



Advanced heterogeneous porous catalysts for desulfurization of diesel

Susana Natércia Oliveira Ribeiro

PhD thesis submitted to

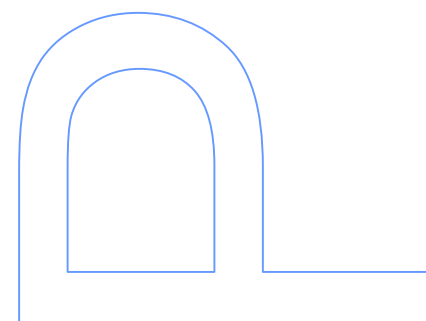
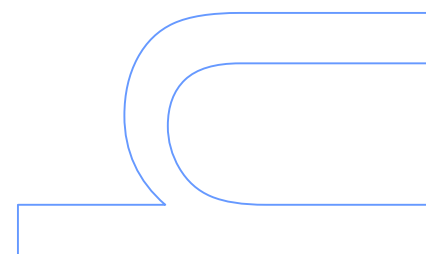
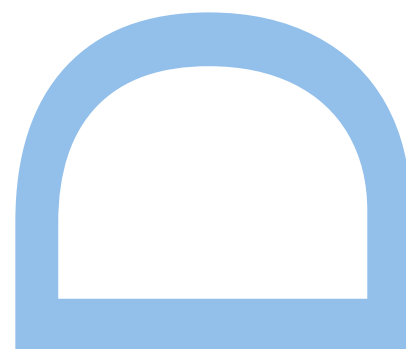
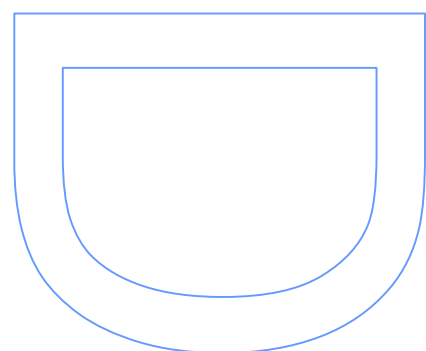
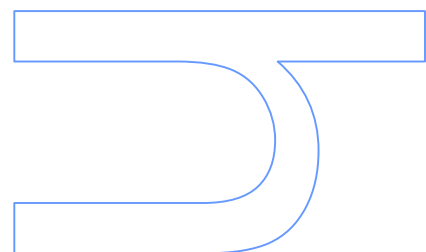
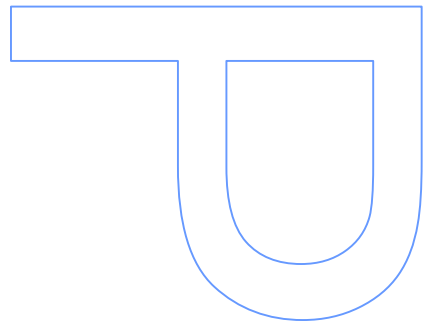
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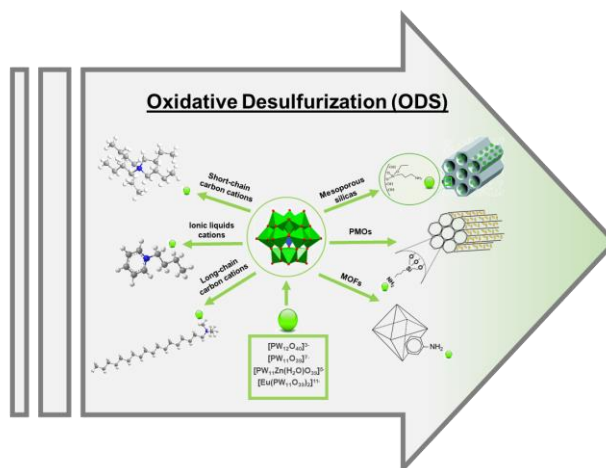
Catalysis

2019





Untreated Diesel



Sulfur-free Diesel

Advanced heterogeneous porous catalysts for desulfurization of diesel

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***To my Daughters
Helena and Isabel***

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Resumo

Esta dissertação teve como principal objetivo, o desenvolvimento de novos catalisadores porosos, para aplicação eficiente em processos de dessulfurização oxidativa de forma a obter-se diesel com baixo teor de enxofre. Para atingir este objetivo, o trabalho foi desenvolvido em três etapas principais: i) preparação de novos catalisadores heterogêneos; ii) otimização dos sistemas catalíticos oxidativos utilizando gasóleos modelo; iii) aplicação dos sistemas otimizados em dessulfurização de amostras de gasóleo real não tratado com diferentes quantidades e composição de enxofre.

Vários polioxometalatos (POMs) do tipo Keggin com diferentes estruturas foram selecionados como centros catalíticos ativos: i) o anião de Keggin $[PW_{12}O_{40}]^{3-}$ (PW_{12}); o monolacunar $[PW_{11}O_{39}]^{7-}$ (PW_{11}); o mono-substituído $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ ($PW_{11}Zn$) e o tipo sanduíche $[Eu(PW_{11}O_{39})_2]^{11-}$ ($Eu(PW_{11})_2$). A preparação dos catalisadores heterogêneos foi efetuada por diferentes métodos: i) solidificação, pela combinação de POMs com o catião octadeciltrimetilamonio (ODA); ii) imobilização em suportes funcionalizados de sílica mesoporosa (SBA-15); iii) imobilização em organossílicas mesoporosas funcionalizadas (PMOs); iv) incorporação num polímero de coordenação funcionalizado (UiO-66-NH₂). Todos os catalisadores foram caracterizados por diferentes técnicas para confirmar a integridade do suporte e das estruturas dos centros ativos após a sua imobilização.

Foram estudados dois sistemas de dessulfurização oxidativa, usando H₂O₂ como oxidante: i) um sistema bifásico (ECODS); ii) um sistema catalítico livre de solvente (CODS). No sistema ECODS, o processo inicia-se com uma extração líquido-líquido com MeCN ou BMIMPF₆, seguindo-se a fase catalítica oxidativa na presença do solvente de extração. No sistema CODS, a fase catalítica oxidativa é realizada na ausência de solvente, seguida por uma extração líquido-líquido final para remover os compostos de enxofre oxidado.

O sistema CODS demonstrou ser mais vantajoso na dessulfurização dos gasóleos modelo, uma vez que se utilizou uma menor quantidade de oxidante e também solventes de extração mais sustentáveis, tal como a água, para remover os produtos de oxidação do gasóleo. No entanto, o sistema ECODS apresentou resultados de dessulfurização, ligeiramente superiores, nas amostras reais de gasóleo. Os catalisadores que tiveram melhor desempenho catalítico foram aqueles contendo os

aniões derivados da estrutura de Keggin: o monolacunar $[PW_{11}O_{39}]^{7-}$ e o mono-substituído $[PW_{11}Zn(H_2O)O_{39}]^5$. A maior eficiência de dessulfurização oxidativa para tratar o gasóleo real (1335 ppm de S) foi de 93,1%, obtida na presença do catalisador $PW_{11}@TMA-SBA-15$. No entanto, os compósitos monolacunares apresentaram uma menor estabilidade em comparação com os mono-substituídos. Os compósitos $PW_{11}Zn@aptesSBA-15$ e $PW_{11}Zn@aptesPMOE$ apresentaram uma atividade e estabilidade semelhantes usando o gasóleo modelo (dessulfurização completa após 1 h), podendo ser reciclados durante 10 ciclos consecutivos sem perda de atividade catalítica; no tratamento do gasóleo real o compósito $PW_{11}Zn@aptesSBA-15$ apresentou uma maior quantidade de centro ativo imobilizado e um melhor desempenho catalítico (87.7%).

Palavras chave: Dessulfurização oxidativa; Peróxido de hidrogénio; Derivados de benzotiofeno; Polioxometalatos; SBA-15; Organossílicas mesoporosas periódicas; Redes metal-orgânicas; UiO-66; Gasóleos não tratados

Abstract

This work had as main objective, the development of new efficient solid catalysts, for application in oxidative desulfurization processes to prepare low-sulfur diesel. To achieve this purpose, the work was developed in three main steps: i) preparation of novel heterogeneous catalysts; ii) optimization of oxidative catalytic systems using model diesel; iii) application of optimized oxidative desulfurization systems to treat different real diesels containing different sulfur amount and composition.

Several Keggin derivative structures of polyoxometalates (POMs) were selected as active catalytic centers: i) the Keggin phosphotungstate anion $[PW_{12}O_{40}]^{3-}$ (PW_{12}); the monolacunar $[PW_{11}O_{39}]^{7-}$ (PW_{11}); the zinc mono-substituted $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ ($PW_{11}Zn$) and the sandwich-type $[Eu(PW_{11}O_{39})_2]^{11-}$ ($Eu(PW_{11})_2$). The preparation of solid catalysts was achieved by different methods: i) solidification, by combining the anionic active center POM and octadecyltrimethylammonium (ODA) cation; ii) immobilization in functionalized mesoporous silica SBA-15 supports; iii) immobilization in functionalized periodic mesoporous organosilicas (PMOs) supports; iv) incorporation in a functionalized Metal-Organic Framework (UiO-66-NH₂). All catalysts were characterized by different techniques to confirm the integrity of support and active center structures after immobilization.

Two different desulfurization systems were studied, using H₂O₂ as oxidant: a biphasic extractive and oxidative desulfurization (ECODS) system and a solvent-free catalytic oxidative desulfurization (CODS) system. The ECODS system consists in an initial liquid-liquid extraction with MeCN or BMIMPF₆, followed by the oxidative catalytic stage in the presence of the extraction solvent. In the CODS system the oxidative catalytic stage is performed in the absence of solvent, followed by a final liquid-liquid extraction to remove the oxidized sulfur compounds.

The solvent-free system demonstrated to be more advantageous, to desulfurize model diesels, since it was able to use less oxidant amount and also more sustainable extraction solvents, such as water, to remove the oxidation products from diesel. However, the biphasic system presented slightly higher desulfurization results using real diesel samples. The most active catalysts were those containing Keggin derivatives: monolacunar $[PW_{11}O_{39}]^{7-}$ and mono-substituted $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ as active center. The highest oxidative desulfurization efficiency to treat real diesel (1335 ppm of S) was 93.1%, achieved using $PW_{11}@TMA-SBA-15$ catalyst. However, lower stability was

found for the monolacunary composites, compared to the mono-substituted composites. Similar activity and stability were found for $PW_{11}Zn@aptesSBA-15$ and $PW_{11}Zn@aptesPMOE$ composites, using model diesel (complete desulfurization after 1 h), being able to be recycled over 10 consecutive cycles without loss of activity. However, higher catalytic performance treating real diesel was achieved using $PW_{11}Zn@aptesSBA-15$ (87.7%).

Keywords: Oxidative desulfurization; Hydrogen Peroxide; Benzothiophene derivatives; Polyoxometalates; SBA-15; Periodic Mesoporous Organosilica; Metal Organic frameworks; UiO-66; Real diesel

Thesis outline

This thesis is divided into ten chapters: Chapter 1 (introduction), Chapters 2-9 published or in submission process for publication results and Chapter 10 the concluding remarks and future perspectives.

The first chapter is an introduction with a general description of the aim of the project and a bibliographic review.

The Chapters 2-9 present an adaptation from published and submitted publications in which the author has a major contribution. Consequently, some similar introductory and experimental information was recurrent between chapters. The Chapters were organized in a manner that does not reflect the order of experimental work execution, but to simplify the overall reading of this thesis and better present the obtained results. Images and additional text were added in order to present additional results, as well as to provide a better work presentation.

Chapter 10 presents a general conclusion of the main results obtained, concerning the global aim of this thesis. Final remarks and some indications for future work activities are also presented in this chapter.

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Abbreviations and symbols

1-BT	1-benzothiophene
4-MDBT	4-methyldibenzothiophene
4,6-DMDBT	4,6-dimethyldibenzothiophene
5-MBT	5-methylbenzothiophene
APDDAB	3-(acryloylamino)propyl]dodecyldimethyl ammonium
API	American Petroleum Institute
aptes	(3-Aminopropyl)triethoxysilane
BMIM	1-butyl-3-methylimidazolium
[BMIM]PF ₆	1-butyl-3-methylimidazolium hexafluorophosphate
BPMS	bi(multi)-functionalized periodic mesoporous organosilica
BPy	1-butylpyridinium
BTC	1,3,5-benzene-tricarboxylate
BzPN	benzyl aminophosphazene
CHP	cumenehydroperoxide
CODS	Catalytic oxidative desulfurization
DBT	dibenzothiophene
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
D _p	Pore diameter
d _w	Wall thickness
ECODS	Extractive catalytic oxidative desulfurization
EDS	Energy dispersive X-ray spectroscopy
EtOH	Ethanol
FT-IR	Fourier transform infrared spectroscopy
FT-RAMAN	Fourier transform Raman spectroscopy
GC-FID	Gas chromatography – flame ionization detector
GC-FID/SCD	Gas chromatography – flame ionization detector /Sulfur Chemiluminescence Detector
GC-FPD	Gas chromatography – flame photometric detector
h	Hours
HDPy	Hexadecylpyridinium
HDS	Hydrodesulfurization
HMS	Hexagonal mesoporous silica

ICP-OES	Inductively coupled plasma optical emission spectrometry
IL	Ionic liquid
HKUST	Hong-Kong University of Science and Technology
LDHs	Layered double hydroxides
MCM-n	Mobil composition of matter
MeCN	Acetonitrile
MIL	Material of Institute Lavoisier
min	Minutes
MOF	Metal organic framework
MPS	Methyl phenyl sulfide
NENU	Northeast Normal University
NMR	Nuclear magnetic resonance
ODA	Trimetyloctadecylammonium
ODS	Oxidative desulfurization
OMS	Ordered mesoporous silica
PAM	Poly(acrylamide) microgels
PCPs	Porous coordination polymers
PEG	Polyethylene glycol
PMO	Periodic mesoporous organosilica
POM	Polyoxometalate
PTA	Phosphotungstic acid
ppm	Parts per million
SBA	Santa Barbara Amorphous type material
S _{BET}	BET (Brunauer–Emmett–Teller) surface area
SEM	Scanning electron microscopy
TBA	Tetra-n-butylammonium
tba	N-(3-trimethoxysilylpropyl)tributylammonium
TBHP	Tert-butyl hydroperoxide
TEOS	Tetraethoxysilane
TGA	Thermal gravimetric analysis
Th	Thiophene
TMA	N-trimethoxysilylpropyl-N,N,N-trimethylammonium
TMU	Tarbiat Modares University
UiO	University of Oslo
UMCM	University of Michigan Crystalline Material
V _p	Total pore volume

wt% Weight percent

XRD Powder X-ray diffraction

ZIF Zeolitic Imidazolate Framework

ν Streching

δ Bending

δ Chemical shift

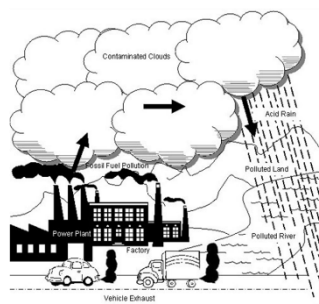
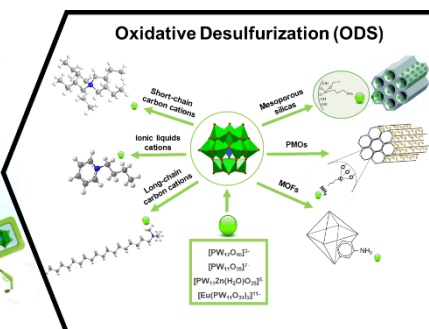
2θ Diffraction angle

Chapter 1

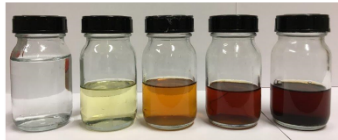
Introduction



Sulfur free diesel



Untreated diesel



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Chapter 1

Introduction

1.1. Context

Sulfur compounds present in liquid fuels are responsible for the release of SO_2 and air borne particulate during combustion. Therefore, the desulfurization of fuels is crucial in the petroleum-processing industry. The current method implemented in refining industries, to remove sulfur compounds from crude oil, is hydrodesulfurization (HDS). This method operates under severe operation conditions using metal catalysts to convert sulfur compounds in H_2S . Despite HDS process effectiveness, it reveals some vital flaws such as the need of high pressures (20-100 atm of H_2) and temperatures (300-400 °C), hydrogen consumption and reduction of octane/cetane number in fuels. Consequently, there is an urgent need for the development of more sustainable and economic desulfurization methods for the production of sulfur-free fuels. [1] An alternative method to HDS is oxidative desulfurization (ODS) that operates in two main steps: oxidation of sulfur compounds in sulfoxides and/or sulfones and their removal by extraction processes. ODS is considered to be an alternative or even a complementary method to the actual HDS, presenting several advantages such as mild operation conditions, low cost of energy and use of less expensive oxidants. [2] The success of ODS process is dependent on the presence of an efficient catalyst in the oxidative step. For a future success industrial application, it is important that the catalyst presents high efficiency and robustness, making possible its recyclability and continuous use in successive cycles. [2, 3]

1.2. Crude oil and desulfurization demand

Although the energy obtained from renewable sources has been increasing during the recent years, fossil fuels remain the larger fraction of energy source (still over 82%) around the world. Half of which is obtained from crude oil, with larger portions of petroleum being used in the transportation sector[4, 5]. Crude oil is a naturally complex mixture of hydrocarbons that can also contain organic compounds with sulfur, nitrogen, oxygen and metals (Table 1.1).

Oil refineries take the advantage of the different weights, volatilities and boiling temperatures of crude oil hydrocarbons in order to separate them and create intermediary and finished products (Figure 1.1). Several refinery streams are used to produce three major types of transportation fuels: gasoline, jet fuels and diesel that differ in composition and properties.

Table 1.1 - Crude oil constituents [6, 7]

Constituent	Chemical type
Hydrocarbons:	Straight chain; branched chain
Paraffinic (Alkanes)	Alkyl cyclopentanes; alkyl cyclohexanes
Naphthenic	Alkyl benzenes; aromatic naphthenic fluorenes; polynuclear aromatics
Dissolved gases	Nitrogen (N ₂); carbon dioxide (CO ₂)
Sulfur compounds	Hydrogen sulfide (H ₂ S) ^a , mercaptans; organic sulfides, disulfides and polysulfides; thiophenes and benzothiophenes; sulfones
Organic nitrogen compounds	Pyridine, quinoline
Organic oxygen compounds	Carboxylic acids (including naphthenic acids) ^b , alcohols, phenols ^b , aldehydes, ketones, esters, ethers, oxyacids
Organic metallic compounds	Porphyrins
Colloidal particles	Asphaltenes; resins; paraffin waxes
Surfactants	Sulfonic acids, sulfonates, sodium naphthenates
Metals	Vanadium, nickel ^c , iron ^c , aluminum, sodium, potassium, calcium, copper
Water (S&W ^d or BS&W ^d) ^e	Fresh or saline
Solids	Sand, dirt, silt, soil dust, mud, corrosion products (metals' oxides, sulfides, salts)

^a Hydrogen sulfide is present as dissolved gas

^b They are surfactants

^c They are present in porphyrins

^d S&W—sediment and water; as previously called BS&W—bottoms sediment and water

^e Microorganisms can be present in crude oils

Crude oil gravity (American Petroleum Institute – API) and sulfur content (sweet for low sulfur and sour for high sulfur) are the most important parameters that define crude oil quality and price. Sulfur content of crude oil and refinery streams is usually expressed in weight percent (wt%) or parts per million by weight (ppm). The average of sulfur content in crude oil varies from less than 0.1% to greater than 5% depending on its type and origin. Sulfur concentration in distilled crude oil tends to increase progressively with increasing carbon number and boiling range (Table 1.2). Therefore, crude fractions obtained in the boiling range of fuel oil and asphalt have higher sulfur content than those in the jet and diesel boiling range. On the other hand, these last have

higher sulfur content than the products obtained in the gasoline boiling range (Figure 1.1). [8]

The presence of sulfur compounds in liquid fuels has shown to cause adverse effects not only on the environment but also on human health. The combustion of sulfur containing fuels promotes the formation of sulfur oxides (SO_2) and sulfate particulate matter. SO_2 can react with water in atmosphere and cause acid rain, which can accelerate the erosion of historical buildings, destroy the automotive paint finishing, acidify soil and lead to the loss of several ecosystems. The sulfur particulate matter can be transported to the lungs and cause respiratory illnesses. Furthermore, sulfur compounds are unwelcome in refining process because they can deactivate some catalysts used in crude oil processing and promote corrosion in equipments. The automobiles are also affected by the presence of sulfur because it has a profound effect in the efficacy of catalytic converters. [4, 9]

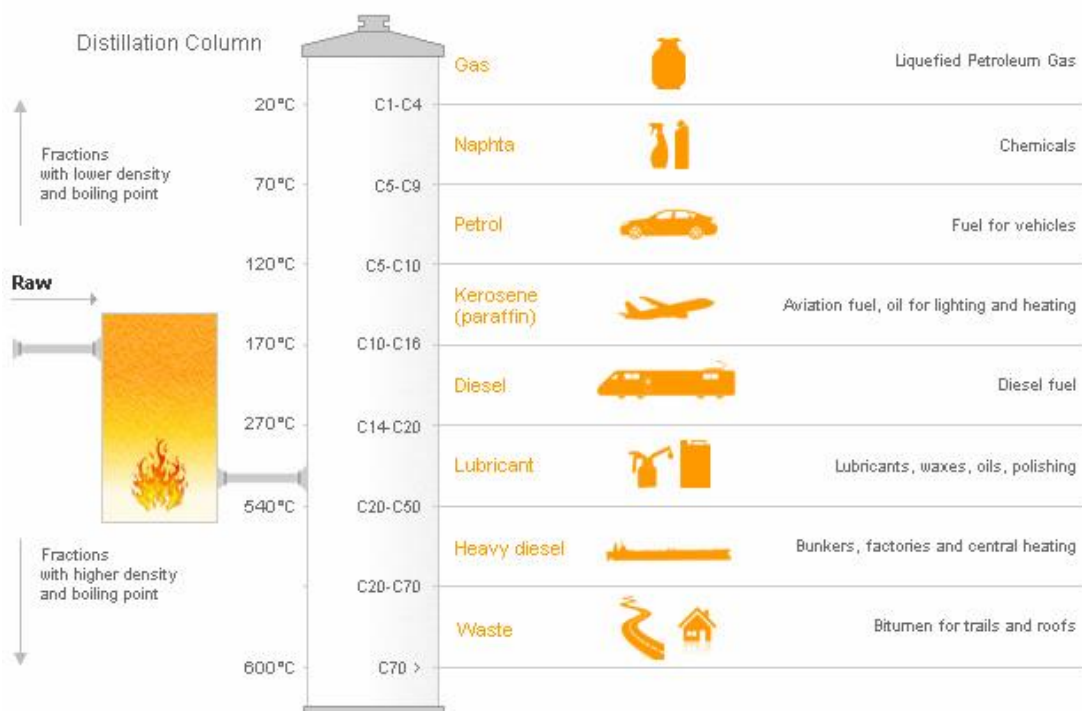


Figure 1.1 - Refining process in Galp (source: <https://www.galp.com/corp/en/about-us/what-we-do/refining-marketing/-sourcing-refining-and-logistics/fundamentals-of-refining>).

In the last few decades, the harmful effects caused by the production of sulfur oxides during combustion of fuels, led worldwide governments to stablish limits for sulfur in diesel fuels to ultra-low levels (<10 ppm) (Figure 1.2). For example, the United States

Environmental Protection Agency has limited, in 2006, the sulfur content of most diesel fuels to 15 ppm from a level of 500 ppm. In Europe, the allowed sulfur content in fuels decreased from 350 ppm to 50 ppm in 2005 and this value was reduced to 10 ppm in 2009. [10-12] As result, the production of diesel with ultra-low sulfur levels increased largely the cost to the refineries of the HDS process. In order to achieve the imposed limits of sulfur, the HDS needs to operate under severe operation conditions (high temperature, high pressure and high H₂ consumption) and/or with higher catalyst volumes, which increases largely the cost of the process. Therefore, the search for alternative or complementary processes to the HDS have attracting researchers' attention and become an important task for oil refining industries to develop new technologies to remove sulfur from diesel using a cost-effective process based in sustainable conditions to accomplish the new specifications.

Table 1.2 - Distribution of Sulfur compounds over the distillation range of a crude oil [13, 14]

Boiling range (°C)	Sulfur content (%)	Sulfur compound distribution (%)			
		Thiols	Sulfides	Thiophenes	Other ^a
70–180 (naphtha)	0.02	50	50	Trace	–
160–240 (kerosene)	0.2	25	25	35	15
230–350 (distillate)	0.9	15	15	35	35
350–550 (vacuum gas oil)	1.8	5	5	30	60
>550 (vacuum residue)	2.9	Trace	Trace	10	90

^a Benzothiophenes, dibenzothiophenes and heavy sulfides

Several desulfurization processes have been proposed in the past to deal with the removal of sulfur from fuels. Alternative or complementary desulfurization processes have been proposed which include extractive desulfurization, adsorptive desulfurization, biodesulfurization, oxidative desulfurization (ODS) and others. Among them, ODS has been the most promising and studied method to remove sulfur from fuels. [4, 9, 10]

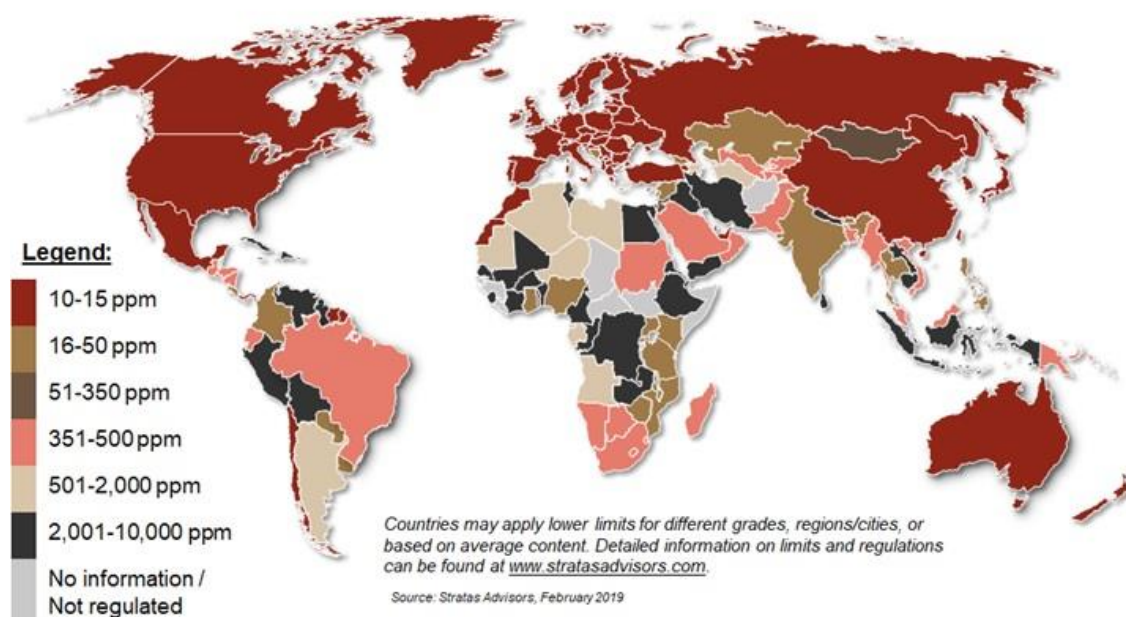


Figure 1.2 - Maximum sulfur limits in on-road diesel, 2019.

1.3. Hydrodesulfurization

Hydrodesulfurization is the most common industrial process in which hydrogen under high pressure (3-7 MPa) and temperature (300-400 °C) is used to decompose sulfur compounds from refinery streams in order to reduce its levels. Usually, the HDS process consists in the catalytic cleavage the C-S bonds within the molecules to form aliphatic hydrocarbons and H_2S , using Co-Mo, Ni-Mo or Ni-W impregnated on Al_2O_3 as catalysts. The H_2S produced by the HDS treatment is eventually converted to elemental sulfur. [4, 13, 15, 16] HDS eliminates easily thiols, sulfides and thiophenes. However, the elimination of refractory sulfur compounds such as dibenzothiophene (DBT) and dibenzothiophenes derivatives is more difficult, requiring more severe experimental conditions to desulfurize these compounds. Figure 1.3 exhibits the relative reactivities of some sulfur compounds from different fuel fractions towards HDS process. The low reactivity of the refractory sulfur compounds is due to both steric hindrance and electronic density. [17, 18]

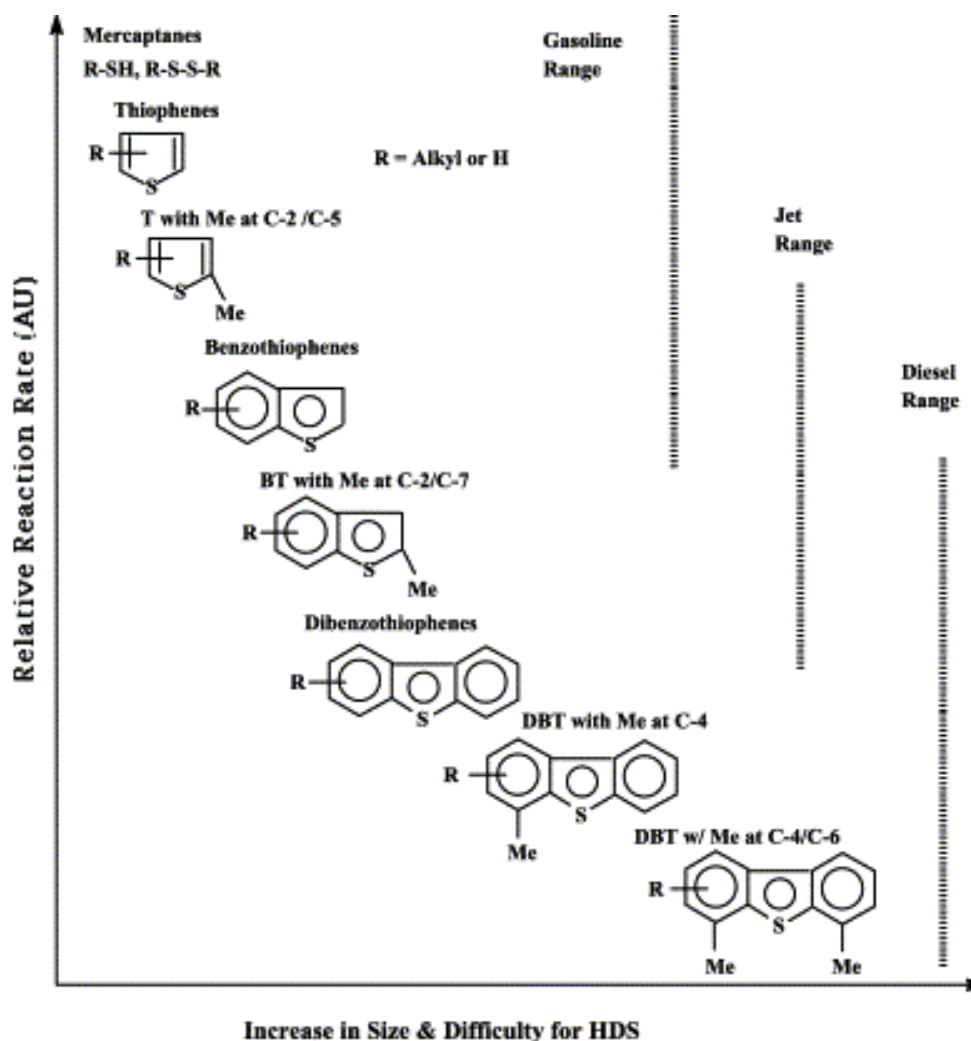


Figure 1.3 - Reactivity of different organic sulfur compounds in HDS process versus their ring sizes and positions of alkyl substitutions on the ring. [18]

Most HDS processes reduces sulfur content in fuels to a range of 200-300 ppm, effectively and relatively inexpensive. However, in order to reach ultra-low levels of sulfur (<10 ppm) demands to remove the refractory sulfur compounds, more severe operation conditions are required, *i.e.*, the use of excess hydrogen at high pressure and temperature and the use of highly active catalysts at slow space velocity. [2]

The use of extreme operational conditions affects not only the cost of the commercial final fuels but also other fuel requirements. Therefore, an alternative or complementary process, able to operate under mild reaction conditions without the use of expensive hydrogen, is required and oxidative desulfurization (ODS) has merged as a potential candidate. [2]

1.4. Oxidative desulfurization (ODS)

Oxidative based desulfurization process is a promising two stage process to reduce sulfur from fuels. The ODS process offers many advantages towards HDS since it operates under mild reaction conditions: low pressure (atmospheric pressure) and temperature ($< 100\text{ }^{\circ}\text{C}$) and the use of expensive hydrogen is not required. Besides, the refractory sulfur-containing compounds [dibenzothiophene (DBT) and benzothiophene (BT) derivatives] can be easily oxidized, increasing their polarity. The oxidation reactivity tends to increase when the electron density of the sulfur species is higher, $\text{DBT} > \text{BT} \gg \text{thiophene (Th)}$ in the reverse reactivity order of HDS. [18] In ODS, sulfur compounds are selectively oxidized by adding one or two oxygen atoms to the sulfur atom using an appropriate combination of oxidant and catalyst, without breaking any carbon–sulfur bonds, yielding sulfoxides and sulfones. In a different step, these are then removed by an extraction, adsorption or distillation process due to their increased relative polarity. [4, 19-22] In scheme 1.4 are presented two possible ODS systems: A) a solvent-free catalytic oxidative desulfurization (CODS) system, where the oxidative step occurs in the absence of other solvent and the oxidized sulfur removal occurs after the oxidative catalytic stage; and B) an extractive and catalytic oxidative desulfurization (ECODS) system, where a biphasic liquid-liquid extraction (diesel/polar immiscible solvent) occurs during the oxidation stage. [20]

1.4.1 General description of the ODS process

In the ODS process, sulfur-containing compounds are converted into oxidized products with increased relative polarity, using an efficient combination of selective oxidants and catalysts. The electronegativity of sulfur and carbon are similar, resulting in sulfur-carbon bound with relatively non-polar properties and sulfur-containing compounds with similar properties to their corresponding non-sulfur organic compounds. As such, the solubility of sulfur-containing compounds and hydrocarbons are very similar in polar and non-polar solvents. [21]

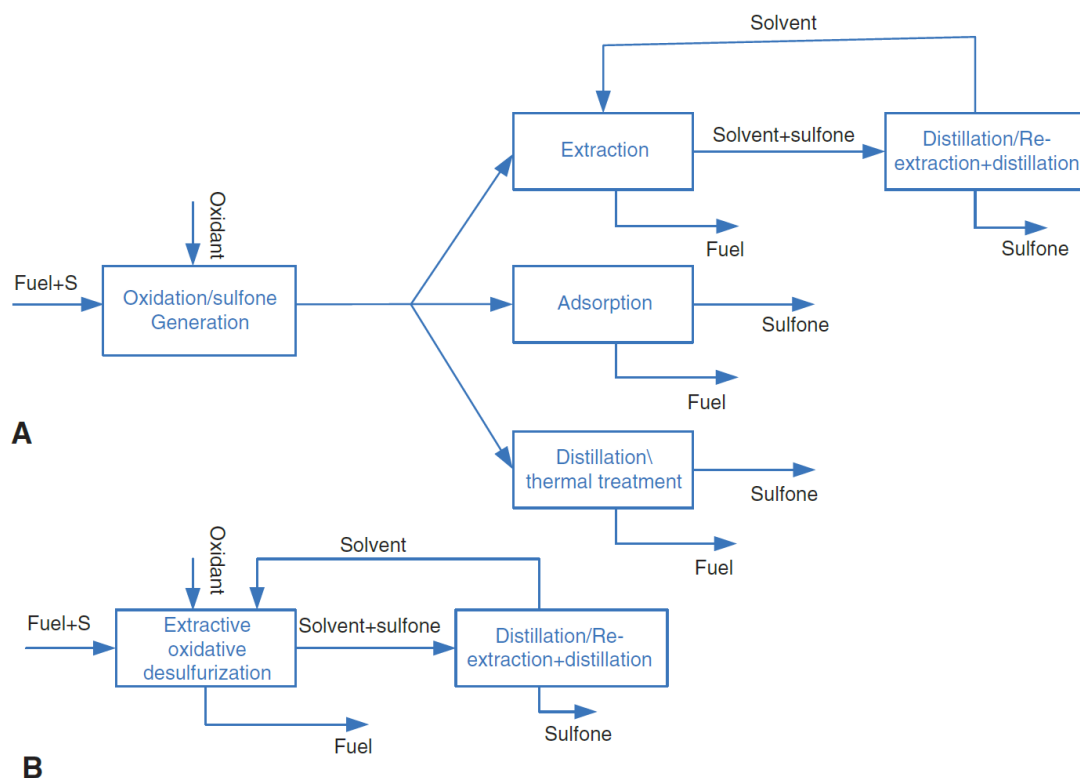


Figure 1.4 – Representation of ODS systems; A) solvent-free CODS system and B) biphasic diesel/polar immiscible solvent ECODS system. [20]

However, the properties of S-containing compounds can be altered by increasing their polarity via oxidation which subsequently increases their solubility in polar solvents, what constitutes the fundament of the ODS process. In order to oxidize the sulfur compounds, the oxidant must be in contact with the fuel under optimum conditions, donating O-atoms to the sulfur-containing compounds until sulfoxides and/or sulfones are formed (Figure 1.5). [2]

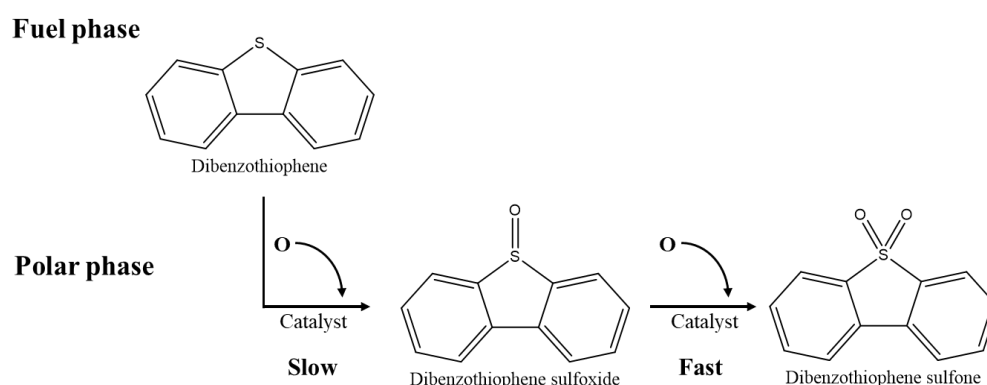


Figure 1.5 – Schematic representation of DBT oxidation

Water-soluble polar solvents such as dimethylsulfoxide (DMSO), dimethylformamide (DMF) and acetonitrile (MeCN) have been applied in ODS systems. [2, 23] The two first solvents present high extractability of sulfones; however, their boiling ranges are near those of some sulfones and their separation by distillation is difficult. Acetonitrile is a preferable extraction solvent, since its lower boiling point (82 °C) allows an easy separation from the sulfones by distillation. [2] Ionic liquids (ILs) have also been applied in ODS to remove sulfur compounds from fuels and are more effective when the compounds are previously oxidized. The first report using ILs for the selective extraction of sulfur compounds from diesel was described by Bössman and his group [24] in 2001, and since then many works in this area have been published. [25] ILs possess many desirable properties such as non-volatility, solubility for organic/inorganic compounds, good thermal/chemical stability, non-flammability, recyclability and have been named 'green' extracting agents. [26, 27] One of the principal limitations of using ILs in desulfurization processes is their high cost, being more expensive than the common organic solvents. However, its recycle capacity and the expected decrease in prices over the years, makes them promising extraction solvents for the removal of sulfur containing compounds present in fuels. [26-30]

In an oxidative catalytic process, the choice of the appropriate oxidant is of crucial importance and some requirements should be taken in to account: percentage of active oxygen, selectivity, cost, reaction time and environmental safety. Several oxidants have been investigated in ODS namely: H_2O_2 , [31] $t\text{-BuOOH}$, [32] O_2 , [33] O_3 , [34] NO_2 [35]. Among the used oxidizing agents, H_2O_2 is the most promising and commonly studied because of its environmental friendliness (water is its only by-product after donating oxygen), high percentage of active oxygen, ease of handling and commercial availability. [2, 22, 36, 37] However, the use of H_2O_2 oxidant requires the presence of an efficient catalyst to activate the H-O-O-H bonds through forming active oxygen species, which will form the active oxygen donor that it will accelerate the oxidative reaction. [2] On the other hand, the catalyst should not catalyze the non-efficient decomposition of H_2O_2 and also should not suffer any degradation during oxidative reaction. The existence of an efficient catalyst in the oxidation stage is one of the keys to the success of the ODS process. Several catalytic systems have been studied in the oxidation of sulfur compounds using H_2O_2 , and among them polyoxometalates based systems. [1, 23, 38-43] Polyoxometalates (POMs) are metal-oxygen anionic clusters that have attracted much attention in several fields, such as materials science, analytical chemistry, medicine, electro-, photo-, magnetic chemistry and one of the most important, acid and oxidative catalysis. [37, 44-49] The reaction of POMs with H_2O_2 can create peroxo

species that can catalyze the oxidative reaction. [50-53] For example, reactions catalyzed by phosphotungstic acid in combination with H_2O_2 give the well-known Ishii-Venturello complex $\{\text{PO}_4[\text{WO}(\text{O}_2)_2]_4\}^{3-}$, a tungstophosphate with oxide and peroxide ligands, which act as catalyst rather than the plenary Keggin anion $[\text{PW}_{12}\text{O}_{40}]^{3-}$. [44] The application of POMs in ODS processes is quite recent. In 2006, the tetrabutylammonium salts of $[\text{W}_6\text{O}_{19}]^{2-}$, $[\text{V}(\text{VW}_{11})\text{O}_{40}]^{4-}$, $[\text{PVW}_{11}\text{O}_{40}]^{4-}$, and $[\text{PV}_2\text{Mo}_{10}\text{O}_{40}]^{4-}$ were used for the first time as catalysts in oxidative desulfurization of model compounds (1-BT, DBT and 4,6-DMDBT). [42] Since then, the application of POMs in ODS processes has been growing due to their effectiveness and efficiency as oxidative catalysts. [38] Different studies have proved that ODS processes, can be conducted under homogeneous catalytic systems, as well as under heterogeneous catalytic conditions. The homogeneous catalytic systems can be efficient; however, the common drawback is the difficulty to separate and reuse the catalysts. Therefore, the use of a heterogeneous catalytic system in the ODS process is of particular interest from an industrial and environmental point of view, since it allows the recovery and reuse of the catalyst. [22]

1.5. Polyoxometalates

Polyoxometalates are known since the beginning of the 19th century, with the discovery of the ammonium salt of phosphomolybdic acid by Berzelius in 1826. [54] With the development of their chemistry, several types of POMs structures have been described, and the Lindqvist $[\text{M}_6\text{O}_{19}]^{n-}$, Anderson $[\text{XM}_6\text{O}_{24}]^n$, Keggin $[\text{XM}_{12}\text{O}_{40}]^{n-}$ and Wells-Dawson $[\text{X}_2\text{M}_{18}\text{O}_{62}]^{n-}$ are the most studied (Figure 1.6). POMs are anionic oxo-clusters of early transition metals in their highest oxidation state, namely Mo^{6+} , W^{6+} , V^{5+} and less frequently Nb^{5+} and Ta^{5+} . POMs can be divided in two main classes based on their chemical composition: isopolyanions ($[\text{M}_m\text{O}_y]^{p-}$) and heteropolyanions ($[\text{X}_x\text{M}_m\text{O}_y]^{q-}$), where M is the main transition metal called *addenda* atom and O is the oxygen atom. The heteropolyanions can also have another incorporated element, the primary heteroatom X, that can be a non-metal (such as P, Si, As, Sb), another element of the p-block or a different transition metal. POMs can have more than one primary heteroatom in their structure; and their presence is essential to complete the basic structure of the heteropolyanion. Therefore, it cannot be substituted or chemically removed without destroying the anion structure. On the other hand, an *addenda* atom can be removed from the structure to form a stable polyoxoanionic subunit. [52, 55-58]

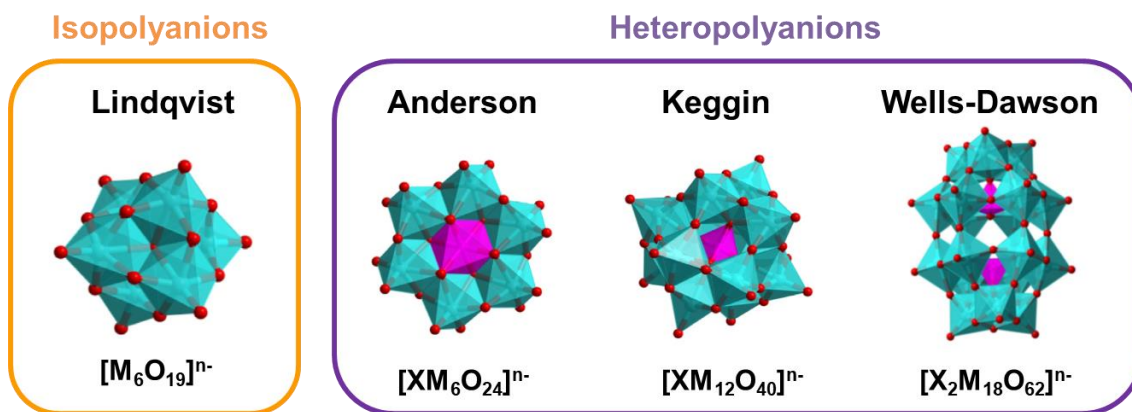


Figure 1.6 – Schematic representation of different POM structure

Through the past of more than two decades, POMs, especially heteropolyanions, have received great attention in the area of catalysis due to their unique molecular properties. POM chemical properties such as acid/base strength and redox potential can be easily adjusted through the selection of appropriate constituent elements and counter cations, which can also modify their physical properties including solubility in different media and surface area. Furthermore, their low environmental impact, facility of synthesis and thermal stability towards oxygen donors also explain the increasing of catalytic reactions employing POMs. Amongst the wide variety of polyoxometalate structures (Figure 1.6), the Keggin derivatives stand for their diversity, unique stability and ease availability, being the most well investigated POM structures in catalysis. [44, 59-62]

1.5.1. Keggin anion

Linus Pauling was the first to suggest the Keggin structure in 1929. [63] However, it was James F. Keggin who solved its structure in 1933, using X-ray diffraction of the phosphotungstic acid. [64] This structure was then used to determine the structure by many other POMs. [65] The Keggin structure, which is represented in figure 1.6, has the general formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ where twelve metal atoms (e.g., $M = W^{VI}, Mo^{VI}, V^{V}$) are arranged around one single heteroatom (e.g., $X = P^V, Si^{IV}, As^V, Ge^{VI}, Si^{IV}, B^{III}, Fe^{III}$).

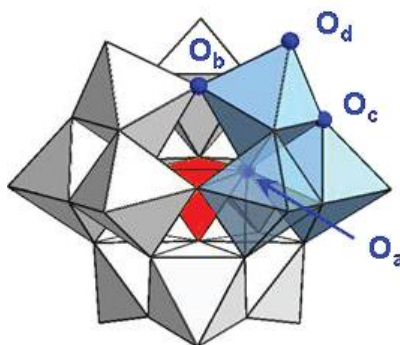


Figure 1.7 - Keggin structure: Mo or W = gray octahedra, heteroatom X = red, one $\{M_3O_{13}\}$ unit = light blue with different types of oxygen shown as blue balls (symbols are explained in the text).

The Keggin structure presents one central tetrahedron XO_4 surrounded by twelve edge- and corner-sharing metal-oxygen octahedral MO_6 assembled in four groups of three M_3O_{13} units. These groups are connected by common vertices and different types of oxygen atoms that can be identified according to its position in the POM structure: connected to the heteroatom (O_a), in shared vertices (O_b), in shared edges (O_c) and terminals (O_d) (Figure 1.7). [46, 60, 61, 66, 67] These four types of addendum-oxygen connections are responsible to the presence of different absorption bands on the infrared spectrum of these heteropolyanions. [61, 68]

Five possible isomers ($\alpha, \beta, \gamma, \delta, \epsilon$) of the Keggin structure can be obtained by a 60° clockwise rotation of each M_3O_{13} group around its O_a atom. However, only three of them (α, β, γ) have been successfully synthesized, isolated and identified and the α is the most described in the literature due to its higher stability. [67]

1.5.1.1. Keggin derivatives

The Keggin anion, treated under proper experimental conditions (e.g., pH, temperature, concentration), can lead to the formation of lacunary POM derivative (most commonly one, two or three vacancies) by removing one or more MO^{4+} groups. Among the possible structures, it stands out the monolacunary Keggin structure represented by the general formula $[XM_{11}O_{39}]^{(n+4)-}$ (XM_{11}), obtained by the removal of one MO^{4+} unit ($M = W^{VI}, Mo^{VI}$). This specie contains a lacuna with 5 potentially coordinator oxygen atoms (Figure 1.7 b)). The monolacunary structure, with the ability of being coordinator, can react with metallic ions M' giving rise to mono-substituted Keggin derivative of the type 1:1 $[XM_{11}M'(L)O_{39}]^{m-}$ [where L is a monodentate ligand, for example water molecule

(Figure 1.8 c)] or to sandwich-type, formed by 1:2 $[M'(XM_{11}O_{39})_2]^{n-}$ (M' is often a lanthanide). [55, 69]

In the present work, various Keggin derivatives POM structures were used:

- i) **The Keggin POM** $[PW_{12}O_{40}]^{3-}$ (abbreviated as PW_{12}), containing the addenda atom, $M = W^{6+}$ and the primary heteroatom, $X = P^{5+}$.
- ii) **The monolacunary Keggin derivative** $[PW_{11}O_{39}]^{7-}$ (abbreviated as PW_{11}), formed from the loss of MO_4^+ unit from the Keggin PW_{12} structure.
- iii) **The mono-substituted** $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ (abbreviated as $PW_{11}Zn$), formed by the coordination of the metal cation Zn^{2+} to the monolacunary PW_{11}
- iv) **The sandwich-type** $[Eu(PW_{11}O_{39})_2]^{11-}$ (abbreviated as $Eu(PW_{11})_2$), formed by the coordination of the lanthanide Eu^{3+} to two monolacunary PW_{11} units.

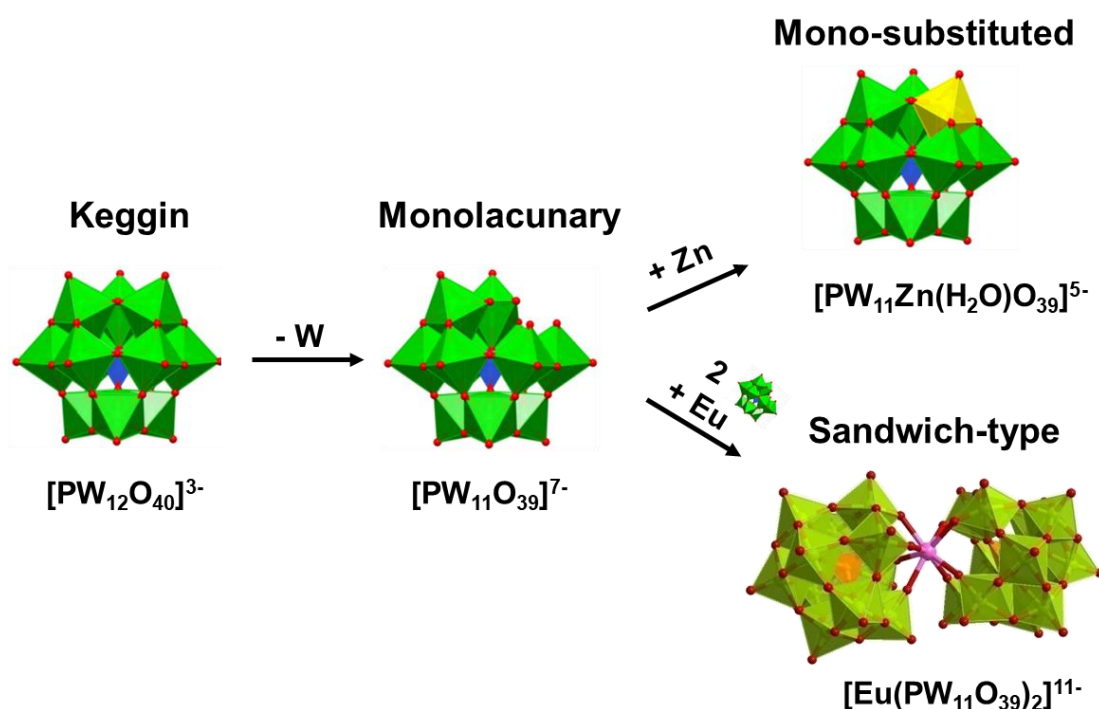


Figure 1.8 – Representation of Keggin derivatives formation.

1.6. POM-based heterogeneous catalysts in ODS processes

Taking in account the unique features of POMs, such as multifunctionality, structural mobility and compatibility with eco-sustainable conditions, various POMs have been extensively used as efficient homogeneous catalysts in a large variety of oxidative reactions, including ODS processes. [70-78] However, most of these catalytic systems take place in homogeneous or biphasic liquid-liquid reaction systems, making catalyst separation and reuse a difficult task, which affects their use in systems that require environmentally friendly efficient transformation and sustainable development. [44] Thus, the design of POM based heterogeneous catalysts is preferable in environmental and industrial terms.

However, the use of heterogeneous catalysts can be affected by two problems: leaching and lower activity when compared to their homogeneous counterparts. Therefore, several strategies have been proposed to overcome those problems. Typically, POM-based heterogeneous catalysts can be prepared via two roots, namely “solidification” and “immobilization” of the catalytically active POMs. [44, 72, 79, 80]

Figure 1.9 represents the adopted strategies in the scope of this thesis to prepare POM-based catalysts. Four Keggin phosphotungstates were selected as active catalytic centers (presented in 1.5.1.1). The heterogenization of these catalytic active centers was accomplished using different strategies:

- i) Combination with **long-carbon chain counter-cations**, namely the octadecyltrimethylammonium cation (ODA),
- ii) Immobilization in various functionalized **mesoporous silica supports** (SBA-15),
- iii) Immobilization in different bifunctional **periodic mesoporous organosilicas** (PMOs),
- iv) Incorporation into porous **Metal Organic Frameworks** (MOFs).

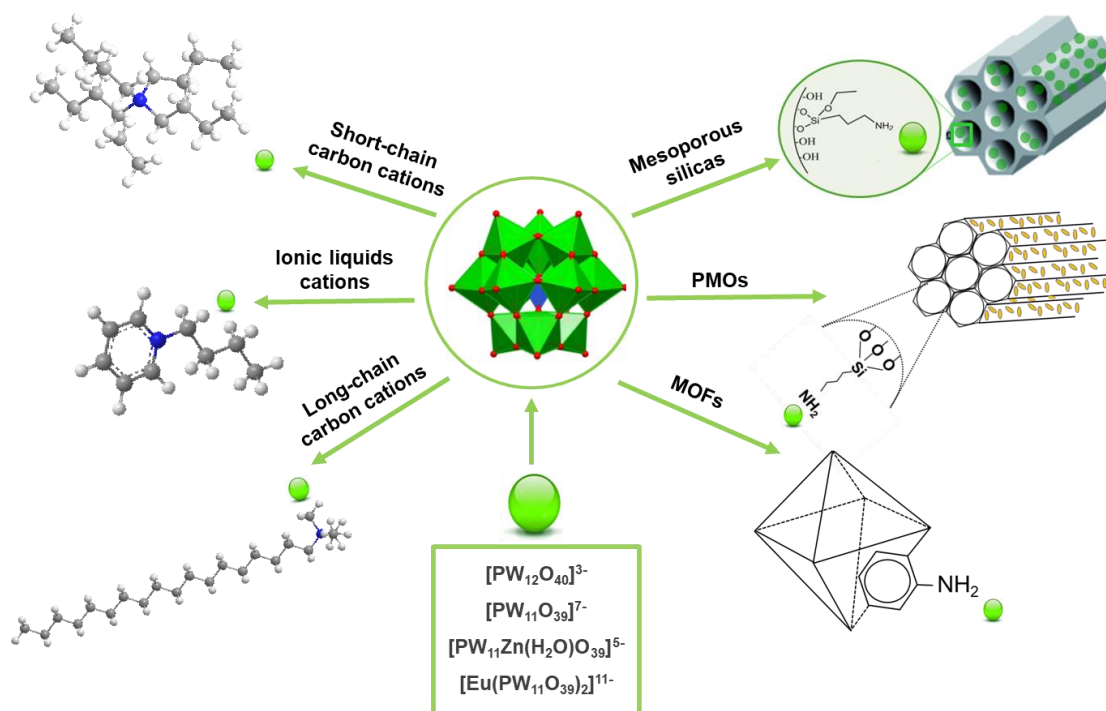


Figure 1.9 – Several strategies to prepare POM-based catalysts.

1.6.1. Solidification of POMs with counter-cations

The solidification method uses counter-cations with appropriate composition, charge, size, shape and hydrophobicity, to create insoluble ionic materials, which can be employed as heterogeneous catalysts. This process avoids the use of support material and is based on a simple synthesis by means of a one-step precipitation process.

The design of POM-based heterogeneous catalysts can be achieved by the combination of POMs with proper organic units, such as surfactants with various carbon-chain lengths and ionic liquids. In recent years, new efficient organic-inorganic hybrid catalysts with the ability of recycling, have been developed and applied on desulfurization processes. [38, 44] Two different heteropolyanions have been reported as precursors to prepare surfactant encapsulated POMs used in ODS processes: the Anderson $[XM_6O_{24}]^{n-}$ [81-83] and the Keggin $[XM_{12}O_{40}]^{n-}$ types. [33, 84-91] Between these two POMs, the Keggin type, specially the phosphotungstic acid $H_3[PW_{12}O_{40}]$ has been the most studied, due to its stability and commercial accessibility. [92]

In 2004, Li *et al.* [93] prepared a $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst assembled in emulsion with diesel containing sulfur compounds. This catalyst could selectively oxidize the sulfur compounds, using H_2O_2 as oxidant, in their correspondent sulfones

that could be separated from the reaction media using an extraction solvent. This catalyst could also be easily separated from the reaction media, after demulsification and sedimentation. Besides, it also reveals good desulfurization capacity of a real diesel containing several alkyl-substituted dibenzothiophenes. One year later, Li and co-workers [85] prepared different quaternary ammonium cations with phosphotungstic acid and studied their behavior in the oxidation of a model diesel containing different sulfur compounds (1-BT, DBT and 4,6-DMDBT), as well as, in the desulfurization of a real diesel. During the catalytic reaction, the catalyst was distributed in the interface of two immiscible liquids and form emulsion droplets. When $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst was applied in the desulfurization of a real diesel, over 96% efficiency of H_2O_2 and ~100% selectivity to sulfones was achieved, and it also demonstrated to be recyclable and stable, maintaining catalytic activity.

POM semitubes and wire assemblies were prepared by Wang and coworkers [89] with the change of $H_3[PW_{12}O_{40}]$ surface by electrostatic interactions between the anionic POM cluster and different cationic surfactants with various alkyl chains. These catalysts were applied in the oxidation of DBT in which amphiphilic units with similar chemical composition presented similar catalytic efficiencies.

A direct reaction system was used to prepare a combined amphiphilic catalyst of octadecyltrimethylammonium bromide and $[PW_{12}O_{40}]^{3-}$ by Luo *et. al* [86] in 2006. This catalyst (with different molar ratio between the quaternary ammonium cation and the POM anion) was tested in DBT oxidation (3000 ppm DBT in *n*-octane) and the highest reaction rate was obtained for a molar ratio 1:1 between the two constituents of the catalyst. Complete DBT conversion was achieved under mild reaction conditions (10 min at 70 °C) using H_2O_2 as oxidant.

Composite microspheres of $H_3[PW_{12}O_{40}]$ were prepared by using an ion-exchange reaction between 3-(acryloylamino)propyl]dodecyldimethyl ammonium (APDDAB) located within the porous of poly(acrylamide) microgels (PAM) and $H_3[PW_{12}O_{40}]$, in aqueous solution. [87] This catalyst was tested in the desulfurization of a DBT model diesel (sulfur content of $\approx$ 2000 ppm in decalin). After 24 h of reaction the sulfur content was less than 25 ppm and the catalyst was recovered by decantation and reused in three cycles maintaining the catalytic performance between cycles.

The octadecyltrimethylammonium (ODA) surfactant was also chosen to prepare several emulsion catalysts using Keggin-type phosphotungstate and its derivatives. [91] The emulsion catalyst with the bare Keggin structure (PW_{12}) was found to be inactive in the oxidation of 1-BT in decalin, using H_2O_2 as oxidant, at 30 °C. However, the catalyst

with monolacunary Keggin-structure (PW_{11}) could completely oxidize 1-BT under the same reaction conditions and the catalytic activity decreased considerably when its lacunary sites were coordinated with transition metal cations.

In 2011, Wang and coworkers [94] presented a highly efficient desulfurization catalyst based on surfactant encapsulated POM with nanocone morphology. The POM nanocones assemblies were prepared by ion exchange reaction between octadecyldimethylammonium bromide and $H_3[PW_{12}O_{40}]$ and later functionalized with magnetite (Fe_3O_4) nanocrystals, conferring the catalyst a magnetic character facilitating its separation from the reaction medium by applying an external magnetic field.

Recently Balula's research group [41] also prepare a highly active heterogeneous catalyst using the quaternary ammonium salt ODA and the monolacunary phosphotungstate PW_{11} . It was demonstrated that the cation exchange confers total heterogeneity to ODA-containing hybrid and the heterogeneous catalyst allowed the complete desulfurization of a multicomponent model diesel (2000 ppm S) after 40 min of reaction, conciliating extraction (using 1-Butyl-3-methylimidazolium hexafluorophosphate $BMIMPF_6$ as solvent) and oxidation (ECODS process using H_2O_2 oxidant).

Another amphiphilic catalyst $[(C_{18}H_{37})N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ [88] assembled in emulsion droplets, was used to separately oxidize sulfur-containing compounds in decalin with a sulfur concentration of 1000 ppm each. The catalytic oxidation reactivity of the sulfur-containing compounds followed the order: BT < 5-methylbenzothiophene (5-MBT) < DBT < 4,6-DMDBT. The produced sulfones could be removed by a polar extraction solvent. Besides, the catalyst was also tested in the desulfurization of two different diesels: a prehydrotreated diesel with 500 ppm of sulfur content and a straight-run diesel with 6000 ppm of sulfur. After oxidation and extraction, the sulfur level of the prehydrotreated diesel lowered to 0.1 ppm and in the case of the straight-run diesel the sulfur content was reduced to 30 ppm.

A Keggin type derivative POM with a mixed-addenda $[PV_2Mo_{10}O_{40}]^{5-}$ has also been used to prepare amphiphilic catalysts and used in emulsion systems to desulfurize a DBT model diesel (in decalin), using molecular oxygen as oxidant and isobutyl aldehyde as sacrificial agent. [33] Under optimized conditions, completely oxidation of DBT was achieved, after 4 hours using $[(C_{18}H_{37})N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$ as catalyst and in the presence of MeCN as extraction solvent. However, there is a lack of information about the activity of the sacrificial agent. Table 1.3 summarizes the experimental conditions and the desulfurization results for the POM-based catalysts referred to above.

Table 1.3 - Experimental conditions and desulfurization efficiency for the various hybrid POM-based catalysts applied in diesel desulfurization.

Catalyst	Diesel (ppm S)	Oxidant	T (°C)	Time	Efficiency	Ref.
[(C ₁₈ H ₃₇) ₂ N(CH ₃) ₂] ₃ [PW ₁₂ O ₄₀]	4,6-DMDBT in decalin, tetralin and <i>n</i> -dodecane (475)	H ₂ O ₂ /S=2.6	30	80 min	100%	[93]
	Prehydrotreated diesel (500)		30	> 12 h	~100%	
[(C ₁₈ H ₃₇) ₂ N(CH ₃) ₂] ₃ [PW ₁₂ O ₄₀]	1-BT or DBT or 4,6-DMDBT in decalin, tetralin and <i>n</i> -dodecane (475)	H ₂ O ₂ /S=2.6	60	90 min	100%	[85]
	Prehydrotreated diesel (500)		30	> 12 h	~100%	
[(C ₁₈ H ₃₇)N(CH ₃) ₃] ₃ [PW ₁₂ O ₄₀]	DBT in hexane (174 ppm S)	H ₂ O ₂ /S=37	50	20 min	100%	[89]
[(C ₁₈ H ₃₇)N(CH ₃) ₃] ₃ [PW ₁₂ O ₄₀]	DBT in <i>n</i> -octane (521)	H ₂ O ₂ /S=30	70	10 min	100%	[86]
PAM/APDDAB ₃ [PW ₁₂ O ₄₀]	DBT in decalin (305)	H ₂ O ₂ /S=16	50	22 h	100%	[87]
[(C ₁₈ H ₃₇)N(CH ₃) ₃] ₅ Na ₂ [PW ₁₁ O ₃₉]	1-BT in decalin (1000)	H ₂ O ₂ /S=3,5	30	60 min	98%	[91]
[(C ₁₈ H ₃₇) ₂ N(CH ₃) ₂] ₃ [PW ₁₂ O ₄₀]	DBT in hexane (174)	H ₂ O ₂ /S=12	50	38 min	100%	[94]
[(C ₁₈ H ₃₇)N(CH ₃) ₃] ₇ [PW ₁₁ O ₃₉]	1-BT, DBT, 4-MDBT and 4,6-DMDBT in <i>n</i> -octane (2000)	H ₂ O ₂ /S=8	70	70 min	100%	[41]
[C ₁₈ H ₃₇ N(CH ₃) ₃] ₄ [H ₂ NaPW ₁₀ O ₃₆]	1-BT, 5-MBT, DBT, or 4,6-DMDBT in decalin (1000)	H ₂ O ₂ /S=3	40	1-BT (120min) 5-MDBT (90 min) DBT (40 min) 4,6-DMDBT (40 min)	100%	[88]
	Prehydrotreated diesel (500)	H ₂ O ₂ /S=7	22	60 min	~100%	
	straight-run diesel (6000)	H ₂ O ₂ /S=3	30	120 min	99.6%	
[C ₁₈ H ₃₇ N(CH ₃) ₃] ₅ [PV ₂ Mo ₁₀ O ₄₀]	DBT in decalin (511)	O ₂ (bubbled)	60	4 h	100%	[33]

PAM: poly(acrylamide) microgels; APDDAB: 3-(acryloylamino)propyl]dodecyldimethyl ammonium

The preparation of POM-based ionic liquids is quite recent, beginning around 2004, where the first class of these catalysts was obtained through partial proton exchange of phosphotungstic acid with a bulky PEG-containing quaternary ammonium cations. [95] Over the last years, there has been a growing effort to develop hybrid POMs using ionic liquids (ILs) cations as counter-cation to prepare recoverable and recyclable heterogeneous catalysts. [44] There are few examples of the use of these hybrid catalysts in ODS processes. Most of the reports describe biphasic systems using ILs both as solvents and reaction media, resulting in efficient catalytic systems that could be reused for several times. [21, 96, 97] On the other hand, Rafiee *et al.* [90] synthesized several organic-inorganic POMs composed of sulfonated pyridinium cations and

phosphotungstate anion $[PW_{12}O_{40}]^{3-}$ that were used efficiently in catalytic oxidation of sulfur containing model diesel (methyl phenyl sulfide (MPS), thiophenes and DBT). Moreover, the catalysts could be easily separated upon cooling the reaction solution and reused five times without loss of catalytic activity.

1.6.2. Immobilization of POMs in support materials

The heterogenization of POM active catalytic centers can also be achieved by its immobilization onto different support materials. A wide diversity of materials has been used to prepare heterogeneous POM based catalysts namely: mesoporous silica, metal organic frameworks (MOFs), carbon based materials, polymers, mesoporous metal oxides, magnetic nanoparticles... [38, 44, 98] The application of these type of catalysts in ODS processes are mainly based on MOFs and silica supports. [38] However, other supports such as activated carbon, [99] magnetic materials, [100] layered double hydroxides (LDHs), [101] alumina [102] and titania [103] have also been reported.

1.6.2.1. Ordered mesoporous silica

Ordered mesoporous silica (OMS) were the first mesoporous materials prepared through template direct synthesis which were reported in the early 1990s by Mobil Oil Company researchers. [104] Since their discovery, extensive research has been addressed due to its ease of synthesis, well-defined pore size (2–50 nm), relatively large surface areas and high pore volume. [105, 106] In order to enhance the use of OMS in different fields of application, namely catalysis, adsorption, separation and sensing, organic functionalities can be added. The surface functionalization of mesoporous silica has been accomplished by post synthesis (“grafting”) or in-situ (“co-condensation”) processes using organosilanes containing appropriate functional groups (Figure 1.10). [38, 105, 106]

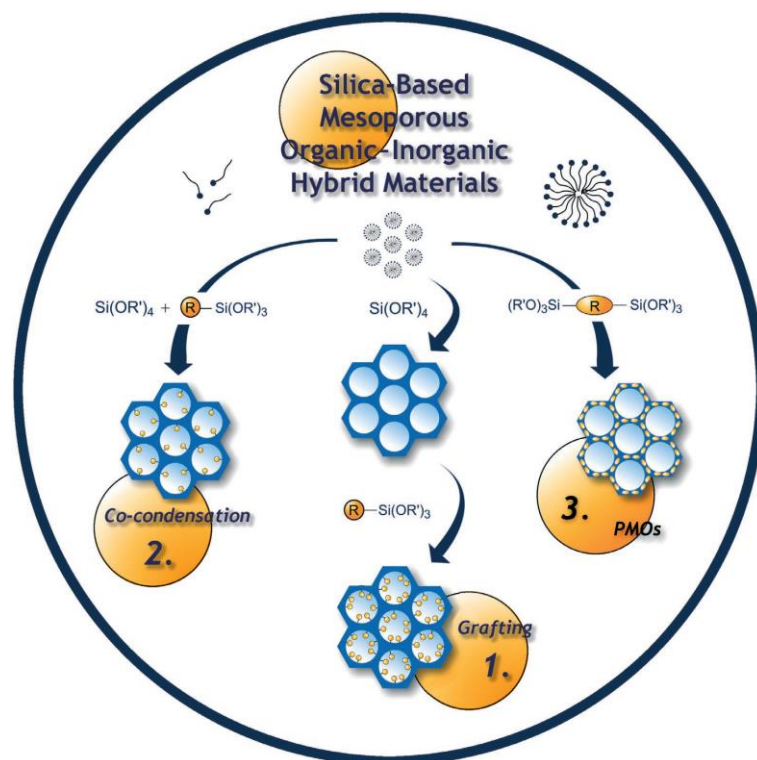


Figure 1.10 - Different approaches to create functionalized mesoporous silica materials [107]

Over the last years, mesoporous silica materials with uniform mesoporous channel structure and high specific surface areas, thermal stability, lightweight, and extending framework composition have been employed as supports to form novel robust heterogeneous catalysts. Different mesoporous silica families (SBA-n, MCM-n, HMS-n, etc.) have been used to create POMs based heterogeneous catalysts, mainly using the Keggin type POMs, and applied in ODS processes. The POM immobilization method (impregnation, sol-gel techniques, electrostatic interactions, ion-exchange or covalent bond) has revealed to be crucial to the structural robustness of these type of catalysts. [38, 44]

The use of POMs supported in silica materials as heterogeneous catalysts in a ODS process, is quite recent. In 2009, the monolacunary POM $(\text{C}_{19}\text{H}_{42}\text{N})_4\text{H}_3[\text{PW}_{11}\text{O}_{39}]$ was incorporated in a silica matrix *via* a co-condensation sol-gel methodology and the formed catalyst was tested in the desulfurization of a model diesel containing DBT (500 ppm) using H_2O_2 as oxidant ($\text{O/S}=4$) at 60°C . The catalyst revealed to be highly active and reusable; however, some leaching of the POM from the silica surface was detected resulting in some loss of activity during recycling cycles. [108] In the same year, $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ was immobilized on the surface of a Ag^+ modified mesoporous silica and applied in desulfurization of DBT model diesel and in real diesel. This heterogeneous

catalyst joined together the adsorptive capacity of the free Ag^+ centers and the catalytic capacity of the POM. The desulfurization of the real diesel presented some drawbacks because the presence of alkenes and aromatic hydrocarbons present in the diesel oil were adsorbed on the heterogeneous catalyst sites, which slightly decreased the efficiency of the catalyst. [109]

Since then, several approaches have been made to prepare efficient heterogeneous catalysts Keggin POM based silicas for ODS processes. Hu *et al.* immobilized $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ in silica magnetic nanoparticles functionalized with long cationic carbon chain by ionic interaction. The improvement of this approach resulted in the ease recover of the catalyst by the application of an external magnetic field. [100] In 2013, Yan *et al.* prepared a stable catalyst by incorporating $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$, by evaporation-induced self-assembly method, in a mesoporous silica containing titanium. [110]

In 2014 three other Keggin derivatives POMs were immobilized in silica supports. Cesium salts of tungsten-substituted molybdophosphoric acid $\text{Cs}_x\text{H}_{3-x}[\text{PMo}_{12-y}\text{W}_y\text{O}_{40}]$ with diverse Mo/W ratio were supported on platelet SBA-15 and applied in a ODS process using tert-butyl hydroperoxide (TBHP) as oxidant and without the presence of an extraction solvent to desulfurize a DBT model diesel. [111] $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ was also immobilized in a porous silica-alumina $\text{SiO}_2\text{-Al}_2\text{O}_3$ and the prepared catalyst was applied in BT desulfurization using MeCN as extraction solvent and H_2O_2 as oxidant. Balula and co-workers also reported for the first time, a zinc mono-substituted phosphotungstate encapsulated into silica nanoparticles using a cross-linked organic-inorganic core. This structural stable catalyst was tested in a model diesel containing DBT and 4,6-DMDBT using a biphasic system with MeCN as extraction solvent and H_2O_2 as oxidant. [43]

One year later (2015), POM-based ILs were successfully embedded into a silica matrix by hydrothermal process and employed in ODS process using a model diesel (1-BT, DBT and 4,6-DMDBT). The catalyst $[\text{C}_4\text{mim}]_3\text{PW}_{12}\text{O}_{40}/\text{SiO}_2$ had moderate hydrophilic–hydrophobic balanced surface leading to high sulfur removal. [112] A vanadium-substituted molybdophosphoric acid was supported on zirconium modified mesoporous silica (SBA-15) and its catalytic activity was evaluated in DBT desulfurization. [113]

More recently, the immobilization of different Keggin POMs in phosphazene-functionalized silica was performed by Craven *et al.*, [39] which were then used in desulfurization of several sulfur compounds (1-BT, DBT and 4,6-DMDBT).

Since the first application of Keggin POM based silica catalysts in ODS processes, the catalytic efficiency of these systems have been improved and currently total

conversion of DBT can be achieved after 30min under sustainable conditions. Table 1.4 summarizes the experimental conditions and the desulfurization results for the POM-based silica catalysts referred in this section.

Table 1.4 - Experimental conditions and desulfurization efficiency for the various POM-based silica catalysts applied in diesel desulfurization presented in this section.

Catalyst	Diesel (ppm S)	Oxidant	T (°C)	Time	Efficiency	Ref.
$(C_{19}H_{42}N)_4H_3[PW_{11}O_{39}]/SiO_2$	DBT in <i>n</i> -octane (500)	$H_2O_2/S=4$	60	90 min	100%	[108]
$Ag_2-H_3[PW_{12}O_{40}]/SiO_2$	DBT in petroleum ether (800)	$H_2O_2/S=12$	70	120 min	100%	[109]
MSN/AEM- $H_3[PW_{12}O_{40}]$	DBT in Decalin (434)	$H_2O_2/S=9$	50	22h	100%	[100]
$H_3[PW_{12}O_{40}]-TiO_2-SiO_2$	DBT in petroleum ether (1000)	$H_2O_2/S=12$	60	120 min	100%	[110]
$Cs_xH_{3-x}[PMo_8W_4O_{40}]/SBA-15$	DBT in <i>n</i> -hexane (505)	TBHP/S=5	60	60 min	100%	[111]
$K_5[PW_{11}Zn(H_2O)O_{39}]-aptes@SiO_2$	DBT and 4,6-DMDBT in <i>n</i> -octane (1000)	$H_2O_2/S=32$	50	180 min	93.4%	[43]
$[BMIM]_3[PW_{12}O_{40}]/SiO_2$	1-BT (250) or DBT(500) or 4,6-DMDBT (250) in <i>n</i> -octane	$H_2O_2/S=3$	60	30 min	1-BT-85.1% DBT-100% 4,6-DMDBT-100%	[112]
$H_3[PMo_{12}O_{40}]/BzPN-SiO_2$	1-BT or DBT or 4,6-DMDBT in heptane (1600 each)	$H_2O_2/S=3$	60	1-BT-6h DBT-3h 4,6-DMDBT-4h	1-BT-90% DBT-100% 4,6-DMDBT-100%	[39]

MSN: magnetic silica nanospheres; AEM: 3-(trimethoxysilyl)-propyldimethyloctadecyl ammonium chloride; TBHP: *tert*-Butyl hydroperoxide; BMIM: 1-Butyl-3-methylimidazolium; BzPN: benzyl aminophosphazene

1.6.2.2. Periodic mesoporous organosilicas

Periodic mesoporous organosilicas, known as PMOs, are attractive composite materials since they combine in a single solid both the properties of a rigid 3D silica network (high surface areas and pore volume, tunable pore size, highly ordered mesostructure) with the particular chemical reactivity of the organic component(s). [114] These recent materials (first synthesis in 1999), [115-117] are prepared through the surfactant-templated polycondensation of bridge silsesquioxane organic molecules with general formula $(R'O)_3-Si-R-Si-(OR')_3$, where R represents the organic bridging group and R' usually a methyl or ethyl group (Figure 1.9.). Their channel walls contain uniformly distributed inorganic and organic fragments bonded by covalent bonds of two or more terminal silyl groups. [118, 119] Several organic groups have been successfully incorporated within the PMOs pore walls such as methylene, phenylene, biphenylene,

thiophene, ferrocene etc. Besides, other groups bearing specific functions can also be incorporated in PMOs frameworks thereby creating bi(multi)-functionalized periodic mesoporous organosilicas (BPMOs). [106, 120-124]

In comparison with the SiO_2 -based mesoporous materials, PMOs exhibit some advantages such as tunable surface hydrophobicity/hydrophilicity and higher hydrothermal stability and mechanical stability, over their silica counterparts, due to the incorporation of high loading of organic moieties into their framework. [105, 106, 125] Moreover, while functional groups must be added to ordered mesoporous silicas, PMOs already possess organic functional moieties incorporated directly into the pore walls which overcome some problems related to grafting and co-condensation processes. The introduction of different organic bridges into the PMOs framework allowed its application in different areas such as, chromatography, bio-sensors, adsorption, controlled drug delivery systems and catalysis, being this last field undoubtedly one of their main applications. [106, 126-129] The use of PMOs as catalysts has been achieved by the introduction of different organic groups (BPMOs) and the incorporation of Bronsted acid sites, metal sites and metal complexes. [129] The incorporation of catalytic active species such as POMs in PMOs is practically unexplored and few examples are described in the literature. [130, 131] As so, the application of POM@PMOs in ODS processes is also an open field to explore.

1.6.2.3. Metal-organic frameworks

Metal-organic frameworks (MOFs) also called porous coordination polymers (PCPs) are a recent class of crystalline porous materials, comprising metallic centers linked by multidentate organic linkers into extended one-, two- or three-dimensional ordered networks. This new class of materials have gain an exponential development over the last twenty years, due to its high surface area and porosity, structural diversity and tailorability. As consequence of these unique features, a new generation of functional MOFs has emerged as excellent candidates in diverse technological and industrial applications such as gas storage and separation, guest exchange, sensors based in magnetic or optical proprieties, biomedicine [132, 133] and, in particular, catalysis has been one of the earliest fields of application. [134-137] Several MOFS have been reported in ODS processes acting as catalysts and as supports for active species such as POMS, these MOFs are presented in Table 1.5 with respective monomer units.

Table 1.5 - Metal organic frameworks applied in oxidative desulfurization processes.

Material	Monomer unit	Reference
HKUST-1	$\text{Cu}_3(\text{BTC})_2(\text{H}_2\text{O})_3$	[138]
MIL-100(Fe)	$\text{Fe}_3\text{O}(\text{H}_2\text{O})_2\text{F} \cdot \{\text{C}_6\text{H}_3(\text{CO}_2)_3\}_2 \cdot n\text{H}_2\text{O}$	[139]
MIL-101 (Cr)	$\text{Cr}_3\text{F}(\text{H}_2\text{O})_2\text{O}[(\text{O}_2\text{C})-\text{C}_6\text{H}_4-(\text{CO}_2)]_3 \cdot n\text{H}_2\text{O}$	[140]
MIL-125 (Ti)	$\text{Ti}_8\text{O}_8(\text{OH})_4(\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2)_6$	[141]
MIL-125 (Ti)-NH ₂	$\text{Ti}_8\text{O}_8(\text{OH})_4-(\text{O}_2\text{C}-\text{C}_6\text{H}_5-\text{CO}_2-\text{NH}_2)_6$	[142]
MOF-808	$\text{Zr}_6\text{O}_4(\text{OH})_4(-\text{CO}_2)_6(\text{HCOO})_6$	[143]
NENU-9	$[(\text{CH}_3)_4\text{N}]_2\{[\text{Cu}_2(\text{BTC})_{4/3}(\text{H}_2\text{O})_2]_6[\text{H}_3\text{PV}_2\text{Mo}_{10}\text{O}_{40}]\}$	[144]
TMU-10	$[\text{Co}_6(\text{oba})_5(\text{OH})_2(\text{H}_2\text{O})_2(\text{DMF})_4]_n \cdot 5\text{DMF}$	[145]
TMU-12	$[\text{Co}_3(\text{oba})_3(\text{O}) (\text{Py})_{0.5}]_n \cdot 4\text{DMF} \cdot \text{Py}$	[145]
UiO-66	$\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BDC})_{12}$	[146]
UMCM-309	$[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{BTB})_2(\text{OH})_6(\text{H}_2\text{O})_6]$	[147]
Zif-8	$\text{Zn}[\text{mIM}]_2$	[148]

BTC: 1,3,5-benzene-tricarboxylate; BDC: dicarboxylate; oba: 4,4'-oxybisbenzoic acid; Py: pyrazine; mIM: methylimidazole

1.6.2.3.1. Metal-organic frameworks as catalysts

The catalytic properties of a pristine MOF can be related to the presence of active sites generated by the choice of metal-connected nodes and/or of the bridge ligands. In addition, multiple catalytic active sites can also be added to enhance its catalytic activity. The generation of active sites can be accomplished by different ways: removal of labile solvent molecules of the MOF structure by exposing the metal site, creation of defects within their structures (Figure 1.11), introduction of functional organic sites during the construction of the frameworks, incorporation of catalytic guests molecules within the MOFs cavities. [135, 136]

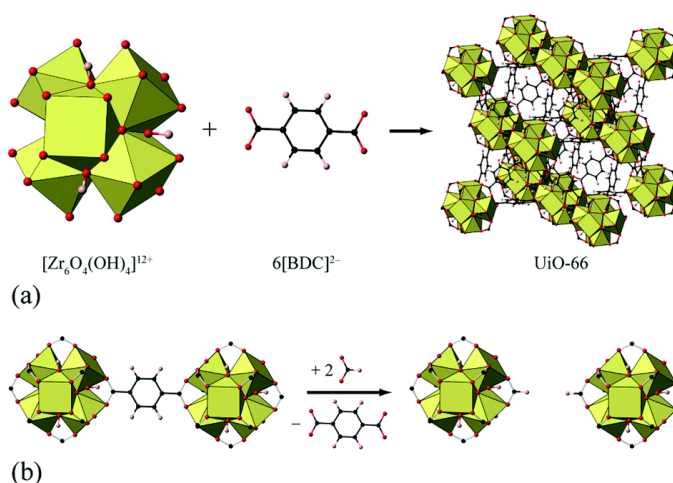


Figure 1.11 – a) structure of non-defective UiO-66 (UiO stands for University of Oslo) is comprised of $[\text{Zr}_6\text{O}_4(\text{OH})_4]$ clusters connected by terephthalate linkers. (b) Inclusion during framework synthesis of monocarboxylate modulators, can lead to correlated linker vacancies where a single terephthalate linker is replaced by two monocarboxylates in an opposing geometry. [149]

The employment of MOFs in ODS processes has been mainly as a support material for catalytic species such as POMs. The MOFs' properties improve the catalytic activity of active POMs, even without using any inherent activity of the MOF network. [1, 150, 151] However, some reports of MOFs acting as catalysts in ODS processes have also been described in the literature over the last few years.

A titanium based MOF (MIL-125: MIL stands for Material of Institute Lavoisier) and the amine functionalized MIL-125 (MIL-125-NH₂) were tested in DBT oxidation using cumene hydroperoxide (CHP) as oxidant. MIL-125 showed better catalytic performance in oxidative desulfurization of DBT, probably due to less steric hindrance to the active sites. [152] More recently, these two last catalysts (MIL-125 and MIL-125-NH₂) were also tested in H₂O₂-based ECODS system using a model diesel. The desulfurization rate of model diesel sulfur compounds increases in the order of 4,6-DMDBT < Th < BT < DBT. The best performance was attained by MIL-125 due to the presence of the amine group in MIL-125-NH₂ which prevented sulfur compounds from contacting with Ti active sites to a certain extent. The activity of MIL-125 had also been enhanced by the introduction of mesopores. [153]

Two cobalt-based MOFs (TMU-10 and TMU-12; TMU: Tarbiat Modares University) were also tested in a DBT model diesel (n-hexane as solvent) desulfurization. TMU-12 showed higher catalytic activity compared to TMU-10 possibly because of a difference in their coordinate Co centers and void space. Under optimized conditions almost complete desulfurization was achieved after 6 h. [145]

In 2018, Zhang *et al.* reported the application of the zirconium based MOF UiO-66 in desulfurization of several sulfur compounds (Th, BT, DBT, 4,6-DMDBT) using H₂O₂ as oxidant (O/S=12). Complete desulfurization of DBT was achieved after 150 min at 60 °C; however, the recycling tests revealed loss of catalytic activity after five consecutive ODS cycles, probably due to the sulfones adsorption in UiO-66 active sites. [154] During the same year, two other zirconium MOFs (UMCM-309, MOF-808) were used as catalysts for oxidative desulfurization of sulfur compounds using TBHP as oxidant. A post-synthetic approach, targeting the removal of the coordinated formed ligands was applied to further improve the catalytic activity of MOFs, resulting in the formation of additional open sites. The MOF-808-M exhibited high catalytic activity, as well as high selectivity and reusability. [150]

In short, the application of MOFs in ODS processes as catalyst is still limited, having been tested only in model diesel and more studies needed to be addressed in

order to improve the catalytic results. Table 1.6 summarizes the experimental conditions and the desulfurization results for MOFs acting as catalysts, referred in this section.

Table 1.6 - Experimental conditions and desulfurization efficiency for the various MOFs applied in diesel desulfurization presented in this section.

Catalyst	Diesel (ppm S)	Oxidant	T (°C)	Time	Efficiency	Ref.
MIL-125(Ti)	DBT in <i>n</i> -heptane (80%) and toluene (20%) (200)	CHP/S=15	60	180 min	36%	[152]
MIL-125(Ti)	Th, 1-BT, DBT or 4,6-DMDBT (240 each)	H ₂ O ₂ /S=8	60	240 min	Th ~70% 1-BT ~92% DBT ~100% 4,6-DMDBT~63%	[153]
TMU-12	DBT in <i>n</i> -hexane (500)	H ₂ O ₂ /S=3	60	8 h	75.2%	[145]
UIO-66(Zr)	Th, 1-BT, DBT or 4,6-DMDBT (500 each)	H ₂ O ₂ /S=12	60	180 min	Th ~47% 1-BT ~61% DBT ~100% 4,6-DMDBT~72%	[154]
MOF-808-M	1-BT, DBT or 4,6-DMDBT in toluene (500 each)	TBHP/S=2.5	60	8h	1-BT ~90% DBT ~98% 4,6-DMDBT~42%	[150]

1.6.2.3.2. Metal-organic frameworks as supports

MOFs with high surface area and permanent porosity are outstanding support candidates to accommodate catalytic active species, such as POMs. Several POM structures have been used to prepare POM-based MOF heterogeneous catalysts and the Keggin type have also been the most used. A strong effort has been made to immobilize active POMs in MOFs to prepare efficient heterogeneous catalysts. The most common methods are the impregnation [140] and one pot synthesis [155]. The impregnation method consists in a post-synthetic method, where the incorporation of POMs within the MOFs pores is made by their presence in a POM solution. In the one pot method, the MOF synthesis occurs in the presence of the POM.

An important breakthrough in POM based MOFs was the incorporation of lacunary phosphotungstate K₇[PW₁₁O₃₉] within the cages of 3D chromium terephthalate MIL-101(Cr), reported by Férey *et al* in 2005. [140] This MOF has a rigid crystal structure, large pores and surface area and also good stability. Latter, Kholdeeva and coworkers reported that some Keggin anions could be electrostatically bound to MIL-101(Cr) and applied as heterogeneous catalysts in oxidative reactions. [155] Since then the mesoporous MIL-100 (M) and -terephthalate MIL-101 families (M = Fe, Cr, Al) have been the most investigated host matrices.

The application of POM based MOFs catalysts in ODS processes is quite recent, dating from 2013, when Hu and coworkers [156] reported the preparation of different amounts of $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ encapsulated within the nanocages of MIL-101(Cr), via one-pot synthesis, and its application in the desulfurization of a model diesel containing sulfur compounds (1-BT, DBT and 4,6-DMDBT in *n*-heptane). The catalyst with higher loading of POM (50% $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\text{@MIL-101}$) revealed to be the best in the desulfurization of the model diesel. The catalyst was recovered and recycled in four consecutive cycles with a slight decrease of catalytic activity probably due to some leaching of the POM. Balula's research group also reported several works where the MIL-101(Cr) was used to incorporate other POMs, via impregnation method, and applied in ODS processes. [1, 40, 151, 157] These studies were conducted in biphasic liquid-liquid systems with an extraction solvent immiscible with the diesel phase. The evaluation and optimization of the extractive and catalytic components of the ODS processes were performed and complete desulfurization of multicomponent model diesel was achieved after a few hours. The amine-functionalized MIL-101(Cr)- NH_2 was also used to impregnate POM active species and these were applied in ECODS systems. [40, 158] The catalyst ($\text{H}_3[\text{PW}_{12}\text{O}_{40}]\text{@MIL-101(Cr)-NH}_2$) presented high catalytic activity and could be easily separated and recycled several times without leaching or apparent loss of activity. More recently a new hybrid material was synthesized via phosphotungstic acid template self-construction of MIL-101(Cr) in the pore of diatomite, to prevent POM leaching to the solution. [159]

Besides the MIL-101(Cr), other MOFs have been used as supports for catalytic active POMs species such as Cu-BTC frameworks (BTC = 1,3,5-benzenetricarboxylate), also known as HKUST-1 (HKUST stands for Hong-Kong University of Science and Technology), and others as the NENU-n (Northeast Normal University) series and the UiO family. [59, 160]. The UiO family is built up from $\{\text{Zr}^{\text{IV}}_6\text{O}_4(\text{OH})_4\}$ oxocluster nodes and linear dicarboxylate is also one of the most studied MOFs in the last few years. [160]

Liu *et al.* encapsulate $\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}$ within the pores of a MOF structure in which the organic ligands act as hydrophobic groups (NENU-9) and then studied its desulfurization ability in a model and real diesels. [144] Rafiee and Nobakht reported the encapsulation of several Keggin heteropolyacids in HKUST-1 for selective oxidation of sulfides and deep desulfurization of model fuels. [161] Wang *et al.* encapsulate $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$, via one-pot synthesis, in different robust MOFs including MIL-100(Fe), UiO-66 and ZIF-8 (Zeolitic Imidazolate Framework) and studied the correlations between the desulfurization activity, in model and real gasolines, and the window size of used MOFs.

[162] The mesoporous MIL-100(Fe) with larger window size revealed to be the best in the desulfurization of model diesel containing 1-BT, DBT and 4,6-DMDBT, as well as in the recycling experiments. Recently in 2018, a heterogeneous catalyst was prepared, also *via* one-pot synthesis, with $H_3[PW_{12}O_{40}]$ and UiO-67 to be used in a ECODS system. The heterogeneous catalyst revealed high catalytic activity in the desulfurization of a model diesel containing 1-BT, DBT and 4,6-DMDBT and could be recycled during eight consecutive cycles without significant loss of catalytic activity. [163] Table 1.7 summarizes the experimental conditions and the desulfurization results for POM-based MOFs, referred in this section.

Table 1.7 - Experimental conditions and desulfurization efficiency for the various POM-based metal-organic frameworks applied in diesel desulfurization presented in this section.

Catalyst	Diesel (ppm S)	Oxidant	T (°C)	Time	Efficiency	Ref.
$H_3[PW_{12}O_{40}]@MIL-101(Cr)$	DBT in <i>n</i> -heptane (640)	$H_2O_2/S=50$	50	6h	99%	[156]
$K_{11}[Tb(PW_{11}O_{39})_2]@MIL-101(Cr)$	1-BT, DBT and 4,6-DMDBT in <i>n</i> -octane (1500)	$H_2O_2/S=21$	50	3h	98.9%	[1]
$H_3[PMo_{12}O_{40}]@NH_2-MIL-101(Cr)$	1-BT, DBT, 4-MDBT and 4,6-DMDBT in <i>n</i> -octane (2000)	$H_2O_2/S=6$	50	2h	95%	[40]
	untreated diesel (2300)				80%	
$[C_4H_9)_4N]_3[PW_{12}O_{40}]@MIL-101(Cr)$	1-BT, DBT and 4,6-DMDBT in <i>n</i> -octane (1992)	$H_2O_2/S=21$	50	2h	98.7%	[151]
$Na_9[PW_9O_{34}]@MIL-101(Cr)$	1-BT, DBT and 4,6-DMDBT in <i>n</i> -octane (1707)	$H_2O_2/S=21$	50	1h	99.7%	[157]
$H_3[PW_{12}O_{40}]@NH_2-MIL-101(Cr)$	1-BT, DBT or 4,6-DMDBT in <i>n</i> -heptane (950 each)	$H_2O_2/S=4$	50	1h	DBT 100%	[158]
		$H_2O_2/S=10$			1-BT ~70.5% 4,6-DMDBT ~88.2%	
$H_3[PW_{12}O_{40}]@MIL-101(Cr)$ -diatomite	DBT in <i>n</i> -heptane (500)	$H_2O_2/S=5$	60	2h	98.6%	[159]
NENU-9	DBT in decalin (500)	O_2 (bubbled)	80	1.5h	100%	[144]
	Prehydrotreated gasoline					
$H_3[PMo_{12}O_{40}]@HKUST-1$	Th, MPS and DBT in <i>n</i> -hexane (1000)	$H_2O_2/S=6$	65	3h	92%	[161]
$H_3[PW_{12}O_{40}]@MIL-100(Fe)$	1-BT, DBT or 4,6-DMDBT in <i>n</i> -heptane (950 each)	$H_2O_2/S=4$	70	24h	1-BT 61.8% DBT 100% 4,6-DMDBT 92.8%	[162]
	untreated gasoline (473)				85%	
$H_3[PW_{12}O_{40}]@UiO-66$	1-BT, DBT or 4,6-DMDBT in <i>n</i> -heptane (950 each)	$H_2O_2/S=4$	70	24h	1-BT 94.8% DBT 100% 4,6-DMDBT 39.1%	
	untreated gasoline (473)				75%	
$H_3[PW_{12}O_{40}]@UiO-67$	1-BT, DBT or 4,6-DMDBT in <i>n</i> -heptane (1000 each)	$H_2O_2/S=13$	70	1h	1-BT 75% DBT 99.5% 4,6-DMDBT 85%	[163]

1.7. General plan

The work presented in this thesis has as main goal the development of efficient heterogeneous catalysts for oxidative desulfurization processes (ODS), to prepare low-sulfur diesel. To achieve this, the developed work was focused in three main targets: i) preparation of novel catalysts; ii) optimization of oxidative catalytic systems; iii) application of optimized ODS systems to deep desulfurization of untreated real diesel.

The Keggin phosphotungstate and the Keggin derivatives presented in 1.5.1.1 were selected as active catalytic centers. The catalytic activity of the active centers was investigated/analyzed following different approaches to prepare POM based catalysts with high ODS performance (figure 1.9):

- i) **Homogeneous catalysts:** the counter-cation of potassium salt prepared POMs was replaced by ionic-liquid cations or by quaternary amine counter-cation (tetrabutylammonium);
- ii) **Heterogeneous catalysts** were prepared using three methodologies:
 - ii.i) solidification method, by combining POMs and long-carbon chain lengths, using octadecyltrimethylammonium (ODA) counter-cation, forming solid hybrid catalysts;
 - ii.ii) immobilization on the surface of strategic functionalized support materials based in SBA-15 mesoporous silica, and periodic mesoporous organosilica (PMOs), forming novel POM@SBA-15, POMs@PMOs composites;
 - ii.iii) incorporation into a metal-organic framework (UiO-66-NH₂), forming new POMs@MOFs composites.

All compounds and materials were characterized by several solid-state techniques. The catalytic performance of catalysts was studied, initially using model diesel containing various sulfur compounds. Three different model diesels were prepared by dissolving refractory sulfur compounds in n-octane, with a concentration of approximately 500 ppm of S for each compound:

Model diesel A (~1500 ppm S): (1-BT, DBT and 4,6-DMDBT);

Model diesel B (~2000 ppm S): (1-BT, DBT, 4-MDBT and 4,6-DMDBT);

Model diesel C (~1500 ppm S): (DBT, 4-MDBT and 4,6-DMDBT).

Further studies with the most efficient catalysts were used in ODS processes of untreated real diesels:

Galp diesel (2300 ppm S) containing mainly benzothiophenes and dibenzothiophenes derivatives;

CEPSA diesel (1335 ppm S) containing mainly dibenzothiophenes derivatives.

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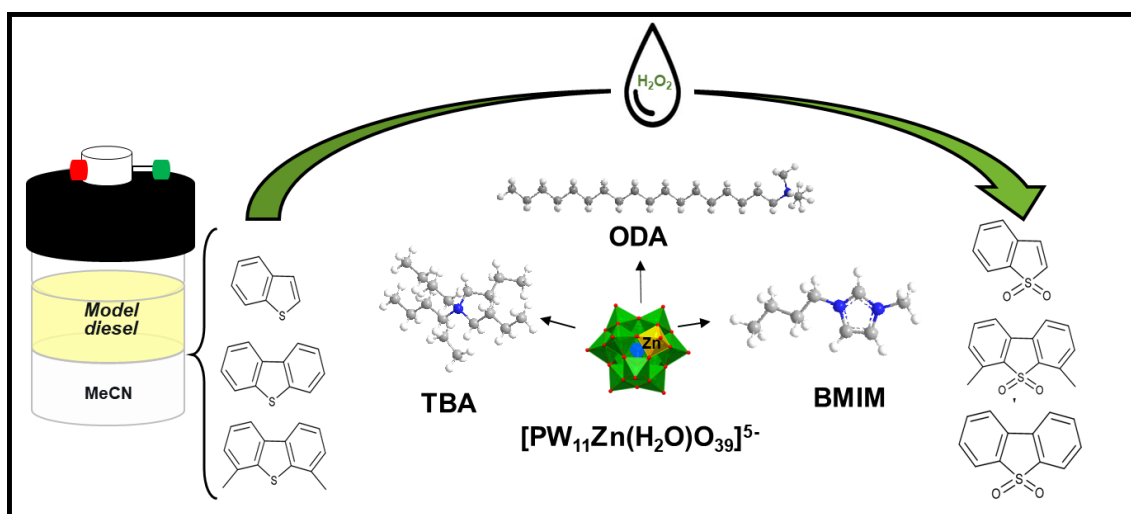
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Chapter 2

Catalytic oxidative/extractive desulfurization of model and untreated diesel using hybrid based zinc-substituted polyoxometalates^{1,2}



¹ Adapted from: Susana O. Ribeiro, Diana Julião, Luís Cunha-Silva, Valentina F. Domingues, Rita Valença, Jorge C. Ribeiro, Baltazar de Castro, Salete S. Balula, *Catalytic oxidative/extractive desulfurization of model and untreated diesel using hybrid based zinc-substituted polyoxometalates*, Fuel, 166 (2016) 268-275, doi:10.1016/j.fuel.2015.10.095.

² Susana O. Ribeiro contribution to the publication: Preparation and characterization of zinc mono-substituted polyoxometalates containing different cationic surfactants; investigation of their catalytic performance in the desulfurization of model diesel and also of a high-sulfur content real diesel (supplied by Galp); manuscript preparation.

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Chapter 2

Catalytic oxidative/extractive desulfurization of model and untreated diesel using hybrid based zinc-substituted polyoxometalates

Abstract

The desulfurization efficiency of various hybrid zinc-substituted polyoxometalates ($[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$, abbreviated as PW_{11}Zn) was here investigated and optimized using sustainable systems coupling the liquid-liquid extraction and the oxidative catalytic process (ECODS). Initially, the desulfurization studies were performed using a model diesel containing a mixture of the most refractory sulfur compounds and later extended to an untreated real diesel. In both cases, acetonitrile was used as the extraction solvent and aqueous H_2O_2 as the oxidant. High degree of desulfurization was achieved using either model or untreated diesels, after few hours. The quaternary ammonium catalysts $[\text{TBA}]\text{PW}_{11}\text{Zn}$ (TBA: tetrabutylammonium) and $[\text{ODA}]\text{PW}_{11}\text{Zn}$ (ODA: octadecyltrimethylammonium) showed higher catalytic desulfurization efficiency than the ionic liquid catalyst $[\text{BMIM}]\text{PW}_{11}\text{Zn}$ (BMIM: 1-n-butyl-3-methylimidazolium). The $[\text{TBA}]\text{PW}_{11}\text{Zn}$ behaved as a homogeneous catalyst confined in the extraction solvent, while $[\text{ODA}]\text{PW}_{11}\text{Zn}$ with the long carbon chain behaved as a heterogeneous catalyst capable to be recovered from the system. Both quaternary ammonium catalysts were successfully reused/recycled for various consecutive desulfurization cycles.

2.1 Introduction

Polyoxometalates (POMs) have received special interest in oxidative desulfurization because they have showed high sulfur removal efficiency due to their unique features. [1-3] The catalytic activity of Keggin POM compounds $Q_n[XM_{12}O_{40}]^{p-}$ is strongly influenced by the nature of the counter-cation Q, the central atom X and the metal M. [4-6] At present, new organic-inorganic hybrid materials based in Keggin-type POMs and various organic cations have aroused worldwide attention, especially for the application in oxidative desulfurization (ODS) processes. [7-14] Modifications of POMs with organic units have been applied as an efficient strategy to achieve POMs-based hybrid catalysts with higher catalytic efficiency and recovery and reusability capacity. Different organic groups such as ionic liquids, [13, 15-19] organic polymers [20-22] and surfactants with different carbon-chain lengths [1, 7-10, 14, 23-27] have been applied, leading to improved catalytic activity and possibility to be recycled. The cationic surfactant octadecyldimethylammonium with the long alkyl chain attached to the POM active catalyst center, may act as a dynamic trap to enhance the probability of interaction between substrate, oxidant and catalyst center, what will increase the catalytic efficiency. [1, 7-10, 14, 27, 28] The formed POM amphiphilic structures based on surfactant molecules not only increase the catalyst activity but also provide easy and fast catalyst recovery from reaction system. [1, 7-10, 14, 27, 28] On the other hand, the high-valence POMs anions have been employed as counter negative ions for ionic liquids (ILs), producing new ILs with catalytic activity. Some studies in the literature demonstrate that the resulting ILs based POMs are highly active catalysts, possible to be recovered and reusable. [13, 29] Some of these ILs based POMs were synthesized from imidazole ionic liquids, such as 3-methylimidazolium [4-8, 11, 13, 25]. However, only a couple of examples were reported in the literature using ILs based POMs for ODS systems. [11, 12].

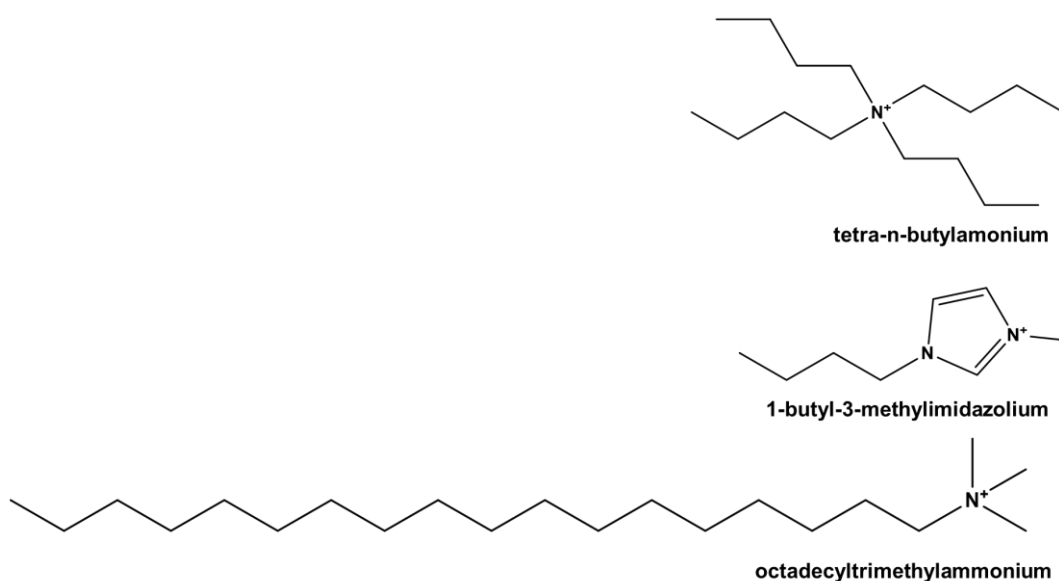
Recently, it has been reported the efficiency of zinc-substituted POM ($[PW_{11}Zn(H_2O)O_{39}]^{5-}$ (abbreviated as $PW_{11}Zn$) for olefin oxidation and for ODS processes, using H_2O_2 as oxidant. In these studies the catalytic performance of $PW_{11}Zn$ was investigated with this active center was encapsulated into the metal-organic framework MIL-101(Cr) support [30] or encapsulated into silica nanoparticles [31]. In the present work, different hybrid organic- $PW_{11}Zn$ compounds have been prepared based in the cationic surfactant ODA and the cationic 1-butyl-3-methylimidazolium (BMIM) to form $[BMIM]PW_{11}Zn$ ionic liquid. The catalytic performance of these hybrid $PW_{11}Zn$ based compounds was investigated in the desulfurization of multicomponent model diesel A (1-

benzothiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene in *n*-octane; containing approximately 1500 ppm S) and also using an untreated diesel supplied by Galp (2300 ppm S).

2.2. Results and discussion

2.2.1. Hybrid catalysts characterization

The potassium salt of the zinc-substituted polyoxometalate $[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$ ($\text{K}_5[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}] \cdot n\text{H}_2\text{O}$ (KPW_{11}Zn)) was initially prepared and used as precursor for the preparation of various hybrid based PW_{11}Zn : $(\text{C}_4\text{H}_9)_4\text{N}^+\text{H}[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 4\text{H}_2\text{O}$ ($[\text{TBA}]\text{PW}_{11}\text{Zn}$), $(\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3)_5[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 4\text{H}_2\text{O}$ ($[\text{ODA}]\text{PW}_{11}\text{Zn}$) and $(\text{C}_8\text{H}_{15}\text{N}_2)_5[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}] \cdot 4\text{H}_2\text{O}$ ($[\text{BMIM}]\text{PW}_{11}\text{Zn}$) (Scheme 2.1).



Scheme 2.1 – Representation of the chemical structure of the used counter-cations.

The FT-IR spectra of these compounds (Figure 2.1) display the characteristic asymmetric vibration bands of the Keggin-type frameworks: $\nu_{\text{as}}(\text{P}-\text{O})$ between 1090–1050 cm^{-1} , terminal $\nu_{\text{as}}(\text{W}-\text{O}_{\text{t}})$ at ca. 956-948 cm^{-1} , corner-sharing $\nu_{\text{as}}(\text{W}-\text{O}_{\text{b}}-\text{W})$ at ca. 890-882 cm^{-1} , and edge-sharing $\nu_{\text{as}}(\text{W}-\text{O}_{\text{e}}-\text{W})$ at ca. 826-800 cm^{-1} . [32] The similarity of the FT-IR spectra between the KPW_{11}Zn and the hybrid $[\text{TBA}]\text{PW}_{11}\text{Zn}$, $[\text{ODA}]\text{PW}_{11}\text{Zn}$ and $[\text{BMIM}]\text{PW}_{11}\text{Zn}$ indicates that the structure of the zinc-substituted phosphotungstate remains intact after assembling with the organic cations. The bands at 2962, 2936, 2874

and 1484 cm^{-1} are characteristic to the vibrations of the quaternary ammonium cation. [33] The bands observed at 2918 , 2850 , 2362 and 1468 cm^{-1} for $[\text{ODA}]\text{PW}_{11}\text{Zn}$ can identify the organic surfactant cation. [23] In addition, the bands observed between 3068 and 2872 cm^{-1} and also the bands between 1654 and 1338 cm^{-1} are attributed to the ionic liquid cation. [17]

The amount of organic cations per mole of POM was determined by the elemental analysis of C, H and N. By thermogravimetric analysis (Figure 2.2) was possible to quantify the presence of hydration water molecules, as well as to identify the water molecule coordinated to the zinc-substituted center. Four water molecules were found for all hybrid POMs, corresponding to the weight loss observed below 150 , 130 and $120\text{ }^{\circ}\text{C}$ for $[\text{TBA}]\text{PW}_{11}\text{Zn}$, $[\text{ODA}]\text{PW}_{11}\text{Zn}$ and $[\text{BMIM}]\text{PW}_{11}\text{Zn}$, respectively. The coordinated water molecule was identified for all hybrid POMs by the weight loss observed in the temperature range 150 - 225 , 130 - 190 and 120 - $295\text{ }^{\circ}\text{C}$ for $[\text{TBA}]\text{PW}_{11}\text{Zn}$, $[\text{ODA}]\text{PW}_{11}\text{Zn}$ and $[\text{BMIM}]\text{PW}_{11}\text{Zn}$, respectively.

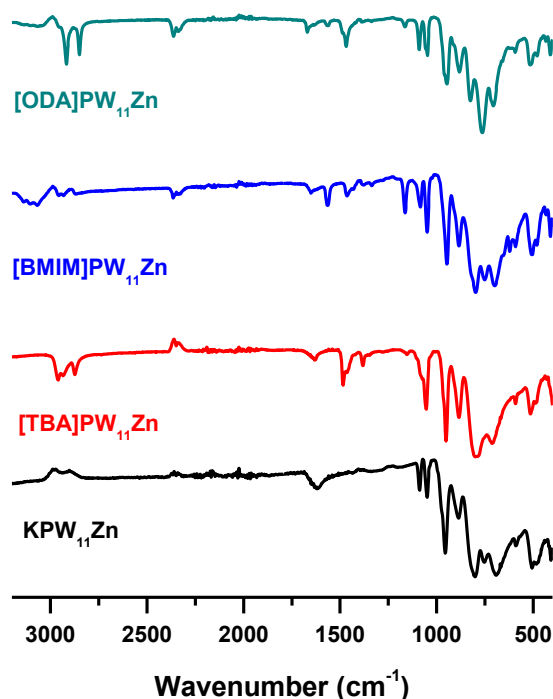


Figure 2.1 - FT-IR spectra of the KPW_{11}Zn and the hybrid zinc substituted polyoxometalates: $[\text{TBA}]\text{PW}_{11}\text{Zn}$, $[\text{ODA}]\text{PW}_{11}\text{Zn}$ and $[\text{BMIM}]\text{PW}_{11}\text{Zn}$.

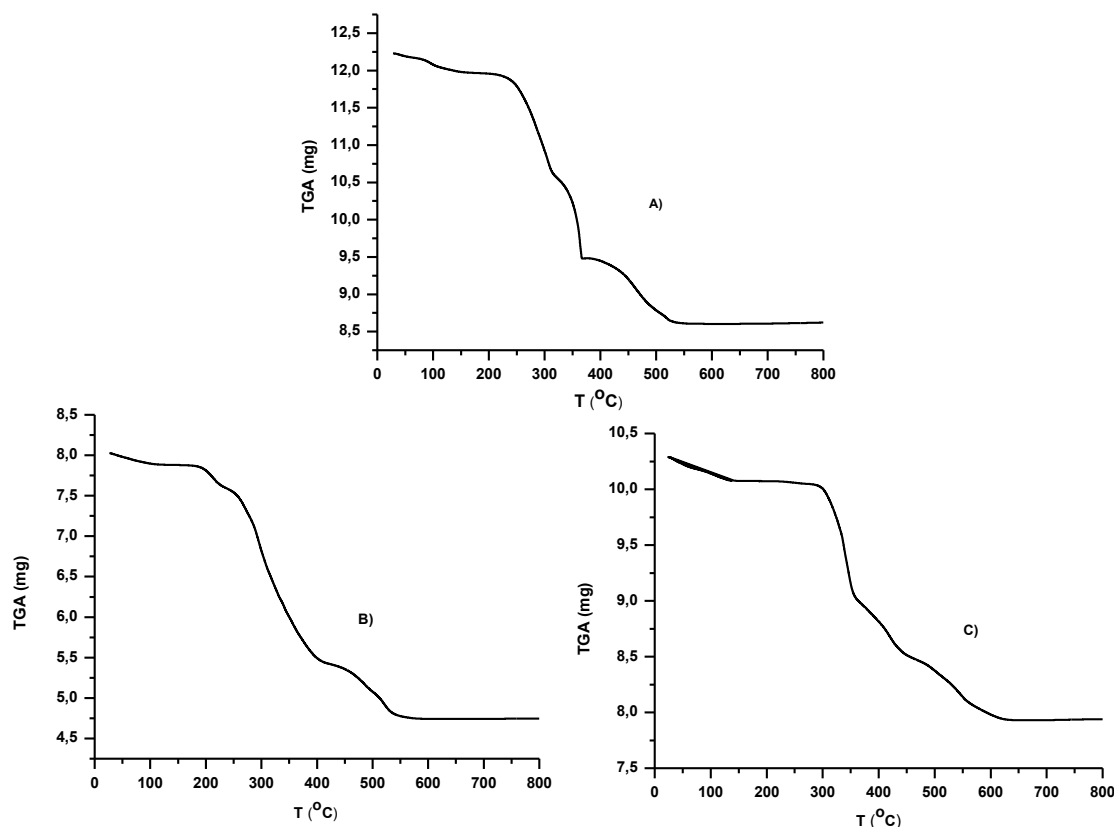


Figure 2.2 - TGA curves of A) [TBA]PW₁₁Zn, B) [ODA]PW₁₁Zn and C) [BMIM]PW₁₁Zn

The KPW₁₁Zn and hybrid zinc-substituted POMs were also characterized by ³¹P NMR (Figure 2.3). A single peak was observed for each zinc-substituted compound. The spectrum of KPW₁₁Zn in D₂O solution exhibits one signal at $\delta = -11.41$ ppm. The same characteristic ³¹P NMR single peak was observed by Johnson and Stein. [34] For the [TBA]PW₁₁Zn in CD₃CN the ³¹P NMR analysis presented the same single peak at -10.65 ppm what confirm the previous result obtained by our research group. [30] Also only one single peak was found for [BMIM]PW₁₁Zn in CD₃CN solution at -11.41 ppm. Solid ³¹P MAS NMR analysis of [ODA]PW₁₁Zn resulted a single peak at -12.39 ppm. These results confirm that the integrity of the PW₁₁Zn structure was maintain after exchanging the potassium cation by a larger organic cation (Figure 2.3). On the other hand, it is also possible to verify that the nature of the cation has some influence on the environment around the central phosphorus atom, as the chemical shift vary with the nature of the cation.

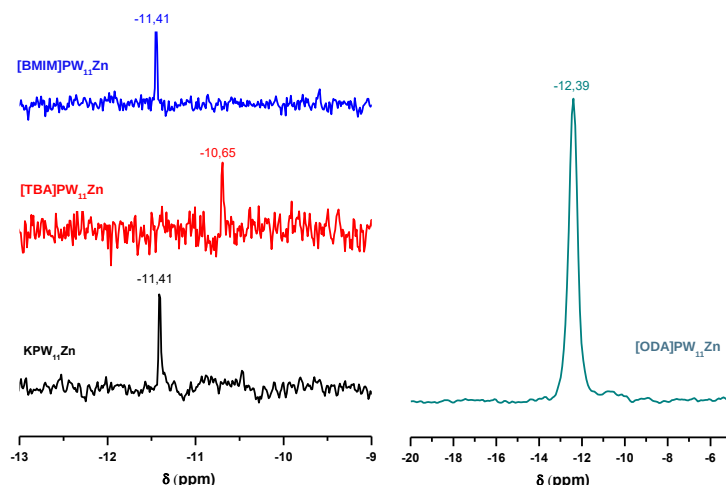


Figure 2.3 - A) ^{31}P NMR spectra of the KPW_{11}Zn in D_2O , $[\text{TBA}]\text{PW}_{11}\text{Zn}$ and the $[\text{BMIM}]\text{PW}_{11}\text{Zn}$ in CD_3CN **B)** ^{31}P MAS NMR spectra of $[\text{ODA}]\text{PW}_{11}\text{Zn}$

2.2.2. Biphasic extractive and catalytic oxidative desulfurization (ECODS) using a model diesel

The ECODS studies were performed using the model diesel A (see Chapter 1 section 1.7). The desulfurization of model diesel was carried out in the presence of H_2O_2 as oxidant and using MeCN as extraction solvent. The ECODS processes were investigated using a biphasic system between two immiscible liquid-liquid phases, the model diesel and an extraction solvent, with equal volume ratio. The ECODS system is performed in two main steps: the initial extraction and the catalytic oxidative stage. Initially, the extraction of the non-oxidized sulfur compounds from the model diesel to the MeCN phase occurs during 10 min at 50 °C. After this time, the distribution the sulfur compounds between the two phases achieve the equilibrium and the desulfurization of the model diesel stopped. To continue the desulfurization of the model diesel, the oxidant H_2O_2 was added to the ECODS system to oxidize the sulfur components present in the MeCN phase to the corresponding sulfones and/or sulfoxides, which promote a continue transfer of more sulfur compounds from the model diesel to the MeCN extraction phase. No oxidative products were detected in the model diesel phase what suggest that the catalytic oxidative reaction must only occur in the MeCN extractive phase. Furthermore, no further desulfurization of the model diesel occurred after the initial extraction phase in the presence of H_2O_2 and absence of the hybrid- PW_{11}Zn catalyst.

2.2.2.1. Optimization of ECODS system

An initial optimization using the model diesel was performed with the [TBA]PW₁₁Zn catalyst. The influence of various parameters was investigated, such as catalyst and oxidant amounts and reaction temperature, in order to achieve the best operation conditions.

Different amounts of [TBA]PW₁₁Zn were used in the ECODS process: 1, 3, 9 and 12 μmol , maintaining all the other reaction conditions (temperature 50 °C, 75 μL of oxidant; $\text{H}_2\text{O}_2/\text{S} = 21$), 0.75 mL of multicomponent model diesel and 0.75 mL of MeCN extraction solvent). The desulfurization of each sulfur compound during the initial extraction step seemed to do not differ with the various amounts of [TBA]PW₁₁Zn catalyst. In fact, as described in the literature, the simple liquid-liquid diesel/MeCN extraction of DBT and 1-BT is higher than 4,6-DMDBT. This is due to the lower molecular dimension of 1-BT and the higher solubility of DBT in MeCN. [35]

In Figure 2.4 is displayed the efficiency obtained with different amounts of [TBA]PW₁₁Zn catalyst during the catalytic oxidative stage of the ECODS. It is possible to observe that the highest desulfurization in shorter time was achieved using 9 μmol of catalyst. However, after 4 h of the ECODS process practically complete desulfurization was found in the presence of 3, 9 and 12 μmol of catalyst. Using only 1 μmol of catalyst the desulfurization is much lower than with 3 μmol ; however, the difference of activity using 3 and 12 μmol is only significant during the first hour of the process.

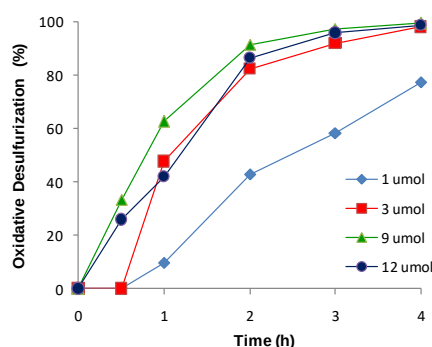


Figure 2.4 - Kinetic profile, after the initial extraction step, for the oxidative catalytic stage of the desulfurization process using the model diesel (0.75 mL), catalyzed by different amounts of [TBA]PW₁₁Zn catalyst, in the presence of MeCN as extraction solvent (0.75 mL) and H_2O_2 as oxidant ($\text{H}_2\text{O}_2/\text{S} = 21$), at 50°C.

Figure 2.5 displays the desulfurization for each sulfur compound after 4 h in the presence of the different amounts of [TBA]PW₁₁Zn. It is possible to observe that the 1-BT is the most difficult sulfur compound to remove from diesel and consequently the

most difficult to oxidize. The desulfurization of DBT and 4,6-DMDBT is similar in the presence of 3, 9 and 12 μmol , but considerable different in the presence of 1 μmol of catalyst. In fact, the oxidative reactivity order $\text{DBT} > 4,6\text{-DMDBT} > 1\text{-BT}$ is well described in the literature and is related to the electronic density at the sulfur atom and to some steric hindrance. [17, 36, 37]

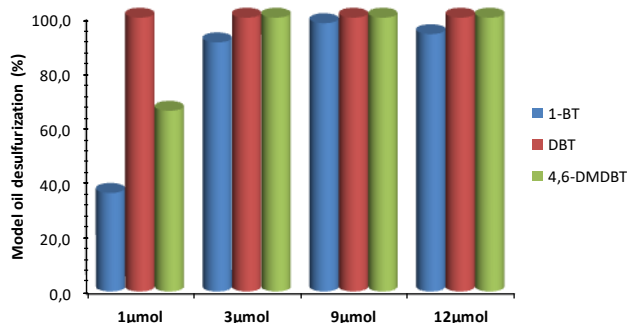


Figure 2.5 - Desulfurization data obtained for each sulfur compound present in the model diesel after 4 h at 50°C, in the presence of H_2O_2 as oxidant and catalyzed by different amounts of $[\text{TBA}]\text{PW}_{11}\text{Zn}$.

The influence of the oxidant amount was also investigated using 0.33 and 0.66 mmol of H_2O_2 . These different amounts of oxidant were added to the ECODS system after the initial extraction step, maintaining the temperature at 50 °C, using 9 μmol of $[\text{TBA}]\text{PW}_{11}\text{Zn}$ catalyst and 1:1 volume ratio of diesel/MeCN liquid-liquid system (0.75 mL of each). Figure 2.6 display the desulfurization profile of the multicomponent diesel using different amount of H_2O_2 and also in the absence of oxidant. It is possible to observe that the presence of oxidant is crucial to maintain desulfurization after the initial extraction step. Also, the higher desulfurization was obtained using higher H_2O_2 amount, since after 3 h of the process only 10 ppm of sulfur was present in the model diesel using 0.66 mmol of oxidant, instead of 230 ppm still present when 0.33 mmol were used. Total desulfurization was achieved after 4 h using 0.66 mmol of H_2O_2 ; however, still 185 ppm of sulfur was present when lower amount of oxidant was used.

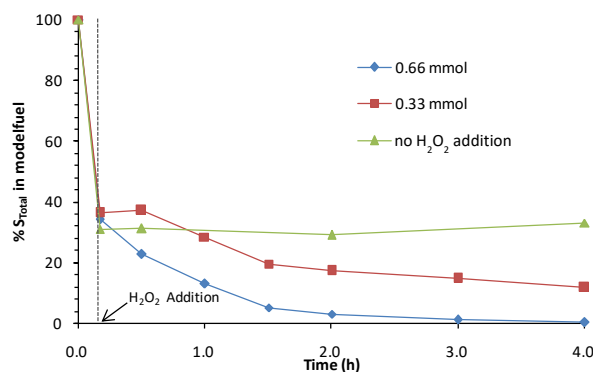


Figure 2.6 - Desulfurization profile of a multicomponent model diesel in the presence of MeCN as extraction solvent, at 50 °C, catalyzed by [TBA]PW₁₁Zn (9 μmol), using different amounts of oxidant H₂O₂.

The optimized model diesel/MeCN ECODS system, *i.e.* using 9 μmol of [TBA]PW₁₁Zn catalyst and 0.66 mmol of oxidant (H₂O₂/S=21), was also studied at room temperature. The comparison of the desulfurization profile obtained at room temperature and at 50 °C is presented in Figure 2.7. While the initial extraction of sulfur from model diesel to MeCN extraction phase was not drastically affected by the temperature (total initial sulfur extraction of 62 and 66% obtained at room temperature and at 50 °C, respectively), remarkable differences of desulfurization efficiency were found during the oxidative catalytic stage of the process at room temperature and at 50 °C. After 4 h of the ECODS process at room temperature only 72% of desulfurization occurred, instead of the total desulfurization observed at 50 °C.

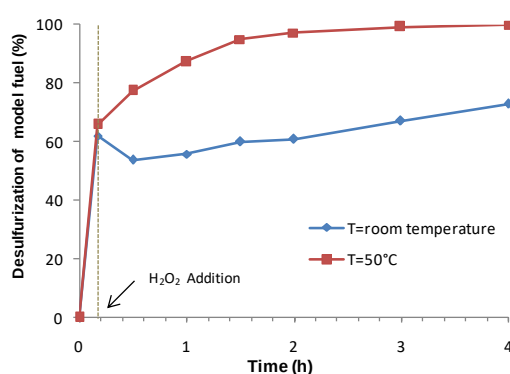


Figure 2.7 - Desulfurization profile of a multicomponent model diesel in the presence of MeCN as extraction solvent, at 50 °C and at room temperature, catalyzed by [TBA]PW₁₁Zn (9 μmol) and using H₂O₂/S=21.

2.2.2.2. Comparison of desulfurization efficiency between hybrid $PW_{11}Zn$ catalysts

The previous optimized conditions were used to investigate the desulfurization performance of other $PW_{11}Zn$ catalysts based on the ionic liquid $[BMIM]PW_{11}Zn$ and the surfactant $[ODA]PW_{11}Zn$. The desulfurization profile of these catalysts (9 μmol of each) were compared with the previous $[TBA]PW_{11}Zn$ using the biphasic liquid-liquid model diesel/MeCN system, in the presence of 0.66 mmol of H_2O_2 at 50 °C (Figure 2.8).] The initial extraction of sulfur compounds from model diesel to the MeCN phase was similar in the presence of the different hybrid catalytic ODS systems, before the addition of oxidant (total sulfur desulfurization of 65.8, 58.8 and 68.6% for $[TBA]PW_{11}Zn$, $[BMIM]PW_{11}Zn$ and $[ODA]PW_{11}Zn$, respectively). Wang et al. have referred that the long carbon chain of the quaternary ammonium cations from the hybrid catalysts could facilitate the adsorption of sulfide molecules on its long alkyl chains, which facilitate the desulfurization; [10] however, this behavior was not observed here and the extraction of non-oxidized sulfur compounds from model diesel was similar in the presence of a short carbon chain as TBA and the long carbon chain as ODA cations.

When the desulfurization efficiency of the various hybrid catalysts was evaluated conciliating the extractive and catalytic properties of the ODS system, it was found that the lowest desulfurization performance was observed using the IL $[BMIM]PW_{11}Zn$, while the highest performance was found using the $[TBA]PW_{11}Zn$. After the addition of the oxidant, during the first 2 h of the catalytic stage a significant difference of catalytic performance is observed between the $[BMIM]PW_{11}Zn$, $[TBA]PW_{11}Zn$ and $[ODA]PW_{11}Zn$. Also using the $[BMIM]PW_{11}Zn$ catalyst was possible to observe a decrease on the rate of desulfurization during the first minutes of the catalytic stage of the process, probably caused by the introduction of water from the aqueous oxidant in the ECODS process and also by the lower catalytic activity of this catalyst. This behavior was previously observed by our group using the biphasic liquid-liquid system. [38] After 4 h of the process, the complete desulfurization of the model diesel was achieved in the presence of $[TBA]PW_{11}Zn$, while only 91% and 89% were achieved using $[ODA]PW_{11}Zn$ and $[BMIM]PW_{11}Zn$ catalysts, respectively.

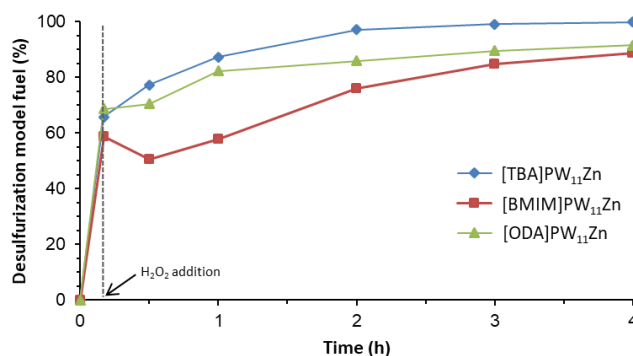


Figure 2.8 - Profile of desulfurization of a multicomponent model diesel catalyzed by various hybrid PW₁₁Zn based catalysts (9 μ mol), in the present of MeCN as extraction solvent, at 50 °C and using 0.66 mmol of H₂O₂.

In Table 2.1 is presented the desulfurization percentage for each sulfur compound during the catalytic oxidative stage. After 1 h of the process, the DBT is almost complete desulfurized from the model diesel and the 4,6-DMDBT was also largely removed when the [TBA]PW₁₁Zn and the [ODA]PW₁₁Zn were used as catalysts. Using the [BMIM]PW₁₁Zn only 10% of DBT was oxidized and removed from model diesel during the first hour of the oxidative catalytic stage. After the 4 h, the desulfurization of the model diesel is not completed in the presence of [ODA]PW₁₁Zn and [BMIM]PW₁₁Zn due to the remaining 1-BT (Table 2.1). As mentioned before, it is well reported in the literature that the reactivity of the studied refractory sulfur compounds decreases in the order of DBT > 4,6-DMDBT > 1-BT and the lowest reactivity of 1-BT is attributed to the significant lower electron density on its sulfur atom. [17, 36, 37]

Table 2.1- Desulfurization percentage of the various sulfur compounds present in the model diesel after 1 and 4 h of the ECODS process, catalyzed by different hybrid catalysts at 50 °C in the presence of MeCN as extraction solvent.

Catalyst	Sulfur compound	1h	4h
[TBA]PW ₁₁ Zn	1-BT	13	97
	DBT	98	100
	4,6-DMDBT	63	100
[BMIM]PW ₁₁ Zn	1-BT	0	21
	DBT	10	100
	4,6-DMDBT	0	87
[ODA]PW ₁₁ Zn	1-BT	3	44
	DBT	83	99
	4,6-DMDBT	78	99

The lower desulfurization efficiency observed for [BMIM]PW₁₁Zn must be related with the lowest affinity of the counter-cation part of the catalytic ionic liquid with the model diesel. In opposite, the quaternary ammonium catalysts probably have a higher affinity with the model diesel; however, no catalyst was identified by ³¹P NMR in this apolar phase. Still, quaternary ammonium cations of catalysts may behave as phase-transfer agents between model diesel and MeCN extraction solvent, which probably promote a higher desulfurization.

Li et al. reported that the length of carbon chains of quaternary ammonium cations of surfactant-type decatungstates play an important role in the catalytic performance of these catalysts, claiming that those catalysts with longer carbon chain had better activity. [39] More recently, Lü et al. also compared the catalytic activity of an Anderson-type POM with a TBA cation and a long carbon chain [(C₁₆H₃₃)N(CH₃)₃]⁺ cation in the oxidation of DBT, and in this case the TBA catalyst presented higher activity than the long carbon chain catalyst. [40] In this case, the authors referred that the steric effects of the long carbon quaternary ammonium cations are responsible for the decrease of catalyst reactivity. In this work, the [TBA]PW₁₁Zn also showed to be slightly better catalyst than the [ODA]PW₁₁Zn from the first minutes of the ECODS process. However, it appears that this difference of activity is due to the solubility of the [TBA]PW₁₁Zn catalyst in MeCN contrasting with the insolubility observed for [ODA]PW₁₁Zn. In fact, ³¹P NMR analysis from the MeCN extraction phase using [ODA]PW₁₁Zn demonstrated the absence of the polyanion [PW₁₁Zn(H₂O)O₃₉]⁵⁻ (PW₁₁Zn) or any phosphorus signal in solution, which indicate the insolubility of [ODA]PW₁₁Zn in the MeCN extraction phase. The same analysis performed in the model diesel also demonstrated the absence of phosphorus in solution. These results indicate that [ODA]PW₁₁Zn acts as a pure heterogeneous catalyst.

The solid [ODA]PW₁₁Zn catalyst was dispersed in both model diesel and MeCN extraction phases during the ECODS process (Figure 2.9); however, this did not allow an improvement of catalyst activity. In opposite, the [TBA]PW₁₁Zn was immobilized in the MeCN extraction phase during the ECODS process, which probably promotes an easier interaction between the catalyst, the oxidant and the sulfur compounds, necessary to form the peroxo intermediate active species, [26, 31] which must be the reason for the higher catalytic performance of this soluble catalyst containing the TBA cations as transfer-phase agent between model diesel and MeCN solvent.

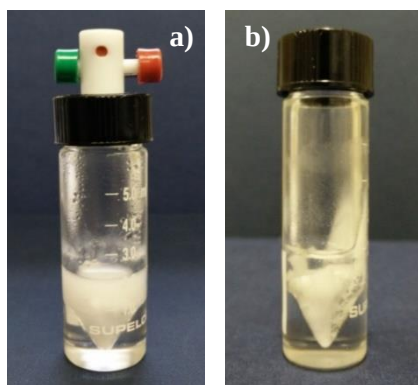


Figure 2.9 - a) Image of the emulsion of [ODA]PW₁₁Zn catalyst during the ECODS process, dispersed between model diesel and MeCN extraction phase, b) at the end of ECODS process after centrifugation (5000 rpm, 3 min).

2.2.2.3. Recyclability of the ECODS system

The reusability of the hybrid catalyst [TBA]PW₁₁Zn immobilized in the extraction phase was investigated. The catalyst could not be isolated from the ECODS system; however, the MeCN extraction phase containing the soluble catalyst could be reused for at least five consecutive cycles without losing activity (Figure 2.10). At the end of each cycle, the sulfur-free model diesel is removed from the system and an additional fresh portion of model diesel was added to the system. After the first 10 min at 50 °C of the initial extraction step, a new portion of H₂O₂ was also added to the system to initiate the oxidative catalytic stage. Figure 2.10 presents the total desulfurization occurred during the initial extraction step and after 3 h of the catalytic oxidative stage. It is possible to observe that the desulfurization, occurred during the initial extraction step for the various consecutive ECODS cycles, slightly increased mainly after the second ECODS cycle. In fact, after the second cycle, a white precipitate is observed in the extraction phase and this could be identified as the corresponding sulfones from the sulfur compounds present in the model diesel. However, this did not prevent the occurrence of a continuous transfer of sulfur compounds from the model diesel to the extraction phase. The catalytic stage of the ECODS is crucial to achieve total desulfurization and after 3 h a sulfur-free model diesel was produced.

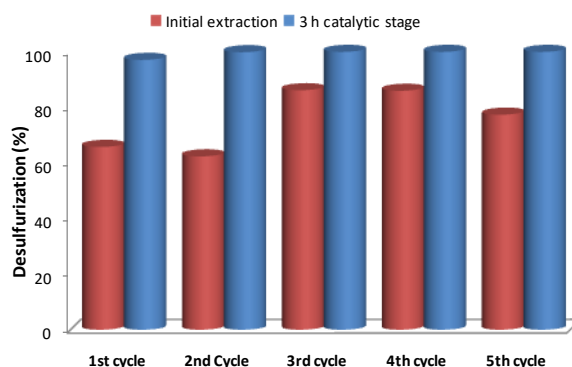


Figure 2.10 - Desulfurization data for five consecutive ECODS cycles catalyzed by [TBA]PW₁₁Zn (9 μ mol), using a model diesel and MeCN as extraction solvent, at 50 °C and 0.66 mmol of the oxidant H₂O₂.

Due to the heterogeneity of the [ODA]PW₁₁Zn, the recyclability of this catalyst could be performed by isolating, with centrifugation, the solid hybrid compound from the liquid-liquid ECODS system at the end of each ECODS cycle. After washing it with ethyl acetate and drying at room temperature, the solid catalyst was reused in a new ECODS cycle maintaining the same experimental conditions. Figure 2.11 presents the recyclability for three consecutive ECODS cycles. Only a small decrease in desulfurization efficiency is noticed from the first to the second and the third ECODS cycle (96, 93 and 91%, respectively).

The stability of [ODA]PW₁₁Zn catalyst was investigated by FT-IR after the third catalytic ECODS cycle. The characteristic bands of this hybrid catalyst could be identified and the spectra before and after catalytic use are similar (Figure 2.12).

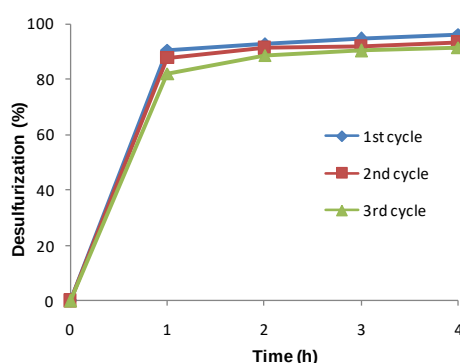


Figure 2.11 - Recyclability for [ODA]PW₁₁Zn catalyst (9 μ mol) for desulfurization of a model diesel in the presence of MeCN extraction solvent, at 50 °C and H₂O₂ oxidant (0.66 mmol).

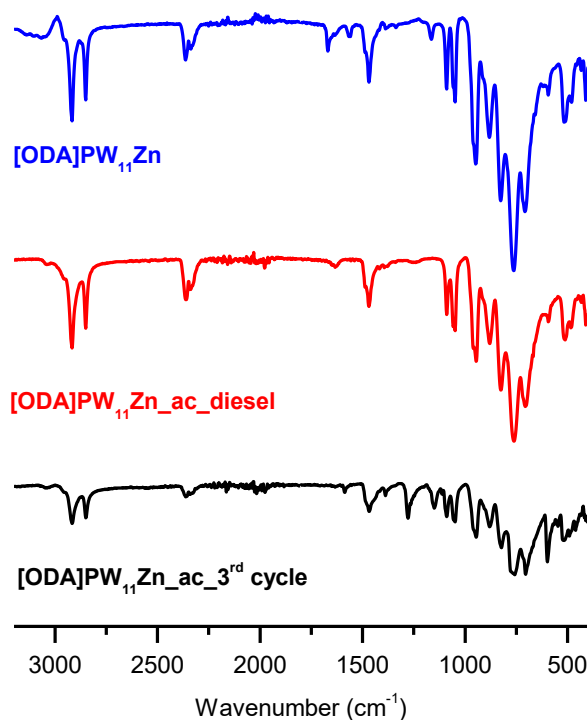


Figure 2.12 - FT-IR spectra of [ODA]PW₁₁Zn before (a) and after catalytic use for the desulfurization of an untreated real diesel (b) and a model diesel after three consecutive ECODS cycles (c).

2.2.3. Desulfurization of untreated diesel

The most efficient hybrid catalysts ([TBA]PW₁₁Zn and [ODA]PW₁₁Zn) were used in the oxidative desulfurization of an untreated diesel containing 2300 ppm of total sulfur, supplied by Galp. The desulfurization of the real diesel was also performed conciliating the liquid-liquid extraction, using MeCN as extraction solvent, and the oxidative catalytic stage of the process. The diesel was analyzed by GC-FPD (gas-chromatography using a flame photometric detector) where it could be observed the various families of sulfur compounds, mainly benzothiophene and dibenzothiophenes derivatives (Figure A1 in Appendix). Furthermore, it was possible to identify the peaks attributed to 1-BT, DBT, 4,6-DMDBT and 4-methyldibenzothiophene (4-MDBT), presented in Figure A1. The desulfurization process of real diesel was initiated by performing three consecutive liquid-liquid extraction cycles using equal volume of real diesel and MeCN. In each extraction cycle, both immiscible phases were stirred at 50 °C for 10 min. Figure A2 in Appendix A displays the chromatogram (GC-FPD) of the MeCN extraction phase after treating the diesel by liquid-liquid extraction. It is possible to observe that both benzothiophenes and dibenzothiophene derivatives were extracted to the MeCN phase. The amount of total sulfur, quantified by X-ray fluorescence after the first and the third cycle of extraction, is

displayed in Table 2.2 (experiments A and B). After three extraction cycles only 34% of desulfurization was achieved; however, a continuous extraction of sulfur compounds was observed during the different cycles (12% of desulfurization for the first extraction cycle and 34% for the third cycle).

Table 2.2 - Experiments performed for desulfurization of an untreated real diesel, using MeCN as extraction solvent at 50 °C.

Experiment	Catalyst ^b	Nr. extractive processes ^a	Time (h)	Nr. extractive processes after ECODS ^c	Diesel Sulfur content (ppm)	Desulfurization efficiency (%) ^d
A	-	1	-	-	2024	12
B	-	3	-	-	1507	34
C	[TBA]PW ₁₁ Zn	-	4	-	901	61
D	[ODA]PW ₁₁ Zn	-	5	-	763	67
E	[ODA]PW ₁₁ Zn	3	8	-	770	66
F	[ODA]PW ₁₁ Zn	3	8	1	643	72

^a liquid-liquid diesel/MeCN extraction of non-oxidized sulfur compounds during 10 min at 50 °C.

^b Oxidative catalytic desulfurization in a biphasic diesel/MeCN system using H₂O₂ as oxidant at 50 °C.

^c liquid-liquid treated diesel/MeCN extraction of oxidized sulfur compounds after ECODS process during 10 min at 50 °C.

^d Calculated based on untreated diesel containing 2300 ppm of sulfur supplied by Galp.

The same real diesel was also desulfurized using the oxidative catalytic process, using the biphasic diesel/MeCN system in the presence of [TBA]PW₁₁Zn and [ODA]PW₁₁Zn catalysts and an excess of H₂O₂, at 50 °C (Table 2.2). In this study, two different samples were used: the untreated diesel (with 2300 ppm of sulfur) and the diesel treated with three liquid extraction cycles (with 1507 ppm of sulfur). When the ECODS process was applied for 4 h with the untreated diesel, the efficiency of desulfurization found in the presence of [ODA]PW₁₁Zn and [TBA]PW₁₁Zn was 67% and 61%, respectively. The ECODS process was also applied with the diesel treated with previous liquid extraction, but using the solid [ODA]PW₁₁Zn catalyst and a H₂O₂/S ratio equal to 27; however, the level of remaining sulfur in diesel was not improved even for

higher reaction time (8 h, experiment E in Table 2.2). A small increase in the diesel desulfurization was achieved when a liquid-liquid extraction was performed after 8 h of the ECODS process (experiment F in Table 2.2), using equal volume of ECODS treated diesel and MeCN, under stirring for 10 min at 50 °C. In this case, the desulfurization increased from 66% to 72%. The chromatograms (GC-FPD) from treated diesel and MeCN extraction phase are displayed in Figures A3 and A4 in Appendix A. From the diesel chromatogram it was possible to verify that the sulfur compounds that remained in treated diesel are benzothiophene derivatives and seems that all dibenzothiophene derivatives were removed. The chromatogram of the extraction MeCN phase confirms the extraction of oxidized sulfur products during this last extraction process.

In conclusion, the results performed based on ECODS processes demonstrate that a large number of liquid-liquid extraction cycles are not crucial to improve the desulfurization of an untreated diesel, mainly if the oxidative catalytic stage of the process could be performed for a longer time. Contrastingly, a liquid-liquid extraction executed after the oxidative catalytic stage is important to remove probably some oxidized sulfur compounds presented in the treated diesel, in order to increase the desulfurization efficiency.

2.3. Conclusions

The comparison of desulfurization efficiency between different zinc-substituted polyoxometalate hybrid catalysts ([TBA]PW₁₁Zn, [ODA]PW₁₁Zn and [BMIM]PW₁₁Zn) was here presented and enlarged for the first time to model and untreated diesels. The ionic liquid catalyst containing 1-butyl-3-methylimidazolium cations ([BMIM]PW₁₁Zn) was less efficient than the quaternary ammonium catalysts containing a short ([TBA]PW₁₁Zn) and a long carbon chain ([ODA]PW₁₁Zn) cations. The quaternary ammonium counter-cations of catalysts may behave as phase-transfer agents. Using the model and the untreated diesels it was possible to confirm that the length of the carbon chain from the cation (TBA or ODA) seems do not have a remarkable influence during the liquid-liquid extraction step and also in the oxidative catalytic desulfurization stage of the ECODS process. The desulfurization efficiency of [TBA]PW₁₁Zn and [ODA]PW₁₁Zn is similar and the main difference is attributed to the fact that [TBA]PW₁₁Zn behave as a homogeneous catalyst immobilized in the acetonitrile extraction phase, while the [ODA]PW₁₁Zn is a heterogeneous catalyst without solubility in diesel and acetonitrile phases. Practically, complete desulfurization of model diesel was obtained after 4 h of the process, while 72% was achieved using the real untreated diesel after 8 h. After the extraction/oxidative

catalytic treatment, the only sulfur-compounds that remained in the real diesel were the benzothiophene derivatives.

2.4. Experimental section

2.4.1. Materials and Methods

All the reagents, 1-butyl-3-methylimidazolium bromide (Fluka), octadecyltrimethylammonium bromide (Aldrich), tetra-n-butylammonium bromide (Merck), sodium tungstate dehydrate (Aldrich), sodium phosphate dehydrate (Aldrich), zinc acetate di-hydrated (M&B), hydrochloric acid (Fisher Chemicals), 4,6-dimethyldibenzothiophene (Alfa Aesar GmbH & Co KG), dibenzothiophene (Aldrich), 1-benzothiophene (Fluka), n-octane (VWR international S.A.S.), ethyl acetate (Merck), acetonitrile (Fisher Chemical), 1-butyl-3-methylimidazolium hexafluorophosphate (Sigma- Aldrich), H₂O₂ 30% (Aldrich) were used as received without further purification.

Elemental analysis for C, N, O and H were performed on a Leco CHNS-932 at the University of Santiago de Compostela. Hydration water contents were determined by thermogravimetric analysis performed in air between 20°C and 800°C, with a heating rate of 5 °C min⁻¹, using a TGA-50 Shimadzu thermobalance (CICECO, Universidade de Aveiro). Infrared absorption spectra were recorded for 400-4000cm⁻¹ region on a Perkin Elmer Spectrum 100 series with ATR accessory, a resolution of 4 cm⁻¹ and 64 scans. ³¹P NMR spectra were collected for liquid solutions using a Bruker Avance III 400 spectrometer and chemical shifts are given with respect to external 85% H₃PO₄. Solid state ³¹P MAS NMR spectra were recorded with a 7 T (300MHz) AVANCE III Bruker spectrometer under a magic angle spinning of 10Hz at room temperature. The catalytic reactions were monitored by a Bruker 430-GC-FID gas chromatograph, with hydrogen as carried gas (55 cm³s⁻¹) and a Supelco capillary column SPB-5 (30m x 250µm id.; 25 µm film thickness) was used. Sulfur content in real diesel was measured by ultraviolet fluorescence test method in Galp by Rita Valença, using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-Ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125. Sulfur compounds in real diesel were identified by Susana O. Ribeiro using a Shimadzu GC-FPD gas chromatograph, with helium as carrier gas and a TRB-1 column (50 m, ID = 0.32).

2.4.2. Synthesis of hybrid zinc-substituted polyoxometalates

K₅[PW₁₁Zn(H₂O)O₃₉].nH₂O (KPW₁₁Zn) was prepared by following a previously described procedure [41]. Na₂HPO₄ (1,8 mmol) and Na₂WO₄·2H₂O (20 mmol) were dissolved in 40 ml of water, the mixture was heated at 90°C for 4 h and the pH was adjusted to 4.8 with HCl 4M. Zinc acetate (2,4 mmol) was then added and the pH was corrected to 4.8. An excess of potassium chloride was added and the formed solid was filtered, washed and dried at room temperature. ³¹P NMR (161.9 MHz, D₂O 298 K): δ = −11.41 ppm. FT-IR (cm^{−1}): ν = 2952 (w), 2938 (w), 1622 (m), 1088 (s), 1050 (s), 956 (vs), 886 (s), 800 (s), 754 (m), 700 (m), 590 (w), 506 (w), 484 (w), 408 (w).

(C₄H₉)₄N)₄H[PW₁₁Zn(H₂O)O₃₉].4H₂O ([TBA]PW₁₁Zn, TBA = (C₄H₉)₄N) was prepared following the procedure described in the literature. [41, 42] Elemental and thermogravimetric analysis, vibrational spectra (FT-IR) and ³¹P NMR data confirmed the successful preparation of [TBA]PW₁₁Zn. Anal. Calcd (%) for C₆₄H₁₅₅N₄O₄₄PW₁₁Zn (3802,36): C, 20.20; H, 4.11; N, 1.47. Found: C, 20.66; H, 4.27; N, 1.72. TGA showed a mass loss of 2,03% in the range of 30-150°C (calcd, for loss of 4 hydrated H₂O molecules: 1,89%), in the range of 150-225°C the mass loss was 0,47% (calcd, for loss 1 coordinated water molecule: 0,47%). ³¹P NMR (161.9 MHz, CD₃CN, 298 K): δ = −10.65 ppm. FT-IR (cm^{−1}): ν = 2962 (s), 2936 (s), 2874 (s), 1644 (m), 1484 (s), 1382 (m), 1054 (s), 952 (vs), 884 (s), 802 (vs), 714 (sh), 592 (m), 514 (m).

(C₁₈H₃₇N(CH₃)₃)₅[PW₁₁Zn(H₂O)O₃₉].4H₂O ([ODA]PW₁₁Zn) was prepared for the first time adapting a procedure reported in the literature. [8] A solution of octadecyltrimethylammonium bromide (5 mmol dissolved in 20 mL of ethanol) was added dropwise to the aqueous solution of previously prepared KPW₁₁Zn (1 mmol in 40 mL), with continuous stirring for 2h. The mixture was filtered and the obtained solid was dried in vacuum at 60°C. The hybrid compound was characterized by elemental and thermogravimetric analysis, vibrational spectroscopy (FT-IR) and solid-state ³¹P NMR data. Anal. Calcd (%) for C₁₀₅H₂₄₀NPW₁₁ZnO₄₄ (4394,03): C, 28,67; H, 5,50; N, 1,59. Found: C, 30,04; H, 6,04; N, 1.80. TGA showed a mass loss of up to 130 °C of 1,79% (calcd, for loss of 4 hydrated H₂O molecules: 1,63%). In the range of 130-190 °C the loss was 0,39% which represents the loss of one coordinated water molecule (calcd, for loss of 1 H₂O molecule: 0,41%). ³¹P MAS NMR (δ = −12.39 ppm). FT-IR (cm^{−1}): ν = 2918 (s), 2850 (s), 2362 (s), 1670 (m), 1564 (w), 1468 (m), 1164 (w), 1090 (s), 1048 (m), 948 (s), 882 (s), 826 (s), 764 (vs), 708 (s), 594 (w), 516 (m) 434 (w) 412 (m).

(BMIM)₅[PW₁₁Zn(H₂O)O₃₉]·4H₂O ([BMIM]PW₁₁Zn, BMIM abbreviated for 1-butyl-3-methylimidazolium, C₈H₁₅N₂) was prepared adapting a procedure reported in the literature. [11] An aqueous solution of 1-*n*-butyl-3-methylimidazolium bromide (5 mmol) was added dropwise to the aqueous solution of zinc substituted phosphotungstate (1 mmol) at room temperature under constant stirring during two hours. The resulting precipitate was washed with distilled water, filtered and dried under vacuum at 60 °C overnight. Elemental and thermogravimetric analysis, vibrational spectra (FT-IR) and ³¹P NMR data confirmed the successful preparation of [BMIM]PW₁₁Zn. Anal. Calcd (%) for (C₈H₁₅N₂)₅O₄₀PW₁₁Zn (3730.32): C, 20.59; H, 3.97; N, 1.50. Found: C, 20.66; H, 4.27; N, 1.72. TGA showed a mass loss of 2.07% up to 120 °C (calcd, for loss of 4 H₂O hydration molecules: 2.04%) In the range of 120-295°C the mass loss was 0.51% which corresponds to one coordinated water molecule (calcd, for loss of 1H₂O molecule: 0.51%). ³¹P NMR (161.9 MHz, D₂O, 298 K): δ = -11.41 ppm. FT-IR (cm⁻¹): ν = 3068 (w), 2962 (w), 2934 (w), 2872 (w), 2366 (w), 2328 (w), 1654 (w), 1566(m), 1464 (m), 1338 (w), 1166(s), 1086 (m), 1050 (s), 948 (vs), 890 (s), 800 (s), 754 (m), 710 (m), 656(w), 620 (m), 594 (w), 508 (m), 486 (w), 434 (w), 410 (m).

2.4.3. ECODS process using a model diesel

The ECODS experiments were carried out under air (atmospheric pressure) in a closed borosilicate 5 mL reaction vessel equipped with a magnetic stirrer, and immersed in a thermostatic oil bath at 50 °C. Hydrogen peroxide (30 wt%) was used as oxidant. A model diesel was prepared by dissolving the most refractory sulfur compounds (1-BT, DBT and 4,6-DMDBT, approximately 500 ppm S of each) in *n*-octane. ECODS experiments were performed with equal volume of model diesel and acetonitrile to prepare the biphasic liquid-liquid system (0.75 mL each). An initial extraction of sulfur compounds from model diesel to the extraction solvent was analyzed. The biphasic system was stirred for 10 min until the initial extraction equilibrium was reached and an aliquot from the upper model diesel phase was taken and analyzed by GC-FID. After this stage, the oxidant H₂O₂ was added to the system. Samples from model diesel were taken from the system at periodic time and analyzed by GC-FID. Tetradecane was used as standard. The ECODS system was reused by removing the desulfurized model diesel and adding a new amount of model diesel containing the various sulfur compounds.

2.4.4. ECODS process of untreated diesel

The used untreated diesel was supplied by Galp containing approximately 2300 ppm of total sulfur. An initial extraction was performed using MeCN as extraction solvent. The biphasic system 1:1 diesel/MeCN (15 mL of each) was stirred for 10 min at 50 °C. After this time, the diesel was removed from the system (loss of diesel weight of 8%) and added to a new portion of clean MeCN. This initial extraction procedure was repeated for three times. In the next step, the resulted diesel was, usually, mixed with the hybrid $PW_{11}Zn$ catalyst (0.2 mmol) in MeCN and with an excess of H_2O_2 oxidant ($H_2O_2/S = 27$). The mixture was heated at 50 °C for 8 h. After this time, the diesel was removed from the mixture and washed with equal volume of MeCN at 50 °C for 10 min (loss of total diesel weight of 18%). The analysis of sulfur content of the treated diesel was performed by Galp.

2.5. References

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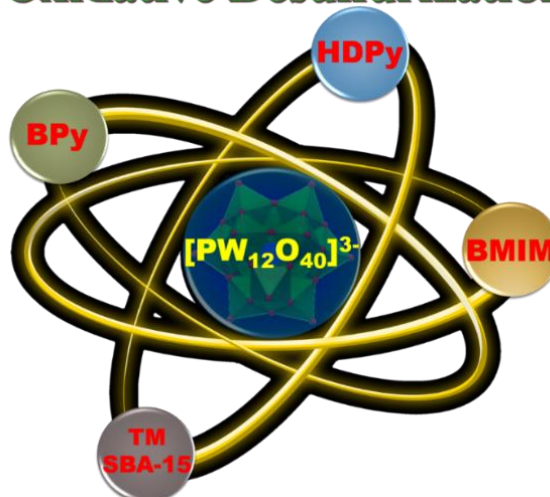
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Chapter 3

Improving the catalytic performance of Keggin $[PW_{12}O_{40}]^{3-}$ for oxidative desulfurization: ionic liquids versus silica composite

Oxidative Desulfurization



¹ Adapted from: Susana O. Ribeiro, Beatriz Duarte, Baltazar de Castro, Carlos M. Granadeiro and Salette S. Balula, *Improving the Catalytic Performance of Keggin $[PW_{12}O_{40}]^{3-}$ for Oxidative Desulfurization: Ionic Liquids versus SBA-15 Composite*, Materials, 11 (2018) 1196, doi:10.3390/ma11071196.

² Susana O. Ribeiro contributions to the publication: Preparation and characterization of the composite material ($PW_{12}@TM-SBA-15$); characterization of hybrid catalysts; investigation of catalytic performance of all catalysts in the desulfurization of a model diesel and real diesel supplied by Galp; manuscript preparation.

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Chapter 3

Improving the catalytic performance of Keggin $[PW_{12}O_{40}]^{3-}$ for oxidative desulfurization: ionic liquids versus silica composite

Abstract

Different methodologies were used to increase the oxidative desulfurization efficiency of the Keggin phosphotungstate $[PW_{12}O_{40}]^{3-}$ (PW_{12}). One possibility was to replace the acid proton by one of three different ionic liquid cations, forming the novel hybrid polyoxometalates: $[BMIM]PW_{12}$ (BMIM: 1-butyl-3-methylimidazolium), $[BPy]PW_{12}$ (BPy: 1-butylpyridinium) and $[HDPy]PW_{12}$ (HDPy: hexadecylpyridinium). These hybrid Keggin compounds showed high oxidative desulfurization efficiency in the presence of $[BMIM]PF_6$ solvent, achieving complete desulfurization of multicomponent model diesel (~2000 ppm of S) after only 1 h, using a low excess of oxidant ($H_2O_2/S = 8$) at 70 °C. However, their stability and activity showed some weakness in continuous reused oxidative desulfurization cycles. An improvement of stability in continuous reused cycles was reached by the immobilization of the Keggin polyanion in a strategic positively-charged functionalized-SBA-15 support (SBA: Santa Barbara Amorphous). The $PW_{12}@TMA-SBA-15$ composite (TMA: *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium) presented similar oxidative desulfurization efficiency to the homogeneous IL- PW_{12} compounds, having the advantage of a high recycling capability in continuous cycles, increasing its activity from the first to the consecutive cycles. Therefore, the oxidative desulfurization system catalyzed by the Keggin-type composite has high performance under sustainable operational conditions, avoids waste production during recycling and allows catalyst recovery.

3.1 Introduction

Extractive and catalytic oxidative desulfurization (ECODS) is one of the most advantageous technologies for producing ultra-clean fuels due to its ability to efficiently remove the aromatic sulfur compounds from fuel under mild operating conditions. [1] The sulfur compounds are initially oxidized to polar compounds which can then be easily removed from the diesel phase by extraction with a polar solvent. Over the last few years, numerous catalysts have been reported for ECODS application, such as mixed metal oxides, [2, 3] ionic liquids, [4, 5] metal–organic frameworks, [6, 7] titanium–zeolites, [8–10] titanium-containing mesoporous silicas [11, 12] and polyoxometalates (POMs). [13, 14]

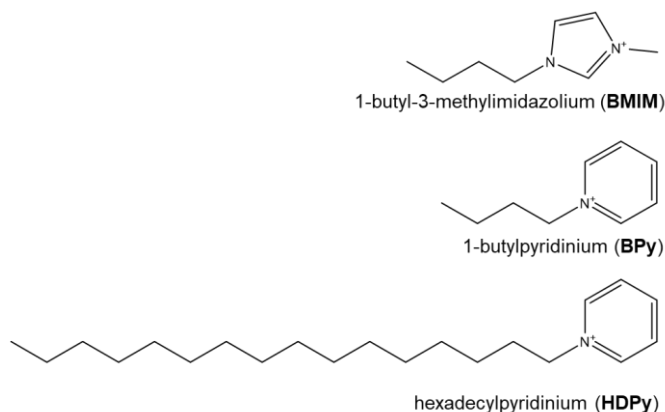
The preparation of organic POM hybrids has become a widespread methodology in POM chemistry, [15] and in the case of catalysis, it has been used to enhance the efficiency and allow the separation of catalysts from reactional media. [16, 17] Cationic surfactants, ionic liquids and copolymers have been used in the construction of organic POM hybrids, including those used for application in oxidative desulfurization. [18–22] Zhu et al. prepared a series of ionic liquid POM hybrids using different imidazolium cations and Keggin-type POMs. [19] The hybrids were tested as catalysts in the oxidation of dibenzothiophene (DBT) through an ECODS process. The authors showed that the catalytic activity is strongly influenced by the type of cations and metals, with the best catalysts achieving complete oxidation of DBT ($S = 500$ ppm) after 1 h. [19]

In this work, two different type of catalysts based on the Keggin $[PW_{12}O_{40}]^{3-}$ anion (PW_{12}) were prepared. The first consisted of ionic liquid POM hybrids obtained by substitution of the starting protons of phosphotungstic acid by cations of ionic liquids (ILs). The ILs used were the bromide salts of 1-butyl-3-methylimidazolium (BMIM), 1-butylpyridinium (BPy) and hexadecylpyridinium (HDPy) (see Scheme 3.1). The second type of catalyst studied was a composite material obtained by the incorporation of PW_{12} into the mesoporous channels of positively-charged functionalized-SBA-15 ($PW_{12}@TMA-SBA-15$) (see Scheme 3.2). All the prepared catalysts were tested in a biphasic ECODS process of multicomponent model diesel containing the most refractory sulfur compounds in diesel. The desulfurization studies were performed using H_2O_2 as oxidant and an IL ($[BMIM]PF_6$) or organic solvent (acetonitrile) as the extracting solvent. The influence of the solvents on the desulfurization performance was evaluated, and the reusability of the catalysts was investigated for consecutive ECODS cycles.

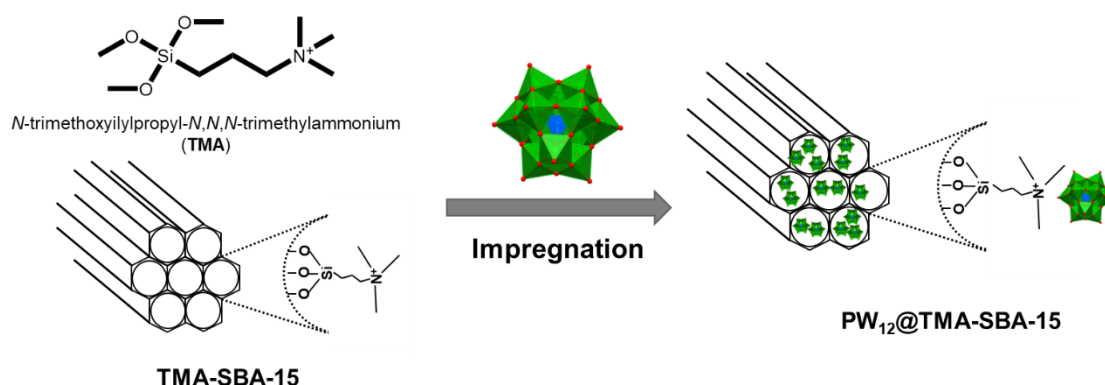
3.2. Results and discussion

3.2.1. Catalysts characterization

Different catalysts have been prepared based on the Keggin $[PW_{12}O_{40}]^{3-}$ anion (PW_{12}), namely ionic liquid- PW_{12} (IL- PW_{12}) hybrids compounds and a composite material. The hybrids were prepared by replacing the protons of phosphotungstic acid by the cations of the ionic liquids 1-butyl-3-methylimidazolium (BMIM), 1-butylpyridinium (BPy) and hexadecylpyridinium (HDPy) (Scheme 3.1). The number of ionic liquid cations in the hybrids structures was determined by elemental analysis. The composite material was obtained through incorporation of PW_{12} on the mesoporous channels of trimethylammonium-functionalized SBA-15 (Scheme 3.2).



Scheme 3.1 – Ionic liquid cations used to prepare the hybrid PW_{12} catalysts.



Scheme 3.2 – Representation of the preparation of the $PW_{12}@TMA-SBA-15$ composite.

The vibrational spectra of IL- PW_{12} (Figure 3.1A and 3.2A) exhibit the characteristic bands associated with the anionic PW_{12} together with the bands ascribed to the cationic counterpart. In all spectra, the bands associated with PW_{12} stretching modes can be

clearly observed in the $1100\text{--}800\text{ cm}^{-1}$ range, namely $\nu_{as}(P\text{--}O)$, terminal $\nu_{as}(W=O)$, corner-shared $\nu_{as}(W\text{--}O_b\text{--}W)$ and edge-shared $\nu_{as}(W\text{--}O_c\text{--}W)$ by decreasing wavenumber. [23–25] The bands associated with the ionic liquid cations can be observed in the $3164\text{--}3064\text{ cm}^{-1}$ and $2970\text{--}2850\text{ cm}^{-1}$ ranges corresponding to $\nu(C\text{--}H)$ of the aromatic heterocycles and aliphatic chains, respectively. [17, 26] Moreover, the bands located in the $1173\text{--}1165\text{ cm}^{-1}$ range, which are more clear in the FT-IR spectra, can be assigned to the $\delta(H\text{--}C\text{--}C)$ and $\delta(H\text{--}C\text{--}N)$ modes in the heterocycles. [19, 26, 27]

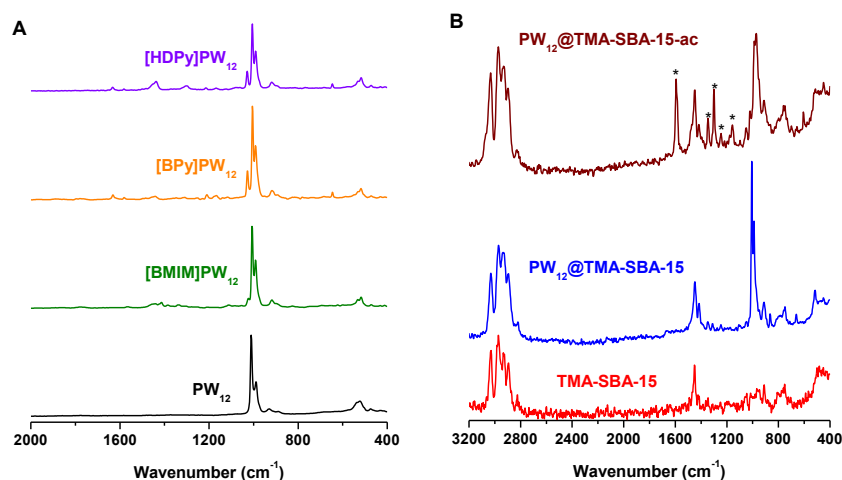


Figure 3.1 - FT-Raman spectra of (A) the PW_{12} -hybrids and (B) the trimethylammonium -functionalized TMA-SBA-15 and the corresponding $PW_{12}@TMA\text{--}SBA\text{--}15$ composite before and after catalysis (ac).

Regarding the $PW_{12}@TMA\text{--}SBA\text{--}15$ composite, the FT-IR spectrum (Figure 3.2B) is dominated by the intense bands associated with the SBA-15 support, namely the $\nu_{as}(Si\text{--}O\text{--}Si)$, $\nu_s(Si\text{--}O\text{--}Si)$ and $\delta(O\text{--}Si\text{--}O)$ vibrational modes located at 1082 , 808 and 459 cm^{-1} , respectively. [28, 29] Some of the PW_{12} vibrational modes are occluded by the intense silica bands. However, the appearance of an additional band at 951 cm^{-1} and the increased relative intensity of the band at 808 cm^{-1} , which can be assigned to $\nu(W=O)$ and $\nu(W\text{--}O_c\text{--}W)$ stretches, respectively, point out to the presence of PW_{12} in the composite material.

The FT-Raman is an extremely useful technique for the characterization of siliceous-based composite due to their relatively weak Raman signal. [30–32] Therefore, the presence of PW_{12} on the composite is more evident in the FT-Raman spectrum since the FT-Raman spectrum of $PW_{12}@TMA\text{--}SBA\text{--}15$ (Figure 3.1B) exhibits very intense bands in the $1010\text{--}860\text{ cm}^{-1}$ range associated with the characteristic PW_{12} vibrations. [23,

33] The spectrum also displays the bands arising from the presence of trimethylammonium groups, namely $\nu(\text{C-H})$ and $\delta(\text{CH}_2)$ vibrational modes in the $3031\text{--}2890\text{ cm}^{-1}$ and $1450\text{--}1410\text{ cm}^{-1}$ ranges, respectively. [34, 35] The successful preparation of $\text{PW}_{12}\text{@TMA-SBA-15}$ was further confirmed by elemental analysis which determined a PW_{12} loading of 0.056 mmol/g .

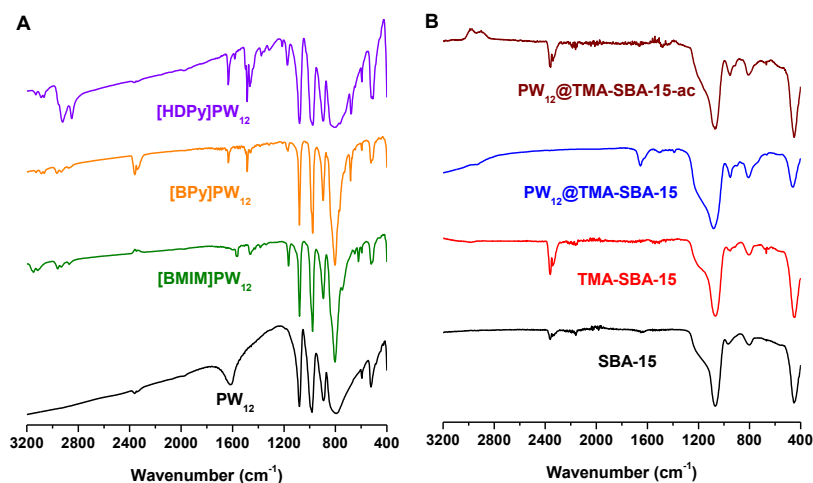


Figure 3.2 - FT-IR spectra of (A) the PW_{12} -hybrids and (B) the starting SBA-15 support, the functionalized TMA-SBA-15 and the corresponding $\text{PW}_{12}\text{@TMA-SBA-15}$ composite before and after catalysis.

The $\text{PW}_{12}\text{@TMA-SBA-15}$ composite and support were analyzed by powder XRD (Figure 3.3). The TMA-SBA-15 pattern exhibits the typical low-angle three peaks of SBA-15 materials which can be indexed as (100), (110) and (200) reflections of a $p6mm$ hexagonal symmetry. [36, 37] After the PW_{12} incorporation, a shift to higher 2θ can be observed in the $\text{PW}_{12}\text{@TMA-SBA-15}$ pattern, in particular for the peaks assigned to the (110) and (200) reflections. Previous works dealing with POM-incorporated SBA-15 materials have reported this shift to higher angles which has been attributed to the occupancy of SBA-15 channels by the guest species. [29, 38-40]

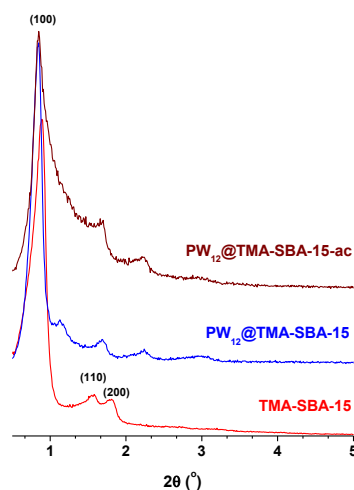


Figure 3.3 - Powder XRD patterns of trimethylammonium -functionalized SBA-15 (TMA-SBA-15) and the corresponding $PW_{12}@TMA-SBA-15$ composite before and after catalysis (abbreviated as ac).

The SEM images of $PW_{12}@TMA-SBA-15$ (Figure 3.4) reveal that the morphology of the starting support is retained in the final composite. The images show hexagonal particles assembled in elongated structures which are typical of the mesoporous SBA-15 framework. [29, 36, 41] The chemical composition of $PW_{12}@TMA-SBA-15$ was evaluated by EDS spectroscopy (Figure 3.4D). The spectrum is mainly composed by the intense peak assigned to silicon from the SBA-15 support but also by the peaks assigned to tungsten which are consistent with the presence of the PW_{12} in the composite material.

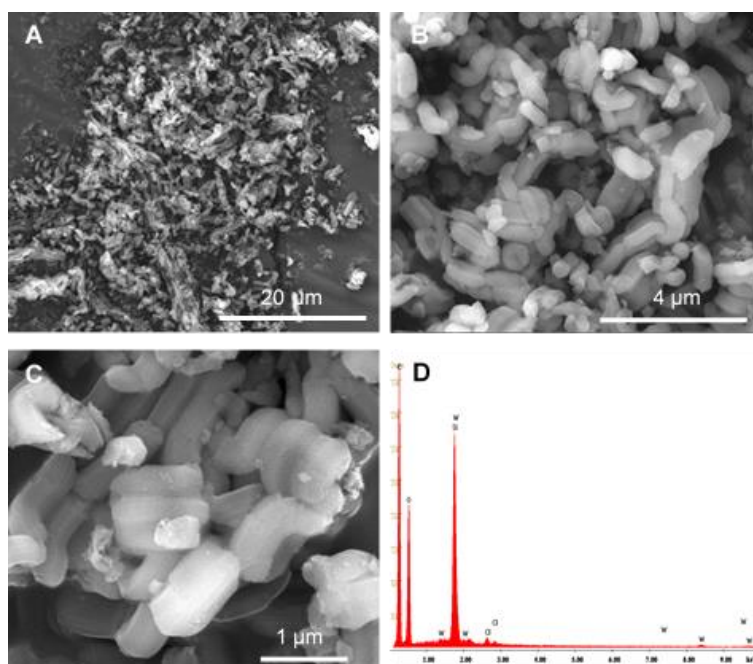


Figure 3.4 - SEM images of the $PW_{12}@TMA-SBA-15$ composite material at different magnifications: (A) x5000, (B) x25000, (C) x60000 and (D) EDS spectrum.

3.2.2. Biphasic extractive and catalytic oxidative desulfurization (ECODS) process

The oxidative desulfurization studies were performed using the model diesel B containing the representative refractory sulfur compounds in diesel: 1-benzothiophene (1-BT), dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) and 4-methyldibenzothiophene (4-MDBT) in *n*-octane (500 ppm S each). The ECODS of model diesel was carried out in the presence of an extraction solvent with ratio 1:1 and in the presence of H_2O_2 as oxidant. Two different extraction solvents were tested: acetonitrile (MeCN) and an ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate ($[BMIM]PF_6$). The biphasic ECODS system is performed in two main steps: the initial extraction and the catalytic stage. Initially, the extraction of the non-oxidized sulfur compounds from the model diesel to the extraction phase occurs during 10 min at 70 °C. After this time the distribution the sulfur compounds between the two phases achieve the equilibrium and the desulfurization of the model diesel stopped. To continue the desulfurization of the model diesel, the oxidant H_2O_2 was added to the system ($H_2O_2/S = 8$) to oxidize the sulfur components present in the extraction phase to the corresponding sulfones and/or sulfoxides, which will promote a continuous transfer of more sulfur compounds to the extraction phase. No oxidative products were detected in the model diesel phase which suggests that the catalytic oxidative reaction must occurs only in the extraction phase (MeCN and $[BMIM]PF_6$). The ECODS system was catalyzed by three different homogeneous catalysts based in ionic liquids of Keggin polyanion ($[PW_{12}O_{40}]^{3-}$ (abbreviated as PW_{12}).

These IL- PW_{12} compounds have distinct organic cations: 1-butyl-3-methylimidazolium ($[BMIM]PW_{12}$), 1-butylpyridinium ($[BPy]PW_{12}$) and hexadecylpyridinium ($[HDPy]PW_{12}$). A heterogeneous catalyst based on the same catalytic active center PW_{12} immobilized on trimethylammonium-functionalized SBA-15 (SBA: Santa Barbara Amorphous) support ($PW_{12}@TMA-SBA-15$) was also used.

3.2.2.1. ECODS using homogeneous IL- PW_{12}

Initially, a comparative study was performed between the different IL- PW_{12} compounds using both biphasic systems: model diesel/MeCN and model diesel/ $[BMIM]PF_6$. Figure 3.5 displays the desulfurization results obtained using MeCN and $[BMIM]PF_6$ extraction solvents. It is possible to verify that the activity of the three IL- PW_{12} compounds is similar using the $[BMIM]PF_6$ extraction solvent (Figure 3.5A). Figure

3.5B demonstrates that the $[BPy]PW_{12}$ catalyst did not promote any oxidation using the model diesel/MeCN ECODS system, since the desulfurization stopped after the initial extraction step (after the first 10 min). On the other hand, using the model diesel/ $[BMIM]PF_6$ system, the three IL- PW_{12} catalysts achieved complete desulfurization after 1 h of oxidation (Figure 3.5A). Only slightly lower activity was observed using PW_{12} as the precursor; this is probably due to the cationic exchange occurred between the cation of PW_{12} and the $[BMIM]^+$ from the reaction medium, which may decrease the initial catalytic performance. By comparing the results obtained with $[BMIM]PF_6$ and MeCN solvents, it is possible to confirm that the $[BMIM]PF_6$ as extraction solvent has a collaborative performance when activating the catalyst, since in the absence of IL- PW_{12} , the ECODS systems did not promote any oxidative desulfurization (Figure 3.5A). This behavior has been observed previously in the literature where $[BMIM]PW_{12}$ was used as a catalyst for the epoxidation of olefins, and low activity was found in the presence of MeCN solvent and a high catalytic performance was observed using $[BMIM]PF_6$ IL solvent. [42] In fact, this IL can be used not only as a solvent, but also should create a special environment that facilitates the formation of the active peroxotungstate compounds through the interaction of IL- PW_{12} and H_2O_2 .

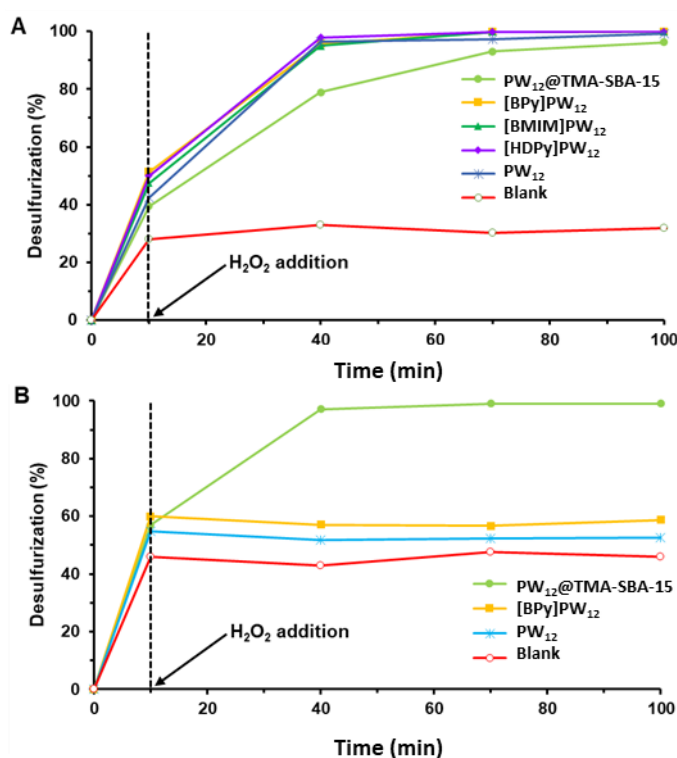


Figure 3.5 - Kinetic desulfurization profiles of the extractive and catalytic oxidative desulfurization (ECODS) process catalyzed by PW_{12} , IL- PW_{12} compounds, composite material $PW_{12}@TMA-SBA-15$ (3 μ mol of PW_{12} active catalytic center) and blank experiments (without catalyst) using (A) $[BMIM]PF_6$ and (B) MeCN as extraction solvents at 70 °C and $H_2O_2/S = 8$.

Moreover, the literature suggests that the mechanism for the oxidation of benzothiophene derivatives catalyzed by polyoxometalates (POMs) and using H_2O_2 as an oxidant starts with the formation of active species through the interaction of the oxidant (H_2O_2) and the W^{VI} atoms of the POM (PW_{12} in this study). [14, 31, 43-47] The resulting hydroperoxy- or peroxy-POM species are able to oxidize the sulfur compounds into the corresponding sulfoxides through a nucleophilic attack. The subsequent oxidation of the sulfoxides leads to the formation of sulfones. The oxidation promotes the continuous mass transport of sulfur compounds from the model diesel into the extraction phase ($[BMIM]PF_6$) in order to restore the equilibrium of the extraction process. After 2 h of ECODS process, the IL extraction phase was also analyzed by GC, and only sulfones and a vestigial amount of 1-BT sulfoxide was detected.

In previous published works, it was possible to demonstrate the reusability of $POM@[BMIM]PF_6$ systems in various consecutive cycles [25, 48]. In these works, the ECODS systems were recycled by washing the IL phase with a mixture of strategically chosen organic solvents to remove the oxidized and non-oxidized sulfur compounds. More recently, our group published a successful reused system that performs by only replacing the desulfurized diesel with new sulfurized diesel and a new aliquot of oxidant. [49] The same procedure was adopted in this work using the $[BPy]PW_{12}@[BMIM]PF_6$ system, i.e., the $[BPy]PW_{12}$ compound confined in the IL extraction phase. This can be considered a continuous recycling system without the need for organic polar solvent and without the possibility of leaching active species during the IL cleaning process. Since the catalytic activities of the different IL- PW_{12} compounds were similar, the reusability was only performed for one of the three hybrid compounds ($[BPy]PW_{12}$). Figure 3.6 presents the reuse data for three consecutive ECODS cycles. It is possible to observe that the catalytic performance of the $[BPy]PW_{12}@[BMIM]PF_6$ system was essentially maintained from the first to the second cycle. However, from the second to the third cycle, a decrease in desulfurization was observed. In fact, a decrease in the initial extraction, i.e., the desulfurization obtained during the first 10 min of stirring at 70 °C (before H_2O_2 addition), decreased from the first to the second cycle and also from the second to the third cycle. This is probably due to the number of oxidized sulfur compounds accumulated in the extraction phase ($[BMIM]PF_6$) over the reusability cycles that decelerate the transfer of more non-oxidized sulfur compounds. This phenomenon also contributes for the lower oxidative catalytic activity of the IL- PW_{12} catalyst. On the other hand, a leaching of the active homogeneous catalyst $[BPy]PW_{12}$ to the model diesel phase can also promote a decrease in oxidative desulfurization efficiency. Therefore, the model diesel phase was analyzed by ^{31}P NMR and by UV-Vis spectroscopy (a

characteristic transition charge band at approximately 250 nm is attributed to the presence of Keggin-type polyoxometalate), but the presence of $[BPy]PW_{12}$ in the model diesel phase was not detected. These results suggest the absence of catalyst leaching from the $[BMIM]PF_6$ phase.

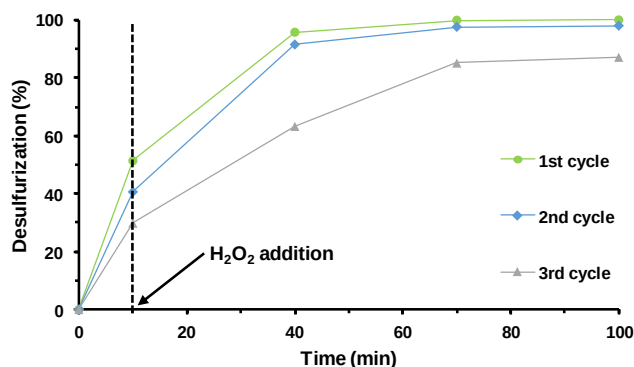


Figure 3.6 - Kinetic desulfurization profiles catalyzed by $[BPy]PW_{12}$ ($3\ \mu\text{mol}$) for three consecutive ECODS cycles using ionic liquid ($[BMIM]PF_6$) as extraction solvent at $70\ ^\circ\text{C}$ and $H_2O_2/S = 8$.

3.2.2.2. ECODS using heterogeneous $PW_{12}@TMA\text{-}SBA\text{-}15$

A new heterogeneous catalyst was prepared by the immobilization of PW_{12} into positively-charged functionalized-SBA-15 (TMA-SBA-15). The SBA-15 has proven to be a suitable support to immobilize POMs when functionalized with appropriate functional groups. [24, 29, 39, 50] In addition, this support has demonstrated that it can be used efficiently in oxidative desulfurization processes. [39, 42, 51-56] In this work, the trimethylammonium functional group was strategically selected to immobilize effectively the anionic PW_{12} by ionic interaction. The preparation of $PW_{12}@TMA\text{-}SBA\text{-}15$ allows the straightforward removal of catalysts from the ECODS system.

The ECODS studies were performed using this heterogeneous catalyst under the same conditions that were previously presented for the homogeneous $IL\text{-}PW_{12}$. The model diesel was desulfurized using MeCN and $[BMIM]PF_6$ extraction solvents (Figure 3.5). Contrary to what was observed with $IL\text{-}PW_{12}$ catalysts, the catalytic activity of the composite $PW_{12}@TMA\text{-}SBA\text{-}15$ was considered similar in the presence of MeCN and IL extraction solvents. The difference in desulfurization efficiency observed during the first 30 min of the oxidation step was attributed to the lower initial extraction obtained with the IL extraction solvent (39% using IL instead of 57% using MeCN, Figure 3.5 and Table 3.1).

Table 3.1 - Individual and total desulfurization efficiency in the initial extraction (10 min) of the sulfur compounds from model diesel to the extraction phase (MeCN or IL) using TMA-SBA-15, $[BPy]PW_{12}$ and $PW_{12}@TMA-SBA-15$ as catalysts (3 μ mol of PW_{12} active catalytic center).

Desulfurization (%)						
Catalyst	Solvent	1-BT	DBT	4-MDBT	4,6-DMDBT	TOTAL
TMA-SBA-15	MeCN	63	66	61	56	62
	IL	53	55	45	37	47
$[BPy]PW_{12}$	MeCN	61	65	60	54	60
	IL	66	58	45	34	51
$PW_{12}@TMA-SBA-15$	MeCN	63	62	55	47	57
	IL	54	50	34	21	40

Based on the superior activity of the composite compared to the IL- PW_{12} using the model diesel/MeCN system, the catalytic contribution of the support TMA-SBA-15 was investigated (Figures 3.7 and 3.8). It was demonstrated that this support material does not have any oxidative catalytic performance, since the desulfurization stopped after the initial extraction process, even in the presence of excess H_2O_2 oxidant ($H_2O_2/S = 8$), using either MeCN or IL extraction solvents. Using the model diesel/IL ECODS system it was possible to observe that desulfurization profile of the composite is slightly lower than the IL- PW_{12} homogeneous catalysts, since complete desulfurization was achieved after 1.5 h using the composite and 1 h using the IL- PW_{12} catalysts. By comparing the initial liquid-liquid sulfur extraction that occurred during the first 10 min for the homogeneous and heterogeneous ECODS catalytic systems, it is possible to observe that this was slightly higher in the absence of solid material, which may have contributed to the lower activity found with the $PW_{12}@TMA-SBA-15$ composite

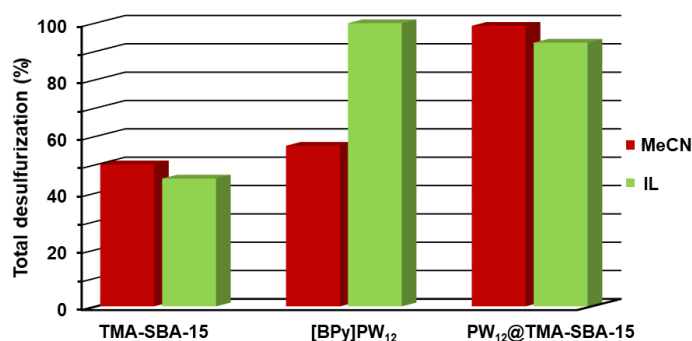


Figure 3.7 - Desulfurization data of multicomponent model diesel obtained after 1 h in the presence of the support (TMA-SBA-15), $[BPy]PW_{12}$, PW_{12} and $PW_{12}@TMA-SBA-15$ (3 μ mol of active PW_{12}) with MeCN or IL ($[BMIM]PF_6$) as extraction solvent, at 70 °C and using $H_2O_2/S = 8$.

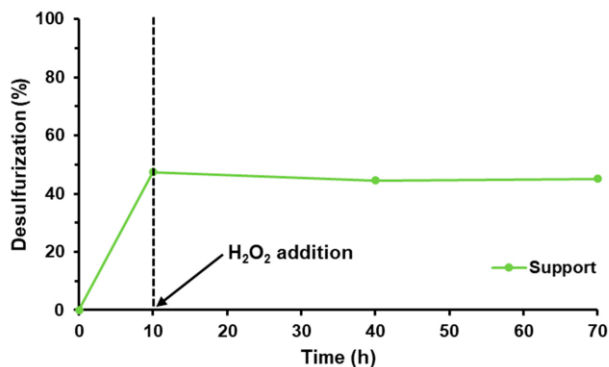


Figure 3.8 - Desulfurization profiles for a multicomponent model diesel using the TMA-SBA-15 support using the ECODS model diesel/[BMIM]PF₆ system at 70 °C and using H₂O₂/S = 8.

The continuous reuse of the composite catalyst PW₁₂@TMA–SBA-15 was performed following the previously described procedure for the reuse of the homogeneous IL–PW₁₂. At the end of an ECODS cycle, after stopping the stirring, all solid catalyst remained in the extraction phase and the sulfur-free model diesel was removed and replaced by new sulfurized model diesel and a new aliquot of oxidant. The continuous reusability of the composite was evaluated for three consecutive cycles. The desulfurization profiles for the various cycles are displayed in Figure 3.9. When comparing the desulfurization performance of the composite catalyst in the three ECODS cycles, some differences were detected, mainly from the first to the consecutive cycles. In particular, an increase in sulfur removal was observed in the second and third cycles when compared with the first cycle. The complete desulfurization of the model diesel was achieved after just 1 h instead of the 1.5 h that was necessary during the first ECODS cycle. This increase observed in the second and consecutive ODS cycles should be related to the presence of previously formed catalytically active peroxo species. [24, 29, 31, 48, 57]

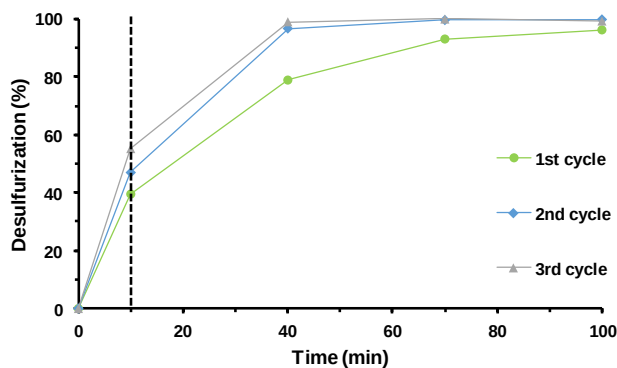


Figure 3.9 - Kinetic desulfurization profiles of multicomponent model diesel catalyzed by PW₁₂@TMA–SBA-15 for three continuous reused cycles using ionic liquid ([BMIM]PF₆) as an extraction solvent at 70 °C and H₂O₂/S = 8.

3.2.3. Catalyst stability

The stability of the heterogeneous catalyst was evaluated after catalytic use ($PW_{12}@TMA-SBA-15-ac$) with different characterization techniques. The vibrational spectra (Figures 3.1B and 3.2B) before and after catalysis were similar without significant changes. Both displayed the typical bands assigned to the vibrational modes of PW_{12} and SBA-15 support, suggesting that the main structure of the composite was retained. In the case of FT-Raman, the spectrum after catalytic use displayed some additional bands (marked with an asterisk). These bands are related to the presence of model diesel and related components, as previously observed by our group. [29] These species remain strongly adsorbed onto the catalyst, even after the washing procedure, and are most likely the corresponding sulfones of the initial sulfur compounds. [58] The crystalline structure of the SBA-15 support was investigated by powder XRD. The pattern of $PW_{12}@TMA-SBA-15-ac$ still exhibited the same three main peaks of the hexagonal symmetry of SBA-15 at the same 2θ (Figure 3.3). Nevertheless, a broadness of the peak indexed to the (100) reflection was observed after catalysis which could be due to a small loss of crystallinity during the consecutive ECODS cycles. The $PW_{12}@TMA-SBA-15-ac$ material was also studied by SEM/EDS techniques (Figure 3.10). The images obtained revealed an identical morphology with the initial composite composed of the same typical elongated structures. Moreover, the EDS analysis revealed the presence of silicon and tungsten at similar relative intensities before and after catalysis.

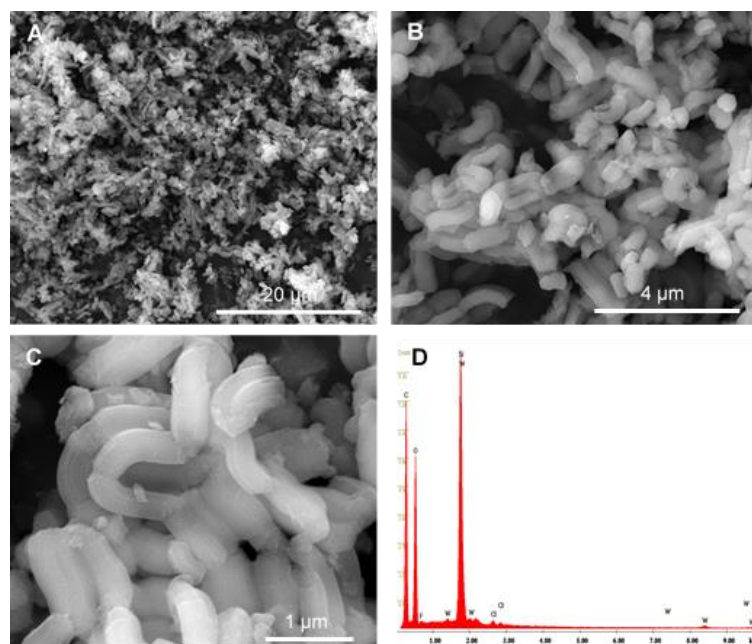


Figure 3.10 - SEM images of the $PW_{12}@TMA-SBA-15-ac$ material at different magnifications: (A) x5000, (B) x25000, (C) x60000 and (D) EDS spectrum.

An elemental analysis of the recovered catalyst was also performed to investigate the occurrence of leaching. The results indicated a PW_{12} loading of 0.046 mmol/g in the $PW_{12}@TMA-SBA-15-ac$ composite, corresponding to a leaching of 17%. Such value is most likely related to the interactions established between the trimethylammonium groups and PW_{12} that help to keep POM molecules in the composite during catalytic use. The characterization of $PW_{12}@TMA-SBA-15-ac$ shows that the heterogeneous catalyst was stable under the experimental ECODS conditions and retained its main structure and chemical composition.

The integrity of the homogeneous $[BPy]PW_{12}$ catalyst was assessed by ^{31}P NMR. The spectra of the starting catalyst after one and three ECODS cycles are represented in Figure 3.11. The spectrum of $[BPy]PW_{12}$ before catalytic use exhibited a single peak at $\delta = -13.89$ ppm. The recovered catalyst after the first ECODS cycle using the biphasic system model diesel/MeCN also presented a ^{31}P NMR spectrum with the initial single peak at -13.89 ppm. This result indicates that no formation of active peroxo-species occurred, which can explain the absence of catalytic activity observed in this homogeneous system. Regarding the ^{31}P NMR spectra obtained after the first and the third ECODS cycles using the model diesel/[BMIM]PF₆ system, these exhibited three main peaks located at $\delta = 1.86$, -2.91 and -8.52 ppm. These species should correspond to peroxo-complexes (known as PW_xO_y) with different P/W ratios which are formed during the decomposition of the Keggin structure in the presence of H_2O_2 . [16, 38, 42, 59, 60] The interaction between PW_{12} and the IL [BMIM]PF₆ can also promote shifts in the ^{31}P signals of the known peroxo-complexes which makes it extremely difficult to perform unequivocal assignment. For instance, Liu *et al.* reported alkene epoxidation using a PW_{12} -based catalyst and ionic liquids as solvents. After catalytic use, an additional ^{31}P NMR signal at $\delta = -8.6$ ppm was observed which the authors were unable to identify. [59] Interestingly, the intensity of the peak at a higher chemical shift (1.86 ppm) increased along the ECODS cycles when compared with the intensities of the other two peaks. At the end of the third cycle, the peak at $\delta = 1.86$ became the main peak in the ^{31}P NMR spectrum and should therefore correspond to the most active species in the studied reaction.

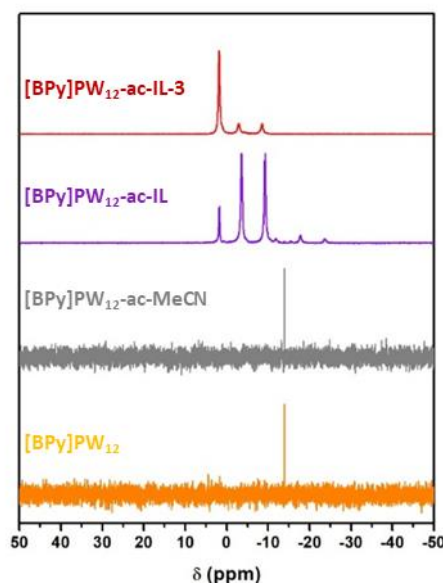


Figure 3.11- ^{31}P NMR spectra of $[BPy]PW_{12}$ before and after catalytic use (ac) in the presence of MeCN or IL extraction solvents. $[BPy]PW_{12}$ -ac-IL means after the first ECODS cycle and $[BPy]PW_{12}$ -ac-IL-3 means after the third ECODS cycle.

3.2.4. ECODS of untreated Diesel

The homogeneous $[BPy]PW_{12}$ and the heterogeneous $PW_{12}@TMA-SBA-15$ catalysts were used in the desulfurization of an untreated real diesel containing 2300 ppm of sulfur. The studies were conducted using the untreated diesel as received and a biphasic ECODS system formed by 1:1 diesel/ $[BMIM]PF_6$. The desulfurization treatment was performed using the same experimental conditions as used with the model diesel ($H_2O_2/S = 8$, 3 μ mol of active catalytic center, at 70 °C). At the end of oxidative catalytic step, the oxidized diesel was extracted with MeCN (1:1 to remove the oxidized products). The desulfurization performed with the homogeneous catalyst was slightly higher than using the heterogeneous, since 75% of efficiency was achieved with $[BPy]PW_{12}$, instead of 65% obtained with the composite after 2 h. The lower reactivity of $PW_{12}@TMA-SBA-15$ might be due to the more complex matrix of the real diesel that contains, besides sulfur compounds, aromatic hydrocarbons that can be adsorbed onto the composite catalytic sites.

3.3. Conclusions

In this work, various ionic–liquid Keggin-type phosphotungstate compounds were prepared using 1-butyl-3-methylimidazolium cation $[BMIM]PW_{12}$, 1-butylpyridinium

cation $[BPy]PW_{12}$ and hexadecylpyridinium cation $[HDPy]PW_{12}$. These compounds showed high catalytic activity during the desulfurization of a multicomponent model diesel (total desulfurization after 1 h). This diesel was treated efficiently in two main steps: initial liquid–liquid sulfur extraction and catalytic sulfur oxidation (ECODS) using a low excess of H_2O_2 oxidant ($H_2O_2/S = 8$) at $70\text{ }^{\circ}C$.

The catalytic performance of these homogeneous catalysts was higher in the present of the biphasic system 1:1 diesel/ionic liquid $[BMIM]PF_6$ than in the 1:1 diesel/acetonitrile system. In the first ECODS system, the high activity of the Keggin catalysts was due to their decomposition into different peroxy-compounds. The various ionic liquids cations used in the homogeneous catalysts did not confer different catalytic performances. Furthermore, the continuous recycling of the extraction $[BMIM]PF_6$ phase containing the homogeneous catalyst caused some loss of oxidative catalytic activity after the first ECODS cycle.

The disadvantages associated with the homogeneous catalytic systems were overcome by the application of the $PW_{12}@TMA-SBA-15$ heterogeneous catalyst, prepared by the immobilization of the same PW_{12} catalytic center on the trimethylammonium functionalized-SBA-15. In this case, the solid catalyst presented a similar oxidative desulfurization efficiency using acetonitrile or ionic liquid $[BMIM]PF_6$ solvents. On the other hand, similar catalytic performances of the composite and IL- PW_{12} homogeneous compounds were found, resulting in complete desulfurization after approximately 1 h. Moreover, the high reuse capacity of the composite was observed, whereby the ionic liquid solvent and the solid catalysts were reused together for consecutive ECODS cycles, and an increase in oxidative desulfurization efficiency was observed after the first cycle. At the end, the solid catalytic composite was isolated, and its structural stability was confirmed. Therefore, the high catalytic performance obtained with the $PW_{12}@TMA-SBA-15$ composite indicates that the trimethylammonium–SBA-15 support confers an optimal environment for promoting efficient catalytic sulfur oxidation, ensuring its activity and robustness.

3.4. Experimental section

3.4.1. Materials and Methods

The following chemicals and reagents were purchased from commercial suppliers and used without further purification: phosphotungstic acid hydrate ($H_3PW_{12}O_{40} \cdot xH_2O$,

Sigma-Aldrich), 1-butyl-3-methylimidazolium (BMIM) bromide (Fluka, 97%), 1-butylpyridinium (BPy) bromide (Aldrich, 99%), hexadecylpyridinium (HDPy) bromide (Aldrich, 97%), Pluronic P123 (Aldrich), hydrochloric acid (HCl, Fluka), tetraethyl orthosilicate (TEOS, 98%), *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (TMA, 50% in methanol, ABCR) and anhydrous toluene (Aldrich, 99.8%). The reagents for ECODS studies were used as received, namely dibenzothiophene (DBT, Sigma-Aldrich, 98%), 1-benzothiophene (BT, Fluka, 95%), 4-methyldibenzothiophene (4-MDBT, Sigma-Aldrich, 96%), 4,6-dimethyldibenzothiophene (4,6-DMDBT, Alfa-Aesar, 97%), *n*-octane (Sigma-Aldrich, 98%), tetradecane (Aldrich, 99%), acetonitrile (MeCN, Merck, 99.5%), 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIM]PF₆, Sigma-Aldrich, 98%) and hydrogen peroxide (H₂O₂, Sigma-Aldrich, 30% w/v aq).

Elemental analysis for C, N, and H was performed on a Leco CHNS-932 at the University of Santiago de Compostela. Infrared spectra were recorded in the 400–4000 cm⁻¹ region on a Jasco 460 Plus Spectrometer using KBr pellets. ³¹P NMR spectra were collected for liquid solutions using a Bruker Avance III 400 spectrometer and chemical shifts are given with respect to external 85% H₃PO₄. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at the “Centro de Materiais da Universidade do Porto” (CEMUP, Porto, Portugal) using a JEOL JSM 6301F scanning electron microscope operating at 15 kV equipped with an Oxford INCA Energy 350 energy-dispersive X-ray spectrometer. The samples were studied as powders and were previously subjected to gold sputtering. Powder X-ray diffraction analyses were performed by the “Departamento de Física e Astronomia from Faculdade de Ciências da Universidade do Porto” and collected at ambient temperature in Bragg-Brentano para-focusing geometry using a Rigaku Smartlab diffractometer, equipped with a D/teX Ultra 250 detector and using Cu K- α radiation ($K_{\alpha 1}$ wavelength 1.54059 Å), 45 kV, 200 mA, in continuous mode, step 0.01°, speed 15°/min, in the range $1 \leq 2\theta \leq 50^\circ$. GC-FID analysis was carried out in a Bruker 430-GC-FID gas chromatograph using hydrogen as the carrier gas (55 cm³ s⁻¹) and fused silica SPB-5 Supelco capillary columns (30 m × 0.25 mm i.d.; 25 μm film thickness). The analysis of sulfur content of the treated diesel was performed by Rita Valença in Galp Company by ultraviolet fluorescence using Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

3.4.2. Synthesis of catalysts

3.4.2.1. Ionic liquid-polyoxometalates

The hybrids were prepared following an adaptation of the method by Zhang *et al.* [61] as described in Chapter 2 section 2.4.2. An aqueous solution of $H_3[PW_{12}O_{40}] \cdot nH_2O$ (1 mmol in 5 mL) was added dropwise to a solution containing the ionic liquid (5 mmol). The [BMIM]Br and [BPy]Br ionic liquids were dissolved in water while [HDPy]Br was dissolved in acetonitrile. The mixture was stirred for 1 h at room temperature. The resulting solid was recovered by filtration, washed with water and dried in a desiccator over silica gel.

[BMIM]PW₁₂. Anal. Found (%): C, 8.89; N, 2.52; Calcd. (%) $[C_8H_{15}N_2]_3(PW_{12}O_{40}) \cdot nH_2O$ (3295.55): C, 8.74, H, 1.38, N, 2.55. ^{31}P NMR (161.9 MHz, CD_3CN , 25 °C): $\delta = -12.27$ and -13.88 ppm. Selected FT-IR (cm^{-1}): $\nu = 3465$ (w), 3147 (m), 3114 (m), 2960 (m), 2931 (m), 2871 (m), 1562 (w), 1464 (w), 1385 (w), 1165 (m), 1080 (s), 978 (vs), 895 (s), 804 (vs), 746 (m), 650 (w), 621 (m), 596 (m), 521 (m); selected FT-Raman (cm^{-1}): 3164 (w), 2958 (m), 2871 (w), 1562 (w), 1442 (m), 1414 (m), 1385 (w), 1336 (w), 1112 (w), 1023 (m), 1006 (vs), 991 (s), 918 (m), 826 (w), 517 (m), 472 (w).

[BPy]PW₁₂. Anal. Found (%): C, 10.17; N, 1.22; Calcd. (%) $[C_9H_{14}N]_3(PW_{12}O_{40}) \cdot nH_2O$ (3286.52): C, 9.86, H, 1.29, N, 1.28. ^{31}P NMR (161.9 MHz, CD_3CN , 25 °C): $\delta = -13.89$ ppm. Selected FT-IR (cm^{-1}): $\nu = 3435$ (w), 3126 (w), 3086 (w), 3064 (w), 2966 (w), 2933 (w), 2875 (w), 1633 (m), 1487 (m), 1464 (w), 1317 (w), 1169 (w), 1080 (vs), 976 (vs), 897 (s), 802 (vs), 683 (s), 596 (w), 524 (m); selected FT-Raman (cm^{-1}): 3093 (m), 2969 (m), 2937 (m), 2937 (m), 2875 (w), 1631 (m), 1581 (w), 1442 (m), 1309 (w), 1210 (w), 1167 (w), 1027 (s), 1005 (vs), 991 (s), 917 (m), 826 (w), 646 (m), 518 (m), 472 (w).

[HDPy]PW₁₂. Anal. Found (%): C, 20.49; N, 1.08; Calcd. (%) $[C_{21}H_{38}N]_3PW_{12}O_{40} \cdot nH_2O$ (3791.08): C, 19.94, H, 3.03, N, 1.11. ^{31}P NMR (161.9 MHz, CD_3CN , 25 °C): $\delta = -14.13$ ppm. Selected FT-IR (cm^{-1}): $\nu = 3130$ (m), 3087 (m), 3066 (m), 2922 (vs), 2850 (vs), 1633 (s), 1583 (w), 1500 (m), 1487 (s), 1466 (s), 1377 (w), 1354 (w), 1315 (w), 1215 (w), 1173 (m), 1080 (vs), 978 (vs), 895 (vs), 808 (vs), 766 (sh), 679 (vs), 594 (m), 521 (s), 509 (s); selected FT-Raman (cm^{-1}): 3094 (m), 2891 (s), 2850 (s), 1633 (w), 1582 (w), 1438 (m), 1301 (w), 1214 (w), 1168 (w), 1028 (m), 1005 (vs), 991 (s), 918 (m), 646 (w), 517 (m), 472 (w).

3.4.2.2. $PW_{12}@TMA-SBA-15$ composite

The SBA-15 support was initially functionalized with *N*-trimethoxypropyl-*N,N,N*-trimethylammonium chloride as described in the literature. [34] Briefly, The support material SBA-15 was activated by drying at 120°C for 1 h under vacuum to remove any physisorbed water. Afterwards 2 g of SBA-15 material with *N*-trimethoxypropyl-*N,N,N*-trimethylammonium chloride (5 mmol) was refluxed in anhydrous toluene (25mL) for 24 h under argon. The composite material was prepared through an impregnation method previously described by our group. [38] A solution of PW_{12} (1 g in 20 mL of water) was added to the trimethylammonium functionalized support (TMA-SBA-15, 0.5 g) and the mixture was stirred for 72 h. The solid was filtrated, washed thoroughly with water and dried in a desiccator over silica gel.

SBA-15. Anal. Found (%): N, 0.3; C, 4.5; H, 0.9. Selected FT-IR (cm^{-1}): $\nu = 3400$ (vw), 1652 (vw), 1198 (sh), 1070 (vs), 968 (m), 804 (m), 452 (vs); selected FT-Raman (cm^{-1}): no significant FT-Raman bands were observed.

TMA-SBA-15. Anal. Found (%): N, 1.4; C, 7.6; H, 2.2; 0.098 mmol of TMA per g of material. Selected FT-IR (cm^{-1}): $\nu = 3736$ (w), 2360 (m), 2342 (m), 1196 (sh), 1068 (vs), 952 (w), 804 (m), 668 (m), 446 (vs); selected FT-Raman (cm^{-1}): 3028 (vs), 2972 (vs), 2934 (vs), 2893 (s), 2825 (w), 1451 (s), 911 (m), 753 (m).

$PW_{12}@TMA-SBA-15$. Anal. Found (%): N, 1.5; C, 7.7; H, 1.8; W, 12.3%; Si, 3.8%. loading of $PW_{12} = 0.056$ mmol g^{-1} . Si/W (molar) = 2.0; ratio of TMA/POM = 19.1. Selected FT-IR (cm^{-1}): $\nu = 3435$ (m), 2939 (sh), 1655 (m), 1508 (w), 1388 (w), 1192 (sh), 1082 (vs), 951 (s), (m), 901 (w), 808 (s), 741 (sh), 667 (w), 459 (s); selected FT-Raman (cm^{-1}): 3031 (m), 2971 (s), 2936 (s), 2894 (m), 1448 (m), 1415 (m), 1348 (w), 1007 (vs), 990 (s), 912 (m), 864 (w), 749 (w), 516 (m).

3.4.3. Extractive and catalytic oxidative desulfurization process

The ECODS studies were performed using the multicomponent model diesel B containing ~2000 ppm of sulfur content dissolved in *n*-octane. This solution is composed by approximately, 500 ppm of dibenzothiophene (DBT), 500 ppm of benzothiophene (BT), 500 ppm of 4-methyldibenzothiophene (4-MDBT) and 500 ppm of 4,6-dimethyldibenzothiophene (4,6-DMDBT). A biphasic system was composed by equal volumes of model diesel and extraction solvent (0.75 mL each one). The process begins with an initial extraction in the presence of the catalyst (3 μ mol) with stirring for 10 min at

70 °C. The catalytic stage is then initiated with the addition of aqueous H_2O_2 30% (40 μ L). The reactions were monitored by analyzing the upper model diesel phase by gas chromatography using tetradecane as standard. The reusability of the catalysts was evaluated by removing the desulfurized model diesel at the end of an ECODS cycle and adding a new portion of untreated model diesel and oxidant. Real unthread diesel was also desulfurized using the same experimental conditions as the model diesel.

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Chapter 4

Oxidative desulfurization strategies using Keggin-type polyoxometalate catalysts: biphasic versus solvent-free systems^{1,2}



¹ Adapted from: Susana O. Ribeiro, Carlos M. Granadeiro, Pedro L. Almeida, João Pires, Maria C. Capel-Sanchez, José M. Campos-Martin, Sandra Gago, Baltazar de Castro and Salette S. Balula, *Oxidative desulfurization strategies using Keggin-type polyoxometalate catalysts: biphasic versus solvent-free systems*, *Catalysis Today*, 333 (2018) 226-236, doi: <https://doi.org/10.1016/j.cattod.2018.10.046>

² *Susana O. Ribeiro contribution to the publication:* Preparation and characterization of catalysts; investigation of catalytic performance of all catalysts in the desulfurization of a model diesel and real diesel supplied by CEPESA. Part of the experimental work was performed at Instituto de Catálisis y Petroleoquímica, Madrid, in collaboration with Doctor Jose M. Campos-Martin. S. O. Ribeiro is responsible for most of the performed experimental work and the manuscript preparation.

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Chapter 4

Oxidative desulfurization strategies using Keggin-type polyoxometalate catalysts: biphasic versus solvent-free systems

Abstract

Keggin-type polyoxometalate structural modification was performed to increase the oxidative catalytic performance to desulfurize model and real diesels. The most active lacunar structure $[\text{PW}_{11}\text{O}_{39}]^{7-}$ (PW_{11}) showed to complete desulfurize a simulated diesel after 60 min oxidation at 70 °C. Its application as homogeneous catalyst using a biphasic extractive and catalytic oxidative desulfurization (ECODS) system 1:1 diesel/acetonitrile required a moderate excess of oxidant (ratio $\text{H}_2\text{O}_2/\text{S} = 8$). The immobilization of the PW_{11} on amine-functionalized mesoporous silica (aptSBA-15 and tbaSBA-15) originated two heterogeneous catalysts $\text{PW}_{11}@\text{aptSBA-15}$ and $\text{PW}_{11}@\text{tbaSBA-15}$. The best results were attained with the $\text{PW}_{11}@\text{aptSBA-15}$ catalyst, which shows identical oxidative desulfurization performance as the homogeneous analogue. As advantage, this heterogeneous catalyst promotes the complete desulfurization of simulated diesel using a solvent-free catalytic oxidative desulfurization (CODS) system, i.e. without the need of acetonitrile use, and achieved the same desulfurization efficiency using half amount of oxidant ($\text{H}_2\text{O}_2/\text{S} = 4$). The oxidative desulfurization of the real diesel achieved a remarkable 83.4% of efficiency after just 120 min. The recycle capacity of $\text{PW}_{11}@\text{aptSBA-15}$ catalyst was confirmed for eight consecutive cycles using the biphasic and the solvent-free systems, however its stability was higher in the solvent-free system than in the biphasic system, without practically any occurrence of PW_{11} leaching in the first case. On the other hand, the Venturello peroxocomplex $[\text{PO}_4\{\text{W}(\text{O}_2)_2\}_4]^{3-}$, recognized as active intermediated in the homogeneous biphasic system, was not identified in the heterogeneous catalytic systems.

4.1 Introduction

Polyoxometalates (POMs) are metal-oxygen anionic clusters that have been attracting much interest due to their unique properties in oxidative catalysis [1-3], with the Keggin-type ($[XM_{12}O_{40}]^{n-}$) POMs being the most investigated in this area of application (also previously studied in chapter 3). Most of the published work reports the phosphotungstic acid $H_3[PW_{12}O_{40}]\cdot nH_2O$ as catalyst or catalyst precursor for various oxidative catalysis. [4-6] Important Keggin-type derivatives include the lacunar polyanions ($[XM_{11}O_{39}]^{(n+4)-}$) that results by the removal of one MO^{4+} unit. The lacunar POM contains free oxygen atoms with coordinative capacity to incorporate different transition metals in their structure. In this case, mono-substituted POMs ($[XM_{11}M'(H_2O)O_{40}]^{p-}$) can be prepared by the coordination of M' transition metal with five O^{2-} ligands from the lacuna (for example the zinc-substituted $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ prepared in chapter 2). The application of transition-metal-substituted POMs as catalysts uses the advantage of open coordination sites on the transition metal by displacement of the water ligand. [5]

The performance of the lacunary phosphotungstate $[PW_{11}O_{39}]^{7-}$ (PW_{11}) in oxidative catalysis is well-reported, especially using H_2O_2 as oxidant. [7] In fact, several PW_{11} -based materials have proved to be efficient catalysts in several reactions, such as aldehyde [8] and alcohol esterification, [9] monoterpenes oxidation [10-12] alcohol oxidation and oxidative desulfurization. [13, 14] Recently, there has been given some attention to the zinc-substituted phosphotungstate $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ (its application in oxidative desulfurization is presented in chapter 2), since it revealed high catalytic activity in oxidative desulfurization. [15-18]

Several approaches have been made to prepare efficient and reusable heterogeneous POM-based catalysts for oxidative desulfurization of fuels. [19] Various strategies have been followed to incorporate active catalytic POMs in different materials, including metal-organic frameworks, [12, 16, 20] activated carbon, [21] layered double hydroxides, [22] mesoporous silica [13, 15, 23-26] and also by hybridization methodologies. [14, 18] Among these approaches, mesoporous silicas have the advantage of high specific surface areas, thermal stability, lightweight and extended framework composition. Moreover, the surface of silica can be easily modified by reacting with organosilanes containing appropriate functional groups. In particular, SBA-15 has been successfully used as support material due to its high hydrothermal stability and large pore size (as presented in chapter 3). [10, 27-30] Anchoring catalytically active POM species on amine-functionalized SBA-15 has proved to be highly efficient in

minimizing leaching owing to the strong interaction between the POM and the amine-functionalized surface via dative bonding. [5, 31] Recently POMs supported on amine-functionalized SBA-15 were prepared for application in oxidative desulfurization. [28, 29] The support has proved to be crucial in providing remarkable robustness and stability to the heterogeneous catalysts which enabled a high recycling capacity in consecutive catalytic cycles. In chapter 3, the trimethylammonium-functionalized SBA-15 demonstrated to be a suitable support to immobilize the Keggin PW_{12} structure via electrostatic interaction to form an active and a robust heterogeneous catalyst for oxidative catalytic desulfurization.

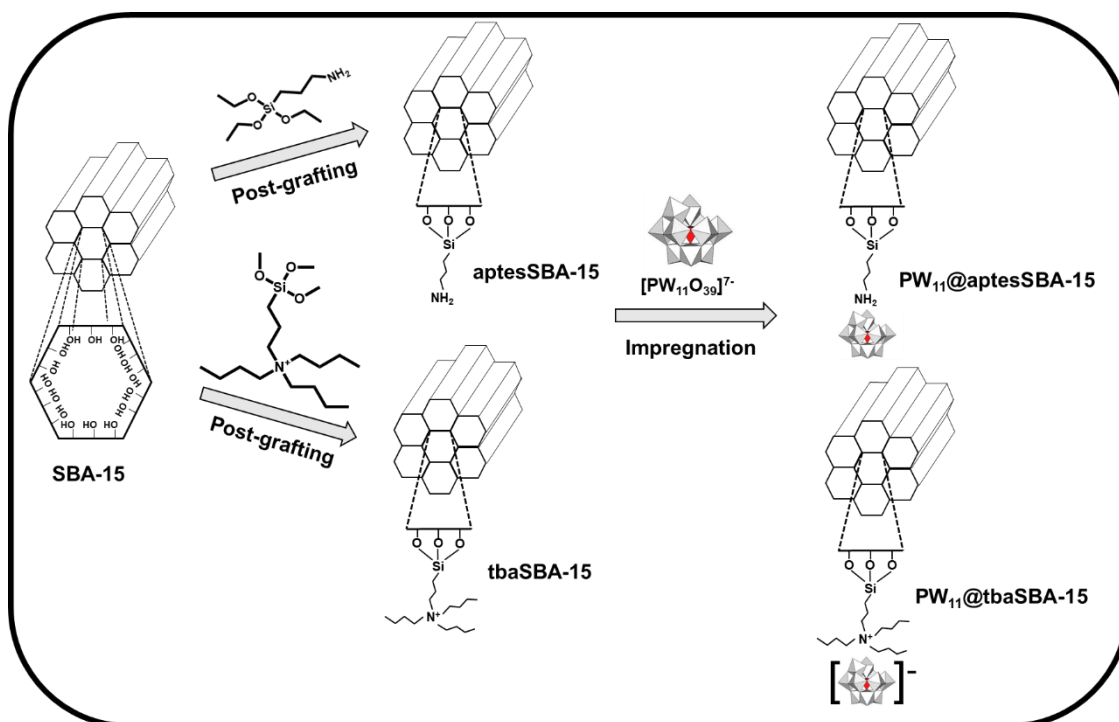
A comparison between the catalytic activity of various Keggin-POM derivatives structures was initially performed and afterwards, the homogeneous catalyst showing the best catalytic activity was immobilized in two different amine-functionalized SBA-15 supports. Therefore, different strategies were adopted in the oxidative desulfurization process to remove the most refractory sulfur compounds from model diesel B (containing ~ 2000 ppm S) and a real diesel (supplied by CEPISA). All desulfurization reactions were carried out with hydrogen peroxide as oxidant. The sustainability of the process and the efficiency of the most active catalytic system were optimized. Total model diesel desulfurization was achieved under mild reaction after only 60 min and after 120 min and 83.4% of desulfurization efficiency was attained for the real untreated diesel. The recyclability of the heterogeneous catalyst was investigated and its robustness was analyzed.

4.2. Results and discussion

4.2.1. Catalysts characterization

The tetra-n-butylammonium salt (TBA) of different Keggin derivative POM structure were prepared and characterized: the Keggin $[PW_{12}O_{40}]^{3-}$ (**PW₁₂**), the lacunar $[PW_{11}O_{39}]^{7-}$ (**PW₁₁**) and the zinc-mono-substituted $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ (**PW₁₁Zn**). Synthesis and characterization data is presented in 4.4.2.1. Composite materials were also prepared via an impregnation method, through the incorporation of lacunar PW_{11} anion in two amine-functionalized SBA-15 supports: aptesSBA-15 [apt: (3-aminopropyl)triethoxysilane] and tbaSBA-15 [tba: N-(3-trimethoxysilylpropyl)tributylammonium] (Scheme 4.1). Experimental details are presented in sections 4.4.2.2, 4.4.2.3 and 4.4.2.4. The prepared composites were characterized by several techniques including vibrational spectroscopy (FT-IR and FT-Raman), powder XRD, inductively

coupled plasma optical emission spectrometry (ICP-OES), solid state ^{31}P , ^{13}C and ^{29}Si MAS NMR, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and textural analysis (N_2 adsorption isotherms).



Scheme 4.1 – Preparation route of the $\text{PW}_{11}@\text{aptSBA-15}$ and $\text{PW}_{11}@\text{tbaSBA-15}$ composites.

The FT-IR spectra (wavenumber region between 400 and 3200 cm^{-1}), display the characteristic bands of the Keggin-type POM derivatives and of the SBA-15 supports (Figure 4.1 left). The spectra of the composite materials are dominated by the characteristic bands of the silica support in the region between 400–1100 cm^{-1} , i.e. the typical Si–O–Si bands around 1078, 802 and 457 cm^{-1} , associated with the formation of a condensed silica network. [20, 32, 33] However, the appearance of two extra bands located at 940 and 879 cm^{-1} , which are attributed to the terminal $\nu_{\text{as}}(\text{W}-\text{O}_\text{t})$ and corner-sharing $\nu_{\text{as}}(\text{W}-\text{O}_\text{b}-\text{W})$ vibrational modes, respectively, indicate the presence of PW_{11} in the composite [18, 20, 34]. As described in the literature, the FT-Raman signal of the silica support is far weaker than the FT-IR allowing a better observation of the bands arising from the PW_{11} . Therefore, the bands associated with $\nu_{\text{as}}(\text{P}-\text{O})$, $\nu_{\text{as}}(\text{W}-\text{O}_\text{d})$ and $\nu_{\text{as}}(\text{W}-\text{O}_\text{b}-\text{W})$ stretching modes can be observed at 1039, 956 and 856 cm^{-1} and 1056, 986 and 880 cm^{-1} for $\text{PW}_{11}@\text{aptSBA-15}$ and $\text{PW}_{11}@\text{tbaSBA-15}$, respectively (Figure 4.1 right). [29, 34, 35] Additionally, a small shift of these bands to lower wavenumbers

was noticed when the PW_{11} is incorporated in the SBA-15 supports, as has been reported in the literature for the immobilization of POMs in to silica materials. [20, 36] The smaller intensity of the bands associated with the POM in the $PW_{11}@tbaSBA-15$ spectrum suggests that the incorporation was less efficient than in $PW_{11}@aptesSBA-15$. In fact, ICP analysis reveals a PW_{11} loading of 0.037 and 0.096 mmol per gram of material for $PW_{11}@tbaSBA-15$ and $PW_{11}@aptesSBA-15$, respectively.

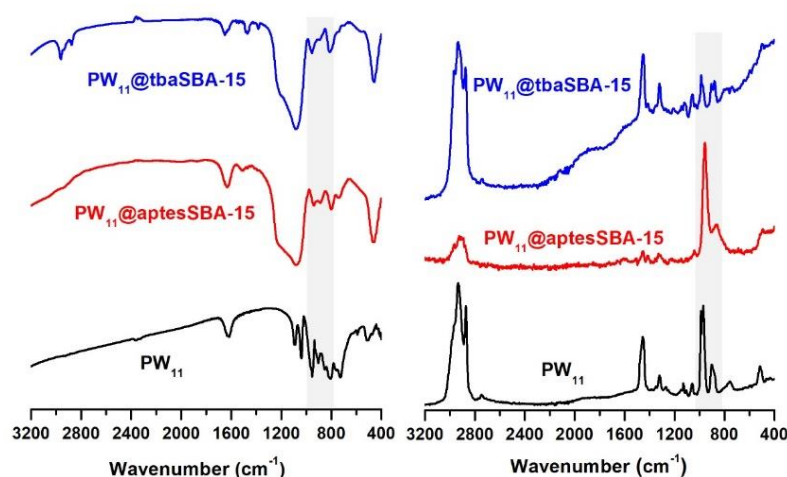


Figure 4.1 - FT-IR (left) and FT-Raman (right) spectra of the isolated PW_{11} and the composite materials $PW_{11}@aptesSBA-15$ and $PW_{11}@tbaSBA-15$.

The integrity of the lacunar PW_{11} structure, before and after its incorporation on silica support was investigated by ^{31}P MAS-NMR (Figure 4.2). The spectra of the composites present a main peak at -12.73 and -13.06 ppm for $PW_{11}@aptesSBA-15$ and $PW_{11}@tbaSBA-15$, respectively, while the free PW_{11} displays a single peak at -12.81 ppm. These results indicate the maintenance of the PW_{11} structure after its incorporation on the silica material. [18, 20] The $PW_{11}@aptesSBA-15$ composite was also analyzed by ^{13}C CP MAS-NMR spectroscopy and this spectrum exhibit three peaks located at 43.6, 21.9 and 10.0 ppm (Figure 4.3 left). These peaks correspond to the C3, C2 and C1 carbon atoms of the aptes fragment, $Si-^1CH_2-^2CH_2-^3CH_2-NH_2$. [29, 37] Moreover, the nonexistence of ^{13}C signals of the pluronic P123 template (67–77 ppm) indicates an efficient removal of the surfactant. [37] The spectrum of the $PW_{11}@tbaSBA-15$ exhibits five peaks located at 59.4, 25.0, 20.8, 14.9 and 10.5 ppm corresponding to the carbon atoms of the tba fragment, $Si-^1CH_2-^2CH_2-^3CH_2-N-(^3CH_2-^2CH_2-^4CH_2-^5CH_3)_3$, respectively.

The ^{29}Si MAS NMR spectra of both composites reveal a broad and intense band and two shoulders that correspond to Q^4 ($\delta \approx -112$ ppm), Q^3 ($\delta \approx -104$ ppm) and Q^2 ($\delta \approx -94$ ppm) species, where $\text{Q}^n = \text{Si}(\text{OSi})_{4-n}(\text{OH})_n$, $n = 2-4$ (Figure 4.3 right). [38, 39] The spectra exhibit a similar profile to the spectrum of the SBA-15 support indicating that the main structure of the silica material was maintained after the PW_{11} incorporation. Spectra of both composites also exhibit two additional peaks related to T^3 and T^2 species ($\text{T}^n = \text{CSi}(\text{OSi})_{3-n}(\text{OH})_n$, $n = 1-3$), located at -65.68 and -58.76 ppm for $\text{PW}_{11}@\text{aptesSBA-15}$ and -68.08 and -60.91 ppm for $\text{PW}_{11}@\text{tbaSBA-15}$. [40] The appearance of T^2 and T^3 peaks suggest the formation of siloxane bonds between Si atoms of the amino groups and SBA-15. [30, 41-44]

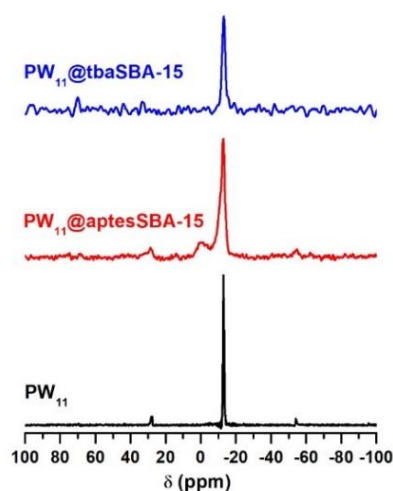


Figure 4.2 - Solid state ^{31}P MAS NMR spectra of the isolated PW_{11} and the composite materials $\text{PW}_{11}@\text{aptesSBA-15}$ and $\text{PW}_{11}@\text{tbaSBA-15}$.

The powder XRD patterns of the PW_{11} -based composites and of the support material are shown in Figure 4.4. The pattern of the SBA-15 presents three well-resolved peaks in the low-angle area which are typical of the SBA-15 materials. [41, 44, 45] These peaks correspond to the (100), (110) and (200) reflections of a hexagonal symmetry lattice P6mm . The peaks of the (110) and (200) reflections in the pattern of the composite materials are shifted to higher 2θ , has been reported in the literature for POMs@SBA-15 composites. [20, 45, 46] The absence of peaks related to the lacunar PW_{11} strongly indicates its incorporation within the porous channels of the porous support.

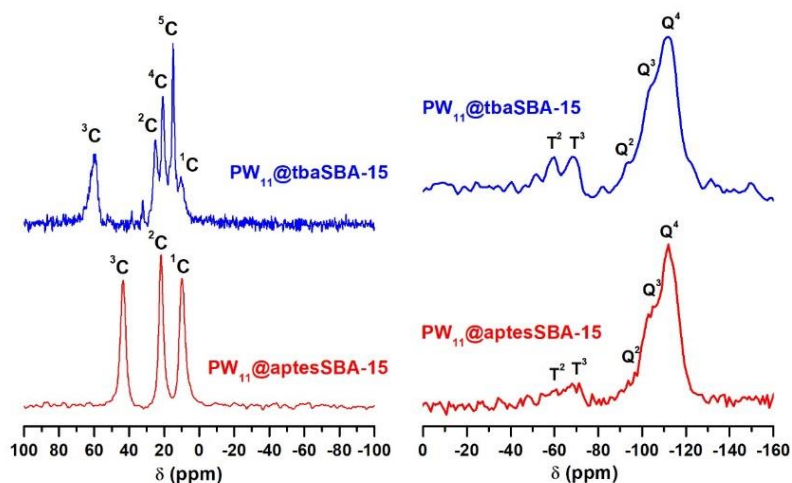


Figure 4.3 - Solid-state ^{13}C CP MAS (left) and ^{29}Si MAS (right) NMR spectra of $\text{PW}_{11}@\text{aptesSBA-15}$ and $\text{PW}_{11}@\text{tbaSBA-15}$.

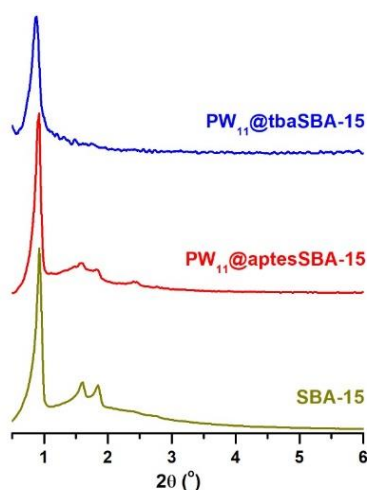


Figure 4.4 - Powder XRD patterns of the support SBA-15 and composite materials $\text{PW}_{11}@\text{aptesSBA-15}$ and $\text{PW}_{11}@\text{tbaSBA-15}$.

Table 4.1 displays the surface area (S_{BET}) and total pore volume (V_p) of the starting support, the amine functionalized support and of the PW_{11} -composites. There is a decrease in S_{BET} and V_p when going from SBA-15 to amine-functionalized aptesSBA-15, which indicates a successful functionalization with aptes that is anchored into the surface of SBA-15. A simultaneous decrease in S_{BET} and V_p could also be observed for both composites when compared with SBA-15. The $\text{PW}_{11}@\text{aptesSBA-15}$ composite displays values in good agreement with previously reported data for $\text{POM}@\text{aptesSBA-15}$ materials which strongly suggest the successful incorporation of PW_{11} on the channels of aptesSBA-15. [29, 36] However, the $\text{PW}_{11}@\text{tbaSBA-15}$ composite exhibited very

small values which are most likely related with the bulkier size of tba groups when compared with aptes ligands. The branched structure of tba, in contrast with the more linear geometry of the aminopropyl groups of aptes (Scheme 4.1), could promote the blockage of a significant amount of porosity what could explain the different catalytic performance of the catalysts as will be further discussed (section 4.2.2.2.).

The N₂ adsorption isotherms for SBA-15, aptesSBA-15 and PW₁₁@aptesSBA-15 (Figure 4.5) are of type IV classification with a H1 hysteresis loop typical of these type of mesoporous materials. [29, 31, 47] The amine-functionalized aptesSBA-15 support and the PW₁₁@aptesSBA-15 composite retain the same shape of the isotherms of bare SBA-15.

Table 4.1 - Textural parameters of SBA-15 and the composite materials, PW₁₁@aptesSBA-15 and PW₁₁@tbaSBA-15.

	S_{BET} (m ² g ⁻¹)	V_p (cm ³ g ⁻¹)
SBA-15	725	0.971
aptesSBA-15	337	0.589
PW₁₁@aptesSBA-15	240	0.399
PW₁₁@tbaSBA-15	10	0.035

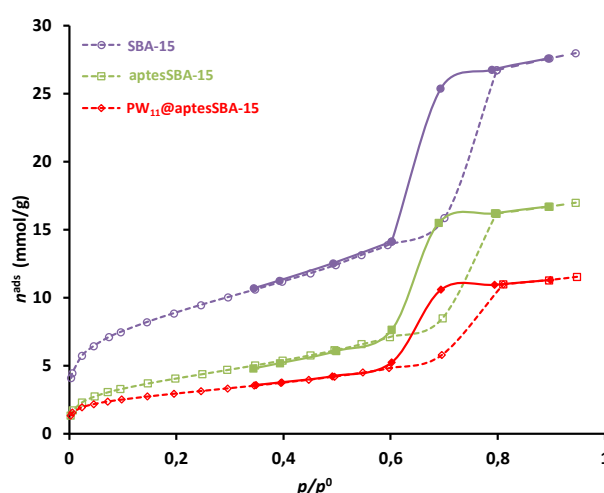


Figure 4.5 - N₂ adsorption-desorption isotherms of the support material SBA-15, the functionalized aptesSBA-15 and the PW₁₁@aptesSBA-15 composite.

The SEM images of the composite materials reveal the characteristic morphology of the SBA-15 materials with hexagonal elongated particles with diameters of approximately 950 nm, indicating that the morphology of the silica support was maintained in both composites after PW_{11} incorporation (Figure 4.6). [18, 46, 48] The presence of PW_{11} in the composite materials was further confirmed by the detection of tungsten in the EDS analysis (Figure 4.6E and 4.6F).

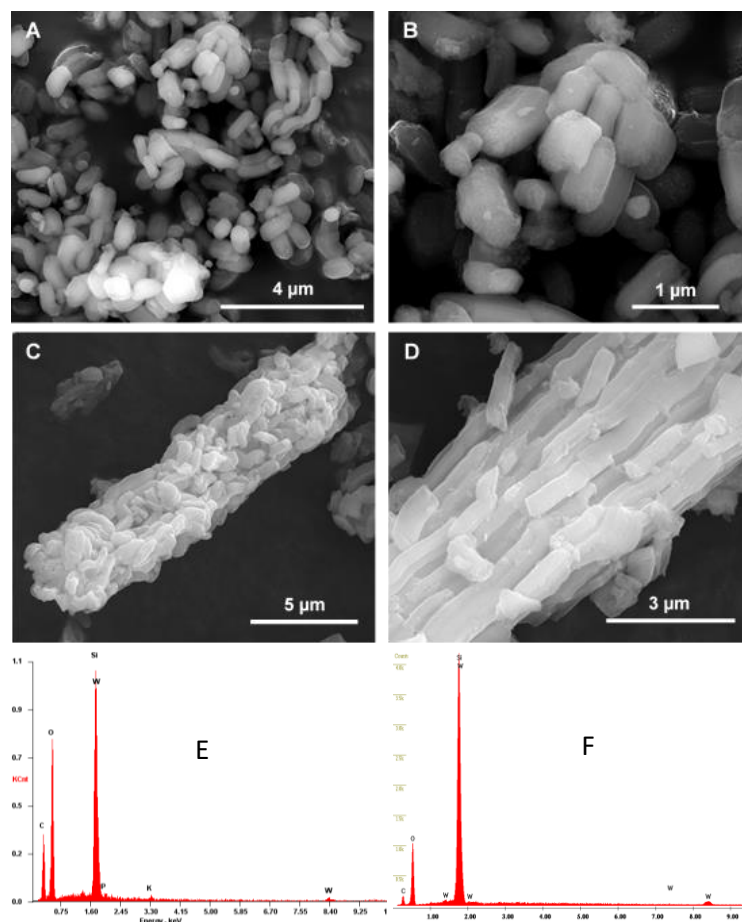
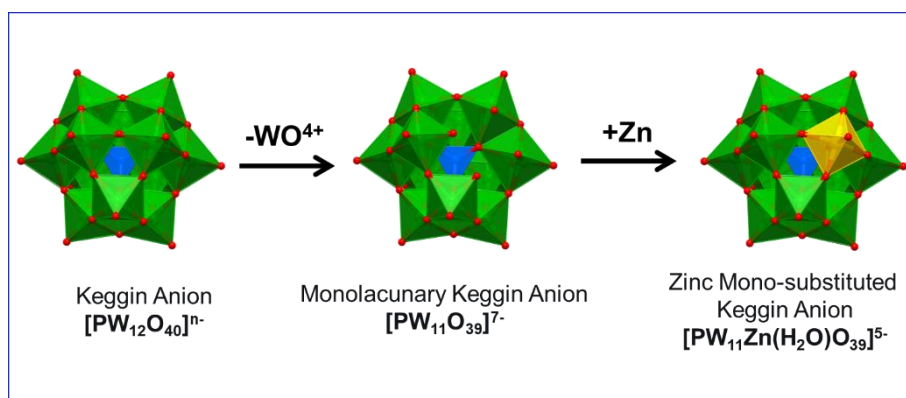


Figure 4.6 - SEM images of (A, B) PW_{11} @aptesSBA-15 and (C,D) PW_{11} @tbaSBA-15 composite materials. EDS spectra of the PW_{11} @aptesSBA-15 (E) and PW_{11} @tbaSBA-15 (F) composite materials.

In conclusion, the comparative study by different techniques between the isolated PW_{11} and its corresponding PW_{11} @aptesSBA-15 and PW_{11} @tbaSBA-15 composites indicate a successful immobilization of the PW_{11} on the amine-functionalized SBA-15 materials without degradation of the PW_{11} structure.

4.2.2. Oxidative desulfurization processes using model diesel

The preliminary studies with the prepared catalysts were performed using the model diesel B (see Chapter 1 section 1.7). The desulfurization studies were performed initially using various homogeneous catalysts based in TBA salts of various Keggin derivative POMs: the Keggin anion PW_{12} , the monolacunary PW_{11} and the zinc mono-substituted $PW_{11}Zn$ (Scheme 4.2). The main goal of these studies was to relate the catalytic efficiency in oxidative desulfurization with POM structure, using a biphasic system (1:1 model diesel/MeCN extraction solvent). These desulfurization studies consisted in an initial liquid-liquid extraction (10 min of stirring at 70 °C), followed by an oxidative catalytic stage ($H_2O_2/S = 8$, at 70 °C).



Scheme 4.2 – Structures of the Keggin phosphotungstate PW_{12} and its derivatives the monolacunary PW_{11} and the zinc mono-substituted $PW_{11}Zn$

The most active homogeneous POM was immobilized in amine-functionalized SBA-15 to create heterogeneous $PW_{11}@aptesSBA-15$ and $PW_{11}@tbaSBA-15$ catalysts. Their catalytic performance was initially compared using the biphasic ECODS system model diesel/MeCN (1:1) and the solvent-free CODS system. In this latter system, the sulfur catalytic oxidation takes place without the presence of any extraction solvent, followed by a liquid-liquid extraction to remove the oxidized sulfur from diesel. This final extraction was performed using MeCN or a greener solvent, such as ethanol and/or water. [17]

4.2.2.1. Homogeneous catalysts: activity and stability

The homogeneous desulfurization catalytic studies, using the TBA salts of the different Keggin-type POMs were performed using a biphasic model diesel/MeCN

system. An initial extraction occurred where non-oxidized sulfur compounds were transferred from the model diesel to the polar organic phase (MeCN). After 10 min the sulfur transfer equilibrium was reached and the oxidative catalytic step was initiated by the addition of the oxidant (H_2O_2 , 0.4 mmol). In this stage the sulfur compounds were oxidized to the correspondent sulfoxides and/or sulfones, which remained in the extraction phase. The distribution of non-oxidized sulfur compounds between diesel and MeCN phases arises to an equilibrium point and the amount of non-oxidized sulfur decrease in MeCN phase (promoted by their oxidation) originates a continuous transfer of sulfur from diesel to MeCN phase, which decreases the sulfur amount in diesel phase.

In figure 4.7 is displayed the desulfurization profiles catalyzed by the different Keggin derivative POMs. The initial extraction step was responsible for the major removal of sulfur from the model diesel to the MeCN phase, and this desulfurization efficiency was similar for the various POM catalysts (from 53.0 % to 58.0%), which indicates that the structure of the homogeneous POMs does not have any influence in this step of the process. To increase desulfurization, the oxidant was added to initiate the catalytic sulfur-oxidation step.

It can also be observed that the lacunar PW_{11} was the most active catalyst reaching ultra-low sulfur levels (< 10 ppm) after 2 h of reaction (99.7% of total desulfurization). Instead of it, the Keggin structure PW_{12} was the less efficient homogeneous catalyst reaching only 68.0 % of total desulfurization after 2 h of reaction (initial extraction plus the catalytic stage) and only 28.1% of oxidation was achieved, in the catalytic stage of the process. The zinc-substituted PW_{11}Zn achieved 85.6 % of total desulfurization after the same period of time.

It is important to note, that after the addition of the aqueous H_2O_2 oxidant (10 min of the process) a decrease of desulfurization was observed using Keggin PW_{12} and zinc-substituted PW_{11}Zn catalysts. This is probably caused by the water introduced in the biphasic system after the addition of the aqueous oxidant, associated to the lower oxidative catalytic efficiency of these two catalysts. This behavior was previously reported using similar biphasic systems. [18] The low reactivity of PW_{12} in MeCN medium has been already reported and justified by the difficult formation of active species (also referred in chapter 3). [20]

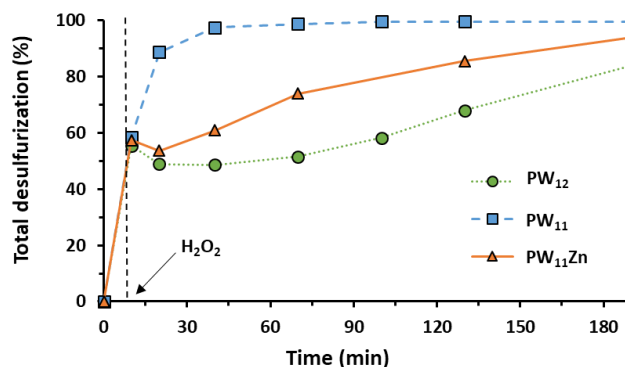


Figure 4.7 - Desulfurization profile of the multicomponent model diesel in the presence of different homogeneous catalysts, PW₁₂, PW₁₁ and PW₁₁Zn (3 μ mol), using MeCN as extraction solvent and H₂O₂/S=8, at 70 °C.

To understand the correlation between POMs catalytic activity and their structure, i.e. complete Keggin structure (PW₁₂), the lacunar Keggin structure losing a WO₄⁺ unit (PW₁₁) and also the incorporation of a zinc metallic center in the lacunary space of the lacunar structure (PW₁₁Zn), the analysis of ³¹P NMR from the polar organic reaction medium (MeCN phase containing the POM) was performed at the end of the process (Figure 4.8). The spectrum of PW₁₂ reveals a single peak at -13.86 ppm which is equal to the spectrum before catalysis. This result indicates that the Keggin structure is stable since does not suffer any degradation but also this is the less active POM. For the zinc substituted PW₁₁Zn (δ = -10.65 ppm before catalysis), the ³¹P NMR spectrum after catalytic use presents a peak at -10.59 ppm is indicating that the zinc-substituted structure is stable despite being active under the used catalytic conditions. Therefore, the substitution of a tungsten atom by a zinc atom in the Keggin structure produces an appreciable increase of catalytic activity. In fact, the higher catalytic activity observed for the PW₁₁Zn instead of the low performance attributed to the Keggin PW₁₂ can be attributed to the facility of PW₁₁Zn structure to form active peroxo intermediates by the interaction of the labile water ligand coordinated to the zinc metal. The formed active peroxo intermediates can easily oxidize the sulfur compounds. [15, 17]

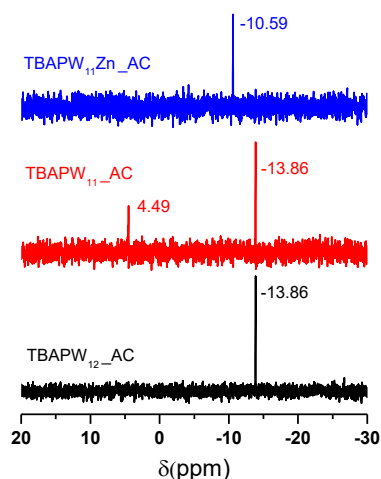


Figure 4.8 ^{31}P NMR spectra of the homogeneous catalysts in the extraction phase medium, after catalytic use (abbreviated as AC): PW_{12} , PW_{11} and PW_{11}Zn .

In the case of lacunar PW_{11} , the ^{31}P NMR spectrum after catalysis shows that the original peak at -11.41 ppm is shifted to -13.86 ppm and a smaller peak appears at 4.49 ppm (Figure 4.8). This last peak can be assigned to $[\text{PO}_4\{\text{W}(\text{O}_2)_2\}_4]^{3-}$ Venturello complex. [49, 50] The peak observed at -13.86 ppm was previously suggested to be assigned as a PW_xO_y -type anion considered to be an intermediated to synthesize the Venturello peroxocomplex.[14, 51, 52]

4.2.2.2. Homogeneous vs Heterogeneous monolacunar catalysts

The most active catalyst in the homogeneous studies (PW_{11}) was incorporated in amine functionalized SBA-15 supports to prepare heterogeneous catalysts that could be easily recovered from the desulfurization system after the experiments. The resulting $\text{PW}_{11}@\text{aptesSBA-15}$ and $\text{PW}_{11}@\text{tbaSBA-15}$ heterogeneous catalysts were tested in the biphasic system using the same conditions of the homogeneous catalytic studies (3 μmol of POM active center, $\text{H}_2\text{O}_2/\text{S} = 8$). It can be seen in Figure 4.9 the desulfurization profiles of model diesel B, catalyzed by the homogeneous PW_{11} and the heterogeneous $\text{PW}_{11}@\text{aptesSBA-15}$ and $\text{PW}_{11}@\text{tbaSBA-15}$ catalysts. The initial extraction of sulfur compounds from model diesel to the MeCN phase (10 min at 70 °C) was similar using for the homogeneous PW_{11} (58.5%) and $\text{PW}_{11}@\text{aptesSBA-15}$ (55.1%), while for $\text{PW}_{11}@\text{tbaSBA-15}$ only removal of 41.1% was achieved. The transfer of sulfur compounds from the model diesel to the extraction phase follows the previously reported order: 1-BT > DBT > 4-MDBT > 4,6-DMDBT (Figure 4.10). [18, 20] In fact, the initial liquid-liquid extraction step (10 min) is responsible for the major removal of sulfur. In this

step, 1-BT is the sulfur compound most efficiently removed due to its low molecular diameter. However, its low electron density on the sulfur atom, when compared with the other sulfur compounds, makes it less reactive in the oxidation step and therefore more difficult to be completely oxidized and removed. The other studied sulfur compounds have similar sulfur electron densities; however, DBT is more soluble in MeCN than the other dibenzothiophene derivatives and the methyl derivatives (4-MDBT and 4,6-DMDBT) present some steric hindrance by the methyl groups. [15, 18, 20]

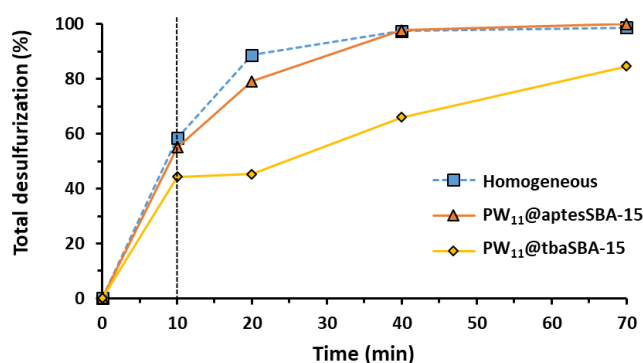


Figure 4.9 - Desulfurization profile of the model diesel using the homogeneous PW₁₁ and the heterogeneous PW₁₁@aptSBA and PW₁₁@tbaSBA catalysts (containing 3 μ mol of active PW₁₁) using MeCN as extraction solvent and H₂O₂/S=8, at 70 °C.

From Figure 4.10 can easily be seen that the sulfur compounds more difficult to oxidize in the biphasic system follows the order 1-BT, 4,6-DMDBT, 4-MDBT and DBT. After 30 min of oxidation, total desulfurization was achieved for DBT and 4-MDBT, using PW₁₁ and PW₁₁@aptSBA-15 catalysts. The 4,6-DMDBT reached 99.0% of desulfurization using the heterogeneous catalyst and 98.9% when the homogeneous catalyst was used. In the case of 1-BT, which was the most difficult to oxidize, the obtained desulfurization was 91.8% for the heterogeneous catalyst and 83.0% for the homogeneous.

The PW₁₁@tbaSBA-15 catalyst exhibited a different catalytic behavior with an induction period in the beginning of the catalytic stage. [15, 53] In fact, practically no oxidation occurred in the first 10 min past the oxidant addition. This phenomenon could be related with the bulkier size of tba groups comparing with aptes which can difficult the diffusion of reactants (substrate and/or oxidant) inside the porous channels of SBA-15.

Figure 4.9 presents similar total desulfurization profiles for the homogeneous PW₁₁ and the PW₁₁@aptSBA-15 catalysts reaching a practically complete desulfurization

after 60 minutes of oxidation (97% using the homogeneous catalyst and 100% using the heterogeneous catalyst). Despite exhibiting similar oxidative catalytic performance, the $\text{PW}_{11}@ \text{aptesSBA-15}$ has the advantage of being easily recovered from the system at the end and able to be reused in a new cycle.

To investigate a possible leaching of the active catalytic centers, the solid $\text{PW}_{11}@ \text{aptesSBA-15}$ catalyst was separated from the reactional medium by hot filtration after 15 min (5 min after the oxidant addition). The results show that the oxidation practically stops after catalyst removal (Figure 4.11) confirming the catalyst heterogeneity.

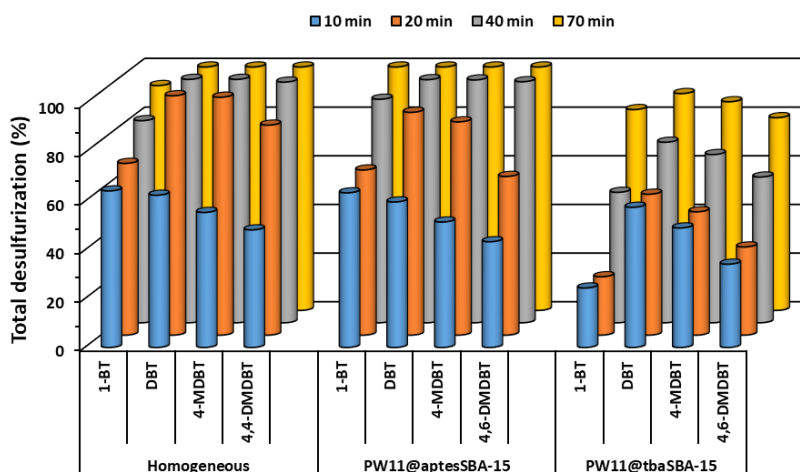


Figure 4.10 - Desulfurization data of the various sulfur compounds present in the model diesel, using the homogeneous PW_{11} and heterogeneous $\text{PW}_{11}@ \text{aptesSBA-15}$ and $\text{PW}_{11}@ \text{tbaSBA-15}$ catalysts (containing $3 \mu\text{mol}$ of active PW_{11}) using a biphasic diesel/MeCN systems, $\text{H}_2\text{O}_2/\text{S} = 8$, at 70°C .

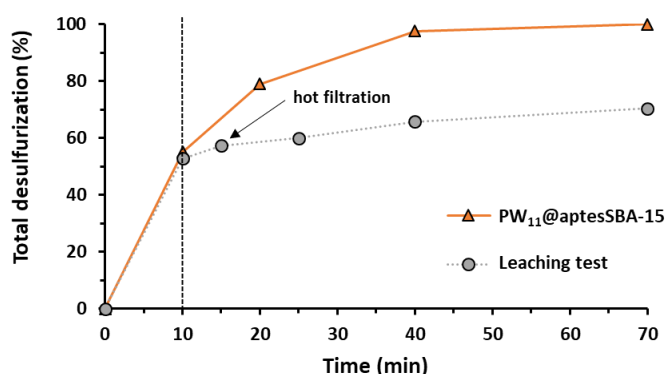


Figure 4.11 - Kinetic profiles for the desulfurization of model diesel using the $\text{PW}_{11}@ \text{aptesSBA-15}$ catalyst ($3 \mu\text{mol}$ of PW_{11}) and the corresponding leaching test., using $\text{H}_2\text{O}_2/\text{S} = 8$, at 70°C

4.2.2.3. Biphasic vs Solvent-free systems using $PW_{11}@apt\text{esSBA-15}$ catalyst

The oxidative catalytic performance of the catalyst exhibiting the best performance ($PW_{11}@apt\text{esSBA-15}$) was also evaluated in the solvent-free system and compared with the biphasic system (reported in 4.2.2.2). The kinetic profiles for the desulfurization of the multicomponent model diesel using the solvent-free and biphasic systems are presented in Figure 4.12. Both systems exhibit similar profiles and were able to achieve complete desulfurization after just 60 min of reaction. The homogeneous PW_{11} catalyst tested under the solvent-free conditions only reached 51.6 % of total conversion for the same period of time and only 68.7 % after 120 min (Figure 4.13). The use of $PW_{11}@apt\text{esSBA-15}$ composite in the solvent-free conditions has the advantage of reaching total oxidation of sulfur compounds without the need of a polar organic solvent. In this system, the oxidation occurs in the diesel phase. Furthermore, the final extraction of the oxidized products can be conducted with a choice of more sustainable and more cost-effective solvents, which is important for future industrial applications.

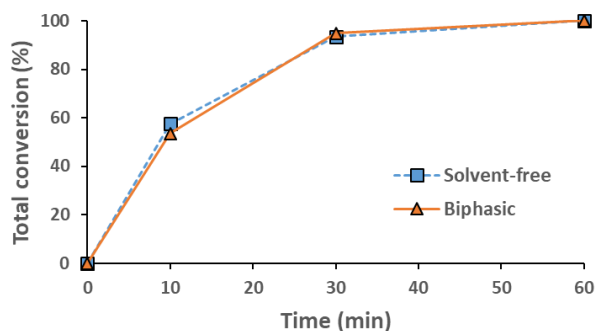


Figure 4.12 - Kinetic profiles for the desulfurization of a model diesel using the solvent-free or biphasic (model diesel/MeCN 1:1) systems with $PW_{11}@apt\text{esSBA-15}$ composite (containing 3 μmol of PW_{11}), using $\text{H}_2\text{O}_2/\text{S} = 8$, at 70 °C.

Further optimization of the solvent-free system was performed concerning the catalyst and oxidant amounts. Two different amounts of composite catalyst were used in the ODS solvent-free process optimization (1 μmol and 3 μmol) and these were tested using a ratio $\text{H}_2\text{O}_2/\text{S}$ of 2, 4 and 8, at 70 °C. The optimization results are presented in Figure 4.14. It was possible to observe that using the lowest amount of oxidant ($\text{H}_2\text{O}_2/\text{S} = 2$) the total oxidation of sulfur compounds was not achieved during the experimental time. Using a $\text{H}_2\text{O}_2/\text{S}$ equal to 4, complete conversion was achieved after only 60 min. With the highest ratio ($\text{H}_2\text{O}_2/\text{S} = 8$) total conversion was achieved after 90 min.

Consequently, the optimum $\text{H}_2\text{O}_2/\text{S}$ ratio was considered to be 4 (using $3 \mu\text{mol}$ of catalyst). When the amount of catalyst was decreased from 3 to $1 \mu\text{mol}$ of active catalytic center, total oxidation was achieved after only 90 min. Therefore, the optimized system should use $3 \mu\text{mol}$ of active catalytic center and a ratio $\text{H}_2\text{O}_2/\text{S} = 4$.

The heterogeneous catalyst $\text{PW}_{11}@ \text{aptesSBA-15}$ was tested, using this solvent-free optimized conditions, in the biphasic system. The results revealed that this biphasic system was less effective than the reported above (using $\text{H}_2\text{O}_2/\text{S}=8$), reaching 97,1 % after 60 min of oxidation and 99,7% after 120 min (Figure 4.15). These results show that the solvent-free system has an extra advantage of using less oxidant amount to achieve total oxidation in 60 min.

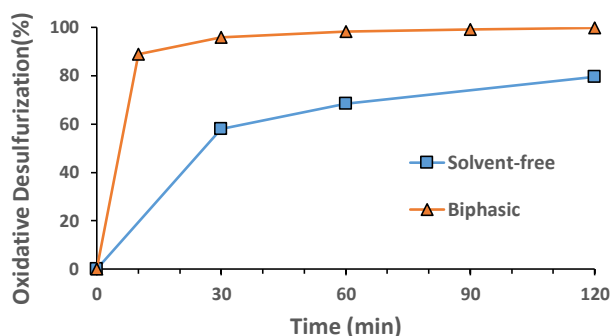


Figure 4.13 - Kinetic desulfurization profiles of a multi-component model diesel using the solvent-free or biphasic (model diesel/MeCN 1:1) systems with the homogeneous PW_{11} catalyst ($3 \mu\text{mol}$), using $\text{H}_2\text{O}_2/\text{S} = 8$, at 70°C .

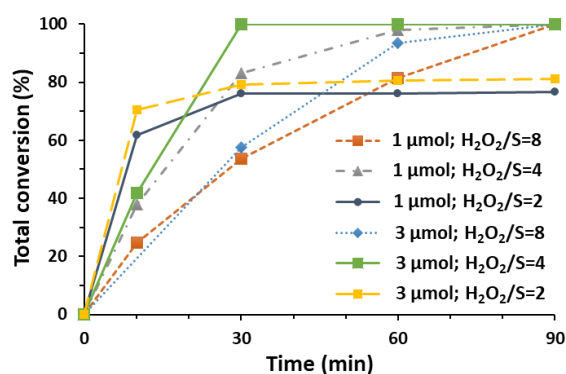


Figure 4.14 - Kinetic desulfurization profiles of a multi-component model diesel using a solvent-free system, catalyzed by different amounts of composite $\text{PW}_{11}@ \text{aptesSBA-15}$ (1 and $3 \mu\text{mol}$ of PW_{11}) and oxidant ($\text{H}_2\text{O}_2/\text{S} = 2, 4, 8$) at 70°C .

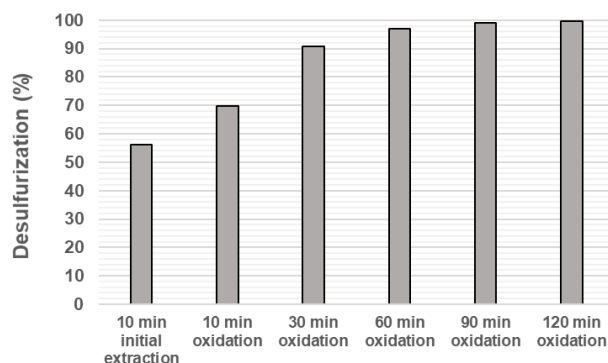


Figure 4.15 – Desulfurization of a multi-component model diesel using the biphasic (model diesel/MeCN 1:1) systems with the heterogeneous $PW_{11}@aptesSBA-15$ catalyst ($3 \mu\text{mol}$ of PW_{11}), using $H_2O_2/S = 4$, at 70°C .

4.2.3. Comparison with other lacunary based catalysts

Table 4.2 summarizes the catalytic performance of various monolacunary based catalysts used in the oxidative desulfurization systems. Entries 1-3 correspond to silica heterogeneous catalysts having PW_{11} as active center. These catalysts showed high performance but only DBT single model diesel was used. Similar catalytic performance was achieved using $PW_{11}@aptesSBA-15$, but in this case a multicomponent model oil (2000 ppm of S instead of 500 ppm) containing more difficult oxidized components was used. [13,26,27] The monolacunary PW_{11} was also used to prepare hybrid catalysts ($ODAPW_{11}$) via ion exchange, entries 4 and 5. Entry 4 presents desulfurization results only for 1-BT model diesel. Entry 5 presents similar desulfurization results for a multicomponent model diesel as used in this work. However, in this work a desulfurization system requiring a less amount of oxidant ($O/S = 4$, instead of 8) was presented, achieving complete conversion of sulfur compounds without the presence of a polar organic solvent. [14]

Table 4.2 - Comparison of desulfurization efficiency and experimental conditions used, in the presence for various PW₁₁ based catalysts applied in the desulfurization of model diesel.

Entry	Catalyst	Model diesel ^a (ppm S)	time (min)	T (°C)	O/S molar ratio	Conversion (%)	Ref.
1	PW ₁₁ /MSPM	DBT (500)	120	60	4	99.7	[24]
2	PW ₁₁ /MCM-41	DBT (500)	60	70	4	99.82	[13]
3	PW ₁₁ /SiO ₂	DBT (500)	90	60	4	99.96	[23]
4	[ODA] ₅ Na ₂ PW ₁₁	1-BT (1000)	60	30	3.5	98	[2]
5	[ODA] ₇ PW ₁₁	1-BT; DBT; 4- MDBT; 4,6-DMDBT (2000)	70	70	8	100	[14]
6	PW ₁₁ @aptSBA- 15	1-BT; DBT; 4- MDBT; 4,6-DMDBT (2000)	60*	70	4	100	This work

^a in *n*-octane; MSPM: mesoporous silica pillared montmorillonite; ODA: octadecyltrimethylammonium; * Still needs sulfones removal

4.2.4. Recycling capacity and stability of PW₁₁@aptSBA-15

The recycle capacity of the heterogeneous catalyst PW₁₁@aptSBA-15 was studied in biphasic and in solvent-free desulfurization systems. In both systems, 3 μmol of catalyst were used and ratios H₂O₂/S of 8 and 4 were used for the biphasic and solvent-free systems, respectively. The recycling ability of the heterogeneous catalyst was evaluated for eight consecutive cycles under biphasic system. After each cycle, the solid catalyst was recovered, washed with ethanol, dried and reused in a new desulfurization cycle maintaining the same experimental conditions. Figure 4.16 display the desulfurization results obtained for the consecutive cycles after 1h of oxidation. It can be observed that the catalyst maintained its performance during all the cycles and no loss of catalytic activity was detected.

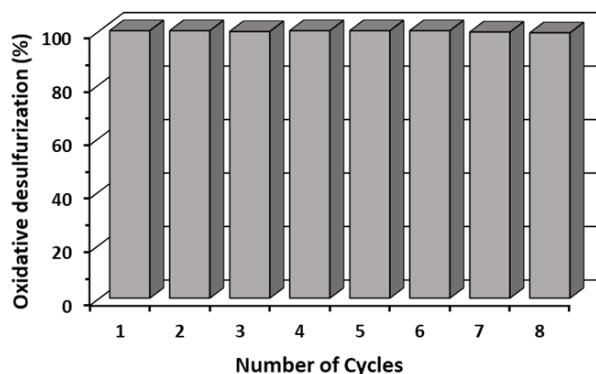


Figure 4.16 - Desulfurization results of a multicomponent model diesel after 1 h, performed for eight consecutive cycles, using the biphasic system diesel/MeCN (1:1) and $\text{H}_2\text{O}_2/\text{S}=8$, catalyzed by $\text{PW}_{11}@ \text{aptesSBA-15}$ at 70 °C.

The recycling ability of the $\text{PW}_{11}@ \text{aptesSBA-15}$ catalyst was also tested in the solvent-free conditions, i.e. in the absence of MeCN extraction solvent. At the end of each cycle the catalyst was recovered by centrifugation, washed with ethanol and dried to be used in a new oxidative desulfurization cycle under the same reaction conditions. At the end of the oxidative step, a liquid-liquid extraction (1:1 model diesel/MeCN or ethanol/water) was performed during 10 min at room temperature, in order to remove the oxidized sulfur compounds from model diesel. Figure 4.17 presents the oxidative desulfurization data for eight consecutive cycles. The results reveal similar catalytic performances along the cycles and without apparent loss of catalytic activity.

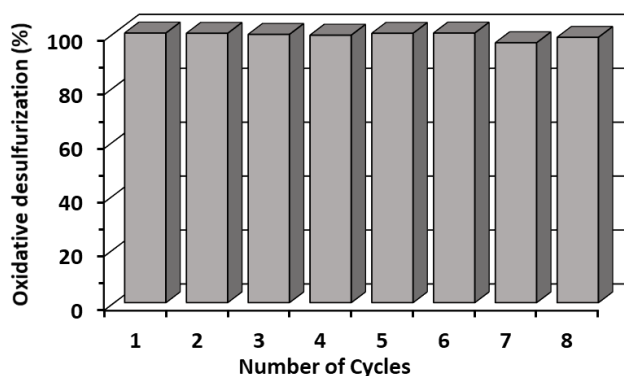


Figure 4.17 – Oxidative desulfurization results obtained after 1 h for eight consecutive cycles using $\text{PW}_{11}@ \text{aptesSBA}$ catalyst under a solvent-free system and $\text{H}_2\text{O}_2/\text{S}=4$ at 70 °C.

The stability of the $\text{PW}_{11}@ \text{aptes SBA-15}$ composite after catalytic use was investigated using several techniques. The catalyst was retrieved after one

desulfurization cycle performed in biphasic and also in solvent-free system. The recovered solids were analyzed by ICP-OES that reveals that the catalyst presents similar Si/W (molar) ratio before (1.55) and after catalysis (1.65), under the solvent free system, indicating that practically no loss of active PW_{11} center occurred during reaction. The same analysis was performed using the solid recovered from the biphasic system; however, in this case some leaching was detected since the Si/W (molar) ratio increased from 1.55 to 2.28 after catalysis. The same recovered solid was also analyzed by powder X-ray diffraction, vibrational spectroscopy (FT-IR and FT-Raman), SEM/EDS and ^{31}P MAS NMR. The powder X-ray patterns of the $PW_{11}@apt\text{esSBA-15}$ before and after oxidative catalysis exhibit identical profiles concerning the position and diffraction peaks relative intensity (Figure 4.18).

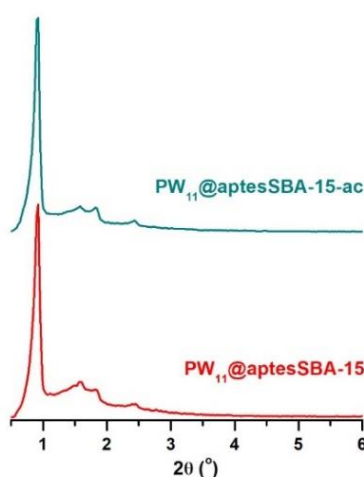


Figure 4.18 - Powder XRD of the $PW_{11}@apt\text{esSBA-15}$ composite before and after catalytic use (ac) in a biphasic (model diesel/MeCN 1:1) system.

The FT-IR spectrum of $PW_{11}@apt\text{esSBA-15-ac}$ (ac is the abbreviation for after catalysis) (Figure 4.19 left) reveals that the characteristic bands of the POM, in particular in the region of $800\text{--}900\text{ cm}^{-1}$, were maintained, which can indicate that the POM structure was maintained after catalytic use. Besides, the FT-Raman spectrum of the composite after catalytic use (Figure 4.19 right) also points out to the preservation of the PW_{11} structure, since the bands assigned to the PW_{11} stretching modes ($990\text{--}959\text{ cm}^{-1}$) are still preserved. The bands that appear in the $1200\text{--}1700\text{ cm}^{-1}$ region in the FT-Raman spectrum are most likely related to the presence of oxidized sulfur compounds from model diesel that remained adsorbed on the catalyst as previously observed. [14, 29]

In fact, the SEM/EDS results reveal the presence of sulfones in the composite after catalysis (Figure 4.20). This is evident in the EDS spectrum in Z1 zone, where the sulfur

presence is revealed. The EDS analysis of the $PW_{11}@apt\text{esSBA-15-ac}$ also shows well the presence of tungsten from the PW_{11} . The SEM images show that the material has maintained its morphology with no visible degradation of the silica support.

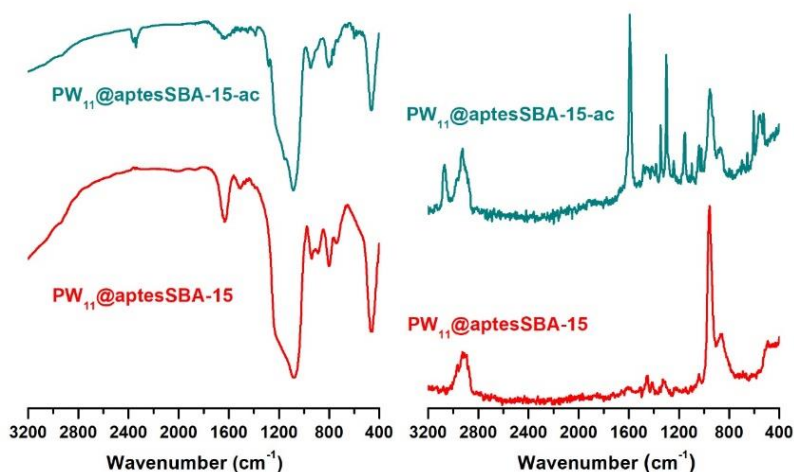


Figure 4.19 - FT-IR (left) and FT-Raman (right) of the $PW_{11}@apt\text{esSBA-15}$ composite before and after catalytic use (ac) in a biphasic (model diesel/MeCN 1:1) system.

The ^{31}P MAS NMR analysis of the composite after catalytic use demonstrates the appearance of a small peak at -12.91 ppm, assigned to the starting PW_{11} structure (Figure 4.21). Another peak shows up at 5.59 ppm, which indicates the occurrence of a transformation of the lacunar PW_{11} structure in a new active specie that must be assigned to a peroxopolyoxometalate such as $\{\text{HPO}_4[\text{W}(\text{O})(\text{O}_2)_2]_2\}^{2-}$. [54] This result reveals the low stability of the lacunar structure even when immobilized on a functionalized aptesSBA-15 support. The new specie formed may also be catalytically active since no loss of activity was detected in the recycling studies.

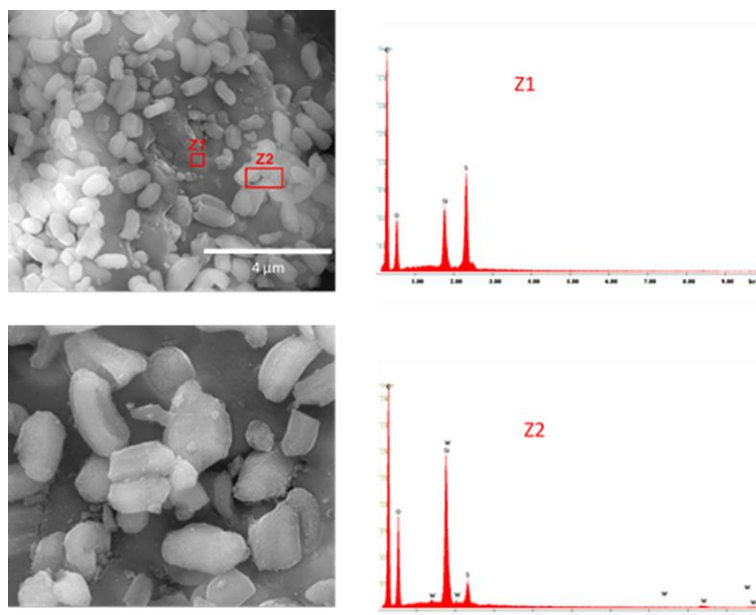


Figure 4.20 - SEM images and EDS spectra of the $PW_{11}@aptSBA-15$ composite after catalytic use in a biphasic (model diesel/MeCN 1:1) system.

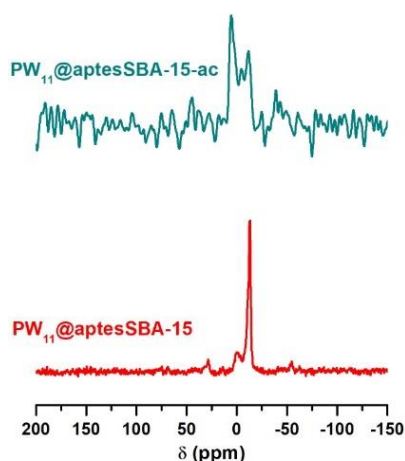


Figure 4.21 - ^{31}P MAS NMR spectra of the $PW_{11}@aptSBA-15$ composite before and after catalytic use in a biphasic (model diesel/MeCN 1:1) system.

4.2.5 Desulfurization of untreated diesel

The remarkable oxidative catalytic performance of $PW_{11}@aptSBA-15$ composite to desulfurize the model diesel has led to its application in the desulfurization of an untreated real diesel supplied by CEPESA (containing 1335 ppm of total sulfur-containing compounds). This work was performed at Instituto de Catálisis y Petroleoquímica de Madrid in collaboration with José Campos-Martin. The analysis by GC-FID/SCD (Sulfur Chemiluminescence Detector) of this diesel and the model diesel B (Figure A.5 in Appendix) reveals that dibenzothiophenes derivatives are mainly present in the

untreated diesel. The desulfurization experiments were performed using the biphasic system (1:1 diesel/MeCN) and also the solvent-free system (Table 4.3). In this last case a final liquid-liquid extraction with MeCN and 1:1 EtOH/H₂O was performed to remove the oxidized sulfur compounds.

Table 4.3 reveals that the highest desulfurization efficiency was achieved using the biphasic system (83.4%), performing an initial extraction with MeCN for 10 min and also using this solvent (with 1:1 ratio) with real diesel during oxidative catalytic step. For the solvent-free system, without performing any initial diesel extraction, the desulfurization efficiency reached only 23.1%. In this case, the majority of the sulfur oxidized compounds still remain in the diesel. However, the 23.1% of desulfurization is indicative of some possible sulfur compounds adsorption on the composite, which was confirmed to occur by SEM analysis (Figure 4.20). When a final extraction was performed for 10 min with EtOH/H₂O (1:1), the desulfurization efficiency increased from 23.1% to 43.1%. However, using MeCN as final extraction solvent the desulfurization efficiency achieved 72.2%.

Table 4.3 - Results of the experiments for desulfurization of untreated real diesel obtained after 2 hours of oxidation using H₂O₂/S = 8, at 70 °C.

	Diesel sulfur content (ppm)	Total desulfurization (%)
Solvent-free (without extraction)	1026	23.1
Solvent-free (final extraction EtOH/H ₂ O)	759	43.1
Solvent-free (final extraction MeCN)	374	71.9
Biphasic	222	83.4

Since the biphasic system was the most efficient to desulfurize the real diesel, the heterogeneous catalyst was recycled for three consecutive cycles. After each cycle the catalyst was recovered by filtration, washed with ethanol and dried to be used in a new cycle under the same reaction conditions. Figure 4.22 presents the results obtained for three consecutive cycles after 3 h of reaction. The desulfurization efficiency was maintained during the 3 cycles, indicating that the catalyst performance was retained and can be used to desulfurize continuously various aliquots of untreated diesel.

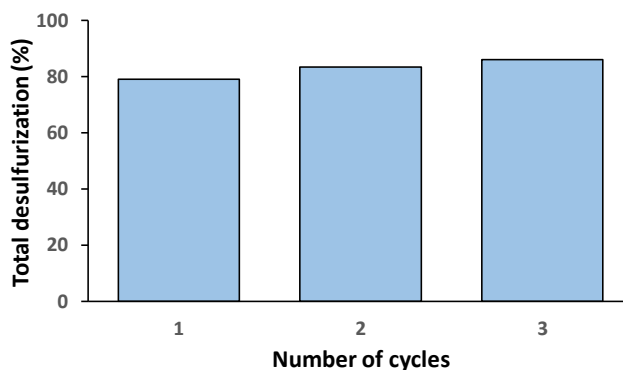


Figure 4.22 - Desulfurization results of a real untreated diesel after 3 h, performed for three consecutive cycles, using the biphasic system (diesel/MeCN 1:1) and $\text{H}_2\text{O}_2/\text{S}=8$, catalyzed by $\text{PW}_{11}@\text{aptesSBA-15}$ (containing 3 μmol of PW_{11}), at 70 $^\circ\text{C}$.

4.3. Conclusions

This work presents the investigation of various Keggin polyoxometalates derivatives as homogeneous catalysts for the oxidative desulfurization of a multicomponent model diesel formed by the most refractory sulfur compounds.

An efficient catalytic performance was only observed using a biphasic diesel/acetonitrile system with a ratio $\text{H}_2\text{O}_2/\text{S} = 8$ and 3 μmol of catalyst at 70 $^\circ\text{C}$. Structural modifications performed in the Keggin-type compound (PW_{12}), such as the removal of a WO_4^{4-} unit, forming the lacunar PW_{11} compound and the substitution of a tungsten atom by a zinc metal center, to form PW_{11}Zn , provided a significant increase in the catalytic activity. The most active catalyst was the lacunar PW_{11} compound, achieving a total desulfurization after only 60 min of reaction. However, this compound showed low structural stability after catalytic use and the Venturello peroxocomplex was identified as the active catalytic specie.

To investigate the stability and the activity of the lacunar PW_{11} in the solid state, this homogeneous PW_{11} was immobilized by a post-grafting method on amine-functionalized SBA-15 supports. The catalytic activity of the composite $\text{PW}_{11}@\text{aptesSBA-15}$ was similar to the homogeneous PW_{11} under the biphasic diesel/acetonitrile system, while $\text{PW}_{11}@\text{tbaSBA-15}$ showed a poorer performance with an initial induction period. Furthermore, the $\text{PW}_{11}@\text{aptesSBA-15}$ composite also presents a high oxidative desulfurization performance in a solvent-free system, i.e.

without the need of acetonitrile. In this case, complete desulfurization was also achieved after 60 min and half amount of oxidant was used (ratio $\text{H}_2\text{O}_2/\text{S} = 4$).

The $\text{PW}_{11}\text{@aptesSBA-15}$ composite was also used as catalyst for the oxidative desulfurization of a real untreated diesel. Experiments performed under biphasic system (1:1 diesel/acetonitrile) originated higher desulfurization efficiency (83.4%) than the solvent-free system (71.9%); however, double amount of oxidant was consumed in the first case. The recycle capacity of the composite was confirmed for eight consecutive cycles in both systems and its stability showed to be higher under the solvent-free system than the biphasic system. In the first case, low leaching of polyoxometalate active species was observed. Finally, the composite showed to have interesting adsorptive capacity to oxidized-sulfur compounds. Therefore, the solvent-free desulfurization system seems to be more advantageous than the biphasic since promotes the stability of the active catalyst and the use of less excess of oxidant.

4.4. Experimental section

4.4.1. Materials and Methods

All the reagents used in the polyoxometalates (POMs) synthesis, support and composite preparation, namely (3-aminopropyl)triethoxysilane (aptes, Aldrich), anhydrous toluene 99.8% (Aldrich), ethanol (Aga), hydrochloric acid (HCl, Fisher Chemicals), pluronic P123 (Aldrich), phosphotungstic acid (Fluka), potassium chloride (Aldrich), sodium hydrogen phosphate dihydrate (Aldrich), sodium tungstate dihydrate (Aldrich), tetra-*n*-butylammonium bromide (TBA, Merck), tetraethoxysilane (TEOS, Aldrich) and zinc acetate dehydrate (M&B) were used as received. The reagents for oxidative desulfurization reactions, including 1-benzothiophene (1-BT, Fluka), dibenzothiophene (DBT, Aldrich), 4-methyldibenzothiophene (4-MDBT, Aldrich), 4,6-dimethyldibenzothiophene (4,6-DMDBT Alfa Aesar), acetonitrile (MeCN, Fisher Chemical), hydrogen peroxide aq. 30% (Aldrich) and *n*-octane (Aldrich) were purchased from chemical suppliers and used without further purification.

Elemental analyses for C, H and N elements were performed in a Leco CHNS-932 instrument and Si, W and P by ICP-OES on a Perkin-Elmer Optima 4300 DV instrument; at the University of Santiago de Compostela. FT-IR spectra were obtained on a Jasco 460 Plus spectrometer using KBr pellets. The FT-Raman spectra were recorded by the research group of Isabel Gonçalves in CICECO Associate Laboratory, University of

Aveiro, using a RFS-100 Bruker FT-spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm and the laser power set to 350 mW. Powder X-ray diffraction (XRD) patterns were obtained at room temperature on a X'Pert MPD Philips diffractometer, equipped with a X'Celerator detector and a flat-plate sample holder in a Bragg-Brentano para-focusing optics configuration (45 kV, 40 mA). Intensity data were collected by the step-counting method (step 0.013°), in continuous mode, in the ca. $0.3 \leq 2\theta \leq 10^\circ$ range (CICECO, Universidade de Aveiro). ^{31}P NMR spectra were collected for liquid solutions using a Bruker Avance III 400 spectrometer and chemical shifts are given with respect to external 85% H_3PO_4 . Solid state ^{13}C , ^{31}P and ^{29}Si MAS NMR spectra were acquired with a Bruker AVANCE III 300 spectrometer (7 T) operating respectively at 75 MHz (^{13}C), 121 MHz (^{31}P) and 60 MHz (^{29}Si), equipped with a BBO probe head. These measurements were performed by Professor Pedro L. Almeida at CENIMAT/I3N, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa. The samples were spun at the magic angle at a frequency of 5 kHz in 4 mm-diameter rotors at room temperature. The ^{13}C MAS NMR experiments were acquired with proton cross polarization (CP MAS) with a contact time of 1.2 ms, and the recycle delay was 2.0 s. The ^{29}Si MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 4.5 μs at a power of 40 W, and a relaxation delay of 10.0 s. The ^{31}P MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 5.0 μs at a power of 20 W, and a relaxation delay of 2.0 s. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at "Centro de Materiais da Universidade do Porto" (CEMUP, Porto, Portugal) using a high-resolution (Schottky) scanning electron microscope with X-ray microanalysis and electron backscattered diffraction analysis Quanta 400 FEG ESEM/EDAX Genesis X4 M. The samples were studied as powders and were coated with an Au/Pd thin film by sputtering using the SPI Module Sputter Coater equipment. The textural characterization was obtained from physical adsorption of nitrogen at -196°C , using a Quantachrome NOVA 2200e instrument at Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa by Professor João Pires. Samples were degassed at 120°C for at least 5 h prior to the measurements. The BET surface area (S_{BET}) was calculated by using the relative pressure data in the 0.05–0.3 range. The total pore volume (V_p) was evaluated on the basis of the amount adsorbed at a relative pressure of about 0.95. GC-FID was carried out in a Varian CP-3380 chromatograph to monitor the ODS multicomponent model oil experiments. Hydrogen was used as the carrier gas (55 cm s^{-1}) and fused silica Supelco capillary columns SPB-5 (30 m x 0.25 mm i.d.; 25 μm film thickness) were used. The sulfur content of untreated diesel was qualified by

GC-FID/SCD in an Agilent 7890A and quantified based in coulombiometric measurements in a TOX-100 S, at *Instituto de Catálisis y Petroleoquímica*, CSIC in Madrid (Spain) by Susana O. Ribeiro and Maria C. Capel-Sanchez under the supervision of José M. Campos-Martin.

4.4.2. Synthesis and preparation of the materials

4.4.2.1. Synthesis of polyoxometalates

The tetra-*n*-butylammonium (TBA, $(C_4H_9)_4N$) salt of Keggin type polyoxometalates were prepared: $[PW_{11}Zn(H_2O)O_{39}]^{5-}$ (**PW₁₁Zn**), $[PW_{11}O_{39}]^{7-}$ (**PW₁₁**) and $[PW_{12}O_{40}]^{3-}$ (**PW₁₂**). The zinc mono-substituted phosphotungstate ($PW_{11}Zn$) was prepared as described in Chapter 2 section 2.4.2. [18, 55] Briefly, Na_2HPO_4 (1.8 mmol) and $Na_2WO_4 \cdot 2H_2O$ (20 mmol) were dissolved in 40 ml of water, the mixture was heated at 85 °C for 1 hour and the pH was adjusted to 4.8 with HCl 4 M. Zinc acetate (2.4 mmol) was then added and stirred until completely dissolved. An excess of TBA bromide was added and after cooling to room temperature, the former white precipitate was filtered and dried in a desiccator over silica gel. The lacunar PW_{11} was prepared similarly, except for the addition of zinc acetate. The TBA salt of the Keggin polyanion PW_{12} was prepared by simply dissolving the phosphotungstic acid in water and adding an excess of TBA bromide. [20] The successful preparation of the POMs was confirmed by FT-IR, and ^{31}P NMR spectroscopies.

PW₁₁Zn: ^{31}P NMR (161.9 MHz, D_2O 298 K): $\delta = -10.65$ ppm. Selected FT-IR (cm^{-1}): $\nu = 2952$ (w), 2938 (w), 1622 (m), 1088 (s), 1050 (s), 956 (vs), 886 (s), 800 (s), 754 (m), 700 (m), 590 (w), 506 (w), 484 (w), 408 (w).

PW₁₁: ^{31}P NMR (161.9 MHz, D_2O 298 K): $\delta = -11.41$ ppm. Selected FT-IR (cm^{-1}): $\nu = 3445$ (m), 2359 (w), 2343(sh), 1616 (w), 1090(s), 1040(s), 953(s), 904 (m), 852 (w), 807 (m), 761 (sh), 728 (m), 593 (w), 511 (m), 417 (w)

PW₁₂: ^{31}P NMR (161.9 MHz, D_2O 298 K): $\delta = -13.86$ ppm.

4.4.2.2. Preparation of aptesSBA-15 support

SBA-15 was hydrothermally synthesized according to a previously reported procedure. [28] Typically, Pluronic P123 (1.0 g) was dissolved in aqueous HCl (2M, 30 mL) and distilled water (7.5 mL) under stirring at 40 °C and then TEOS (2.2 g) was added

dropwise. The mixture was stirred for 24 h at 40 °C, and then the temperature was raised to 100 °C for another 24 h in a Teflon autoclave. The resulting precipitate was filtered, dried and calcinated at 550 °C for 5h with a ramp of 1 °C min⁻¹.

The surface of SBA-15 was functionalized via a post-grafting methodology [27] by refluxing the dried SBA-15 support (1 g) under argon, for 24h in dry toluene with 3-(aminopropyl)triethoxysilane (aptès, 0.5 mmol). The resulting material was filtered, washed with toluene and dried under vacuum at 60 °C for 2 h. Elemental analysis shows that aptèsSBA-15 contains 1.3 mmol of aptès per g of material.

aptèsSBA-15: Anal. Found (%): N, 2.8.; C, 10.1; H, 2.4; Selected FT-IR(cm⁻¹): 3421 (m); 2933 (w); 2360 (w); 2341 (w); 1635 (w); 1199 (sh); 1078 (vs); 970 (sh); 802 (m); 547 (w); 457 (s).

4.4.2.3. Preparation of tbaSBA-15 support

Initially, the hydroxide salt of N-(3-trimethoxysilylpropyl)tributylammonium (tba) was prepared following published procedures (prepared by Sandra Gago in FCT, Nova University). [56] Afterwards, tba (0.5 mmol) was added to previously dried SBA-15 support (1 g) in dry toluene and the mixture was refluxed under argon for 24h. The solid was filtered, washed with toluene and dried under vacuum at 60 °C for 2 h.

4.4.2.4 Preparation of PW₁₁-based composites

The immobilization of PW₁₁ in the amine-functionalized SBA-15 supports was performed via an impregnation method adapted from previously reported procedures [10, 36]. Briefly, a solution of the potassium salt of the lacunar ([PW₁₁O₃₉]⁷⁻) (1 g of in 10mL of deionized water) was added to aptèsSBA-15 or tbaSBA-15 (0.5 g, previously dried under vacuum at 60 °C for 2h) and the mixture was stirred for 3 days at room temperature. The solid was separated by filtration, washed with deionized water and dried in a desiccator over silica gel.

PW₁₁@aptèsSBA-15: Anal. Found (%) W, 19.4; Si, 4.6; loading of POM: 0.096 mmol/g, Si/W (molar) = 1.55; Selected FT-IR (cm⁻¹): 3445 (vs); 1626 (s); 1505 (w); 1221 (sh); 1085 (vs); 940 (w); 879 (w); 799 (m); 743 (w); 457 (s); selected FT-Raman (cm⁻¹): 2964 (m), 2925 (m), 2914 (w), 1450 (w), 1412 (w), 1327 (w), 1039 (w), 956 (vs), 856 (m).

PW₁₁@tbaSBA-15: Anal. Found (%) W, 7.5; loading of POM: 0.037 mmol/g; selected FT-IR (cm⁻¹): 3435 (m), 2962 (m), 2875 (w), 1653 (w), 1471 (w), 1213 (sh), 1086 (vs), 956 (m), 895 (w), 814 (m), 740 (w), 698 (vw), 459 (s); selected FT-Raman (cm⁻¹): 2936 (vs), 2875 (s), 1451 (s), 1321 (m), 1056 (w), 986 (s), 904 (m), 880 (m).

4.4.3. Desulfurization processes using model diesel

The desulfurization experiments were conducted with **model diesel B** (1-benzothiophene (1-BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), in *n*-octane, ~500 ppm S each) in a 5 mL reactor immersed in a thermostatically controlled liquid paraffin bath at 70 °C, under atmospheric pressure. Desulfurization studies were performed in the absence (solvent-free system) and in the presence of acetonitrile (MeCN) as extraction solvent (biphasic system). The use of 70 °C was based in a previous optimization study performed for heterogeneous silica PW₁₁ catalyst. [13] Hydrogen peroxide was used as oxidant: H₂O₂/S molar = 8 (0.4 mmol of H₂O₂) for the biphasic system and H₂O₂/S molar = 4 (0.2 mmol of H₂O₂) for the solvent-free system. Desulfurization experiments were performed with the TBA salt of POMs as well as the PW₁₁@aptSBA-15 composite. In a typical biphasic system experiment, 1:1 model diesel/MeCN (0,75mL of each) were added to 3 μmol of POM or to an amount of PW₁₁@aptSBA-15 or PW₁₁@tbaSBA-15 composites containing 3 μmol of PW₁₁. The mixture was stirred for 10 min at 70 °C until the initial extraction equilibrium was reached. An aliquot of the upper phase from the model diesel was taken and the oxidative catalytic step was initiated by the addition of the oxidant. The solvent-free system experiments were performed without the presence of the MeCN and maintaining all the experimental conditions as the biphasic system. In this process only the oxidative catalytic process occurred and at the end of this step the oxidized sulfur compounds present in model diesel were removed by a liquid-liquid extraction. The sulfur content of model diesel was quantified by GC analysis using tetradecane as standard. For the experiments using the heterogeneous catalysts, a centrifugation was carried out to recover the catalyst, which was washed with ethanol and dried in a desiccator over silica gel.

4.4.4. Desulfurization processes using untreated diesel

The untreated diesel was supplied by CEPISA with 1335 ppm of sulfur-containing compounds. This diesel was tested in both biphasic and solvent-free systems,

maintaining the same ratio $\text{H}_2\text{O}_2/\text{S}/\text{catalyst}$ as used in the model diesel experiments (4.4.3). In the biphasic system 10 mL of diesel (containing about 0,40 mmol of S) was added to 10 mL of MeCN with the solid catalyst $\text{PW}_{11}\text{@aptesSBA-15}$. This mixture was stirred for 10 min and then the oxidative catalytic stage was initiated by the addition of the oxidant ($\text{H}_2\text{O}_2/\text{S}=8$). The real diesel was also desulfurized using the solvent-free system and, in this case, at the end of the oxidative reaction, the treated diesel was subjected to a liquid-liquid extraction with MeCN or a mixture of EtOH/ H_2O 1:1 to remove the oxidized-sulfur compounds.

4.5. References

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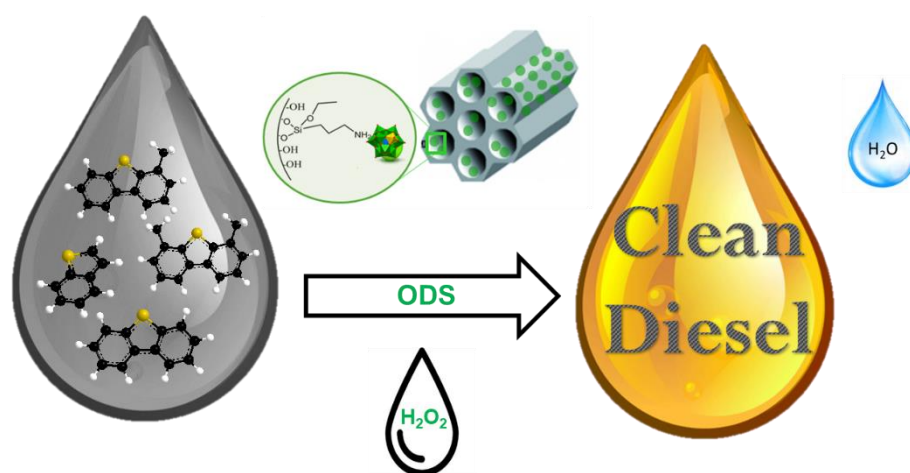
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Chapter 5

An effective zinc-substituted Keggin composite to catalyze the removal of sulfur from real diesels under solvent-free system



¹ Adapted from: Susana O. Ribeiro, Carlos M. Granadeiro, Pedro L. Almeida, João Pires, Rita Valença, José M. Campos-Martin, Jorge C. Ribeiro, Baltazar de Castro and Salette S. Balula, *An effective zinc-substituted Keggin composite to catalyze the removal of sulfur from real diesels under solvent-free system*, submitted to Industrial & Engineering Chemistry Research.

² Susana O. Ribeiro contributions to the publication: Preparation and characterization of polyoxometalates-based silica composites; investigation of its catalytic performance in the desulfurization of a model diesel and also high-sulfur content real diesels supplied by Galp and CEPISA. S. O. Ribeiro is responsible for all experimental work and also for the manuscript preparation.

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Chapter 5

An effective zinc-substituted Keggin composite to catalyze the removal of sulfur from real diesels under solvent-free system

Abstract

A biphasic extractive and catalytic oxidative desulfurization (ECODS) system and a solvent-free catalytic oxidative desulfurization (CODS) system were used to evaluate the desulfurization efficiency of the Keggin phosphotungstate (PW_{12}) and its zinc mono-substituted derivative ($PW_{11}Zn$) immobilized in mesoporous silica ($PW_{12}@apt\text{esSBA-15}$ and $PW_{11}Zn@apt\text{esSBA-15}$). Desulfurization experiments were performed at 70 °C using 3 μmol of catalyst active center and H_2O_2 as oxidant ($H_2O_2/S = 8$ and 4). Overall, the $PW_{11}Zn@apt\text{esSBA-15}$ composite presented better results proving to be highly efficient achieving complete desulfurization after only 60 min, using the solvent-free system. The recyclability of $PW_{11}Zn@apt\text{esSBA-15}$ composite was evaluated for ten consecutive cycles, revealing a preservation of its catalytic efficiency along the cycles. Therefore, the substitution of the tungsten center by zinc in the Keggin structure exhibited improved catalyst activity. Moreover, this catalyst was applied in the desulfurization of two untreated diesels supplied by CEPESA and Galp with different amounts of sulfur (1335 ppm and 2300 ppm, respectively). The combination of $PW_{11}Zn@apt\text{esSBA-15}$ with the solvent-free system revealed to be a promising process for the desulfurization of untreated diesel, since a sulfur removal of 88 % could be reached for CEPESA diesel and the catalyst could be recycled over three consecutive ODS cycles without apparent loss of catalytic activity.

5.1 Introduction

The development of highly efficient catalytic systems for the removal of sulfur compounds, such as benzothiophenes and dibenzothiophenes, from fuels is of great importance considering current environmental concerns. [1] Oxidative desulfurization (ODS) process consists in the oxidation of such compounds into sulfoxides and sulfones followed by their removal through solvent extraction and/or adsorption. [2, 3] Our research group has been developing ODS systems in which the liquid-liquid extraction occurs simultaneously with the catalytic stage or after the oxidation step. [4, 5] The latter offers the advantage of maintaining the desulfurization efficiency while avoiding/reducing the use of harmful organic solvents.

The design of selective, active and recyclable catalysts is also an important task in the pursuit of efficient ODS systems. Polyoxometalates (POMs) are metal-oxygen clusters constituted by early transition metals in their highest oxidation state. [6] The application of POMs as catalysts and H_2O_2 as oxidant, has proved extremely beneficial in creating efficient ODS systems. In particular, the Keggin-type ($[\text{XM}_{12}\text{O}_{40}]^{n-}$) structure is the most explored POM for ODS applications. Transition metal mono-substituted Keggin structures usually present high catalytic activity and its corresponding supported catalysts exhibit low leaching owing to the strong interactions between supports surface and mono-substituted POMs. [6, 7] Recently, zinc mono-substituted phosphotungstate $[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$ (PW_{11}Zn) has been used in ODS studies, proving to be an efficient catalyst in this type of processes, both in homogeneous and heterogeneous conditions, as has been seen in chapters 2 and 4. [8-10] However, in the previous chapters 2 and 4 the PW_{11}Zn catalyst was not heterogenized using suitable solid supports. In fact, the heterogenization of POMs using solid supports has the advantage of combining the selectivity and activity of the homogeneous catalyst with the ability of recovery and recyclability. Among the various applied supports, SBA-15 has been widely used due to its features such as narrow pore size distribution and high hydrothermal stability (examples in chapters 3 and 4) [4, 11-14].

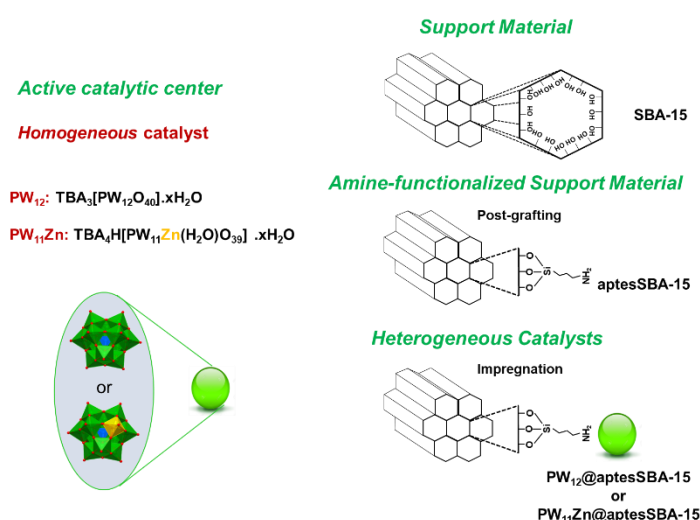
In the present work, the Keggin phosphotungstate $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (PW_{12}) and the corresponding zinc mono-substituted PW_{11}Zn were immobilized in amine-functionalized SBA-15 via the impregnation method described in chapter 4. The composite materials were tested as heterogeneous catalysts in the desulfurization of model diesel containing some of the most refractory sulfur compounds and two real diesels supplied by CEPESA (1335 ppm) and Galp (2300 ppm). Two different desulfurization systems were studied: a biphasic ECODS system, where a liquid-liquid extraction occurs simultaneously with the

oxidation stage, and a solvent-free CODS system where liquid-liquid extraction was performed at the end of the oxidation step. The catalyst exhibiting the best desulfurization performance was recycled for consecutive cycles and its stability was evaluated with both desulfurization systems.

5.2. Results and discussion

5.2.1. Catalysts characterization

The incorporation of both Keggin PW_{12} and $PW_{11}Zn$ POMs in a previously amine-functionalized SBA-15 was achieved via an impregnation process as presented in Scheme 5.1 (experimental procedure in 5.4.2). The confirmation of the successful preparation of POMs@aptesSBA-15 composites was achieved through several characterization techniques including vibrational spectroscopy (FT-IR and FT-Raman), powder XRD, solid-state NMR, inductively coupled plasma optical emission spectrometry (ICP-OES), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and textural analysis (N_2 adsorption isotherms).



Scheme 5.1 – Representation of the preparation of POM based silica catalysts.

The characterization of the SBA-15 support and the amine-functionalized SBA-15 was already presented in Chapter 4; however, some results will be also presented here, for comparison with POM composites. The FT-IR spectra of the composite materials are dominated by the characteristic intense bands of the siliceous support in the 1100-400 cm^{-1} region. These bands can be ascribed to $\nu_{as}(Si-O-Si)$, $\nu_s(Si-O-Si)$ and $\delta(O-Si-O)$

vibrations located at 1081 and 1084 cm^{-1} ; 808 and 803 cm^{-1} ; 458 and 468 cm^{-1} for $\text{PW}_{12}@ \text{aptesSBA-15}$ and $\text{PW}_{11}\text{Zn}@ \text{aptesSBA-15}$, respectively. [4, 15] Additional bands can be observed in both spectra that strongly suggest the presence of the Keggin POMs on the composite materials. In fact, those bands can be attributed to the terminal $\nu_{\text{as}}(\text{W}-\text{O}_\text{t})$ and corner-sharing $\nu_{\text{as}}(\text{W}-\text{O}_\text{b}-\text{W})$ vibrational modes of POMs as they are located at 950 and 944 cm^{-1} for $\text{PW}_{12}@ \text{aptesSBA-15}$ and 900 and 902 cm^{-1} for $\text{PW}_{11}\text{Zn}@ \text{aptesSBA-15}$. [5, 9, 16, 17]

The FT-Raman spectra of the functionalized silica support, the Keggin POMs and the composites are presented in Figure 5.1-B. The presence of the POMs in the composites can be unequivocally confirmed by FT-Raman since the Raman signal from siliceous materials is much weaker allowing a clear observation of the bands associated with POMs. [4, 8] The spectra of both composites exhibit the bands associated with $\nu_{\text{as}}(\text{W}-\text{O}_\text{t})$ and $\nu_{\text{as}}(\text{W}-\text{O}_\text{b}-\text{W})$ stretching modes in the 989-968 cm^{-1} and 885-864 cm^{-1} ranges, respectively [5, 9, 17-19]. Furthermore, elemental analysis reveals a POM loading of 0.143 mmol and 0.111 mmol per gram of material for $\text{PW}_{12}@ \text{aptesSBA-15}$ and $\text{PW}_{11}\text{Zn}@ \text{aptesSBA-15}$, respectively.

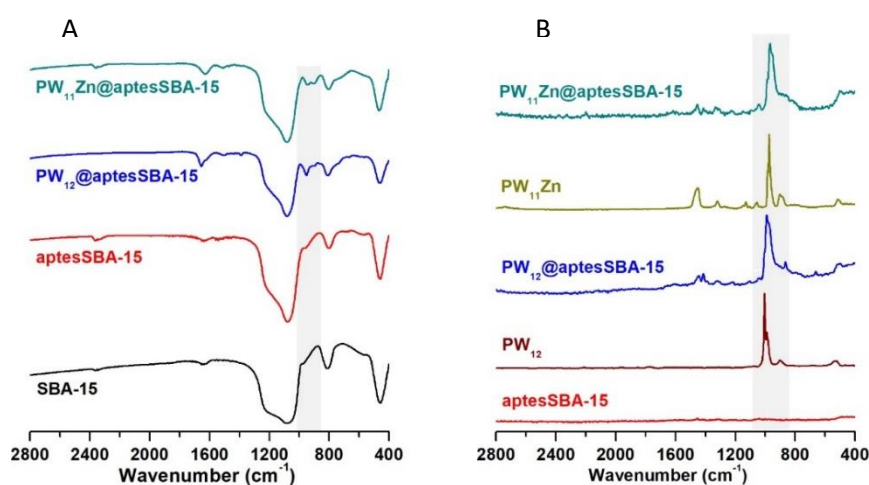


Figure 5.1 - FT-IR (A) and FT-Raman (B) spectra of the SBA-15, the amine-functionalized aptesSBA-15, the isolated POMs and the $\text{PW}_{12}@ \text{aptesSBA-15}$ and $\text{PW}_{11}\text{Zn}@ \text{aptesSBA-15}$ composites.

Figure 5.2 shows the low angle XRD patterns of the composites and the support material in the 2θ range of 0.5-6°. The patterns of both SBA-15 and aptesSBA-15 materials displays the characteristic peaks of SBA-15 materials in the low-angle area corresponding to the (100), (110) and (200) reflections of the hexagonal symmetry lattice $P6mm$. The pattern of $\text{PW}_{11}\text{Zn}@ \text{aptesSBA-15}$ reveals the retention of such peaks at the

same angles as the starting support. Regarding $PW_{12}@aptesSBA-15$, the pattern shows a shift towards higher 2θ for the peaks of the (110) and (200) reflections as previously reported for other $POM@SBA-15$ as in Chapter 4 for PW_{11} composites. [20-22] Moreover, the absence of peaks arising from the Keggin POMs suggests that these molecules are located within the channels of the porous support.

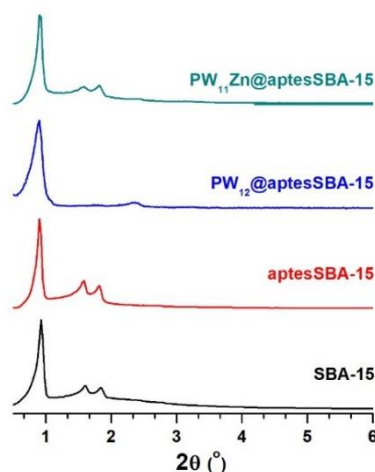


Figure 5.2 - Powder XRD patterns of the support SBA-15, the functionalized aptesSBA-15 and the $PW_{12}@aptesSBA-15$ and $PW_{11}Zn@aptesSBA-15$ composites.

The presence and integrity of the Keggin POMs in the amine-functionalized silica support was also investigated by ^{31}P MAS NMR (Figure 5.3). The spectrum of $PW_{11}Zn@aptesSBA-15$ displays a main peak at -13.98 ppm which matches well the reported data for encapsulated $[PW_{11}Zn(H_2O)]O_{39}^{5-}$ anions. [23] A broad peak centered at -13.19 ppm can be observed for $PW_{12}@aptesSBA-15$ with a shoulder at approximately -14.95 ppm. The latter is consistent with the presence of free $[PW_{12}O_{40}]^{3-}$ anion, [24] while the first may correspond to the Keggin structure interacting with the porous support. In fact, in literature several reports describe the occurrence of a downfield shift, compared to that of the free $[PW_{12}O_{40}]^{3-}$, caused by an electrostatic interaction of the Keggin anions with the $Si-OH_2^+$ groups from the silica support. [5, 25]

The $PW_{11}Zn@aptesSBA-15$ composite was also studied by ^{13}C CP MAS and ^{29}Si MAS NMR spectroscopy. The ^{13}C CP MAS NMR spectrum (Figure 5.4-left) displays three peaks located around 43.56, 21.95 and 10.00 ppm, that correspond to the C3, C2 and C1 atoms of the aminopropyl group, $Si-^1CH_2-^2CH_2-^3CH_2-NH_2$, respectively. [4, 16, 26] The ^{29}Si MAS NMR spectrum of the SBA-15 (Figure 5.4-right) displays a broad peak at $\delta = -111.07$ ppm with a shoulder at $\delta = -103.90$ ppm and a smaller peak at $\delta = -93.67$

ppm assigned to Q^4 , Q^3 and Q^2 species, respectively, where $Q^n = \text{Si}(\text{OSi})_{4-n}(\text{OH})_n$, $n = 2-4$. [14, 27-30] The ^{29}Si MAS NMR spectra of the functionalized SBA-15 also exhibits these peaks together with additional peaks at $\delta = -66.03$ and -59.89 ppm. These correspond to T^3 and T^2 species, where $T^n = \text{CSi}(\text{OSi})_{3-n}(\text{OH})_n$ for $n = 1-3$, which indicate the formation of siloxane bonds between aptes and SBA-15. [4, 30, 31]

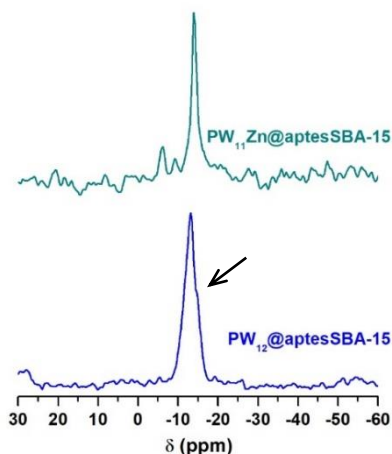


Figure 5.3 - ^{31}P MAS NMR spectra of the $\text{PW}_{12}@apt\text{SBA-15}$ and $\text{PW}_{11}\text{Zn}@apt\text{SBA-15}$ composites.

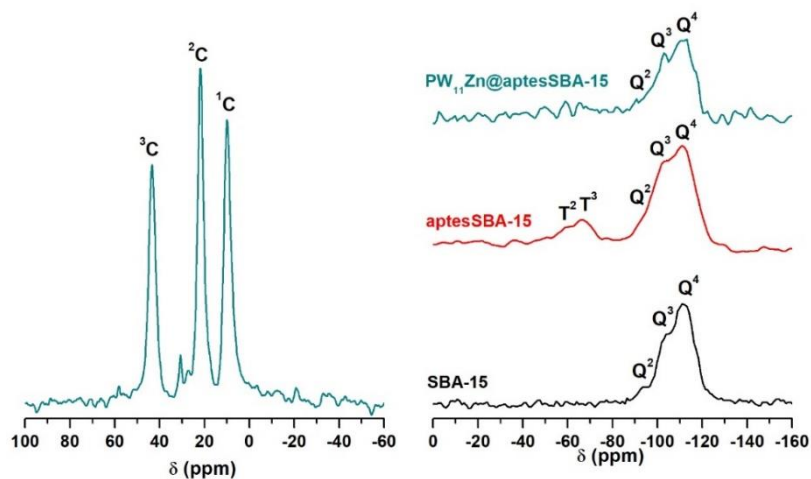


Figure 5.4 - Solid-state ^{13}C CP MAS NMR spectrum of $\text{PW}_{11}\text{Zn}@apt\text{SBA-15}$ (left) and ^{29}Si MAS NMR spectra (right) of SBA-15, aptSBA-15 and $\text{PW}_{11}\text{Zn}@apt\text{SBA-15}$.

The N_2 adsorption studies for SBA-15 (Figure 5.5) show type IV isotherms with H1 hysteresis loops, typical of these mesoporous materials. [4, 7] The amino-functionalized SBA-15 and the POMs@aptSBA-15 materials retain the same shape of the isotherms of starting support. A simultaneous decrease in the surface area (S_{BET})

and pore volume (V_p) (Table 1) could be observed when going from SBA-15 to aptesSBA-15 and then to the final composites, which confirms the successful functionalization with amine groups and the occupancy of the support pores with POM molecules. [4, 19]

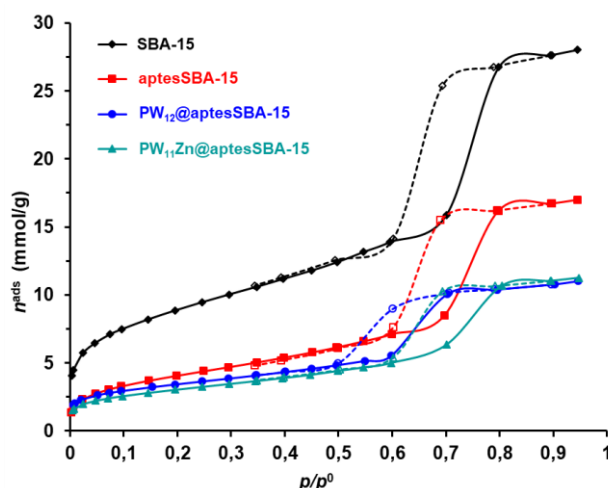


Figure 5.5 - N_2 adsorption-desorption isotherms of the support material SBA-15, the functionalized aptesSBA-15 and the composite materials, $PW_{11}Zn@aptesSBA-15$ and $PW_{12}@aptesSBA-15$.

Table 5.1 Textural parameters of SBA-15, aptesSBA-15 and the composite materials, $PW_{12}@aptesSBA-15$ and $PW_{11}Zn@aptesSBA-15$.

	S_{BET} (m^2g^{-1})	V_p (cm^3g^{-1})
SBA-15	725	0.971
aptesSBA-15	337	0.589
$PW_{11}Zn@aptesSBA-15$	247	0.391
$PW_{12}@aptesSBA-15$	277	0.381

The SEM images of the composite materials (Figure 5.6) reveal the characteristic morphology of the SBA-15 materials with hexagonal and elongated particles with diameters of approximately 415 nm indicating that the morphology of the silica support was maintained after the POMs incorporation. [16, 20, 32] The presence of the POMs in the composite materials could be confirmed by the presence of its main elements in the EDS spectra.

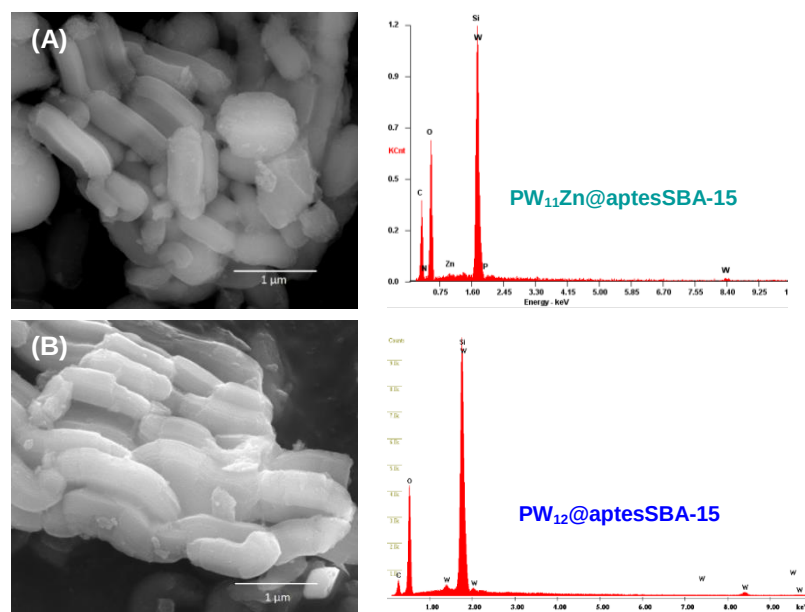


Figure 5.6 - SEM images and EDS spectra of (A) $PW_{11}Zn@aptesSBA-15$ and (B) $PW_{12}@aptesSBA-15$ composites.

In conclusion, the combination of the several characterization techniques allowed to confirm the successful incorporation of the Keggin POMs in the aptesSBA-15 support and that both guest and host structures were retained in the final composites.

5.2.2. Oxidative desulfurization processes using model diesel

The performance of the prepared catalysts in desulfurization systems was initially evaluated using the model diesel B (see Chapter 1 section 1.7). Homogeneous studies, using tetra-*n*-butylammonium (TBA) salts of PW_{12} and $PW_{11}Zn$, and heterogeneous studies, using POMs@aptesSBA-15 composites, were conducted in a biphasic extractive and oxidative desulfurization (ECODS) system, as well as in a solvent-free oxidative desulfurization (ODS) system. The biphasic liquid-liquid system was composed by equal volumes of model diesel and extraction solvent (acetonitrile) using a H_2O_2/S ratio of 8. This process begins with a liquid-liquid extraction for 10 min at 70 °C, during which non-oxidized sulfur compounds are transferred from the model diesel to the polar solvent phase. After reaching the transfer equilibrium, it is necessary to add oxidant in order to continue the sulfur removal from model diesel.

In the solvent-free system, the oxidative catalytic stage was performed at 70 °C without any solvent using a $\text{H}_2\text{O}_2/\text{S}$ ratio of 4. After achieving total oxidation of the sulfur compounds, a liquid-liquid extraction of the oxidized products is necessary to remove them from the model diesel, which was performed with acetonitrile or water. [4]

Figure 5.7 displays the results for the removal of the initial sulfur compounds from the model diesel (1-BT, DBT, 4-MDBT and 4,6-DMDBT) after 60 min of the oxidant addition. In the biphasic system, an initial extraction step was performed for 10 min, during which non-oxidized sulfur compounds are transferred to the solvent phase. In the case of the solvent-free system, the results are only related with the catalytic oxidative step of the ODS process. The overall oxidative reactivity of the sulfur compounds for all desulfurization systems follows the order as previously described in Chapters 3 and 4, typical of ODS systems catalyzed by POMs with H_2O_2 . [4, 13, 22, 33-35] It is also possible to observe that the TBA salts of PW_{11}Zn and PW_{12} present better results in the biphasic systems than in the solvent-free systems. The difference is most likely due to the low solubility of the TBAPOMs catalysts in the model diesel.

The initial extraction step occurring in the biphasic ECODS system is responsible for removing a considerable amount of sulfur compounds from model diesel, namely 56, 57, 60 and 56% for PW_{12} , PW_{11}Zn , $\text{PW}_{12}@\text{aptesSBA-15}$ and $\text{PW}_{11}\text{Zn}@\text{aptesSBA-15}$ biphasic systems, respectively. The extractive ability of the individual components followed the order: 1-BT > DBT > 4-MDBT > 4,6-DMDBT, as a consequence of the different molecular diameters. [4, 5, 36] The solvent-free system has proved to be inefficient using the TBA salts of PW_{11}Zn and PW_{12} catalysts since, after 60 min of the oxidant addition, only 27% and 2% of desulfurization was obtained for PW_{12} and PW_{11}Zn , respectively. Under the biphasic ECODS system, the performance of these catalysts improved allowing to remove, during the same period of time, 52 and 74% using PW_{12} and PW_{11}Zn catalysts, respectively. The lower activity of PW_{12} when compared with lacunary or mono-substituted POMs (chapter 4) has been previously reported and justified by the more difficult formation of catalytic active species (peroxotungstate species) starting from the whole structure of phosphotungstate. [16, 19, 37]

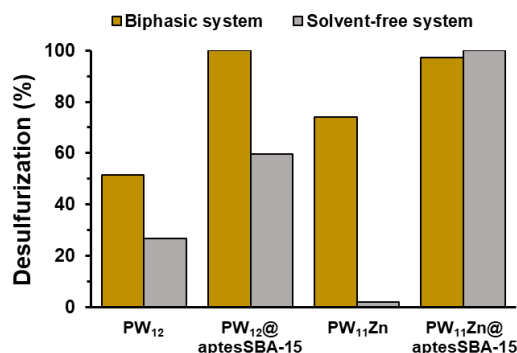


Figure 5.7 - Desulfurization of model diesel in the presence of different catalysts (3 μmol of active center) using the biphasic system (model diesel /MeCN 1:1, $\text{H}_2\text{O}_2/\text{S}=8$) and the solvent-free system ($\text{H}_2\text{O}_2/\text{S}=4$) at 70 $^\circ\text{C}$, after 60 min of the oxidant addition.

Figure 5.7 also evidences that, for biphasic and solvent-free desulfurization systems, the heterogeneous catalysts have a greater desulfurization performance than the homogeneous analogues. The $\text{PW}_{11}\text{Zn}@aptes\text{SBA-15}$ composite achieved complete desulfurization in the solvent-free system and 97% of desulfurization in the biphasic system after 60 min of initiating the catalytic step (oxidant addition). For the same period of time, the $\text{PW}_{12}@aptes\text{SBA-15}$ catalyst reached complete desulfurization in the biphasic system and 60% in the solvent-free system. The immobilization of both homogeneous POMs in the amine-functionalized SBA-15 seems to improve their catalytic ability. The choice of a suitable support is crucial to create a robust heterogeneous catalyst able to be recycled for consecutive cycles but also that promotes an increase of catalytic activity. The SBA-15 support has already demonstrated to be highly suitable in the preparation of heterogeneous catalysts for efficient oxidative desulfurization, [4, 13, 38, 39] and its adsorptive desulfurization capacity has also been reported. [40, 41] Control experiments have been performed using the $aptes\text{SBA-15}$ support as catalyst as well as leaching tests. The oxidative catalytic results show that, using only $aptes\text{SBA-15}$ as catalyst, 16 and 13% of desulfurization is attained for the biphasic [4] and solvent-free systems, respectively. The enhancement of the desulfurization performance observed for the heterogeneous catalysts can result from the combination of adsorptive and oxidative processes of sulfur compounds occurring simultaneously at the surface of the same material.

The investigation of the heterogeneity of the $\text{POMs}@aptes\text{SBA-15}$ composites was conducted in the biphasic system, since any leached active species would promote a homogeneous reaction after the removal of the solid catalyst. Figure 5.8 presents the kinetic profiles for sulfur conversion of model diesel in the biphasic system using both

composites and the corresponding leaching tests. The catalysts were removed by hot filtration 5 and 7 min past the oxidant addition using $PW_{12}@aptesSBA-15$ and $PW_{11}Zn@aptesSBA-15$ catalysts, respectively, and the ECODS process was allowed to continue with the filtrated solution. The leaching results confirm the heterogeneity of both catalysts since the conversion practically stops after catalyst removal. At the end of the leaching tests, the extraction phases (MeCN) were analyzed by ^{31}P NMR spectroscopy. In the case of ECODS system using $PW_{11}Zn@aptesSBA-15$ catalyst, no peak could be observed in the ^{31}P NMR spectrum indicating the absence of leached species in the MeCN phase. Regarding $PW_{12}@aptesSBA-15$ ECODS catalytic system, the spectrum shows a single peak at -13.86 ppm (Figure 5.9). Despite being close to the chemical shift of the isolated PW_{12} (-13.89 ppm), the fact that the reaction stops after the catalyst removal, strongly suggests that it should not correspond to the active species.

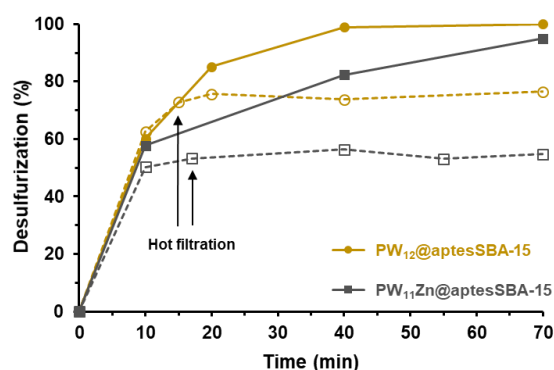


Figure 5.8 - Kinetic profiles for the desulfurization of model diesel using the heterogeneous $PW_{12}@aptesSBA-15$ and $PW_{11}Zn@aptesSBA-15$ catalysts (containing 3 μ mol of POM, using $H_2O_2/S = 8$ and at 70 $^{\circ}C$), and the corresponding leaching tests (dotted lines) under the biphasic system.

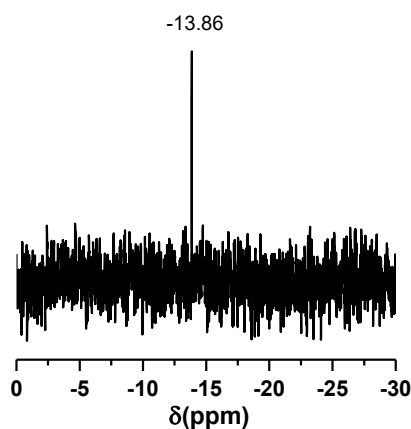


Figure 5.9 - ^{31}P NMR spectrum of the extraction MeCN phase at the end of the leaching test using the $PW_{12}@aptesSBA-15$ catalyst.

The overall results obtained with the $\text{PW}_{11}\text{Zn@aptesSBA-15}$ composite has led us to consider it the most advantageous catalyst due to its remarkable performance in both systems together with the absence of leaching. As so, the catalytic performance of $\text{PW}_{11}\text{Zn@aptesSBA-15}$ in the biphasic and solvent-free systems was assessed in more detail. In Figure 5.10 is possible to compare the desulfurization profiles of model diesel catalyzed by $\text{PW}_{11}\text{Zn@aptesSBA-15}$ using both systems and two different $\text{H}_2\text{O}_2/\text{S}$ ratios. The solvent-free system exhibits superior desulfurization performance than the biphasic system for both $\text{H}_2\text{O}_2/\text{S}$ ratios, mainly for 30 minutes after oxidant addition. In fact, using the solvent-free system, complete oxidation could be reached after just 60 min of reaction whereas the best result with the biphasic system ($\text{H}_2\text{O}_2/\text{S}=8$) removed 97% after 70 min (10 min extraction + 60 min oxidation).

The mechanism of the ODS process in the biphasic system may follow the formerly reported mechanism for PW_{11}Zn -catalyzed desulfurization using aqueous H_2O_2 as oxidant [8, 9, 16]. The interaction of the oxidant with the terminal $\text{W}^{\text{VI}}=\text{O}$ bonds or the substituted $\text{Zn}-\text{OH}_2$ (water as labile ligand) leads to the formation of active peroxo species. These species are then able to oxidize sulfur compounds into the corresponding sulfoxides and/or sulfones while simultaneously regenerating the W^{VI} -species. [42]

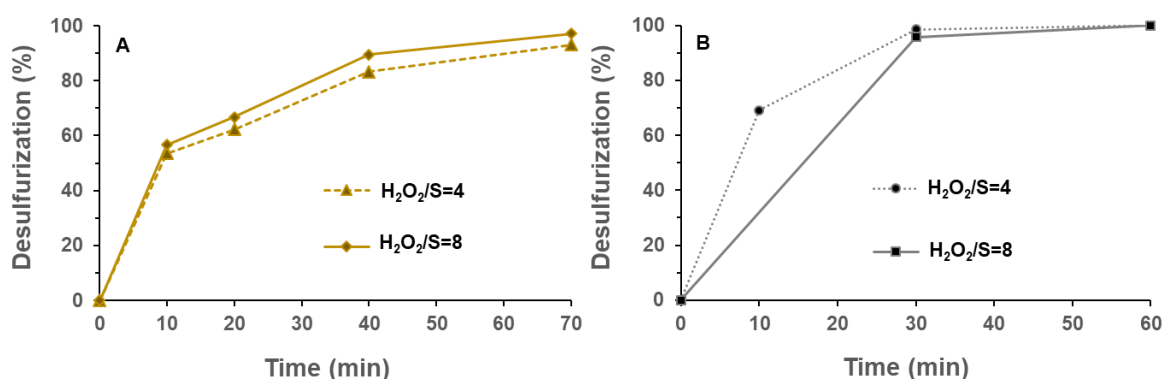


Figure 5.10 Desulfurization profiles of model diesel B catalyzed by $\text{PW}_{11}\text{Zn@aptesSBA-15}$ composite (containing 3 μmol of PW_{11}Zn) using different oxidant amounts under the (A) biphasic (model diesel/MeCN 1:1) and (B) solvent-free systems, at 70 $^{\circ}\text{C}$.

5.2.2.1 Recycling of $\text{PW}_{11}\text{Zn@aptesSBA-15}$ catalyst

In order to assure the sustainability of the desulfurization systems, the recycling ability of the $\text{PW}_{11}\text{Zn@aptesSBA-15}$ catalyst was evaluated for several consecutive cycles using both desulfurization systems. After each cycle, the catalyst was recovered by centrifugation, washed with ethanol and dried to be used in another ODS cycle under

the same experimental conditions. The desulfurization efficiency of the $PW_{11}Zn@aptesSBA-15$ catalyst in both systems has been compared for five consecutive cycles after 60 min of oxidation (Figure 5.11). The results show that the desulfurization efficiency was maintained along the five consecutive cycles without any significant loss of catalytic activity for both systems. Besides the slightly superior performance using the solvent-free system, it also allowed to perform five additional ODS cycles (ten in total) while maintaining the catalytic activity (Figure 5.12).

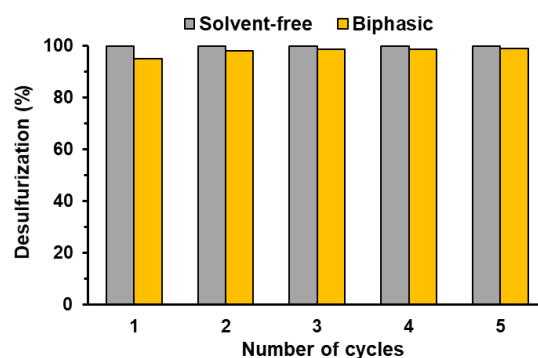


Figure 5.11 - Recycling desulfurization results using the $PW_{11}Zn@aptesSBA-15$ composite (containing $3\ \mu\text{mol}$ of $PW_{11}Zn$) after 60 min of the oxidant addition using the solvent-free ($H_2O_2/S=4$) or biphasic ($H_2O_2/S=8$) systems at $70\ ^\circ\text{C}$.

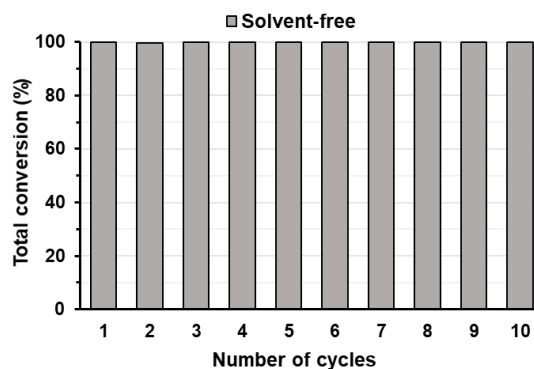


Figure 5.12 - Desulfurization results for ten cycles, using the $PW_{11}Zn@aptesSBA-15$ composite (containing $3\ \mu\text{mol}$ of $PW_{11}Zn$) after 60 min of the oxidant addition using the solvent-free system ($H_2O_2/S=4$) at $70\ ^\circ\text{C}$.

5.2.3 Catalysts materials stability

The structural stability of the $POMs@aptesSBA-15$ catalysts was evaluated after catalytic use (ac) under the biphasic ECODS system. Different characterization techniques of the recovered solids after one ECODS cycle was performed. The ICP-OES of the composites after catalytic use in the biphasic system reveals some loss of POM

center during the process. An increase of the Si/W (molar) ratio after catalysis was observed corresponding to a loss of 27 and 26 % for $PW_{12}@aptesSBA-15$ and $PW_{11}Zn@aptesSBA-15$, respectively. Nevertheless, as it was seen in the recycling studies of $PW_{11}Zn@aptesSBA-15$ (Figures 5.11 and 5.12), the catalytic activity over consecutive cycles was not affected. The FT-IR spectra of the composites before and after catalytic use were compared (Figure 5.13). The main bands of the composites remain unchanged, and specifically the characteristic bands associated to the POM stretching modes in the $1000-800\text{ cm}^{-1}$ region, suggest the preservation of its structures after catalytic use.

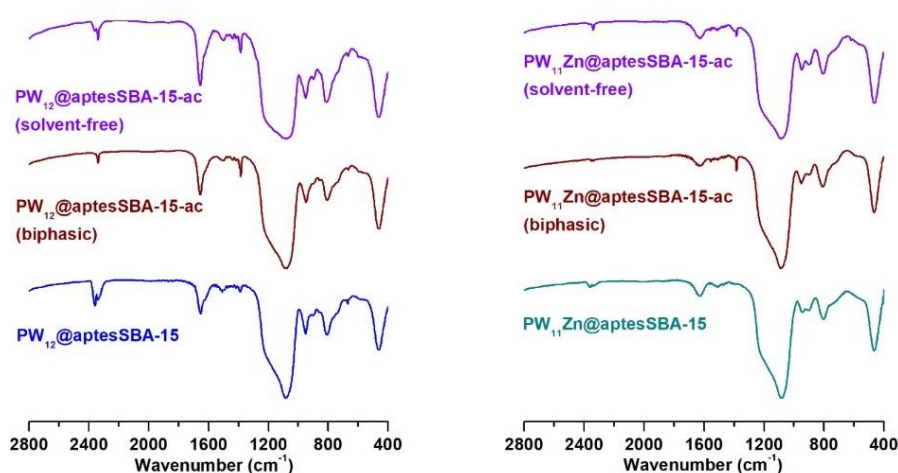


Figure 5.13 - FT-IR spectra of the $PW_{12}@aptesSBA-15$ and $PW_{11}Zn@aptesSBA-15$ composites before and after catalytic use (ac is the abbreviation for after catalysis).

Therefore, the ^{31}P MAS NMR analyses of the recovered catalysts were performed (Figure 5.14). Regarding the $PW_{12}@aptesSBA-15$ catalysts, the spectra of both recovered catalysts display two peak located at -13.19 and -14.95 ppm, previously assigned to different PW_{12} interaction with the support. This result indicates that there must be a continuous equilibrium between these species occurring during the ECODS processes. The spectrum of $PW_{11}Zn@aptesSBA-15-ac$ exhibit a main peak at -11.93 ppm just slightly shifted when compared with the ^{31}P signal before catalysis. A smaller peak located at -4.65 ppm can also be observed that corresponds to the $[PO_4\{W(O_2)_2\}_4]^{3-}$ Venturello complex. [5, 43]

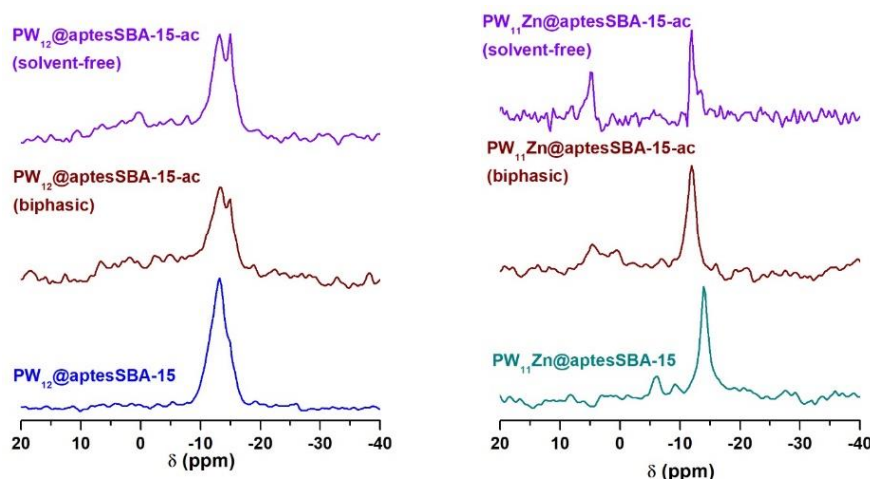


Figure 5.14 - ^{31}P MAS NMR spectra of the $\text{PW}_{12}@aptes\text{SBA-15}$ and $\text{PW}_{11}\text{Zn}@aptes\text{SBA-15}$ composites before and after catalytic use (ac stands for after catalysis).

The powder XRD patterns of the POMs@aptesSBA-15 composites before and after the ECODS process (Figure 5.15) exhibit similar main diffraction peaks. A decrease of intensity of the (110) reflection is detected in the pattern of $\text{PW}_{11}\text{Zn}@aptes\text{SBA-15-ac}$ in the biphasic system. A closer observation confirms that the peak is still present (Figure 5.14-inset) and therefore that the structure of the support has also been preserved. The SEM images (Figure 5.16) still present the elongated structures of the initial composites suggesting that the morphology of the catalysts was maintained after the ECODS process. Besides, the EDS spectra also display tungsten, indicating the POM presence in both catalysts. Moreover, the EDS spectra of $\text{PW}_{11}\text{Zn}@aptes\text{SBA-15}$ after catalysis reveal a considerable amount of sulfur adsorbed to the composite material.

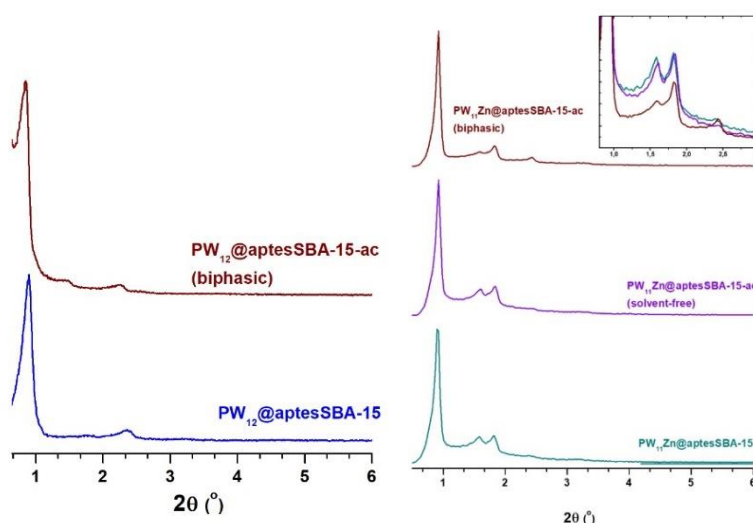


Figure 5.15 - Powder XRD patterns of the composites $\text{PW}_{11}\text{Zn}@aptes\text{SBA-15}$ and $\text{PW}_{12}@aptes\text{SBA-15}$ before and after catalytic use (ac is the abbreviation for after catalysis).

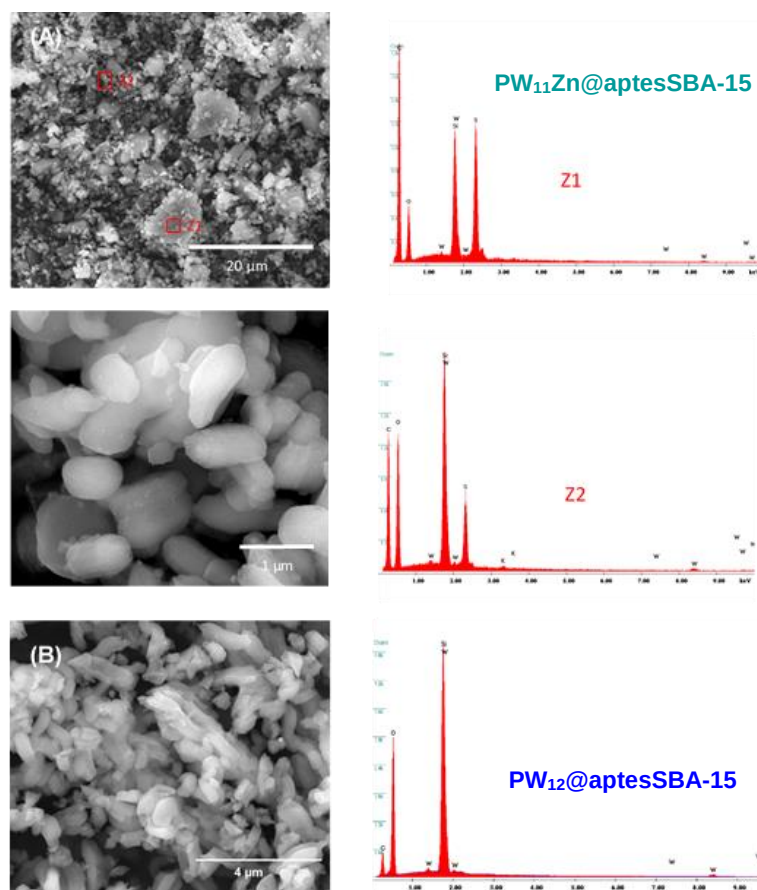


Figure 5.16 - SEM images and EDS spectra of (A) $PW_{11}Zn@aptSBA-15$ after ten cycles under the solvent-free system and (B) $PW_{12}@aptSBA-15$ after one cycle under the biphasic system.

5.2.4. Oxidative desulfurization processes using real diesel

Taking in account its promising catalytic performance, the $PW_{11}Zn@aptSBA-15$ composite was tested in the desulfurization of real diesels. Two untreated diesel samples with different composition and amount of sulfur compounds were used, one supplied by CEPISA with 1335 ppm S (mainly dibenzothiophenes derivatives) and the other by Galp with 2300 ppm S (mainly benzothiophenes and dibenzothiophenes derivatives). An initial extraction with acetonitrile (1:1 diesel/MeCN during 10 min at room temperature) was performed to the latter which allowed to remove 300 ppm S. Afterwards, this sample was further desulfurized using the biphasic system (1:1 diesel/MeCN) under the $H_2O_2/S/catalyst$ proportions as used in model diesel experiments ($H_2O_2/S=8$ and 3 μmol of active center) at 70 °C for 2 h oxidation. After the catalytic step, all diesel samples were treated with a liquid-liquid extraction with acetonitrile (1:1) at room temperature for 10 min, to remove oxidation products and some non-oxidized sulfur compounds. After each ODS cycle, the catalyst was separated by centrifugation, washed with ethanol and dried to be used in another ODS cycle with a

new portion of untreated diesel. Figure 5.17 presents the desulfurization results obtained for three ODS cycles after 2h the oxidant addition, for all experiments. Overall, it can be observed that the catalyst maintained the desulfurization efficiency between cycles. In the first cycle, the desulfurization efficiency for the CEPESA diesel using the biphasic system corresponds to 85 %.

The Galp diesel, under the biphasic system, after one ODS cycle reached 73%. Without the final extraction with MeCN, that value considerably decreased to 58%. After three ODS cycles with the same catalyst, the desulfurization efficiency of the system reached 82%, which is indicative that the catalyst retained its catalytic activity, and can be used in successive ODS cycles to desulfurize untreated diesel.

For efficiency comparison between biphasic and solvent-free systems, the CEPESA diesel was desulfurized as it was, also using solvent-free system in the same conditions as the biphasic system. Similar results were obtained between the solvent-free and biphasic systems (88%); however, the solvent-free system needed a smaller amount of extraction solvent to reach similar desulfurization efficiency, since the biphasic system uses MeCN during the catalytic stage and in the final extraction.

In summary, the $PW_{11}Zn@aptesSBA-15$ catalyst and the ODS systems herein proposed have all shown very promising features for the production of sulfur-free diesels. In fact, the results obtained with real diesel samples have shown that the systems are highly efficient removing sulfur compounds in a relatively short period of time. In particular, the solvent-free system matches the desulfurization performance of the biphasic system while reducing the amount of toxic solvents used in the process.

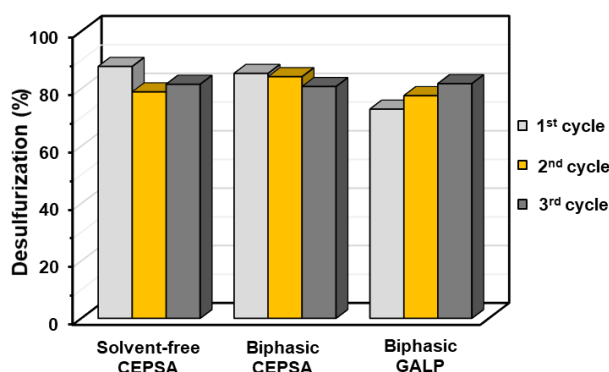


Figure 5.17 - Desulfurization results obtained of untreated diesel for three ODS cycles 2 h after the oxidant addition, catalyzed by $PW_{11}Zn@aptesSBA-15$ composite, using the solvent-free ($H_2O_2/S=8$) or biphasic ($H_2O_2/S=8$) systems at 70 °C.

5.3. Conclusion

In conclusion, the Keggin phosphotungstate (PW_{12}) and its zinc mono-substituted derivative ($PW_{11}Zn$) were immobilized in amine-functionalized mesoporous silica SBA-15 and applied in the desulfurization of multicomponent model diesel. Two different ODS systems were tested, a biphasic system, where the oxidation step occurs in the presence of an extraction solvent and a solvent-free system, without the presence of an extraction solvent during the catalytic reaction.

The desulfurization efficiencies of the TBA salts of PW_{12} and $PW_{11}Zn$ catalysts, using both systems, as well as its corresponding composites ($PW_{12}@apt\text{esSBA-15}$ and $PW_{11}Zn@apt\text{esSBA-15}$) were compared. The homogeneous (PW_{12}) and the heterogeneous ($PW_{12}@apt\text{esSBA-15}$) catalysts have shown superior performance under the biphasic system. However, the best results were achieved with the $PW_{11}Zn@apt\text{esSBA-15}$ composite. Its performance was similar in both systems (>97 % after just 60 min) although the solvent-free system required only half the oxidant amount.

The stability of both composites after catalytic use was assessed, which revealed higher POM stability for $PW_{11}Zn$ than for PW_{12} . The high stability of $PW_{11}Zn@apt\text{esSBA-15}$ was demonstrated by maintaining its catalytic activity in ten consecutive ODS cycles without any apparent loss of desulfurization efficiency. Moreover, the $PW_{11}Zn@apt\text{esSBA-15}$ was also tested in the desulfurization of two untreated diesels with different sulfur amounts (CEPSA 1335 ppm and Galp 2300 ppm). After one ODS cycle, the desulfurization efficiency for the CEPSA diesel was 88 % and 85 %, using the solvent-free and the biphasic systems, respectively. Lower desulfurization efficiency was found using the Galp diesel under biphasic system, reaching a desulfurization of 73 % after one ODS cycle. The $PW_{11}Zn@apt\text{esSBA-15}$ catalyst (especially under the solvent-free system) has shown remarkable desulfurization properties, namely efficiency and recyclability, with great potential for application in sustainable industrial processes.

5.4. Experimental section

5.4.1. Materials and Methods

All the reagents used in the polyoxometalates (POMs) synthesis, support and composite preparation, namely (3-aminopropyl)triethoxysilane (apt\text{es}, Aldrich), anhydrous toluene 99.8% (Aldrich), ethanol (Aga), hydrochloric acid (HCl, Fisher Chemicals), pluronic P123 (Aldrich), phosphotungstic acid (Fluka), potassium chloride

(Aldrich), sodium hydrogen phosphate dihydrate (Aldrich), sodium tungstate dihydrate (Aldrich), tetra-*n*-butylammonium bromide (TBA, Merck), tetraethoxysilane (TEOS, Aldrich) and zinc acetate dehydrate (M&B) were used as received. The reagents for oxidative desulfurization reactions, including 1-benzothiophene (1-BT, Fluka), 4,6-dimethyldibenzothiophene (4,6-DMDBT Alfa Aesar), 4-methyldibenzothiophene (4-MDBT, Aldrich), dibenzothiophene (DBT, Aldrich), acetonitrile (MeCN, Fisher Chemical), hydrogen peroxide aq. 30% (Aldrich) and *n*-octane (Aldrich) were purchased from chemical suppliers and used without further purification.

Elemental analyses for C, H and N elements were performed in a Leco CHNS-932 instrument, and Si and W by ICP-OES on a Perkin-Elmer Optima 4300 DV instrument at the University of Santiago de Compostela. FT-IR spectra were obtained on a Jasco 460 Plus spectrometer using KBr pellets. The FT-Raman spectra were recorded by the research group of Isabel Gonçalves in CICECO Associate Laboratory, University of Aveiro, using a RFS-100 Bruker FT-spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm and the laser power set to 350 mW. Powder X-ray diffraction analyses were performed by the “Departamento de Física e Astronomia from Faculdade de Ciências da Universidade do Porto” and collected at ambient temperature in Bragg-Brentano para-focusing geometry using a Rigaku Smartlab diffractometer, equipped with a D/teX Ultra 250 detector and using Cu K- α radiation ($K_{\alpha 1}$ wavelength 1.54059 Å), 45 kV, 200 mA, in continuous mode, step 0.01°, speed 15°/min, in the range $1 \leq 2\theta \leq 50^\circ$. ^{31}P NMR spectra were collected for liquid solutions using a Bruker Avance III 400 spectrometer and chemical shifts are given with respect to external 85% H_3PO_4 . Solid state ^{13}C , ^{31}P and ^{29}Si MAS NMR spectra were acquired with a Bruker AVANCE III 300 spectrometer (7 T) operating at 75 MHz (^{13}C), 121 MHz (^{31}P) and 60 MHz (^{29}Si), respectively, equipped with a BBO probe head. The samples were spun at the magic angle at a frequency of 5 kHz in 4 mm-diameter rotors at room temperature. The ^{13}C MAS NMR experiments were acquired with proton cross polarization (CP MAS) with a contact time of 1.2 ms, and the recycle delay was 2.0 s. The ^{29}Si MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 4.5 μs at a power of 40 W, and a relaxation delay of 10.0 s. The ^{31}P MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 5.0 μs at a power of 20 W, and a relaxation delay of 2.0 s. Solid state ^{13}C , ^{31}P and ^{29}Si MAS NMR spectra were performed by Pedro Almeida at CENIMAT/I3N, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at “Centro de Materiais da Universidade do Porto” (CEMUP, Porto, Portugal) using a high-resolution (Schottky)

scanning electron microscope with X-ray microanalysis and electron backscattered diffraction analysis Quanta 400 FEG ESEM/EDAX Genesis X4 M. The samples were studied as powders and were coated with an Au/Pd thin film by sputtering using the SPI Module Sputter Coater equipment. The textural characterization was obtained from physical adsorption of nitrogen at $-196\text{ }^{\circ}\text{C}$, using a Quantachrome NOVA 2200e instrument at Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa by Professor João Pires. Samples were degassed at $120\text{ }^{\circ}\text{C}$ for at least 5 h prior to the measurements. The BET surface area (S_{BET}) was calculated by using the relative pressure data in the 0.05–0.3 range. The total pore volume (V_p) was evaluated on the basis of the amount adsorbed at a relative pressure of about 0.95. GC-FID was carried out in a Varian CP-3380 chromatograph to monitor the ODS multicomponent model oil experiments. Hydrogen was used as the carrier gas (55 cm s^{-1}) and fused silica Supelco capillary columns SPB-5 ($30\text{ m} \times 0.25\text{ mm i.d.}$; $25\text{ }\mu\text{m}$ film thickness) were used. Sulfur content in Galp diesel was measured by ultraviolet fluorescence test method in Galp by Rita Valença, using a Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125. CEPESA sulfur content quantification was obtained by X-ray Fluorescence Spectrometry, using an Spectrace 450 spectrometer at the University of Santiago de Compostela.

5.4.2 Preparation of the POMs@aptesSBA-15 composites

The potassium and tetra-*n*-butylammonium (TBA) salts of the zinc mono-substituted phosphotungstate $[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$ (**PW₁₁Zn**) as well as the TBA salt of the Keggin polyanion $[\text{PW}_{12}\text{O}_{40}]^{3-}$ (**PW₁₂**) were prepared and characterized according to previously reported methods. [16, 44] The hydrothermal synthesis of the SBA-15 support, as well as, its surface functionalization via post-grafting method were also described elsewhere. [11, 13]

The immobilization of the Keggin POMs in the functionalized aptesSBA-15 was achieved via an impregnation method adapted from previously reported procedures from our group [5, 12, 19]. Briefly, the potassium salt of **PW₁₁Zn** and the commercial phosphotungstic acid (1.0 g of each POM) were dissolved in deionized water (10 mL) and added to aptesSBA-15 (0.5 g), previously dried under vacuum at $60\text{ }^{\circ}\text{C}$ for 2h. The mixture was stirred for 3 days and the solid was separated by filtration, washed with deionized water and dried in a desiccator over silica gel.

PW₁₂@aptSBA-15: Anal. Found (%) W, 23.0; loading of POM: 0.143 mmol/g⁻¹; selected FT-IR (cm⁻¹): 3434 (s); 2938 (w); 1654 (m); 1621 (sh); 1498 (w); 1388 (w); 1191 (sh); 1081 (vs); 950 (m); 900 (w); 808 (m); 667 (w); 458 (s); selected FT-Raman (cm⁻¹): 2958 (s); 2935 (s); 2898 (s); 1442 (m); 1414 (m); 989 (vs); 978 (sh); 864 (m).

PW₁₁Zn@aptSBA-15: Anal. Found (%) W, 22.6; Si, 5.1; loading of POM: 0.111 mmol/g⁻¹, Si/W (molar) = 1.49; selected FT-IR (cm⁻¹): 3445 (vs); 2359(w); 2341 (w); 1626 (m); 1445 (w); 1213 (sh); 1084 (vs); 944 (w); 902 (w); 803 (m); 468 (s); selected FT-Raman (cm⁻¹): 2927 (s); 2900 (s); 1454 (m); 1414 (m); 1333 (m); 1043 (vs); 968 (sh); 885 (m).

5.4.3. Oxidative desulfurization processes using model diesel

To evaluate the catalysts ability to be used in oxidative desulfurization the model diesel B was prepared (1-benzothiophene (1-BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), with a concentration of approximately 500 ppm S each, in *n*-octane). The ODS experiments were conducted under atmospheric pressure in a 5 mL reactor immersed in a thermostatically controlled liquid paraffin bath at 70 °C. The ODS studies were performed in the presence (MeCN, acetonitrile was used for the biphasic system) or in the absence of extraction solvent (solvent-free system). Hydrogen peroxide 30% was used as oxidant. ODS experiments in homogeneous conditions were performed with the TBA salts while the heterogeneous studies were performed with the POMs@aptSBA-15 composites. In a typical biphasic system experiment, 1:1 model diesel/MeCN (0.75 mL of each) were added to 3 μmol of POM (for POMs@aptSBA-15 composites, the equivalent amount containing 3 μmol of POM) and the resulting mixture was stirred for 10 min at 70 °C until the extraction equilibrium was reached. An aliquot of the upper phase oil was taken and the catalytic step was initiated by the addition of the oxidant. The solvent-free system experiments were performed with the catalyst, model diesel (0.75 mL) and the oxidant. In the solvent-free system, a final liquid-liquid extraction with a solvent (MeCN or EtOH and/or water) was performed to remove the oxidized sulfur compounds from model diesel. The sulfur content was quantified by GC analysis using tetradecane as standard. In the end of the heterogeneous experiments, the catalyst was recovered by centrifugation, washed with ethanol and dried in a desiccator over silica gel. For the recycling studies, the recovered catalyst was reused in new ODS cycles under the same reactional conditions.

5.4.4. Oxidative desulfurization processes using untreated diesels

Two different untreated diesel samples were tested in desulfurization processes. The untreated diesel samples were supplied by CEPISA (ca. 1335 ppm of sulfur) and Galp (ca. 2300 ppm of sulfur). The latter (Galp) was subjected to one liquid-liquid extraction 1:1 with MeCN before the ODS process, during 10 minutes at room temperature. Both diesel samples were tested in the biphasic system using the $PW_{11}Zn@aptesSBA-15$ catalyst. The diesel samples were mixed with the zinc composite (containing 3 μmol of POM) in MeCN using a H_2O_2/S ratio of 8. After the oxidant addition, the mixture was heated at 70 °C for 2 h. After this time, the diesel samples were removed from the system and washed with an equal volume of MeCN for 10 min and separated by decantation. The solvent-free system was also evaluated in the desulfurization of CEPISA diesel for comparison with the biphasic system. In this case, the catalyst and oxidant were mixed with the diesel sample and heated at 70 °C during 2 h. The diesel was separated from the catalyst by centrifugation and washed with MeCN during 10 min. Recycling tests were also performed for three consecutive cycles. After catalytic use the composite was recovered, washed with ethanol and dried in a desiccator over silica gel overnight.

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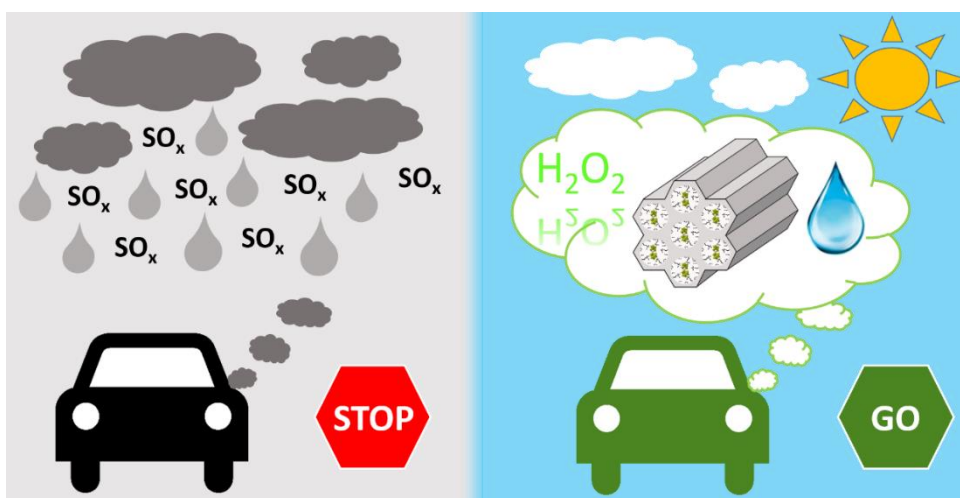
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Chapter 6

Desulfurization Process conciliating Heterogeneous Oxidation and liquid extraction: Organic Solvent or Centrifugation/Water?^{1,2}



¹ Adapted from: Susana O. Ribeiro, Lucie S. Nogueira, Sandra Gago, Pedro L. Almeida, Marta C. Corvo, Baltazar de Castro, Carlos M. Granadeiro and Salete S. Balula, *Desulfurization Process conciliating Heterogeneous Oxidation and liquid extraction: Organic Solvent or Centrifugation/Water?*, Applied Catalysis A: General, 542 (2017) 359-367, doi: 10.1016/j.apcata.2017.05.032

² Susana O. Ribeiro contribution to the publication: Support material preparation; investigation of catalytic performance of the prepared composite in the desulfurization of the model diesel and manuscript preparation.

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Chapter 6

Desulfurization Process conciliating Heterogeneous Oxidation and liquid extraction: Organic Solvent or Centrifugation/Water?

Abstract

The present work presents a novel oxidative desulfurization system based in a sandwich-type polyoxometalate composed by two Keggin derivative units, connected by the Eu^{3+} lanthanide, $[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$ (abbreviated as $\text{Eu}(\text{PW}_{11})_2$). This behaved as an efficiently catalyst in the oxidative desulfurization of a multicomponent model diesel, operating under sustainable conditions, *i.e.* using an eco-friendly oxidant and without the need of extractive organic solvents. The catalytic performance of the homogeneous $\text{Eu}(\text{PW}_{11})_2$ and the heterogeneous $\text{Eu}(\text{PW}_{11}\text{O}_{39})_2@\text{aptesSBA-15}$ composite was evaluated using a biphasic (extractive and catalytic oxidative desulfurization – ECODS) system and, the latter was also tested in a solvent-free (catalytic and extractive desulfurization – CODS) system ($\text{H}_2\text{O}_2/\text{S} = 12$ at 70°C). The results, using the composite, reveal its remarkable desulfurization performance achieving complete desulfurization after just 2 h of reaction. Moreover, the composite has shown a high recycling ability without loss of catalytic activity for ten consecutive oxidative desulfurization cycles. Interestingly, under solvent-free conditions it was possible to maintain the desulfurization efficiency of the biphasic system while being able to avoid the use of harmful organic solvents. In this case, a successful extraction of oxidized sulfur compounds was found conciliating centrifugation and water as extraction solvent. Therefore, this work reports an important step towards the development of novel eco-sustainable desulfurization systems with high industrial interest.

6.1 Introduction

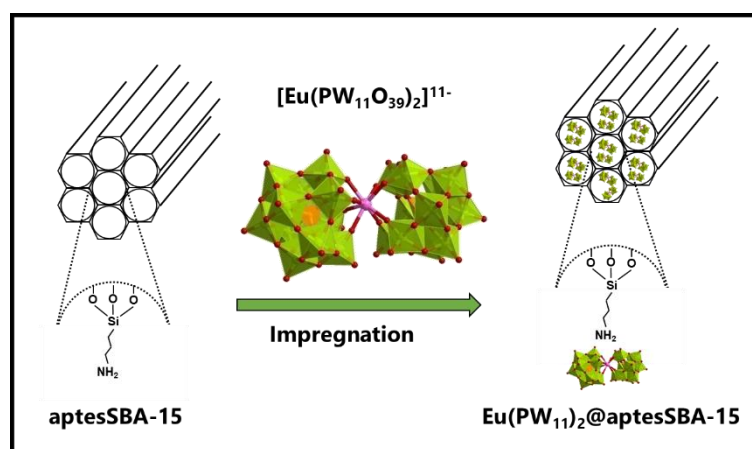
The immobilization of POM in solid supports arises from the need to prepare stable heterogeneous catalysts that allow its recovery and recycling. The SBA-15 (SBA: Santa Barbara Amorphous) mesoporous silica has been extensively used as solid support in the heterogenization of homogeneous catalysts due to its large internal surface area, high hydrothermal stability and narrow pore size distribution. [1-4] In particular, several catalytic active POMs have been incorporated/immobilized in mesoporous silica SBA-15 for application in heterogeneous catalysis (see chapters 3, 4 and 5 and references [5-22]). Recently, Chamack *et al.* have reported the immobilization of different tungsten-substituted molybdophosphoric acids on platelet SBA-15 for application in oxidative desulfurization (ODS). [18] The authors have shown that the tungsten substitution content influences the catalytic activity of the materials. Despite reporting complete desulfurization in short reaction periods, the studied model fuel contained only one sulfur compound.

In this chapter, we report a novel composite prepared through the impregnation of the sandwich-type $[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$ anion in the porous framework SBA-15 functionalized with (3-aminopropyl)triethoxysilane (aptès), designated as aptèsSBA-15. This catalytic active center is formed by two lacunar $[\text{PW}_{11}\text{O}_{39}]^{7-}$ units coordinated by the Eu^{3+} center. The main goal to use this sandwich-type active center is to investigate the influence of using two units of active Keggin derivatives (in chapter 4 only one unit was used) in ODS. Therefore, $\text{Eu}(\text{PW}_{11})_2@\text{aptèsSBA-15}$ composite was evaluated as heterogeneous catalyst in the desulfurization of model diesel B (see section 1.7) using H_2O_2 as oxidant and its catalytic performance was compared with the homogeneous $\text{Eu}(\text{PW}_{11})_2$. The ODS studies were performed using either a solvent-free or a biphasic system and the catalytic oxidative desulfurization performances were compared. Furthermore, the most desired sustainable solvent, *i.e.* water, was used as an efficient extraction solvent to remove oxidized sulfur compounds from model diesel. The recyclability and stability of the catalyst in the studied oxidative catalytic systems was also investigated.

6.2. Results and discussion

6.2.1. Catalysts characterization

The potassium and tetra-n-butylammonium (TBA) salts of the europium polyoxotungstate: $K_{11}[Eu(PW_{11}O_{39})_2] \cdot H_2O$ ($Eu(PW_{11})_2$), $TBA_7H_4[Eu(PW_{11}O_{39})_2]$ ($[TBA] Eu(PW_{11})_2$) were initially prepared and the $Eu(PW_{11})_2$ was incorporated in the apts-functionalized SBA-15 via impregnation method as presented previously in Chapters 4 and 5 (Scheme 6.1; detailed experimental procedure in 6.4.2).



Scheme 6.1 – Representation of the composite $Eu(PW_{11})_2@aptesSBA-15$ preparation.

The resulting $Eu(PW_{11})_2@aptesSBA-15$ composite was thoroughly studied by several characterization techniques including vibrational spectroscopy (FT-IR and FT-Raman), elemental analysis, powder XRD, solid-state ^{13}C CP MAS, ^{31}P MAS and ^{29}Si CP MAS spectroscopies, scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) elemental mapping and textural analysis (N_2 adsorption isotherms).

The FT-IR spectrum of the composite was compared with the spectra of the aptsSBA-15 support and POM (Figure 6.1 – left). The FT-IR spectrum of $Eu(PW_{11})_2@aptesSBA-15$ is dominated by the intense bands in the $1100-400\text{ cm}^{-1}$ range assigned to the $\nu_{as}(Si-O-Si)$, $\nu_s(Si-O-Si)$ and $\delta(O-Si-O)$ vibrations of the siliceous support. [15, 23] The presence of the POM in the composite material is confirmed by the additional bands located at ca. 958 and 893 cm^{-1} assigned to the terminal $\nu_{as}(W-O_d)$ and corner-sharing $\nu_{as}(W-O_b-W)$ vibrational modes of the $Eu(PW_{11})_2$, respectively. [24-26] As presented in Chapters 4 and 5, the Raman signal from the siliceous support is rather weak and consequently, no significant interference is observed in the main POM

stretches range ($1100\text{--}800\text{ cm}^{-1}$). [14, 27, 28] Therefore, the typical bands associated with the POM stretching modes can be clearly seen in the $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ spectrum (Figure 6.1 – right), namely two intense bands (986 and 970 cm^{-1}) associated with the $\nu_{\text{as}}(\text{W-O}_d)$ stretches and a smaller band (ca. 878 cm^{-1}) assigned to the $\nu_{\text{as}}(\text{W-O}_b\text{-W})$ vibrational mode. [26, 29] The incorporation process has led to a small shift in these bands towards lower wavenumbers, as previously reported for other POM-immobilized aptesSBA-15 composite materials. [15, 16] Elemental analysis further confirms the presence of the $\text{Eu}(\text{PW}_{11})_2$ in the composite material revealing a $\text{Eu}(\text{PW}_{11})_2$ loading of 0.063 mmol/g .

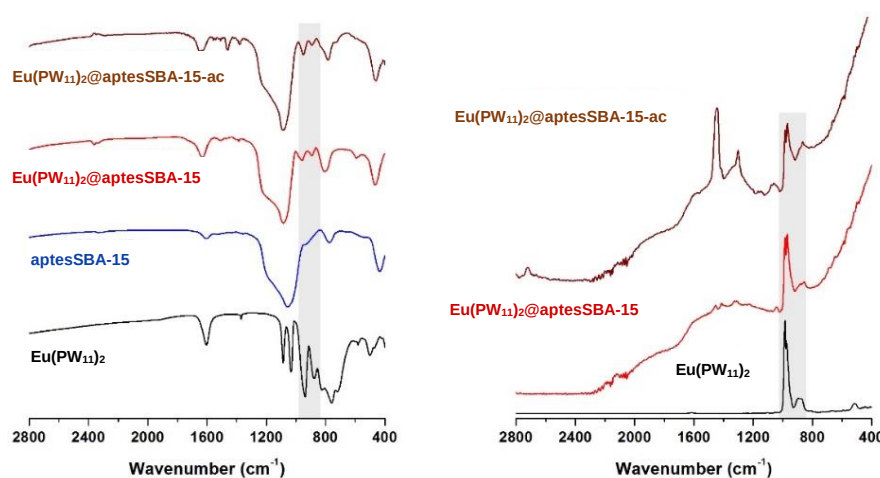


Figure 6.1 - FT-IR (left) and FT-Raman (right) spectra of the isolated $\text{Eu}(\text{PW}_{11})_2$, the functionalized support aptesSBA-15 and the corresponding $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ composite before and after catalysis (ac).

The structure of the solid support and the composite material was studied by powder XRD (Figure 6.2). The patterns of SBA-15 and aptesSBA-15 exhibit three well-resolved peaks in the low-angle range, characteristic of SBA-15-type materials. [4] The peaks can be indexed to the (100), (110) and (210) reflections of a hexagonal symmetry lattice. The XRD pattern of $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ shows that, after the incorporation, the peaks are shifted to higher 2θ when compared with those of aptesSBA-15. This shift has been previously reported for POM-incorporated SBA-15 composites. [8, 17, 18] The absence of peaks from the $\text{Eu}(\text{PW}_{11})_2$ (Figure 6.2 – inset) in the pattern of the composite gives a good indication of its successful incorporation suggesting that the $\text{Eu}(\text{PW}_{11})_2$ molecules are located inside the porous channels of the siliceous framework rather than on its surface.

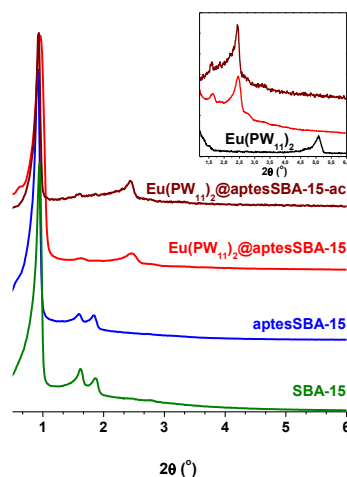


Figure 6.2 - Powder XRD patterns of the starting SBA-15, the functionalized aptesSBA-15 and the $\text{Eu(PW}_{11}\text{)}_2\text{@aptSBA-15}$ composite before and after catalysis (ac).

Figure 6.3 exhibits the ^{13}C CP MAS spectrum of the $\text{Eu(PW}_{11}\text{)}_2\text{@aptSBA-15}$ composite, with three main peaks located at 10.45, 22.41 and 43.82 ppm ascribed to C1, C2 and C3 of aptes, $\text{Si-}^1\text{CH}_2\text{-}^2\text{CH}_2\text{-}^3\text{CH}_2\text{-NH}_2$, respectively. [1, 10] The results confirm that the structure of the incorporated aminopropyl groups is preserved in the final composite and also the absence of peaks from pluronic P123 (67-77 ppm) indicates a very efficient surfactant extraction.

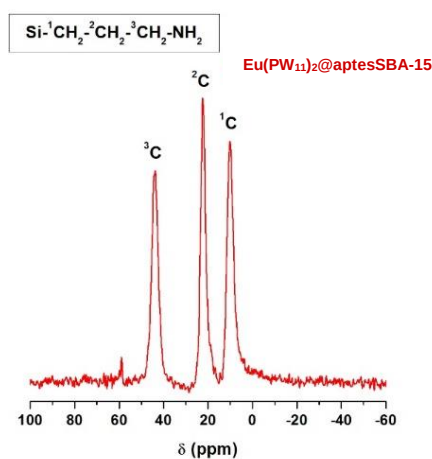


Figure 6.3 - Solid-state ^{13}C CP MAS spectrum of $\text{Eu(PW}_{11}\text{)}_2\text{@aptSBA-15}$.

The composite material was studied by ^{31}P MAS NMR spectroscopy and its spectrum was compared with the one of the isolated $\text{Eu(PW}_{11}\text{)}_2$ (Figure 6.4 - Left). The ^{31}P MAS NMR spectrum of the $\text{Eu(PW}_{11}\text{)}_2$ exhibits a main peak at $\delta = -2.64$ ppm with a

shoulder at $\delta = -0.63$ ppm as a result of the slight asymmetry of the two $[\text{PW}_{11}\text{O}_{39}]^{7-}$ fragments surrounding the Eu^{3+} ion. [29-31] After the incorporation, the ^{31}P MAS NMR spectrum presents a single broad peak centered at $\delta = -0.86$ ppm. The interaction between the $\text{Eu}(\text{PW}_{11})_2$ and the siliceous matrix is probably responsible for this shift of the main peak since the ^{31}P nucleus is extremely sensitive to the local environment. The shift observed is in good agreement with previous reports dealing with phosphometalate anions immobilized on amine-functionalized SBA-15 supports. [7, 10, 16] For all of the above, the ^{31}P MAS NMR data strongly points out to the preservation of the $\text{Eu}(\text{PW}_{11})_2$ structure after the incorporation on aptesSBA-15. The different orientations of the $\text{Eu}(\text{PW}_{11})_2$ molecules within aptesSBA-15 are responsible for the broadness of the ^{31}P signal due to the slightly different environments around phosphorus atoms. [28]

The isotropic chemical shifts were obtained by evaluating the intensities of the spinning sidebands in the MAS NMR spectra at slow to moderate sample spinning (5, 6 and 10 kHz). The intensities of the spinning sidebands are a function of the chemical shift tensor (CST), and although the knowledge of the principal values of the CST alone is useful for structural analysis, this subject falls outside the scope of the present work. The analysis of the spinning sideband envelopes at different frequencies allowed an unambiguous determination of the isotropic chemical shifts (Figure 6.4 - Right).

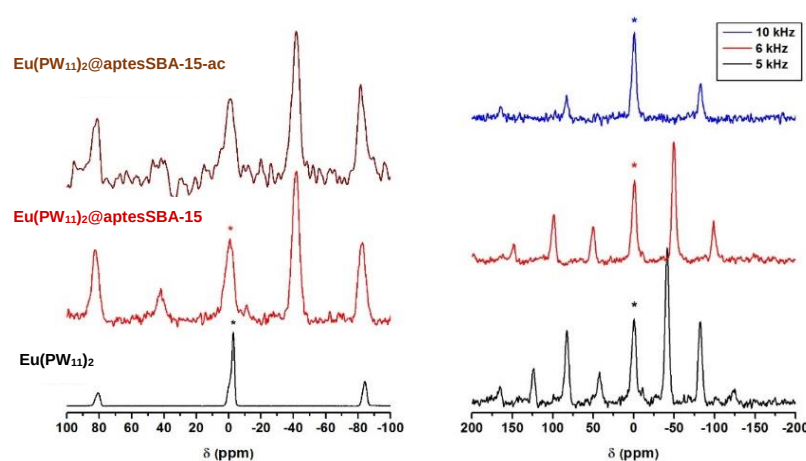


Figure 6.4 – Left - Solid-state ^{31}P MAS NMR spectra of the isolated $\text{Eu}(\text{PW}_{11})_2$ and the $\text{Eu}(\text{PW}_{11})_2@aptes\text{SBA-15}$ composite before and after catalysis (ac). Right - ^{31}P MAS NMR spectra of $\text{Eu}(\text{PW}_{11})_2@aptes\text{SBA-15}$ at different spinning frequencies 5, 6 and 10 kHz. The isotropic chemical shifts are indicated with an asterisk (*).

The structure of the aptesSBA-15 support and of the $\text{Eu}(\text{PW}_{11})_2@aptes\text{SBA-15}$ composite was also studied by ^{29}Si MAS NMR spectroscopy (Figure 6.5). The ^{29}Si MAS spectrum of the support exhibits an intense broad peak at $\delta = -110.54$ ppm with a

shoulder at $\delta = -101.32$ ppm and a smaller resonance peak at $\delta = -89.03$ ppm corresponding to the Q^4 , Q^3 and Q^2 species, respectively, where $Q^n = \text{Si}(\text{OSi})_{4-n}(\text{OH})_n$, $n = 2-4$. [2, 10, 12] As expected, the use of cross-polarization (CP) via ^1H allowed to confirm the presence of aminopropyl groups in the silica structure by greatly enhancing the intensity of the T peaks. [1, 10] In fact, the ^{29}Si CP MAS spectrum of aptesSBA-15, besides the previously discussed Q^n peaks, displays two extra resonance peaks at $\delta = -68.29$ ppm and $\delta = -60.31$ ppm assigned to T^3 and T^2 species, respectively, where $T^n = \text{CSi}(\text{OSi})_{3-m}(\text{OH})_m$, $m = 1-3$. [13, 32] These peaks indicate the formation of new siloxane bonds (Si-O-Si) between the Si atoms of aptes and Si atoms of the SBA-15 surface. [32] The relative intensity of T^3 is slightly higher than T^2 which indicates that the reaction of surface silanols occurs predominantly with three alkoxysilyl groups of aptes. The ^{29}Si NMR spectra (MAS and CP MAS) of $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ exhibit similar profiles to the ones of aptesSBA-15 which suggests that the main structure of the siliceous matrix is preserved after the incorporation of $\text{Eu}(\text{PW}_{11})_2$ moieties.

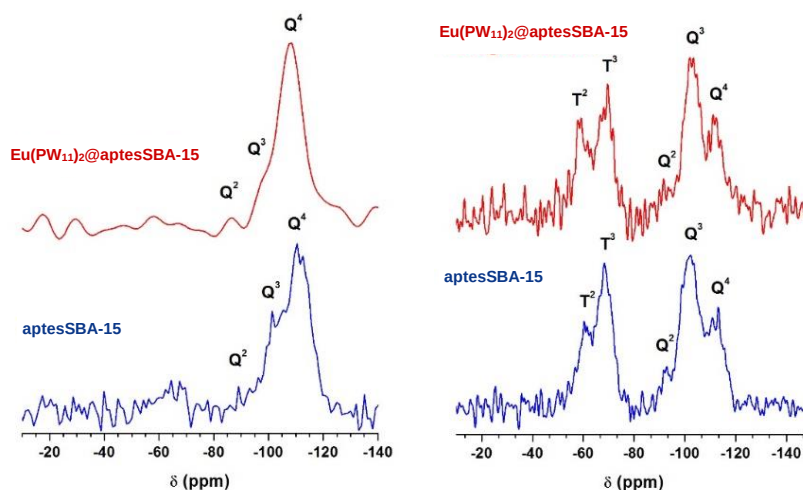


Figure 6.5 - ^{29}Si MAS (left) and CP MAS (right) NMR spectra of the functionalized SBA-15 and $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ composite.

The morphology and chemical composition of $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ were evaluated by SEM/EDS techniques (Figure 6.6). The SEM images show that the composite exhibits the typical morphology of mesoporous SBA-15 consisting in hexagonal particles organized in elongated structures with diameters of approximately 500 nm. [4, 7, 33] SEM studies clearly show that the morphology of the silica support is preserved after the $\text{Eu}(\text{PW}_{11})_2$ incorporation. The EDS spectrum confirms the presence of the POM in the composite material by showing its main elements (Eu, P and W).

Moreover, the EDS mapping confirms the homogeneity of the prepared sample by revealing a uniform distribution of these elements throughout the siliceous matrix.

The textural properties of SBA-15 materials were evaluated by N₂ adsorption experiments. Type IV isotherms with H1 hysteresis loops were obtained (Figure 6.7) which is typical of these mesoporous materials. [4] Table 6.1 shows the textural parameters obtained from combined data of N₂ adsorption experiments and powder X-ray diffractograms. A simultaneous decrease in the surface area (S_{BET}), pore volume (V_p) and pore diameter (D_p) is observed when going from the pristine SBA-15 material to the final Eu(PW₁₁)₂@aptesSBA-15 composite which confirms that the aptes groups were successfully anchored onto the surface wall of SBA-15 with subsequent immobilization of the Eu(PW₁₁)₂ moieties. [15, 18] On the other hand, the wall thickness (d_w) increases which is in good agreement with the inclusion of the guest species on the pore wall. [12, 23]

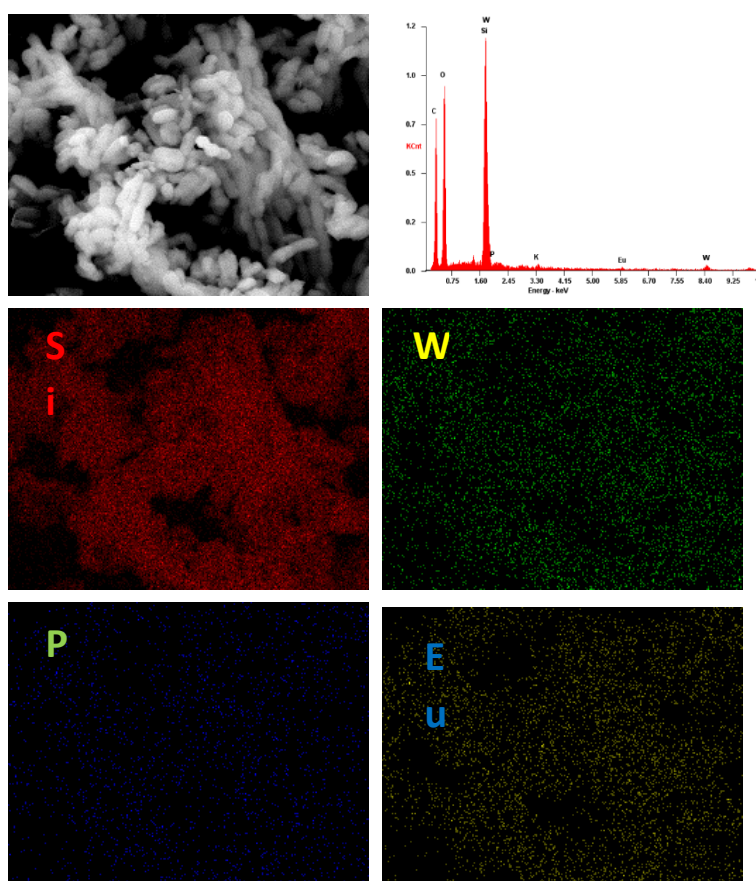


Figure 6.6 - SEM image, EDS and elemental mapping for the Eu(PW₁₁)₂@aptesSBA-15 composite.

Table 6.1 - Textural parameters of SBA-15, aptes-functionalized SBA-15 and Eu(PW₁₁)₂@aptSBA-15 composite.

Materials	d_{100} (nm)	a_0 (nm) ^[a]	D_p (nm)	d_w (nm) ^[b]	S_{BET} (m ² /g)	V_p (cm ³ /g) ^[c]
SBA-15	9.32	10.76	6.77	3.99	752	1.16
aptSBA-15	9.73	11.23	6.37	4.86	363	0.68
Eu(PW₁₁)₂@aptSBA-15	9.19	10.61	5.22	5.39	138	0.23

[a] $a_0 = 2d_{100}/\sqrt{3}$. [b] $d_w = a_0 - D_p$. [c] V_p is the total pore volume determined at the relative pressure of 0.95.

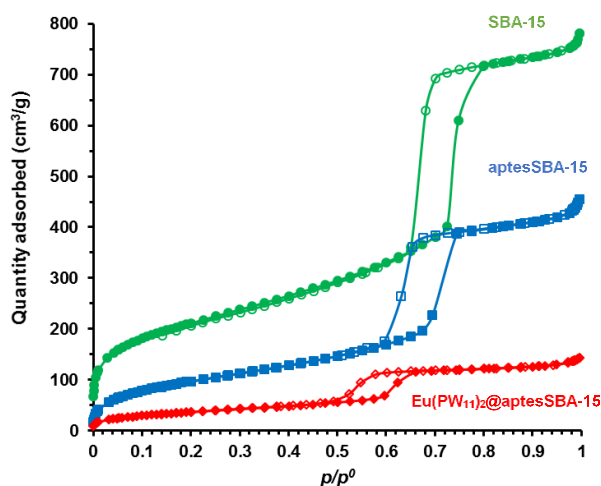


Figure 6.7 - Nitrogen adsorption-desorption isotherms at -196 °C of the mesoporous SBA-15, aptes-functionalized SBA-15 and the Eu(PW₁₁)₂@aptSBA-15 composite. Filled and unfilled symbols represent the adsorption and desorption processes, respectively.

6.2.2. Oxidative desulfurization processes

The Eu(PW₁₁)₂@aptSBA-15 sample was used as heterogeneous catalyst in the oxidative desulfurization (ODS) of model diesel B (see section 1.7), but with a total sulfur concentration of approximately 2350 ppm. The desulfurization studies were performed using (i) solvent-free and (ii) biphasic systems.

The biphasic ECODS system is formed by a mixture of equal volumes of model diesel and an immiscible polar organic solvent (acetonitrile). In this case, the desulfurization system conciliates a liquid-liquid extraction and an oxidative catalytic process. On the other hand, the solvent-free desulfurization system consists in an

oxidative catalytic process, without the need of polar organic solvents, only the model diesel, the oxidant H_2O_2 and the catalyst are present. After complete oxidation of all sulfur compounds under these sustainable conditions, the oxidized products were removed from the diesel by liquid-liquid extraction, using water or acetonitrile for comparative extraction performance.

6.2.2.1 Biphasic extractive and catalytic oxidative desulfurization system (ECODS) system

In figure 6.8 is possible to compare the desulfurization of the multicomponent model diesel catalyzed by the heterogeneous $\text{Eu}(\text{PW}_{11}\text{O}_{39})_2@\text{aptesSBA-15}$ and the homogeneous $[\text{TBA}]\text{Eu}(\text{PW}_{11})_2$. The biphasic ODS process of the model diesel occurs in two distinct steps. First, the sulfur compounds from the multicomponent model diesel are extracted to the organic solvent by simply stirring the biphasic system for 10 min at 70 °C. The second step corresponds to the catalytic stage and is initiated by the addition of the oxidant (H_2O_2) after the initial equilibrium is reached. In this stage, the sulfur compounds are oxidized to the corresponding sulfoxides and/or sulfones which are much more soluble in the extraction phase than in the model diesel phase. The desulfurization profiles obtained for the ODS systems using the $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ and $[\text{TBA}]\text{Eu}(\text{PW}_{11})_2$ as catalysts are very similar. After only 2 h of reaction, 92 and 89% of desulfurization were achieved using the heterogeneous $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ and the homogeneous $[\text{TBA}]\text{Eu}(\text{PW}_{11})_2$ systems, respectively. The individual desulfurization percentages for each sulfur compound using the composite material after the initial extraction stage (10 min), 30 min and 2 h of reaction are presented in Figure 6.9. The overall desulfurization of the studied sulfur components follows the order as previously reported for POM-catalyzed ODS systems with H_2O_2 and in the previous Chapters 3-5. [31, 34-37] The low molecular diameter of 1-BT is responsible for the 58 % of desulfurization in the initial extraction. However, the lower electron density on the sulfur atom when compared with the other studied compounds and consequent lower reactivity [36, 37] results in a desulfurization percentage of only 82 % after 2 h of reaction (24 % during the catalytic stage). DBT and its methyl-derivatives (4-MDBT and 4,6-DMDBT) exhibit similar electron densities on the sulfur atom. [38] The distinct desulfurization performance between these substrates is justified by the higher solubility of DBT as well as the steric hindrance promoted by the methyl groups. [28, 31, 35, 39]

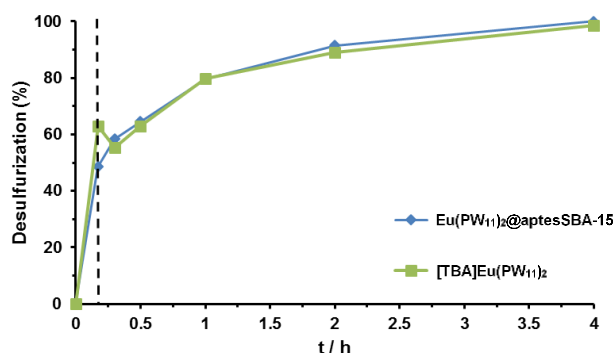


Figure 6.8 - Desulfurization of the multicomponent model diesel in a biphasic system (diesel/MeCN 1:1) showing the initial extraction stage (before the dashed line) and the catalytic stage (after the dashed line) in the presence of the homogeneous and heterogeneous catalysts (containing 3 μmol of $\text{Eu}(\text{PW}_{11})_2$) at 70 °C and using $\text{H}_2\text{O}_2/\text{S} = 12$.

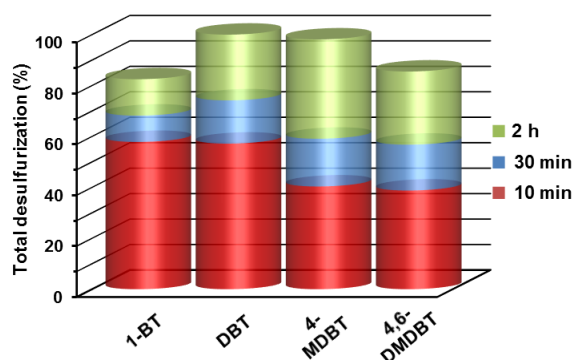


Figure 6.9 - Percentage of each sulfur component removed from the model diesel in the presence of the heterogeneous $\text{Eu}(\text{PW}_{11})_2$ @aptesSBA-15 catalyst (containing 3 μmol of $\text{Eu}(\text{PW}_{11})_2$).

The proposed mechanism for the studied ODS process follows the previously reported mechanism for POM-catalyzed desulfurization using H_2O_2 as the oxidant. [28, 31, 35, 37, 40-42] The mechanism starts with the formation of active species by the interaction of the oxidant (H_2O_2) with the W^{VI} atoms of the $[\text{TBA}]\text{Eu}(\text{PW}_{11})_2$. The resulting hydroperoxy- or peroxy-POM species are able to oxidize the sulfur compounds, extracted from the model diesel, into the corresponding sulfoxides through a nucleophilic attack. By doing so, the starting W^{VI} -POM species are regenerated and able to restart the catalytic cycle. The subsequent oxidation of the sulfoxides leads to the formation of sulfones. The oxidation promotes the continuous mass transport of sulfur compounds from the model diesel into the organic phase (MeCN) in order to restore the equilibrium of the extraction process.

Different control experiments have been performed, namely with the aptesSBA-15 support as the catalyst, single extraction (without any oxidant) and a blank experiment without any catalyst (Figure 6.10). The results show that the desulfurization stops after the initial extraction period when no oxidant is added (single extraction) or no catalyst is used (blank experiment). The obtained desulfurization profile using aptesSBA-15 reveals that the support can give a small contribution to the overall desulfurization performance of the composite material with a desulfurization of 16 % during the catalytic stage.

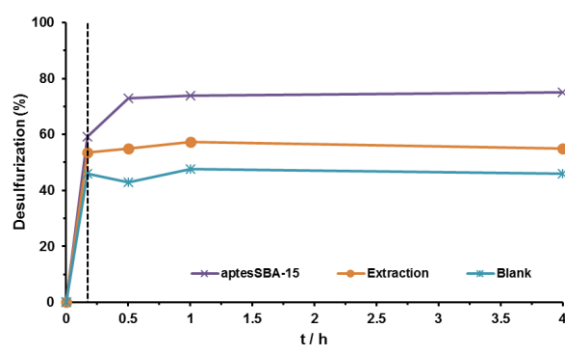


Figure 6.10 Kinetic profiles for the desulfurization of model diesel using the aptesSBA-15 support, blank experiment (without any catalyst), using $\text{H}_2\text{O}_2/\text{S} = 12$ and single extraction (without oxidant), at 70°C .

The recycling ability of the heterogeneous catalyst in the studied desulfurization process was evaluated for ten consecutive cycles. At the end of each cycle, the catalyst was recovered, washed thoroughly with ethanol, dried and reused in a new ECODS cycle under the same experimental conditions. The desulfurization of the model diesel using the $\text{Eu}(\text{PW}_{11})_2@\text{apt}\text{esSBA-15}$ catalyst for ten consecutive ECODS cycles is depicted in Figure 6.11a. Comparing the desulfurization profile of the heterogeneous catalyst for the first three ECODS cycles, some differences are detected from the first to the consecutive cycles (Figure 6.11b). In particular, an increase of sulfur removal is observed after the first cycle. The complete desulfurization of the multicomponent model diesel is achieved after just 2 h instead of the 4 h necessary during the first ECODS cycle. This increase observed after the first ECODS cycle should be related with the presence of previously formed catalytic active species. [28, 35, 43]

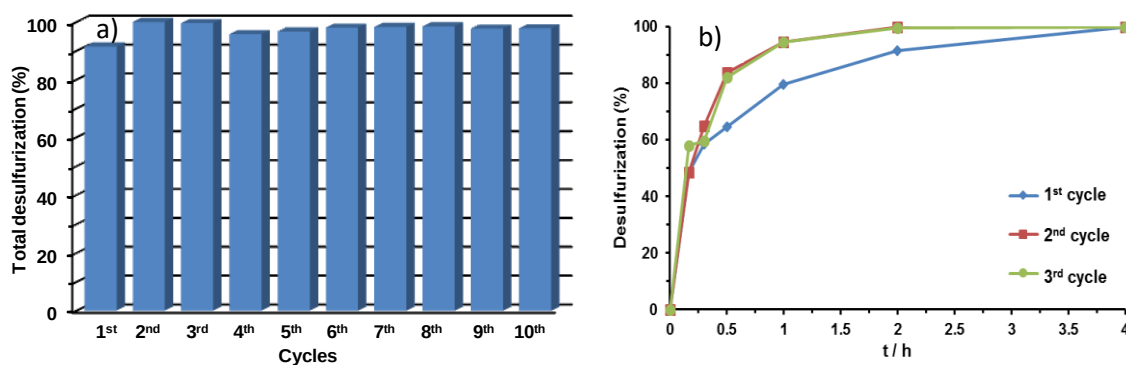


Figure 6.11 a) Results obtained for ten consecutive ECODS cycles after 2 h, using a multicomponent model diesel in the biphasic system catalyzed by $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ composite (containing $3 \mu\text{mol}$ of $\text{Eu}(\text{PW}_{11})_2$). b) Kinetic profiles for the desulfurization of the model diesel for the first three ECODS cycles, using $\text{H}_2\text{O}_2/\text{S} = 12$ at 70°C .

6.2.2.2. Solvent-free catalytic oxidative desulfurization (CODS) system

The oxidative catalytic performance of the homogeneous and heterogeneous catalysts using the solvent-free CODS system (without the presence of MeCN extraction solvent during oxidative process) is depicted in Figure 6.12.

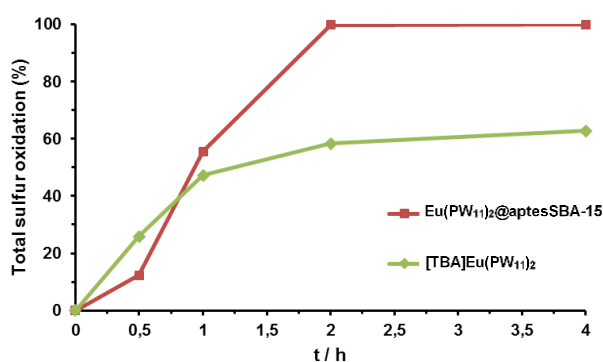


Figure 6.12 - Total sulfur oxidation of the multicomponent model diesel in the solvent-free system in the presence of the $[\text{TBA}]\text{Eu}(\text{PW}_{11})_2$ and $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ catalysts (containing $3 \mu\text{mol}$ of $\text{Eu}(\text{PW}_{11})_2$), using $\text{H}_2\text{O}_2/\text{S} = 12$ at 70°C .

The oxidation of the sulfur compounds present in the model diesel using the $[\text{TBA}]\text{Eu}(\text{PW}_{11})_2$ catalyst has only reached 63% after 4 h of reaction whereas the complete oxidation was achieved after 2 h of reaction using $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ as a heterogeneous catalyst. The poor performance of the $[\text{TBA}]\text{Eu}(\text{PW}_{11})_2$ catalyst is most likely related with its low solubility in the model diesel. On the other hand, the SBA-15 support material in the heterogeneous catalyst may have some positive contribution

in the catalytic efficiency of $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ catalyst. In fact, the adsorptive desulfurization capacity of SBA-15 materials has been well reported in the literature [44, 45] and a combination of oxidation with a possible adsorption of sulfur-compounds in the same material could lead to a considerable oxidative desulfurization efficiency.

The individual oxidation percentage for each sulfur component using the heterogeneous catalyst has also been investigated (Figure 6.13). Similarly to the previously discussed for the biphasic system, the oxidation reactivities also follow the characteristic order for POM-catalyzed ODS systems with H_2O_2 : $\text{DBT} > 4\text{-MDBT} > 4,6\text{-DMDBT} > 1\text{-BT}$. [31, 34-37] At the end of the oxidative reaction, an extraction with acetonitrile (1 mL) or conciliating centrifugation and extraction with water (three consecutive cycles with 1 mL) was performed to remove the oxidized sulfur compounds from the model diesel (1 mL). Figure A.6 (see Appendix) presents the chromatograms corresponding to the model diesel after 4 h of sulfur oxidation (Figure A.6-A), the oxidized model diesel after centrifugation (10 min at room temperature, Figure A.6-B), after liquid-liquid extraction with 1 mL of acetonitrile (Figure A.6-C), and after three consecutive liquid extraction cycles with water (Figure A.6-D). Figure A.6-A exhibits the sulfone and the sulfoxide from the 1-BT oxidation, as well as the sulfones produced from DBT, 4-MDBT and 4,6-DMDBT oxidation. After 10 min of centrifugation at room temperature, it is possible to observe that some of the previous products precipitate and their concentration in model diesel considerably decreases (Figure A.6-B). After liquid extraction with acetonitrile or water, it is possible to observe that the model diesel is practically completely desulfurized (Figure A.6-C and A.6-D, respectively).

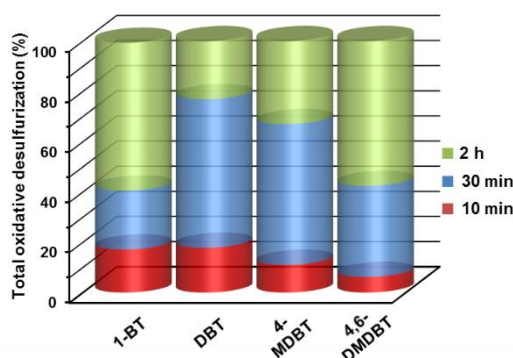


Figure 6.13 - Percentage of each sulfur component removed from the model diesel in the presence of the heterogeneous $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ catalys (containing $3\ \mu\text{mol}$ of $\text{Eu}(\text{PW}_{11})_2$), using $\text{H}_2\text{O}_2/\text{S} = 12$ at $70\ ^\circ\text{C}$, in the solvent-free system.

Comparing the kinetic profiles for the solvent-free and biphasic systems (Figure 6.14) catalyzed by $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$, lower desulfurization performance is observed for the solvent-free system during the first hour of reaction. This induction period should be related with the slower formation of the hydroperoxy- or peroxo-POM active species in the solvent-free conditions, caused by the fact that the aqueous oxidant and the sulfur compounds were present in immiscible phases. In fact, the diffusion of the oxidant in an apolar phase (model diesel) is expected to be more difficult than when the oxidant is dispersed in a polar organic phase as occurs in the biphasic system using the extraction solvent (MeCN). Nevertheless, a higher desulfurization of the model diesel is attained using the solvent-free system reaching the complete desulfurization after 2 h of reaction when compared with the 4 h necessary in the case of the biphasic system.

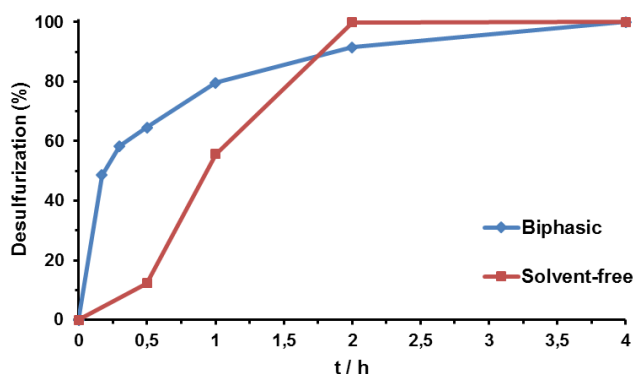


Figure 6.14 - Kinetic profiles for the desulfurization of a model diesel using solvent-free or biphasic (diesel/MeCN) systems with $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ as catalyst (containing $3 \mu\text{mol}$ of $\text{Eu}(\text{PW}_{11})_2$), using $\text{H}_2\text{O}_2/\text{S} = 12$ at 70°C .

The recycling ability of the heterogeneous catalyst has also been evaluated in the solvent-free conditions. At the end of each CODS cycle, the complete oxidized model diesel was separated from the solid catalyst by centrifugation. In the next step, the oxidized sulfur compounds were removed from the model diesel by means of a liquid-liquid extraction with water. The heterogeneous catalyst was washed with ethanol and dried at room temperature. After this, the catalyst was reused in a new CODS cycle under the same experimental conditions. The total oxidative desulfurization values obtained for ten consecutive CODS cycles after 2 h are summarized in Figure 6.15, which also displays the results obtained after 30 min, 1 h and 2 h for the first three consecutive CODS cycles. These results reveal that the slow desulfurization period only occurs during the first cycle. In the following cycles, a much faster desulfurization rate is observed with desulfurization percentages higher than 50% after 30 min of reaction when

compared with only 12% achieved in the first cycle. The difference observed is most likely related with the fact that the hydroperoxy- or peroxy-POM active species which have already been formed during the first cycle are present at the beginning of the following cycles hence leading to a faster initial desulfurization rate. The results obtained for these following cycles reveal similar catalytic performance between them as shown by the total desulfurization percentages obtained along the cycles (30 min: 56 and 50%, 1 h: 82% and 79% for the second and third cycle, respectively).

In summary, the solvent-free conditions allow to achieve total desulfurization of the model diesel within the same period of time as the biphasic or even faster as in the case of the first cycle, without needing the presence of a polar organic extraction solvent. Furthermore, the solvent-free system allows the application of a more sustainable choice for the extraction of oxidized sulfur products without compromising the desulfurization efficiency. This constitutes a very important step towards the development of eco-sustainable yet efficient desulfurization systems.

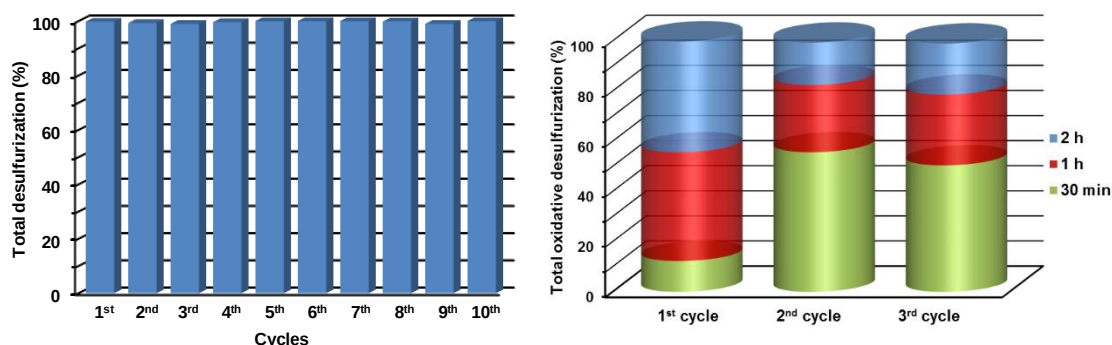


Figure 6.15 – Left - Results obtained for ten consecutive ODS cycles after 2 h catalyzed by $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ composite (containing 3 μmol $\text{Eu}(\text{PW}_{11})_2$) under solvent-free system. Right - Total oxidative desulfurization of the model diesel in the solvent-free system for the first three consecutive ODS cycles at 70 °C, using $\text{H}_2\text{O}_2/\text{S} = 12$.

Recently, has been reported the incorporation of the $[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$ anion in different porous MOF supports. [31] The influence of the support in the catalytic activity of the materials was evaluated for the desulfurization of a multicomponent model diesel. The best desulfurization performance was achieved for the desulfurization system using $\text{Eu}(\text{PW}_{11})_2@ \text{NH}_2\text{-MIL-53(Al)}$ as the catalyst (complete desulfurization after 2 h of reaction). Nevertheless, a small decrease of the desulfurization performance has been observed during the recycling studies due to some leaching of the $\text{Eu}(\text{PW}_{11})_2$ from the material. The oxidative desulfurization system herein reported exhibits similar desulfurization performance, but the $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ composite displays a better overall performance in the desulfurization of the model diesel. In fact, the

composite has shown an exceptional robustness and high recycling ability without loss of activity throughout the desulfurization cycles.

6.2.3. Catalyst material stability

The structural stability of the $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ catalyst was evaluated through the extensive characterization of the solid recovered after the oxidative desulfurization process ($\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15-ac}$). Elemental analyses reveal that the composite retains its chemical composition after catalytic use and that no leaching of the $\text{Eu}(\text{PW}_{11})_2$ occurs by presenting identical values to the ones before catalysis for Si/W (molar) and aptes/ $\text{Eu}(\text{PW}_{11})_2$ ratios (0.50 and 19, respectively).

The vibrational spectroscopy data of $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15-ac}$ (Figure 6.1) show that the characteristic bands of the material remain unaltered. In particular, no changes are observed in the bands assigned to the $\text{Eu}(\text{PW}_{11})_2$ stretching modes ($1000\text{--}850\text{ cm}^{-1}$) both in FT-IR and FT-Raman, suggesting that the $\text{Eu}(\text{PW}_{11})_2$ structure is preserved after the oxidative desulfurization process. The additional bands observed in both $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15-ac}$ spectra ($1500\text{--}1200\text{ cm}^{-1}$) should be related with the presence of diesel-related compounds adsorbed to the catalyst.

The powder XRD patterns before and after catalytic use (Figure 6.2) display identical profiles, both in the position and relative intensity of the diffraction peaks. Furthermore, the ^{31}P MAS NMR spectra of the composite before and after catalytic exhibit a single broad peak at identical chemical shifts, indicating the preservation of the POM structure after the oxidative desulfurization process.

SEM/EDS techniques were also used to study the morphology and chemical composition of $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15-ac}$. The SEM image (Figure 6.16 left) reveal a similar morphology to the as-prepared sample composed by elongated structures with no evidence of degradation of the mesoporous silica support. EDS analysis of $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15-ac}$ (Figure 6.16 right) also show an identical chemical composition to the sample before catalysis. The characterization data points out to the high structural stability of the heterogeneous catalyst after the ODS process.

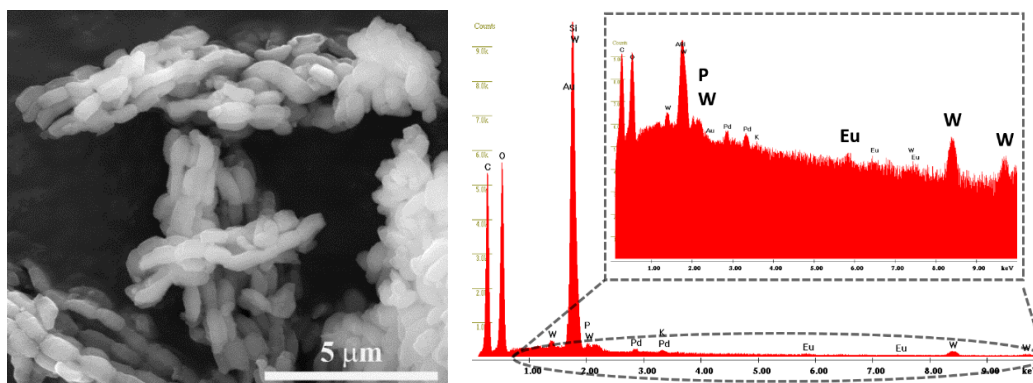


Figure 6.16 – Sem image and EDS spectra of the $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ after catalytic use.

6.3 Conclusion

The present work proposes a desulfurization process formed by oxidative catalytic step and an oxidized-sulfur removal stage performed by centrifugation and model diesel/water extraction. The novel composite $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$, was evaluated as heterogeneous catalyst in the oxidative desulfurization of a multicomponent model diesel. The desulfurization performance of the heterogeneous catalyst was compared using a solvent-free and biphasic systems. Regarding the biphasic system, the results show that the composite maintains the catalytic activity of the isolated $[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]^{11-}$ while providing a robust support for the active species and enabling catalyst recovery. Moreover, the heterogeneous catalyst exhibited a high recycling ability without any loss of catalytic activity for ten consecutive ODS cycles.

On the other hand, the solvent-free ODS studies have revealed very promising features. Indeed, the desulfurization performance obtained in the solvent-free system matches the one under biphasic conditions, with the important advantage of avoiding the use of organic solvents to achieve a sulfur-free model diesel. The $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ does not demonstrated to have a higher catalytic efficiency than the the previous $\text{PW}_{11}@ \text{aptesSBA-15}$ (chapter 4) and $\text{PW}_{11}\text{Zn}@ \text{aptesSBA-15}$ (chapter 5) catalysts; however, its structural stability was confirmed through characterization after the oxidative desulfurization process.

6.4. Experimental section

6.4.1. Materials and Methods

All the reagents used in the POM synthesis and silica composite, namely sodium tungstate dihydrate (Aldrich), sodium hydrogen phosphate dihydrate (Aldrich), europium chloride hexahydrate (Aldrich), (3-aminopropyl)triethoxysilane (aptès, Aldrich), ethanol (Aga), tetraethoxysilane (TEOS, Aldrich) and ammonia 25% (Merck) were used as received. The reagents for ODS tests, including 1-benzothiophene (1-BT, Fluka), dibenzothiophene (DBT, Aldrich), 4-methyldibenzothiophene (4-MDBT, Aldrich), 4,6-dimethyldibenzothiophene (4,6-DMDBT, Alfa Aesar), *n*-octane (Aldrich), acetonitrile (MeCN, Fisher Chemical) and hydrogen peroxide 30% (Aldrich) were purchased from chemical suppliers and used without further purification.

Elemental analyses for Si, W and Eu were performed by ICP-OES on a Perkin-Elmer Optima 4300 DV instrument, and C, H and N analyses in a Leco CHNS-932 instrument; both techniques were performed at the University of Santiago de Compostela. FT-IR spectra were obtained on a Jasco 460 Plus spectrometer using KBr pellets. The FT-Raman spectra were recorded by the research group of Isabel Gonçalves in CICECO Associate Laboratory, University of Aveiro, using a RFS-100 Bruker FT-spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm and the laser power set to 350 mW. Powder X-ray diffraction (XRD) patterns were obtained at room temperature on a X'Pert MPD Philips diffractometer, equipped with a X'Celerator detector and a flat-plate sample holder in a Bragg-Brentano parafocusing optics configuration (45 kV, 40 mA). Intensity data were collected by the step-counting method (step 0.013°), in continuous mode, in the ca. $0.3 \leq 2\theta \leq 10^\circ$ range (CICECO, Universidade de Aveiro). Solid state ^{13}C MAS, ^{31}P MAS and ^{29}Si MAS NMR spectra were acquired with a 7 T (300 MHz) AVANCE III Bruker spectrometer operating respectively at 75 MHz (^{13}C), 121 MHz (^{31}P) and 60 MHz (^{29}Si), equipped with a BBO probehead. The samples were spun at the magic angle at a frequency of 5, 6 or 10 kHz in 4 mm-diameter rotors at room temperature. The ^{13}C MAS NMR experiments were acquired with proton cross polarization (CP MAS) with a contact time of 1.2 ms, and the recycle delay was 2.0 s. The ^{29}Si MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 4.5 μs at a power of 40 W, and a relaxation delay of 10.0 s. The ^{29}Si CP MAS NMR experiments were acquired with a contact time of 1.2 ms, and the recycle delay was 5.0 s. The ^{31}P MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 5.0 μs at a power of 20 W, and a relaxation delay of 2.0 s. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS)

studies were performed at “Centro de Materiais da Universidade do Porto” (CEMUP, Porto, Portugal) using a high-resolution (Schottky) scanning electron microscope with X-ray microanalysis and electron backscattered diffraction analysis Quanta 400 FEG ESEM /EDAX Genesis X4M. The samples were studied as powders and were coated with an Au/Pd thin film by sputtering using the SPI Module Sputter Coater equipment. The textural characterization was performed by Sandra Gago from Departamento de Química/ Faculdade de Ciências e Tecnologia-Universidade NOVA de Lisboa, and obtained from physical adsorption of nitrogen at -196 °C, using a Micrometrics ASAP 2010 instrument. Samples were degassed at 120 °C for at least 5 h prior to the measurements. The BET surface area (S_{BET}) was calculated by using the relative pressure data in the 0.05-0.3 range. The total pore volume (V_p) was evaluated on the basis of the amount adsorbed at a relative pressure of about 0.95. The pore size distributions were obtained from the adsorption branches of the isotherms, applying the BJH method with the modified Kelvin equation and a correction for the statistical film thickness of the pore walls. The statistical film thickness was calculated using the Harkins-Jura equation in the p/p_0 range of 0.3-1.0. GC-FID was carried out in a Varian CP-3380 chromatograph to monitor the ODS experiments. Hydrogen was used as the carrier gas (55 cm s^{-1}) and fused silica Supelco capillary columns SPB-5 (30 m x 0.25 mm i.d.; 25 μm film thickness) were used.

6.4.2. Synthesis of catalysts

6.4.2.1. Europium polyoxotungstate

The potassium and tetrabutylammonium ($\text{C}_{16}\text{H}_{36}\text{N}$, TBA) salts of the europium polyoxotungstate: $\text{K}_{11}[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2] \cdot \text{H}_2\text{O}$ ($\text{Eu}(\text{PW}_{11})_2$), $\text{TBA}_7\text{H}_4[\text{Eu}(\text{PW}_{11}\text{O}_{39})_2]$ ($[\text{TBA}]\text{Eu}(\text{PW}_{11})_2$) were prepared according to previously reported methods by our group. [26, 29] Briefly, an aqueous solution of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was added dropwise to an aqueous solution of $\text{K}_7[\text{PW}_{11}\text{O}_{39}] \cdot 10\text{H}_2\text{O}$ in a 1:2 stoichiometric ratio. The mixture was stirred for 1 h at 90 °C and an excess of KCl was added. After cooling to room temperature, the white precipitate was filtered and dried in a desiccator over silica gel. The corresponding TBA salt used in the homogeneous reaction was prepared by addition of solid tetrabutylammonium bromide to an aqueous solution of the potassium salt. The identity of both compounds was confirmed by vibrational spectroscopy (FT-IR and FT-Raman), ^{31}P NMR spectroscopy, elemental and thermal analyses.

6.4.2.2. $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ composite

The preparation of the composite was performed through the immobilization of the POM in previously functionalized SBA-15 support. The parent SBA-15 was synthesized according to a previously reported procedure [4] using P123 and TEOS under acidic conditions. The surface of the support was functionalized with aptes via a post-grafting methodology.[46] Briefly, activated SBA-15 (1 g) was refluxed with aptes (5 mmol) in anhydrous toluene (25 mL) for 24 h under argon. The functionalized support (hereafter referred as aptesSBA-15) was filtered, washed with toluene and dried in a desiccator under silica gel. Elemental analyses reveal that aptesSBA-15 contained 1.2 mmol of NH_2 per g of material. The incorporation of the $\text{Eu}(\text{PW}_{11})_2$ was achieved through an impregnation procedure previously reported by our group for polyoxometalate-supported aptesSBA-15 composites.[15, 16] An aqueous solution of the $\text{Eu}(\text{PW}_{11})_2$ (0.17 mmol in 8 mL) was added to aptesSBA-15 (0.5 g) and the mixture was stirred for 24 h at room temperature. Afterwards, the solid was isolated by filtration, washed with water and dried in a desiccator over silica gel.

$\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$: Anal. Found (%): W, 25.7; Eu, 1.4; C, 7.1; H, 1.7; N, 1.8; loading of POM: 0.063 mmol per 1 g, Si/W (molar) = 0.49 and ratio of aptes/POM = 21. Selected FT-IR (cm^{-1}): ν = 3452, 2929, 1633, 1506, 1385, 1084, 958, 893, 806, 667, 592, 467; selected FT-Raman (cm^{-1}): 2957, 2899, 1042, 986, 970, 878, 855.

6.4.3. Oxidative desulfurization processes

The oxidative desulfurization studies were performed using a model diesel B containing the most representative sulfur-compounds in diesel, namely 1-benzothiophene (1-BT), dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), in *n*-octane (with a total sulfur concentration of 2350 ppm). The oxidative desulfurization experiments were carried out under air (atmospheric pressure) in a closed borosilicate 5 mL reaction vessel, equipped with a magnetic stirrer and immersed in a thermostatically controlled liquid paraffin bath at 70 °C. The oxidative desulfurization process in homogeneous conditions was performed using the TBA salt of $\text{Eu}(\text{PW}_{11})_2$ while the heterogeneous oxidative desulfurization studies were performed using the $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ composite. The heterogeneous oxidative desulfurization studies were performed using either a solvent-free or a biphasic system. The catalytic performance of the homogeneous POM and heterogeneous $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ was compared for both systems. In a

typical biphasic experiment, 3 μmol of $\text{Eu}(\text{PW}_{11})_2$ or 47 mg of $\text{Eu}(\text{PW}_{11})_2@\text{aptesSBA-15}$ [containing the equivalent of 3 μmol of POM] were added to 1:1 model diesel/MeCN (1 mL of each) and the resulting mixture was stirred for 10 min. The catalytic step of the process is initiated by the addition of aqueous hydrogen peroxide 30% (90 μL ; $\text{H}_2\text{O}_2/\text{S}$ molar = 12). The solvent-free system experiments were performed using the model diesel (1 mL), the catalyst and the H_2O_2 oxidant ($\text{H}_2\text{O}_2/\text{S}$ molar = 12). A liquid-liquid extraction using an extraction solvent (water or MeCN) was only performed when complete oxidation was achieved to remove the oxidized sulfur compounds from the model diesel. Centrifugation was carried out after oxidation to separate the solid catalyst from model diesel. The sulfur content in the model diesel was periodically quantified by GC analysis using tetradecane as a standard. For the recycling studies, in the case of the biphasic system after each cycle the heterogeneous catalyst was recovered by filtration, washed thoroughly with ethanol, dried in a desiccator over silica gel and reused in a new ODS cycle under the same reactional conditions. Regarding the solvent-free system, the catalyst is easily removed from the model diesel phase conciliating centrifugation and addition of extraction solvent (water or MeCN).

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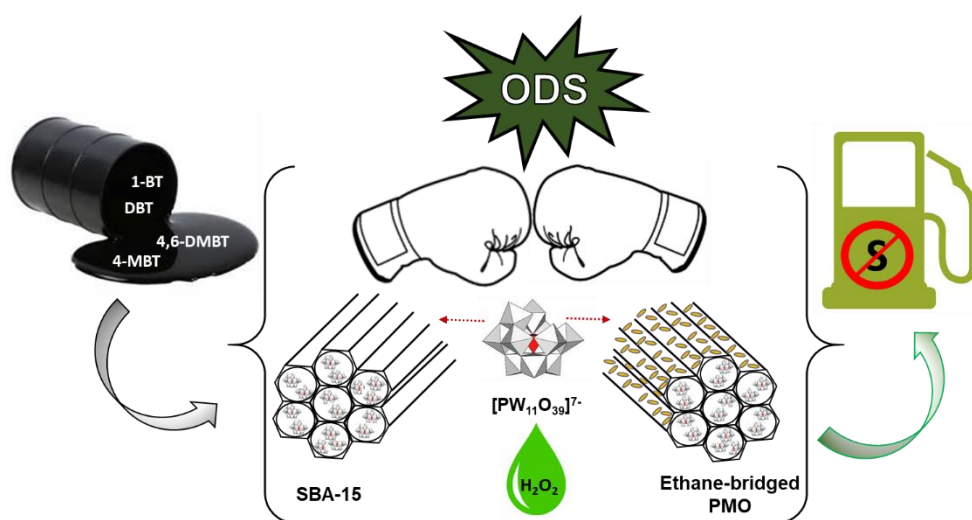
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Chapter 7

Catalytic oxidative desulfurization performance of mesoporous silica versus organosilica composites to treat model and real diesels^{1,2}



¹ Adapted from: Susana O. Ribeiro, Carlos Granadeiro, Marta Corvo, João Pires, José M. Campos-Martin, Baltazar de Castro and Salete S. Balula, *Catalytic oxidative desulfurization performance of mesoporous silica versus organosilica composites to treat model and real diesels*, submitted to *Frontiers in Chemistry*.

² Susana O. Ribeiro contribution to the publication: Catalysts preparation and characterization; investigation of its catalytic performance in the desulfurization of a model diesel and real diesel; manuscript preparation.

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Chapter 7

Catalytic oxidative desulfurization performance of mesoporous silica versus organosilica composites to treat model and real diesel

Abstract

The monolacunary Keggin-type $[PW_{11}O_{39}]^{7-}$ (PW_{11}) heteropolyanion was immobilized onto the porous framework of mesoporous silicas, namely SBA-15 and an ethylene-bridged periodic mesoporous organosilica (PMOE). The supports were previously functionalized with a cationic functional group (*N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium, TMA) for the successful anchoring of the anionic polyoxometalate. The $PW_{11}@TMA-SBA-15$ and $PW_{11}@TMA-PMOE$ composites were evaluated as heterogeneous catalysts in the oxidative desulfurization of a model diesel. The $PW_{11}@TMA-SBA-15$ catalyst has shown a remarkable desulfurization performance by reaching ultra-low sulfur levels ($<10\text{ppm}$) after only 60 min using either a biphasic extractive and catalytic oxidative desulfurization (ECODS) (1:1 MeCN/diesel) or a solvent-free catalytic oxidative desulfurization (CODS) system. Furthermore, the mesoporous silica composite was able to be recycled for 6 consecutive cycles without any apparent loss of activity. The promising results have led to the application of the catalyst in the desulfurization of an untreated real diesel supplied by CEPESA (1335 ppm S) using the biphasic system. The system has proved to be a highly efficient process by reaching desulfurization values higher than 90% for real diesel during 3 consecutive cycles.

7.1 Introduction

Over the last years, ordered mesoporous silicas (OMS) have attracted researchers' attention in catalysis, due to its well-ordered structures, large surface areas, high pore volumes and well-defined pore size (2–50 nm). [1] Moreover, the surface of mesoporous silicas can be easily modified through the introduction of organic functionalities by reaction with organosilanes.

Periodic mesoporous organosilicas (PMOs) are a recent class of ordered organic-inorganic hybrid mesoporous materials. These materials offer the possibility to adjust the surface (hydrophilicity/hydrophobicity) and physical properties (morphology, porosity), as well as offering mechanical stability through the incorporation of different functional organic moieties. [1, 2] Usually, the preparation of PMOs is conducted, in the presence of a structure-directing agent, by hydrolysis and condensation reactions of bridged silsesquioxane precursors with general formula $(R'O)_3-Si-R-Si-(OR')_3$, where R represents the organic bridging group and R' usually a methyl or ethyl group. This synthesis is similar to the process for the preparation of mesoporous silica materials, such as SBA-15. [3, 4] The functional organic moieties in PMO are also built directly into the channel walls, which contribute to the rigidity or flexibility of the walls and to the general structural characteristics of the materials. [3] The unique properties of PMOs make them suitable candidates for catalytic applications; however, the number of applications that exploit their hybrid nature is quite limited and in particular its application in oxidative desulfurization is inexistent. [5]

The high catalytic activity of the monolacunary Keggin phosphotungstate $[PW_{11}O_{39}]^{7-}$ in oxidative reactions [6-10] has driven the preparation of several PW_{11} -based heterogeneous catalysts for desulfurization of fuels (for example the $PW_{11}@aptesSBA-15$ presented in Chapter 4, among others). [11-15]

In this chapter, novel composites have been prepared through the impregnation of the $[PW_{11}O_{39}]^{7-}$ (PW_{11}) heteropolyanion in the porous framework of mesoporous silicas functionalized with *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium (TMA). Three different mesoporous silica supports were selected to prepare novel composites: the ordered mesoporous silica SBA-15, an ethylene-bridged (PMOE) and a benzene-bridge (PMOB) periodic mesoporous organosilicas. This is the first work reporting the application of a POM-based PMO ($PW_{11}@TMA-PMOE$) in the oxidative desulfurization of the multicomponent model diesel. The catalytic performance of $PW_{11}@TMA-SBA-15$

and $\text{PW}_{11}@\text{TMA-PMOE}$ are compared. The low loading of PW_{11} in the TMA-PMOB did not allowed its application in catalytic experiments.

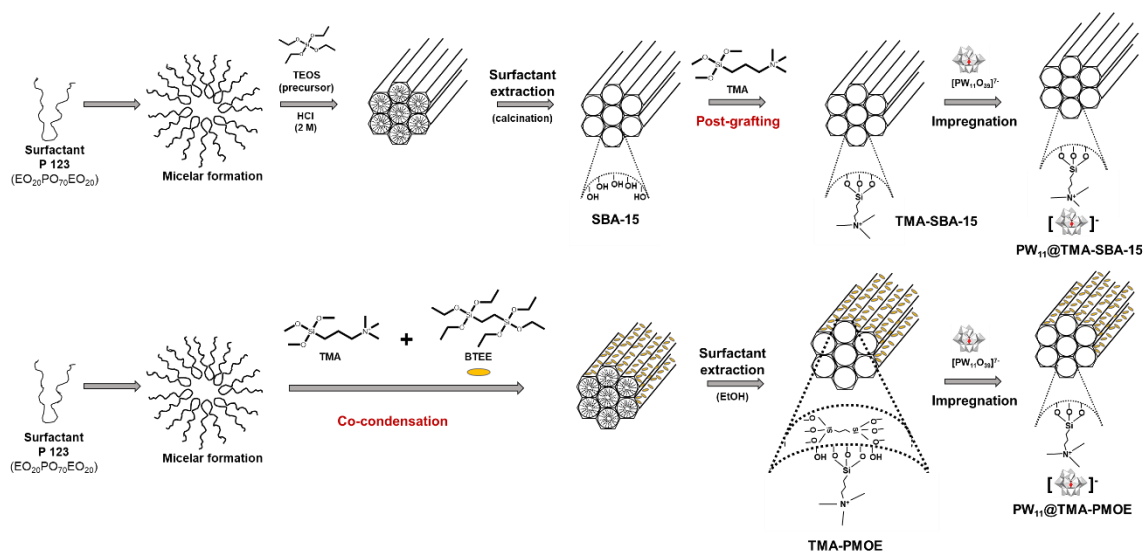
7.2. Results and discussion

7.2.1. Catalysts characterization

The synthesis of TMA-functionalized silica materials is described in scheme 7.1. The synthesis of ethylene-bridge PMO is performed by the co-condensation of the bridged bis-silane (1,2-bis(triethoxysilyl)ethane; BTEE) and the terminal silane (TMA) in the presence of the micelles of surfactant ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$; Pluronic P123) in acid medium. After an ageing period, the surfactant is removed by ethanol extraction. The formation of SBA-15 is also based in the same surfactant using TEOS (tetraethyl orthosilicate) as silica precursor in acid medium. The surfactant is removed by calcination after an ageing period. The functionalization of SBA-15 was performed *via* post-grafting with the same terminal silane (TMA). [3, 16]

The incorporation of the PW_{11} anion in TMA-functionalized silicas was performed via an impregnation method by electrostatic interactions (Scheme 7.1). Several characterization techniques were used to assess the successful preparation of the materials. Some characterization results of the functionalized SBA-15 support have already been presented in Chapter 3 (section 3.2.1), namely the vibrational spectra and XRD patterns; however, for comparison with the correspondent composite they will also be presented in this chapter.

The FT-IR spectrum of $\text{PW}_{11}@\text{TMA-SBA-15}$ presents similar profile to that for TMA-SBA-15. The typical bands assigned to the siliceous support located at 1100-400 cm^{-1} range namely the $\nu_{\text{as}}(\text{Si-O-Si})$, $\nu_{\text{s}}(\text{Si-O-Si})$ and $\delta(\text{O-Si-O})$ vibrational modes, respectively, [17-20] mask the bands that could be assigned to the POM incorporation and no extra bands can be recognized. However, the FT-RAMAN spectra, displayed in Figure 7.2-left, evidence the presence of the POM in the composite, since it exhibits very intense bands in the 1010-860 cm^{-1} range associated with the characteristic PW_{11} vibrations. The spectrum also displays the bands arising from the presence of amine groups, namely $\nu(\text{C-H})$ and $\delta(\text{CH}_2)$ vibrational modes in the 3035-2902 cm^{-1} and 1450-1412 cm^{-1} ranges, respectively. The presence of POM in this composite material was also confirmed by the presence of W in the EDS spectrum (Figure 7.2 B) and elemental analysis with a loading of PW_{11} of 0.099 mmol per g of material. [19, 21]



Scheme 7.1 – Representation of the synthetic pathway for the different PW_{11} -based composites.

The FT-IR spectrum of the TMA-PMOE material (Figure 7.1 B) presents the typical bands of silsesquioxane frameworks namely the intense band in at 1093 cm^{-1} assigned to $\nu_{as}(\text{Si-O-Si})$, as well as the bands located at 912 , 763 and 441 cm^{-1} associated with the $\nu_{as}(\text{Si-OH})$, $\nu_s(\text{Si-O-Si})$ and $\delta(\text{Si-O-Si})$, respectively. [4, 22-24] The band at 2898 cm^{-1} (stretching) and at 1413 cm^{-1} (bending) can be associated to the C-H vibrational modes of bridging-ethylene and the alkyl groups of TMA. [4, 23, 24] The absence of bands located around 1340 and 1380 cm^{-1} suggest that the pluronic P123 surfactant has been successfully removed during the extraction process. [25] The FT-IR spectrum of the $PW_{11}@TMA-PMOE$ composite suggests that the structure of the support, previously described, have been maintained. The presence of PW_{11} in the composite material is not evident in the FT-IR spectrum, due to the presence of intense bands arising from TMA-PMOE. As previously discussed, the lower intensity of the silica-related vibrational modes in FT-Raman allows a better identification of the POM vibrational bands. [12, 26, 27]

The FT-RAMAN spectrum of $PW_{11}@TMA-PMOE$ (Figure 7.2 B) is mainly dominated by the bands from the periodic mesoporous ethanesilica, in particular, the bands in the $3000\text{-}2800\text{ cm}^{-1}$ range ascribed to the $\nu(\text{C-H})$ stretch, at 1412 and 1271 cm^{-1} to $\delta(\text{CH}_2)_{\text{twist}}$ and $\delta(\text{CH}_2)_{\text{wagg}}$ modes, respectively, and the band at 515 cm^{-1} assigned to the vibration of the ethylene unit against the siliceous framework together with $\delta(\text{Si-O-Si})$ vibrations. [4, 28] The presence of PW_{11} is suggested by the band at 980 cm^{-1} which can be attributed to the $\nu_{as}(\text{W-O}_d)$ vibrations. [15] Further suggest the presence of PW_{11} in the composite material was confirmed by EDS (Figure 7.3 D) with

the presence of W in the EDS spectrum, as well as by elemental analysis of W with a loading of 0.057 mmol of PW_{11} per g of material.

In the case of benzene-bridged PMO materials, the FT-IR spectra are also dominated by the bands of the support (Figure 7.1 C). The band located at 1074 cm^{-1} can be assigned to the $\nu_{as}(\text{Si-O-Si})$ mode while the band located at 809 cm^{-1} to the stretching vibration of Si-O, which can indicate siloxane network in PMO framework. The benzene ring vibrations are present at 1488 cm^{-1} pointing out the successfully load of benzene group in the silica framework by covalent bounding. The band at 1155 cm^{-1} can be ascribed to the stretching vibration of Si-C and the strong band at 536 cm^{-1} to the out of plane aromatic $\delta_{\text{Csp}^2\text{-H}}$ bending. [29, 30] The amount of POM in the composite material was determined by elemental analysis of W, with a loading of 0.028 mmol of PW_{11} per g of material; however, this loading was too low to allow its use in catalytic experiments.

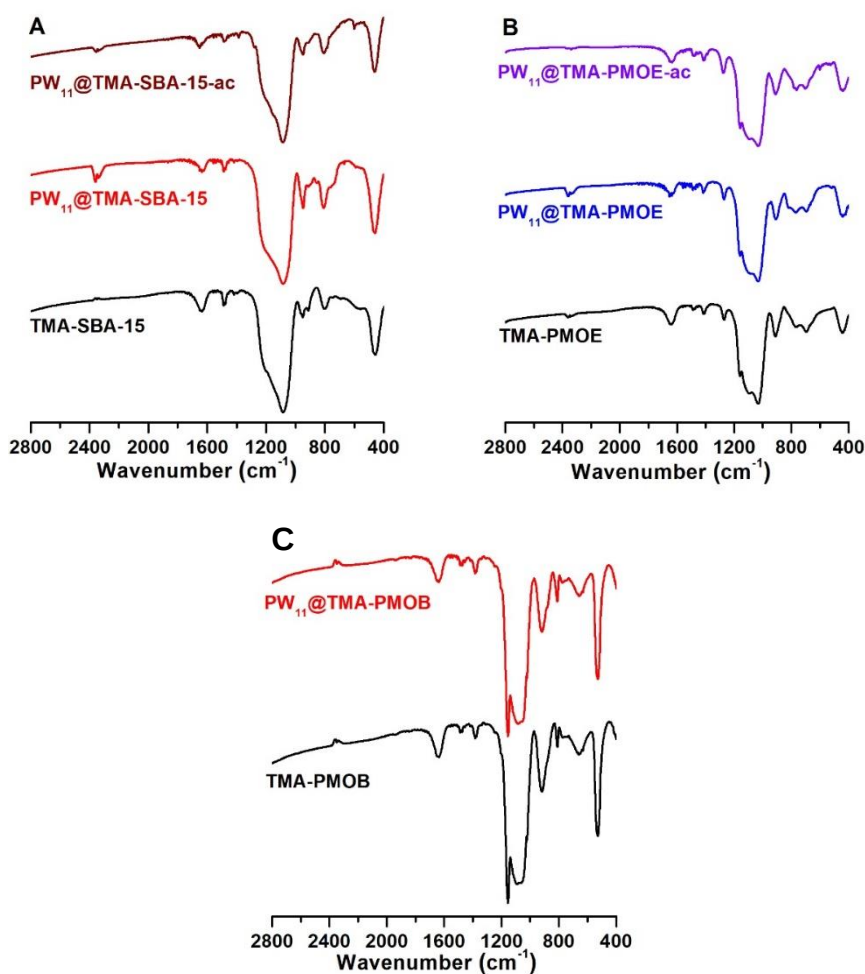


Figure 7.1 – FT-IR spectra of the trimethylammonium-functionalized supports and the resulting PW_{11} composites (ac – after catalysis): (A) TMA-SBA-15 and PW_{11} @TMA-SBA-15 composite; (B) TMA-PMOE and PW_{11} @TMA-PMOE; (C) TMA-PMOB and PW_{11} @TMA-PMOB.

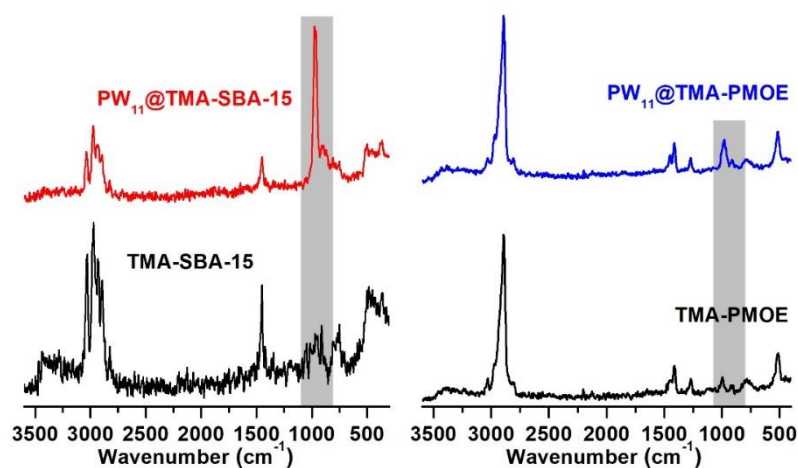


Figure 7.2 – FT-Raman spectra of the trimethylammonium-functionalized supports and the resulting PW_{11} composites: (left) TMA-SBA-15 and $PW_{11}@TMA-SBA-15$ composite, (right) TMA-PMOE and $PW_{11}@TMA-PMOE$.

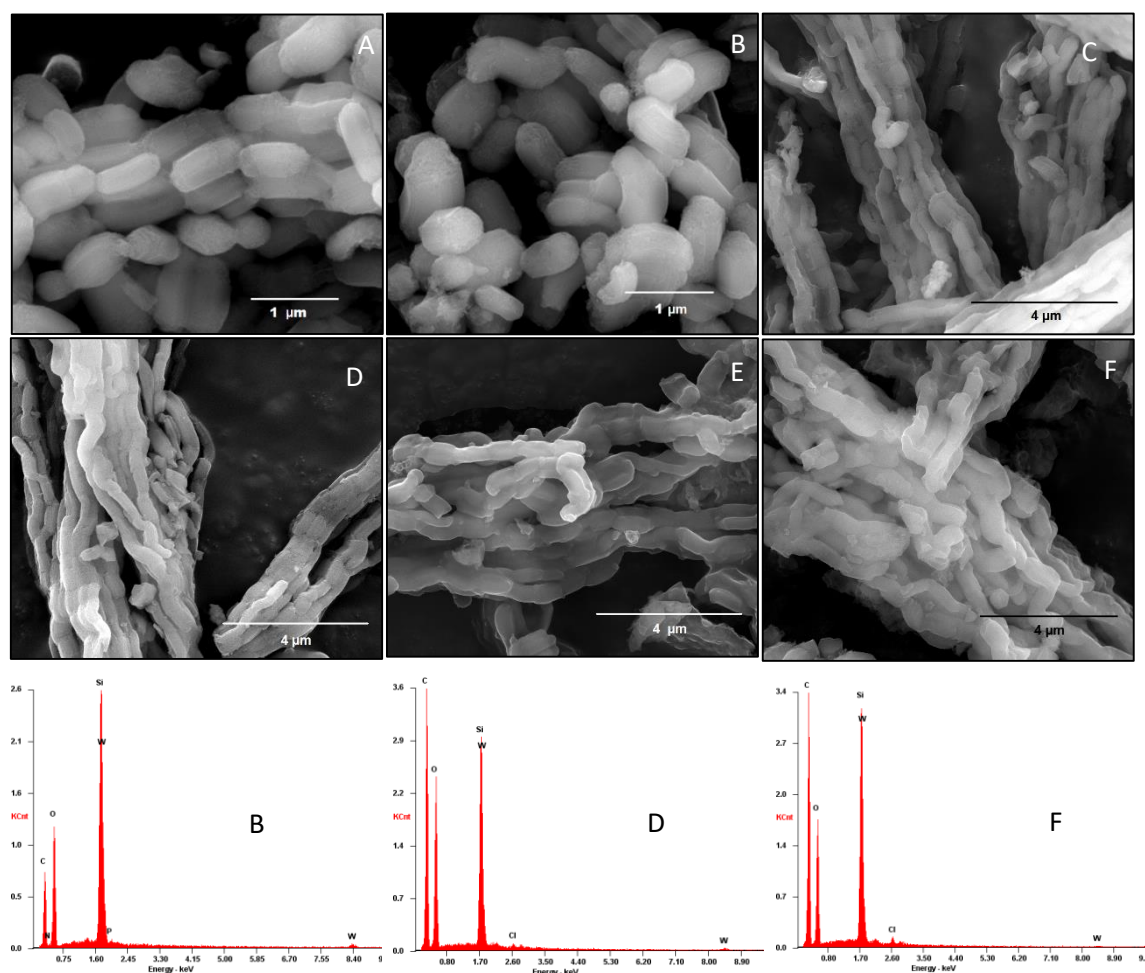


Figure 7.3 –SEM images of the trimethylammonium-functionalized supports and the resulting PW_{11} composites (A - TMA-SBA-15; B - $PW_{11}@TMA-SBA-15$ composite; C - TMA-PMOE; D - $PW_{11}@TMA-PMOE$; E - TMA-PMOE and F - $PW_{11}@TMA-PMOE$). EDS spectra of the PW_{11} composites.

The SEM image of the TMA-SBA-15 support (Figure 7.3-A) presents the typical hexagonal elongated particles of the mesoporous SBA-15 framework. The SEM image of its analogue composite (Figure 7.2-B) reveals that the morphology of the TMA-SBA-15 support was maintained after the POM incorporation. The SEM image of $PW_{11}@TMA-PMOE$ (Figure 7.3-D) still exhibits the same morphology as the support (Figure 7.2-C) composed by ropelike structures with several micrometers in length. [4, 31] The SEM image of TMA-PMOB (Figure 7.3-E) also presents such ropelike structures but with smaller lengths than the previous ones. [25] Once again, a similar morphology could be observed between the $PW_{11}@TMA-PMOB$ composite (Figure 7.3-F) and the support suggesting the structural preservation of the support during the POM incorporation process. The chemical composition of the composites was evaluated by EDS. The results reveal, besides silicon as the main element, the presence of tungsten which is consistent with the incorporation of PW_{11} on the final composites (Figure 7.3).

The powder XRD patterns of the TMA-functionalized supports and the resulting PW_{11} composites are presented in Figure 7.4. The powder XRD of the $PW_{11}@TMA-SBA-15$ composite (Figure 7.4-A) exhibit the typical low-angle three peaks of SBA-15 materials, with a shift to higher 2θ and with lower intensity for the (110) and (200) reflections, as previously reported in other POM-incorporated SBA-15 composites. [32-34] The absence of peaks from the PW_{11} points out that the POM has been successfully incorporated.

In the case of the mesoporous organosilicas supports (TMA-PMOE and TMA-PMOB), both present also the same three peaks as seen in the SBA-15 materials. The highly ordered mesostructure of the prepared PMOs was accomplished by the addition of a KCl as additive which improved the interaction between the organosilica oligomers and the surfactant. [4, 23] The powder XRD pattern of the $PW_{11}@TMA-PMOE$ composite is similar to the TMA-PMOE support, indicating structural preservation of the support. The $PW_{11}@TMA-PMOB$ presents lower intensity for the (110) and (200) reflections as compared with those of the SBA-15 composite, which may indicate the presence of PW_{11} in the porous support.

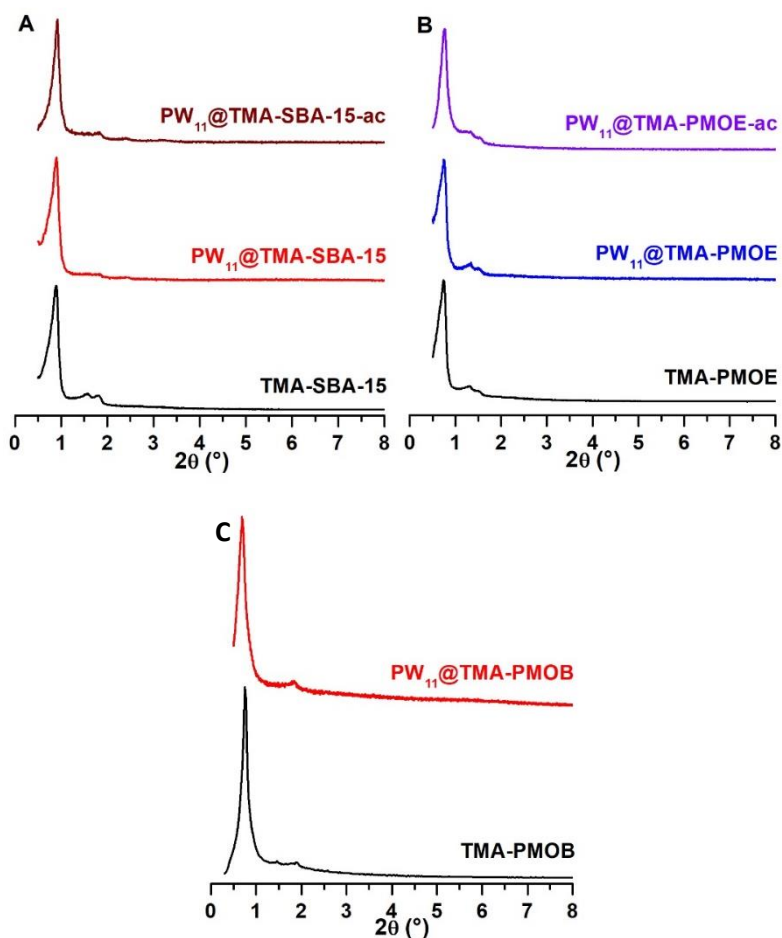


Figure 7.4 – Powder XRD patterns of the trimethylammonium-functionalized supports and the resulting PW_{11} composites (ac – after catalysis). (a) TMA-SBA-15 and $PW_{11}@TMA-SBA-15$ composite; (b) TMA-PMOE and $PW_{11}@TMA-PMOE$; (c) TMA-PMOB and $PW_{11}@TMA-PMOB$.

The textural properties of SBA-15 and ethylene-bridge PMO materials were evaluated by N_2 adsorption experiments. Type IV isotherms with H1 hysteresis loops were obtained (Figure 7.5) for both types of silica, which is characteristic of mesoporous materials. Table 7.1 displays the surface area (S_{BET}) and pore volume (V_p) of the starting supports and the PW_{11} -composites. A simultaneous decrease in S_{BET} and V_p could be observed for both composites when compared with the support, which confirms the incorporation of POM inside the pore channels. [4, 15, 20]

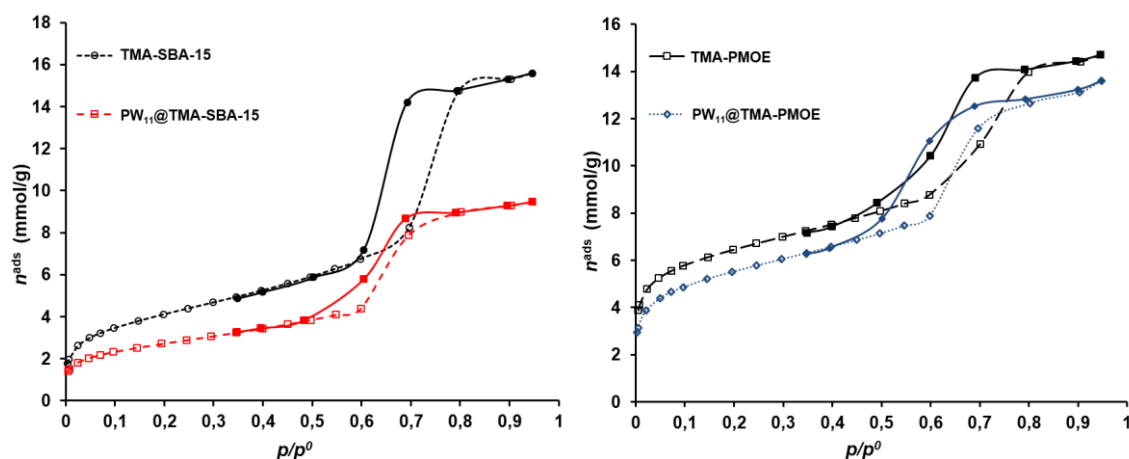


Figure 7.5 – N_2 adsorption-desorption isotherms of the TMA-SBA-15 and $PW_{11}@TMA-SBA-15$ composite (left); TMA-PMOE and $PW_{11}@TMA-PMOE$ (right).

Table 7.1 – Textural parameters of the trimethylammonium-functionalized supports and the resulting PW_{11} composites.

	S_{BET}	V_p
	(m^2g^{-1})	(cm^3g^{-1})
TMA-SBA-15	336	0,54
$PW_{11}@TMA-SBA-15$	221	0,32
TMA-PMOE	521	0,51
$PW_{11}@TMA-PMOE$	449	0,47

The integrity of the lacunar PW_{11} structure after its incorporation in silica supports was investigated by ^{31}P MAS-NMR (Figure 7.6). The spectrum of the $PW_{11}@TMA-SBA-15$ composite presents a broad peak centered at -10.41 ppm with a prominent shoulder at -12.75 ppm. The shoulder corresponds to free PW_{11} anion while the broad peak may be resultant from the interaction of the POM with the siliceous matrix. In fact, a downfield shift in the ^{31}P NMR signal of POMs has been reported as a result of the interaction with $Si-OH^{2+}$ groups of the silica support. [35] This result indicates that the PW_{11} structure was retained after its incorporation in the TMA-SBA-15 support. The spectrum of $PW_{11}@TMA-PMOE$ presents three different peaks with approximately similar intensities at -10.64, -12.79 and -15.16 ppm. The two peaks located at -10.64 and -12.79 ppm should correspond to the free PW_{11} and PW_{11} interacting with the support, respectively, as previously discussed. The peak at -15.16 ppm should correspond to the PW_{11} anion with an occupied lacuna, which is known to promote an upfield shift of the ^{31}P signal. [10, 36]

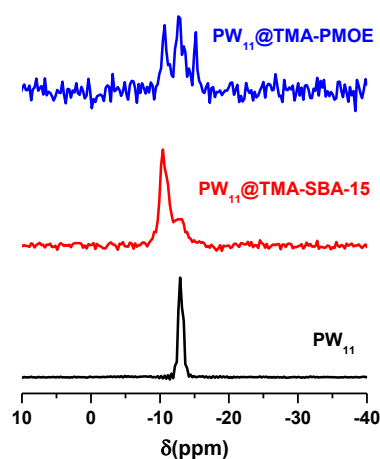


Figure 7.6 – ^{31}P MAS-NMR spectra of PW_{11} and $\text{PW}_{11}@\text{TMA-SBA-15}$ and $\text{PW}_{11}@\text{TMA-PMOE}$ composites.

The TMA-functionalized SBA-15 and ethylene-bridged PMO supports as well as the resulting PW_{11} composites were analyzed by ^{13}C CP MAS-NMR spectroscopy (Figure 7.7). The spectrum of the TMA-SBA-15 support exhibit four peaks located at 70.33, 55.19, 18.59 and 10.94 ppm (Figure 7.7 - left). The peak located at 55.19 ppm correspond to the methyl group and the others can be assigned to the C3 (70.33), C2 (18.59) and C1(10.94) carbon atoms of the TMA group, $\text{Si-}^1\text{CH}_2\text{-}^2\text{CH}_2\text{-}^3\text{CH}_2\text{-N}^+(\text{CH}_3)_3$, respectively. The nonexistence of ^{13}C signals of the Pluronic P123 template (67–77 ppm) indicates an efficient removal of the surfactant. [28] The spectrum of the $\text{PW}_{11}@\text{TMA-SBA-15}$ also presents chemical shifts similar to those of the support material, namely at 70.74, 55.16, 18.61 and 10.53 ppm.

The spectrum of the ethylene-bridged PMO contains a strong peak at 6.63 ppm corresponding to the bridging ethylene group (Figure 7.7 - right), and three peaks at 10.75, 18.85 and 70.50 ppm assigned to the C1, C2 and C3 of TMA, respectively. The spectrum, also presents a peak at 61.37 ppm ascribable to carbon atoms of the ethoxy groups ($\text{CH}_3\text{-CH}_2\text{-O}$) most likely due to incomplete hydrolysis of 1,2-bis(triethoxysilyl)ethane (BTEE) or during the ethanol extraction process of the surfactant. [4, 23, 24]

The ^{29}Si MAS NMR solid state spectrum of the TMA-SBA-15 support presents a broad and intense band and two shoulders that correspond to Q^4 ($\delta \approx -112$ ppm), Q^3 ($\delta \approx -105$ ppm) and Q^2 ($\delta \approx -93$ ppm) species, where $\text{Q}^n = \text{Si}(\text{OSi})_{4-n}(\text{OH})_n$, $n = 2-4$ (Figure 7.8 left). [15, 26, 37] The $\text{PW}_{11}@\text{TMA-SBA-15}$ spectrum exhibits a similar profile to the spectrum of the TMA-SBA-15 support indicating that the main structure of the silica

material was maintained after the PW_{11} incorporation. The ^{29}Si MAS spectrum of the ethylene-bridge PMO (Figure 7.8 - right) presents the characteristic T^n signals attributed to $[\text{C}-\text{Si}(\text{OSi})_2(\text{OH})]$ (T^2 at -60.8 ppm) and $[\text{C}-\text{Si}(\text{OSi})_3]$ (T^3 at -67.1 ppm) and some Q^n signals (Si sites attached to four oxygen atom) between -100 and -115 ppm. This is indicative of some cleavage of the Si-C bond during the synthesis and surfactant extraction process. [4, 29] The incorporation of PW_{11} in the TMA-PMOE support did not result in significant changes in the ^{29}Si MAS spectrum of the composite when compared to the starting support material, which also indicates the preservation of the silicious structure.

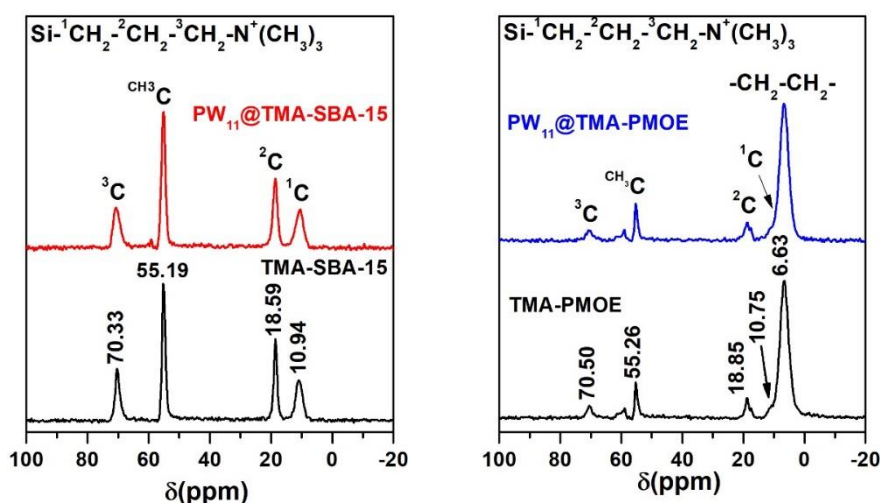


Figure 7.7 ^{13}C MAS NMR spectra of the trimethylammonium-functionalized supports and the resulting PW_{11} composites. TMA-SBA-15 and $PW_{11}@TMA-SBA-15$ composite (left); TMA-PMOE and $PW_{11}@TMA-PMOE$ (right).

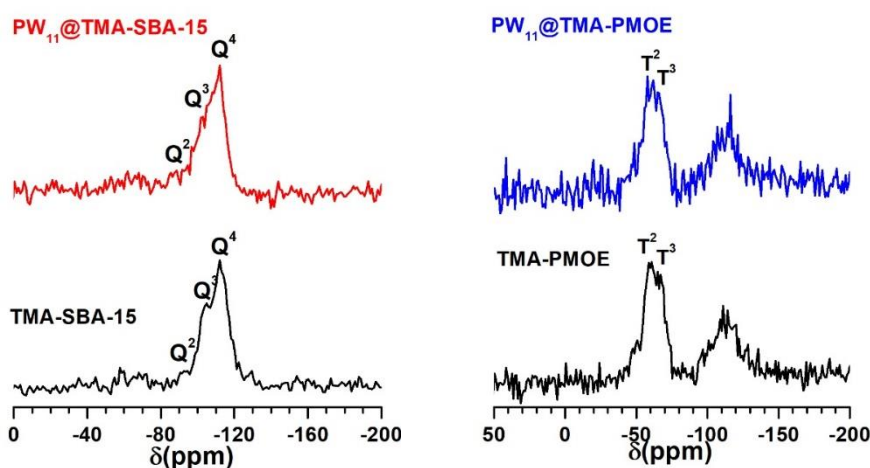


Figure 7.8 ^{29}Si MAS spectra of the trimethylammonium-functionalized supports and the resulting PW_{11} composites. TMA-SBA-15 and $PW_{11}@TMA-SBA-15$ composite (left); TMA-PMOE and $PW_{11}@TMA-PMOE$ (right).

7.2.2. Oxidative desulfurization processes using model diesel

The ODS studies were performed using model diesel B (see Chapter 1 section 1.7) with approximately 2000 ppm S, at 70°C. The PW₁₁@TMA-SBA-15 composite and the PW₁₁@TMA-PMOE composite were tested as heterogeneous catalysts. The oxidative desulfurization of the model diesel was accomplished using either a biphasic ECODS system and a solvent-free CODS system, as described in the previously (Chapters 4,5 and 6). In both systems, 3 µmol of active catalytic center PW₁₁ were used.

In the biphasic system (1:1 model diesel/MeCN extraction solvent) an initial liquid-liquid extraction was performed (10 min of stirring at 70 °C), in the presence of the catalyst. During this step some sulfur-containing compounds were removed from the model oil to the solvent phase, until the transfer equilibrium is reached. Afterwards, the oxidative catalytic stage was initiated by adding the oxidant (ratio H₂O₂/S = 8, at 70 °C). In this step, the sulfur compounds were simultaneously oxidized and extracted to the MeCN phase. The solvent-free system begins with the catalytic stage, in the absence of extraction solvent (ratio H₂O₂/S = 4, at 70 °C), followed by a final extraction step with MeCN or water to remove the oxidized sulfur compounds.

In Figure 7.9 are displayed the results obtained for the biphasic system using both heterogeneous catalysts: PW₁₁@TMA-SBA-15 and PW₁₁@TMA-PMOE. It can be observed that during the initial extraction step (10 min stirring) between 55 and 60% of the model diesel sulfur-containing compounds are transferred to the MeCN phase. This transference follows the order described previously (Chapters 4, 5 and 6), with 1-BT being the most easily extracted, and justified by the size and geometry of each compound. [8, 38] In the oxidative catalytic step, the non-oxidized sulfur compounds, mostly present in the solvent phase, are oxidized and simultaneously more sulfur compounds are transferred to the solvent phase. [27] The PW₁₁@TMA-SBA-15 catalyst was able to achieve complete desulfurization for DBT, 4-MDBT and 4,6-DMDBT and 93,9 % for 1-BT, after 30 min the catalytic step initiation. After 60 min, only 2 ppm of 1-BT remained in the model diesel. The oxidative reactivity follows the expected order, with 1-BT being the most difficult compound to be oxidized, which is related to the electronic density of the sulfur atom and steric hindrance phenomena. [15, 20, 27, 39] Regarding the PW₁₁@TMA-PMOE catalyst, the desulfurization efficiency was slight lower, reaching after 60 min of catalytic oxidation, 92.8% for 1-BT, 98.2% for DBT, 99.0% for 4-MDBT and 99.3% for 4,6-DMDBT, resulting in a total desulfurization of 96.9%.

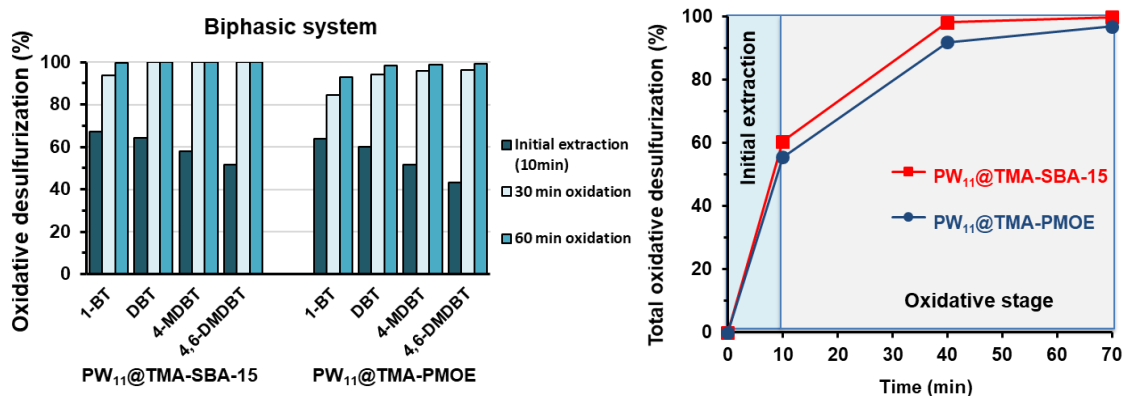


Figure 7.9 – Desulfurization of each sulfur compound from the model diesel (left) and total oxidative desulfurization profile (right) using the biphasic system (1:1 model diesel/MeCN extraction solvent; ratio $\text{H}_2\text{O}_2/\text{S}=8$ at 70 °C), using PW₁₁@TMA-SBA-15 and PW₁₁@TMA-PMOE catalysts (containing 3 μmol of PW₁₁).

In Figure 7.10 are presented the desulfurization results for the solvent-free system, using both composites. During the initial 10 min of catalytic oxidation, the PW₁₁@TMA-PMOE catalyst is faster in the oxidation of sulfur compounds, achieving 72 % of total oxidation, while the PW₁₁@TMA-SBA-15 reached 45.3 %. This might be related to the lower hydrophobicity of the PW₁₁@TMA-PMOE composite that possesses more affinity with the diesel phase than the PW₁₁@TMA-SBA-15. Nevertheless, after 30 min of the process the catalysts performance was similar, achieving total conversion for DBT, 4-MDBT and 4,6-DMDBT and 84.2 and 86.8 % conversion for 1-BT, using for PW₁₁@TMA-PMOE and PW₁₁@TMA-SBA-15 composites, respectively. At the end of 60 min of desulfurization, the SBA-15 composite reached ultra-low levels of sulfur, with only 2 ppm of 1-BT (99.6% conversion) remaining in the model diesel, while with the PMOE composite only 89.6 % of 1-BT has been converted (52 ppm remaining). In fact, continuing the reaction up to 120 min, the conversion of 1-BT, using the PW₁₁@TMA-PMOE is still 93.8 %. It seems that, despite the initial fast reaction rate (first 30 min), desulfurization becomes slower after and total conversion could not be reached even after 120 min. This behavior also occurs with the biphasic system since total desulfurization only reached 98.1 and 98.3 %, after 120 min and 240 min reaction, respectively.

Increasing the amount of oxidant in the solvent-free system to ratio $\text{H}_2\text{O}_2/\text{S} = 8$, ultra-low levels of sulfur could be achieved (7 ppm) with PMOE composite, at the end of 60 min. Contrastingly, increasing the amount of oxidant from $\text{H}_2\text{O}_2/\text{S} = 4$ to $\text{H}_2\text{O}_2/\text{S} = 8$, the desulfurization efficiency of PW₁₁@TMA-SBA-15 shows a slight decrease (figure 7.11). In summary, the PW₁₁@TMA-PMOE needs a higher amount of oxidant than the

SBA-15 composites, that present better desulfurization efficiencies with a $\text{H}_2\text{O}_2/\text{S}=4$ ratio than $\text{H}_2\text{O}_2/\text{S}=8$, as described previously in Chapters 4 and 5. [15]

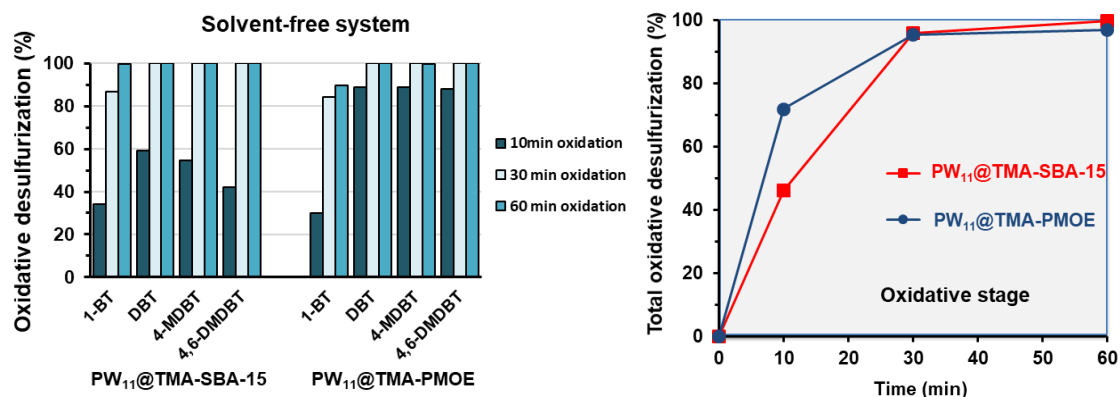


Figure 7.10 – Desulfurization of each sulfur compound in the multicomponent model diesel (left) and total oxidative desulfurization profile (right), using the solvent-free system (ratio $\text{H}_2\text{O}_2/\text{S}=4$ at 70°C) and $\text{PW}_{11}@TMA-SBA-15$ and $\text{PW}_{11}@TMA-PMOE$ as catalysts (containing $3\ \mu\text{mol}$ of PW_{11} active center).

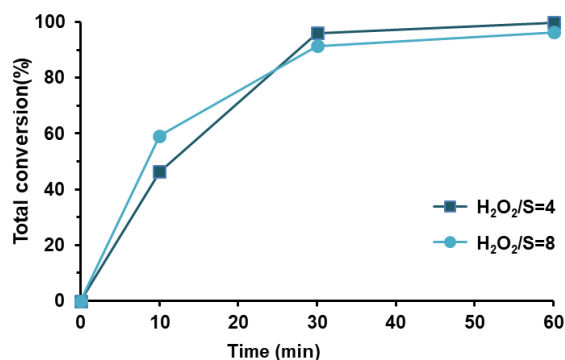


Figure 7.11 – Total conversion for sulfur oxidation presented in the model diesel, using the solvent-free system at 70°C and $\text{PW}_{11}@TMA-SBA-15$ catalyst (containing $3\ \mu\text{mol}$ of PW_{11}), in the presence of two different $\text{H}_2\text{O}_2/\text{S}$ ratios.

7.2.3. Recyclability of $\text{PW}_{11}@TMA-SBA-15$

Since the $\text{PW}_{11}@TMA-SBA-15$ catalyst presented the best desulfurization results, its recycling ability was evaluated for several consecutive cycles using both desulfurization systems (biphasic and solvent-free). After each cycle, the solid catalyst was recovered by centrifugation, washed with ethanol and dried to be used in another desulfurization cycle under the same experimental conditions. In Figure 7.12 is displayed the desulfurization percentages obtained with $\text{PW}_{11}@TMA-SBA-15$ catalyst for eight

consecutive cycles after 60 min of oxidation, using the biphasic or the solvent-free systems. For both systems, the results show that the desulfurization efficiency was maintained along six consecutive cycles. After the six cycle, some loss of catalytic activity was detected probably due to the active site deactivation by the presence of sulfones strongly adsorbed in the catalyst surface, as as previously observed. [14, 20]

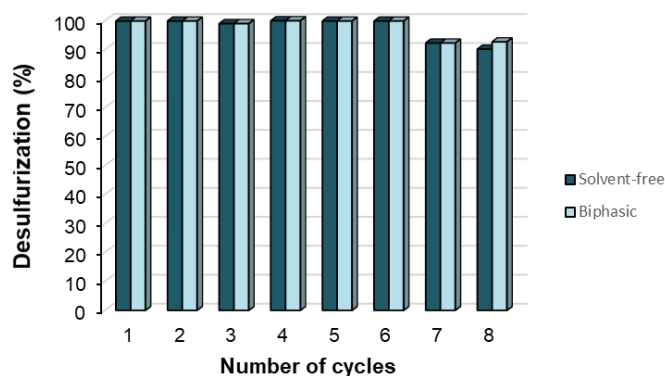


Figure 7.12 – Desulfurization results obtained for six catalytic cycles after 60 min of the oxidant addition, catalyzed by $PW_{11}@TMA-SBA-15$ composite (containing 3 μmol of PW_{11}), using the solvent-free ($H_2O_2/S=4$) and biphasic ($H_2O_2/S=8$) systems, at 70 °C.

7.2.4. Catalysts stability

The chemical robustness and stability of the PW_{11} composites was evaluated by several techniques. The ICP-OES of the $PW_{11}@TMA-SBA-15$ composite reveals that, using the solvent-free system, the catalyst presents similar Si/W (molar) ratio before (1.46) and after catalysis (1.44 after eight desulfurization cycles), indicating that practically no loss of active PW_{11} center occurred during the process even after eight consecutive cycles. The analysis performed after one desulfurization cycle, using the biphasic system, detected some leaching of the PW_{11} from the support material since the Si/W (molar) ratio increased from 1.46 to 1.79 after catalytic use. The $PW_{11}@TMA-PMOE$ composite ICP revealed that after its use in the solvent-free system the Si/W ratio was maintained (1.01 before and 1.00 after catalytic use).

The powder XRD patterns of $PW_{11}@TMA-SBA-15-ac$ and $PW_{11}@TMA-PMOE$, after catalytic use in the biphasic system, exhibit similar profiles to the patterns of the as-prepared materials regarding the position and relative intensity of the peaks (Figure 7.1), which is a good indication of the robustness and stability of the catalyst.

Regarding FT-IR spectra, the main vibrational bands of the composites after catalytic use remain practically unchanged, which is consistent with its structural

retention (Figure 7.4). The morphology of the composites also seems to have been preserved after the desulfurization process as observed by SEM (Figure 7.13), and the corresponding EDS spectra of each composite confirm the presence of PW_{11} by exhibiting the W element (Figure 7.13). Moreover, the EDS spectra of the $PW_{11}@TMA-SBA-15-ac$ also reveals the presence of S, resulting from oxidized sulfur-containing compounds of the model diesel that precipitated in the presence of the composite (Figure 7.13).

The ^{31}P MAS NMR spectra of the composites before and after catalysis, using both desulfurization systems, are presented in Figure 7.14. The spectrum of $PW_{11}@TMA-SBA-15$ after a biphasic ECODS cycle presents a broad peak at -12.68 ppm with a shoulder at -10.92 ppm. The results means that, after the biphasic cycle, the predominant species in the material is now the PW_{11} interacting with the support rather than the free PW_{11} as in the as-prepared composite.

After eight cycles of the solvent-free system, the spectrum displays a main peak at -15.19 ppm that can be assigned to the PW_{11} with saturated lacuna, probably by sulfone or peroxy interactions.

The $PW_{11}@TMA-PMOE$ after one biphasic desulfurization cycle exhibits a broad single peak centered at -10.72 ppm, while after one solvent-free CODS cycle, an additional peak is also observed at -12.27 ppm. These peaks correspond to free PW_{11} (-10.64 ppm) and PW_{11} interacting with the silica support (-12.27 ppm), showing the structural retention of these species from the as-prepared material.

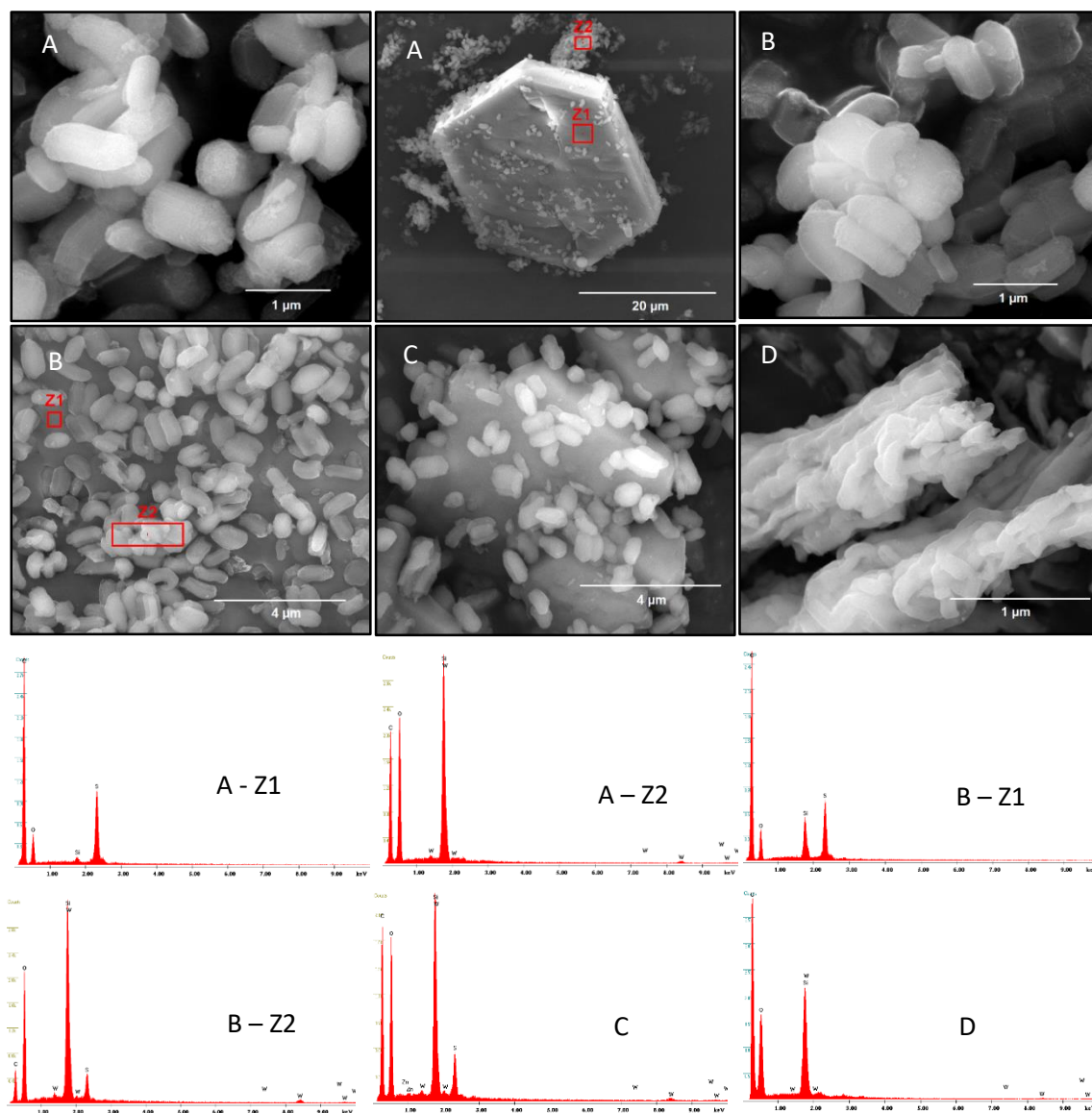


Figure 7.13 –SEM images and EDS spectra of A - PW₁₁@TMA-SBA-15 composite after one cycle using the biphasic system; B - PW₁₁@TMA-SBA-15 composite after one cycle using the solvent-free system; C - PW₁₁@TMA-SBA-15 composite after eight cycles using the solvent-free system and D - PW₁₁@TMA-PMOB composite after catalytic use using the solvent-free system.

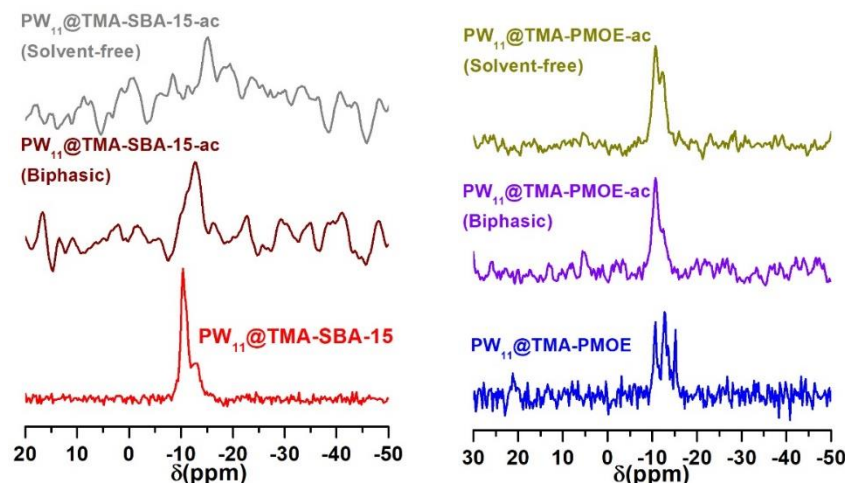


Figure 7.14 – ^{31}P MAS NMR spectra of the $\text{PW}_{11}@TMA\text{-SBA-15}$ composite (left) and $\text{PW}_{11}@TMA\text{-PMOE}$ (right) before and after catalytic use (ac stands for after catalysis).

7.2.5. Oxidative desulfurization process using untreated diesel

The good catalytic performance of $\text{PW}_{11}@TMA\text{-SBA-15}$ has motivated its application in desulfurization of the untreated diesel supplied by CEPISA (1335 ppm). The desulfurization experiments were performed using the biphasic system (1:1 diesel/MeCN), and also the solvent-free system, using a $\text{H}_2\text{O}_2/\text{S}$ ratio of 8 at 70 °C, during 2 hours of oxidation. After the oxidative catalytic process, a liquid-liquid extraction with MeCN/diesel 1:1 at room temperature was performed for all treated diesel samples, during 10 min with stirring.

The desulfurization results are presented in Figure 7.15. The best performance for the first desulfurization cycle was obtained with the biphasic system (93.1%), performing an initial extraction for 10 min (1:1 diesel/MeCN) before oxidation step and also a final extraction after oxidation. Using the solvent-free system, lower desulfurization efficiency was reached (75%).

The solid $\text{PW}_{11}@TMA\text{-SBA-15}$ catalyst was further recycled for two more consecutive cycles. After each cycle, the catalyst was separated from diesel by centrifugation, washed with ethanol and dried to be used in a new cycle under the same reaction conditions. The biphasic system showed higher recycling ability than the solvent-free system, since catalyst efficiency is maintained for three consecutive cycles. On the other hand, an increase of desulfurization efficiency is observed from the second to the third cycle of solvent-free system. This must be related to the formation of catalytic active intermediate during the previous desulfurization cycles. These active intermediate

can be attributed to active peroxy compounds. However, the best desulfurization efficiency was obtained for the first cycle using the biphasic system.

In short, the $PW_{11}@TM-SBA-15$ using the biphasic system revealed to be a promising process for the desulfurization of untreated diesel, since 93.1% desulfurization of CEPSA diesel was achieved and the catalyst could be recycled over three consecutive desulfurization cycles with no apparent loss of catalytic activity.

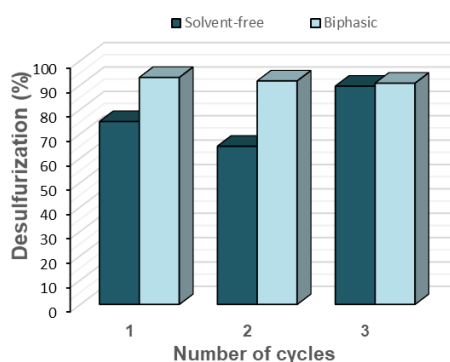


Figure 7.15 - Desulfurization results of a real untreated diesel obtained after 2 h, catalyzed by $PW_{11}@TMA-SBA-15$ at 70 °C, using the solvent-free system and the biphasic system and a ratio $H_2O_2/S=8$.

7.3 Conclusion

In this work, three different POM-based silica composites were prepared via impregnation of PW_{11} on the surface of mesoporous silica materials (SBA-15, ethylene-bridge PMOE and benzene-bridge PMOB) functionalized with TMA. The cationic functional group promotes the immobilization of the anionic PW_{11} by electrostatic interaction. The surface modification of SBA-15 was accomplished by post-synthetic grafting, while the introduction of functional groups in PMOs was achieved *in situ* (“co-condensation”).

Two of these composites, $PW_{11}@TMA-SBA-15$ and $PW_{11}@TMA-PMOE$, were tested as oxidative catalysts in the desulfurization of multicomponent model diesel B. The $PW_{11}@TMA-PMOE$ composite achieved 96.9% of desulfurization after 60 min of oxidative reaction, while the $PW_{11}@TMA-SBA-15$ allowed to reach ultra-low levels of sulfur (<10 ppm) under the same period of time, using the biphasic system.

Using the solvent-free system, complete conversion of DBT, 4-MDBT and 4,6-DMDBT has been achieved for both catalysts after only 30 min. The $PW_{11}@TMA-PMOE$

catalyst revealed to be slightly less active than the PW₁₁@TMA-SBA-15 catalyst, since no complete 1-BT desulfurization was achieved, after 60 min of the process. In comparison, the PW₁₁@TMA-SBA-15 reached ultra-low levels of sulfur (2 ppm) for the same period of time. Moreover, PW₁₁@TMA-SBA-15 has shown a remarkable recycling ability, in both desulfurization systems, by maintaining its catalytic efficiency for six consecutive cycles.

The robustness of the composites was confirmed by characterization studies of the recovered solid catalysts suggesting their structural and chemical preservation after catalytic use.

The promising results obtained with simulant diesel have motivated the application of PW₁₁@TMA-SBA-15 in the desulfurization process of an untreated diesel supplied by CEPSA, under biphasic and solvent-free systems. Furthermore, recycling tests were performed using both systems for three consecutive cycles. The best result was obtained using the biphasic system, removing 93.1 % of sulfur compounds from the diesel after only 2 h and maintained its high desulfurization efficiency for two more cycles. The success of these recycling studies using a real untreated diesel, makes that the use of PW₁₁@TMA-SBA-15 catalyst under biphasic conditions a promising system for the production of sulfur-free fuels.

7.4. Experimental section

7.4.1. Materials and Methods

The following chemicals and reagents were purchased from chemical suppliers and used without further purification: sodium tungstate dihydrate (Aldrich), sodium hydrogen phosphate dihydrate (Aldrich), tetra-*n*-butylammonium bromide (Merck), hydrochloric acid (Fisher Chemicals), Pluronic P123 (Aldrich), *N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride (TMA, ABCR5, 50% in methanol), 1,2-bis(triethoxysilyl)ethane (BTEE, 96%, Aldrich), 1,4-bis(triethoxysilyl)benzene (BTEB, 96%, Aldrich), potassium chloride (Aldrich), ethanol (Aga), tetraethyl orthosilicate (TEOS, 98%, Aldrich), anhydrous toluene (99.8%, Aldrich), 1-benzothiophene (1-BT, Fluka), dibenzothiophene (DBT, Aldrich), 4-methyldibenzothiophene (4-MDBT, Aldrich), 4,6-dimethyldibenzothiophene (4,6-DMDBT, Alfa Aesar), *n*-octane (Aldrich), acetonitrile (MeCN, Fisher Chemical) and hydrogen peroxide (30%, Aldrich).

Elemental analyses for C, H and N elements were performed in a Leco CHNS-932 instrument, and Si, W and P by ICP-OES on a Perkin-Elmer Optima 4300 DV instrument at the University of Santiago de Compostela. FT-IR spectra were obtained on a Jasco 460 Plus spectrometer using KBr pellets. The FT-Raman spectra were recorded by the research group of Isabel Gonçalves in CICECO Associate Laboratory, University of Aveiro, using a RFS-100 Bruker FT-spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm and the laser power set to 350 mW. Powder X-ray diffraction (XRD) patterns were obtained at room temperature in Bragg-Brentano para-focusing geometry using a Rigaku Smartlab diffractometer, equipped with a D/tex Ultra 250 detector and using Cu K- α radiation ($K\alpha_1$ wavelength 1.54059 Å), 45 kV, 200 mA in continuous mode, step 0.01°, speed 0.6°/min in the $0.5 \leq 2\theta \leq 10^\circ$ range. ^{31}P NMR spectra were collected for liquid solutions using a Bruker Avance III 400 spectrometer and chemical shifts are given with respect to external 85% H_3PO_4 . Solid state ^{13}C , ^{31}P and ^{29}Si MAS NMR spectra were acquired with a Bruker AVANCE III 300 spectrometer (7 T) operating at 75 MHz (^{13}C), 121 MHz (^{31}P) and 60 MHz (^{29}Si), respectively, equipped with a BBO probe head. The samples were spun at the magic angle at a frequency of 5 kHz in 4 mm-diameter rotors at room temperature. The ^{13}C MAS NMR experiments were acquired with proton cross polarization (CP MAS) with a contact time of 1.2 ms, and the recycle delay was 2.0 s. The ^{29}Si MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 4.5 μs at a power of 40 W, and a relaxation delay of 10.0 s. The ^{31}P MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 5.0 μs at a power of 20 W, and a relaxation delay of 2.0 s. Solid state ^{13}C , ^{31}P and ^{29}Si MAS NMR spectra were performed by Marta Corvo at CENIMAT/I3N, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at “Centro de Materiais da Universidade do Porto” (CEMUP, Porto, Portugal) using a high-resolution (Schottky) scanning electron microscope with X-ray microanalysis and electron backscattered diffraction analysis Quanta 400 FEG ESEM/EDAX Genesis X4 M. The samples were studied as powders and were coated with an Au/Pd thin film by sputtering using the SPI Module Sputter Coater equipment. The textural characterization was obtained from physical adsorption of nitrogen at -196°C , using a Quantachrome NOVA 2200e instrument at Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa by Susana Ribeiro under the supervision of Professor João Pires. Samples were degassed at 120°C for at least 5 h prior to the measurements. The BET surface area (S_{BET}) was calculated by using the relative pressure data in the 0.05–0.3 range. The total pore volume (V_p) was evaluated

on the basis of the amount adsorbed at a relative pressure of about 0.95. GC-FID was carried out in a Varian CP-3380 chromatograph to monitor the ODS multicomponent model oil experiments. Hydrogen was used as the carrier gas (55 cm s^{-1}) and fused silica Supelco capillary columns SPB-5 (30 m x 0.25 mm i.d.; 25 μm film thickness) were used. Sulfur content in real diesel was measured by X-ray Fluorescence Spectrometry, using an Spectrace 450 spectrometer at the University of Santiago de Compostela.

7.4.2. Synthesis of materials

7.4.2.1. Synthesis of monolacunary phosphotungstate

The tetra-*n*-butylammonium (TBA, $(\text{C}_4\text{H}_9)_4\text{N}$) salt of monolacunary phosphotungstate $[\text{PW}_{11}\text{O}_{39}]^{7-}$ (**PW₁₁**) was prepared as described in Chapter 4 section 4.4.2.1. [15]

7.4.2.2. **PW₁₁@TMA-SBA-15 composite**

The synthesis of mesoporous silica SBA-15 functionalized with N,N,N-trimethylammonium groups with a loading of 0.974 mmol g⁻¹ (TMA-SBA-15), as well as the preparation of POM@TMA-SBA-15 composite were previously described in Chapter 3 section 3.4.2.2.. [19, 20]

TMA-SBA-15: Anal. Found (%): N, 1.4; C, 7.6; H, 2.2; loading of TMA 1.00 mmol per 1g; Selected FT-IR (cm^{-1}): 3436 (vs), 2360 (w), 1868 (w), 1635 (m), 1489 (m), 1479 (m), 1419 (w), 1086 (vs), 951 (m), 806 (s), 692 (w), 678 (w), 553 (w), 460 (s). FT-Raman (cm^{-1}): 3028 (vs), 2981 (sh), 2972 (vs), 2931 (m), 2925 (sh), 2823 (m), 1450 (s), 912 (m). [20]

PW₁₁@TMA-SBA-15: Anal. Found (%) W, 21.3; Si, 4.7; loading of POM: 0.099 mmol per 1g, Si/W (molar) = 1.46; Selected FT-IR (cm^{-1}): 3444 (vs), 2360(m), 2341 (m), 1644 (m), 1447 (m), 1195 (sh), 1085 (vs), 948 (m), 914 (w), 856 (w), 809 (m), 458 (s), Selected FT-Raman (cm^{-1}): 3035 (s), 2979 (s), 2922 (s), 2902 (m), 1444 (m), 976 (vs), 970 (vs)

7.4.2.2. **PW₁₁@TMA-PMO composites**

The ethylene-bridged and benzene-bridge TMA-functionalized PMOs were prepared following a previously reported procedure. [4, 23] Briefly, Pluronic P123 (0.096 mmol) and KCl (47 mmol) were dissolved in aqueous HCl (1.6 M; 29 mmol) under

vigorous stirring at 40 °C during 4 h. Then, BTEE or BTEB (2.84 mmol) and TMA (0.71 mmol) were added to the solution and the mixture was further stirred for 20 h at 40 °C. The mixture was then transferred to an autoclave and heated at 100 °C for 24 h. The solid was recovered by filtration and dried in a desiccator under silica gel. The extracting process of the co-polymer P123 was performed by refluxing the sample in an acidic ethanol solution for 24 h. For each g of material, 200 mL of ethanol and 1.5 g of HCl were used.

The PW₁₁@TMA-PMOs composites were prepared through impregnation method as described in Chapter 3 section 3.4.2.2..

TMA-PMOE: Anal. Found (%): N, 0.85; C, 19.79; H, 4.78; loading of TMA 0.61 mmol per 1g; Selected FT-IR (cm⁻¹): 3434 (vs), 2886 (w), 2360 (w), 1637 (m), 1488 (w), 1413 (m), 1270 (m), 1159 (s), 1093 (sh), 1031 (vs), 912 (s), 763 (m), 696 (m), 441 (s). FT-Raman (cm⁻¹): 2972 (sh), 2891 (vs), 2802 (w), 1441 (sh), 1412 (m), 1271 (m), 995 (m), 902 (w), 770 (m), 511 (s).

TMA-PMOB: Anal. Found (%): N, 1.38; C, 30.95; H, 3.70; loading of TMA 0.98 mmol per 1g; Selected FT-IR (cm⁻¹): 3417 (vs), 2327 (w), 1635 (m), 1488 (w), 1384 (m), 1155 (vs), 1074 (vs), 1022 (sh), 917 (s), 809 (m), 744 (w), 671 (m), 536 (vs).

PW₁₁@TMA-PMOE: Anal. Found (%) W, 10.24; Si, 1.55; loading of POM: 0.050 mmol per 1g, Si/W (molar) = 1.01; Selected FT-IR (cm⁻¹): 3444 (vs), 2975 (w), 2898 (m), 2360 (m), 2343 (w) 1652 (m), 1488 (w), 1417 (m), 1270 (m), 1159 (s), 1079 (sh), 1033 (vs), 908 (s), 815 (w), 767 (m), 696 (m), 501 (w), 441 (s). Selected FT-Raman (cm⁻¹): 3031 (w), 2968 (w), 2891 (vs), 2806 (w), 1450 (m), 1412 (s), 1271 (m), 980 (s), 968 (sh), 928 (w), 760 (m), 515 (s)

PW₁₁@TMA-PMOB: Anal. Found (%) W, 5.67; P, 0.19; loading of POM: 0.028 mmol per 1g; Selected FT-IR (cm⁻¹): 3434 (vs), 3062 (w), 2977 (w), 2348 (w), 1637 (m), 1488 (m), 1384 (m), 1155 (vs), 1081 (vs), 1022 (sh), 917 (s), 811 (m), 775 (w), 657 (m), 528 (vs).

7.4.3. Oxidative Desulfurization processes using model diesel

The ODS experiments were performed using the model diesel B (1-BT, DBT, 4-MDBT and 4,6-DMDBT, 500 ppm each, in n-octane). The ODS studies were performed using either a solvent-free and a biphasic system. In a typical biphasic experiment, 1:1 model diesel/MeCN (750µL mL of each) were added to the heterogeneous composite,

containing the equivalent of 3 μmol of POM, and the resulting mixture was stirred for 10 min and an aliquot of the upper phase oil was taken. The catalytic step of the process was initiated by the addition of aqueous hydrogen peroxide 30% (40 μL ; $\text{H}_2\text{O}_2/\text{S}$ molar = 8). The solvent-free system experiments were performed using the model diesel (750 μL), 3 μmol of active catalyst and the H_2O_2 oxidant ($\text{H}_2\text{O}_2/\text{S}$ molar = 4). A final liquid-liquid extraction, was performed to remove the oxidized sulfur compounds, using an extraction solvent such as MeCN. The sulfur content in the model diesel was periodically quantified by GC analysis using tetradecane as a standard. At the end of oxidation, centrifugation was carried out to separate the solid catalyst, which was washed with ethanol and dried in a desiccator over silica gel. For the recycling studies, the recovered catalyst was reused in new ODS cycles under the same reactional conditions.

7.4.3. Oxidative Desulfurization process using untreated diesel

An untreated diesel sample supplied by CEPESA (containing about 1335 ppm of sulfur) was also desulfurized using the $\text{PW}_{11}\text{@TMA-SBA-15}$ catalyst. The untreated diesel was mixed with the heterogeneous composite (an amount containing 3 μmol of PW_{11}) in MeCN and with a $\text{H}_2\text{O}_2/\text{Sulfur}$ ratio equal to 8. The mixture was heated at 70 $^\circ\text{C}$ for 2 h. After this time, the diesel was removed from the mixture and washed with equal volume of MeCN for 10 min and separated by decantation. The solvent-free system was also evaluated in desulfurization of CEPESA diesel for comparison with the biphasic system. In this case, the catalyst and oxidant were mixed with the diesel sample and heated at 70 $^\circ\text{C}$ during 2h. The diesel was separated from the catalyst by centrifugation and washed with MeCN during 10min. Recycling tests were also performed for three consecutive cycles. After catalytic use the recovered composite was washed with ethanol and dried in a desiccator over silica gel overnight to be used in another ODS cycle with a new portion of untreated diesel.

7.5. References

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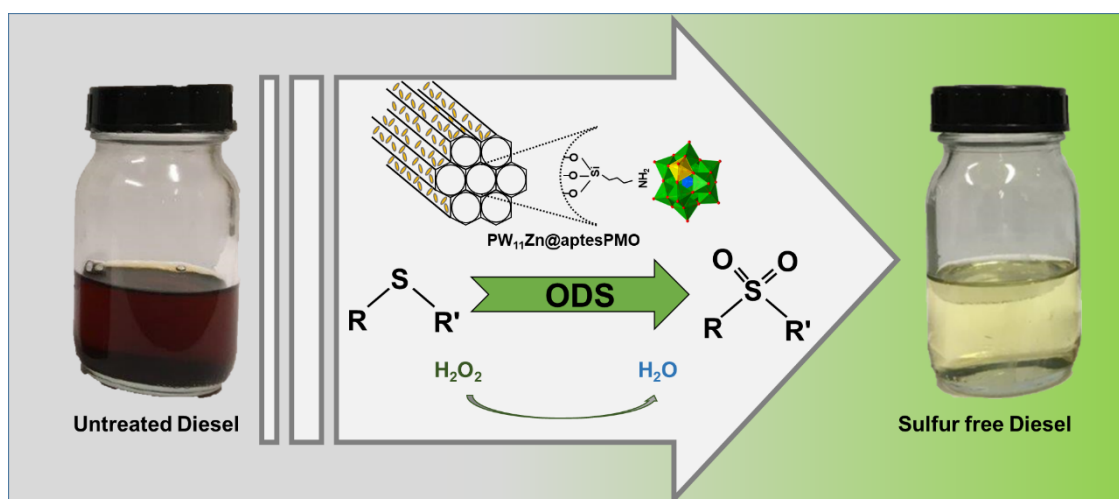
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Chapter 8

Polyoxometalate@Periodic mesoporous organosilicas as effective catalyst for oxidative desulfurization of model and real Diesels^{1,2}



¹ Adapted from: Susana O. Ribeiro, Pedro Almeida, João Pires, Baltazar de Castro and Salette S. Balula, *Polyoxometalate@Periodic mesoporous organosilicas as effective catalyst for oxidative desulfurization of model and real Diesels*, submitted to Catalysis Today special issue "Tailored Porous Materials for Sustainable Catalysis".

² Susana O. Ribeiro contribution to the publication: Catalysts preparation and characterization; investigation of its catalytic performance in the desulfurization of a model and real diesels; manuscript preparation.

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Chapter 8

Polyoxometalate@Periodic mesoporous organosilicas as effective catalyst for oxidative desulfurization of model and real Diesels

Abstract

An ethane-bridge (PMOE) and a benzene bridge (PMOB) periodic mesoporous organosilicas (PMOs) functionalized with (3-aminopropyl)triethoxysilane (aptès) were synthesized through co-condensation process and used as support for $[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})_{39}]^{5-}$ (PW_{11}Zn) active center. The prepared composites ($\text{PW}_{11}\text{Zn}@ \text{aptèsPMOE}$ and $\text{PW}_{11}\text{Zn}@ \text{aptèsPMOB}$) were tested in desulfurization of a model diesel, using two different systems: a biphasic extractive and catalytic oxidative desulfurization (ECODS) system and a solvent-free catalytic oxidative desulfurization (CODS) system. The solvent-free system presented better results, in the presence of both catalysts, reaching ultra-low levels of sulfur compounds after 60 min and using a low ratio of $\text{H}_2\text{O}_2/\text{S} = 4$. The recyclability of both catalysts was verified for ten consecutive cycles. Moreover, the $\text{PW}_{11}\text{Zn}@ \text{aptèsPMOE}$ catalyst improved its catalytic efficiency after the third cycle, achieving complete desulfurization within 30 min. The robustness of the solid $\text{PW}_{11}\text{Zn}@ \text{aptèsPMOE}$ was higher than the $\text{PW}_{11}\text{Zn}@ \text{aptèsPMOB}$, mainly due to the occurrence of some PW_{11}Zn leaching from the PMOB surface. An untreated diesel sample with 1335 ppm of sulfur was also treated using the $\text{PW}_{11}\text{Zn}@ \text{aptèsPMOE}$ catalyst, achieving 75.9% of desulfurization. This catalytic efficiency was maintained over three consecutive ECODS cycles.

8.1 Introduction

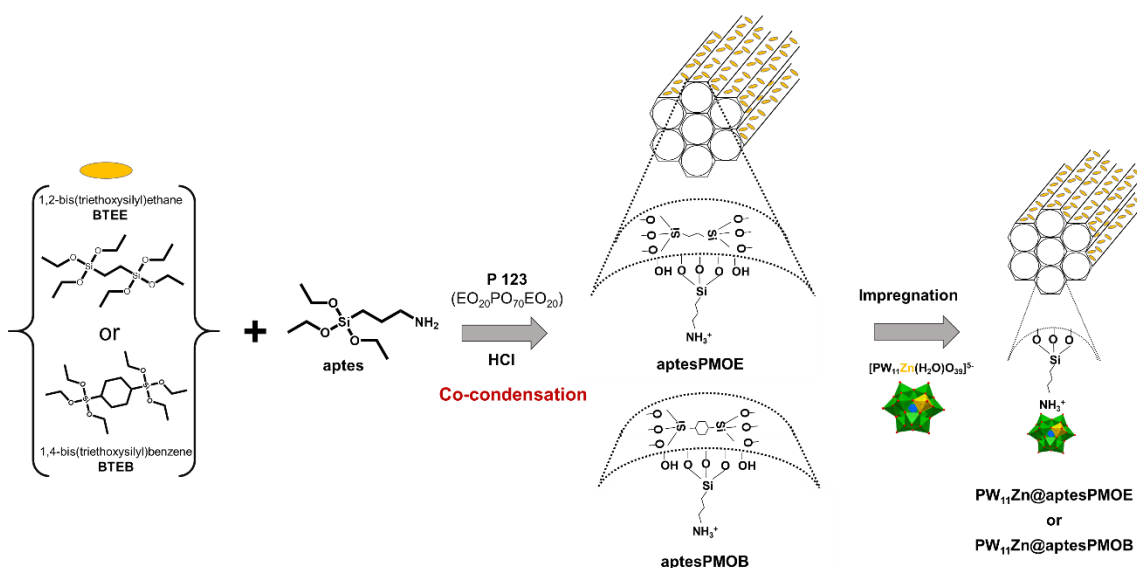
A new class of mesoporous organic-inorganic hybrid materials has been reported for the first time in 1999, called periodic mesoporous organosilicas (PMOs), which are built from bridge silsesquioxane precursors $[(R'O)_3Si-R-Si-(OR')_3]$, using a surfactant self-assembly approach. [1-4] The R in the organic-bridge linker can be methylene ($-CH_2-$), [5-7] ethylene ($-CH_2-CH_2-$), [1, 2, 7] ethenylene ($-CH=CH-$), [8] phenylene ($-C_6H_4-$), [7] biphenylene ($-C_6H_4-C_6H_4-$), [9] thiophene ($-C_5H_4S-$), [10] etc. The OR' can be a hydrolysable alkoxy moiety, mostly methoxy or ethoxy groups. The organic components are homogeneously distributed in the pore walls, which increase the mechanical and hydrothermal stabilities. [4] Moreover, the variety of organic-bridge linkers allows the tunability of several physical and chemical properties of these materials, as for instance the hydrophobicity. Besides the bridge linkers, other groups with specific functionalities can be introduced in the PMOs framework, generating bi(multi)-functionalized periodic mesoporous organosilicas. Amongst the different functional groups, amines are most attractive, owing to the versatile applications provided by their rich chemistry. [11] The exceptional properties of PMOs (high surface areas and pore volume, tunable pore size, highly ordered mesostructure) make them suitable candidates to host catalytic active species such as polyoxometalates (POMs). The zinc mono-substituted phosphotungstate ($PW_{11}Zn$) has been proving to be an efficient catalytic active center for oxidative desulfurization processes, when immobilized in different support materials, as described in Chapters 2 and 5. [12-16]

This chapter reports the preparation of two different PMOs supports containing different bridge linker groups (1,2-bis(triethoxysilyl)ethane: BTEE and 1,4-bis(triethoxysilyl)benzene: BTEB) and the aminopropyl as functional group to promote the immobilization of the $PW_{11}Zn$ active center. Therefore, two novel composites were prepared through the impregnation of $PW_{11}Zn$ in amine-functionalized ethylene-bridge (aptesPMOE) and benzene-bridge (aptesPMOB) PMOs. The prepared composites ($PW_{11}Zn@aptesPMOE$ and $PW_{11}Zn@PMOB$) were tested in the oxidative desulfurization (using H_2O_2 as oxidant) of a model diesel containing the most refractory sulfur compounds present in diesel. The composites $PW_{11}Zn@aptesPMOE$ and $PW_{11}Zn@aptesPMOE$ were tested using either a biphasic extractive and catalytic oxidative desulfurization system (ECODS) and a solvent-free catalytic oxidative desulfurization system (CODS).

8.2. Results and discussion

8.2.1. Catalysts characterization

The PMOE and PMOB supports were prepared by a surfactant-assisted co-condensation method [11, 17] with the surfactant being removed by ethanol extraction. The $\text{PW}_{11}\text{Zn}@PMOs}$ were prepared via impregnation method. The support materials, as well as the $\text{PW}_{11}\text{Zn}@aptesPMOE}$ and $\text{PW}_{11}\text{Zn}@PMOB}$ composites were characterized by several techniques to assess their correct preparation.



Scheme 8.1 – Schematic representation of $\text{PW}_{11}\text{Zn}@aptesPMOE}$ and $\text{PW}_{11}\text{Zn}@aptesPMOB}$ preparation.

FT-IR spectra of PMOs supports and composites (wavenumber region between 400 and 3600 cm^{-1}), display the characteristic bands of amine-functionalized PMOs and of the PW_{11}Zn (Figure 8.1). The apesPMOE FT-IR spectrum is dominated by the characteristic bands of silsesquioxane frameworks namely the intense bands at 1095 and 1031 cm^{-1} assigned to $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si})$, as well as the bands located at 906 , 771 and 441 cm^{-1} associated with the $\nu_{\text{as}}(\text{Si}-\text{OH})$, $\nu_{\text{s}}(\text{Si}-\text{O}-\text{Si})$ and $\delta(\text{Si}-\text{O}-\text{Si})$, respectively. [11, 17-19] The bands at 1270 , 1411 , 2854 and 2923 cm^{-1} can be associated to the C-H vibrational modes of the bridging-ethylene groups. [19] The band at 1457 cm^{-1} can be ascribed to the bending vibrations of C-H in the propyl group of apes. The band at 1635 cm^{-1} is mainly arisen from the adsorbed water (bending). [11, 19, 20] The absence of bands in the region 1340 and 1380 cm^{-1} suggest that the pluronic P123 surfactant has been successfully removed during the extraction process. [21]

The spectrum of the $PW_{11}Zn@aptesPMOE$ composite suggests that the structure of aptesPMOE support was retained after the POM incorporation, since the characteristic bands of the silicious support were maintained. Moreover, two weak additional bands can be observed, which are assigned to the terminal $\nu_{as}(W-O_d)$ at 954 cm^{-1} and edge-sharing $\nu_{as}(W-O_c-W)$ at 809 cm^{-1} of $PW_{11}Zn$. [12]

The FT-IR spectrum of benzene-bridge PMOB presents a strong band at around 3434 cm^{-1} that is attributed to the stretching and deformational vibrations of the residual water (Figure 8.1-right). [22] The band located at 1058 cm^{-1} is assigned to the $\nu_{as}(Si-O-Si)$ mode and the band located at 809 cm^{-1} is attributed to the stretching vibration of $Si-O$, which support the retention of the siloxane network in the PMO framework. [22] The bands at 3062 cm^{-1} and 1155 cm^{-1} correspond to the C-H and Si-C stretching vibration modes of the benzene group, respectively. The benzene ring vibrations are present at 1500 cm^{-1} and 1637 cm^{-1} , which can be indicative of the successfully load of benzene group in the silica framework by covalent bound. The strong band at 524 cm^{-1} corresponds to the out of plane aromatic δ_{Csp^2-H} bending. The band located at 1384 cm^{-1} is due to the pluronic P123 surfactant residues. [21-23] The FT-IR spectrum of $PW_{11}Zn@aptesPMOB$ is also dominated by the characteristic bands of the silicious support; however, the presence of $PW_{11}Zn$ is indicated by two weak bands observed at 948 cm^{-1} and 833 cm^{-1} , attributed to the terminal $\nu_{as}(W-O_d)$ and edge-sharing $\nu_{as}(W-O_c-W)$ of the $PW_{11}Zn$, respectively.

The RAMAN spectrum of $PW_{11}Zn@aptesPMOE$ (Figure 8.2-left) presents the typical bands of the ethylene-bridge PMO, namely the bands in the $3000\text{-}2800\text{ cm}^{-1}$ range ascribed to the $\nu(C-H)$ stretch, at 1415 and at 1271 cm^{-1} to $\delta(CH_2)_{twist}$ and $\delta(CH_2)_{wagg}$ modes, respectively. The band at 509 cm^{-1} corresponds to the vibration of the ethylene unit against the siliceous framework together with $\delta(Si-O-Si)$ vibrations. [17, 24] The spectrum also points out to the presence of $PW_{11}Zn$ by the appearance of additional bands at 986 cm^{-1} and 973 cm^{-1} ascribed to the terminal $\nu_{as}(W-O_d)$ vibrations of $PW_{11}Zn$. [25]

The RAMAN spectrum of $PW_{11}Zn@aptesPMOB$ (Figure 8.2-right) is also dominated by the amine-functionalized PMOB support vibrational bands, namely the bands between 3050 cm^{-1} and 2900 cm^{-1} . The $\nu(C-H)$ stretch at 1596 cm^{-1} corresponds to the C-C stretching vibrations of benzene and at 579 cm^{-1} probably caused by various $\delta(Si-O-H)$ deformation modes. [24] Two strong additional bands appear at 987 cm^{-1} and 972 cm^{-1} , assigned to the terminal $\nu(W-O_d)$ vibrations of the $PW_{11}Zn$. [24, 25]

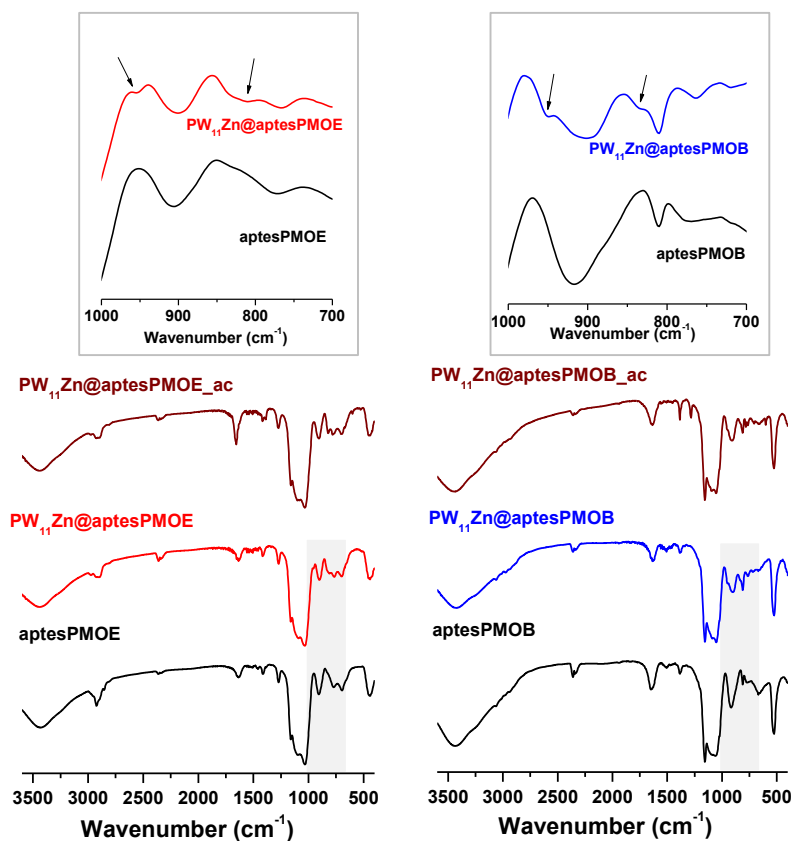


Figure 8.1 – FT-IR spectra of the amine-functionalized supports and the resulting PW₁₁Zn composites, before and after catalytic use (ac stands for after catalysis): Left) aptesPMOE and PW₁₁Zn@aptesPMOE; right) aptesPMOB and PW₁₁Zn@aptesPMOB.

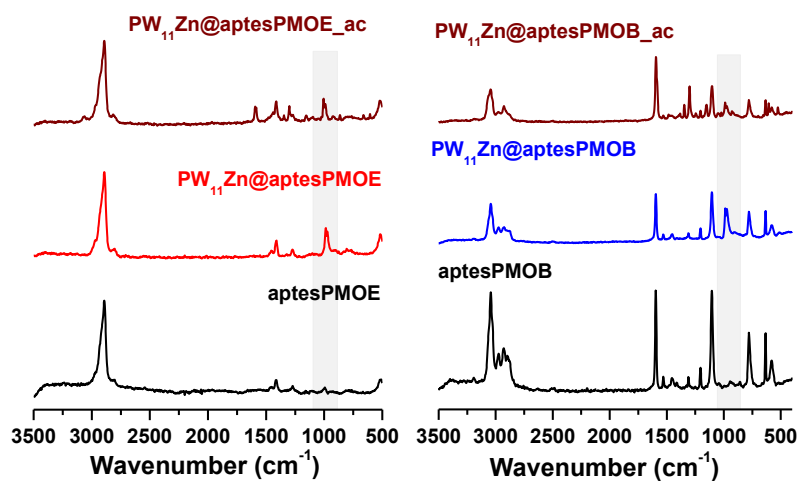


Figure 8.2 – FT-RAMAN spectra of aptesPMOE and PW₁₁Zn@aptesPMOE composite, before and after catalytic use (left); aptesPMOB and PW₁₁Zn@aptesPMOB composite before and after catalytic use (right) (ac stands for after catalysis)

The low-angle powder x-ray patterns of the prepared materials are displayed in Figure 8.3. The amine-functionalized supports aptesPMOE and aptesPMOB present three well-resolved peaks indexed to characteristic (100), (110) and (210) diffractions of a hexagonal mesoporous material, which can be indicative that these supports consist of well-ordered channels. [11, 17, 21, 26] The structure of the supports was maintained after $PW_{11}Zn$ immobilization, since the same pattern of three peaks can be observed in the diffractograms of composite materials.

The amine-functionalized PMOs morphology was assessed by SEM (Figure 8.4 A and B). The SEM images of the support materials reveal ropelike structures with approximately 450 nm diameter and with the majority expanding to several micrometers in length. [17, 21] The SEM images of $PW_{11}Zn$ composites (Figure 8.4 C and D) present the same type of structures as the aptesPMOs supports indicating that its morphology was maintained after the immobilization of $PW_{11}Zn$. The EDS spectra of the $PW_{11}Zn$ composites confirm the presence of the $PW_{11}Zn$ by revealing the presence of W. The presence of $PW_{11}Zn$ in the composites was also confirmed by elemental analysis, with a loading of $PW_{11}Zn$ of 0.062 mmol and 0.054 mmol per g of material for $PW_{11}Zn@apt\text{es}PMOE$ and $PW_{11}Zn@apt\text{es}PMOB$, respectively.

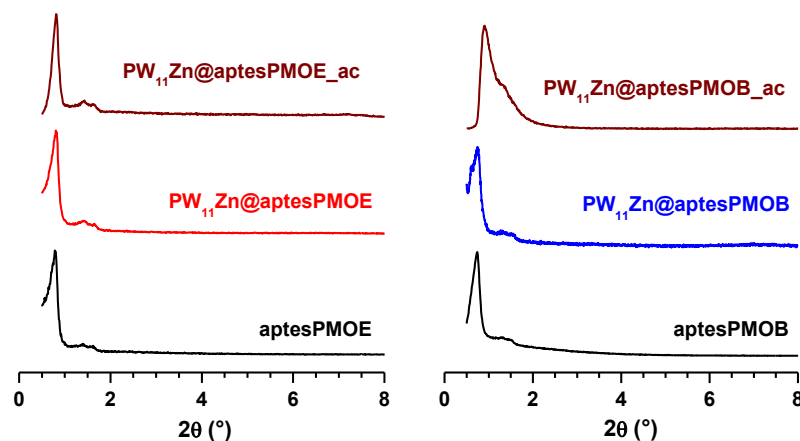


Figure 8.3 – Powder XRD patterns of the amine-functionalized supports and the resulting $PW_{11}Zn$ composites (ac – after catalysis).

The N_2 adsorption-desorption isotherms of the amine-functionalized PMOs and their analogue composites (Figure 8.5) are of type IV with a H1-type hysteresis loop in the range 0.4-0.8 of relative pressure, which is typical of mesoporous materials. [17, 26] The textural parameters presented in Table 8.1 show that the surface area (S_{BET}) and

pore volume (V_p) are smaller for the composites, which supports the presence of $PW_{11}Zn$ within the aptesPMOs channels.

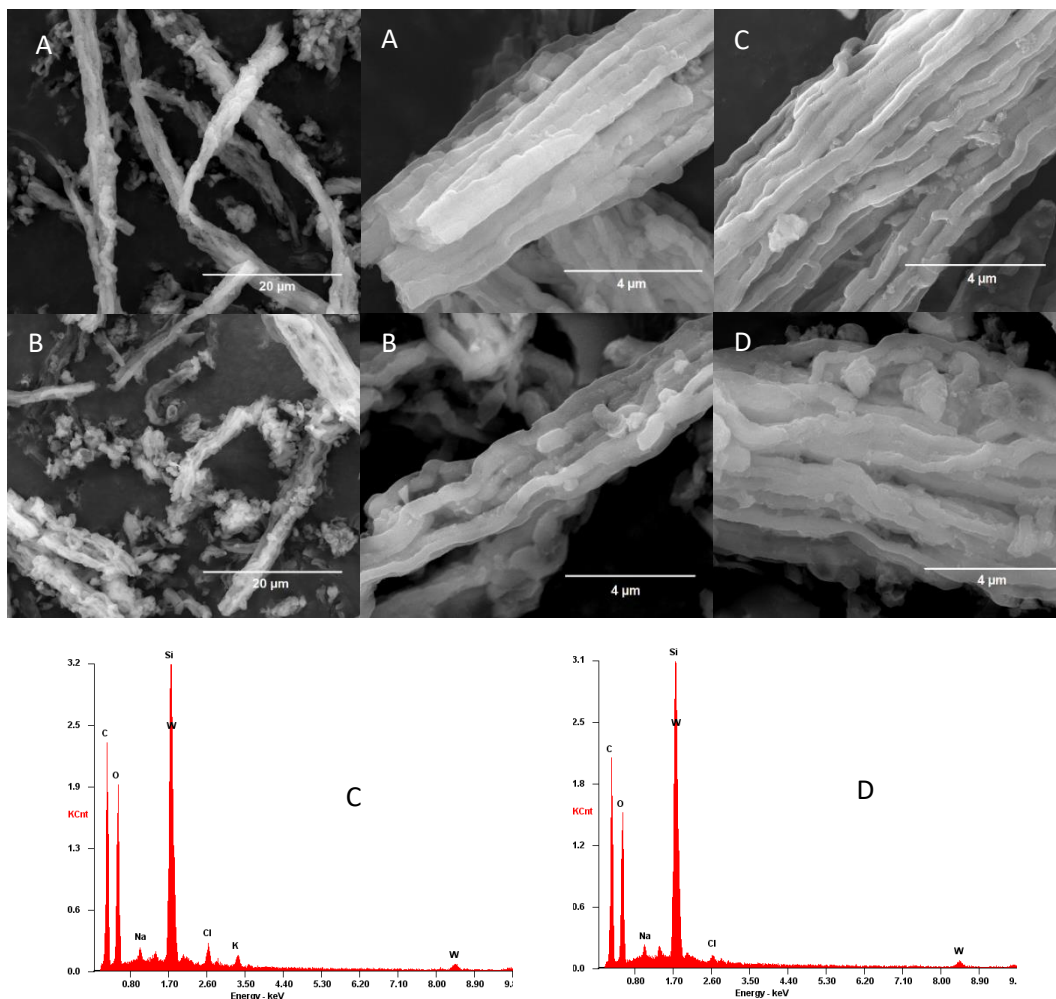


Figure 8.4 –SEM images of the amine-functionalized PMOs and the resulting $PW_{11}Zn$ composites (A - aptesPMOE; B - aptesPMOB; C - $PW_{11}Zn$ @aptesPMOE; D - $PW_{11}Zn$ @aptesPMOB. EDS spectra of the $PW_{11}Zn$ composites.

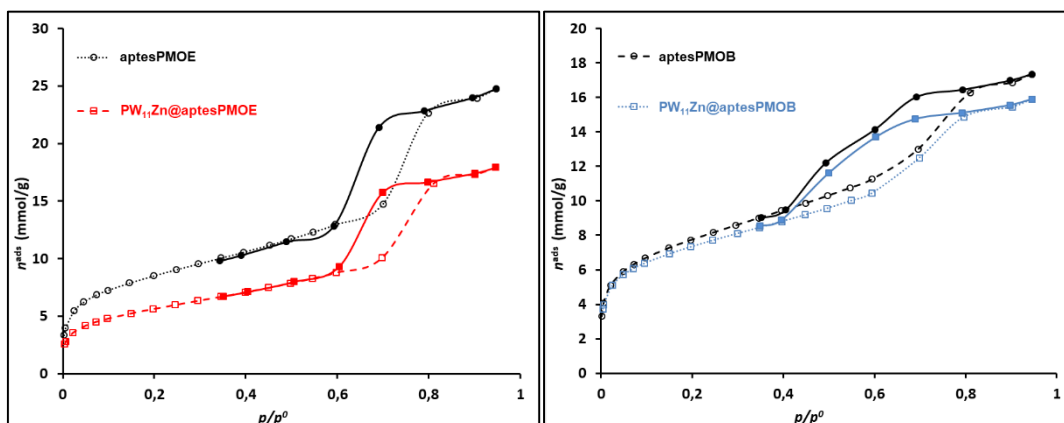


Figure 8.5 – N_2 adsorption-desorption isotherms of the aptesPMOE support and $PW_{11}Zn$ @aptesPMOE composite (left); aptesPMOB support and $PW_{11}Zn$ @aptesPMOB composite (right).

Table 8.1 – Textural parameters of the amine-functionalized supports and the resulting PW₁₁Zn composites.

	S_{BET}	V_p
	(m ² g ⁻¹)	(cm ³ g ⁻¹)
apt_{es}PMOE	692	0,86
PW₁₁Zn@apt_{es}PMOE	460	0,62
apt_{es}PMOB	632	0,60
PW₁₁Zn@apt_{es}PMOB	596	0,55

The presence and integrity of the PW₁₁Zn was also investigated by ³¹P MAS NMR before and after its immobilization in the amine-functionalized silica supports (Figure 8.6). A single peak can be observed at -12.12 ppm for PW₁₁Zn@apt_{es}PMOE and a main peak at -12.22 ppm in the case of PW₁₁Zn@apt_{es}PMOB. The non-immobilized PW₁₁Zn presents a single peak at -13.62 ppm (Figure 8.6). The difference of chemical shift observed between the non-immobilized PW₁₁Zn and the composites may be attributed to the interaction of PW₁₁Zn with the PMO supports. This interaction may occur by a coordination of the amine functional group, present in the surface of PMO supports, to the zinc metal center from PW₁₁Zn. These results are indicative of the maintenance of the PW₁₁Zn structure after its immobilization in the silica materials.

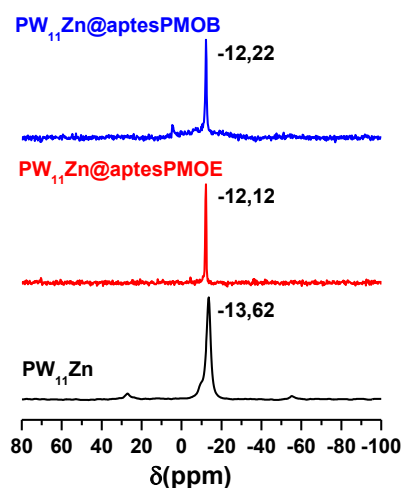


Figure 8.6 – ³¹P MAS NMR spectra of PW₁₁Zn and PW₁₁Zn@apt_{es}PMOE and PW₁₁Zn@apt_{es}PMOB composites.

The amine-functionalized supports and the PW₁₁Zn composites were also analyzed by ¹³C MAS NMR. The ¹³C MAS NMR spectrum of apt_{es}PMOE support (Figure

8.7 - left) presents a strong peak at 5.35 ppm corresponding to the bridging ethylene group. [11, 19, 27] It also exhibits three peaks located at 43.46, 22.26 and 10.60 ppm that correspond to the C3, C2 and C1 carbon atoms of the amine group, respectively, $\text{Si-}^1\text{CH}_2\text{-}^2\text{CH}_2\text{-}^3\text{CH}_2\text{-NH}_2$. [11, 28] The peak located at 58.8 ppm can be ascribed to the ethoxy groups generated during the ethanol extraction process. [11, 17] The $\text{PW}_{11}\text{Zn@aptesPMOE}$ presents a ^{13}C MAS NMR spectrum similar to that of the support PMOE, again indicating the preservation of the support structure after PW_{11}Zn immobilization.

The ^{13}C MAS NMR spectrum of aptesPMOB (Figure 8.7-right) displays a predominant peak at 134.14 ppm corresponding to the superposition of unsolved signals from carbons in the phenylene groups. [29] This signal was also accompanied by spinning sidebands (indicated with an asterisk) due to significant chemical shift anisotropy of the ^{13}C atoms in the benzene ring. [29] The peaks located at 43.49, 21.83 and 11.07 ppm correspond to the C3, C2 and C1 carbon atoms of the amine group. [11, 28] The $\text{PW}_{11}\text{Zn@aptesPMOB}$ composite also presents a profile similar to that of its silica support.

The ^{29}Si spectrum of the aptesPMOE support (Figure 8.8) presents the characteristic T^n signals attributed to $[\text{C-Si}(\text{OSi})_2(\text{OH})]$ (T^2 at -60.58 ppm) and $[\text{C-Si}(\text{OSi})_3]$ (T^3 at -66.92 ppm). [22] Some Q^n signals between -100 and -115 ppm also appear in the spectrum, which suggest that some cleavage of the Si-C bond occurred during the synthesis and surfactant extraction process. [17, 22]

The ^{29}Si MAS NMR spectrum of the benzene-bridged PMO (Figure 8.8) exhibits three T^n signals which can be assigned to the following Si species covalently bonded to the carbon atoms: T^1 $[\text{C-Si}(\text{OSi})(\text{OH})_2]$, $\delta = -62.98$, T^2 $[\text{C-Si}(\text{OSi})_2(\text{OH})]$, $\delta = -72.91$ and T^3 $[\text{C-Si}(\text{OSi})_3]$, $\delta = -81.23$. [30] Some cleavage of the Si-C bond could also be detected by the presence of Q signals.

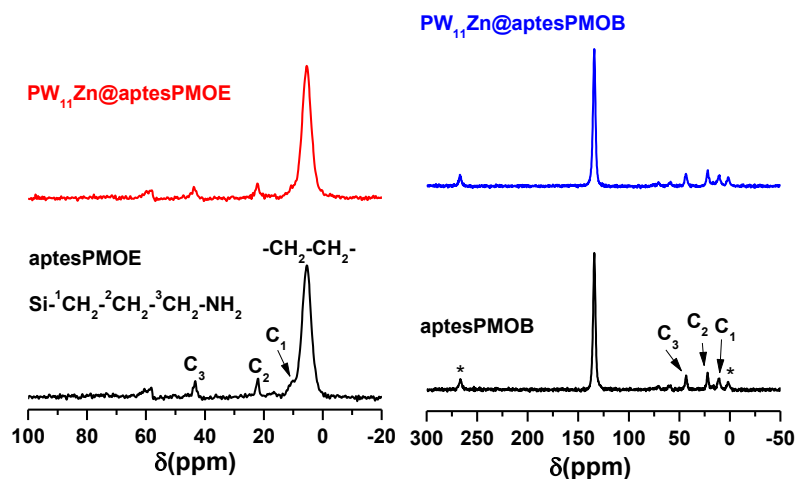


Figure 8.7 ^{13}C MAS NMR spectra of the aptesPMOE support and $\text{PW}_{11}\text{Zn@aptesPMOE}$ composite (left); aptesPMOB support and $\text{PW}_{11}\text{Zn@aptesPMOB}$ composite (right).

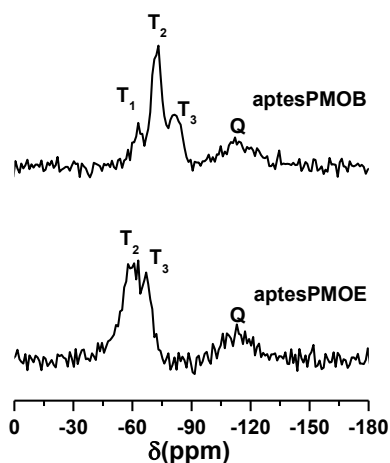


Figure 8.8 ^{29}Si MAS NMR spectra of the amine-functionalized supports aptesPMOE and aptesPMOB.

8.2.2. Oxidative desulfurization process using model diesel

The composites $\text{PW}_{11}\text{Zn@aptesPMOE}$ and $\text{PW}_{11}\text{Zn@aptesPMOB}$ were tested as heterogeneous catalysts in the desulfurization of model diesel B. Two different systems were used in the desulfurization tests: a biphasic extractive and catalytic oxidative desulfurization system (ECODS) and a solvent-free catalytic oxidative desulfurization system (CODS). The biphasic ECODS system was composed by a mixture of equal amounts of model diesel and extraction solvent (acetonitrile) in the presence of $3\ \mu\text{mol}$ of active catalytic center PW_{11}Zn and using a $\text{H}_2\text{O}_2/\text{S}$ ratio of 8, at 70°C . This system was processed in two steps: initial extraction and catalytic stage. During the initial extraction, non-oxidized sulfur-compounds were transferred to the extraction

solvent phase until the distribution of sulfur compounds between the two phases achieved the equilibrium (10 min). After this time, the oxidant was added to the system initiating the catalytic stage. The solvent-free ECODS system was also studied using 3 μmol of active catalytic center PW_{11}Zn and a $\text{H}_2\text{O}_2/\text{S}$ ratio of 4, at 70 °C. A 1:1 liquid-liquid extraction was performed, after complete oxidation of sulfur-compounds.

Figure 8.9 presents the desulfurization results using the biphasic ECODS system catalyzed by both composites $\text{PW}_{11}\text{Zn}@ \text{aptesPMOE}$ and $\text{PW}_{11}\text{Zn}@ \text{aptesPMOB}$. It can be observed that the initial extraction and also the sulfur compounds oxidation follows the same order as has been previously described for POM-catalyzed ECODS systems with H_2O_2 (Chapters 4, 5, 6 and 7). [31-35] The $\text{PW}_{11}\text{Zn}@ \text{aptesPMOE}$ catalyst presents slightly higher desulfurization efficiency than the $\text{PW}_{11}\text{Zn}@ \text{aptesPMOB}$, during the first 120 min of oxidation (94.8% for $\text{PW}_{11}\text{Zn}@ \text{aptesPMOE}$ and 94.6% for $\text{PW}_{11}\text{Zn}@ \text{aptesPMOB}$). However, after this time, similar desulfurization efficiency was found for both composites. After 240 min, complete desulfurization was achieved using both composites. The kinetic desulfurization profiles and leaching tests are displayed in Figure 8.9 –left. To perform the leaching test, the solid catalyst was removed by hot filtration after 30 and 15 min of oxidant addition using $\text{PW}_{11}\text{Zn}@ \text{aptesPMOE}$ and $\text{PW}_{11}\text{Zn}@ \text{aptesPMOB}$ catalysts, respectively. The resultant solution was periodically analyzed until 250 min of ECODS process. The leaching results indicate that both composites behave as solid and heterogeneous catalysts, since the oxidation of sulfur practically stops after the solid catalyst removal.

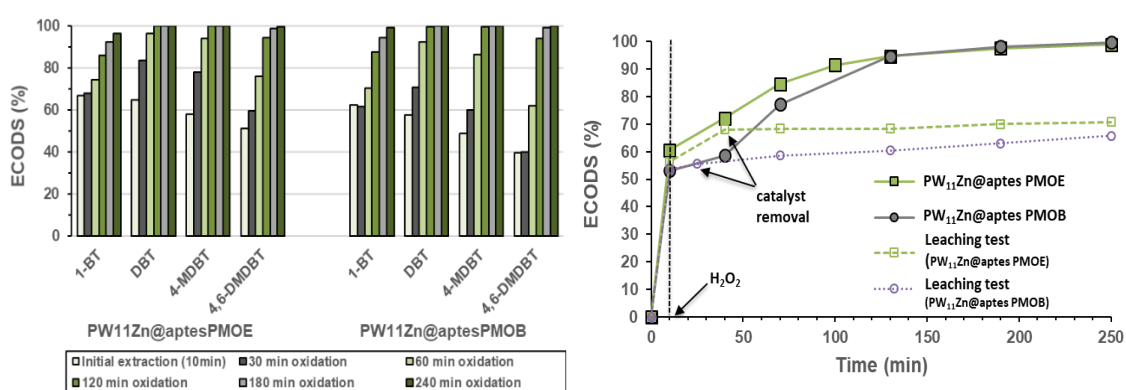


Figure 8.9 – Desulfurization of each sulfur compound present in the model diesel (left) and kinetic desulfurization profile (right) using the biphasic ECODS system (1:1 model diesel/MeCN extraction solvent; ratio $\text{H}_2\text{O}_2/\text{S}=8$, at 70°C) and 3 μmol of PW_{11}Zn active catalytic center present in $\text{PW}_{11}\text{Zn}@ \text{aptesPMOE}$ and $\text{PW}_{11}\text{Zn}@ \text{aptesPMOB}$.

The desulfurization results obtained in the presence of $PW_{11}Zn$ composites, using solvent-free CODS system are presented in Figure 8.10. In this case, the main activity difference between composites was observed after 10 min of H_2O_2 addition, where $PW_{11}Zn@aptesPMOB$ presents higher oxidative desulfurization (77.8%) than $PW_{11}Zn@aptesPMOE$ (32.8%). After 30 min, complete oxidation for DBT, 4-MDBT and 4,6-DMDBT was observed using both $PW_{11}Zn$ composites. After 60 min, ultra-low levels of unoxidized 1-BT was achieved (9 ppm for $PW_{11}Zn@aptesPMOB$ and 1ppm for $PW_{11}Zn@aptesPMOE$) and complete sulfur oxidation was observed after 90 min for both composites. Therefore, the CODS system presents higher desulfurization efficiency than the ECODS system, using a lower ratio of H_2O_2/S (4 for CODS and 8 for ECODS) as previously found in Chapters 4, 5 and 7.

In comparison with the monolacunary $PW_{11}@TMA-PMOE$ catalyst presented in Chapter 7, the $PW_{11}Zn$ based PMOs catalysts present higher desulfurization efficiency, since practically total conversion was achieved, after 60 min. Using $PW_{11}@TMA-PMOE$, efficiency of 96.9% was obtained for the same reaction time. This result may indicate that the occupancy of the lacuna by a zinc metal center contributed to increase catalyst activity and in this case the structure of the POM has an important influence in the desulfurization efficiency.

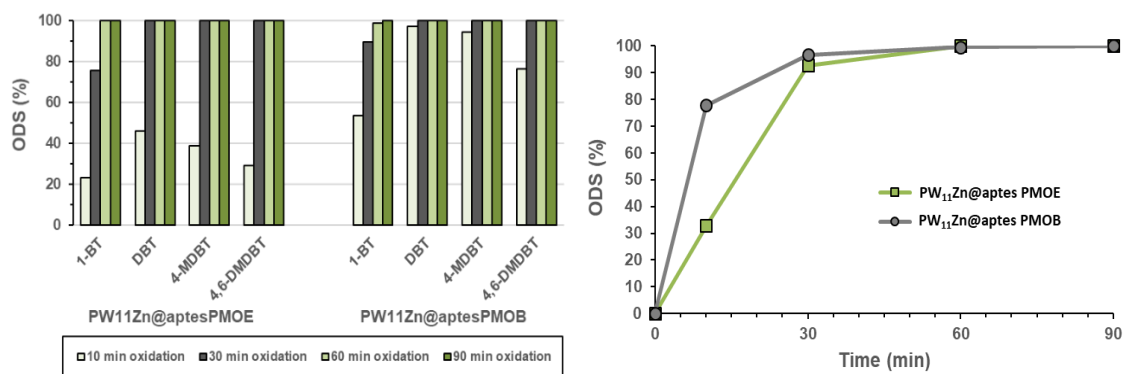


Figure 8.10 – Oxidative desulfurization of various sulfur compounds present in model diesel (left) and total oxidative desulfurization (right) using the solvent-free CODS system (ratio $H_2O_2/S=4$ at $70^\circ C$), using as catalysts: $PW_{11}Zn@aptesPMOE$ and $PW_{11}Zn@aptesPMOB$, containing $3\ \mu mol$ of active $PW_{11}Zn$ center.

8.2.3. Catalysts recyclability

The recycle capacity of both heterogeneous catalysts was tested in the most efficient system - solvent-free CODS system. After each CODS cycle, the solid catalyst was separated from the oxidized model diesel by centrifugation, washed with ethanol

and dried at room temperature. The recovered catalyst was then used in a new CODS cycle, maintaining the experimental conditions.

In Figure 8.11 is presented the total oxidative desulfurization obtained for eight consecutive cycles at the end of 30 min and 60 min using $PW_{11}Zn@aptesPMOE$ catalyst. After 60 min, the results reveal similar catalytic performances along the cycles and without apparent loss of catalytic activity. Moreover, the catalyst presents to increase its activity after the third cycle, achieving total oxidative desulfurization after 30 min reaction after the 3rd cycle. This behavior may be associated with the mechanism involved in the oxidation of the sulfur compounds, that corresponds to the formation of active peroxo species, as already presented in Chapters 2 and 5. The formed active species during the first cycles are already present in the catalyst for the consecutive cycles, what contributes for the enhancement of its catalytic efficiency, especially during the first 30 min of reaction. [12, 14, 36]

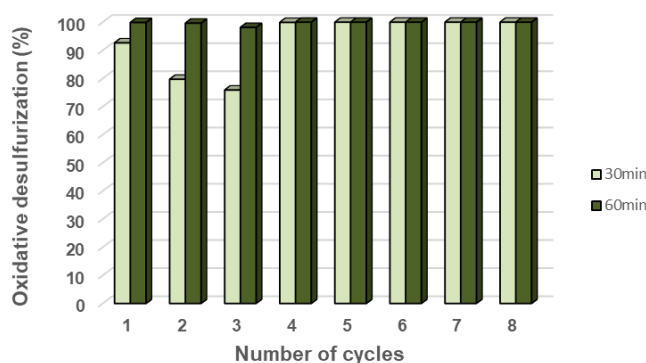


Figure 8.11 – Oxidative desulfurization results obtained for eight CODS cycles after 30 min and 60 min, catalyzed by $PW_{11}Zn@aptesPMOE$ composite (containing 3 μmol of $PW_{11}Zn$), using the solvent-free system and $H_2O_2/S=4$, at 70°C.

The recyclability of $PW_{11}Zn@aptesPMOB$ catalyst was also tested. Figure 8.12 presents the oxidative desulfurization results for ten consecutive cycles after 60 min reaction. The catalyst also maintains the desulfurization efficiency over cycles without apparent loss of catalytic activity.

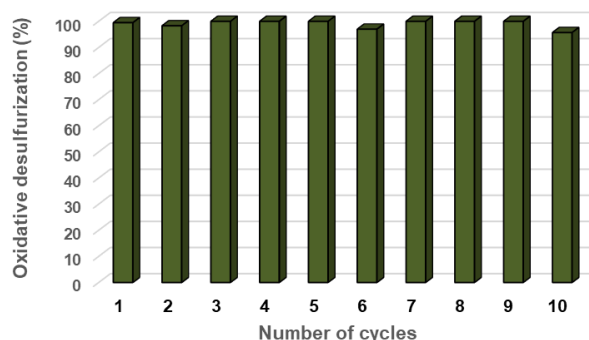


Figure 8.12 – Oxidative desulfurization results obtained for ten CODS cycles after 60 min, catalyzed by $PW_{11}Zn@aptesPMOB$ composite (containing $3\ \mu\text{mol}$ of $PW_{11}Zn$) using the solvent-free system and $H_2O_2/S=4$, at 70°C .

8.2.4. Catalysts stability

After catalytic use, the robustness and stability of the solid catalysts was evaluated using several characterization techniques. The ICP-OES of $PW_{11}Zn@aptesPMOE$ after catalysis reveals that the leaching of POM was negligible since presents similar Si/W (molar) ratio before (0.90) and after catalysis (0.97). On the other hand, the ICP-OES analysis performed with used $PW_{11}Zn@aptesPMOB$ catalyst presents a Si/W (molar) ratio before catalytic use of 1.04 and after catalysis 0.70. This indicates the occurrence of some $PW_{11}Zn$ loss from the solid catalyst during catalytic use.

The powder XRD patterns of $PW_{11}Zn@aptesPMOE$ before and after catalytic use (Figure 8.3-left) displays similar profiles, regarding the position and relative intensity of the diffraction peaks. Contrastingly, the $PW_{11}Zn@aptesPMOB$ composite after catalytic use (Figure 8.3-right) presents a broad peak indexed to the (100) reflection that might be due to a small loss of crystallinity during the ODS process.

The vibrational spectra of both composites, before and after catalytic use, are similar (Figure 8.1 and 8.2), since the typical bands assigned to the vibrational modes of the support material PMO and the $PW_{11}Zn$ can be identified after catalytic use. The RAMAN spectra display the bands attributed to the composites before catalytic use. However, additional bands were found that can be related to the presence of model diesel sulfur components, as previously reported in the literature and presented in the previous Chapters 3, 4 and 6. [36, 37]

The SEM images and EDS spectra (Z1 and Z3) displayed in Figure 8.13 also shows the presence of sulfur aggregates in the presence of the composites after catalytic

use. These SEM images also reveal that the morphology of $PW_{11}Zn@aptesPMOE$ and $PW_{11}Zn@aptesPMOB$ was maintained after the desulfurization process, since they present the same rope like structures as the composites before catalytic use. The EDS analysis (Z2 and Z4) also reveals the presence of $PW_{11}Zn$ by the identification of the W and Zn elements.

The ^{31}P MAS NMR spectra of the zinc mono-substituted phosphotungstate catalysts, before and after catalytic use are displayed in Figure 8.14. The ^{31}P MAS NMR spectrum of the $PW_{11}Zn@aptesPMOE$ composite after its catalytic use, reveals two peaks at -12.15 ppm and -15.17 ppm. The first peak is similar to the as-prepared composite assigned to the $PW_{11}Zn$ structure. The second peak might be related to the interaction of $PW_{11}Zn$ with the oxidant creating a structural change on the Keggin unit by the formation of a new active specie as a peroxopolyoxotungstate. The stability of $PW_{11}Zn@aptesPMOB$ was also studied by ^{31}P MAS NMR after catalytic use. The $PW_{11}Zn@aptesPMOB$ spectrum presents a single peak at -12.45 ppm that can be assigned to the $PW_{11}Zn$ structure.

Overall, the characterization techniques used suggest a higher robustness of the solid $PW_{11}Zn@aptesPMOE$ than the $PW_{11}Zn@aptesPMOB$, mainly due to the occurrence of $PW_{11}Zn$ leaching from the PMOB surface, which may be related to the nature of the PMOB surface and the presence of benzene groups.

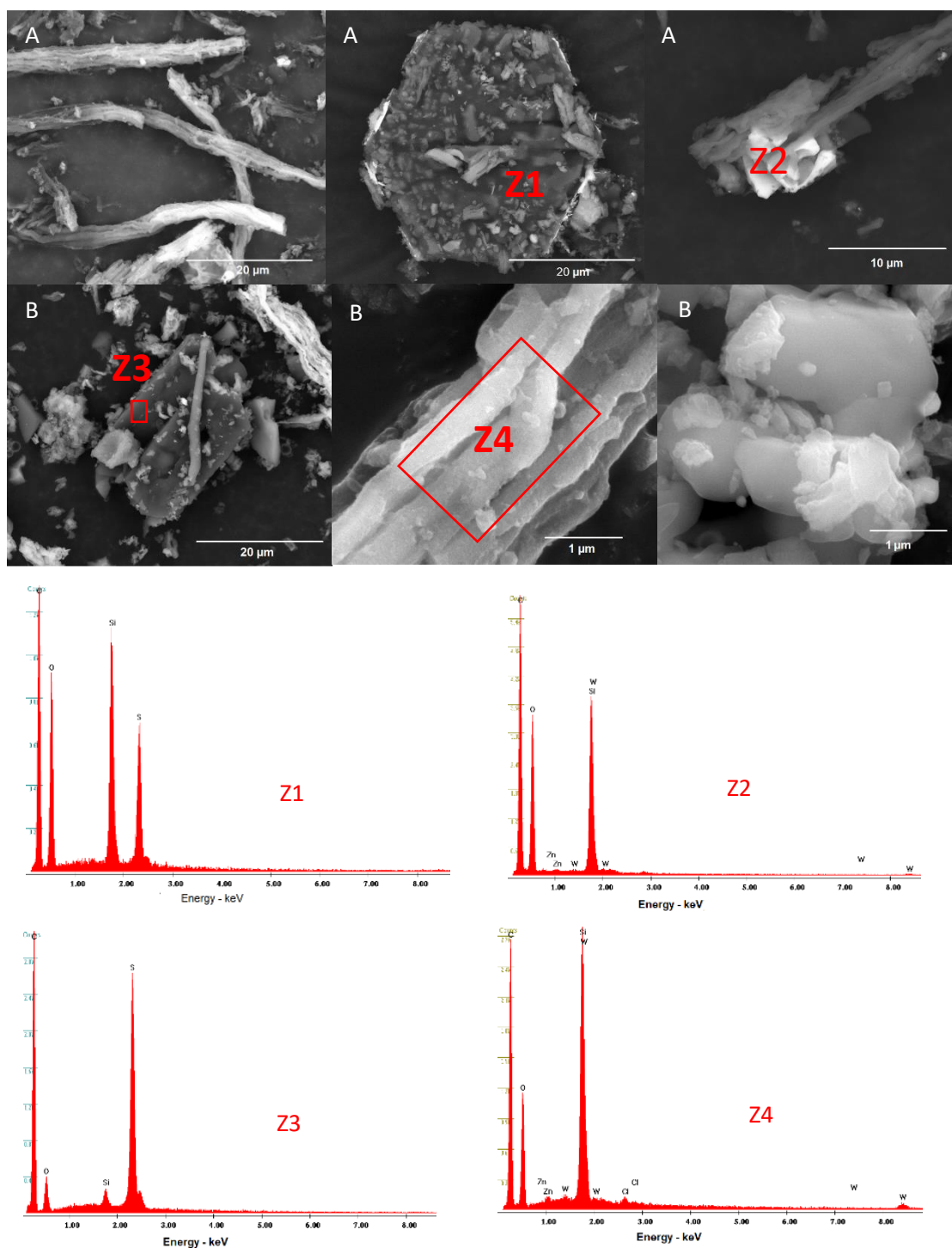


Figure 8.13 - SEM images and EDS spectra after catalytic use of A - $PW_{11}Zn@aptesPMOE$ composite; B - $PW_{11}Zn@aptesPMOB$ composite

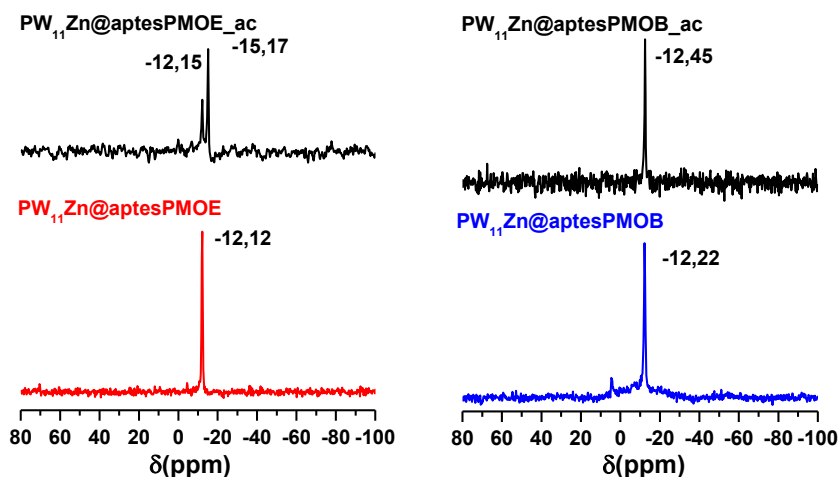


Figure 8.14 - ^{31}P MAS spectra of the $\text{PW}_{11}\text{Zn@aptPMOE}$ composite (left) and $\text{PW}_{11}\text{Zn@aptPMOB}$ (right) before and after catalytic use (ac – after catalysis).

8.2.5. Oxidative desulfurization process using untreated diesel

Since the $\text{PW}_{11}\text{Zn@aptPMOE}$ catalyst presented higher desulfurization efficiency and also higher stability than $\text{PW}_{11}\text{Zn@aptPMOB}$ composite, the first was used for oxidative desulfurization studies using an untreated diesel with a concentration of 1335 ppm of sulfur with a high diversity of sulfur compounds as presented in Chapter 4. These studies were performed using biphasic ECODS system, during 120 min of reaction, using $\text{MeCN/Diesel} = 1:1$; $\text{H}_2\text{O}_2/\text{S} = 8$, at 70 °C. After the oxidative catalytic treatment, the diesel samples were separated from the catalyst by centrifugation and further treated with a 1:1 liquid-liquid extraction with MeCN, during 10 min of stirring at room temperature. Desulfurization results obtained for three consecutive cycles are displayed in figure 8.15. After one ECODS cycle the desulfurization efficiency reached 75.9%, which was maintained after three consecutive cycles.

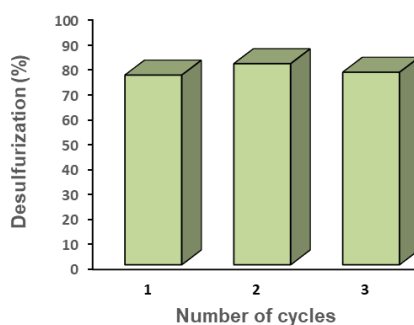


Figure 8.15 - Desulfurization results for the treatment of a real untreated diesel obtained after 2 h, performed for three consecutive ECODS cycles, catalyzed by $\text{PW}_{11}\text{Zn@aptPMOE}$, at 70 °C and using $\text{H}_2\text{O}_2/\text{S}=8$.

8.3 Conclusion

The zinc mono-substituted $PW_{11}Zn$ was immobilized via impregnation method in two different functionalized PMOs: an ethane-bridge (PMOE) and a benzene bridge (PMOB) PMOs functionalized with aminopropyl (apt)es). The supports PMOE and PMOB were prepared through co-condensation process. The prepared composites ($PW_{11}Zn@aptPMOE$ and $PW_{11}Zn@aptPMOB$) were tested as oxidative catalysts for desulfurization of a multicomponent model diesel, using two different systems: a biphasic ECODS system and a solvent-free CODS system.

The best results were obtained with the solvent-free CODS system, probably promoted by the less hydrophilic nature of the support material. Ultra-low levels of sulfur compounds were obtained after 60 min at 70 °C, in the presence of both catalysts and using a low ratio of $H_2O_2/S = 4$.

The recyclability of catalysts was verified for several consecutive cycles. Moreover, the desulfurization efficiency of $PW_{11}Zn@aptPMOE$ increased after the third ECODS cycle, obtaining complete desulfurization after only 30 min. The stability of $PW_{11}Zn@aptPMOE$ and $PW_{11}Zn@aptPMOB$ catalysts was investigated by various characterization techniques. The $PW_{11}Zn@aptPMOE$ presents higher stability than the $PW_{11}Zn@aptPMOB$, since $PW_{11}Zn$ leaching occurred using a benzene bridge PMO.

Desulfurization of an untreated diesel was also performed using the active and robust $PW_{11}Zn@aptPMOE$ catalyst under the biphasic system ($H_2O_2/S = 8$, at 70 °C). For the first ECODS cycle 75.9% of desulfurization was obtained and this catalytic activity was maintained over consecutive cycles.

8.4. Experimental section

8.4.1. Materials and Methods

The following chemicals and reagents were purchased from chemical suppliers and used without further purification: sodium tungstate dihydrate (Aldrich), sodium hydrogen phosphate dihydrate (Aldrich), tetra-n-butylammonium bromide (Merck), hydrochloric acid (Fisher Chemicals), Pluronic P123 (Aldrich), (3-aminopropyl)triethoxysilane (apt)es, Aldrich), 1,2-bis(triethoxysilyl)ethane (BTEE, 96%, Aldrich), 1,4-bis(triethoxysilyl)benzene (BTBE, 96%, Aldrich), potassium chloride

(Aldrich), ethanol (Aga), 1-benzothiophene (1-BT, Fluka), dibenzothiophene (DBT, Aldrich), 4-methyldibenzothiophene (4-MDBT, Aldrich), 4,6-dimethyldibenzothiophene (4,6-DMDBT, Alfa Aesar), *n*-octane (Aldrich), acetonitrile (MeCN, Fisher Chemical) and hydrogen peroxide (30%, Aldrich).

Elemental analyses for C, H and N elements were performed in a Leco CHNS-932 instrument, and Si, W and P by ICP-OES on a Perkin-Elmer Optima 4300 DV instrument at the University of Santiago de Compostela.

FT-IR spectra were obtained on a Jasco 460 Plus spectrometer using KBr pellets.

The FT-Raman spectra were recorded in Aveiro University using a RFS-100 Bruker FT-spectrometer equipped with a Nd:YAG laser with an excitation wavelength of 1064 nm and the laser power set to 350 mW.

Powder X-ray diffraction (XRD) patterns were obtained at room temperature in Bragg-Brentano para-focusing geometry using a Rigaku Smartlab diffractometer, equipped with a D/tex Ultra 250 detector and using Cu K- α radiation ($K\alpha_1$ wavelength 1.54059 Å), 45 kV, 200 mA in continuous mode, step 0.01°, speed 0.6°/min in the $0.5 \leq 2\theta \leq 10^\circ$ range.

^{31}P NMR spectra were collected for liquid solutions using a Bruker Avance III 400 spectrometer and chemical shifts are given with respect to external 85% H_3PO_4 .

Solid state ^{13}C , ^{31}P and ^{29}Si MAS NMR spectra were acquired with a Bruker AVANCE III 300 spectrometer (7 T) operating at 75 MHz (^{13}C), 121 MHz (^{31}P) and 60 MHz (^{29}Si), respectively, equipped with a BBO probe head. The samples were spun at the magic angle at a frequency of 5 kHz in 4 mm-diameter rotors at room temperature. The ^{13}C MAS NMR experiments were acquired with proton cross polarization (CP MAS) with a contact time of 1.2 ms, and the recycle delay was 2.0 s. The ^{29}Si MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 4.5 μs at a power of 40 W, and a relaxation delay of 10.0 s. The ^{29}Si CP MAS NMR experiments were acquired with a contact time of 1.2 ms, and the recycle delay was 5.0 s. The ^{31}P MAS NMR spectra were obtained by a single pulse sequence with a 90° pulse of 5.0 μs at a power of 20 W, and a relaxation delay of 2.0 s. Solid state ^{13}C , ^{31}P and ^{29}Si MAS NMR spectra were performed by Professor Pedro Almeida at CENIMAT/I3N, Faculdade de Ciências e Tecnologia da Universidade Nova de Lisboa.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at “Centro de Materiais da Universidade do Porto” (CEMUP, Porto, Portugal) using a high-resolution (Schottky) scanning electron

microscope with X-ray microanalysis and electron backscattered diffraction analysis Quanta 400 FEG ESEM/EDAX Genesis X4 M. The samples were studied as powders and were coated with an Au/Pd thin film by sputtering using the SPI Module Sputter Coater equipment.

The textural characterization was obtained from physical adsorption of nitrogen at $-196\text{ }^{\circ}\text{C}$, using a Quantachrome NOVA 2200e instrument at Centro de Química e Bioquímica, Faculdade de Ciências da Universidade de Lisboa by Professor João Pires. Samples were degassed at $120\text{ }^{\circ}\text{C}$ for at least 5 h prior to the measurements. The BET surface area (S_{BET}) was calculated by using the relative pressure data in the 0.05–0.3 range. The total pore volume (V_{p}) was evaluated on the basis of the amount adsorbed at a relative pressure of about 0.95.

GC-FID was carried out in a Varian CP-3380 chromatography to monitor the desulfurization multicomponent model diesel experiments. Hydrogen was used as the carrier gas (55 cm s^{-1}) and fused silica Supelco capillary columns SPB-5 (30 m x 0.25 mm i.d.; 25 μm film thickness) were used.

Sulfur content in real diesel was measured by X-ray Fluorescence Spectrometry, using an Spectrace 450 spectrometer at the University of Santiago de Compostela.

8.4.2. Preparation of materials

8.4.2.1. Synthesis of zinc mono-substituted phosphotungstate

The tetra-*n*-butylammonium (TBA, $(\text{C}_4\text{H}_9)_4\text{N}$) salt of the zinc mono-substituted phosphotungstate $[\text{PW}_{11}\text{Zn}(\text{H}_2\text{O})\text{O}_{39}]^{5-}$ (**PW₁₁Zn**) was prepared as described in Chapter 2 section 2.4.2. [25, 38, 39]

8.4.2.2. **PW₁₁Zn@aptesPMOs** composites

The ethylene-bridged and benzene-bridge apes-functionalized PMOs (aptesPMOE and aptesPMOB, respectively) were prepared following a previously reported procedure as described in Chapter 7. [11, 17] Briefly, pluronic P123 (0.096 mmol) and KCl (47 mmol) were dissolved in aqueous HCl (1.6 M; 29 mmol) under vigorous stirring at $40\text{ }^{\circ}\text{C}$ during 4 h. Then, BTEE or BTEB (3,20 mmol or 2.84 mmol, respectively) and apes (0,35 mmol or 0.71 mmol, respectively) were added to the solution and the mixture was further stirred for 20 h at $40\text{ }^{\circ}\text{C}$. The mixture was then

transferred to an autoclave and heated at 100 °C for 24 h. The solid was recovered by filtration and dried in a desiccator under silica gel. The extracting process of the copolymer P123 was performed by refluxing the sample in an acidic ethanol solution for 24 h. For each gram of material, 200 mL of ethanol and 1.5 g of HCl were used.

The $PW_{11}Zn@aptesPMOs$ composites were prepared through impregnation method as described in Chapter 3.

aptesPMOE: Anal. Found (%): N, 0.75; C, 16.96; H, 4.46; Selected FT-IR (cm^{-1}): 3434 (vs), 2923 (m), 2854 (w), 2360 (w), 2341 (w), 1635 (m), 1457 (w), 1411 (m), 1270 (m), 1159 (s), 1095 (sh), 1031 (vs), 906 (s), 771 (m), 696 (m), 441 (s). FT-Raman (cm^{-1}): 2968 (sh), 2891 (vs), 2805 (w), 1455 (m), 1415 (s), 1271 (m), 993 (m), 509 (s).

aptesPMOB: Anal. Found (%): N, 0.62; C, 37.35; H, 4.89; Selected FT-IR (cm^{-1}): 3434 (vs), 3062 (w), 2360 (w), 2341 (w), 1637 (s), 1500 (w), 1384 (m), 1155 (vs), 1058 (vs), 1022 (sh), 916 (s), 809 (m), 769 (w), 659 (m), 524 (vs). Selected FT-Raman (cm^{-1}): 3043 (vs), 2974 (m), 2929 (m), 2897 (w), 1596 (vs), 1530 (m), 1455 (m), 1413 (w), 1204 (w), 1105 (vs), 1045 (w), 943 (w), 779 (s), 633 (s), 579 (s).

$PW_{11}Zn@aptesPMOE$: Anal. Found (%) W, 12.46; Si, 1,71; loading of POM: 0.062 mmol per 1g, Si/W (molar) = 0,90; Selected FT-IR (cm^{-1}): 3446 (vs), 2975 (w), 2910 (m), 2360 (m), 2341 (w) 1635 (m), 1488 (w), 1417 (m), 1270 (m), 1159 (s), 1089 (sh), 1033 (vs), 954 (w), 900 (s), 809 (w), 765 (m), 698 (m), 441 (s). Selected FT-Raman (cm^{-1}): 2967 (sh), 2891 (vs), 2805 (w), 1455 (m), 1411 (s), 1272 (m), 986 (s), 973 (s), 805 (w), 517 (s).

$PW_{11}Zn@aptesPMOB$: Anal. Found (%) W, 10.90; Si, 1,73; loading of POM: 0.054 mmol per 1g; Selected FT-IR (cm^{-1}): 3442 (vs), 3062 (w), 2360 (m), 2341 (w), 1635 (m), 1500 (w), 1384 (m), 1155 (vs), 1089 (vs), 1052 (vs), 1022 (sh), 948 (w), 902 (s), 809 (m), 763 (w), 719 (w), 669 (w), 659 (w), 524 (vs). Selected FT-Raman (cm^{-1}): 3043 (vs), 2974 (m), 2928 (m), 1596 (vs), 1530 (m), 1451 (m), 1309 (m), 1203 (m), 1104 (vs), 987 (s), 972 (s), 779 (s), 633 (s), 579 (s).

8.4.3. Oxidative desulfurization processes using model diesel

The oxidative desulfurization experiments were performed using the model diesel B, using either a solvent-free (CODS) or a biphasic (ECODS) systems. In a typical ECODS experiment, 1:1 model diesel/MeCN (750 μ L mL of each) were added to the catalytic composite, containing an equivalent of 3 μ mol of $PW_{11}Zn$. The resulting mixture

was stirred for 10 min and an aliquot of the upper phase oil was taken. The catalytic step of the process was initiated by the addition of aqueous hydrogen peroxide 30% (40 μL ; $\text{H}_2\text{O}_2/\text{S}$ molar = 8). The CODS experiments were performed using the model diesel (750 μL), the composite containing 3 μmol of active center and H_2O_2 as oxidant ($\text{H}_2\text{O}_2/\text{S}$ molar = 4). A final liquid-liquid extraction was performed to remove the oxidized sulfur compounds from diesel, using MeCN as extraction solvent. The sulfur content in the model diesel was periodically quantified by GC analysis using tetradecane as standard. At the end of oxidation step, centrifugation was carried out to separate and recover the solid catalyst, which was washed with ethanol and dried in a desiccator over silica gel. For the recycling studies, the recovered catalyst was reused in new desulfurization cycles maintaining the reaction conditions.

8.4.3. oxidative desulfurization process using untreated diesel

An untreated diesel sample supplied by CEPESA (containing 1335 ppm of sulfur) was desulfurized using the $\text{PW}_{11}\text{Zn}@ \text{aptesPMOE}$ catalyst under the ECODS conditions. The untreated diesel was mixed with the heterogeneous composite (containing 3 μmol of PW_{11}Zn) in MeCN and with a $\text{H}_2\text{O}_2/\text{S}$ ratio of 8. The mixture was heated at 70 $^\circ\text{C}$ for 2 h. After this time, the diesel was removed from the mixture and washed with equal volume of MeCN for 10 min and separated by decantation. Recycling tests were also performed for three consecutive cycles. After catalytic use the recovered composite was washed with ethanol and dried in a desiccator over silica gel overnight to be used in another ECODS cycle with a new portion of untreated diesel.

8.5. References

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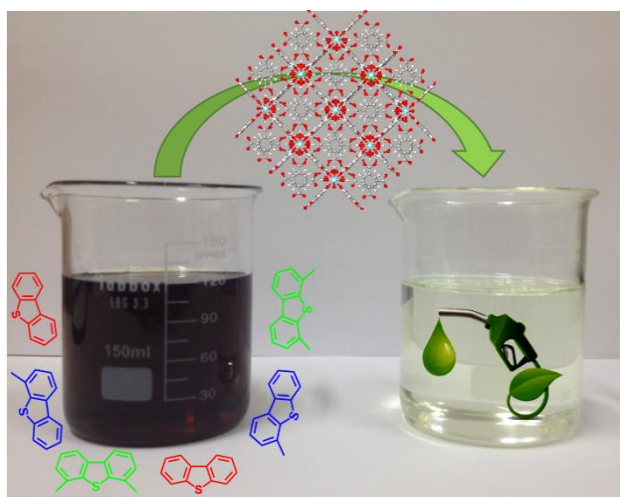
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Chapter 9

Production of Ultra-Deep Sulfur-Free Diesels Using Sustainable Catalytic System Based on UiO-66(Zr)^{1,2}



¹ Adapted from: Carlos M. Granadeiro, SUSANA O. RIBEIRO, Mohamed Karmaoui, Rita Valença, Jorge C. Ribeiro, Baltazar de Castro, Luís Cunha-Silva and Salete S. Balula, *Production of Ultra-Deep Sulfur-Free Diesels Using Sustainable Catalytic System Based on UiO-66*, Chemical Communications, 51 (2015) 13818-13821, doi: 10.1039/C5CC03958D

² Susana O. Ribeiro contribution to the publication: Preparation of the unmodified UiO-66 sample, the amine-functionalized UiO-66 and the PW₁₁Zn@UiO-66-NH₂ composite; desulfurization experiments and manuscript preparation.

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Chapter 9

Production of Ultra-Deep Sulfur-Free Diesels Using Sustainable Catalytic System Based on UiO-66 (Zr)

Abstract

The porous metal-organic framework UiO-66 (UiO: University of Oslo 66) revealed to be an efficient heterogeneous catalyst for the production of diesel with low level of sulfur compounds. An optimized desulfurization method combining liquid-liquid extraction and oxidative catalytic process (ECODS) was applied to a multicomponent model diesel and also to a real diesel sample from Galp. UiO-66 showed a remarkable heterogeneous catalytic performance (100% after 30 min for model diesel) and an easy recovery from diesel systems. The chemical robustness and excellent recycling ability without loss of catalytic activity along various desulfurization cycles make UiO-66 an attractive catalyst to produce sulfur-free fuels (81% desulfurization was achieved for real diesel sample).

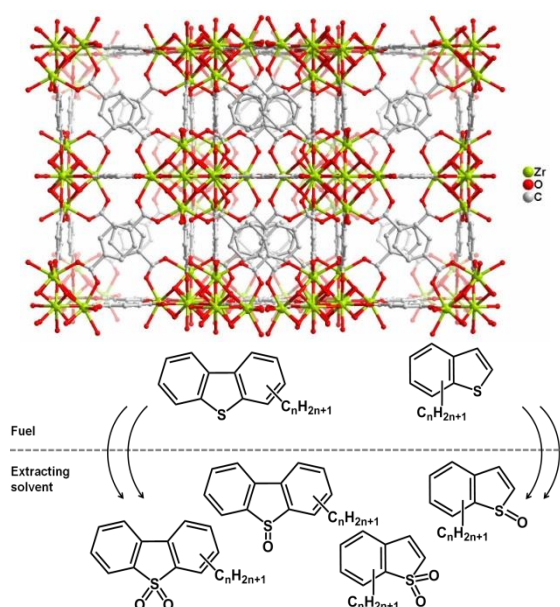
The preparation of an amine-functionalized UiO-66-NH₂ and the composite PW₁₁Zn@UiO-66-NH₂ was also performed. Their oxidative catalytic performance was evaluated and low efficiency was found after 1 h (54.2% for the amine-functionalized UiO-66-NH₂ and 74.6% for the composite).

9.1 Introduction

Novel MOF-based catalytic systems for efficient extractive and catalytic oxidative desulfurization processes (ECODS) have been developed recently. [1-4] The UiO-type materials (UiO stands for University of Oslo) are a class of highly stable MOFs based on $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ secondary building units (Scheme 9.1) that have shown potential applications as sensors, [5] adsorbents [6] and catalysts. [7] In this work the porous Zr(IV) terephthalate UiO-66 was selected due to its high surface area and especially for its exceptional chemical, thermal and mechanical stability. [8-10] Regarding the catalytic field, the non-functionalized UiO-66 has being mainly used as solid support for catalytic active species, almost exclusively metallic nanoparticles, [11, 12] while only a few reports explore the intrinsic catalytic properties of the MOF. [13-16]

Herein, the application of UiO-66 as heterogeneous catalyst for the desulfurization of model diesel C (see Chapter 1 section 1.7) and the Galp real diesel sample (~ 2300 ppm S) is reported in this chapter.

Following the interest in the application of POM-based composites in oxidative desulfurization processes, the amine-functionalized UiO-66 (UiO-66-NH₂) and the composite $\text{PW}_{11}\text{Zn}@$ UiO-66-NH₂ were also prepared and tested as heterogeneous catalysts in the oxidative desulfurization of model diesel B (see Chapter 1 section 1.7).



Scheme 9.1- Schematic representation of the 3D framework of UiO-66 (top) and the oxidative desulfurization process in diesels (bottom).

9.2. Results and discussion

9.2.1. UiO-66 samples

Four different UiO-66 samples were prepared to study the effect of a crystallization agent (HCl) and/or a modulator (trifluoroacetic acid, TFA) on the final structural and chemical properties of the materials:

UiO-66 – (unmodified) was prepared without crystallization agent or modulator

UiO-66_{HCL} - was prepared with crystallization agent

UiO-66_{HCL,mod} - was prepared with crystallization agent and modulator

UiO-66_{mod} - was prepared with modulator

9.2.1.1. Catalysts characterization

The FT-Raman spectra of the prepared UiO-66 samples are presented in Figure 9.1. The bands located at ca. 1435 and 860 cm⁻¹ provide information concerning the degree of homogeneity of the framework and the presence of linker deficiencies. [9] In the ideal UiO-66 structure, two distinct bands associated with the carboxylate-related stretches are observed in the 1445-1420 cm⁻¹ range. The use of HCl as crystallization agent seems to have led to better crystallized frameworks since the spectra of UiO-66_{HCL,mod} and UiO-66_{HCL} show two bands (although not completely separated) associated with the carboxylate stretches. In the other spectra, the presence of a single band in this region suggests differences regarding the presence of carboxylate linkers, namely a higher number of linker defects within the framework. [9]

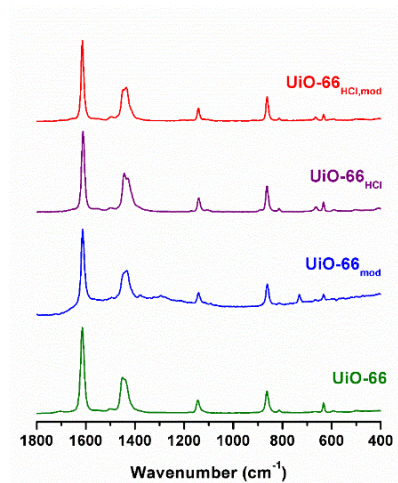


Figure 9.1. FT-Raman spectra of the UiO-66 samples prepared by different synthetic procedures.

The XRD patterns of the UiO-66 samples exhibit the typical diffraction peaks of the MOF in terms of position and relative intensities (Figure 9.2). It is clear that the use of HCl during the synthesis results in more crystalline materials. [9, 17] In fact, the patterns of UiO-66_{HCl,mod} and UiO-66_{HCl} exhibit sharper and well-resolved peaks, while the patterns of UiO-66 and UiO-66_{mod} display broader peaks suggesting more amorphous materials. In this work, the addition of 10 equivalents of a modulator (modulator abbreviated as mod, corresponding to TFA) did not show a significant influence in the overall crystallization of the materials.

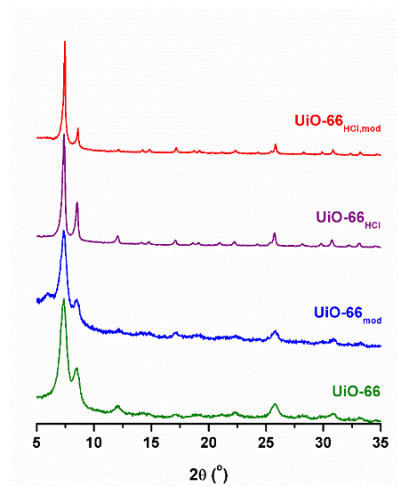


Figure 9.2- Powder XRD patterns of the UiO-66 samples.

The chlorine content of the UiO-66 samples was studied through the quantification of Cl/Zr atomic weight ratios via EDS (Figure 9.3 and Table 9.1). The

amount of residual chlorine (present even after the material being thoroughly washed) in a UiO-66 sample provides an indication of the number of defect sites in a material. The random absence of terephthalate ligands throughout the UiO-66 framework that occurs even in well-crystallized materials, results in charge and coordination deficiencies. [8] Chloride anions can compensate this imbalance by bonding to open zirconium sites, *i. e.*, not coordinated to terephthalate linkers. [9, 18]

Regarding the samples prepared without the modulator, the UiO-66 exhibits a higher content of chlorine when compared with UiO-66_{HCl}. Considering that the chlorine present in each sample is located in defect sites of the framework, such a result suggests that the extent of linker deficiencies in UiO-66 is higher than in UiO-66_{HCl}. As expected, the samples obtained through modulated synthesis contain a smaller amount of chlorine according to previously reported data. [18] In fact, De Vos *et al.* have demonstrated that the charge imbalance promoted by the introduction of trifluoroacetate linkers (CF₃COO)⁻ is compensated by the replacement of OH⁻ ions by O²⁻ ions in the ideal [Zr₆(OH)₄O₄]¹²⁺ cluster resulting in a [Zr₆(OH)_nO_{8-n}]⁽⁸⁺ⁿ⁾⁺ (with $n < 4$) cluster.

In short, different UiO-66 samples were prepared following previously reported methodologies. [18, 19] In particular, the effect of a crystallization agent (HCl) and/or a modulator (trifluoroacetic acid) on the final structural and chemical properties of the materials were addressed. The characterization techniques confirm that the use of HCl results in more crystalline materials. Furthermore, the known linker deficiencies occurring in UiO-66 materials [8, 9, 18] lead to charge compensation by chloride anions at the defect sites or by a rearrangement of the Zr₆(OH)₄O₄ cluster (in the modulated materials).

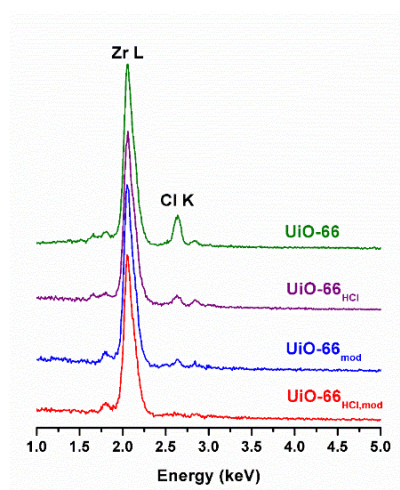


Figure 9.3- EDS spectra of the UiO-66 samples in the 1-5 keV range. All spectra are normalized to the Zr L peak.

Table 9.1- Cl/Zr atomic ratios determined via EDS spectra of the UiO-66 samples.

Sample	Cl/Zr Atomic ratio
UiO-66	0.340
UiO-66 _{HCl}	0.110
UiO-66 _{mod}	0.058
UiO-66 _{HCl,mod}	0.029

9.2.1.2. Biphasic extractive and catalytic oxidative desulfurization (ECODS) process using model diesel

The catalytic performance of each sample was evaluated in the desulfurization of the multicomponent model diesel C (Figure 9.4) with a $\text{H}_2\text{O}_2/\text{S}$ ratio equal to 21, at 50 °C. The best desulfurization performance was achieved with the sample prepared via the non-modulated procedure and without the use of the crystallization agent HCl (herein referred as UiO-66), with a complete desulfurization of the model diesel after only 30 min. The experimental results also show practically complete desulfurization of the multicomponent model diesel after 1 h using the UiO-66_{mod} sample. The well-crystallized UiO-66_{HCl} and UiO-66_{HCl,mod} materials have shown a poorer desulfurization performance. In particular, the UiO-66_{HCl} exhibited no catalytic activity in this ECODS system since the model diesel desulfurization only occurs during the initial extraction step. The results seem to show a correlation between the crystallinity and extent of linker deficiencies of the framework with its desulfurization performance. In fact, the enhanced activity of the more amorphous samples (UiO-66 and UiO-66_{mod}) contrasts with the poor performance observed for the more crystalline samples (UiO-66_{HCl} and UiO-66_{HCl,mod}) during the catalytic stage of the ECODS process.

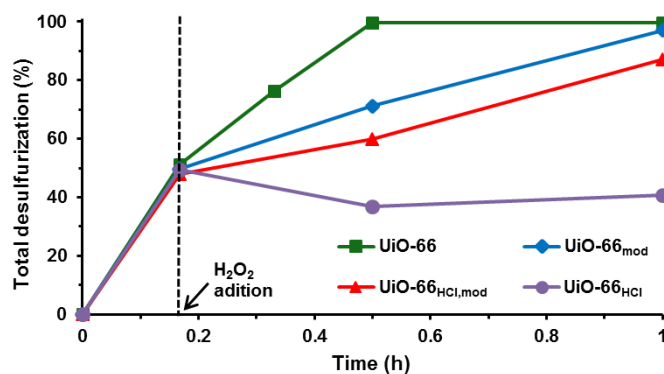


Figure 9.4- Kinetic profile for the desulfurization process of the model diesel using the different UiO-66 samples (9 μmol of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$) at 50 °C, showing the initial extraction stage (before the dashed line) and the catalytic step (after the dashed line).

Recent reports correlate the presence of defect sites occurring within several MOF frameworks with the enhancement of catalytic activity. [20, 21] As the ideal and fully coordinated UiO-66 framework is not expected to exhibit a significant catalytic activity, efforts have been made to promote structural defects while keeping the overall integrity of the framework. [8, 18] In this work, the notable desulfurization performance of the UiO-66 sample is probably related with the low-degree of crystallinity and the considerable number of defect sites in the sample as shown by the amount of residual chlorine via EDS. Comparing the performance of UiO-66 and UiO-66_{mod} materials (both with a similar degree of crystallinity), one can speculate that the presence of chloride ions at the defect sites, observed in UiO-66, plays a key role in the fast desulfurization observed. Moreover, the catalytic activity of different UiO-66 samples also must be related to the presence of active centers in the defect sites, *i.e.* the formation of Zr^{IV}-peroxo groups on the surface of the material by the interaction with H₂O₂. The use of Zr oxoclusters as oxidative catalysts and the formation of Zr^{IV}-peroxo complexes in the presence of H₂O₂ is well reported. [22-24] Oxygen from the Zr^{IV}-peroxo groups are transferred to the sulfur substrates and their oxidized products (sulfones) are formed. The linker deficiencies introduced in the UiO-66 framework will originate structural and electronic modifications that will influence the level of interaction between the H₂O₂ and solid catalyst, and consequently the formation of active Zr^{IV}-peroxo groups, altering their catalytic properties.

The product distribution of the oxidation reactions has been analyzed in diesel and acetonitrile phases, showing that the oxidation of the sulfur compounds results exclusively in the formation of the corresponding sulfones. Regarding the initial extraction stage, no significant differences were detected as similar desulfurization percentages were achieved in all experiments ($\approx 50\%$).

The optimization of the amount of catalyst in the ECODS process was performed for the UiO-66 sample (Figure 9.5). The results revealed a remarkable activity of UiO-66 in the ECODS process, since practically complete desulfurizations ($\geq 96\%$) were attained after only 1 h of reaction for very small amounts of catalyst (3 and 6 μmol of monomer Zr₆O₄(OH)₄(CO₂)₁₂) used. The ECODS process using 12 μmol of catalyst, leads to a notable desulfurization percentage (88 %) after just 20 min. However, since the complete desulfurization of the model diesel is achieved after 30 min using either 9 or 12 μmol (Zr₆O₄(OH)₄(CO₂)₁₂) of UiO-66, we have considered the former as the optimal amount for the ECODS process.

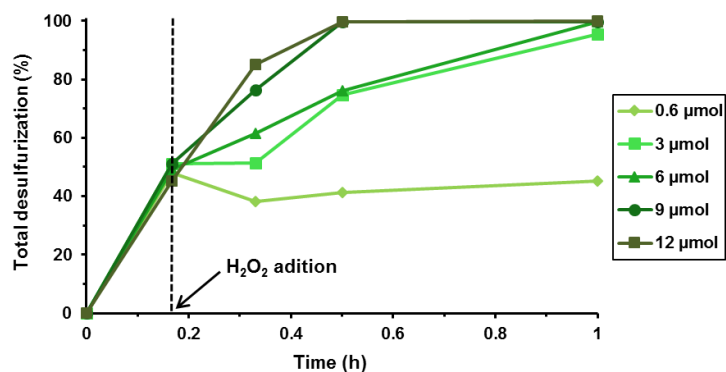


Figure 9.5- Catalytic profile for the desulfurization process of the model diesel using different amounts of the UiO-66 sample (amounts calculated for $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$ monomer) with acetonitrile as the extraction solvent. The desulfurization process comprises two steps: the initial extraction stage (before the dashed line) and the catalytic stage (after the dashed line).

The heterogeneity of UiO-66 was investigated through a leaching test by removing the catalyst after 20 min of reaction. The solid was separated from the mixture and the reaction continued with the remaining filtrate. The leaching test results (Figure 9.6) confirms that the UiO-66 acts as a heterogeneous catalyst as the desulfurization of the model diesel almost immediately stops after its removal.

Furthermore, control experiments using ZrO_2 as catalyst as well as the single extraction (without oxidant) of the model diesel were performed and compared with the desulfurization performance of UiO-66 (Figure 9.7). The results show that the desulfurization stops after the initial extraction stage period (10 min) when no oxidant is added. The desulfurization with ZrO_2 points out that the performance of UiO-66 is not influenced by the possible presence of uncoordinated ZrO_2 since no desulfurization occurs during the catalytic stage of the control experiment.

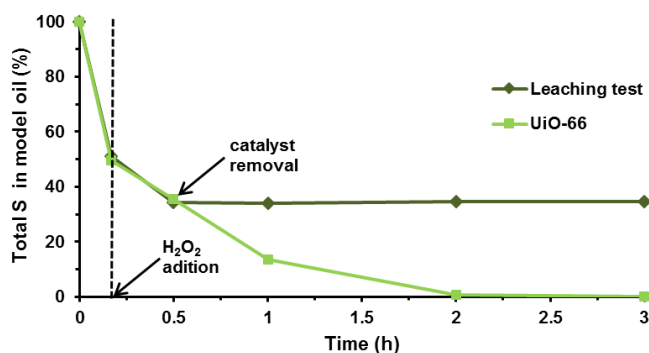


Figure 9.6- Desulfurization of the multicomponent model diesel using UiO-66 ($3 \mu\text{mol}$ of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$) and the corresponding leaching test (catalyst removal after 30 min of reaction).

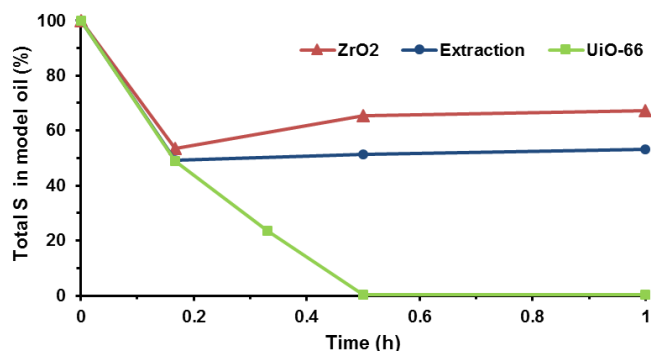


Figure 9.7- Desulfurization profile of a model diesel in the presence of UiO-66 ($9 \mu\text{mol}$ of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$), performing only the extraction liquid-liquid process, and also combining extraction and catalytic steps in the presence of H_2O_2 oxidant. A control experiment replacing the UiO-66 catalyst by ZrO_2 , using an equivalent Zr content, combining extraction and catalytic steps.

9.2.1.3. UiO-66 recyclability and stability

The recycling ability of UiO-66 in the ECODS process was evaluated using the previously optimized amount of catalyst ($9 \mu\text{mol}$ of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$). At the end of each cycle, the catalyst was recovered, washed thoroughly with ethyl acetate, dried and reused in a new cycle under the same experimental conditions. The catalytic data obtained for three consecutive ECODS cycles (Figure 9.8) show values extremely reproducible and display very similar kinetic profiles. Such a result suggests that no chemical degradation and/or structure collapse of the UiO-66 sample occurs throughout the ECODS process. The desulfurization of the model diesel for each component is represented in Figure 9.9 after 10 min of (darker part of the bars) and 1 h (entire bars). The comparison of the desulfurization percentages after 10 min shows a trend in the desulfurization rate of each component for all three cycles. In fact, DBT exhibited a higher initial extraction while for 4-MDBT and 4,6-DMDBT were achieved similar desulfurization percentages. However, after the oxidative catalytic stage the desulfurization efficiency for all the sulfur compounds were similar after 1 h. Before 1 h of ECODS process, the oxidation reactivity observed for this catalytic system decreased in the order of $\text{DBT} > 4,6\text{-DMDBT} \approx 4\text{-MDBT}$. The electron density on the sulfur atom of each component is similar, [25] and therefore the different reactivities observed are related with a steric hindrance effect. [26] As reported, the presence of methyl groups in 4-MDBT and 4,6-DMDBT difficults the interaction between the sulfur atoms and the catalytic active species, decreasing the oxidative reactivity of the methyl-substituted dibenzothiophenes. [27, 28]

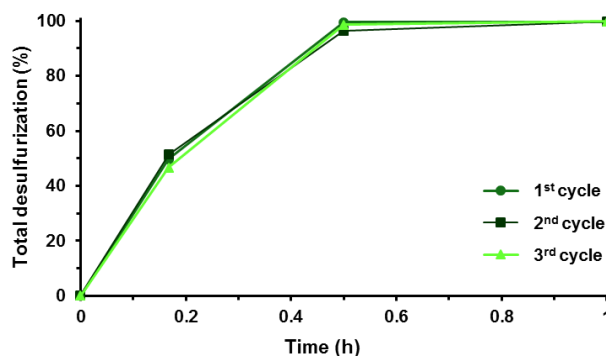


Figure 9.8 - Kinetic profiles for the desulfurization of the model diesel for three consecutive cycles using the UiO-66 sample

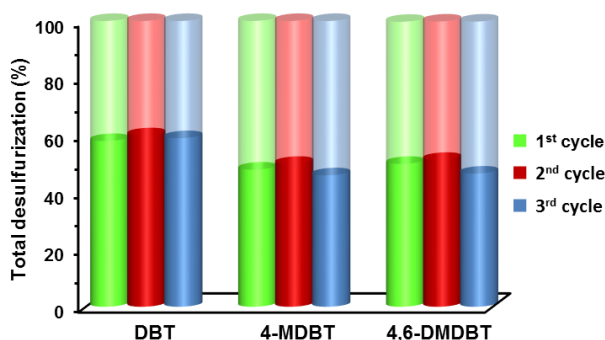


Figure 9.9 - Percentage of each sulfur compound removed from the model diesel after the initial extraction step (darker part of the bars) and after 1 h (entire bars) of the ECODS process for three consecutive cycles.

Different ECODS systems have been proposed for the desulfurization of multicomponent model diesels, including organic acids-, polyoxometalates- and ionic liquids-based systems usually with H_2O_2 , but not allowing the recovery of the catalyst. [28-30] The need for catalyst recycling has recently led to the use of heterogeneous catalysts in desulfurization processes, especially MOF-incorporated or -immobilized composites. [4, 31, 32] The reports in the literature, besides requiring longer reactional times to attain complete desulfurization of the model diesel, also presents some disadvantages, such as leaching of the active species and loss of catalytic activity between cycles. A crucial feature of the ECODS system herein reported is the use of the isolated UiO-66 as heterogeneous catalyst without the need to incorporate/immobilize active species. This prevents the frequently occurring leaching issues and, together with the exceptional robustness of the MOF, promotes a constant catalytic activity in consecutive cycles.

The structural stability of UiO-66 was evaluated through the extensive characterization of the solid recovered after three consecutive ECODS cycles (UiO-66-ac). The vibrational spectroscopy spectra of UiO-66-ac (Figure 9.10) are very similar to the ones before catalysis. Regarding FT-IR, the typical bands of UiO-66 remain unaltered, [8] namely the bands assigned to $\nu_{as}(\text{OCO})$ and $\nu_s(\text{OCO})$ stretches located at 1606 and 1373 cm^{-1} , respectively, as well as the $\nu(\text{Zr-OC})$ stretches located at 638 and 523 cm^{-1} . The FT-Raman of UiO-66-ac also displays the characteristic UiO-66 Raman bands [9] including the bands assigned to the intense in-phase aromatic $\nu(\text{C-C})$ stretch at 1614 cm^{-1} , the symmetric carboxylate $\nu_s(\text{OCO})$ at 1433 cm^{-1} and the symmetric C-C ring breathing at 1142 cm^{-1} .

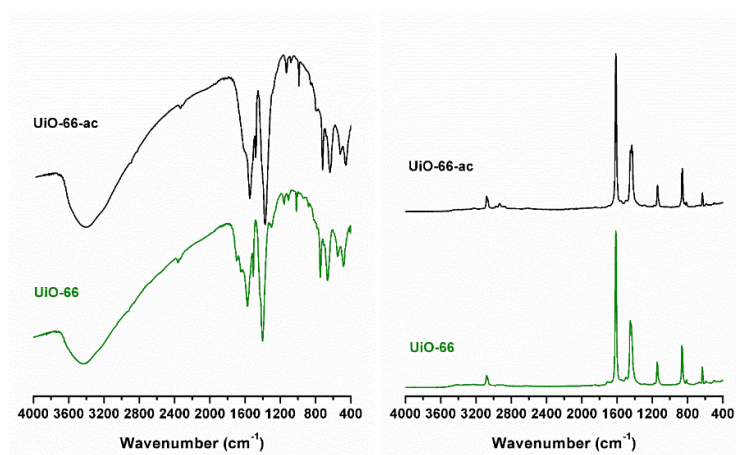


Figure 9.10- FT-IR (left) and FT-Raman (right) spectra of UiO-66 before and after catalytic use (ac).

In the powder XRD patterns before and after catalysis, the main diffraction peaks of UiO-66 (1, 1, 1), (0, 0, 2), (0, 2, 2), (0, 0, 4), (0, 4, 4), (0, 0, 6) and (1, 1, 7)] [33] remain unaffected regarding its position and relative intensity (Figure 9.11). Both XRD patterns are in good agreement with the data reported in the literature for the UiO-66 material. [10, 34]

The SEM images of UiO-66 and UiO-66-ac (Figure 9.12) show identical morphology for both samples indicating that the morphology of the MOF is not altered during the catalytic ECODS cycles. Moreover, the EDS analysis reveals that both samples have an identical chemical composition in terms of elements and their corresponding relative intensity. The combination of evidences from these characterization techniques unequivocally indicates the preservation of the MOF

structure without degradation as a result of the remarkable robustness and stability of UiO-66.

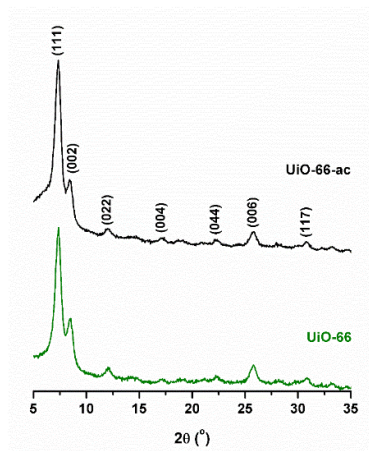


Figure 9.11- Powder XRD patterns of UiO-66 before and after catalytic use (ac).

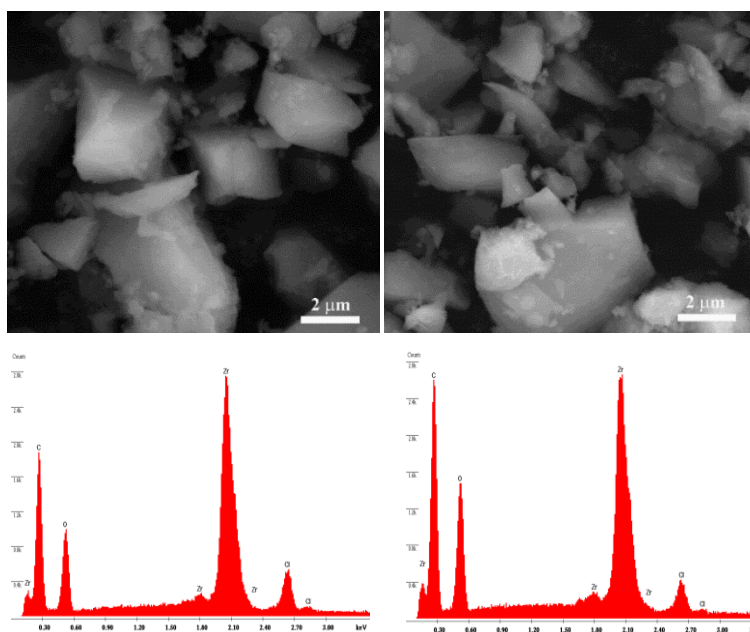


Figure 9.12- SEM micrographs and EDS spectra of UiO-66 before (left) and after catalysis (right).

9.2.1.4. ECODS process using untreated diesel

The outstanding performance of the UiO-66 sample in the desulfurization of the model diesel has motivated its application in the oxidative desulfurization of Galp real diesel sample (sulfur content ca. 2300 ppm).

As described in Chapter 2 (section 2.2.3) the desulfurization process was initiated by performing three consecutive liquid-liquid extraction cycles with equal volume of

MeCN and diesel. This extraction stage with MeCN was responsible for the removal of 793 ppm of sulfur compounds, corresponding to a desulfurization efficiency of 35 %.

The oxidative catalytic stage was crucial to increase the desulfurization of diesel. In fact, this step showed to be the most important to achieve a low-sulfur content in untreated diesel. At the end of the desulfurization process combining extraction (three cycles) and oxidative catalytic desulfurization (two cycles of 8 h each), 81 % of desulfurization was achieved. Such reduction gives a clear indication of the very promising potential of UiO-66 for a future application in industrial desulfurization processes. Several reports can be found in the literature dealing with the desulfurization of untreated diesel fuel using ECODS processes. [35-39] Nevertheless, the systems achieving similar or slightly better desulfurization efficiency than the one herein reported, generally use harsher and less eco-sustainable experimental conditions, such as higher temperatures, longer reaction times and larger amounts of organic solvents due to a higher number of extraction steps performed.

9.2.2. UiO-66-NH₂ and UiO-66-NH₂ composite

9.2.2.1 Catalysts characterization

Amino-functionalized UiO-66 (UiO-66-NH₂) was also prepared using the 2-aminoterephthalic acid. The UiO-66-NH₂ was characterized by elemental analysis and the obtained results were: 6.74% for N, 32.70% for C and 3.90% for H, which corresponds a loading of functional amine groups of 4.78 mmol per g of material. The FT-IR spectrum of UiO-66-NH₂ is displayed in Figure 9.13. In comparison with the spectrum of UiO-66 (Figure 9.10-left) two weak peaks at 3436 cm⁻¹ and 3335 cm⁻¹ are observed in the spectrum of UiO-66-NH₂, which are ascribed to the asymmetrical and symmetrical stretching vibration adsorption of the amine groups. [40] The peaks centered at 1622 cm⁻¹ and 1258 cm⁻¹ correspond to the N-H bending vibration and the characteristic C-N stretching of aromatic amines, respectively. [19, 40] The band at 1568 cm⁻¹ confirmed the interaction between -COOH and Zr (IV). The peak at 764 cm⁻¹ corresponds to the wagging vibrations of N-H. [41, 42]

The functionalized UiO-66-NH₂ was used as support to immobilize the [PW₁₁Zn(H₂O)O₃₉]⁵⁻, abbreviated as PW₁₁Zn (preparation and characterization presented in Chapter 1). The FT-IR spectrum of the novel composite PW₁₁Zn@UiO-66-NH₂ presents similar profile to the support UiO-66-NH₂ without the appearance of extra bands resulting from PW₁₁Zn vibrations. However, the presence of PW₁₁Zn was

confirmed by the presence of W in the EDS spectrum (Figure 9.14) and by ICP analysis with a loading of $PW_{11}Zn$ of 0.039 mmol per g of material. The low loading of POM indicates a small incorporation of this guest compound in the UiO-66-NH₂ support by electrostatic interactions. In fact, the incorporation of $PW_{11}Zn$ units into UiO-66-NH₂ cavities is difficult to occurs since the $PW_{11}Zn$ particles (≈ 12 Å) are larger than the support pores (8-11Å). [43-45]

The SEM images of the UiO-66-NH₂ (Figure 9.14) reveal that its morphology is composed by sphere-like particles. This morphology was maintained after the $PW_{11}Zn$ incorporation as can be seen in SEM image of $PW_{11}Zn@UiO-66-NH_2$.

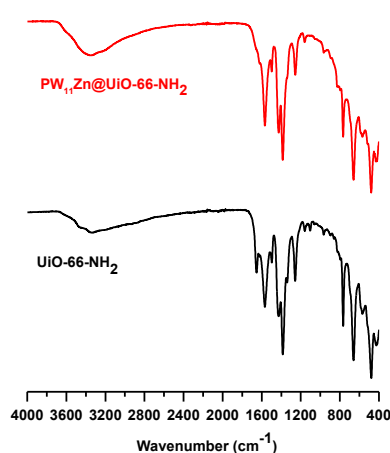


Figure 9.13 - FT-IR spectra of UiO-66-NH₂ and $PW_{11}Zn@UiO-66-NH_2$ composite.

The UiO-66 and UiO-66-NH₂ have isostructural configurations [46] presenting similar diffraction peaks as can be seen in Figures 9.2 and 9.15. The results demonstrate that using the NH₂ groups functionalized terephthalic acid precursors does not affect the skeleton of UiO-66 under the synthesis conditions. However, the UiO-66-NH₂ presents a more crystalline structure since it also exhibit sharper and well-resolved peaks than the UiO-66 sample.

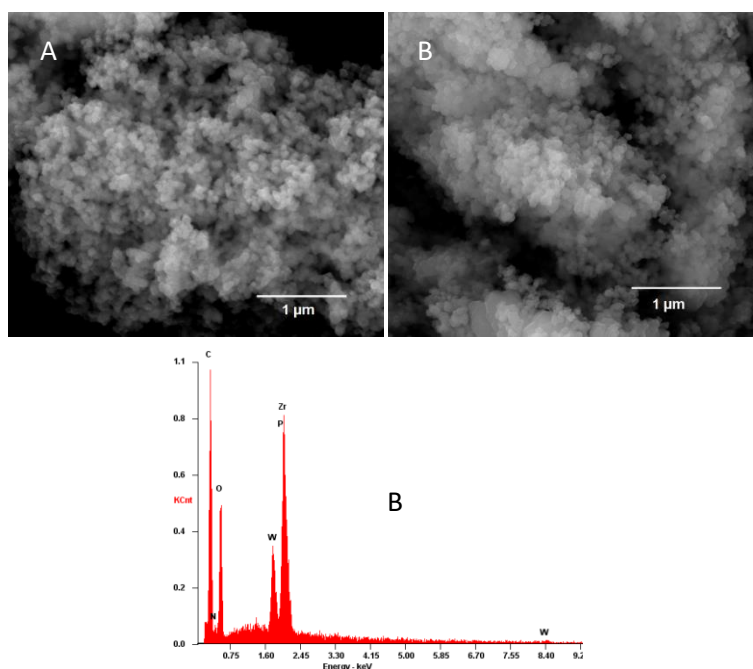


Figure 9.14- SEM micrographs of UiO-66-NH₂ (A) and SEM micrographs and EDS spectra of PW₁₁Zn@UiO-66-NH₂ composite.

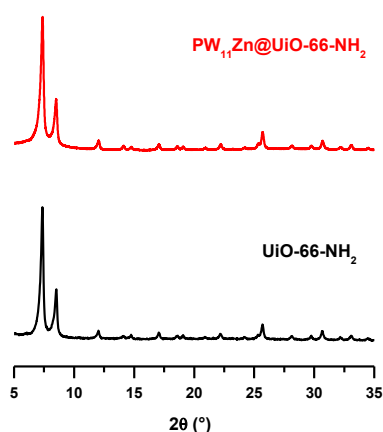


Figure 9.15 - Powder XRD patterns of the UiO-66-NH₂ and PW₁₁Zn@UiO-66-NH₂ composite.

9.2.2.2 ECODS using model diesel

The amine-functionalized UiO-66-NH₂ and the composite PW₁₁Zn@UiO-66-NH₂ were tested as catalysts for the oxidative desulfurization of model diesel B (see Chapter 1 section 1.7). In this case, the experiments were conducted at 70 °C using a H₂O₂/S ratio of 8 and 77 mg of catalyst (corresponding to 3 μmol of PW₁₁Zn in the composite). The results are displayed in Figure 9.16.

Using the UiO-66-NH₂ can be observed that after 60 min of oxidation, the catalyst presents low catalytic activity, since only 54.2% of desulfurization was achieved. After 180 min, the catalyst maintained the desulfurization efficiency (54.1%). Considering the initial extraction results (49.2%), it is possible to confirm the low oxidative efficiency of the catalyst. Although different experimental ECODS conditions have been used to test UiO-66-NH₂ and UiO-66 in model diesel desulfurization, it seems that the UiO-66-NH₂ is less active than the unmodified UiO-66, which is probably due to its higher crystallinity and lack of defects, as seen for the other UiO-66 samples presented in section 9.2.1.2..

In order to improve the catalytic activity of UiO-66-NH₂, the active PW₁₁Zn was immobilized in UiO-66-NH₂ by electrostatic interaction. The results presented in Figure 9.16 confirmed that after the PW₁₁Zn immobilization, the catalytic activity was enhanced, achieving 74.6 % desulfurization after 1 h. However, after this period of time, the catalytic activity seems to stop, since this desulfurization efficiency was maintained even after 180 min of oxidant addition.

In short, the UiO-66-NH₂ should not be the best choice to prepare active POMs@MOFs catalysts, since low improvement of catalytic activity was observed when PW₁₁Zn was immobilized, which may be related with its low loading.

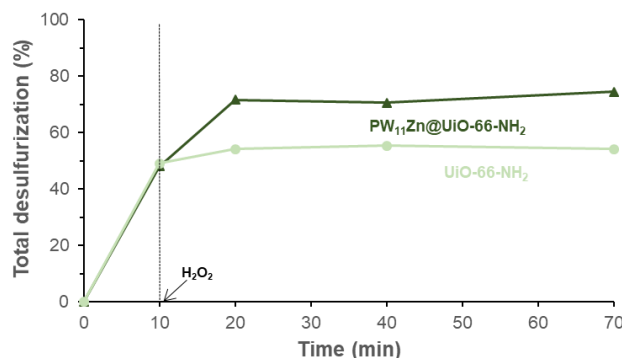


Figure 9.16 - Desulfurization of the multicomponent model diesel using H₂O₂/S=8 and 77 mg of UiO-66-NH₂ and 77 mg PW₁₁Zn@ UiO-66-NH₂ composite (containing 3 μmol of active PW₁₁Zn) at 70°C.

9.3 Conclusion

In summary, we have investigated the application of a sustainable desulfurization system conciliating the liquid-liquid extraction and the oxidative catalytic desulfurization stage based on UiO-66 for the production of low-sulfur/sulfur-free diesels. The system

was tested in the desulfurization of model diesel C and real diesel from Galp. The desulfurization performance of different UiO-66 samples obtained through distinct methodologies was evaluated. For the studied ECODS process, the less crystalline sample UiO-66, obtained through non-modulated synthesis and without a crystallization agent, has shown a superior desulfurization ability over the other samples. The system showed an outstanding efficiency in the removal of sulfur-compounds from the multicomponent model diesel (complete desulfurization achieved after 30 min). The UiO-66 material proved to be a very stable and robust heterogeneous catalyst exhibiting an exceptional recycling ability without any significant loss of catalytic activity for three consecutive ECODS cycles.

In this chapter was also presented the preparation of an amine-functionalized UiO-66-NH₂ and a UiO-66 composite based in the immobilization of the PW₁₁Zn active center. The new composite PW₁₁Zn@ UiO-66-NH₂ was also tested in the desulfurization of model diesel B. However, its catalytic performance was lower than the less crystalline UiO-66 sample (74.6% after 1 h).

According to the high catalytic performance of UiO-66, it was tested using an untreated real diesel. The desulfurization system proved to be highly effective, achieving 81 % of desulfurization.

9.4. Experimental section

9.4.1. Materials and Methods

All the reagents used in the preparation of the materials, such as zirconium(IV) chloride (Aldrich), benzene-1,4-dicarboxylic acid (Aldrich), 2-aminoterephthalic acid (Aldrich), *N,N*-dimethylformamide (DMF, Aldrich), trifluoroacetic acid (TFA, Riedel-de Haën), sodium tungstate dehydrate (Aldrich), sodium phosphate dehydrate (Aldrich), zinc acetate di-hydrated (M&B), hydrochloric acid (Fisher Chemicals), were used as received without further purification. The reagents used in the ECODS processes, dibenzothiophene (DBT, Aldrich), 4-methyldibenzothiophene (4-MDBT, Aldrich) and 4,6-dimethyldibenzothiophene (4,6-DMDBT, Alfa Aesar GmbH & Co Kg), acetonitrile (MeCN, Panreac), ethyl acetate (Merck), H₂O₂ 30% (Aldrich) and *n*-octane (Aldrich) were also used as received.

FT-IR spectra were obtained on a Jasco 460 Plus spectrometer using KBr pellets, while the FT-Raman spectra were acquired on a RFS-100 Bruker FT-spectrometer,

equipped with Nd:YAG laser with a 1064 nm excitation wavelength and laser power set to 350 mW. Powder X-ray diffraction patterns were obtained at room temperature on a X'Pert MPD Philips diffractometer, equipped with an X'Celerator detector and a flat-plate sample holder in a Bragg-Brentano para-focusing optics configuration (45kV, 40 mA). Intensity data were collected by the step-counting method (step 0.04°), in continuous mode, in the $ca. 3 \leq 2\theta \leq 40^\circ$ range (CICECO, Universidade de Aveiro). Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) studies were performed at "Centro de Materiais da Universidade do Porto" (CEMUP, Porto, Portugal) using a high-resolution (Schottky) scanning electron microscope with X-ray microanalysis and electron backscattered diffraction analysis Quanta 400 FEG ESEM/EDAX Genesis X4 M. The samples were studied as powders and were coated with an Au/Pd thin film by sputtering using the SPI Module Sputter Coater equipment. GC-MS analysis were performed using a Hewlett Packard 5890 chromatograph equipped with a Mass Selective Detector MSD series II using helium as the carrier gas ($35 \text{ cm}^3 \text{ min}^{-1}$); GC-FID was carried out in a Varian CP-3380 chromatograph to monitor the catalytic reactions. The hydrogen was used as the carrier gas ($55 \text{ cm}^3 \text{ min}^{-1}$) and fused silica Supelco capillary columns SPB-5 ($30 \text{ m} \times 0.25 \text{ mm i.d.}$; $25 \mu\text{m}$ film thickness) were used. The analysis of sulfur content of the treated diesel was performed by Rita Valença in Galp Company by ultraviolet fluorescence using Thermo Scientific equipment, with TS-UV module for total sulfur detection, and Energy Dispersive X-ray Fluorescence Spectrometry, using an OXFORD LAB-X, LZ 3125.

9.4.1. Synthesis of the materials

9.4.2.1. UiO-66 samples

Different UiO-66 samples were prepared using previously reported experimental procedures. UiO-66 sample was prepared, without acid or modulator, using a modified procedure of the method described by Lillerud et al. [19] Briefly, zirconium(IV) chloride (6.4 mmol) and 1,4-benzenedicarboxylic acid (6.4 mmol) were dissolved in DMF (180 mL) at room temperature. The mixture was placed in an oven at 120°C for 24 h. After cooling to room temperature, the solid was filtered, washed three times with DMF and ethanol each and dried in an oven at 80°C overnight. The samples $\text{UiO-66}_{\text{HCl}}$, $\text{UiO-66}_{\text{mod}}$ and $\text{UiO-66}_{\text{HCl,mod}}$ were prepared following the method described by De Vos and co-workers. [18] The synthetic route involves the use of HCl as a crystallization agent and/or TFA as a modulator. An initial equimolar solution of zirconium(IV) chloride (0.75 mmol) and 1,4-benzenedicarboxylic acid (0.75 mmol) in DMF (7.75 mL) was prepared. The

autoclaves were placed in an oven at 120 °C for 21 h, after which the solids were recovered by centrifugation, washed three times with DMF and methanol, and dried at 80 °C overnight.

9.4.2.2. UiO-66-NH₂ and PW₁₁Zn@UiO-66-NH₂ composite

The UiO-66-NH₂ was prepared as the previous UiO-66, adapting the method described by Lillerud et al. [19] Instead of benzene-1,4-dicarboxylic acid, the 2-aminoterephthalic acid was used. The PW₁₁Zn was prepared as described in Chapter 2 in 2.4.2. [47]. The PW₁₁Zn@UiO-66-NH₂ composite was prepared via impregnation method by electrostatic interactions adapted from previously reported procedures [3, 48].

9.4.3. ECODS using model diesel

The oxidative desulfurization studies were performed using the model diesel C containing the most representative refractory sulfur-compounds in diesel, namely dibenzothiophene (DBT), 4-methyldibenzothiophene (4-MDBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT), in *n*-octane (with a concentration of 500 ppm of sulfur from each compound). The different UiO-66 samples were tested as heterogeneous catalyst in the ECODS process. The reactions were carried out under air in a closed borosilicate reaction vessel with a magnetic stirrer and immersed in a thermostatically controlled liquid paraffin bath at 50 °C. The ECODS reactions were performed in a biphasic system composed by the model fuel and MeCN. In a typical experiment, the catalyst (15 mg, containing 9 μmol of Zr₆O₄(OH)₄(CO₂)₁₂) was added to MeCN (0.75 mL) and model fuel (0.75 mL), and the resulting mixture was stirred for 10 min. The catalytic step of the process is initiated by the addition of aqueous hydrogen peroxide 30% (75 μL, H₂O₂/S = 21). The sulfur content was periodically quantified by GC analysis using tetradecane as a standard. The UiO-66 samples were tested as catalyst in the ODS process. The amount of catalyst used in the ECODS process was optimized for the sample exhibiting the best desulfurization performance (UiO-66). Different ODS experiments were performed using a variable amount of UiO-66 (0.6; 3; 6; 9 and 12 μmol of Zr₆O₄(OH)₄(CO₂)₁₂). The recycling studies were performed using the optimized amount of UiO-66 (9 μmol of Zr₆O₄(OH)₄(CO₂)₁₂). After each cycle, the catalyst was recovered by filtration, washed thoroughly with acetonitrile, dried in a desiccator over silica gel and reused in a new ECODS cycle under the same reactional conditions.

9.4.4. ECODS using untreated diesel

The untreated diesel sample was supplied by Galp containing approximately 2300 ppm of sulfur. An initial extraction was performed using MeCN as the extraction solvent. The biphasic system 1:1 diesel/MeCN was stirred for 10 min at 50 °C. Afterwards, the diesel was removed from the system and a new portion of clean MeCN was added. This initial extraction procedure was repeated for three times. In the next step, the resulting diesel was mixed with a suspension of the heterogeneous catalyst UiO-66 (120 µmol of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{CO}_2)_{12}$) in MeCN (1:1 for diesel/MeCN) followed by the addition of the oxidant H_2O_2 (2 mL, $\text{H}_2\text{O}_2/\text{S} = 21$). The mixture was heated at 50 °C for 8 h under stirring. After this time, the diesel was removed from the mixture and washed with an equal volume of MeCN at 50 °C for 10 min. The solid catalyst was also recovered and washed thoroughly with ethyl acetate. The previously oxidized real diesel was treated once more in the presence of the recovered UiO-66 catalyst and using a fresh portion of MeCN and H_2O_2 for 8 h at 50 °C. At the end of this second catalytic cycle, the treated diesel was recovered from the ECODS system and finally washed with MeCN at 50 °C for 10 min.

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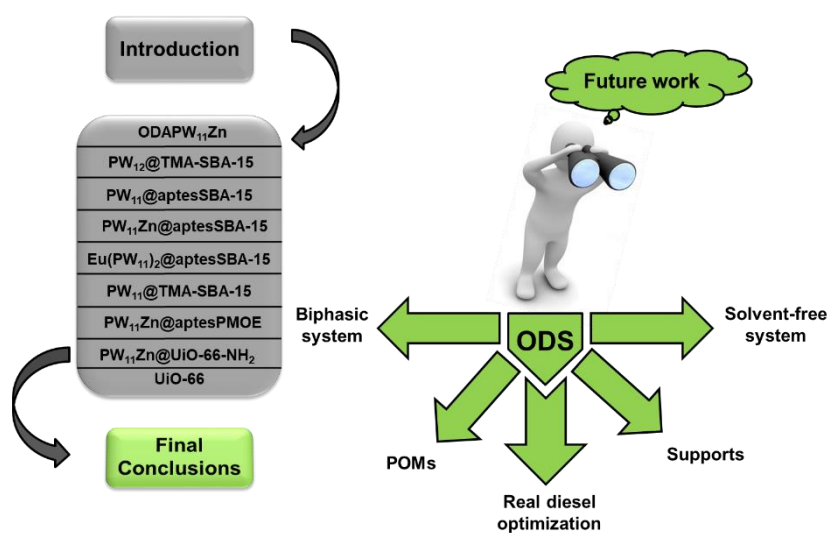
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Chapter 10

Final conclusions and future work



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Chapter 10

Final conclusions and future work

10.1 Final conclusions

The awareness of the hazards effects of SO_2 released to the atmosphere, resultant from the transportation sector, led to the establishment of strict regulations demanding ultra-low levels of sulfur in transportation fuels. This has put pressure in refining oil industries that turns the desulfurization process more expensive to produce low-sulfur fuels. Hydrodesulfurization (HDS) is the standard method in refineries to achieve this purpose. Harsh operational conditions are needed to prepare diesel with sulfur content < 10 ppm, which carries elevated operational costs. As so, complementary methods to HDS are needed and the oxidative desulfurization has emerged as a promising candidate, since it operates under mild reaction conditions and also makes it easier to desulfurize refractory sulfur molecules that are present in a diesel treated by HDS.

Over the last years, polyoxometalates (POMs), specially of the Keggin type (with tunable size, charge and structures and presenting the possibility to include a variety of transition metals) have attracted continuous interest in the area of oxidative desulfurization (ODS), since they have proved to create efficient oxidative catalytic systems under sustainable conditions, using hydrogen peroxide as oxidant.

This project had as main goal the development of novel and efficient heterogeneous catalysts based in POMs able to desulfurize diesel by oxidative process. These catalysts were prepared by the heterogenization of active POMs, following various strategies: i) cationic exchange, using octadecyltrimethylammonium (ODA) cation; ii) immobilization in functionalized SBA-15 supports; iii) immobilization in functionalized periodic mesoporous organosilicas (PMOs); iv) incorporation in a functionalized Metal-Organic Framework (UiO-66- NH_2). Various Keggin structures were studied: i) the Keggin phosphotungstate anion (PW_{12}); the monolacunar PW_{11} ; the zinc mono-substituted PW_{11}Zn and the sandwich-type $\text{Eu}(\text{PW}_{11})_2$. All catalysts were characterized by several techniques to confirm its structures. The oxidative desulfurization studies were performed using H_2O_2 as oxidant, due to its environmental friendliness. Preliminary studies were conducted using different model diesels, containing the most refractory sulfur compounds present in real diesel (1-benzothiophene, dibenzothiophene, 4-

methyldibenzothiophene and 4,6-dimethyldibenzothiophene). Further studies, using the most active, recyclable and stable catalysts, were performed using untreated diesel supplied by Galp (~2300 ppm S) and by CEPISA (~1335 ppm S) companies, containing different sulfur composition (Figures A1 and A5 in Appendix).

Throughout this work there was a permanent concern about the sustainability and the cost-effectiveness of the oxidative desulfurization process and various optimizations were performed, such as the amount of oxidant, the reaction time, the presence or absence of a polar solvent during oxidative step and the nature of the extraction solvent. In fact, the ratio of $\text{H}_2\text{O}_2/\text{S}$ decreased from the initial experiments (21, presented in chapters 2 and 9) to the most recent works (4, presented in Chapters 4, 5, 7 and 8). A remarkable improvement of the reaction time necessary to achieve the highest desulfurization results (from 240 min to 60 min) was also obtained. This was based in the design of more active and robust catalysts and in the optimization of previous mentioned parameters. The application of water/ethanol instead of MeCN to remove the oxidized sulfur compounds from treated diesel (Chapters 4 and 6), was also an important improvement in the desulfurization systems.

The application of polar organic solvents during oxidative desulfurization processes was avoided. Therefore, the efficiency of the biphasic extractive and oxidative desulfurization (ECODS) system was compared with the solvent-free catalytic oxidative desulfurization (CODS) system. The biphasic system consists in an initial liquid-liquid extraction with MeCN or BMIMPF₆, followed by an oxidative catalytic stage (in the presence of the previous extraction solvent). The initial extraction is responsible for removing a large amount of sulfur compounds from the model diesel to the extraction phase, which follow the order 1-BT>DBT>4-MDBT>4,6-DMDBT. The catalytic oxidation occurred mainly in the extraction phase.

In the solvent-free system the oxidation of sulfur compounds occurred without the presence of a polar solvent. The oxidized sulfur compounds were afterwards removed from the treated diesel using more sustainable solvents, such as water and/or ethanol (Chapter 4 and 6). The oxidative reactivity of the sulfur compounds for all desulfurization systems followed the order: DBT>4-MDBT>4,6-DMDBT>1-BT.

In Chapters 2 to 9 is reported the design of several efficient sustainable desulfurization processes containing highly active heterogeneous catalysts that were capable to be recycled over consecutive cycles. Table 10.1 summarizes the best model diesel desulfurization results from each chapter.

When the desulfurization efficiency of the solvent-free system is compared to the biphasic system, it is possible to observe that similar results were obtained using the monolacunar PW_{11} heterogeneous catalysts (chapters 4 and 7). However, for the other studied heterogeneous catalysts ($PW_{11}Zn$ and $Eu(PW_{11})_2$), better desulfurization efficiency was found using the solvent-free system. The solvent-free system presents various advantages associated to sustainability and cost of the process, since no additional organic solvents were used during oxidative step. Additionally, the solvent-free system also seems to increase the stability of the solid catalyst by reducing leaching problems (Chapter 4, 7 and 8).

Among the most active catalysts presented in Table 10.1, it is important to highlight the catalysts that achieved complete desulfurization after 60 min under the most sustainable conditions ($H_2O_2/S = 4$, that corresponds to the stoichiometric ratio to form sulfones, and without the use of solvent during oxidative step): $PW_{11}@aptesSBA-15$, $PW_{11}@TMA-SBA-15$, $PW_{11}Zn@aptesSBA-15$ and $PW_{11}Zn@aptesPMOE$. Lower stability was found for the monolacunar composites, as was observed their transformation in other species, after the catalytic use. The new formed composites should be catalytic active since no loss of activity was noticed in the recycling studies, during six consecutive cycles (Chapter 7). Higher stability was found for $PW_{11}Zn@aptesSBA-15$ and $PW_{11}Zn@aptesPMOE$ composites, that also presented the formation of new active species. These catalysts could be recycled for higher number of consecutive cycles (ten), without loss of activity and without occurrence of leaching.

Similar activity and stability were found for $PW_{11}Zn@aptesSBA-15$ and $PW_{11}Zn@aptesPMOE$ composites. However, higher loading of active center was found for $aptesSBA-15$ composite ($0.111 \text{ mmol/g}^{-1}$) than for $aptesPMOE$ ($0.062 \text{ mmol/g}^{-1}$), which means that a smaller amount of support is needed when the mesoporous silica composite was used.

The preparation of $PW_{11}Zn$ based heterogeneous catalysts by cationic exchange with long-carbon cations (ODA) and incorporation into $UiO-66-NH_2$ originated less efficient catalysts. The $UiO-66$ with the presence of defect sites within its framework, although presenting high desulfurization efficiency (100% for DBT, 4-MDBT and 4,6 DMDBT within 30 min), required a large excess of oxidant ($H_2O_2/S=21$).

Table 10.1 – The most efficient catalytic desulfurization systems based in prepared composites to treat model diesels.

Chapter	Catalyst (amount)	Diesel	ODS Process	Oxidation time (min)	T (°C)	H ₂ O ₂ /S molar ratio	Total desulfurization (%)
2	ODAPW ₁₁ Zn (9 μmol)	A	Biphasic ^a	240	50	21	91.0
3	PW ₁₂ @TMA-SBA-15 (3 μmol)	B	Biphasic ^a	60	70	8	99.0
			Biphasic ^b	60	70	8	93.0
4	PW ₁₁ @aptSBA-15 (3 μmol)	B	Biphasic ^a	60	70	8	100
			Solvent-free	60	70	4	100
5	PW ₁₁ Zn@aptSBA-15 (3 μmol)	B	Biphasic ^a	60	70	8	97.0
			Solvent-free	60	70	4	100
6	Eu(PW ₁₁) ₂ @aptSBA-15 (3 μmol)	B	Biphasic ^a	120	70	12	91.5
			Solvent-free	120	70	12	100
7	PW ₁₁ @TMA-SBA-15 (3 μmol)	B	Biphasic ^a	60	70	8	99.9
			Solvent-free	60	70	4	99.9
8	PW ₁₁ Zn@aptPMOE (3 μmol)	B	Biphasic ^a	120	70	8	94.8
			Solvent-free	60	70	4	99.9
9	PW ₁₁ Zn@UiO-66-NH ₂ (3 μmol)	B	Biphasic ^a	180	70	8	75.9
	UiO-66 (3 μmol)	C	Biphasic ^a	50	50	21	96.0
	UiO-66 (9 μmol)	C	Biphasic ^a	30	50	21	100

^a Biphasic system 1:1 MeCN/Diesel^b Biphasic system 1:1 [BMIM]PF₆/Diesel

A - 1-BT; DBT; 4,6-DMDBT (1500 ppm)

B - 1-BT; DBT; 4-MDBT; 4,6-DMDBT (2000 ppm)

C - DBT; 4-MDBT; 4,6-DMDBT (1500 ppm)

The desulfurization studies performed with real diesels are summarized in Table 10.2. Comparing the efficiency of the composite catalysts to oxidative desulfurization of diesel supplied by CEPESA and by Galp, it is possible to observe a higher efficiency using the CEPESA diesel. This must be related to the appreciable lower sulfur content of CEPESA diesel compared to that of Galp, and also to the lower content of BT derivatives, been those the most difficult to oxidize.

Comparing the performance of PW_{11} based catalysts ($PW_{11}@apt\text{esSBA-15}$ and $PW_{11}@TMA\text{-SBA-15}$) to treat real diesel using biphasic and solvent-free systems, it is possible to observe that their biphasic oxidative desulfurization efficiency was slightly higher than that obtained using the solvent-free system (treating the CEPSA diesel). The initial extraction, that occurs in the biphasic system, may remove more polar molecules, including sulfur compounds that are then oxidized, contributing for the higher desulfurization efficiency observed using this system instead of the solvent-free system, where the sulfur oxidation needs to occur in the diesel phase, in which other various molecules with high potential to be oxidized are also present, since the real diesel presents a highly complex matrix containing sulfur, paraffinic, naphthenic, aromatic and nitrogen compounds, among others.

Using the zinc mono-substituted catalyst $PW_{11}Zn@apt\text{esSBA-15}$, similar oxidative desulfurization efficiency was observed using biphasic and solvent-free system to treat CEPSA diesel. When the nature of the support was changed for a less hydrophilic material, *i.e.* $PW_{11}Zn@apt\text{esPMOE}$, the oxidative desulfurization efficiency decreased markedly. Therefore, the replacement of the mesoporous silica SBA-15 support by a periodic mesoporous organosilica (PMO), did not have an important influence using model diesel, but it is not the best strategy to improve catalytic oxidative performance to desulfurize real diesel.

The best result to treat CEPSA diesel was obtained with $PW_{11}@TMA\text{-SBA-15}$ (93.1%). To treat the diesel with higher sulfur content (Galp), 73% desulfurization was achieved after 2h, using $PW_{11}Zn@apt\text{esSBA-15}$ and H_2O_2/S ratio of 8. Using the hybrid $ODAPW_{11}Zn$ also 73% of desulfurization efficiency was achieved after 8 h of reaction, using a larger oxidant amount and an exhaustive pre-treatment (3 extraction cycles). Using similar experimental conditions and UiO-66 as catalyst, the desulfurization efficiency to treat Galp diesel was increased to 81%; however, two desulfurization cycles of 8 h each were performed.

The main conclusions to be drawn from the oxidative desulfurization studies present in this work are that it is necessary to derivatize the Keggin structure (PW_{12}) to achieve higher catalytic performance. The solvent-free systems using silica catalysts presented higher desulfurization efficiencies to treat model diesels, but slightly lower desulfurization results were found for real diesel. However, since the catalysts presented higher stability and lower leaching under the solvent-free system, further studies should be addressed to optimize this system to treat real diesel samples. This optimization

should be performed using mesoporous silica SBA-15, since its replacement for a less hydrophilic material (PMO) did not promote a higher real diesel desulfurization.

In short, the main goal of this project was achieved since novel efficient and robust POM-based heterogeneous catalysts were successfully prepared and applied in oxidative desulfurization of high sulfur content model and real diesels.

Table 10.2 – The most efficient catalytic desulfurization systems based in prepared composites to treat real diesels

Chapter	Catalyst (amount)	Diesel	n° extractive processes before ODS	ODS Process	Oxidation time (min)	T (°C)	H ₂ O ₂ /S molar ratio	Total desulfurization (%)
2	ODAPW ₁₁ Zn (9 μmol)	Galp	3	Biphasic ^{a,c}	480	50	27	72.0
3	PW ₁₂ @TMA-SBA-15 (3 μmol)	Galp		Biphasic ^{b,c}	120	70	8	65.0
4	PW ₁₁ @aptesSBA-15 (3 μmol)	CEPSA		Biphasic ^a	120	70	8	83.4
				Solvent-free ^c	120	70	8	71.9
5	PW ₁₁ Zn@aptesSBA-15 (3 μmol)	Galp	1	Biphasic ^{a,c}	120	70	8	72.9
		CEPSA		Biphasic ^{a,c}	120	70	8	85.4
				Solvent-free ^c	120	70	8	87.7
7	PW ₁₁ @TMA-SBA-15 (3 μmol)	CEPSA		Biphasic ^{a,c}	120	70	8	93.1
				Solvent-free ^c	120	70	8	75.0
8	PW ₁₁ Zn@aptesPMOE (3 μmol)	CEPSA		Biphasic ^{a,c}	120	70	8	75.9
9	UiO-66 (9 μmol)	Galp	3	Biphasic ^{a,c}	480 (2 cycles)	50	21	81.0

Galp 2300 ppm S; CEPSA 1335 ppm S

^a Biphasic system 1:1 MeCN/Diesel

^b Biphasic system 1:1 [BMIM]PF₆/Diesel

^c liquid-liquid treated diesel/MeCN extraction after ODS process during 10 min

10.2. Future work

Future prospects of this work are essentially focused on the use of a more complex matrix to simulate real diesel. The model diesel should be prepared with a higher carbon chain solvent, such as hexadecane. Also, besides the refractory sulfur compounds, some naphthalenes and other aromatic compounds should also be present to better simulate real diesel.

The optimization of experimental conditions, including the extraction of the oxidized sulfur compounds with water, should be carried out in real diesel samples. At this point, and considering that hydrodesulfurization is relatively unexpensive to desulfurize a diesel stream up to 200-300 ppm and these treated diesel is mainly composed by dibenzothiophene and dibenzothiophene derivatives which are easily oxidized by oxidative desulfurization, the developed desulfurization systems should be applied as a complement to the hydrodesulfurization system from a feedstock up to 200-300 ppm.

At the end of oxidative desulfurization treatment, an evaluation of the real diesel quality should be performed to assess how the desulfurization treatment affects the diesel properties.

Appendix

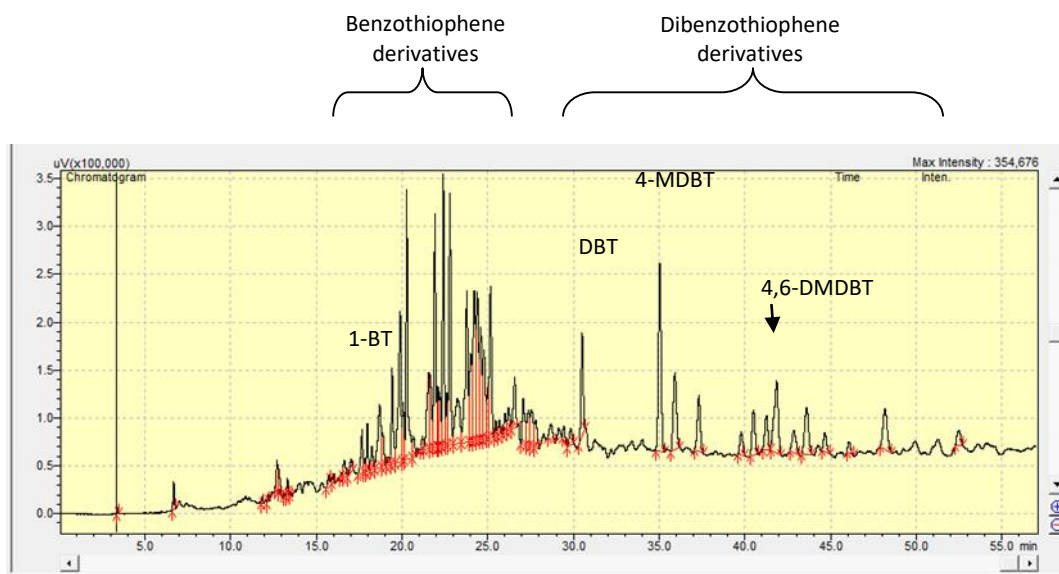


Figure A.1. Chromatogram (GC-FPD) of untreated diesel (10 times diluted in ethyl acetate).

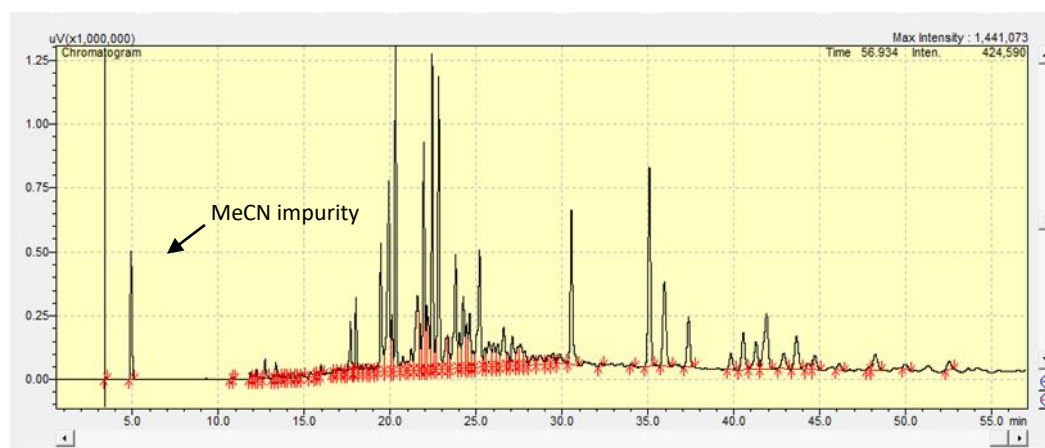


Figure A.2 - Chromatogram (GC-FPD) from the extraction MeCN phase presenting the no oxidized sulfur compounds extracted from untreated diesel, during 10 min at 50 °C.

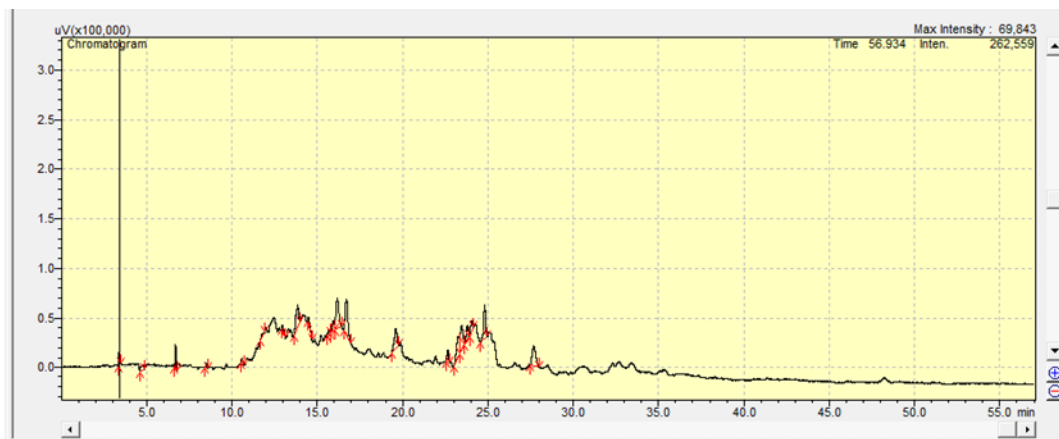


Figure A.3 - Chromatogram (GC-FPD) of treated diesel (10 times diluted in ethyl acetate) by oxidative catalytic desulfurization process.

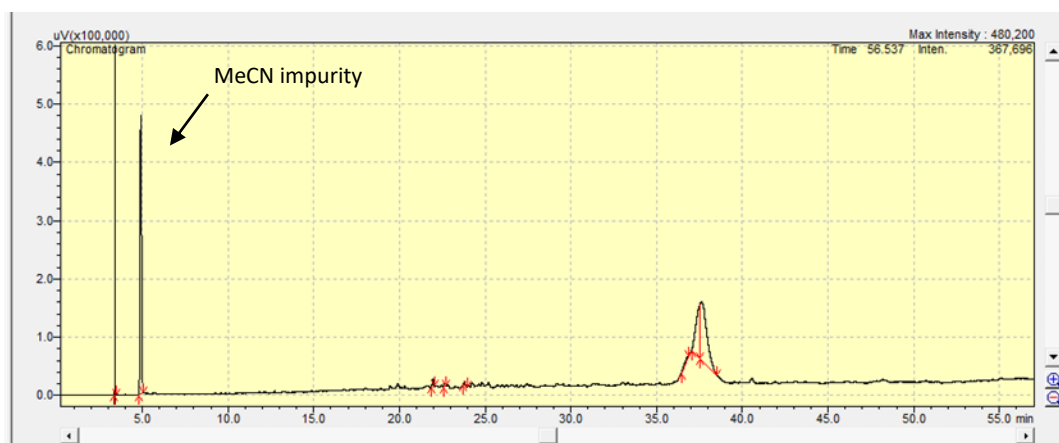


Figure A.4 - Chromatogram (GC-FPD) from the extraction MeCN phase after the final liquid extraction step performed to the diesel treated by ODS process.

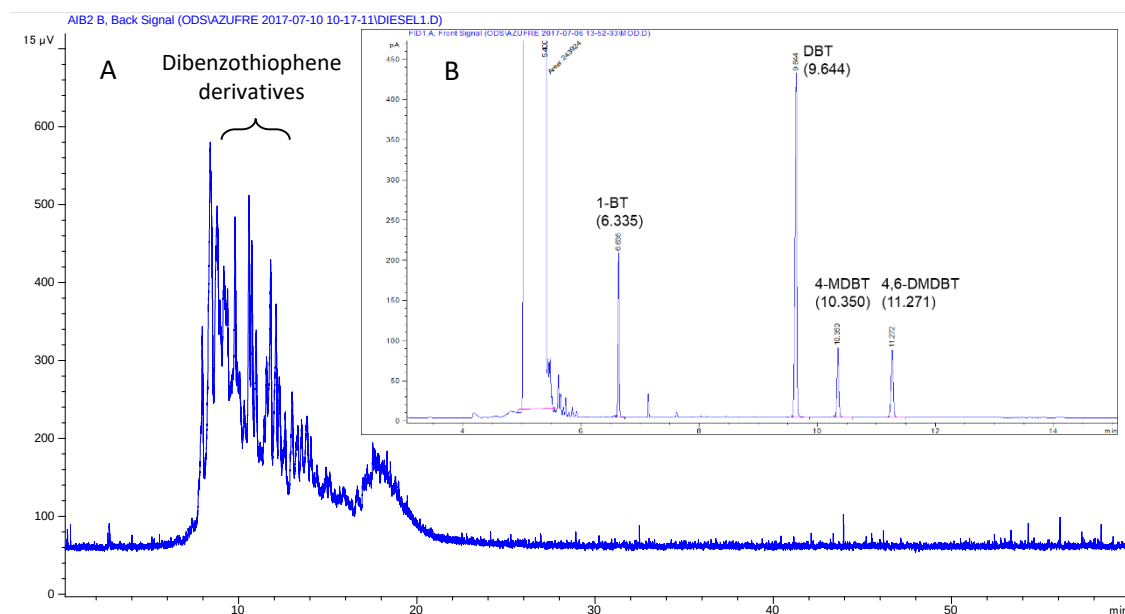


Figure A.5 - Chromatogram obtained by GC-FID/SCD from untreated diesel supplied by CEPISA (A) and model diesel B (B).

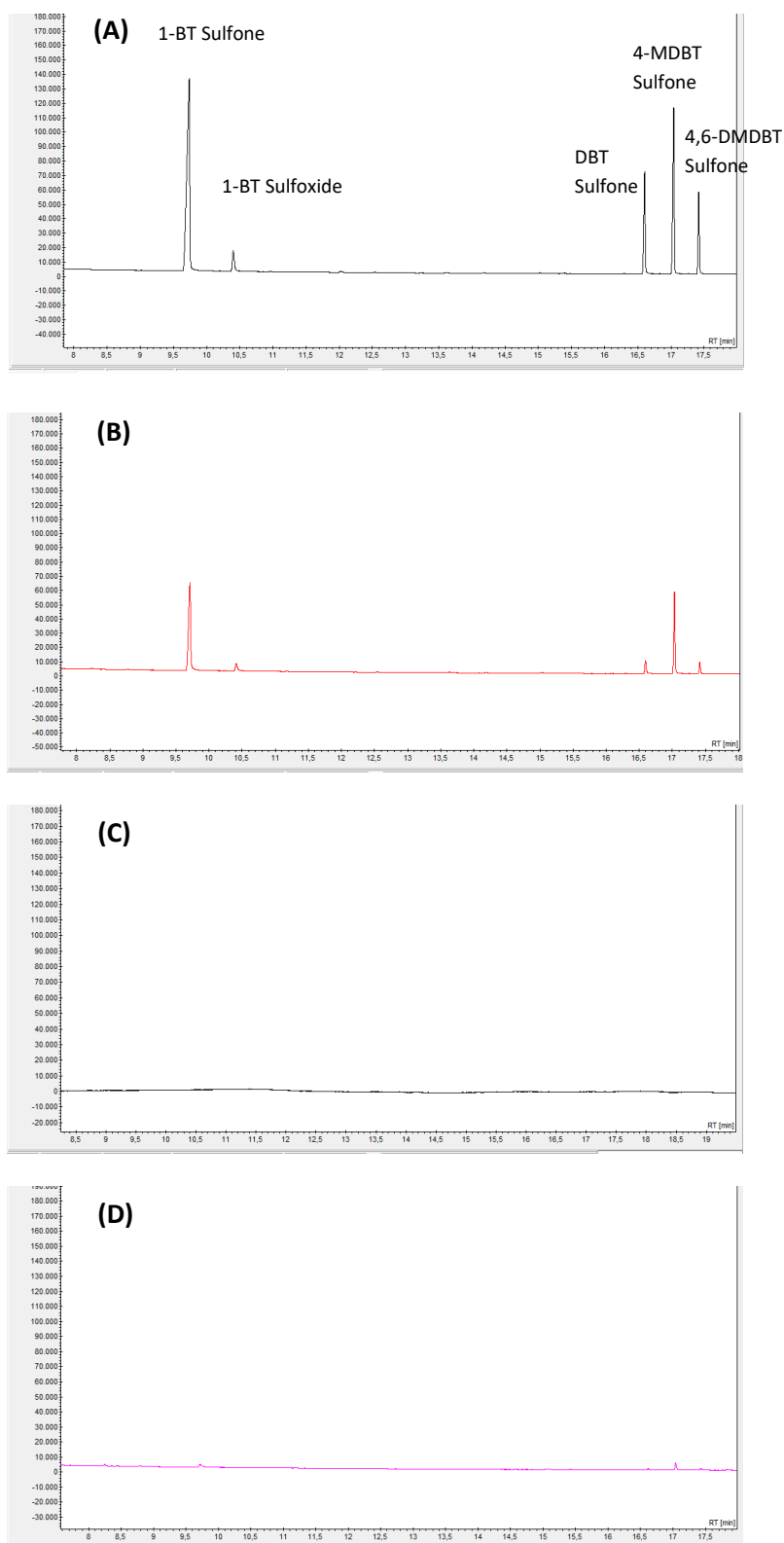


Figure A.6 - Chromatogram displays from the model diesel treated under solvent-free conditions $\text{Eu}(\text{PW}_{11})_2@ \text{aptesSBA-15}$ catalyst and H_2O_2 oxidant). (A) after 4 h of catalytic sulfur oxidative reaction; (B) after 10 min of centrifugation treatment at room temperature; (C) after liquid-liquid extraction with 1 mL of acetonitrile; and (D) after three consecutive liquid extraction cycles with 1 mL of water.