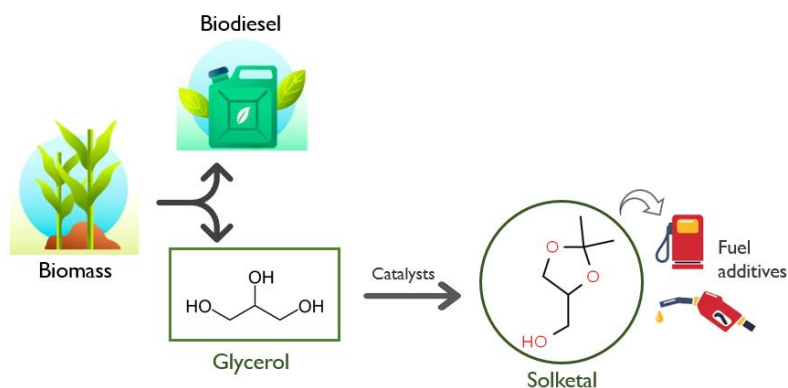




# Preparation of catalysts for the sustainable conversion of glycerol into fuel additives

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Master's Degree in Chemistry – Specialization in Functionalized Materials and Surfaces for Sustainability

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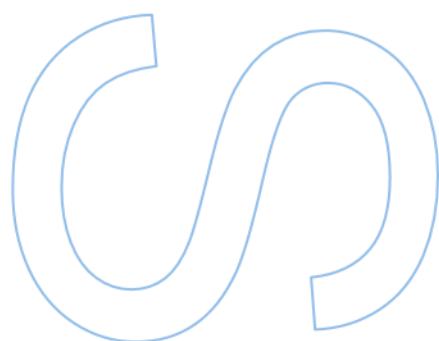
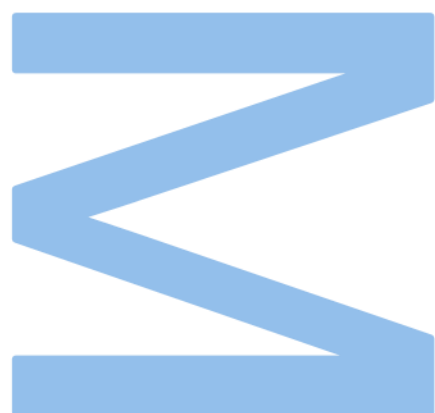
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## Abstract

Fossil fuel consumption is one of the main generators of greenhouse gas emissions, negatively impacting climate change. As such, environmental policies have been widely adopted, with the growing need for new fuel alternatives. Biodiesel is an environmentally friendly fuel, with a strong disadvantage associated to its production, that consists in the formation of a large amount of the by-product glycerol. Valorisation strategies for glycerol repurpose include the acetalization reaction, where in the presence of ketones, glycerol originates solketal, a very attractive oxygenated fuel additive. The glycerol conversion efficiency is very deeply dependent on the catalyst selected for the reaction. One of the ideal choices is the use of acid polyoxometalates (also known as heteropolyacids, HPAs).

This thesis project focused on the preparation of novel heterogeneous catalysts, able to obtain high glycerol conversion and high solketal selectivity. These catalysts are based in HPA active centres ( $\text{H}_3\text{PW}_{12}$ ,  $\text{H}_3\text{PMo}_{12}$  and  $\text{H}_4\text{SiW}_{12}$ ), immobilized in mesoporous silica and polymeric membranes. The active centres were initially applied in glycerol acetalization reactions, as homogeneous catalysts, and experimental parameters were optimized. Then, the best performing HPAs were incorporated in solid supports to form heterogeneous catalysts. Initially, into functionalized APTES-SBA-15 mesoporous silica  $\text{HPAs}@ \text{APTES-SBA-15}$ , through an impregnation procedure, and later in polymeric membranes of polyvinyl alcohol (PVA)  $\text{HPA}@ \text{PVA}$ . Still, the mesoporous silica composites  $\text{HPA}@ \text{APTES-SBA-15}@ \text{PVA}$  were further immobilized in the PVA polymeric matrix, as to increase catalyst robustness and recycling potential.

The homogeneous  $\text{H}_3\text{PW}_{12}$  demonstrated higher glycerol conversion (97%, with 97% of solketal selectivity, after 30 min at 25 °C), when compared to the other HPAs. The influence of catalyst acidity in glycerol acetalization reactions was evaluated, with higher conversions observed using an optimized catalyst acidity of 0.373 mmol  $\text{H}^+/\text{g}$ , value applied for the following acetalization reactions.

The HPAs immobilized in functionalized APTES-SBA-15 support ( $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}@ \text{APTES-SBA-15}$ ), were tested as solid catalysts in glycerol acetalization, under the same optimized reaction conditions as the HPAs. The  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  composite demonstrated superior catalytic performance (97% of conversion with 97% of solketal selectivity, after 60 min at 25 °C). Catalyst stability was investigated for four consecutive reutilization and recycling cycles, with

H<sub>3</sub>PW<sub>12</sub>@APTES-SBA-15 exhibiting a decrease in catalytic efficiency, due to loss of acidic HPA sites.

Then, the catalytic polymeric membranes were prepared, through the immobilization of HPAs in a PVA matrix, with or without the presence of the functional group APTES (H<sub>3</sub>PW<sub>12</sub>@APTES-PVA, H<sub>3</sub>PMo<sub>12</sub>@APTES-PVA, H<sub>3</sub>PW<sub>12</sub>@PVA and H<sub>3</sub>PMo<sub>12</sub>@PVA), and tested as one-piece heterogeneous catalysts. Membranes with APTES exhibited absence of catalytic activity. Polymeric membranes without APTES were also applied in glycerol acetalization reactions, with H<sub>3</sub>PW<sub>12</sub>@PVA demonstrating superior catalytic efficiency (95% of conversion with 98% of solketal selectivity, after 60 min at 60 °C). Catalyst stability of H<sub>3</sub>PW<sub>12</sub>@PVA was studied during ten consecutive reutilization cycles, without loss of catalytic performance.

Finally, polymeric composite membranes (H<sub>3</sub>PW<sub>12</sub>@APTES-SBA-15@PVA and H<sub>3</sub>PMo<sub>12</sub>@APTES-SBA-15@PVA) were also tested as one-piece heterogeneous catalysts with the intension of forming a more robust catalyst than the mesoporous powder HPAs@APTES-SBA-15 composites. However, these composite membranes showed absence of catalytic activity, with no glycerol conversion detected. These results opened the possibility for further work perspectives, namely in possible strategies for the successful preparation and application of catalytically active composite membranes in glycerol acetalization reactions.

**Keywords:** heterogeneous catalysis, solketal, acetalization, polyoxometalates, mesoporous silica, composites, polymeric membranes

## Resumo

O consumo de combustíveis fósseis é um dos maiores responsáveis pela emissão de gases de efeito de estufa, que impactam negativamente as mudanças climáticas. Assim, legislações ambientais têm sido implementadas, fomentando a necessidade de novas alternativas energéticas. O biodiesel é um combustível verde, com uma grande desvantagem associada à sua produção, na qual o glicerol é produzido em larga quantidade como produto secundário. Estratégias para valorizar o glicerol, de modo a ser possível o seu reaproveitamento, incluem a reação de acetilização. Assim, na presença de acetonas, o glicerol origina solketal, um aditivo de combustível oxigenado bastante atrativo. A eficiência da conversão do glicerol está bastante interligada com a escolha do catalisador da reação. Uma das escolhas ideais é o uso de polioxometalatos ácidos (também conhecidos como heteropoliácidos, HPAs).

Este projeto de tese tem como foco a preparação de catalisadores heterogêneos inovadores, de modo a obter valores de conversão de glicerol e seletividade ao solketal altos. Estes catalisadores são baseados em centros ativos HPAs ( $\text{H}_3\text{PW}_{12}$ ,  $\text{H}_3\text{PMo}_{12}$  e  $\text{H}_4\text{SiW}_{12}$ ) imobilizados em sílica mesoporosa e membranas poliméricas. Os centros ativos foram inicialmente usados em reações de acetilização de glicerol, como catalisadores homogêneos, e a otimização de parâmetros experimentais foi realizada. Em seguida, os HPAs com o melhor desempenho foram incorporados em suportes sólidos, de modo a originar catalisadores heterogêneos. Inicialmente, foram incorporados numa sílica mesoporosa funcionalizada APTES-SBA-15, formando  $\text{HPA}@ \text{APTES-SBA-15}$  através de um procedimento de impregnação, e mais tarde em membranas de álcool polivinílico (PVA),  $\text{HPA}@ \text{PVA}$ . Ainda, os compósitos de sílica mesoporosa  $\text{HPA}@ \text{APTES-SBA-15}@ \text{PVA}$  foram imobilizados numa matriz polimérica de PVA, de modo a aumentar a robustez e potencial de reciclagem do catalisador.

O homogêneo  $\text{H}_3\text{PW}_{12}$  demonstrou melhor conversão de glicerol (97% com seletividade ao solketal de 97%, depois de 30 min a 25 °C), quando comparado com os outros HPAs. A influência da acidez do catalisador foi avaliada, com conversões mais altas observadas com uma acidez de 0,373 mmol  $\text{H}^+/\text{g}$ , valor que foi aplicado nas restantes reações de acetilização.

Os HPAs imobilizados no suporte funcionalizado APTES-SBA-15 ( $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  e  $\text{H}_3\text{PMo}_{12}@ \text{APTES-SBA-15}$ ) foram testados como catalisadores sólidos em acetilização de glicerol, com as mesmas condições experimentais previamente otimizadas com os HPAs. O compósito  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  demonstrou o

melhor desempenho catalítico (conversão de 97% com seletividade ao solketal de 97%, depois de 60 min a 25 °C). A estabilidade do catalisador foi estudada durante quatro ciclos consecutivos de reutilização e reciclagem, em que  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  sofreu uma diminuição de eficiência catalítica, devido à perda de centros ativos HPA.

Em seguida, as membranas poliméricas catalíticas preparadas, através da imobilização de HPAs numa matriz de PVA, na presença ou ausência do grupo funcional APTES ( $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$ ,  $\text{H}_3\text{PMo}_{12}\text{@APTES-PVA}$ ,  $\text{H}_3\text{PW}_{12}\text{@PVA}$  e  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ ) foram usadas como catalisadores heterogêneos de peça singular. As membranas poliméricas com APTES não demonstraram atividade catalítica. As membranas poliméricas sem APTES foram também aplicadas em reações de acetilização de glicerol, em que  $\text{H}_3\text{PW}_{12}\text{@PVA}$  demonstrou eficiência catalítica superior (conversão de 95% com seletividade ao solketal de 98%, depois de 60 min a 60 °C). A estabilidade do catalisador  $\text{H}_3\text{PW}_{12}\text{@PVA}$  foi estudada durante dez ciclos consecutivos de reutilização, sem perda de atividade.

Finalmente, membranas poliméricas com compósitos ( $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  e  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$ ) foram também usadas como catalisadores heterogêneos de peça singular, com o objetivo de desenvolver um catalisador mais robusto que os compósitos mesoporosos em pó  $\text{HPAs@APTES-SBA-15}$ . No entanto, estas membranas não demonstraram qualquer atividade catalítica, não sendo detetada nenhuma conversão de glicerol em solketal. Estes resultados abriram a possibilidade de futuras perspetivas de trabalho, nomeadamente sobre possíveis estratégias para a preparação e aplicação bem-sucedida de membranas com compósito cataliticamente ativas, para a reação de acetilização do glicerol.

**Palavras-chave:** catálise heterogênea, solketal, acetilização, polioxometalatos, sílica mesoporosa, compósitos, membranas poliméricas

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## List of Abbreviations

|                |                                                          |
|----------------|----------------------------------------------------------|
| <b>APTES</b>   | 3-aminopropyltriethoxysilane                             |
| <b>ATR</b>     | Attenuated Total Reflectance                             |
| <b>EDS</b>     | Energy Dispersive X-Ray Spectroscopy                     |
| <b>FAAEs</b>   | Fatty acid alkyl esters                                  |
| <b>FTIR</b>    | Fourier Transform Infrared Spectroscopy                  |
| <b>GHG</b>     | Greenhouse gases                                         |
| <b>HPA</b>     | Heteropolyacid                                           |
| <b>ICP-OES</b> | Inductively Coupled Plasma Optical Emission Spectrometry |
| <b>MCM-41</b>  | Mobil Composition of Matter No.41                        |
| <b>NMR</b>     | Nuclear Magnetic Resonance                               |
| <b>P123</b>    | Pluronic P123                                            |
| <b>PEO</b>     | Poly(ethylene oxide)                                     |
| <b>POM</b>     | Polyoxometalate                                          |
| <b>PVA</b>     | Polyvinyl alcohol                                        |
| <b>PXRD</b>    | Powder X-Ray Diffraction                                 |
| <b>SBA-15</b>  | Santa Barbara Amorphous No. 15                           |
| <b>SEM</b>     | Scanning Electron Microscopy                             |
| <b>TEOS</b>    | Tetraethoxysilane                                        |

# 1.Introduction

### 1.1. Societal energy needs: biodiesel and the by-product

The global phenomenon of societal and industrial development has progressively increased energetic demands. In order to answer these needs, fossil fuel consumption has soared in the past decades. However, this increase does not come without consequences, mainly in two areas: energetical and environmental.

Fossil fuels are non-renewable energy sources, meaning that their resources will eventually run out. The exponential rise in their consumption has led to a rapid decrease in raw fossil sources.<sup>1, 2</sup> Nevertheless, these energetic demands have not reduced, and therefore, it is extremely necessary to develop new energy alternatives, focusing on preserving sustainability. One of the biggest concerns of the last century is climate change, with growing awareness leading to the implementation of legislation and environmental policies. It is well known that one of the main contributors for climate change is related to the emission of greenhouse gases (GHG), derived from fossil fuel consumption.<sup>1, 3, 4</sup> Indeed, the European Union has planned to reduce 55% of GHG emissions by 2030, and completely eliminate them until 2050.<sup>5</sup>

Evidently, search for the solution for both situations has increased interest in renewable energy alternatives, with biomass distinguishing itself as a very attractive candidate.<sup>1, 6</sup> Biomass can be defined as the energy derived from organic materials, from either edible or non-edible sources, allowing an improvement of the sustainability in the energetic sector, decreasing its environmental impact.<sup>1, 2, 7</sup> Its use in fuel formulation has led to the appearance of fuel alternatives, such as biodiesel. This is considered a non-toxic and biodegradable fuel, and therefore, its production and interest has increased in recent years.<sup>1, 4, 8</sup> The biodiesel production reaction can be observed in Figure 1.1. Biodiesel is obtained through the transesterification of triglycerides (a type of fat found in vegetable oils) in the presence of an alcohol (usually methanol) and an appropriate catalyst.<sup>3, 9</sup> This reaction originates two products: biodiesel, also known as fatty acid alkyl esters (FAAEs) and glycerol.<sup>1, 3</sup>

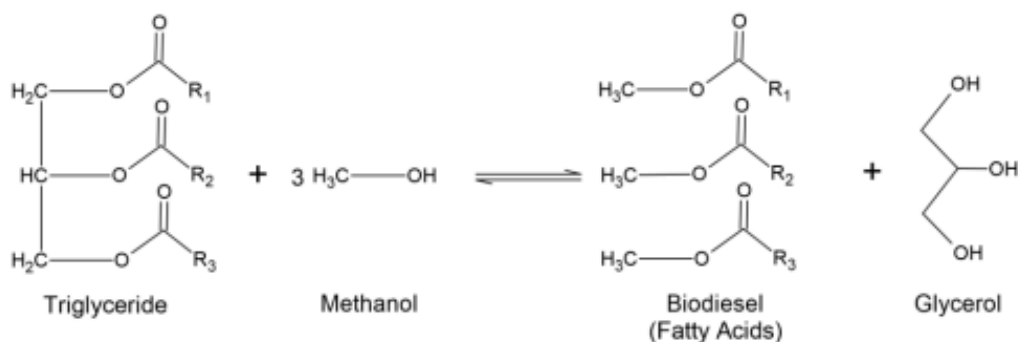


**Figure 1.1** - Biodiesel production reaction, originating glycerol as a by-product. Adapted from literature <sup>3</sup>.

Glycerol is the by-product of the transesterification reaction, obtained in a ratio of 1:10 compared to biodiesel.<sup>6, 9</sup> Due to the increased interest in biodiesel production, there is an excess of crude glycerol in the fuel industry. In fact, glycerol consumption cannot keep up with the rate at which it is being produced.<sup>3, 9</sup>

From the 12 Principles of Green Chemistry, Principle Number 9, Catalysis, intends the decrease, or even complete elimination of waste products in manufacturing reactions, turning the reactions more selective for the desired product.<sup>10</sup> It is crucial for the biodiesel industry to develop sustainable and efficient catalytic processes capable of valorising and utilizing the crude glycerol produced.<sup>3, 8</sup>

## 1.2. Glycerol Valorisation

Propane-1,2,3-triol ( $C_3H_8O_3$ ), commonly referred as glycerol, is a compound composed of three hydroxyl substituents, as seen in Figure 1.2. The presence of these groups allows the formation of hydrogen bonds, and as such, glycerol is soluble in water and insoluble in hydrocarbons.<sup>7, 9</sup> Glycerol has raised interest for its use in many different applications, ranging from cosmetics, pharmaceutical, and for the production of other value-added products.<sup>6, 9</sup> The most important properties of this molecule are the high boiling point, non-toxicity and low volatility.<sup>7</sup>

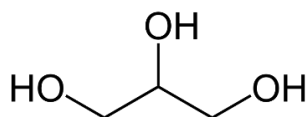


Figure 1.2 - Molecular structure of glycerol.

While glycerol has many different uses, it is important to take into consideration that most of these applications are only viable for pure glycerol. However, glycerol formed from the biodiesel industry, i.e. crude glycerol, possesses impurities related to the biodiesel production reaction, for example salts, water and residue from methanol.<sup>2-4</sup> Therefore, there are two strategies that can be followed: i) refine the crude glycerol or ii) utilize other reactions to obtain glycerol-derived value-added products. Normally, the second strategy is opted, since the purification process can become extremely costly.<sup>11, 12</sup> While focusing on the second strategy, i.e. glycerol valorisation, it is possible to find a variety of catalytic reactions able to transform glycerol. Some examples illustrated in Figure 1.3 can be distinguished, such as etherification<sup>13</sup>, dehydration<sup>14</sup>, hydrogenolysis<sup>15</sup>, carboxylation<sup>16</sup>, oxidation<sup>17</sup> and, the most important for this work, acetalization, which will be discussed in section 1.2.1.

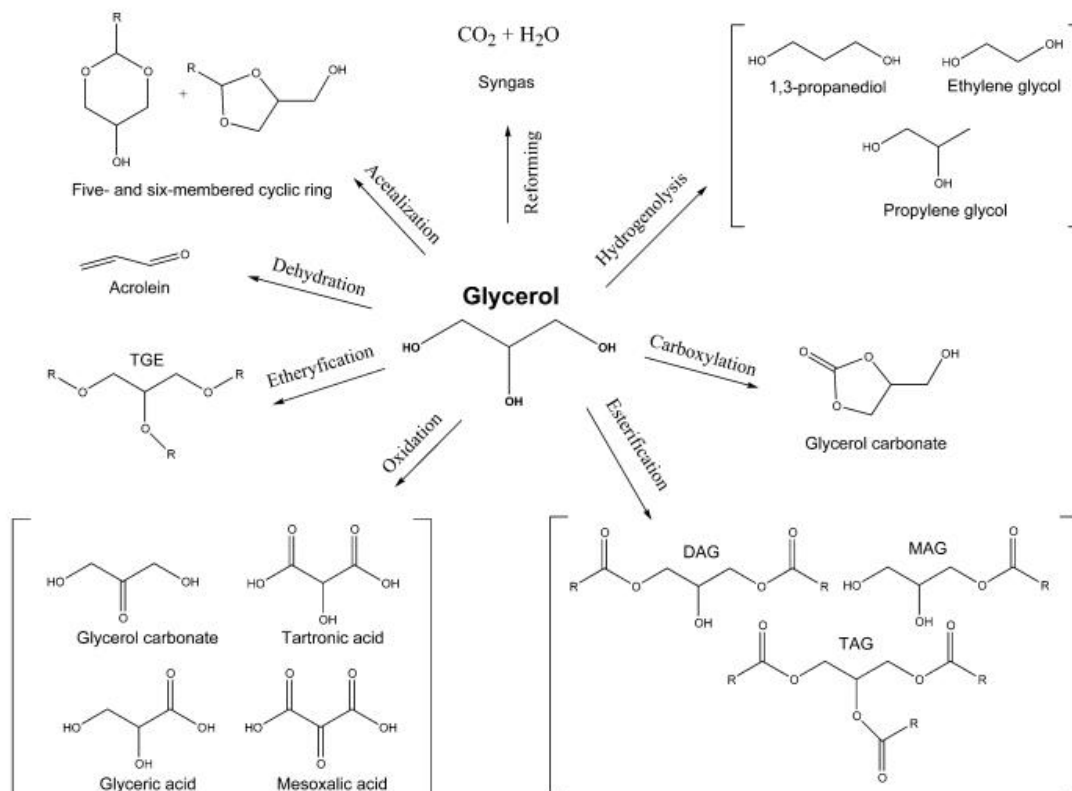


**Figure 1.3** - Various examples of glycerol valorisation reactions and the respective products obtained. Adapted from literature <sup>2</sup>.

Fuel additives derived of glycerol ethers, namely di-ethers and tri-ethers, can be obtained by glycerol etherification, a condensation reaction in the presence of alcohols and catalysts.<sup>13</sup> Acrolein can be obtained by glycerol dehydration, which can be transformed into many other chemicals, including acrylic acid as the most known one, applied in polymer formulation.<sup>14</sup> Hydrogenolysis of glycerol occurs during dehydration, through the addition of a hydrogen source. This addition allows the formation of 1,2-propanediol, 1,3-propanediol, ethylene glycol and propylene glycerol. The first two are mainly applied in polymer synthesis.<sup>15</sup> Glycerol carboxylation, in the presence of dimethyl carbonate, originates glycerol carbonate which is also widely used in polymer formulation.<sup>16</sup> Oxidation of glycerol can originate a variety of products that depend on the catalyst nature and pH used. Some examples of the desired products from glycerol oxidation are tartaric acid and glyceric acid.<sup>17</sup>

### 1.2.1. Acetalization

Acetalization of glycerol occurs in the presence of either aldehydes or ketones, giving rise to the products observed in Figure 1.4: solketal as a five-membered cyclic compound and acetal, a six-membered cyclic compound. Water can be considered a by-product in this reaction.<sup>2, 3, 7</sup>

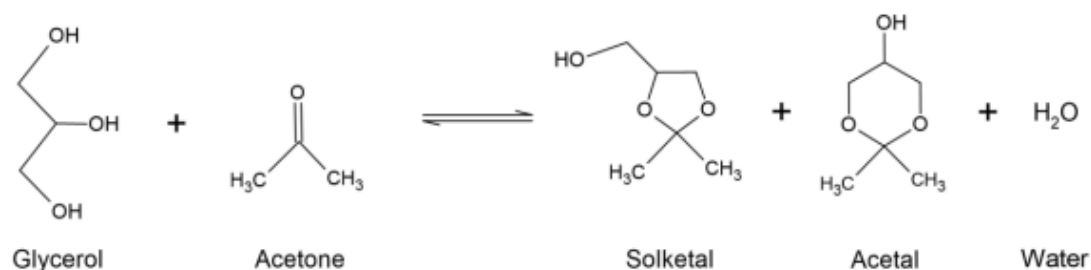


**Figure 1.4** - Glycerol acetalization reaction, with the originated products solketal, acetal and water. Adapted from literature <sup>3</sup>.

One of the main products obtained in the acetalization reaction of glycerol is 2,2-dimethyl-1,3-dioxolane-4-methanol (C<sub>6</sub>H<sub>12</sub>O<sub>3</sub>), also known as solketal. This compound is characterized by its low toxicity and high miscibility in most solvents (especially water and organic solvents), which favours its use as an environmentally friendly substance.<sup>2, 9</sup> Despite having many different applications, solketal has found its purpose in the fuel industry, thanks to its extraordinary performance as an oxygenated fuel additive.<sup>3, 4</sup>

Oxygenated fuel additives are substances that are applied to improve fuel characteristics and properties. To name a few, additives can decrease the viscosity of the fuel, improve cold flow properties, act as cleanliness agents and even reduce particle emission.<sup>2, 3, 7, 9</sup> Particularly, the use of fuel additives in biodiesel is fundamental, since this kind of fuel shows superior viscosity (when compared to fossil fuel and its originated diesels), which could cause engine problems without treatment.<sup>2, 3</sup>

As seen in Figure 1.5, the use of solketal as a fuel additive in biodiesel is environmentally and economically advantageous, through a Circular Economy perspective <sup>3, 7</sup>, when considering the following factors: i) biodiesel reaction forms glycerol as a by-product; ii) glycerol can be repurposed into solketal through acetalization; iii) solketal is used as a very well-performing fuel additive; and finally iv) biodiesel requires the use of fuel additives in order to be commercialized.

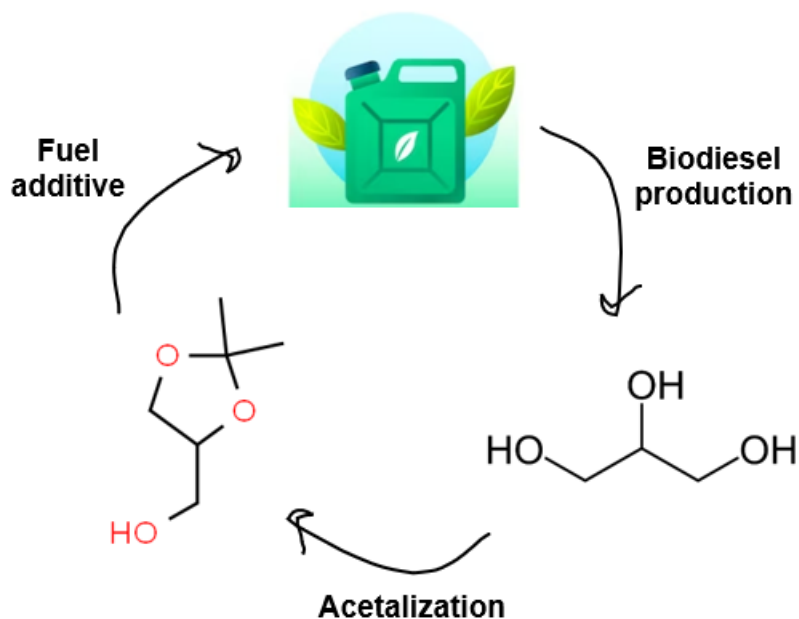


**Figure 1.5** – Schematic illustration of the Circular Economy model followed for the crude glycerol obtained from the biodiesel production process. Solketal is applied as a fuel additive in biodiesel.

### 1.2.2. Optimization of solketal production

An important factor to consider in the acetalization reaction is the existence of a large thermodynamic obstacle. Acetalization of glycerol originates water as a by-product, that decreases largely the yield of solketal obtained.<sup>2-4, 7</sup> Therefore, it is essential to adopt strategies that shift the reaction towards solketal formation, avoiding the presence of water. These strategies are dependent on the correct choice of the substrate, the solvent and the catalyst.

#### 1.2.2.1. Substrate

As discussed in section 1.2.1, the acetalization of glycerol occurs in the presence of oxygen-containing compounds, commonly ketones or aldehydes, which are referred as substrates. Some examples of substrates used can be seen in Figure 1.6: formaldehyde<sup>18</sup>, benzaldehyde<sup>19</sup> and, the focus of this work, acetone<sup>6, 20-22</sup>.

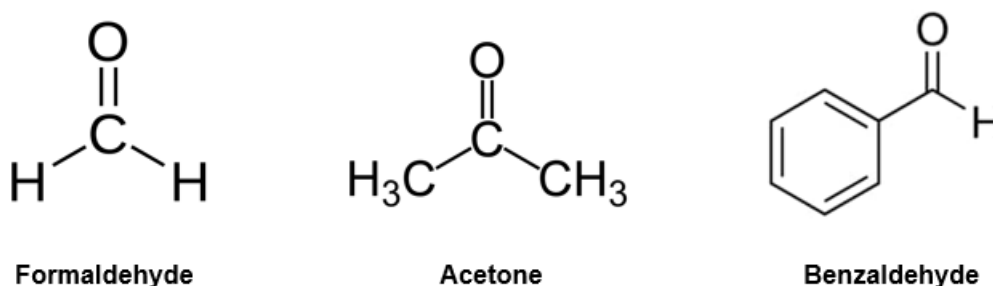


**Figure 1.6** – Most common substrates used in acetalization: formaldehyde, acetone and benzaldehyde.

As mentioned above, the thermodynamic setback of the acetalization reaction must be surpassed. One of the most used strategies for this purpose is to increase the glycerol/substrate ratio.<sup>3, 4, 9</sup> Research studies have shown that acetone is particularly effective, since its excess leads to increased glycerol conversion.<sup>20, 21</sup> Therefore, it is also important to take into consideration the substrate/glycerol ratio, in order to obtain a high solketal yield.

#### 1.2.2.2. Solvent

One other commonly used strategy to increase solketal formation is to remove one of the products from the reactional system.<sup>3, 4, 9</sup> As seen before, there are two other products beside solketal – acetal and water. Removal of water can be obtained through the utilization of desiccants, between other compounds.<sup>3</sup>

Traditionally, acetalization reactions occurred in the presence of organic solvents, in which acetal would be dissolved and removed from the solution.<sup>2, 9</sup> In the last years, breakthroughs in catalyst research have led to the use of solvent-free environments, since optimized catalysts already assure the favourable reaction equilibrium, without needing solvents.<sup>9, 22-24</sup>

#### 1.2.2.3. Catalyst

The function of a catalyst is to improve the kinetic parameters of the reaction, allowing to reach equilibrium faster, all while not being consumed in the reaction.<sup>8, 11</sup> Ideal catalysts need to present a high recycling capacity, to be consequently used while maintaining their catalytic efficiency for various reaction cycles. Also, it is crucial to be able to isolate and recover the catalyst from the reaction medium. Characteristics such as high recuperation and recyclability help reduce costs and, more importantly, waste disposal. Finally, catalysts should also be environmentally friendly, i.e. presenting high activity under sustainable conditions, according to the Green Chemistry Principles.<sup>4, 12</sup>

In glycerol acetalization, the correct choice of the catalyst is essential for the reaction, since without the presence of a catalyst, the reaction practically does not occur.<sup>2</sup> In this case, the catalyst is responsible for activating the carbonyl groups of the substrate, which then kickstarts the reaction.<sup>2</sup> In the past years, research in this area showed that this initial activation is strongly dependent on catalyst acidity.<sup>6, 7, 12, 21</sup>

Further investigation has allowed the proposal of an acetalization mechanism, using catalysts presenting Brönsted acidity. This mechanism is illustrated in Figure 1.7 and two stages can be distinguished: formation of a carbenium ion and formation of the products (acetal and solketal). In the first stage, a  $H^+$  proton of the catalyst attacks the carbonyl of the substrate used (in this work, the acetone). Through this interaction, it is observed the formation of an intermediate structure that, interacting with the  $-OH$  groups belonging to glycerol, forms a hemiketal/hemiacetal. Once the water is removed from the reaction, the formation of a tertiary carbenium ion occurs. As such, the first stage is complete, and the second stage begins.<sup>9, 21</sup> At this stage, the carbenium ion is attacked by a hydroxyl group of glycerol and two different products can be obtained.<sup>9, 21</sup> In the first case, the five-membered cyclic group solketal is originated if the hydroxyl group possesses a secondary  $-OH$ ; in the second case, the six-membered cyclic group acetal is originated if the hydroxyl group possesses a primary  $-OH$ .<sup>2, 6</sup> The formation of solketal is preferred by the reaction since the attack of a secondary  $-OH$  is easier.<sup>11</sup>

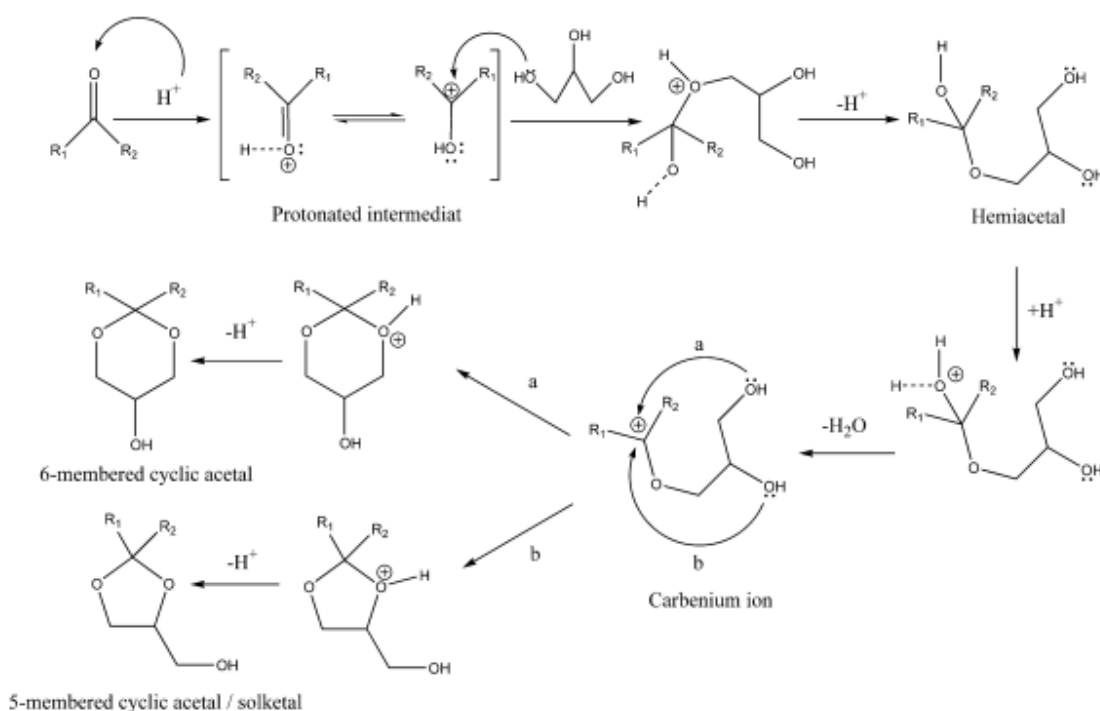


**Figure 1.7** – Acetalization mechanism proposed for Brönsted acids. Adapted from literature <sup>2</sup>.

Conventionally, acetalization resorted to homogeneous catalysts, such as hydrochloric acid, sulfuric acid and p-toluenesulfonic acid (pTSA).<sup>3, 9</sup> However, the use of these catalysts presented major disadvantages, such as difficult recuperation and environmental problems related to toxicity.<sup>3, 4, 9</sup> Heterogeneous catalysts appeared as potential candidates to substitute the previous, preventing the mentioned setbacks while exhibiting high catalytic efficiency.<sup>3, 9</sup> Many different types of catalysts were investigated and are still applied in acetalization, and some examples are: heteropolyacids (HPAs)<sup>21, 22</sup>, mesoporous silicas<sup>6, 25</sup>, zeolites<sup>26-28</sup>, Amberlyst resins<sup>27</sup> and polymers<sup>23, 29</sup>. The acetalization of glycerol using acetone as the substrate, was previously reported and results using different catalysts can be consulted in Table 1.1.

**Table 1.1** – Catalysts applied in acetalization of glycerol using acetone as the substrate, in a solvent-free environment.

| Catalyst                                                            | Gly/Acet Ratio | T (°C) | Conversion (%) | Selectivity (%) | Ref |
|---------------------------------------------------------------------|----------------|--------|----------------|-----------------|-----|
| <b>H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub></b>                   | 1:15           | RT     | 99.2           | 97.0            | 21  |
| <b>H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub></b>                  | 1:15           | RT     | 91.4           | 94              | 21  |
| <b>H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub></b>                  | 1:15           | RT     | 90.7           | 85.7            | 21  |
| <b>Sn<sub>2</sub>SiW<sub>12</sub>O<sub>40</sub></b>                 | 1:12           | RT     | 99             | 97              | 11  |
| <b>Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub></b> | 1:6            | RT     | 94             | 98              | 30  |
| <b>Nb-SBA-15</b>                                                    | 1:3            | RT     | 95             | 100             | 6   |
| <b>Zr-SBA-15</b>                                                    | 1:3            | RT     | 92             | 98              | 6   |
| <b>MoPo/SBA-15</b>                                                  | 1:3            | RT     | 74.2           | 98.2            | 25  |

Gly/Acet ratio refers to the glycerol/acetone ratio used in glycerol acetalization reactions and RT means room temperature.

**Table 1.1 (cont)** – Catalysts applied in acetalization of glycerol using acetone as the substrate, in a solvent-free environment.

| Catalyst                                                          | Gly/Acet Ratio | T (°C) | Conversion (%) | Selectivity (%) | Ref |
|-------------------------------------------------------------------|----------------|--------|----------------|-----------------|-----|
| <b>H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>@SiO<sub>2</sub></b> | 1:6            | 70     | 97             | 97              | 20  |
| <b>PSF/SiO<sub>2</sub></b>                                        | 1:10           | RT     | 86.6           | 98.1            | 31  |
| <b>UAV-20</b>                                                     | 1:10           | 55     | 56             | 90              | 23  |
| <b>Amberlyst-15</b>                                               | 1:2            | RT     | 73.1           | 91              | 27  |
| <b>Zeolite H-Y</b>                                                | 1:2            | RT     | 74.2           | 98.2            | 27  |

Gly/Acet ratio refers to the glycerol/acetone ratio used in glycerol acetalization reactions and RT means room temperature.

### 1.3. Polyoxometalates

Polyoxometalates, also abbreviated as POMs, are inorganic structures composed of structurally stable metal-oxygen anionic clusters.<sup>32</sup> These compounds are constituted of combined building units with the formula MO<sub>x</sub>, where M is called an addenda atom and corresponds to transition metals in their highest oxidation state (metals from Group 5 and 6 of the Periodic Table, commonly Mo and W).<sup>33, 34</sup> Since the building units can be combined in different forms, there are many types of polyoxometalate structures reported. The most known POM families can be observed in Figure 1.8.

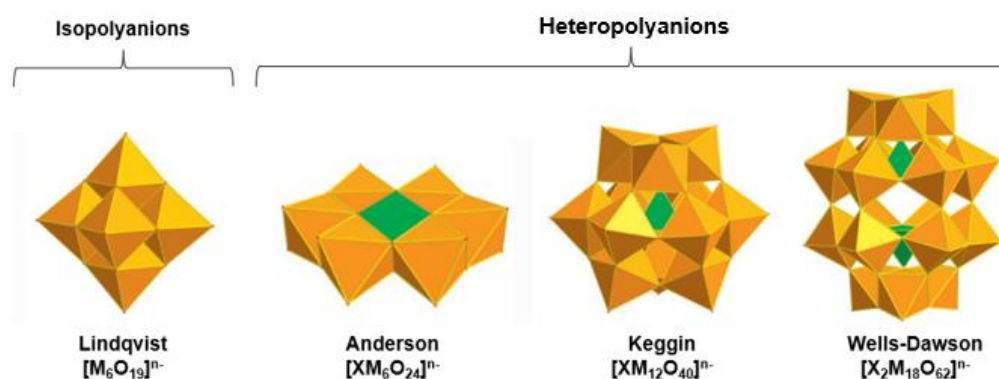


**Figure 1.8** – Different families of polyoxometalates (Lindqvist, Anderson, Keggin and Wells-Dawson), and their corresponding structures. Adapted from literature <sup>33</sup>.

As seen in Figure 1.8, polyoxometalates can be divided into two different classes: isopolyanions and heteropolyanions. Isopolyanions are structures comprised of oxygen and addenda atoms (M), adopting the form  $[M_xO_y]^{n-}$ . The most common type of isopolyanions is the Linqvist type, with structural form  $[M_6O_{19}]^{n-}$ .<sup>33, 35</sup> Then, heteropolyanions that possess structures formed by oxygen, addenda atoms (M) and extra heteroatoms (X). The most common heteropolyanion compounds are the Anderson-type (structural form  $[XM_6O_{24}]^{n-}$ ), Keggin-type (structural form  $[XM_{12}O_{40}]^{n-}$ ) and Wells-Dawson-type (structural form  $[X_2M_{18}O_{62}]^{n-}$ ).<sup>33, 35</sup>

The X heteroatoms present in heteropolyanions are commonly atoms of p-block elements (usually P or Si) and are characterized as primary heteroatoms since the POM structure collapses once removed. Contrarily, M addenda atoms are considered secondary heteroatoms since the structure maintains itself even if removed.<sup>33</sup>

### 1.3.1. Keggin-type polyoxometalates

The present work will be focused on the Keggin-type POMs, as they are the most studied and applied in catalytic reactions<sup>36, 37</sup>, owing to their stability and impressive acid characteristics<sup>36, 38, 39</sup>, which is an important factor for acetalization, as described in previous sections. Keggin-type polyoxometalates show a  $[XM_{12}O_{40}]^{n-}$  structure, with a central  $XO_4$  group, surrounded by four  $M_3O_{13}$  groups, as seen in Figure 1.9. These structures possess three types of bonds: terminal  $M=O$  bonds, bridging  $M-O-M$  bonds, that can be edge sharing (Figure 1.9A) or corner sharing (Figure 1.9B) and, finally,  $X-O-M$  bonding.<sup>34, 35, 38</sup>

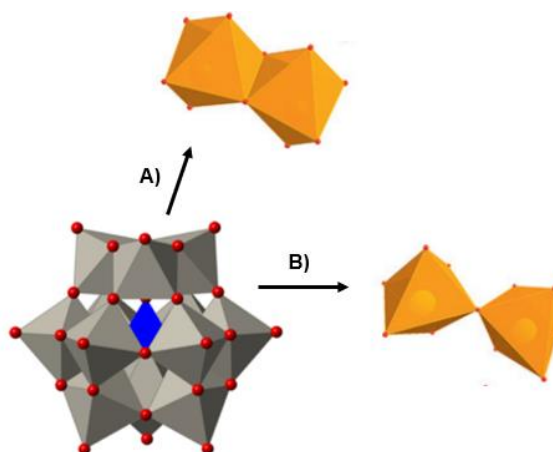


**Figure 1.9** – Structure of the Keggin-type polyoxometalate, containing two types of  $M_3O_{13}$  sharing: A) edge sharing and B) corner sharing. Adapted from literature<sup>33, 40</sup>.

Observing Figure 1.10, four different oxygens can be distinguished: oxygen that connects the primary heteroatom to an addenda atom ( $P-O_a-M$ ); oxygen that connects two addenda atoms of different  $M_3O_{13}$  groups (corner-sharing  $M-O_b-M$ ); oxygen that connects two addenda atoms of the same  $M_3O_{13}$  group (edge sharing  $M-O_c-M$ ) and terminal oxygen in each  $M_3O_{13}$  group ( $M=O_d$ ).<sup>41, 42</sup>

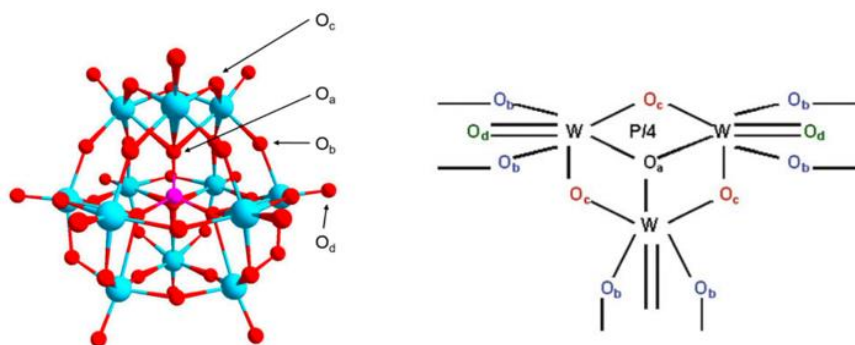


**Figure 1.10** – The different types of oxygen atoms and M-O bonds present in Keggin-type polyoxometalates. Adapted from literature <sup>41, 42</sup>.

Keggin-type polyoxometalates can also be referred as heteropolyacids (HPAs), due to the ability to act as Brønsted acids, owing to the extensive sum of active sites (protons) available in their surface <sup>35, 36</sup>, making them very captivating as catalysts. The commercially available and also most studied Keggin heteropolyacids are the phosphotungstic acid ( $H_3PW_{12}O_{40}$ ), the phosphomolybdic acid ( $H_3PMo_{12}O_{40}$ ) and the silicotungstic acid ( $H_4SiW_{12}O_{40}$ ).<sup>34, 43</sup> From here on forth, these HPAs will be discussed using the following abbreviations:  $H_3PW_{12}$ ,  $H_3PMo_{12}$  and  $H_4SiW_{12}$ , respectively.

Focusing on their catalytic application, HPAs are known to be soluble in most solvents, especially in polar environments.<sup>38, 43, 44</sup> As such, when used as homogeneous catalysts, they normally exhibit good catalytic behaviour, since they allow effective contact between the active sites on their surface and the reaction medium.<sup>22, 36</sup> However, in many types of catalytic reactions, this easy dissolution is a very big setback, hindering the recuperation of the catalyst and troubling its separation from the reaction medium.<sup>38</sup>

### 1.3.2. Heteropolyacids as catalysts for glycerol acetalization

The use of Keggin-type heteropolyacids in glycerol acetalization reactions with acetone has been previously reported.<sup>11, 21, 30</sup>

Kaliaguine et al. studied the application of a cesium salt of phosphotungstate ( $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ) as a catalyst in glycerol acetalization with acetone, obtaining 94% of glycerol conversion (with 98% solketal selectivity), after 1 h of reaction at room temperature.<sup>30</sup> Da Silva et al. investigated the catalytic efficiency of a tin(II) silicotungstate ( $\text{Sn}_2\text{SiW}_{12}\text{O}_{40}$ ) in acetalization of glycerol with acetone, and compared its performance to other heteropolyacids. This silicotungstate catalyst showed to achieve high glycerol conversion with 99% and with 97% of solketal selectivity, after 1 h of reaction, at room temperature.<sup>11</sup> Balula et al. reported the catalytic efficiency of three heteropolyacids: phosphotungstic acid ( $\text{H}_3\text{PW}_{12}$ ), phosphomolybdic acid ( $\text{H}_3\text{PMo}_{12}$ ) and silicotungstic acid ( $\text{H}_4\text{SiW}_{12}$ ). These HPAs were applied as homogeneous catalysts in the acetalization of glycerol with acetone, obtaining high catalytic efficiency and solketal selectivity. The best performing catalyst was  $\text{H}_3\text{PW}_{12}$  with 99.2% of glycerol conversion (97% solketal selectivity), after 5 min of reaction, at room temperature.<sup>21</sup>

It can be seen that heteropolyacids are highly efficient catalysts for glycerol acetalization reactions, with high conversion and selectivity. However, their application is rarely reported in literature since, as mentioned previously, their easy dissolution hinders their separation from the reactional solution, and difficult catalyst recuperation and recycling. The solution to this problem was found by applying HPAs in their heterogeneous form, which can be possible through their immobilization in solid supports. In this case, catalyst recuperation (filtration or centrifugation) and recycling is facilitated, while still maintaining a similar homogeneous catalytic performance.<sup>45</sup>

In the following sections, HPA immobilization will be discussed, in particular through mesoporous silica and polymeric membranes as solid supports.

#### 1.4. Mesoporous silica materials

Porous materials have been widely studied in the last decades, owing to their outstanding performance in various reactions namely adsorption<sup>46</sup>, separation<sup>47</sup> and catalysis.<sup>48</sup> By definition, porous materials are defined by a solid phase matrix, with pores formed by either a gas or liquid phase.<sup>49</sup>

The International Union of Pure and Applied Chemistry (IUPAC) differentiates porous materials into three types, distinguished by their pore size – microporous, mesoporous and macroporous. As such, microporous materials show pore sizes inferior to 2 nm, mesoporous materials with pore sizes between 2 and 50 nm, and finally, macroporous materials with pores superior to 50 nm.<sup>50, 51</sup>

Mesoporous materials are compatible with a wide range of applications due to their interesting characteristics. In particular, these materials are extremely well suited for catalytic reactions thanks to their high surface area, thermal stability, adjustable pore size and adaptability to numerous surface functionalizations.<sup>6, 52, 53</sup>

Mesoporous materials based in silicates and aluminosilicates were one of the first mesoporous materials successfully prepared. Most of the silica materials are considered cost effective, since these combine structural stability and low cost.<sup>52, 54</sup> As mentioned above, mesoporous silicas were first discovered in 1992 by researchers at Mobil Corporation, producing the first mesoporous silica materials, the M41S.<sup>51, 54, 55</sup> The most studied mesophase from this family of silica materials is the Mobil Composition of Matter No.41 (MCM-41), identified by its hexagonal array and pores ranging from 2 to 10 nm.<sup>50, 51, 53</sup> Another breakthrough in mesoporous silica research occurred in 1998, when Zhao et al. obtained a new structure, the Santa Barbara Amorphous (SBA), through the discovery of the SBA-15 silica. Compared with MCM-41, this silica exhibits superior thermal stability and a larger pore size ranging from 4.6 to 30 nm, increasing its interest for catalytic applications.<sup>51, 52, 56</sup> Some examples of mesoporous silica structures can be seen in Figure 1.11.

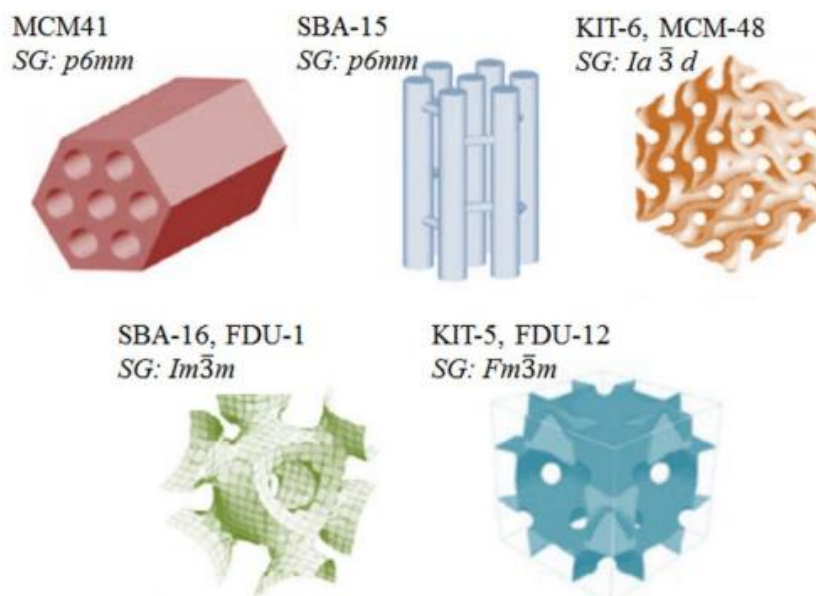


**Figure 1.11** – Examples of different mesoporous silica structures. Adapted from literature <sup>57</sup>.

Bringing the focus to the SBA-15 mesoporous silicas, this structure is prepared through a soft-templating method, using hydrothermal synthesis.<sup>55, 57</sup> A chosen surfactant and the silica precursor are added to an aqueous solution, under acidic conditions, initiating a cooperative self-assembly process.<sup>55, 57</sup> Cooperative self-assembly relies on the notion of two mechanisms: surfactant self-assembly and organic-inorganic interactions between the surfactant and the precursor.

Surfactants are composed of two structures: hydrophilic group (heads) and hydrophobic group (tails). In the presence of an aqueous solution, surfactants show a characteristic self-assembly feature that originates micelles. In this case, spherical micelles can be observed, where the hydrophilic heads are positioned to the outside, in contact with the solution, and the hydrophobic tails are protected inside of the structure.<sup>58</sup>

Then, the silica precursor suffers hydrolysis due to the acidic conditions, which allows organic-inorganic interactions between the precursor and the surfactant micelles. In the case of SBA-15, these interactions are mainly electrostatic forces and hydrogen bonds. The acidic conditions also increase silica condensation and precipitation, which allows the formation of mesoporous structures.<sup>55, 57</sup>

The obtained material goes through hydrothermal treatment and finally calcination, in order to completely remove the surfactant from the structure.<sup>55, 57</sup> The cooperative self-assembly process can be observed in Figure 1.12.

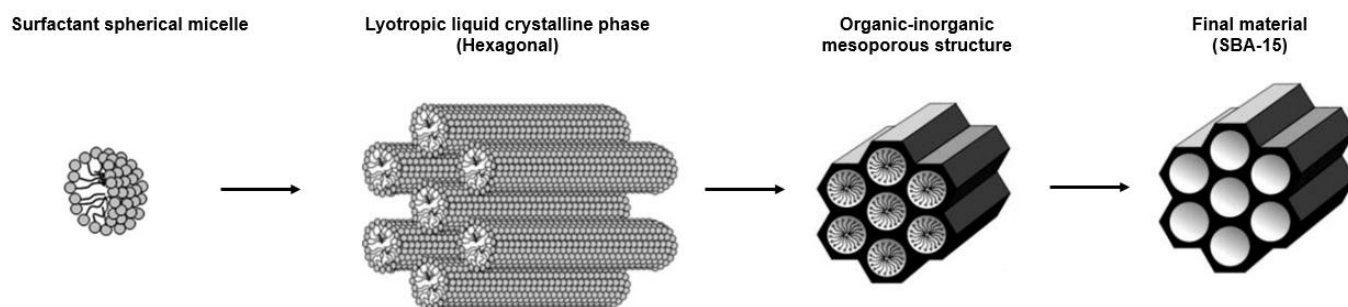


**Figure 1.12** – SBA-15 mesoporous silica preparation, from the formation of spherical micelles, organization into a crystalline phase, formation of the initial silica structure and obtention of the final SBA-15 material, post calcination.

For the preparation of SBA-15 silica, the surfactant used is the triblock copolymer Pluronic P123 (ethylene and propylene oxide repeated units, PEO-PPO-PEO) and the silica precursor is tetraethoxysilane (TEOS).<sup>54, 59</sup> As seen in Figure 1.13, P123 is added to an acidic solution constituted by water and hydrochloric acid (HCl), with temperature and agitation, followed by addition of TEOS.

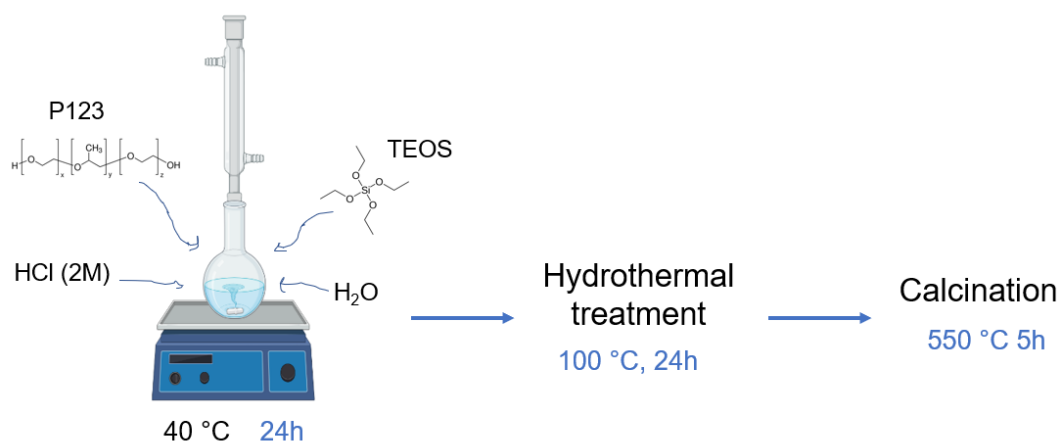


**Figure 1.13** – Experimental procedure used for the SBA-15 preparation.

As seen in Figure 1.11 and Figure 1.14A, SBA-15 exhibits a structure characteristic of the  $p6mm$  plane group: hexagonal cylindrical pores arranged in a hexagonal array.<sup>52, 55</sup> Furthermore, this material is particularly interesting due to the presence of both mesopores (inside the structure) and micropores (inside the walls).<sup>50, 55, 60</sup>

In the cooperation self-assembly process, the PEO chains of the surfactant used (P123) expanded to the silica wall of the structure, as this is a characteristic behaviour of these types of surfactants. As such, during the calcination step, when the surfactant

is removed, microporous channels can be observed inside the walls of the SBA-15 structure, as seen in Figure 1.14B.<sup>50, 55, 60</sup>

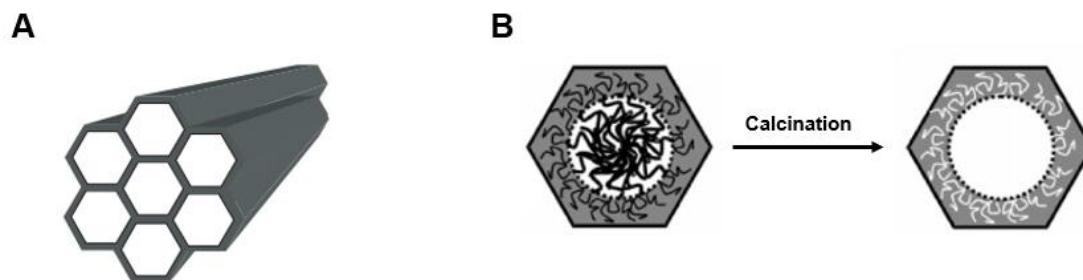


**Figure 1.14** – A) Hexagonal structure of the SBA-15 silica.<sup>50</sup> B) Calcination step and the formation of micropores.<sup>55</sup>

#### 1.4.1. Heterogeneous catalysts based in SBA-15

The dual porosity of SBA-15 makes it a very interesting support material for catalysis, presenting a remarkable possibility of active species incorporation.<sup>52</sup> One of these active species are the HPAs.

As mentioned in section 1.3.1, HPAs are easily dissolved in most known solvents, rendering their recuperation extremely difficult and raising a problem for their application in catalytic systems as homogeneous catalysts. The best solution to solve this problem is through their heterogenization in solid supports, namely mesoporous silica. This way, it becomes possible to combine the advantages of HPAs (efficient acidic catalysts) and silicas (high thermal stability, high surface area), obtaining new solid catalysts that present simultaneous facile recuperation and recycling capacity.<sup>36, 52</sup>

The incorporation of HPAs in SBA-15 silica can be divided into two steps. Firstly, it is necessary to prepare the surface of the material to successfully incorporate the species, through surface functionalization.<sup>50, 52, 61</sup> SBA-15 possesses silanol groups on its surface, which are great anchoring sites for HPA incorporation.<sup>50</sup> Due to the acidic nature of HPAs, the best strategy is surface modification with basic amine groups, in order to increase the interactions between the support and the catalytic active species, preventing leaching.<sup>50, 61</sup> Finally, HPAs can be anchored on the silica surface and the final material obtained.

The most commonly used amine group in SBA-15 functionalization is the 3-aminopropyltriethoxysilane (APTES).<sup>56, 61</sup> Silica functionalization and HPA immobilization can be seen in Figure 1.15.

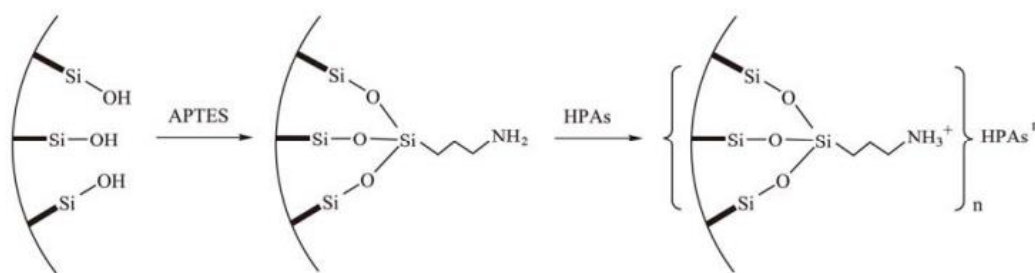


**Figure 1.15** – Surface modification of SBA-15 with APTES groups and consequent HPA immobilization. Adapted from literature.<sup>61</sup>

The incorporation of HPAs in mesoporous silica solid supports exponentially increases its recuperation from the reaction medium, allowing for easy recycling. However, these HPAs@SBA-15 catalysts are applied in catalytic reactions in their powdered forms, being recuperated from the solution by centrifugation or filtration.<sup>6, 25</sup> This recuperation is not ideal since it can be responsible for catalyst loss. Furthermore, powdered catalysts can be more susceptible to deactivation, due to the loss of active sites by adsorption of reaction products.<sup>25, 62</sup>

The present work presented a novel strategy to facilitate catalyst recuperation and reutilization, that consisted in the use of catalytic polymeric membranes, incorporating the HPAs active species or even the HPA@SBA-15 composites.

## 1.5. Polymeric membranes

Polymeric membranes are constituted by polymer materials, exhibiting high mechanical and chemical stability and high surface area, while allowing inexpensive preparation and being generally environmentally friendly.<sup>63-65</sup> There are various polymers available in the market, each one having its own specific characteristics. As such, depending on the material chosen for membrane formulation, it is possible to have facilitated tunability depending on the application pretended.<sup>63, 66</sup> Examples of the most used polymers for membrane formulation can be found in Figure 1.16.

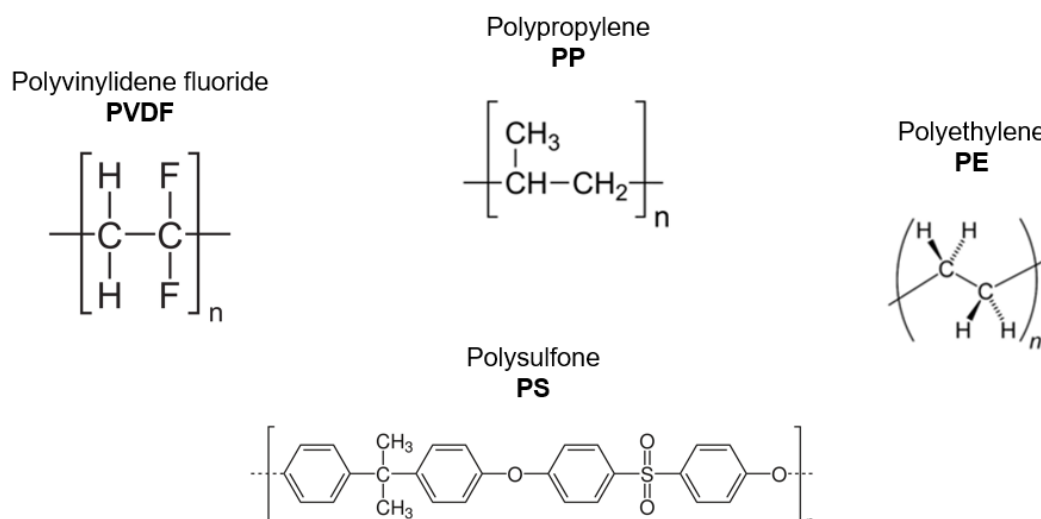


**Figure 1.16** – Structures of the most used polymeric materials for membrane preparation.

As seen before, due to their excellent stability and properties, polymeric membranes can be employed in many different applications. Research is commonly focused on their use in three main processes: adsorption<sup>67, 68</sup>, separation<sup>69, 70</sup> and catalysis<sup>62</sup>, being the latter the focus of this work.

An ideal catalyst should have outstanding catalytic efficiency in the reaction employed, while also assuring facile recuperation for recycling process. As such, a clever strategy to obtain the ideal catalyst is to incorporate catalytic active species in solid supports – combining the advantages of both materials. The solid support can be a powder, as previously described for the preparation of HPAs@SBA-15, or even a one-piece of solid catalyst. This last can be formed by preparing catalytic membranes, that consist in the incorporation of active catalysts in a polymeric matrix.<sup>42, 65, 71</sup>

The catalytic membranes can be prepared by various techniques, such as phase inversion, interfacial polymerization, stretching, track-etching or electrospinning<sup>66, 72, 73</sup>, with phase inversion being the most used method.

Furthermore, inside the phase inversion method, there are many different strategies, with the most commonly adopted being immersion precipitation and evaporation-induced phase separation.<sup>66, 72</sup> In immersion precipitation, there is formation of a solution between the polymer and a chosen solvent, which suffers casting on a support. Then, this casted solution is soaked in a bath constituted by a non-solvent. These two species, the solvent and non-solvent, interact and the final membrane is formed.<sup>66, 72, 73</sup> In evaporation-induced phase separation, there is formation of a solution

between the polymer and a volatile solvent. The solution is casted on a support, and the solvent starts to evaporate, leading to the formation of the final membrane.<sup>66, 73</sup>

In this work, the selected polymer for membrane formulation was polyvinyl alcohol, also known as PVA (Figure 1.17). This compound presents a stable polymeric structure characterized by its facilitated handling, non-toxicity and non-solubility in ketones<sup>73, 74</sup>, which is particularly important for application in acetalization reactions, in the presence of acetone.

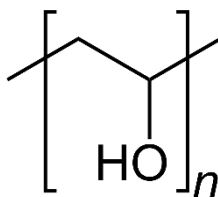


**Figure 1.17** – Structure of polyvinyl alcohol, also known as PVA.

The PVA membranes were prepared according to Figure 1.18, in which the polymer was dissolved in a solution with a solvent, in this case water, since PVA is highly soluble in aqueous environments.<sup>63, 73</sup> Then, a chosen catalyst was added, and the mixture left to age under stirring. Finally, the solution was casted on a support, where the solvent was evaporated, originating the final membrane. After evaporation, it was necessary to immerse the membrane in a non-solvent (in this case ethanol), to allow its removal from the support.

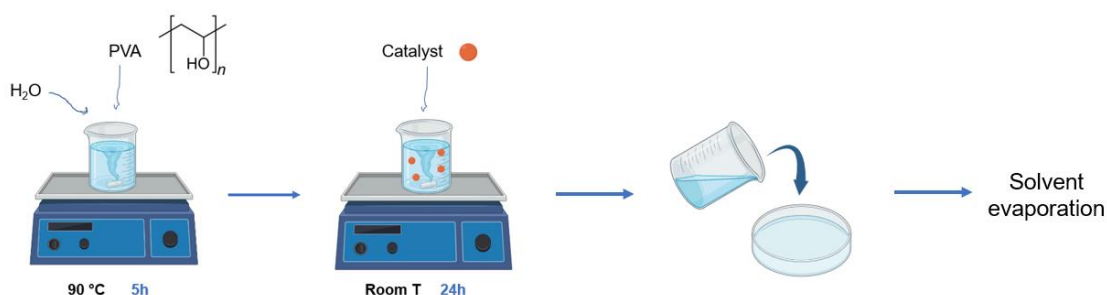


**Figure 1.18** – Experimental procedure used for catalyst@PVA membrane preparation. In this, the catalyst was HPAs or HPAs@silica.

### 1.5.1. Catalytic membranes of Polyvinyl alcohol for glycerol acetalization

The use of polymeric membranes in acetalization of glycerol is mainly constricted to their use in membrane reactors for water removal.<sup>75</sup> As mentioned in section 1.2.2.2, the conversion of glycerol into solketal originates water as a by-product, which hinders the solketal conversion efficiency.

Focusing on the use of catalytically active polymeric membranes in acetalization of glycerol, to our knowledge, only two examples can be found in literature.<sup>29, 75</sup> Qing et al. developed a multilayer membrane reactor, which was applied in a reactional system with glycerol and acetone as a substrate. The membrane was constituted by three layers, which all had different functions: one was responsible for holding the catalyst used, another for separation and removal of water from the reaction.<sup>75</sup> Castanheiro et al. reported the use of a catalytic membrane in acetalization of glycerol with acetone. This membrane was formed by a PVA matrix functionalized with sulfonic acid groups, responsible for the catalytic behaviour.<sup>29</sup>

However, single-layer membranes, that exhibit only catalytic behaviour due to catalyst immobilization (i.e. HPA and SBA-15 composites), have never been applied in glycerol acetalization reactions, and this Master work intends to be an innovation in this topic.

## 1.6. Aim and methodology

This dissertation project has as the main objective the development of advanced catalysts for glycerol conversion, through acetalization reactions with acetone. Therefore, novel catalysts were developed and applied in this reaction, such as the homogeneous polyoxometalates (HPAs) and the heterogeneous HPAs incorporated in different supports: i) mesoporous silica (HPAs@silica), ii) polymeric matrix to prepare catalytic polymeric membranes (HPAs@membrane) and iii) HPAs incorporated in mesoporous silica and further immobilized in polymeric membranes (HPAs@silica@membrane).

This work is organized in different chapters, according to the nature of the catalysts prepared.

**Chapter 2** - Characterization of HPAs ( $\text{H}_3\text{PW}_{12}$ ,  $\text{H}_3\text{PMo}_{12}$  and  $\text{H}_4\text{SiW}_{12}$ ). Application in acetalization of glycerol with acetone. Optimization of experimental parameters.

**Chapter 3** – Preparation and characterization of SBA-15 support. Preparation and characterization of functionalized APTES-SBA-15 silica. Incorporation of HPAs and characterization of composites:  $\text{H}_3\text{PW}_{12}$ @APTES-SBA-15 and  $\text{H}_3\text{PMo}_{12}$ @APTES-SBA-15. Application in acetalization of glycerol with acetone. Optimization of experimental parameters. Catalyst stability studies and characterization.

**Chapter 4** – Preparation and characterization of HPAs immobilized in polymeric membranes:  $\text{H}_3\text{PW}_{12}$ @APTES-PVA,  $\text{H}_3\text{PMo}_{12}$ @APTES-PVA,  $\text{H}_3\text{PW}_{12}$ @PVA and  $\text{H}_3\text{PMo}_{12}$ @PVA. Application in acetalization of glycerol with acetone. Optimization of experimental parameters. Catalyst stability studies and characterization.

**Chapter 5** – Preparation and characterization of composites immobilized in polymeric membranes:  $\text{H}_3\text{PW}_{12}$ @APTES-SBA-15@PVA and  $\text{H}_3\text{PMo}_{12}$ @APTES-SBA-15@PVA. Application in acetalization of glycerol with acetone.

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## **2. HPAs for glycerol acetalization**

This chapter presents the characterization and the application of the Keggin-type heteropolyacids (HPAs), used as homogeneous catalysts for the acetalization of glycerol with acetone. Potentiometric titration was used to characterize catalyst acidity of three different HPAs: phosphotungstic acid, phosphomolybdic acid and silicotungstic acid. The catalyst efficiency of the different HPAs was compared and optimized.

## 2.1. Characterization by Potentiometric titration

Potentiometric titration was used to quantify the amount of acidic sites present in the three homogeneous catalysts: phosphotungstic acid ( $\text{H}_3\text{PW}_{12}$ ), phosphomolybdic acid ( $\text{H}_3\text{PMo}_{12}$ ) and silicotungstic acid ( $\text{H}_4\text{SiW}_{12}$ ). HPAs solutions were prepared with NaCl 2M, in order to promote the exchange of cation (Equation 2.1). Then, the resulting solutions were filtrated, and potentiometric titration proceeded using a NaOH solution, acting as the titrant. The results obtained from the potentiometric analysis can be observed in Table 2.1, where the acidity of the catalyst was posteriorly calculated.



**Table 2.1** – Potentiometric measurements obtained for the three HPAs, followed by the calculation of acidity.

| Catalyst                    | pH  | V (NaOH)<br>(mL) | Acidity<br>(mmol $\text{H}^+$ /g) |
|-----------------------------|-----|------------------|-----------------------------------|
| $\text{H}_3\text{PMo}_{12}$ | 2.2 | 9.74             | 9.74                              |
| $\text{H}_3\text{PW}_{12}$  | 2.2 | 1.93             | 1.93                              |
| $\text{H}_4\text{SiW}_{12}$ | 2.6 | 0.995            | 0.995                             |

According to the potentiometric measurements,  $\text{H}_3\text{PMo}_{12}$  exhibits the highest acidity, when compared to the other HPAs. Such results were expected when considering that Mo is more susceptible to oxidation than W <sup>1-3</sup>, and as such, there is a directly

proportional correlation between this susceptibility and the amount of titrant used, leading to a higher value of acidity.

Then, comparing the two tungsten HPAs,  $\text{H}_3\text{PW}_{12}$  and  $\text{H}_4\text{SiW}_{12}$ , it can be seen that the former exhibits higher acidity. Tungsten HPAs are less susceptible to oxidation, and inside all types of tungstates, the  $\text{H}_4\text{SiW}_{12}$  presents a lower oxidation potential, leading to a lower amount of titrant used and the lowest value of acidity.<sup>1</sup> To resume, it is seen that HPAs exhibit the following oxidation trend:  $\text{H}_3\text{PMo}_{12} > \text{H}_3\text{PW}_{12} > \text{H}_4\text{SiW}_{12}$ , which is in agreement with the potentiometric measurements and acidities obtained.

## 2.2. Acetalization studies

As mentioned in section 1.2.2.1., the correct choice of substrate and glycerol/substrate ratio are some of the most important factors for efficient glycerol conversion. Acetone is the substrate most used in the literature<sup>4-7</sup>. It has been confirmed that when acetone is used in excess, there is an exponential increase in solketal conversion.<sup>8</sup>

Balula et al. previously studied the influence of different glycerol/acetone ratios, ranging from 1:1 to 1:15.<sup>8</sup> The optimized glycerol conversion was increased when using a ratio of 1:15. This optimized ratio will be maintained in the catalytic studies performed here on forth.

Glycerol acetalization reactions proceeded under air in a closed borosilicate 5 mL vessel used as a reactor, with constant stirring and temperature. The reactor was filled with 120  $\mu\text{L}$  of glycerol and 1.880 mL of acetone (1:15), and left under agitation for 10 min, in order to homogenize the solution. Then, the appropriate catalyst was added, and glycerol conversion evaluated during 120 min. Glycerol conversion results were evaluated by gas chromatography.

The catalytic activity of the three HPAs ( $\text{H}_3\text{PW}_{12}$ ,  $\text{H}_3\text{PMo}_{12}$  and  $\text{H}_4\text{SiW}_{12}$ ) was compared and optimized, using two different temperatures, 25 °C and 60 °C, and different catalyst amounts (section 2.2.3).

Initial blank experiments were conducted, without the presence of catalysts, using the ratio of 1:15 glycerol/acetone, at constant stirring for 60 min, at both 25 °C and 60 °C. At both temperatures, no glycerol conversion was observed. Such results were expected since in acetalization reactions, the catalyst is responsible for activating the substrate, which initiates its interaction with glycerol. Without substrate activation, no glycerol conversion was exhibited.<sup>7, 9, 10</sup>

### 2.2.1. Catalyst acidity

The previous work reported by Balula et al. studied the effect of the catalyst amount in the conversion of glycerol, in acetalization reactions. In this case, optimized results were found using 3% of HPA, when compared to glycerol weight. This results corresponds to the usage of 3  $\mu\text{mol}$  of catalyst approximately.<sup>8</sup>

High glycerol conversion was achieved using the various HPAs: 99.2% for  $\text{H}_3\text{PW}_{12}$ , 91.4% for  $\text{H}_3\text{PMo}_{12}$  and 90.7% for  $\text{H}_4\text{SiW}_{12}$ .<sup>8</sup> In this work it was investigated the effect of catalyst efficiency in glycerol conversion by evaluating the influence of catalyst acidity, instead of its molarity, as previously performed by Balula et al.<sup>8</sup> To do such, potentiometric measurements were performed to normalize catalyst acidity between catalytic experiments. In Table 2.2, it is possible to observe the potentiometric results that show the acidity of the three HPAs for the 3  $\mu\text{mol}$ , the optimized amount of HPA previously used.<sup>8</sup>

**Table 2.2** – Calculation of the acidity for the three HPAs, corresponding to the 3  $\mu\text{mol}$  of HPA catalyst.

| Catalyst                    | Catalyst amount for 3 $\mu\text{mol}$<br>(mg) | Acidity<br>(mmol $\text{H}^+/\text{g}$ ) |
|-----------------------------|-----------------------------------------------|------------------------------------------|
| $\text{H}_3\text{PMo}_{12}$ | 3.06                                          | 1.192                                    |
| $\text{H}_3\text{PW}_{12}$  | 4.84                                          | 0.373                                    |
| $\text{H}_4\text{SiW}_{12}$ | 4.83                                          | 0.192                                    |

The catalytic studies using HPA for acetalization reactions were performed using the acidity of 0.373 mmol  $\text{H}^+/\text{g}$ , that corresponds to the 3  $\mu\text{mol}$  of  $\text{H}_3\text{PW}_{12}$ . Such choice was made based on the fact that  $\text{H}_3\text{PW}_{12}$  has been described to be the best catalyst for solketal conversion, in acetone.<sup>8, 11</sup> To maintain this acidity for the other HPA catalysts, calculations were performed to know the amount of each HPA needed, and the results can be observed in Table 2.3.

**Table 2.3** – The quantity of each HPA catalyst to be used in glycerol acetalization reactions, as to maintain the optimized catalyst acidity of 0.373 mmol H<sup>+</sup>/g.

| Catalyst                         | Catalyst amount (mg) |
|----------------------------------|----------------------|
| H <sub>3</sub> PMo <sub>12</sub> | 0.959                |
| H <sub>3</sub> PW <sub>12</sub>  | 4.84                 |
| H <sub>4</sub> SiW <sub>12</sub> | 9.38                 |

2.2.2. Comparative HPAs catalytic performance

HPAs were applied in acetalization reactions as homogeneous catalysts, owing to their rapid dissolution in the reaction medium, as mentioned in section 1.3.1. A ratio of 1:15 glycerol/acetone was used together with an appropriate amount of HPA catalyst, to maintain the acidity of the catalyst at 0.373 mmol H<sup>+</sup>/g. The comparative study of the HPAs catalytic performance was performed at 25 °C, since previous reported results showed higher glycerol conversion at this temperature.<sup>8, 9</sup> Reactions were studied during 120 min, through quantification of the glycerol conversion using gas chromatography.

The results obtained for the three catalysts can be observed in Figure 2.1. The following times were chosen in order to obtain conversion results at the beginning (5 min), middle (30 min) and at the end (60 min) of the reaction. The highest glycerol conversion result was obtained at 60 min.

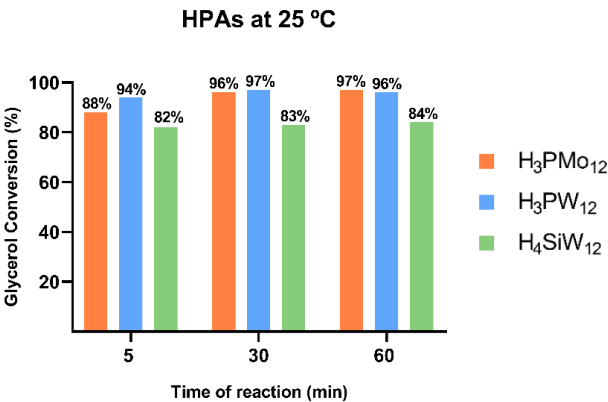


**Figure 2.1** – Glycerol conversion obtained after 5, 30 and 60 min of reaction, catalysed by three different HPAs, using a ratio of 1:15 glycerol/acetone, catalyst acidity of 0.373 mmol H<sup>+</sup>/g, at 25 °C.

The  $\text{H}_3\text{PMo}_{12}$  exhibited a maximum glycerol conversion of 97%, with solketal selectivity of 98%, after 60 min. Likewise,  $\text{H}_3\text{PW}_{12}$  exhibited a similar conversion of 97% with solketal selectivity of 97%, only after 30 min. However, the differences observed between  $\text{H}_3\text{PW}_{12}$  and  $\text{H}_3\text{PMo}_{12}$  were close to the experimental error calculated for these studies (equal or inferior to 5%). Finally,  $\text{H}_4\text{SiW}_{12}$  had the lowest catalytic efficiency with a maximum conversion of 84% with solketal selectivity of 98%, after 60 min.

In general, all catalysts demonstrated satisfactory catalytic efficiency, with the expected catalytic behaviour trend of  $\text{H}_3\text{PW}_{12} > \text{H}_3\text{PMo}_{12} > \text{H}_4\text{SiW}_{12}$ .  $\text{H}_3\text{PW}_{12}$  is extensively reported as the most acidic out of the three <sup>1, 2</sup>, which becomes very evident when observing the acid dissociation constants, demonstrated as pKa, for the three HPA in acetone, as shown in Table 2.4.

**Table 2.4** – HPA acid dissociation constants (expressed as pKa), obtained in acetone at 25 °C.

| HPA                         | pKa <sub>1</sub> | pKa <sub>2</sub> | pKa <sub>3</sub> | Ref       |
|-----------------------------|------------------|------------------|------------------|-----------|
| $\text{H}_3\text{PW}_{12}$  | 1.6              | 3.0              | 4.0              | 1, 12, 13 |
| $\text{H}_3\text{PMo}_{12}$ | 2.0              | 3.6              | 5.3              | 1, 13     |
| $\text{H}_4\text{SiW}_{12}$ | 2.0              | 3.6              | 5.3              | 1, 13     |

The acid dissociation constant, also known as Ka, measures the strength of an acid, i.e. higher Ka corresponds to stronger acid. When Ka is expressed as pKa, it can be attributed that lower pKa corresponds to stronger acid.

$$Ka = \frac{[H^+][A^-]}{[HA]} \quad (2.2)$$

$$pKa = -\log Ka \quad (2.3)$$

As observed in Table 2.4, it is seen that  $\text{H}_3\text{PW}_{12}$  shows the smaller  $\text{pK}_a$  of the three acid catalysts, which indicates that it must be the strongest acid and, consequently, the most efficient catalyst. For  $\text{H}_3\text{PMo}_{12}$  and  $\text{H}_4\text{SiW}_{12}$  the difference in acidity behaviour is not derived from the  $\text{pK}_a$ , as they present the same values. In this case, the presence of a different principal heteroatom in their structure (P for  $\text{H}_3\text{PMo}_{12}$  and Si for  $\text{H}_4\text{SiW}_{12}$ ) must have an influence in their acidity. This influence is documented in literature, where it is reported that the acidity decreases when the charge of the heteroatom decreases ( $\text{P}^{\text{V}}$  to  $\text{Si}^{\text{IV}}$ ).<sup>2, 13</sup>

### 2.2.3. Optimization of catalytic acetalization

#### 2.2.3.1. Temperature

While the choice of substrate and catalyst are the main factors for a high conversion of glycerol, other experimental factors can be optimized to improve glycerol conversion and solketal selectivity. One important parameter that can influence catalyst efficiency is the temperature of the reaction. Figure 2.2 displays the catalytic performance of the different HPAs, allowing comparison of the kinetic profiles and glycerol conversion results after 30 min, obtained at 25 and 60 °C.

After increasing the temperature from 25 to 60 °C, it is possible to observe that the catalytic efficiency of the HPAs did not increase. Furthermore, the highest conversion result was obtained at 60 min, and the solketal selectivity maintained around 98%, similar to the results obtained at 25 °C.

At 60 °C,  $\text{H}_3\text{PW}_{12}$  achieved a maximum conversion of 92% after 30 min, showing slightly lower results than those obtained at 25 °C, with a maximum conversion of 97% after 30 min.  $\text{H}_3\text{PMo}_{12}$  exhibited a maximum conversion of 97% and 94% after 60 min at 25 and 60 °C, respectively. Finally,  $\text{H}_4\text{SiW}_{12}$  once again showed the lowest catalytic efficiency, with a maximum conversion of 78% after 30 min at 60 °C.

From all the experiments, it was possible to observe that the best glycerol conversion result was achieved using the  $\text{H}_3\text{PW}_{12}$  catalyst, after only 30 min at 25 °C. Furthermore, it can be seen that for all catalysts, the optimized reaction temperature was 25 °C, which corresponds to the results obtained in literature.<sup>8, 9</sup>

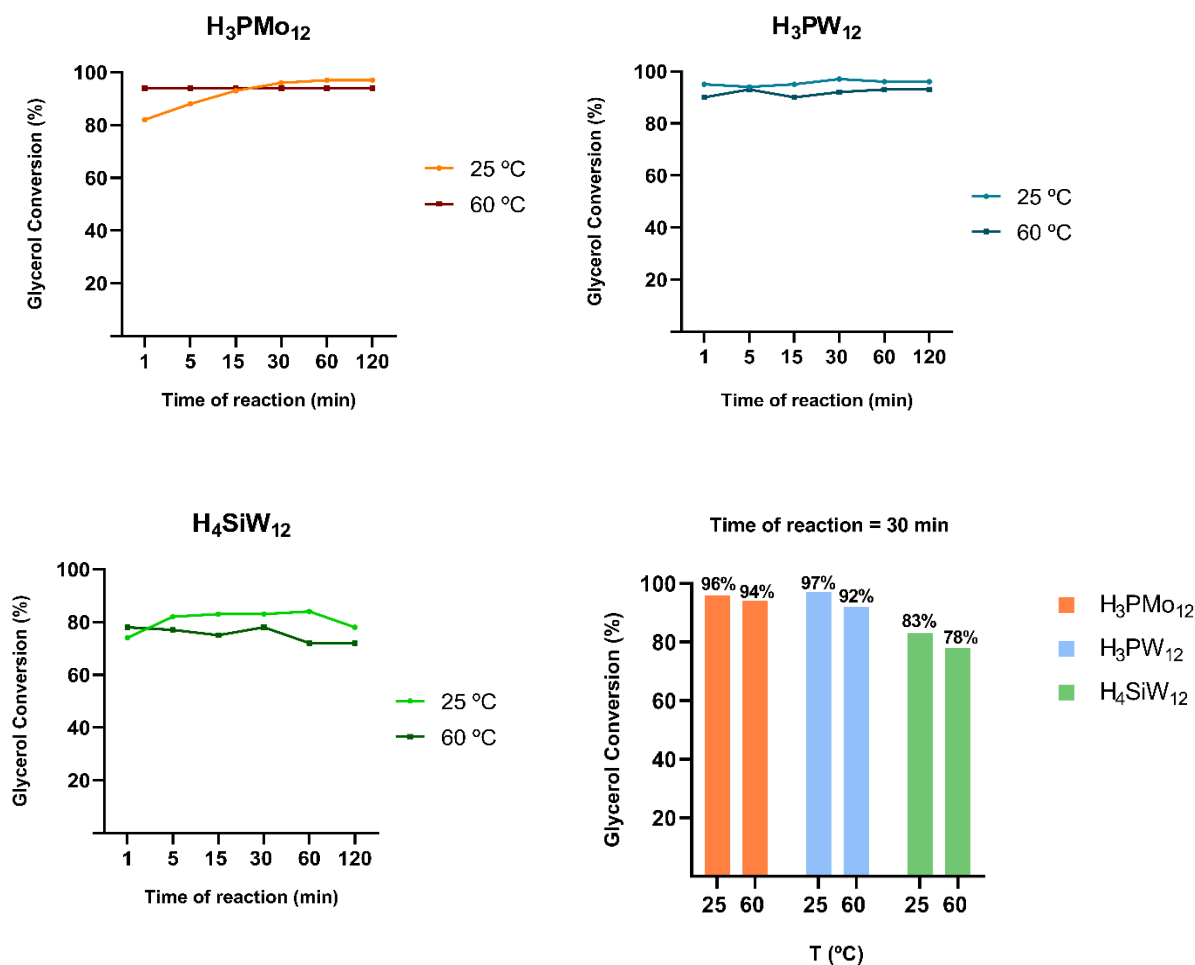


**Figure 2.2** – Kinetic profile and glycerol conversion results obtained after 30 min, for the acetalization of glycerol catalysed by three HPAs, using a ratio of 1:15 glycerol/acetone, catalyst acidity of 0.373 mmol H<sup>+</sup>/g, at 25 and 60 °C.

### 2.2.3.2. Catalyst acidity

Catalyst acidity is probably the principal factor that influences the efficiency for glycerol acetalization. In order to obtain the highest conversion results of glycerol into solketal, the previous catalyst acidity of 0.373 mmol H<sup>+</sup>/g was also optimized, using the two best performing catalysts: H<sub>3</sub>PW<sub>12</sub> and H<sub>3</sub>PMo<sub>12</sub>.

This optimization proceeded using the same experimental conditions as before (ratio of 1:15 glycerol/acetone), at 25 °C. Different acidities were tested, and the glycerol conversion was evaluated. The acidities and the results obtained can be observed in Figure 2.3 and 2.4 for H<sub>3</sub>PW<sub>12</sub> and H<sub>3</sub>PMo<sub>12</sub>, respectively.

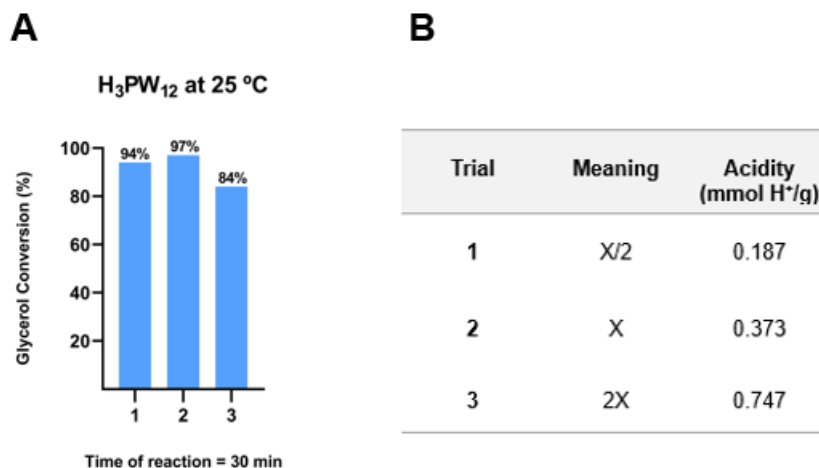


**Figure 2.3 – A)** Glycerol conversion results obtained after 30 min, using different acidities of the H<sub>3</sub>PW<sub>12</sub> catalyst, at 25 °C. **B)** Explanation of the trial number and corresponding acidity, i.e. X/2 is half of the initial amount used and 2X is the double.

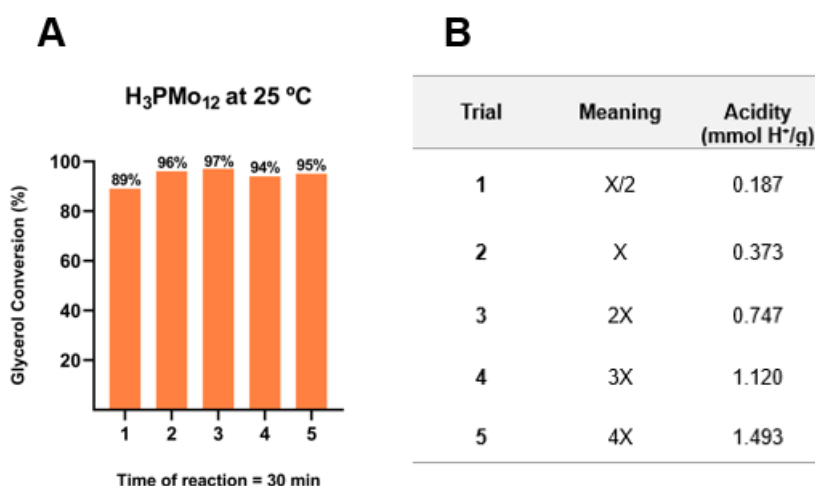


**Figure 2.4 - A)** Glycerol conversion results obtained after 30 min, using different acidities of the H<sub>3</sub>PMo<sub>12</sub> catalyst, at 25 °C. **B)** Explanation of the trial number and corresponding acidity, i.e. X/2 is half of the initial amount used and 2X is the double, etc.

Using the H<sub>3</sub>PW<sub>12</sub> catalyst, three different acidities were studied (Trial 1 to 3, in Figure 2.3). The best glycerol conversion result (97%) was observed in Trial 2, which corresponds to the acidity of 0.373 mmol H<sup>+</sup>/g. It can also be seen that, when the acidity is decreased to half of the amount, the catalyst still maintains high catalytic performance (94%) further acknowledging the acidic strength of H<sub>3</sub>PW<sub>12</sub>. Using the

double acidity, it is observed that the catalytic performance of this catalyst dropped to 84% after 30 min, highlighting the importance of finding the optimized acidity.

Using the  $\text{H}_3\text{PMo}_{12}$  catalyst, five different acidities were studied (Trial 1 to 5, in Figure 2.4). For this catalyst, five different amounts were studied in order to reach the acidity corresponding to 3  $\mu\text{mol}$  of  $\text{H}_3\text{PMo}_{12}$ , with a value of 1.192 mmol  $\text{H}^+/\text{g}$ . In general, all trials exhibited very satisfactory glycerol conversion, with the lowest result corresponding to the lowest acidity amount used (89% after 30 min). Trials 2 and 3 present the best catalytic results, achieving 96% and 97% after 30 min, respectively. Since the conversion data and solketal selectivity obtained for these two last acidity amounts were similar, the optimized acidity was chosen to be 0.373 mmol  $\text{H}^+/\text{g}$  (Trial 2), corresponding to the lower catalyst usage.

### 2.3. Final remarks

During this chapter, the efficiency of different Keggin-type HPA catalysts ( $\text{H}_3\text{PW}_{12}$ ,  $\text{H}_3\text{PMo}_{12}$  and  $\text{H}_4\text{SiW}_{12}$ ) was evaluated for the acetalization of glycerol with acetone. Blank reactions containing only glycerol and acetone, without catalyst, demonstrated the absence of glycerol conversion, highlighting the importance of the catalyst for the formation of solketal as reaction products.

Initially, potentiometric titration analysis was performed to calculate the acidity for each HPA. The acidity amount used initially in the catalytic experiments (0.373 mmol  $\text{H}^+/\text{g}$ ) was maintained by the three different catalysts, and their catalytic efficiency was compared. The best catalytic efficiency was achieved for the  $\text{H}_3\text{PW}_{12}$  catalyst, obtaining 97% of conversion and 97% of selectivity for solketal after 30 min of reaction, at 25 °C.

Optimization of experimental conditions was performed by studying the effect of temperature (25 and 60 °C) and catalyst amount, in the catalytic efficiency of  $\text{H}_3\text{PW}_{12}$  and  $\text{H}_3\text{PMo}_{12}$ . Higher glycerol conversion results were achieved at 25 °C and using an acidity amount of 0.373 mmol  $\text{H}^+/\text{g}$ .

In the following chapters, only the two best performing catalysts  $\text{H}_3\text{PW}_{12}$  and  $\text{H}_3\text{PMo}_{12}$  will be used. These will be heterogenized and studied as heterogeneous catalysts. Furthermore, previous optimized conditions will be applied in all following acetalization reactions in this work.

## 2.4. References

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### **3. Mesoporous Silica Composites for Glycerol Acetalization**

This chapter will present the preparation and catalytic application of heterogeneous catalysts based in the previously used active HPAs supported in mesoporous silica SBA-15.

Initially, the support SBA-15 was prepared using a hydrothermal synthesis process <sup>1</sup>, and its surface was functionalized with 3-aminopropyltriethoxysilane (APTES), following a post-grafting method <sup>1</sup>, and originating APTES-SBA-15 (Figure 3.1). Then, the active HPAs were incorporated into the silica structure, originating the composites  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ . All materials were characterized by various techniques: zeta potential, elemental analysis, FTIR-ATR, PXRD, SEM-EDS, ICP-OES and potentiometric titration. Finally, the composites were applied as heterogeneous catalysts in glycerol acetalization reactions, and their catalytic efficiency was studied and discussed.



**Figure 3.1** – Mesoporous silica materials prepared: SBA-15 (on the left) and APTES-SBA-15 (on the right).

### 3.1. Silica support and composites characterization

#### 3.1.1. Zeta potential

Zeta potential of the prepared SBA-15 and APTES-SBA-15 materials was studied, in order to understand the efficiency of the surface functionalization of SBA-15. From these results it is possible to investigate surface charge and particle stability. The results obtained can be observed in Table 3.1.

**Table 3.1** – Zeta potential measurements of SBA-15 and APTES-SBA-15.

| Material     | Zeta Potential<br>(mV) |
|--------------|------------------------|
| SBA-15       | -17.5                  |
| APTES-SBA-15 | +29.3                  |

Before functionalization, SBA-15 presents a zeta potential of -17.5 mV and after functionalization with APTES, the zeta potential increases to +29.3 mV. The change of negative value to positive indicates a successful surface functionalization, since pure SBA-15 contains silanol groups on its surface, which have a negative charge, that revealed negative zeta values. When the surface was functionalized with APTES, rich in amino groups (Figure 3.2), an abundance of positive charge on the surface was performed, leading to positive zeta values.

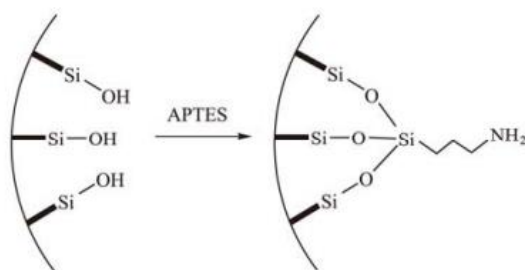


**Figure 3.2** – Surface functionalization of SBA-15, with APTES. Adapted from literature.<sup>2</sup>

Finally, highly stable particles exhibit zeta values higher than  $\pm 30$  mV.<sup>3</sup> It can be seen that through surface functionalization of SBA-15, the silica particles became more stable, and their surface is now presenting a functional group suitable for HPA incorporation.

### 3.1.2. Elemental analysis

The technique of elemental analysis, performed for the functionalized APTES-SBA-15 silica, was used to verify, and quantify the presence of the APTES functional group. As such, the amount of nitrogen, carbon and hydrogen were analysed, and the results obtained can be seen in Table 3.2.

**Table 3.2** – Results of the elemental analysis (C, H and N) of the functionalized APTES-SBA-15.

| Material     | Nitrogen (%) | Carbon (%) | Hydrogen (%) |
|--------------|--------------|------------|--------------|
| APTES-SBA-15 | 2.41         | 7.05       | 2.16         |

From these results it was possible to confirm the presence of nitrogen on the surface of the functionalized APTES-SBA-15. The amount of APTES present in the structure was also quantified, with 2.41% of nitrogen corresponding to 1.1 mmol of APTES per g of material.

### 3.1.3. FTIR-ATR

The preparation of the mesoporous silica materials, support SBA-15 and functionalized support APTES-SBA-15, was evaluated through FTIR-ATR analysis. In Figure 3.3, it is possible to observe the results obtained.

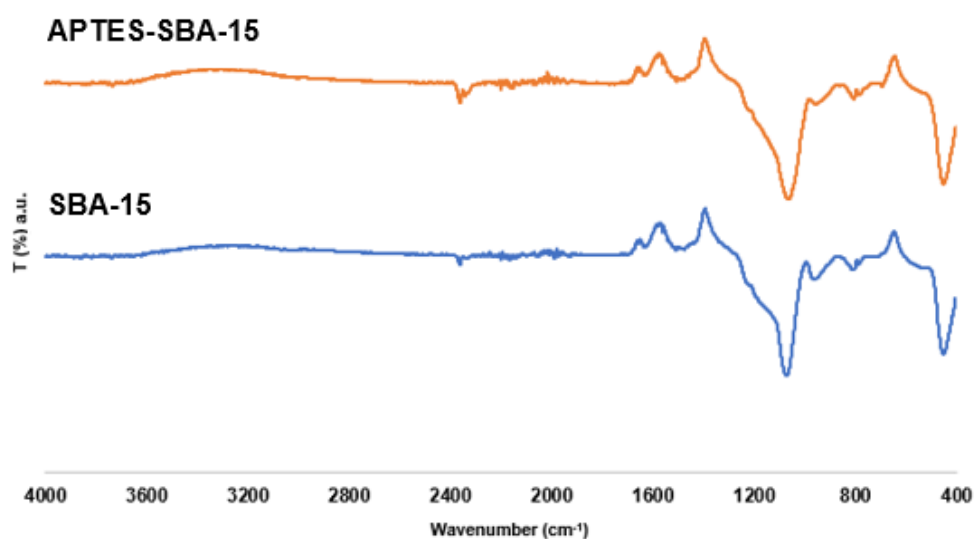


**Figure 3.3** – FTIR-ATR spectra obtained for SBA-15 (in blue) and APTES-SBA-15 (in orange), in a wavenumber range between 400 and 4000  $\text{cm}^{-1}$ .

Both materials exhibited characteristic SBA-15 vibration bands:  $\nu_{as}$  (Si-O-Si) (asymmetric stretching) at  $1070\text{ cm}^{-1}$ ,  $\nu_s$  (Si-O-Si) (symmetric stretching) at  $804\text{ cm}^{-1}$  and  $\delta$  (Si-O-Si) (bending) at  $451\text{ cm}^{-1}$  (Table 3.3).<sup>4-6</sup>

The presence of amino groups attributed to the functional group in APTES-SBA-15, was not able to be distinctly identified by this technique. In fact, the spectra of SBA-15 and APTES-SBA-15 are similar, and no extra bands in the functionalized APTES-SBA-15 could be identified. Some examples of characteristic bands of APTES can be observed in Table 3.4, highlighting those at  $3200\text{ cm}^{-1}$  and  $2800\text{ cm}^{-1}$ , correspondent to the  $\nu$  (N-H) and  $\nu$  (C-H), respectively.<sup>7, 8</sup>

**Table 3.3** – Vibration modes characteristic of SBA-15, with their experimental and literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes      | Experimental<br>( $\text{cm}^{-1}$ ) | Literature <sup>4-6</sup><br>( $\text{cm}^{-1}$ ) |
|----------------------|--------------------------------------|---------------------------------------------------|
| $\nu_{as}$ (Si-O-Si) | 1070                                 | 1080 - 1090                                       |
| $\nu_s$ (Si-O-Si)    | 804                                  | 800 - 810                                         |
| $\delta$ (Si-O-Si)   | 451                                  | 450 - 470                                         |

**Table 3.4** – Vibration modes characteristic of APTES, with their literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes      | Literature <sup>9-11</sup><br>( $\text{cm}^{-1}$ ) |
|----------------------|----------------------------------------------------|
| $\nu$ (N-H)          | 3200 - 3400                                        |
| $\nu$ (C-H)          | 2800 - 3000                                        |
| $\nu_{as}$ (Si-O-Si) | 1080 - 1090                                        |
| $\nu_s$ (Si-O-Si)    | 800 - 810                                          |

Figure 3.4 presents the spectra of the prepared composites, where it is possible to observe the results obtained for  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}@ \text{APTES-SBA-15}$ .

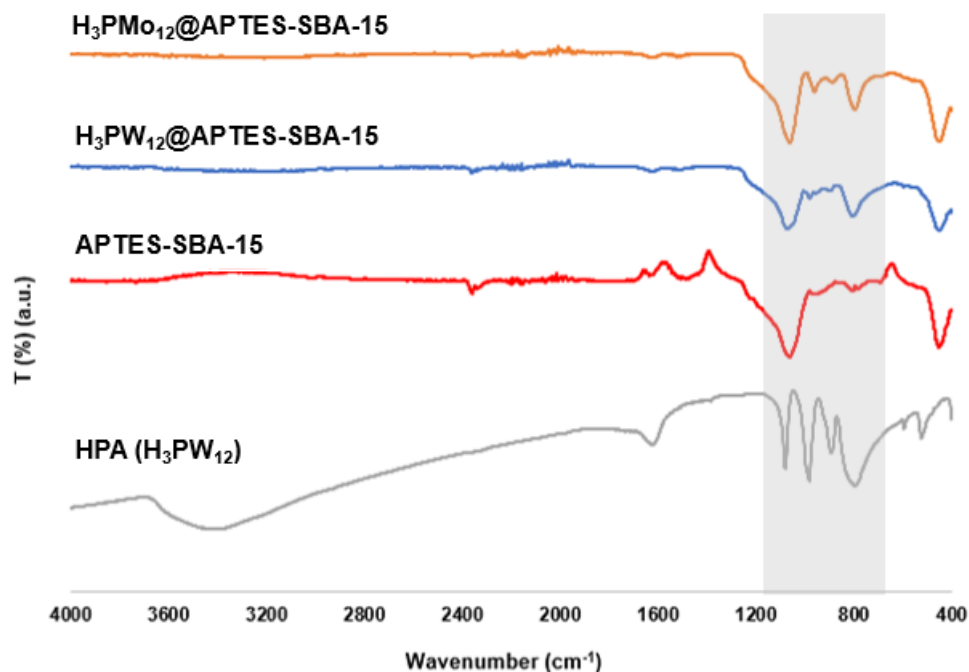


**Figure 3.4** - FTIR-ATR spectra obtained for APTES-SBA-15 support (in red),  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  (in blue) and  $\text{H}_3\text{PMo}_{12}@ \text{APTES-SBA-15}$  (in orange), in a wavenumber range between 400 and 4000  $\text{cm}^{-1}$ .

Both composites maintained the original SBA-15 structure, as shown by the appearance of the characteristic SBA-15 peaks presented in Table 3.3. Furthermore, it is also possible to observe the characteristic HPA vibration bands (highlighted area), as summarized in Table 3.5.

**Table 3.5** - Vibration modes characteristic of HPA ( $\text{H}_3\text{PW}_{12}$  and  $\text{H}_3\text{PMo}_{12}$ ), with their experimental and literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes                           | Experimental<br>( $\text{cm}^{-1}$ ) |                             | Literature <sup>12-14</sup><br>( $\text{cm}^{-1}$ ) |                             |
|-------------------------------------------|--------------------------------------|-----------------------------|-----------------------------------------------------|-----------------------------|
|                                           | $\text{H}_3\text{PW}_{12}$           | $\text{H}_3\text{PMo}_{12}$ | $\text{H}_3\text{PW}_{12}$                          | $\text{H}_3\text{PMo}_{12}$ |
| $\nu_{\text{as}} (\text{P-O}_a)$          | 1074                                 | 1062                        | 1079                                                | 1060 - 1080                 |
| $\nu_{\text{as}} (\text{M=O}_d)$          | 980                                  | 960                         | 979                                                 | 960 - 1000                  |
| $\nu_{\text{as}} (\text{M-O}_b\text{-M})$ | 898                                  | 888                         | 895                                                 | 840 - 910                   |
| $\nu_{\text{as}} (\text{M-O}_c\text{-M})$ | 802                                  | 798                         | 802                                                 | 760 - 800                   |

3.1.4. PXRD

The crystalline structure of the prepared materials was evaluated through low-angle Powder X-Ray Diffraction (PXRD) and the patterns obtained are shown in Figure 3.5.

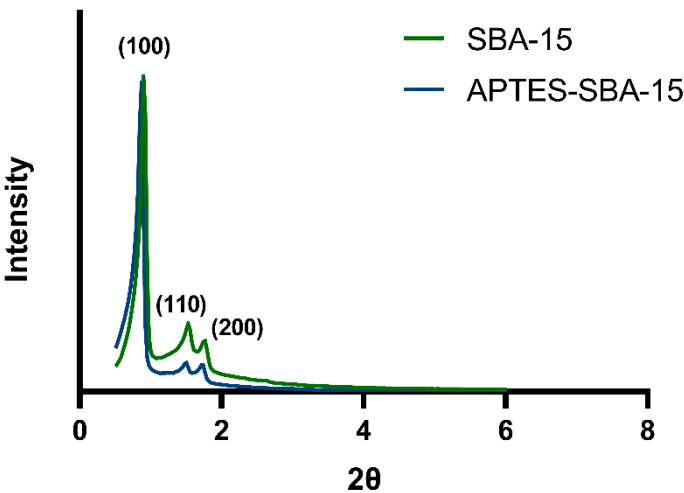


**Figure 3.5** – Diffraction pattern obtained for the SBA-15 support (in green) and functionalized APTES-SBA-15 (in blue).

The SBA-15 support possesses a hexagonal structure, with three characteristic diffraction peaks, localized at  $0.8^\circ$ ,  $1.5^\circ$  and  $1.8^\circ$ ,  $2\theta$  values. These peaks correspond to the (100), (110) and (200) planes, respectively.<sup>6, 14</sup> The functionalized APTES-SBA-15 exhibits the same peaks, showing that the surface functionalization did not compromise the structure and crystallinity of the material.

Further, the prepared composites were also analysed by PXRD, in order to verify their structural crystallinity and the obtained diffraction patterns are present in Figure 3.6.

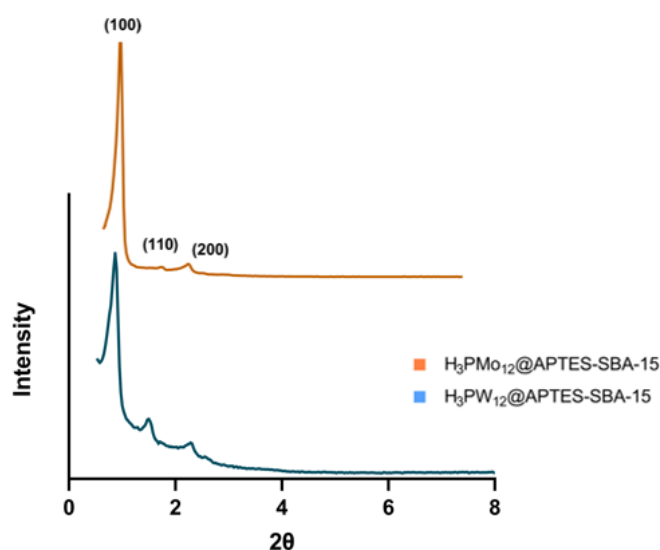


**Figure 3.6** – Diffraction pattern obtained for  $\text{H}_3\text{PW}_{12}@APTES\text{-SBA-15}$  (in blue) and  $\text{H}_3\text{PMo}_{12}@APTES\text{-SBA-15}$  (in orange).

The crystalline structure of the functionalized APTES-SBA-15 support after HPA incorporation was maintained, confirmed by the appearance of the characteristic diffraction peaks relative to (100), (110) and (200) planes. It is also possible to observe that the  $2\theta$  suffered shifts for higher values, due to a shrinkage of the mesoporous silica structure after HPA incorporation, similarly to previous reports.<sup>14-16</sup>

### 3.1.5. SEM-EDS

The morphology and composition of all the prepared materials was evaluated through SEM-EDS (Figures 3.7 to 3.10). The SBA-15 support exhibited particles with the characteristic hexagonal shape (Figure 3.7A), which was expected due to its hexagonal arrangement.<sup>5, 14, 15</sup> After functionalization with APTES, the particles adhere more to each other and adopt a more elongated shape (Figure 3.7B), while still maintaining its hexagonal structure.<sup>7, 17</sup>

In agreement to the PXRD analysis, SEM results indicate that the surface functionalization of SBA-15 with APTES did not compromise its structural morphology. The EDS spectra obtained for both materials (Figure 3.8) showed the expected peak for silicon (Si) from the support. The amount of amino groups on the surface of APTES-SBA-15 was probably lower than the detection limit of this technique, and therefore, the presence of nitrogen was not observed. Peaks correspondent to gold (Au) are derived from coating of the materials with an Au/Pd film, necessary for sample analysis.

For the composites,  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$  (Figure 3.9 A and B, respectively), the morphology of the silica support was not altered after HPA incorporation, as previously confirmed by PXRD.<sup>1, 14</sup> The incorporation of HPAs in the silica structure can be confirmed by the EDS analysis (Figure 3.10), where the peaks for tungsten (W) and molybdenum (Mo) could be observed, alongside the peak of silicon, derived from the support material.

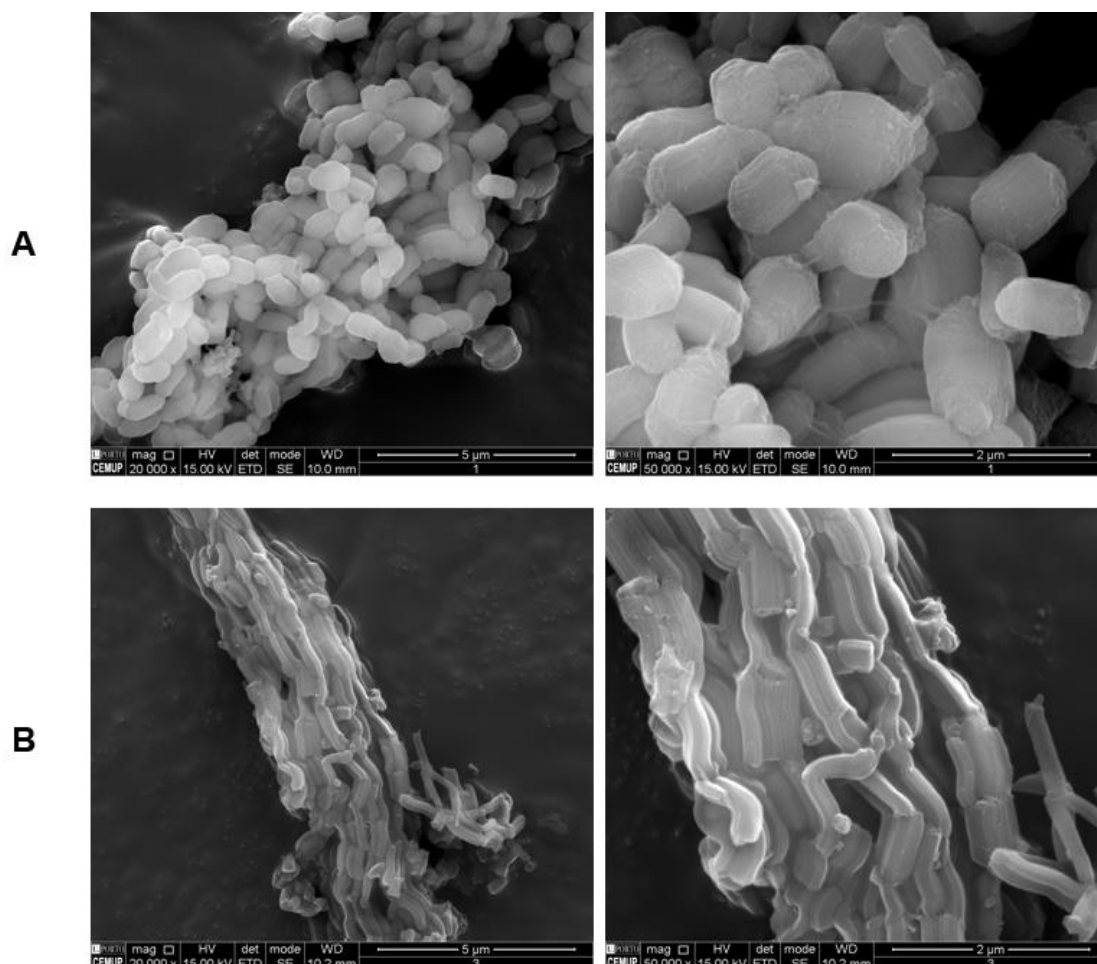


**Figure 3.7** – SEM images obtained for A) SBA-15 and B) APTES-SBA-15.

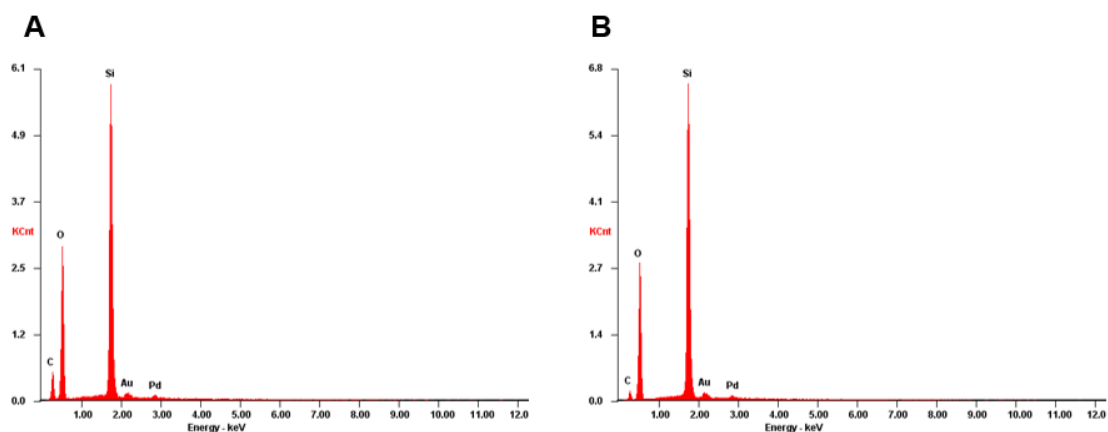


Figure 3.8 – EDS spectra obtained for A) SBA-15 and B) APTES-SBA-15.

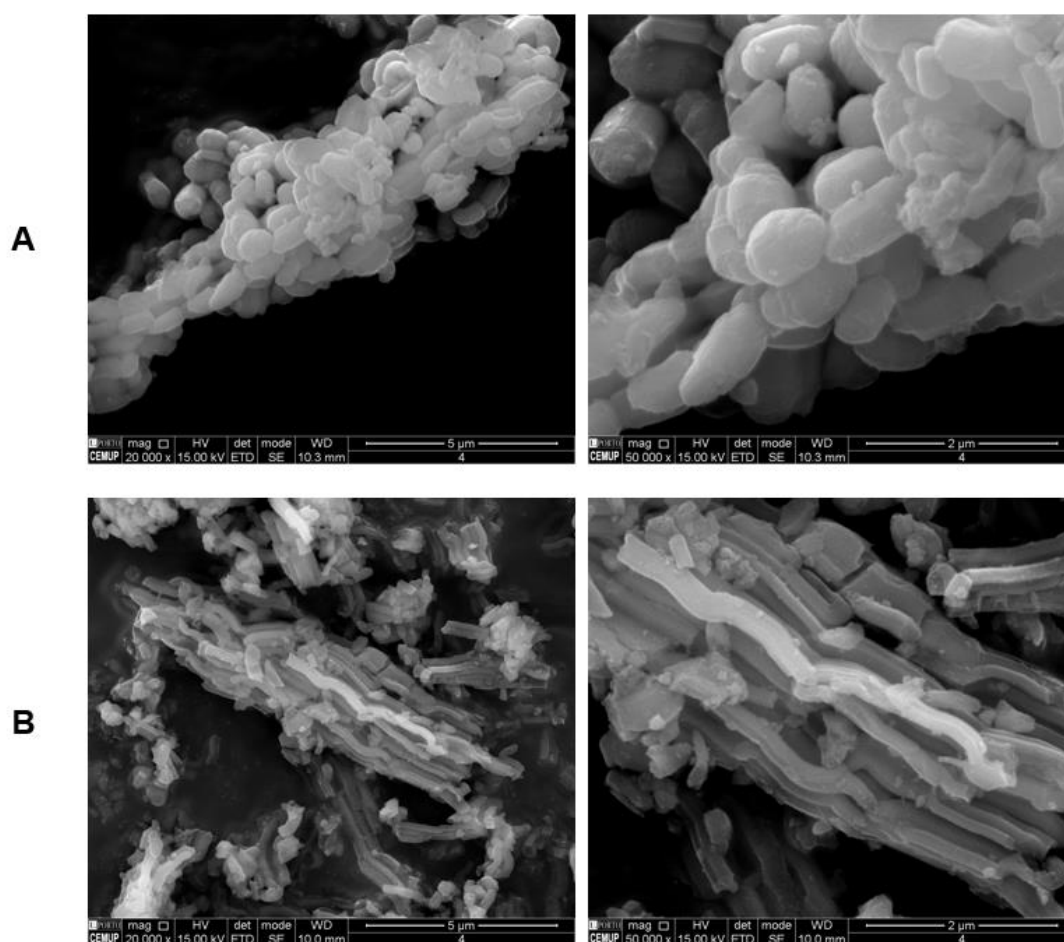


Figure 3.9 – SEM images obtained for A) H<sub>3</sub>PW<sub>12</sub>@APTES-SBA-15 and B) H<sub>3</sub>PMo<sub>12</sub>@APTES-SBA-15.

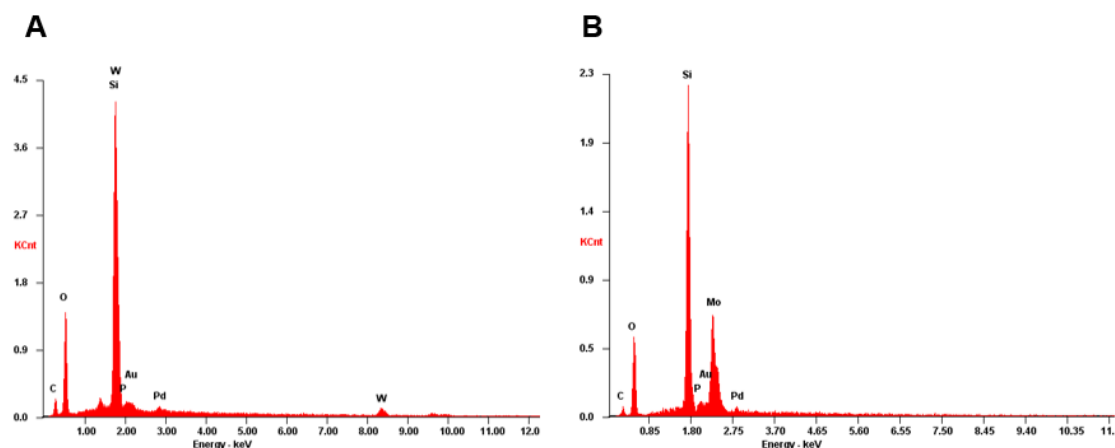


**Figure 3.10** – EDS spectra obtained for A)  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and B)  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ .

### 3.1.6. ICP-OES

The quantification of HPAs incorporated into APTES-SBA-15 was evaluated for each composite through ICP-OES analysis. Therefore, the amount of W and Mo in  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ , respectively, was analysed. The results obtained can be consulted in Table 3.6. After this, the loading of HPA for each composite could be calculated, converting grams of W or Mo per g of material into moles of HPA per g of composite. For  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$ , it was obtained a loading of 159  $\mu\text{mol}$  of  $\text{H}_3\text{PW}_{12}$  per g of composite and for  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ , a slightly higher loading of HPA was achieved, 188  $\mu\text{mol}$  of  $\text{H}_3\text{PMo}_{12}$  per g of composite.

**Table 3.6** – ICP-OES results for the quantity of HPAs loading for each composite, where X corresponds to W in  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$ , and Mo in  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ .

| Composite                                       | $m_X$ (g / kg of composite) | $n_{\text{HPA}}$ ( $\mu\text{mol}$ / g of composite) |
|-------------------------------------------------|-----------------------------|------------------------------------------------------|
| $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  | 350.1                       | 159                                                  |
| $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ | 216.9                       | 188                                                  |

### 3.1.7. Potentiometric titration

Potentiometric titration was used to quantify the amount of acidic sites present in the two composites materials:  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ .

The composite materials were dispersed in NaCl 2M solutions, with NaCl acting as the exchange cation. Then, these solutions were titrated with a NaOH solution (0.025M), acting as the titrant. The results obtained can be observed in Table 3.7, where the acidity of the heterogeneous catalysts was posteriorly calculated.

**Table 3.7** – Potentiometric measurements obtained for the two composites, followed by the calculation of acidity.

| Composite                                       | pH   | V (NaOH)<br>(mL) | Acidity<br>(mmol $\text{H}^+$ /g) |
|-------------------------------------------------|------|------------------|-----------------------------------|
| $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  | 3.39 | 0.2815           | 0.469                             |
| $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ | 3.41 | 2.014            | 3.357                             |

Similar results as the previously obtained for homogeneous HPAs (chapter 2, Table 2.1) were here observed, i.e. the composite containing  $\text{H}_3\text{PMo}_{12}$  present a higher acidity than the composite containing  $\text{H}_3\text{PW}_{12}$ . However, it is also possible to observe that the acidity for both composites is much lower than the acidity of the isolated HPAs. This difference is probably caused by the nature of the support material of the heterogeneous catalysts, since mesoporous silica is known to have low acidic nature.<sup>4</sup>

### 3.2. Acetalization studies

The optimal experimental conditions found for the active homogeneous HPAs (described in Chapter 2), were initially used for the catalytic experiments involving the mesoporous silica-based catalysts in glycerol acetalization reactions with acetone.

Therefore, the glycerol acetalization reactions proceeded in catalytic reactors immersed in paraffin baths, with constant stirring and temperature. The reactor was filled with a ratio of 1:15 glycerol/acetone, and left under agitation for 10 min, at 25°C, in order to homogenize the solution. Then, the heterogeneous catalyst was added, and

glycerol conversion was evaluated during 120 min. Glycerol conversion results were determined by gas chromatography analysis.

Initially, a blank reaction was performed by analysing the catalytic activity of the functionalized support APTES-SBA-15 (section 3.2.1.). Then, the two composites ( $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ ) were applied as heterogeneous catalysts for the glycerol acetalization reaction, using two different temperatures: 25 °C and 60 °C. These results can be observed in section 3.2.3. The optimization of experimental factors was performed, and the results are discussed in section 3.2.4. The stability of the catalysts was studied through reutilization and recycling experiments, and the results are presented in section 3.3. Finally, characterization of the most active catalyst after catalytic use was reported in section 3.4.

### 3.2.1. Catalytic activity of APTES-SBA-15 support

The influence of the APTES-SBA-15 support in glycerol acetalization reactions was studied by applying it as a heterogeneous catalyst. As such, catalytic reactors with 1:15 glycerol/acetone ratio and an amount of catalyst were placed under constant stirring, at 25 °C.

Even after 120 min of reaction, no glycerol conversion was observed. The absence of support activity was expected since in acetalization reactions, one of the most important factors to achieve high glycerol conversion is high acidity of the catalyst and the functionalized SBA-15 support is known to have very low acidity.<sup>4, 18, 19</sup> These results were confirmed through potentiometric titration analysis performed with this support, where a pH of 8.6 was obtained.

### 3.2.2. HPAs@APTES-SBA-15 catalytic performance

Initially, the necessary amount of each heterogeneous catalyst ( $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ ) was calculated based on the previous optimized catalyst acidity (0.373 mmol  $\text{H}^+$ /g, Chapter 2). Table 3.8 presents the catalyst amounts needed from each composite, in order to maintain the catalyst acidity.

**Table 3.8** – The quantity of each HPA@APTES-SBA-15 composite to be used in glycerol acetalization reactions, maintaining the optimized catalyst acidity of 0.373 mmol H<sup>+</sup>/g.

| Composite                                         | Catalyst used (mg) |
|---------------------------------------------------|--------------------|
| <b>H<sub>3</sub>PW<sub>12</sub>@APTES-SBA-15</b>  | 11.934             |
| <b>H<sub>3</sub>PMo<sub>12</sub>@APTES-SBA-15</b> | 1.668              |

The performance of HPAs as heterogeneous catalysts (H<sub>3</sub>PW<sub>12</sub>@APTES-SBA-15 and H<sub>3</sub>PMo<sub>12</sub>@APTES-SBA-15) was studied for two different temperatures, 25 and 60 °C. The obtained results are represented in Figure 3.11A (kinetic profiles) and Figure 3.11B (comparison of conversion at 5 and 60 min). Reactions were analysed at the same times as the reactions using homogeneous catalysts: beginning of the reaction at 5 min and end of the reaction at 60 min.

H<sub>3</sub>PMo<sub>12</sub>@APTES-SBA-15 showed the lowest catalytic efficiency of the two composites, with a maximum glycerol conversion of 31% (solketal selectivity of 69%), after 5 min at 25 °C. When the reaction temperature was increased to 60 °C, the conversion increased to 40%, with solketal selectivity of 76%, after 5 min. It can also be observed that, even after 60 min, the conversion of this catalyst did not increase (Figure 3.11B).

Contrarily, H<sub>3</sub>PW<sub>12</sub>@APTES-SBA-15 exhibited a maximum glycerol conversion of 97% with solketal selectivity of 97%, after 60 min at 25 °C. Increasing the reaction temperature to 60 °C, the conversion and solketal selectivity are practically maintained: 96% of conversion and solketal selectivity of 97%, after 60 min.

In fact, between the two reaction temperatures used, the only distinction observed in the kinetic profile occurs during the first 5 min of reaction, where the catalyst used at 60 °C reaches higher conversions faster.<sup>20</sup> This indicates that the acetalization of glycerol with acetone, catalysed by HPAs@APTES-SBA-15, is a fast occurring reaction, even using room temperature (25 °C).

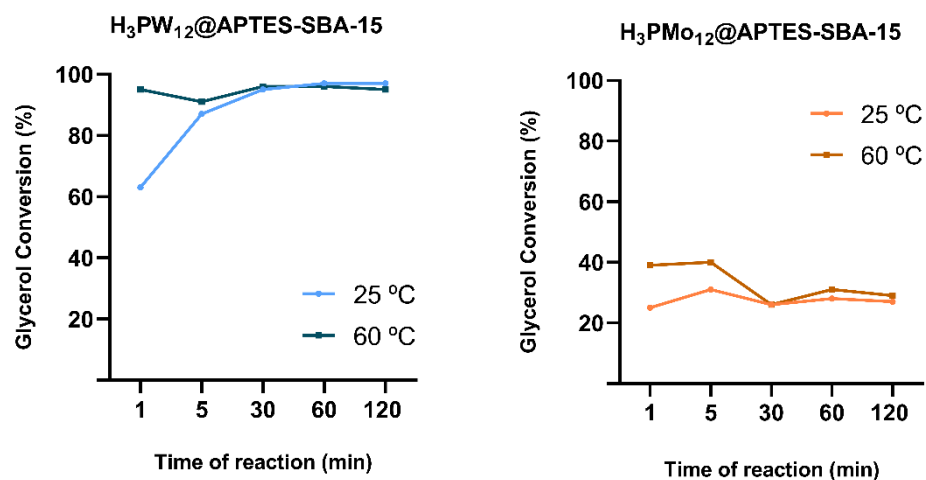
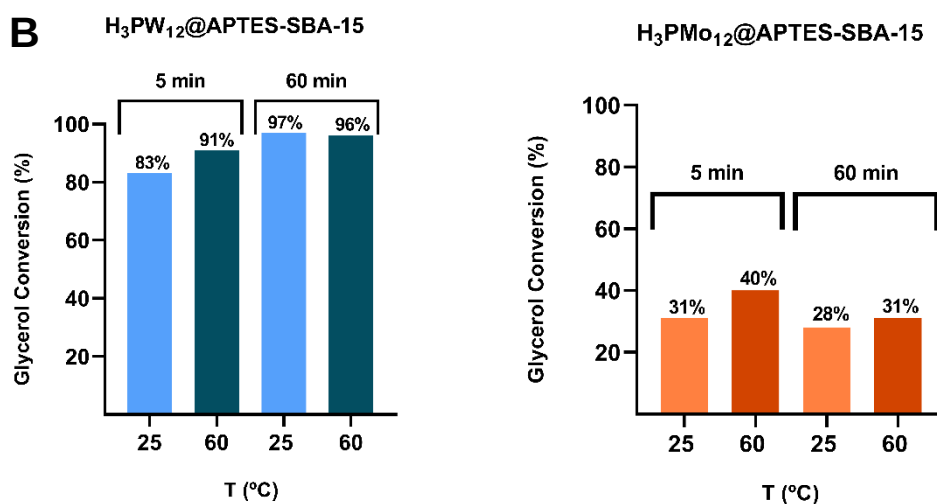
**A****B**

**Figure 3.11 – A)** Kinetic profiles of glycerol acetalization catalysed by HPAs@APTES-SBA-15 heterogeneous catalysts, using a ratio of 1:15 glycerol/acetone, 0.373 mmol H<sup>+</sup>/g catalyst acidity, at 25 and 60 °C. **B)** Glycerol conversion data obtained after 5 and 60 min, using HPAs@APTES-SBA-15 catalysts, for both 25 and 60 °C.

Using these HPAs heterogeneous catalysts, it was also possible to observe the following catalytic behaviour trend:  $H_3PW_{12}@APTES-SBA-15 > H_3PMo_{12}@APTES-SBA-15$ . This result is similar to the trend observed for the homogeneous catalyst (chapter 2).

After the  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$  catalyst was used in a catalytic cycle, it was removed from the reaction medium and analysed. It was possible to observe that the solid had changed its colour after catalysis, from a yellowish solid (yellow colour is characteristic of the  $\text{H}_3\text{PMo}_{12}$ ) to a blue solid (Figure 3.12). This change has been very well documented<sup>21, 22</sup> and is related to the reduction of  $\text{Mo}^{\text{VI}}$  to  $\text{Mo}^{\text{V}}$ , due to the susceptibility of the HPA to redox reactions.<sup>23</sup>



**Figure 3.12** – Image of the  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA}$  composite after catalytic reaction.

### 3.3. Catalyst stability tests

When a catalyst exhibits good catalytic behaviour, it is important to study its stability in the reaction, in order to find if the catalytic behaviour is maintained after consecutive catalytic cycles. The ideal catalyst for future industrial application needs to show high catalytic performance, while being consecutively applied.

Therefore, the most active catalyst,  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$ , was selected to study catalyst stability. Firstly, the catalyst was reused, i.e. catalyst was used under consecutive reaction cycles without washing treatment (Figure 3.13). After the 1<sup>st</sup> cycle, the reactional solution (containing glycerol, acetone and products) was removed and the solid catalyst was isolated. After, a new batch (1:15 glycerol/acetone ratio) was placed in the reactor and a new catalytic cycle begins. The process was repeated for four cycles, and the results discussed in section 3.3.1.

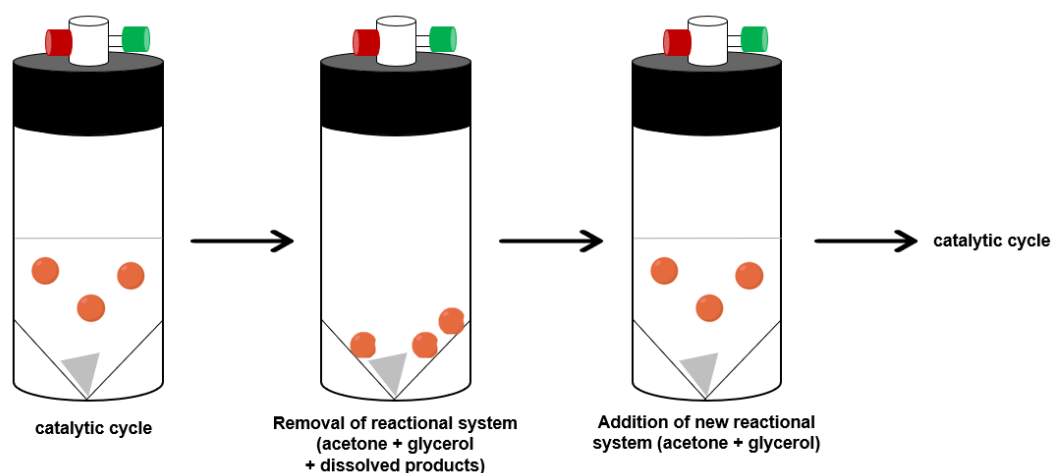


**Figure 3.13** – Experimental scheme for catalyst reutilization studies.

The catalyst recycling process was also investigated. In this case, the catalyst was removed after a catalytic cycle and washed. After drying, the catalyst was weighted, to adjust the reaction conditions, and a new batch of glycerol and acetone was added, beginning the new catalytic cycle (Figure 3.14). The process was repeated for four cycles, and the results discussed in section 3.3.2.

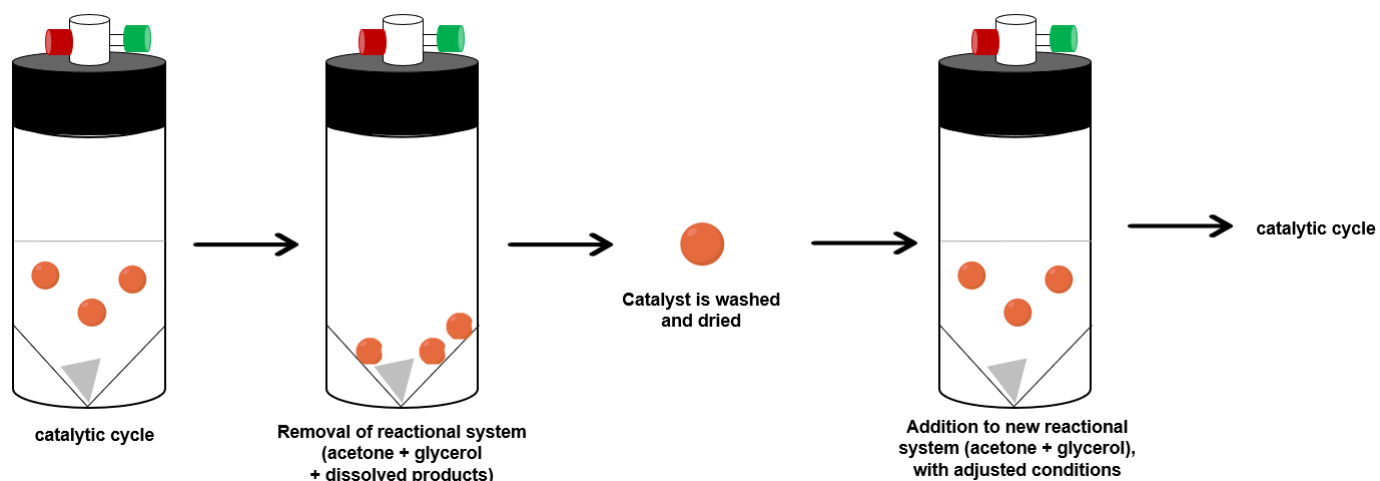


**Figure 3.14** – Experimental scheme for catalyst recycling studies.

As such, it was possible to study the catalyst stability when the catalyst was continuously used without any treatment (reutilization), and also when the catalyst was washed between each cycle (recycling).

### 3.3.1. Reutilization

The catalyst,  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$ , was applied in acetalization reactions for 4 consecutive reutilization cycles, at two different temperatures: 25 and 60 °C. The results obtained can be observed in Figure 3.15.

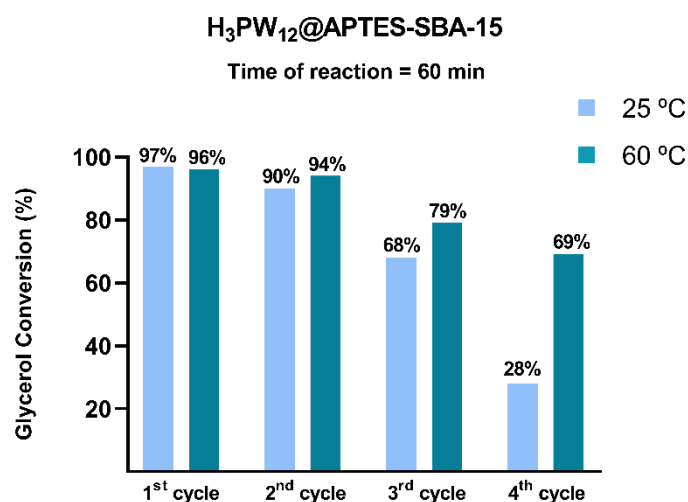


**Figure 3.15** – Glycerol conversion results obtained after 60 min, reusing the  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  catalyst for four consecutive cycles. Reactions were performed at 25 and 60 °C.

For the 1<sup>st</sup> cycle, the highest catalytic efficiency was observed (glycerol conversion of 97% and 96%, obtained after 60 min, for 25 and 60 °C, respectively). After the 1<sup>st</sup> cycle, catalytic activity decreased. The reutilization performed at 25 °C showed a continuous decrease in catalyst efficiency, with an accentuated drop after the 3<sup>rd</sup> catalytic cycle, where the catalyst reached only 28% of glycerol conversion. Furthermore, the solketal selectivity also consecutively decreased between cycles, from 94% (2<sup>nd</sup> cycle) to 71% (4<sup>th</sup> cycle). Reutilization performed at 60 °C showed a less accentuated decrease of catalyst efficiency between cycles. However, after the 4<sup>th</sup> cycle, glycerol conversion reached 69%. Therefore, performing the reaction at 60 °C is preferred than at 25 °C, since the reutilization of the catalysts is slightly better.

This decrease of catalytic efficiency in the reutilization process must be associated to the loss of catalyst acidity, since the higher the acidity, the better the catalyst efficiency. Two main factors can contribute for the loss of catalyst activity between cycles: i) the reactional solution cannot come in contact with the  $\text{H}_3\text{PW}_{12}$  active centres inside the pores of the SBA-15 support, due to pore impediment or ii) there is  $\text{H}_3\text{PW}_{12}$  leaching from the solid support to the reaction medium between cycles.

In order to investigate the possibility of leaching of active species, recycling studies were conducted. In this case, after each catalytic cycle,  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  was washed and dried, decreasing the possibility of accumulated products on the surface and pores of the support.

### 3.3.2. Recycling

The catalyst,  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$ , was recycled in glycerol acetalization reactions for four consecutive recycling cycles. Experiments were performed at 25 and 60 °C. The results obtained can be observed in Figure 3.16.

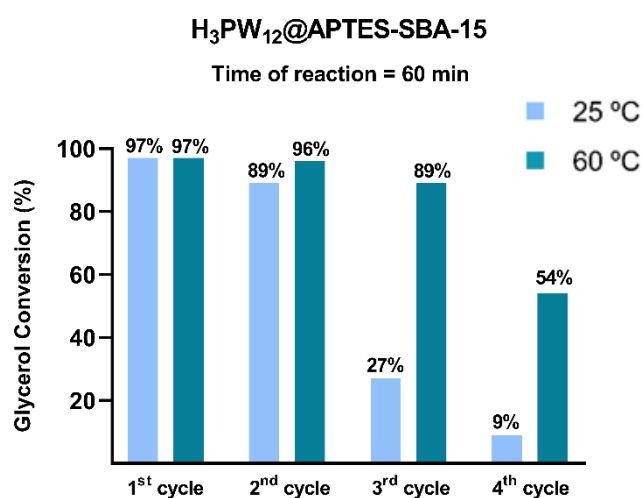


**Figure 3.16** – Glycerol conversion results obtained after 60 min, recycling the  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15}$  catalyst for four consecutive cycles. Reactions were performed at 25 and 60 °C.

Similarly to the reutilization process, the catalyst suffers a drastic loss of activity, at 25 °C. From the 2<sup>nd</sup> to the 3<sup>rd</sup> cycle, the glycerol conversion decreased from 89% to 27%. After the 4<sup>th</sup> cycle, only 9% of conversion was achieved, rendering the material inactive. Recycling at 60 °C, similarly to reutilization, showed a less drastic decrease of catalytic performance, reaching 54% after the 4<sup>th</sup> cycle. Therefore, using a reaction temperature of 60 °C for recycling studies is also preferred.

Comparing reutilization and recycling, it is possible to observe that in both processes the catalyst suffered loss of efficiency. This may indicate that the problem is not related with pore impediment, which could be caused by surface adsorption of products from the reaction, since the washing procedure between recycling cycles should remove adsorbed products. Therefore, this decrease of catalytic activity may be caused by a

decrease in catalyst acidity, which must be related with leaching of  $\text{H}_3\text{PW}_{12}$  from the APTES-SBA-15 support. Previous reports have stated some examples involving the occurrence of leaching of species from APTES-SBA-15.<sup>18, 24</sup>

In order to confirm this possibility,  $\text{H}_3\text{PW}_{12}$ @APTES-SBA-15 was characterized after catalytic reactions.

### 3.4. Catalyst characterization after catalysis

#### 3.4.1. Potentiometric titration

Potentiometric titration was used to quantify the amount of acidic sites present in the  $\text{H}_3\text{PW}_{12}$ @APTES-SBA-15 catalyst after three cycles of recycling process, in order to confirm if the loss of catalytic activity was linked to a decrease of acidity. The result obtained can be consulted in Table 3.9.

Comparing the catalyst acidity before and after catalytic use, it is possible to observe a decrease of acidity after the catalyst is used in acetalization reactions (from 0.469 to 0.277 mmol  $\text{H}^+$ /g), accompanied by a significant difference in pH: after recycling, the pH of the catalyst is similar to the pH of the support without incorporating  $\text{H}_3\text{PW}_{12}$  (8.6). This result may indicate that a large leaching occurred after the 3 recycling cycles. Recycling differs from reutilization due to a specific step: catalyst washing after each catalytic cycle. This step can, in fact, contribute to the loss of active catalytic centres.

**Table 3.9** – Potentiometric measurements obtained for the  $\text{H}_3\text{PW}_{12}$ @APTES-SBA-15 composite, before and after three catalytic recycling reactions, followed by the calculation of acidity.

| $\text{H}_3\text{PW}_{12}$ @APTES-SBA-15 | pH   | Acidity (mmol $\text{H}^+$ /g) |
|------------------------------------------|------|--------------------------------|
| Before catalysis                         | 3.39 | 0.469                          |
| After 3 cycles of recycling              | 8.57 | 0.277                          |

### 3.4.2. SEM-EDS

The morphology and composition of  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  after catalysis was evaluated through SEM-EDS analysis. After one catalytic cycle (Figure 3.17A), the particles seem to maintain its characteristic hexagonal shape, previously observed in Figure 3.17, before catalysis. After three recycling cycles (Figure 3.17B), particle dispersion can be seen, with the formation of smaller aggregates. The presence of W in both cases was confirmed by EDS (Figure 3.18).

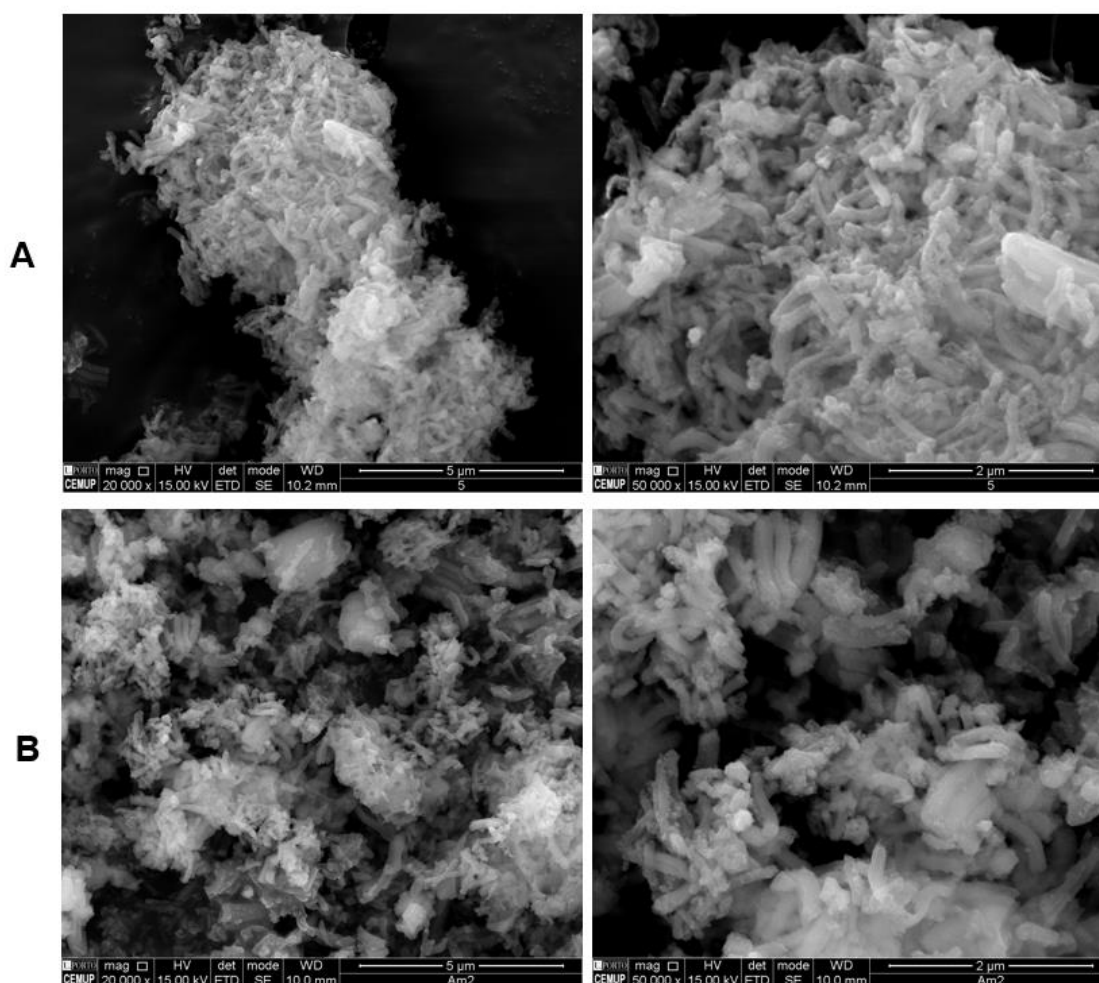


**Figure 3.17** – SEM images obtained for A)  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  after one catalytic cycle, B)  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  after three recycling cycles.

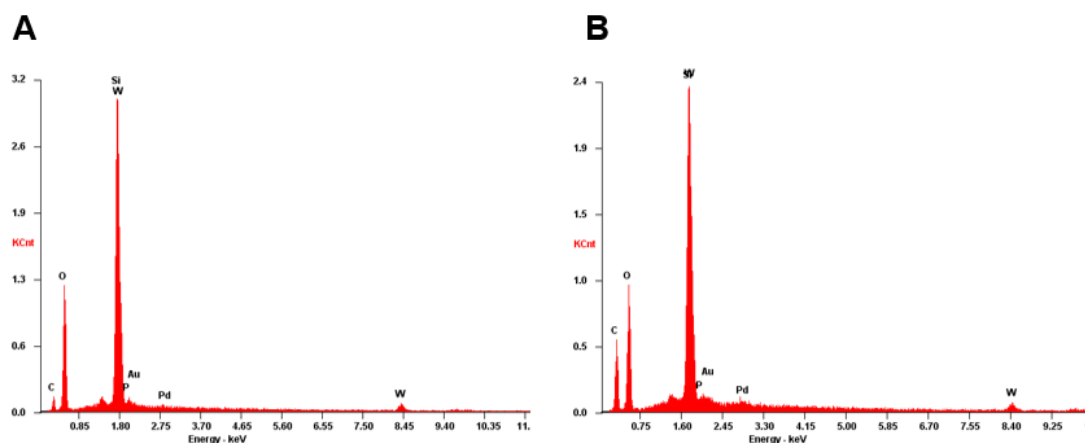


**Figure 3.18** – EDS spectra for A)  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  after one catalytic cycle, B)  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  after three recycling cycles.

### 3.4.3. PXRD

The  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  composite was analysed by PXRD, in order to verify the crystalline structure after catalytic application. The pattern obtained is shown in Figure 3.19.

When compared with the diffraction pattern obtained before catalysis (Figure 3.6), it becomes clear that the SBA-15 structure suffered loss of crystallinity. The well-defined peak around  $0.8^\circ$  to  $2\theta$  corresponds to the (100) plane, and the remaining planes (110) and (200) were not able to be clearly identified.

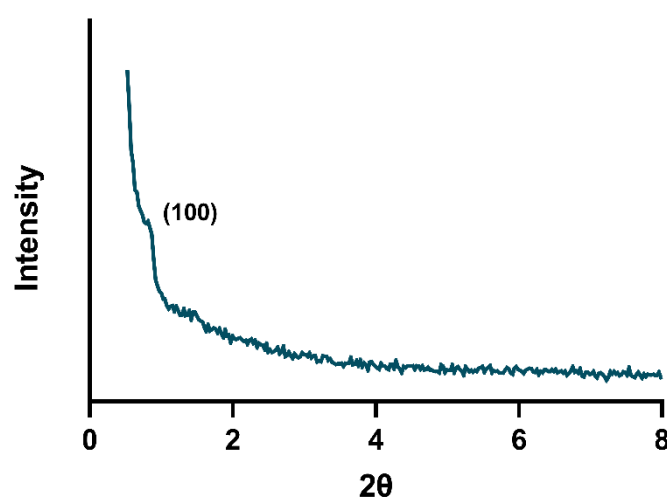


**Figure 3.19** – Diffraction pattern obtained for  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$ , after catalytic application.

### 3.4.4. ICP-OES

Quantification of  $\text{H}_3\text{PW}_{12}$  present in  $\text{H}_3\text{PW}_{12}@\text{APTES-SBA-15}$  after catalytic application was evaluated through ICP-OES, after the first and third recycling reaction. The results obtained can be consulted in Table 3.10.

After the first catalytic cycle, it was obtained 137  $\mu\text{mol}$  of  $\text{H}_3\text{PW}_{12}$  per g of composite. After three cycles of recycling, it was found a value of 105  $\mu\text{mol}$  of  $\text{H}_3\text{PW}_{12}$  per g of composite. Comparing these values with the initial loading of 159  $\mu\text{mol}$  of  $\text{H}_3\text{PW}_{12}$  per g of composite, it is possible to conclude that a loss of HPA of 14% and 34% was obtained for the first and third recycling cycles, respectively.

**Table 3.10** – ICP-OES results and the quantity of  $\text{H}_3\text{PW}_{12}$  loading for the composite, after one and three recycling cycles.

| Material                                                                                          | $m_w$ (g / kg of composite) | $n_{\text{HPA}}$ ( $\mu\text{mol}$ / g of composite) |
|---------------------------------------------------------------------------------------------------|-----------------------------|------------------------------------------------------|
| <b><math>\text{H}_3\text{PW}_{12}@\text{APTES-SBA-15}</math><br/>after catalytic cycle</b>        | 301.26                      | 137                                                  |
| <b><math>\text{H}_3\text{PW}_{12}@\text{APTES-SBA-15}</math><br/>after three recycling cycles</b> | 231.15                      | 105                                                  |

### 3.5. Final remarks

During this chapter, the preparation and characterization of support materials and HPA@APTES-SBA-15 composites were evaluated, confirming the successful preparation of the solid supports (SBA-15 and APTES-SBA-15) and composites ( $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ ). This characterization was performed by different techniques that allowed to study the crystalline structure of these materials, and also identify and quantify the amino functional groups and HPA active centres.

The composites were applied in acetalization reactions as heterogeneous catalysts, and their influence in glycerol acetalization reaction with acetone was studied. The APTES-SBA-15 support showed no catalytic activity, owing to its characteristic low acidity. On the contrary, both composites showed catalytic activity, with  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  exhibiting very good glycerol conversion results. Catalyst stability tests were performed for four consecutive cycles with the most efficient heterogeneous catalyst, the  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  (97% of glycerol conversion achieved after 60 min, with 97% solketal selectivity). A decrease in catalytic activity was observed during reusing and recycling cycles. This loss of activity was more pronounced after the second cycle, in both cases. Characterization post-catalysis of the  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  catalyst confirmed the occurrence of HPA leaching from the solid support, which caused the loss of activity observed.

The next two chapters of this dissertation will present a strategy to solve this problem, by the further immobilization of HPA and HPA@SBA-15 into polymeric membranes. As such, this strategy will be tackled, through the preparation and application of polymeric membranes as heterogeneous catalysts.

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## **4. Catalytic Membranes for Glycerol Acetalization**

This chapter will discuss the preparation and catalytic application of polymeric membranes as heterogeneous catalysts. The HPA active centres were incorporated in a polymer material, polyvinyl alcohol (PVA), forming the HPA@PVA catalysts.

Therefore, four catalytic membranes were prepared based in the active  $\text{H}_3\text{PW}_{12}$  and  $\text{H}_3\text{PMo}_{12}$ . Two different procedures were followed, one containing the functional group 3-aminopropyltriethoxysilane (APTES):  $\text{H}_3\text{PW}_{12}$ @APTES-PVA and  $\text{H}_3\text{PMo}_{12}$ @APTES-PVA, and the other without APTES:  $\text{H}_3\text{PW}_{12}$ @PVA and  $\text{H}_3\text{PMo}_{12}$ @PVA. In the first case, APTES was added to previously prepared PVA solutions, at room temperature. After some time, solutions of the respective HPAs were added, and the membranes were casted and left to dry. For the membranes without APTES, the procedure of preparation was similar, through addition of HPAs to solutions of PVA. The membranes were also casted and left to dry. Therefore, two types of membranes were prepared in this work: type I membranes (with the presence of APTES) and type II membranes (without the presence of APTES). Images of prepared membranes are presented in Figure 4.1. The preparation procedure was adapted from the literature.<sup>1</sup>

All the materials were characterized by various techniques: FTIR-ATR, SEM-EDS, ICP-OES and potentiometric titration. Finally, all the membranes were applied in glycerol acetalization reactions with acetone, and their catalytic efficiency was studied and discussed.

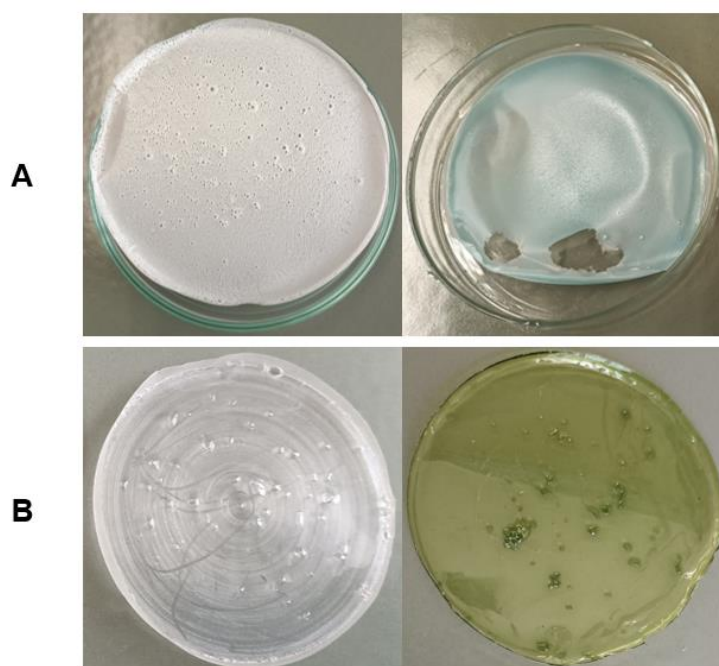


**Figure 4.1** – Polymeric membranes incorporating HPAs: **A)** type I membranes:  $\text{H}_3\text{PW}_{12}$ @APTES-PVA (on the left) and  $\text{H}_3\text{PMo}_{12}$ @APTES-PVA (on the right). **B)** type II membranes:  $\text{H}_3\text{PW}_{12}$ @PVA (on the left) and  $\text{H}_3\text{PMo}_{12}$ @PVA (on the right).

## 4.1. Characterization of catalytic membranes

### 4.1.1. FTIR-ATR

The prepared membranes were evaluated through FTIR-ATR, and the results are presented in Figure 4.2A for HPA@APTES-PVA membranes and Figure 4.2B for HPA@PVA membranes.

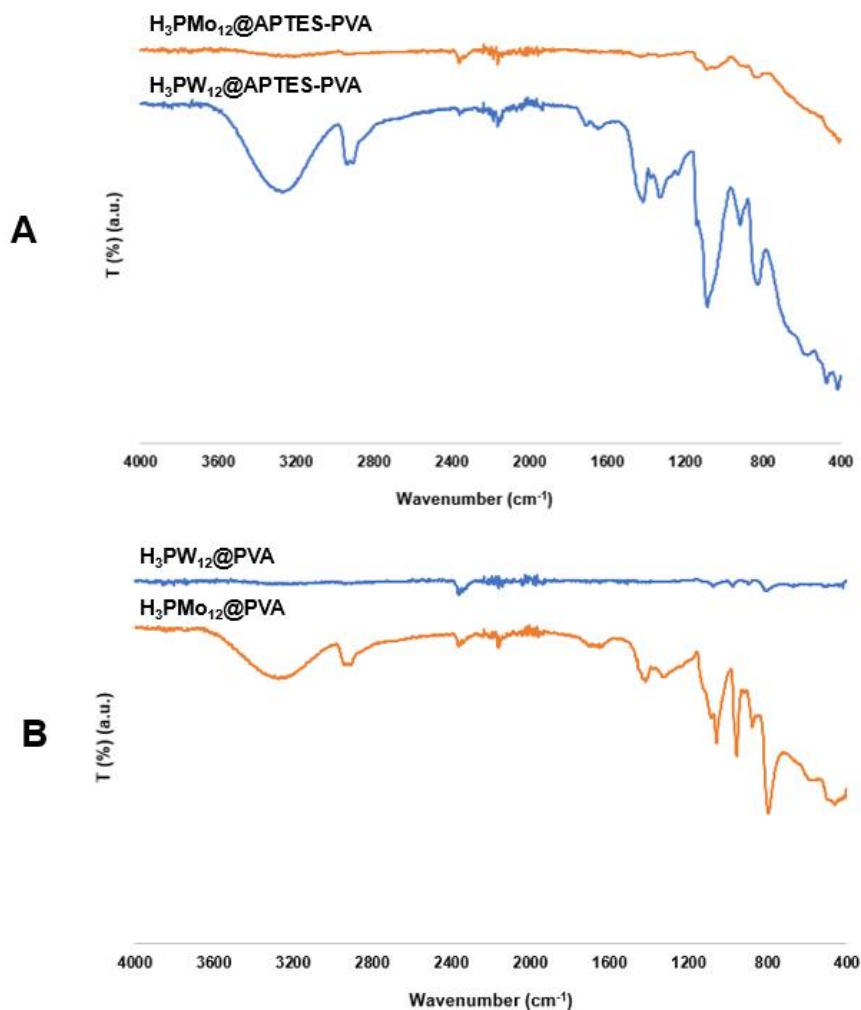


**Figure 4.2** - FTIR-ATR spectra obtained for A) HPA@APTES-PVA membranes and B) HPA@PVA membranes, in a wavenumber range between 400 and 4000 cm<sup>-1</sup>.

Spectra of H<sub>3</sub>PMo<sub>12</sub>@APTES-PVA and H<sub>3</sub>PW<sub>12</sub>@PVA do not present very well-defined bands. This interference with the analysis could be due to the thickness of these membranes since this factor could not be controlled during preparation.

Focusing on the spectra obtained for H<sub>3</sub>PW<sub>12</sub>@APTES-PVA and H<sub>3</sub>PMo<sub>12</sub>@PVA, characteristic PVA bands can be identified. The characteristic vibration modes of this material are summarized in Table 4.1, highlighting the  $\nu(\text{O-H})$  around 3270 cm<sup>-1</sup>,  $\nu(\text{C-H})$

at  $2912\text{ cm}^{-1}$ ,  $\delta$  (C-H) at  $1418\text{ cm}^{-1}$  and C-H deformation at around  $1320\text{ cm}^{-1}$ , for both types of membranes.<sup>2, 3</sup> The incorporation of HPA in the membranes was also confirmed, with the appearance of characteristic HPA bands, summarised in Table 4.2. The characteristic  $\nu_{\text{as}}$  (M=O<sub>d</sub>) vibration mode was not clearly identified for H<sub>3</sub>PW<sub>12</sub>@APTES-PVA, due to overlap with APTES characteristic bands.

**Table 4.1** – Vibration modes characteristic of PVA, with their experimental and literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes | Experimental<br>( $\text{cm}^{-1}$ )       |                                       | Literature <sup>2-5</sup><br>( $\text{cm}^{-1}$ ) |
|-----------------|--------------------------------------------|---------------------------------------|---------------------------------------------------|
|                 | H <sub>3</sub> PW <sub>12</sub> @APTES-PVA | H <sub>3</sub> PMo <sub>12</sub> @PVA |                                                   |
| $\nu$ (O-H)     | 3276                                       | 3274                                  | 3200 - 3500                                       |
| $\nu$ (C-H)     | 2912                                       | 2912                                  | 2800 - 3000                                       |
| $\delta$ (C-H)  | 1418                                       | 1418                                  | 1410 - 1430                                       |
| C-H deformation | 1328                                       | 1326                                  | 1320 - 1330                                       |

**Table 4.2** - Vibration modes characteristic of HPA, with their experimental and literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes                         | Experimental<br>( $\text{cm}^{-1}$ )       |                                       | Literature <sup>6-8</sup><br>( $\text{cm}^{-1}$ ) |                                  |
|-----------------------------------------|--------------------------------------------|---------------------------------------|---------------------------------------------------|----------------------------------|
|                                         | H <sub>3</sub> PW <sub>12</sub> @APTES-PVA | H <sub>3</sub> PMo <sub>12</sub> @PVA | H <sub>3</sub> PW <sub>12</sub>                   | H <sub>3</sub> PMo <sub>12</sub> |
| $\nu_{\text{as}}$ (P-O <sub>a</sub> )   | 1088                                       | 1058                                  | 1079                                              | 1060 - 1080                      |
| $\nu_{\text{as}}$ (M=O <sub>d</sub> )   | 1086*                                      | 958                                   | 979                                               | 960 - 1000                       |
| $\nu_{\text{as}}$ (M-O <sub>b</sub> -M) | 914                                        | 876                                   | 895                                               | 840 - 910                        |
| $\nu_{\text{as}}$ (M-O <sub>c</sub> -M) | 824                                        | 796                                   | 802                                               | 760 - 800                        |

\*band overlapped with  $\nu_{\text{as}}$  (Si-O-Si) band, characteristic vibration mode of APTES.

For type I membranes, the presence of APTES was also verified. As observed in Table 4.3, the characteristic peaks of this material overlap with both PVA and HPA areas on the spectra. As such, it is possible to observe a higher band intensity in those zones in the membrane of type I when compared with the membrane of type II. For example, the bands at  $3200\text{ cm}^{-1}$  and  $1080\text{ cm}^{-1}$  are more intense in  $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$  than  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ , since they correspond to the N-H stretching and Si-O-Si stretching vibrations of APTES, respectively.<sup>9, 10</sup>

**Table 4.3** – Vibration modes characteristic of APTES, present in  $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$ , with their experimental and literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes             | Experimental ( $\text{cm}^{-1}$ ) | Literature <sup>9-11</sup> ( $\text{cm}^{-1}$ ) |
|-----------------------------|-----------------------------------|-------------------------------------------------|
| $\nu$ (N-H)                 | 3276                              | 3200 - 3400                                     |
| $\nu$ (C-H)                 | 2912                              | 2800 - 3000                                     |
| $\nu_{\text{as}}$ (Si-O-Si) | 1088                              | 1080 - 1090                                     |
| $\nu_{\text{s}}$ (Si-O-Si)  | 828                               | 800 - 810                                       |

#### 4.1.2. SEM-EDS

The morphology and composition of the catalytic membranes were evaluated through SEM-EDS analysis.

As seen in Figure 4.3, type I membranes demonstrate the existence of small agglomerates of HPA, probably a result of the presence of APTES. Therefore,  $\text{HPA@APTES-PVA}$  presents a limitation of the free dispersion of HPA inside the membrane material. Furthermore, it is possible to observe that the HPA agglomerations are probably not exposed to the surface of the PVA matrix, since their particles seem to be involved by the PVA polymer. This picture becomes even more clear in Figure 8.1 and 8.2 (presented in the Attachments section at the end of this Master Thesis), observing the SEM images obtained with elemental composition contrast, with the lighter areas being HPA and the darker areas being the PVA matrix

(mostly carbon and oxygen). This was confirmed by EDS where the two distinct zones were studied for both membranes: one next to the HPA cluster (Z1) and one in the polymer matrix (Z2), obtaining the results present in Figure 4.4 and 4.5. Finally, the presence of APTES was confirmed through the appearance of the Si peak in EDS analysis.

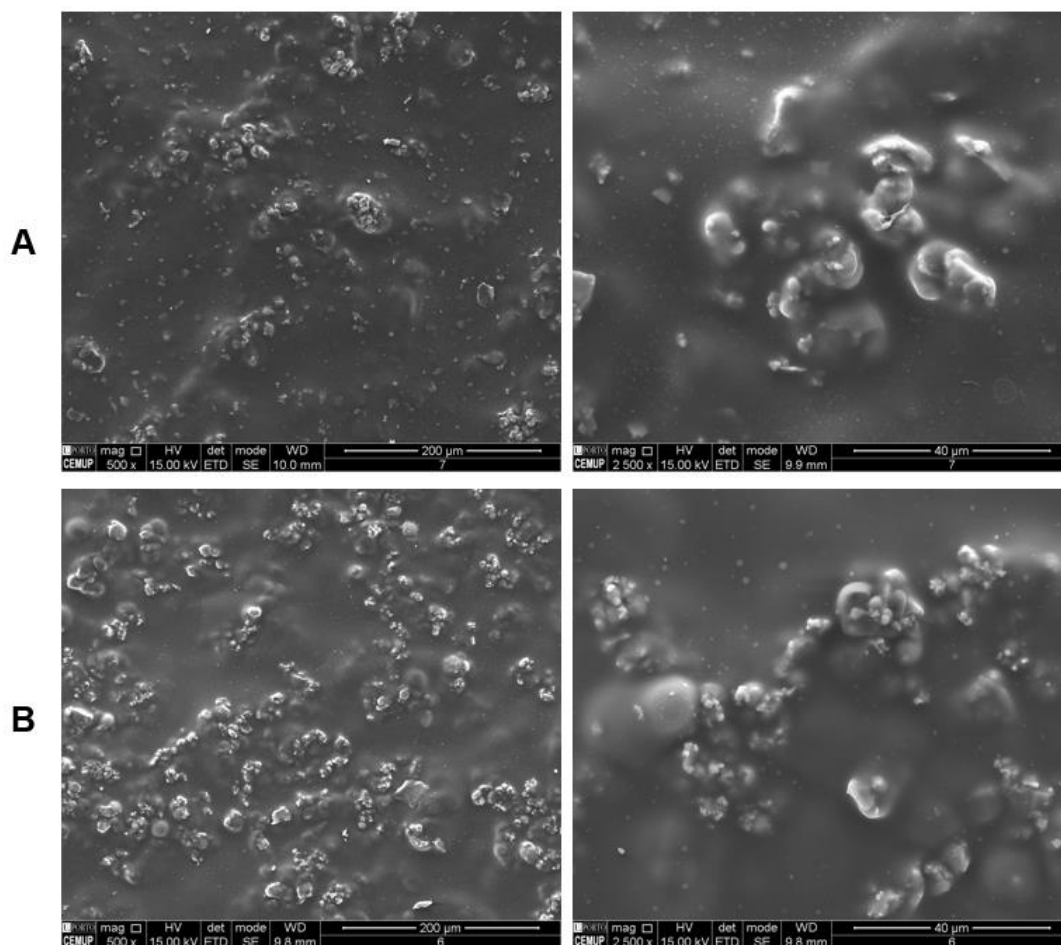


**Figure 4.3** – SEM images obtained for A) H<sub>3</sub>PW<sub>12</sub>@APTES-PVA and B) H<sub>3</sub>PMo<sub>12</sub>@APTES-PVA.

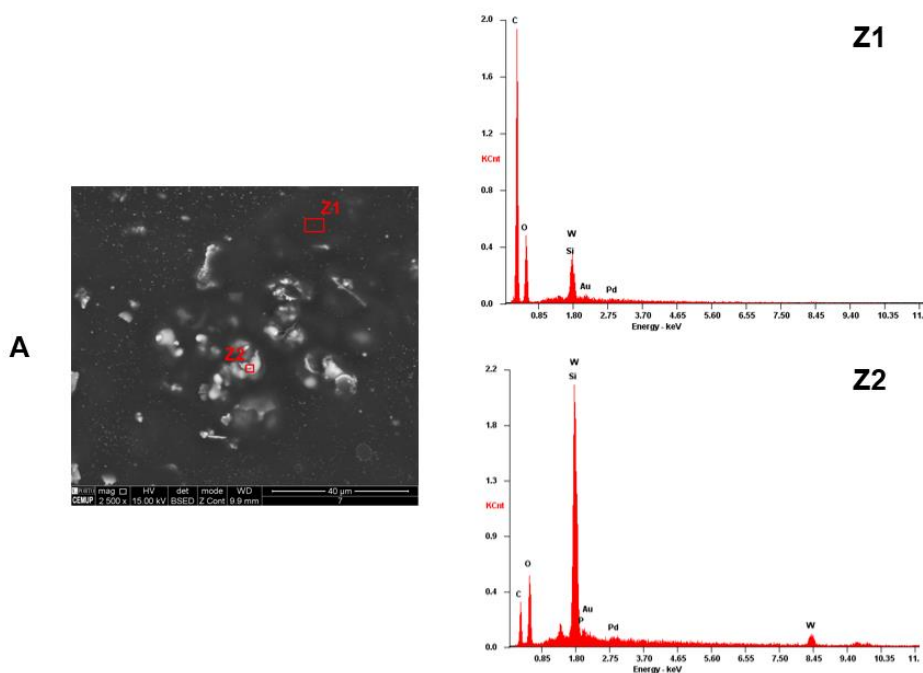


**Figure 4.4** – EDS spectra obtained for A) H<sub>3</sub>PW<sub>12</sub>@APTES-PVA, in two distinct membrane zones (Z1 and Z2).

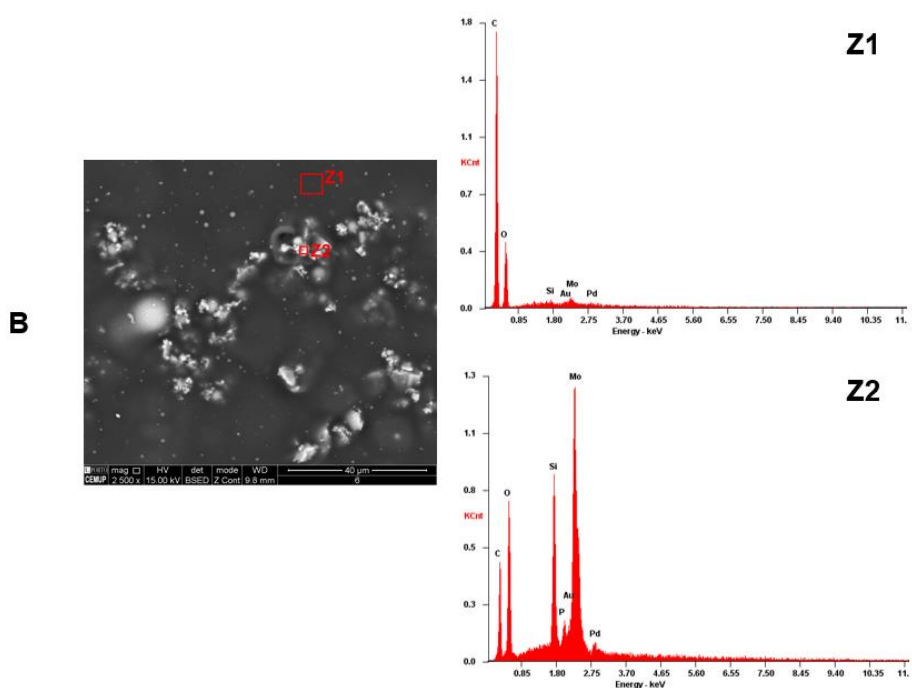


**Figure 4.5** – EDS spectra obtained for B) H<sub>3</sub>PMo<sub>12</sub>@APTES-PVA, in two distinct membrane zones (Z1 and Z2).

Unlike type I membranes, the morphology of type II membranes differed from each other, as seen in Figure 4.6. Since these two membranes were prepared without APTES, the molecules of HPA were free to disperse inside the PVA matrix, leading to the absence of HPA clusters, unlike those in type I. Focusing in the  $\text{H}_3\text{PW}_{12}\text{@PVA}$  membrane (Figure 4.6C), there is the formation of ridge-like structures, with a seemingly homogeneous HPA dispersion in the entire matrix. This homogeneity is confirmed by the EDS spectra present in Figure 4.7, with the presence of the expected C, O and W peaks, with the latter being due to the HPA active centres.

Contrarily, for  $\text{H}_3\text{PMo}_{12}\text{@PVA}$  (Figure 4.6D), it seemed to occur HPA precipitation in certain areas of the membrane, with the presence of a lighter area, probably containing the HPA compounds, and a darker area, without the presence of HPA precipitation. In the EDS spectra presented in Figure 4.8, the membrane zone Z2 is probably attributed the occurrence of HPA precipitation, and Z1 a region where the HPA is more homogeneously dispersed in the membrane. The presence of an intense Mo peak was observed in both regions; however, the low intensity of the C peak in Z2 could correspond to a lower amount of polymeric material PVA.

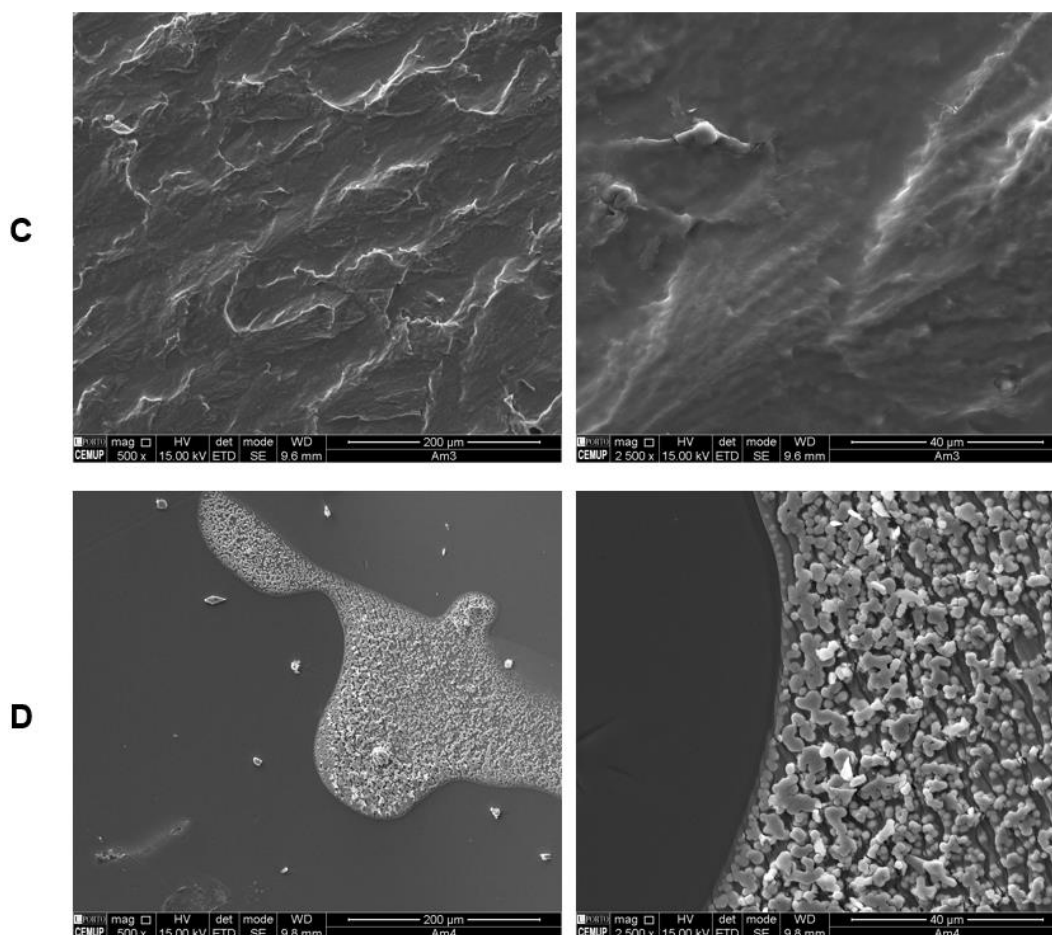


**Figure 4.6** – SEM images obtained for C)  $\text{H}_3\text{PW}_{12}\text{@PVA}$  and D)  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ .

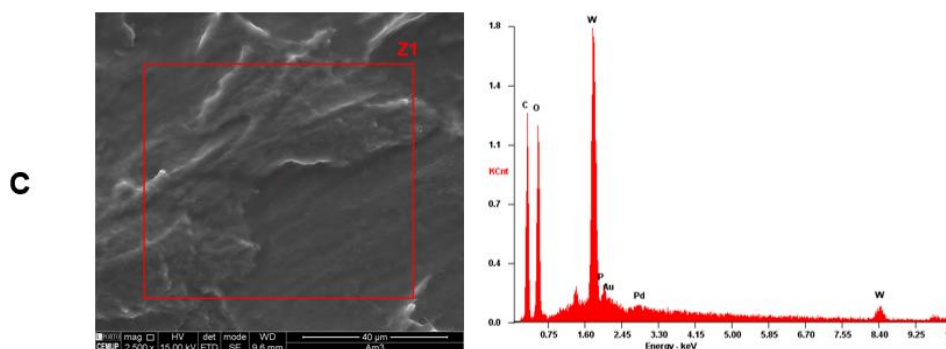


Figure 4.7 – EDS spectrum obtained for C) H<sub>3</sub>PW<sub>12</sub>@PVA.

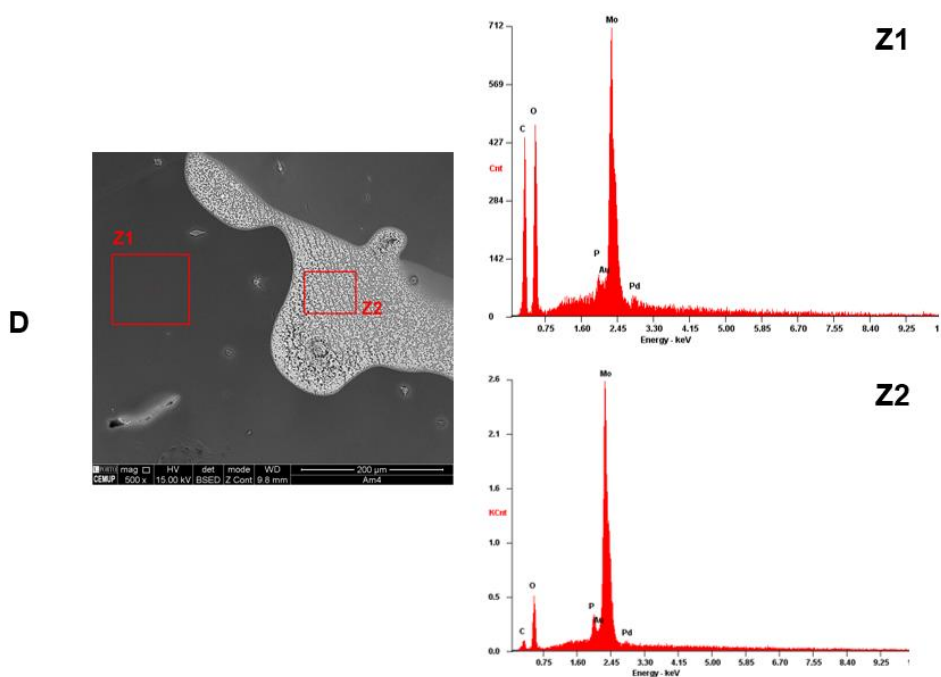


Figure 4.8 – EDS spectra obtained for D) H<sub>3</sub>PMo<sub>12</sub>@PVA, in two distinct membrane zones (Z1 and Z2).

### 4.1.3. ICP-OES

Quantification of HPA incorporated in each membrane was evaluated through ICP-OES, by analysis of the amount of W in  $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$  and  $\text{H}_3\text{PW}_{12}\text{@PVA}$ , and the amount of Mo in  $\text{H}_3\text{PMo}_{12}\text{@APTES-PVA}$  and  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ . The results obtained can be observed in Table 4.4. The loading of HPA for each membrane was determined from the values of grams of W or Mo per g of membrane.

For the type I membranes: the  $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$  presented a loading of 88  $\mu\text{mol}$  of  $\text{H}_3\text{PW}_{12}$  per g of membrane and for  $\text{H}_3\text{PMo}_{12}\text{@APTES-PVA}$ , it was obtained a loading of 114  $\mu\text{mol}$  of  $\text{H}_3\text{PMo}_{12}$  per g of membrane.

For the type II membranes: the  $\text{H}_3\text{PW}_{12}\text{@PVA}$  presented a loading of 67  $\mu\text{mol}$  of  $\text{H}_3\text{PW}_{12}$  per g of membrane and for  $\text{H}_3\text{PMo}_{12}\text{@PVA}$  it was obtained a loading of 149  $\mu\text{mol}$  of  $\text{H}_3\text{PMo}_{12}$  per g of membrane.

**Table 4.4** – ICP-OES results and the quantity of HPAs loading for each membrane, where X corresponds to W in  $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$  and  $\text{H}_3\text{PW}_{12}\text{@PVA}$ , and Mo in  $\text{H}_3\text{PMo}_{12}\text{@APTES-PVA}$  and  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ .

| Membrane                                     | $m_x$ (g / kg of membrane) | $n_{\text{HPA}}$ ( $\mu\text{mol}$ / g of membrane) |
|----------------------------------------------|----------------------------|-----------------------------------------------------|
| $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$  | 193.4                      | 88                                                  |
| $\text{H}_3\text{PMo}_{12}\text{@APTES-PVA}$ | 131.1                      | 114                                                 |
| $\text{H}_3\text{PW}_{12}\text{@PVA}$        | 148.2                      | 67                                                  |
| $\text{H}_3\text{PMo}_{12}\text{@PVA}$       | 171.4                      | 149                                                 |

#### 4.1.4. Potentiometric titration

Potentiometric titration was used to determine the acidity of the four membranes previously prepared. Therefore, a certain amount of each membrane was stirred in a NaCl 2M solution, with NaCl acting as the exchange cation. Then, the resulted solution was titrated using NaOH (0.025M) as the titrant. The results obtained can be observed in Table 4.5, where the acidity of the catalyst was posteriorly calculated.

**Table 4.5** - Potentiometric measurements obtained for the four membranes, followed by calculated acidity.

| Membrane                                    | pH   | V (NaOH)<br>(mL) | Acidity<br>(mmol H <sup>+</sup> /g) |
|---------------------------------------------|------|------------------|-------------------------------------|
| H <sub>3</sub> PW <sub>12</sub> @APTES-PVA  | 5.8  | 0.035            | 0.058                               |
| H <sub>3</sub> PMo <sub>12</sub> @APTES-PVA | 3.88 | 0.16             | 0.267                               |
| H <sub>3</sub> PW <sub>12</sub> @PVA        | 3.09 | 0.57             | 0.950                               |
| H <sub>3</sub> PMo <sub>12</sub> @PVA       | 2.92 | 1.083            | 3.305                               |

Type I membranes exhibited lower acidities than their corresponding type II membranes. This difference is probably caused due to the presence of APTES and HPA agglomeration. In these type I membranes, APTES probably promoted the agglomeration of HPA, securing these particles inside the membrane matrix, and therefore, the interaction of available HPAs with NaCl is lower, leading to lower quantities of acidic sites present for titration. From all four membranes, the membrane with the highest acidity is H<sub>3</sub>PMo<sub>12</sub>@PVA, as expected following the results obtained previously for the isolated H<sub>3</sub>PMo<sub>12</sub> (chapter 2) and also the H<sub>3</sub>PMo<sub>12</sub>@APTES-SBA-15 composite (chapter 3).

## 4.2. Acetalization studies

The optimized experimental conditions, already used for homogeneous HPAs (chapter 2) and mesoporous silica HPAs@APTES-SBA-15 composites (chapter 3), were also applied for the study of the catalytic efficiency of polymeric membranes in glycerol acetalization reactions with acetone.

Catalytic reactions were performed in reactors immersed in paraffin baths, with constant stirring and temperature. The reactor was filled with a ratio of 1:15 glycerol/acetone. Then, the appropriate catalyst was added, and glycerol conversion was evaluated during 180 min. Glycerol conversion results were evaluated by gas chromatography analysis.

Catalytic membranes HPA@APTES-PVA and HPA@PVA were used as heterogeneous catalysts for the acetalization of glycerol, at 25 and 60 °C. The results obtained are discussed in section 4.2.2 and 4.2.3, respectively. The stability of the catalysts was investigated through catalyst reutilization, whose results are presented in section 4.3. Finally, characterization of the catalysts after catalytic use was reported and discussed in section 4.4.

### 4.2.1. Catalytic membrane configuration

Initially, the amount of each catalytic membrane used for glycerol acetalization reactions, containing the optimized acidity of 0.373 mmol H<sup>+</sup>/g was calculated. Results are presented in Table 4.6.

**Table 4.6** – The quantity of each catalytic membrane, HPA@APTES-PVA and HPA@PVA, to be used in glycerol acetalization reactions, maintaining the optimized catalyst acidity of 0.373 mmol H<sup>+</sup>/g.

| Catalytic membranes                         | Catalyst used (mg) |
|---------------------------------------------|--------------------|
| H <sub>3</sub> PW <sub>12</sub> @APTES-PVA  | 95.981             |
| H <sub>3</sub> PMo <sub>12</sub> @APTES-PVA | 20.996             |
| H <sub>3</sub> PW <sub>12</sub> @PVA        | 5.894              |
| H <sub>3</sub> PMo <sub>12</sub> @PVA       | 1.694              |

#### 4.2.2. HPA@APTES-PVA catalytic membrane performance

H<sub>3</sub>PW<sub>12</sub>@APTES-PVA and H<sub>3</sub>PMo<sub>12</sub>@APTES-PVA catalytic membranes were applied in acetalization of glycerol with acetone, at 25 and 60 °C, using the previously optimized conditions: 1:15 glycerol/acetone and 0.373 mmol H<sup>+</sup>/g of acidity. Under these conditions, no catalytic performance was observed, and no glycerol conversion was found.

Some suggestions can be presented as the reason for the absence of catalytic efficiency:

- i) the PVA membranes containing APTES are not permeable enough for the reactional solution to come into contact with the HPAs active centres. These can be incorporated inside the polymeric matrix in deeper locations, not allowing the interaction of the substrate with the HPA acidic sites;
- ii) the electrostatic interaction between the HPA compounds inside the polymeric matrix and APTES is strong enough to prevent the interaction between the HPAs active centres and the substrate.

In order to confirm this situation, membranes without APTES (type II membranes) were also applied in glycerol acetalization studies, under the same conditions.

#### 4.2.3. HPA@PVA catalytic membrane performance

The catalytic performance of HPA@PVA membranes, H<sub>3</sub>PW<sub>12</sub>@PVA and H<sub>3</sub>PMo<sub>12</sub>@PVA, was studied at 25 and 60 °C, under the optimized conditions used previously, and glycerol conversion was analysed at different reaction times: 5, 30, 60, 120 and 180 min. The results obtained are presented in Figure 4.8.

The acetalization of glycerol that occurred at 25 °C exhibited no glycerol conversion; therefore, the catalytic membranes H<sub>3</sub>PW<sub>12</sub>@PVA and H<sub>3</sub>PMo<sub>12</sub>@PVA did not show any catalytic activity. Castanheiro et al. had previously applied PVA functionalized membranes as catalysts in acetalization reactions, verifying that glycerol conversion increased with temperature.<sup>12</sup> Similarly, Qing et al. also used PVA in a pervaporation membrane reactor in acetalization reactions, also concluding that an increase in temperature is beneficial for conversion efficiency.<sup>13</sup>

Therefore, catalytic reactions using PVA membranes were performed at 60 °C, while maintaining all the other experimental conditions.

Results of the acetalization reactions performed at 60 °C presented high catalytic performance of the HPA@PVA membranes, mainly after the first hour of reaction. The  $\text{H}_3\text{PW}_{12}\text{@PVA}$  membrane exhibited an increase of glycerol conversion since the first minutes of reaction, reaching its end with 95% of glycerol conversion, after 60 min (Figure 4.9). After that point, the conversion rate was maintained. On the other hand, the  $\text{H}_3\text{PMo}_{12}\text{@PVA}$  membrane showed an induction period during the first 30 min of reaction. After this time, the glycerol conversion increased and the catalytic reaction reached its end with 95% of conversion, after 120 min (Figure 4.9).

As previously observed with the homogeneous HPAs (chapter 2) and the heterogeneous HPA@APTES-SBA-15 catalysts (chapter 3), the phosphomolybdic catalyst showed lower catalytic activity when compared to the phosphotungstic. In this case as well, the  $\text{H}_3\text{PMo}_{12}\text{@PVA}$  membrane showed lower catalytic performance than the  $\text{H}_3\text{PW}_{12}\text{@PVA}$  membrane. This occurrence must be related to the lower morphologic uniformity of the  $\text{H}_3\text{PMo}_{12}\text{@PVA}$  membrane. By SEM-EDS analysis (Figures 4.6D and 4.8), it was possible to observe that the  $\text{H}_3\text{PMo}_{12}\text{@PVA}$  membrane did not present a uniform morphology, with regions where the HPA seemed to be precipitated, and this precipitation could cause lower catalytic activity. When the HPA acidic sites are uniformly distributed in the PVA matrix, as is the case of the  $\text{H}_3\text{PW}_{12}\text{@PVA}$  membrane, higher catalytic activity was presented, allowing higher glycerol conversion.

As such, type II catalytic membranes are the ideal membranes for glycerol acetalization reactions, using a required reaction temperature of 60 °C. Temperatures higher than 60 °C were not tested, since the boiling point of acetone is close to that temperature, and therefore could cause its evaporation from the solution.

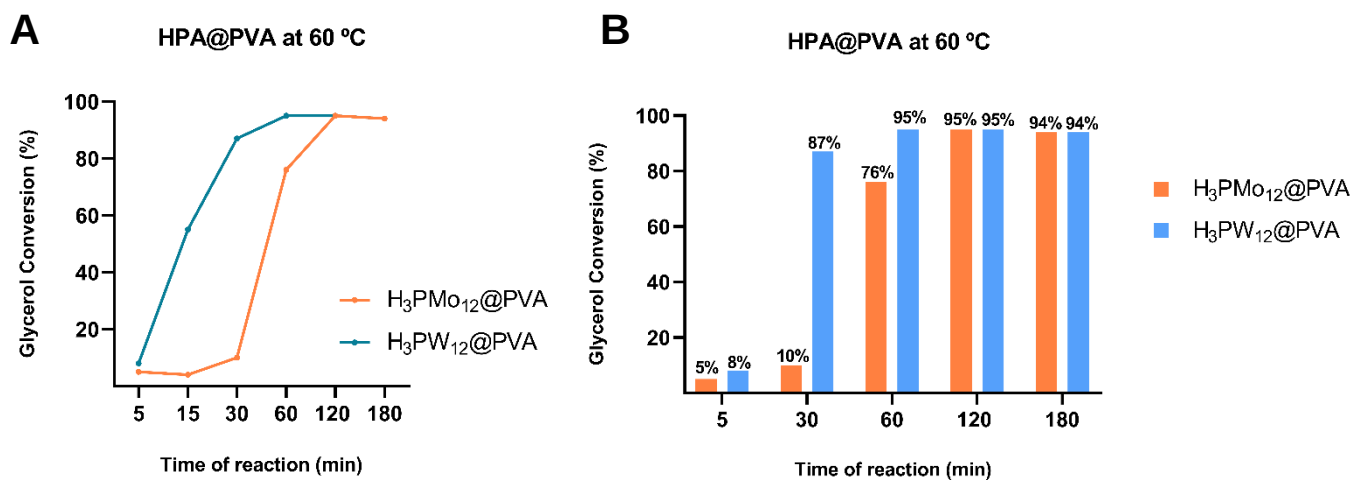


**Figure 4.9 – A)** Kinetic profiles for the glycerol acetalization reactions catalysed by HPA@PVA membranes, using a ratio of 1:15 glycerol/acetone and 0.373 mmol  $H^+$ /g of catalyst acidity, at 60 °C. **B)** Glycerol conversion data after 5, 30, 60, 120 and 180 min, at 60 °C.

### 4.3. Catalysts reutilization

Considering the positive results obtained with the HPA@PVA catalytic membranes for the glycerol acetalization reaction, the catalyst reutilization was investigated, in order to study the membranes behaviour after consecutive catalytic studies.

Both membranes,  $H_3PW_{12}@PVA$  and  $H_3PMo_{12}@PVA$  were used in reutilization studies at 60 °C, maintaining the optimal experimental conditions: ratio of 1:15 glycerol/acetone and 0.373 mmol  $H^+$ /g of catalyst acidity. After the 1<sup>st</sup> cycle, the reactional solution was removed, and a new batch of acetone and glycerol was added to the same reactor, beginning a new catalytic cycle. In reutilization studies, the membrane catalyst was left in the reactor without any washing or drying.

The  $H_3PMo_{12}@PVA$  catalytic membrane was applied in acetalization reactions for 4 consecutive reutilization cycles, and the results obtained are shown in Figure 4.10.

In general, the membrane showed a continuously satisfactory glycerol conversion, reaching 95% until the 2<sup>nd</sup> cycle. Afterwards, a small drop of activity was observed reaching 89% after the 4<sup>th</sup> cycle, accompanied by a loss in solketal selectivity, from 97% (1<sup>st</sup> cycle) to 86% (4<sup>th</sup> cycle). It would be important to continue the reutilization study for a few more cycles, in order to understand if the membrane maintains its stability after the 4<sup>th</sup> cycle or if the decrease of activity continues, showing a behaviour trend. Unfortunately, continuation of the tests was not possible at the present time, due to time constraints.

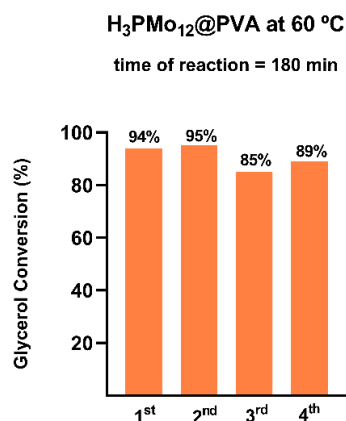


**Figure 4.10** – Glycerol conversion data obtained after 180 min, using the H<sub>3</sub>PMo<sub>12</sub>@PVA membrane for various reutilization cycles, maintaining the experimental conditions: 1:15 glycerol/acetone ratio and 0.373 mmol H<sup>+</sup>/g, at 60 °C.

The H<sub>3</sub>PW<sub>12</sub>@PVA catalytic membrane was applied in glycerol acetalization reactions during 10 consecutive reutilization cycles, and the results obtained are shown in Figure 4.11. Unlike H<sub>3</sub>PMo<sub>12</sub>@PVA, this membrane maintained its catalytic efficiency, not showing loss of activity (glycerol conversion always higher than 93% and 97% of solketal selectivity maintained during the ten cycles). This result is also indicative of the superior catalytic acidic stability of the H<sub>3</sub>PW<sub>12</sub>@PVA membrane, when compared to the H<sub>3</sub>PMo<sub>12</sub>@PVA membrane.

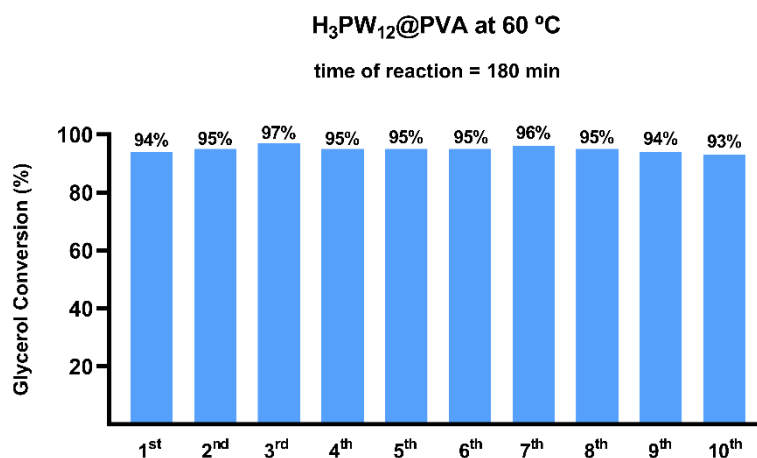


**Figure 4.11** – Glycerol conversion data obtained after 180 min, using the H<sub>3</sub>PW<sub>12</sub>@PVA membrane for various reutilization cycles, maintaining the experimental conditions: 1:15 glycerol/acetone ratio and 0.373 mmol H<sup>+</sup>/g, at 60 °C.

#### 4.4. Catalyst stability

Besides catalytic behaviour, the physical stability of PVA as a solid support for HPA immobilization was also observed. The membranes maintained their integrity for the duration of the reutilization catalytic studies, a very welcoming advantage for catalyst application in industrial settings, without the occurrence of mass loss between reaction cycles.

The membrane used for ten consecutive cycles,  $\text{H}_3\text{PW}_{12}@ \text{PVA}$ , demonstrated a change in colour after a few cycles, which seemed to progress as acetalization reactions continued, as seen in Figure 4.12. This colour change can occur due to the interaction of the membrane with the acetone.

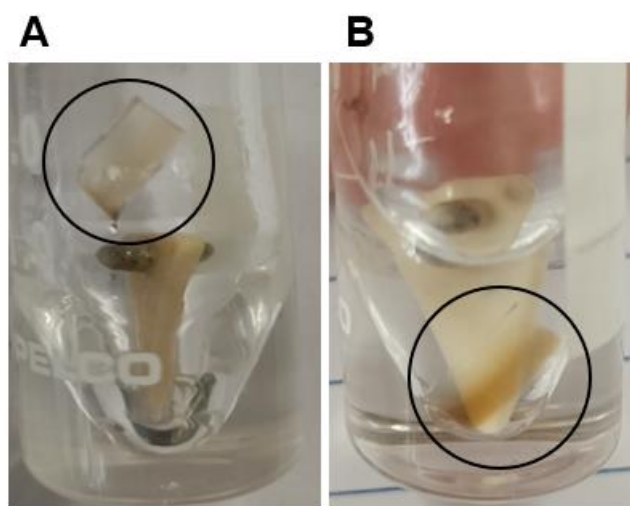


**Figure 4.12** –  $\text{H}_3\text{PW}_{12}@ \text{PVA}$  membrane after ten reutilization reactions.

Finally, it was important to confirm the occurrence of HPA leaching from the membrane. As such, the reactional solution after a catalytic cycle with  $\text{H}_3\text{PW}_{12}@ \text{PVA}$  was collected and analysed by  $^{31}\text{P}$  NMR. The obtained results are shown in Figure 4.13. The spectrum obtained does not show any chemical shifts characteristic of the HPA area (near  $-13.86 \text{ ppm}^{14}$ ), highlighted in the figure below. As such, it seems that the  $\text{H}_3\text{PW}_{12}$  active centres are well immobilized in the PVA matrix, without the occurrence of leaching.

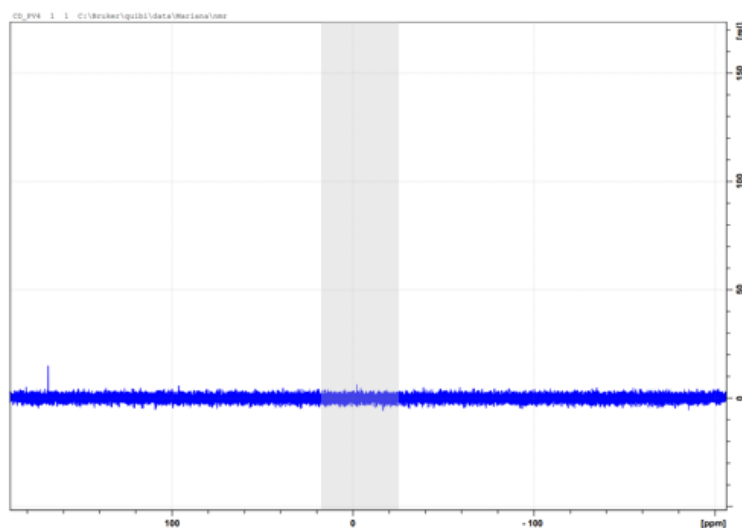


**Figure 4.13** –  $^{31}\text{P}$  NMR spectrum obtained from the reactional solution, recovered after the catalytic reaction of glycerol acetalization catalysed by the  $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{PVA}$  membrane.

#### 4.5. Final remarks

During this chapter, the preparation and characterization of catalytic membranes based in the polymeric material PVA were investigated. By the different characterization techniques used, it was possible to confirm the successful preparation of type I and type II membranes:  $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$ ,  $\text{H}_3\text{PMo}_{12}\text{@APTES-PVA}$ ,  $\text{H}_3\text{PW}_{12}\text{@PVA}$  and  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ .

Afterwards, the membranes were applied in glycerol acetalization reactions, as heterogeneous catalysts. Type I membranes,  $\text{HPA@APTES-PVA}$ , were initially tested as catalysts; however, no catalytic activity was shown. This could be due to the HPA agglomeration, observed for these membranes, promoted by the strong interaction between APTES and HPA inside the membrane matrix, which caused an impediment for the active acidic sites to interact with the reactional system. Later, type II membranes,  $\text{HPA@PVA}$ , were tested as catalysts and showed very good catalytic efficiency at 60 °C, with both membranes reaching 95% conversion, after 60 min for  $\text{H}_3\text{PW}_{12}\text{@PVA}$  and after 120 min for  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ . These results were obtained after the optimization of reaction temperature, with 60 °C being the ideal temperature for glycerol conversion using PVA membranes. The catalyst stability of  $\text{HPA@PVA}$  membranes was also investigated, with  $\text{H}_3\text{PW}_{12}\text{@PVA}$  reaching ten consecutive reutilization cycles without loss of catalytic activity. Further, the leaching of active centres in the  $\text{H}_3\text{PW}_{12}\text{@PVA}$  membrane was analysed by  $^{31}\text{P}$  NMR, and no HPA leaching seems to occur. Therefore, the choice of PVA as the polymeric material for the integration of HPA active centres was a success, allowing the preparation of active and selective one-piece heterogeneous catalysts.

In the previous chapter, the application of  $\text{HPA@SBA-15}$  catalysts in glycerol acetalization was discussed, where very good catalytic results were obtained. However, one of the major limitations of those catalysts was the occurrence of HPA leaching. As such, a possible strategy to solve this problem may be the incorporation of  $\text{HPA@SBA-15}$  catalysts in PVA membranes, allowing their application in glycerol acetalization without loss of active catalyst for the reactional system. This possibility will, therefore, be explored in the following chapter.

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## **5. Mesoporous Silica Composites Immobilized in Membranes for Glycerol Acetalization**

This chapter will discuss the preparation and catalytic application of heterogeneous catalytic membranes prepared by the incorporation of active catalytic mesoporous silicas into PVA polymeric materials, HPA@APTES-SBA-15@PVA.

Two membranes were prepared following similar procedures as described previously in chapter 4, whose procedure was adapted from literature.<sup>1</sup> Solutions of PVA were placed in stirring at constant temperature, for a period of time, followed by the addition of the silica composites ( $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ , previously dispersed in deionised water). Then, the membranes were casted and left to dry, as seen in Figure 5.1.

The prepared membranes were characterized by various techniques: FTIR-ATR, PXRD, SEM-EDS, ICP-OES and potentiometric titration measurements. Finally, the two composite membranes were applied in glycerol acetalization reactions with acetone, and their catalytic efficiency was studied and discussed.

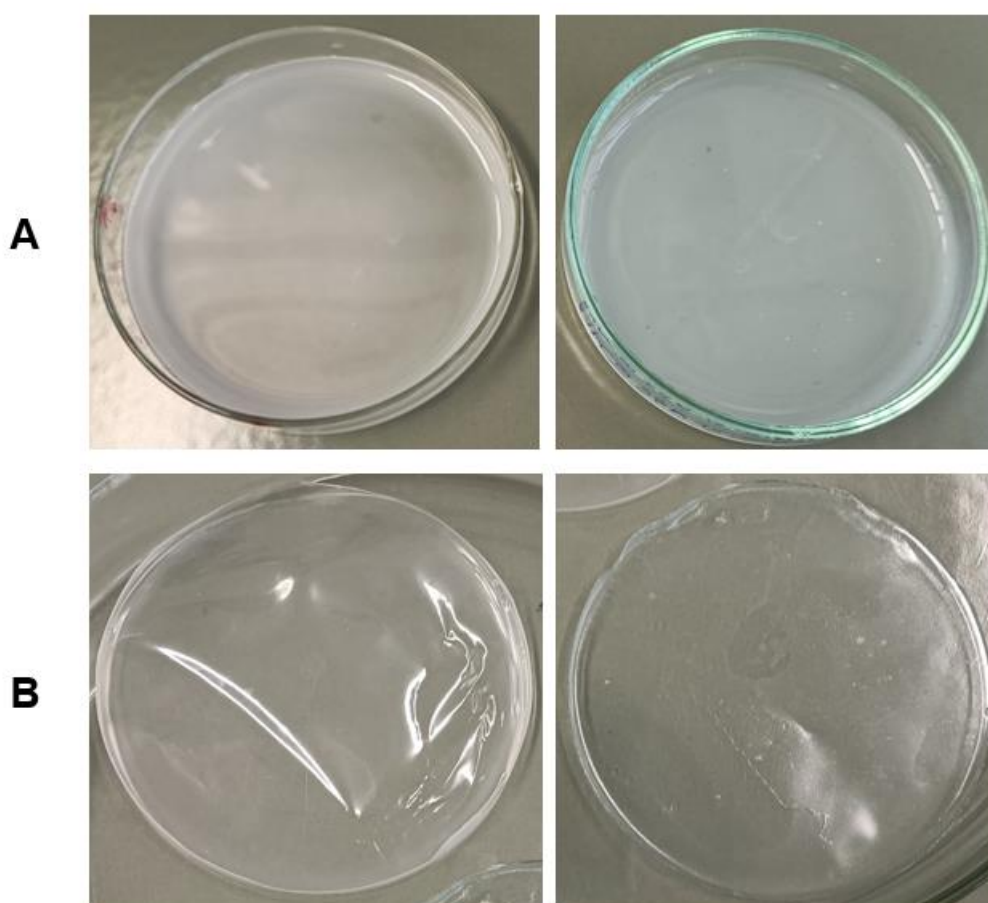


**Figure 5.1** – HPA@APTES-SBA-15@PVA membranes prepared:  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  (on the left) and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$  (on the right). **A)** before drying and **B)** after drying.

## 5.1. Characterization of composite membranes

### 5.1.1. FTIR-ATR

The prepared composite membranes were evaluated through FTIR-ATR, and the results are presented in Figure 5.2, for  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15@PVA}$  and  $\text{H}_3\text{PMo}_{12}@ \text{APTES-SBA-15@PVA}$ .

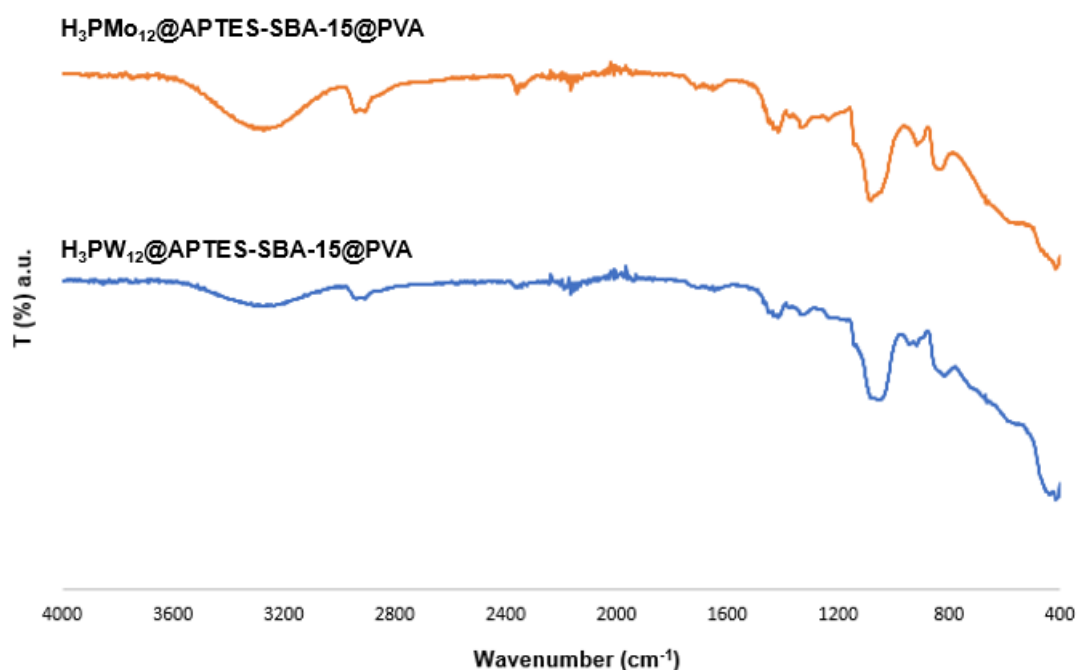


**Figure 5.2** – FTIR-ATR spectra obtained for  $\text{H}_3\text{PW}_{12}@ \text{APTES-SBA-15@PVA}$  (in blue) and  $\text{H}_3\text{PMo}_{12}@ \text{APTES-SBA-15@PVA}$  (in orange), in a wavenumber range between 400 and 4000  $\text{cm}^{-1}$ .

The presence of the PVA polymer matrix, mesoporous silica support and HPA active centres was confirmed by FTIR-ATR. Characteristic PVA bands can be identified, and their vibration modes are summarised in Table 5.1:  $\nu$  (O-H) at around 3270  $\text{cm}^{-1}$ ,  $\nu$  (C-H) at 2912  $\text{cm}^{-1}$ ,  $\delta$  (C-H) at 1416  $\text{cm}^{-1}$  and C-H deformation at 1326  $\text{cm}^{-1}$ .<sup>2, 3</sup> The presence of characteristic SBA-15 bands (Table 5.2) was confirmed, highlighted by the  $\nu_{\text{as}}$  (Si-O-Si) band at around 1080  $\text{cm}^{-1}$ .<sup>4, 5</sup> Finally, the presence of HPA was confirmed by the bands between 900 and 800  $\text{cm}^{-1}$ , owing to  $\nu_{\text{as}}$  (M-O<sub>b</sub>-M) and  $\nu_{\text{as}}$  (M-O<sub>c</sub>-M), respectively (Table 5.3).<sup>6</sup> Some of the HPA bands were not clearly identified in the composite membranes, due to overlap with SBA-15 characteristic bands.

**Table 5.1** – Vibration modes characteristic of PVA, with their experimental and literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes | Experimental ( $\text{cm}^{-1}$ ) | Literature <sup>2, 3</sup> ( $\text{cm}^{-1}$ ) |
|-----------------|-----------------------------------|-------------------------------------------------|
| $\nu$ (O-H)     | 3270                              | 3200 - 3500                                     |
| $\nu$ (C-H)     | 2912                              | 2800 - 3000                                     |
| $\delta$ (C-H)  | 1416                              | 1410 – 1430                                     |
| C-H deformation | 1326                              | 1320 - 1330                                     |

**Table 5.2** – Vibration modes characteristic of SBA-15, with their experimental and literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes             | Experimental ( $\text{cm}^{-1}$ ) | Literature <sup>4, 5, 7</sup> ( $\text{cm}^{-1}$ ) |
|-----------------------------|-----------------------------------|----------------------------------------------------|
| $\nu_{\text{as}}$ (Si-O-Si) | 1080                              | 1080 - 1090                                        |
| $\nu_{\text{s}}$ (Si-O-Si)  | 818*                              | 800 - 810                                          |

\*band overlapped with  $\nu_{\text{as}}$  (M-O<sub>c</sub>-M) band, characteristic vibration mode of HPAs.

**Table 5.3** - Vibration modes characteristic of HPA, with their experimental and literature values (expressed in  $\text{cm}^{-1}$ ).

| Vibration modes                         | Experimental ( $\text{cm}^{-1}$ )                 |                                                    | Literature <sup>6, 8</sup> ( $\text{cm}^{-1}$ ) |                                  |
|-----------------------------------------|---------------------------------------------------|----------------------------------------------------|-------------------------------------------------|----------------------------------|
|                                         | H <sub>3</sub> PW <sub>12</sub> @APTES-SBA-15@PVA | H <sub>3</sub> PMo <sub>12</sub> @APTES-SBA-15@PVA | H <sub>3</sub> PW <sub>12</sub>                 | H <sub>3</sub> PMo <sub>12</sub> |
| $\nu_{\text{as}}$ (P-O <sub>a</sub> )   | 1064*                                             | 1082*                                              | 1079                                            | 1060 - 1080                      |
| $\nu_{\text{as}}$ (M=O <sub>d</sub> )   | 1064*                                             | 1082*                                              | 979                                             | 960 - 1000                       |
| $\nu_{\text{as}}$ (M-O <sub>b</sub> -M) | 914                                               | 918                                                | 895                                             | 840 - 910                        |
| $\nu_{\text{as}}$ (M-O <sub>c</sub> -M) | 816                                               | 814                                                | 802                                             | 760 - 800                        |

\*bands overlapped with  $\nu_{\text{as}}$  (Si-O-Si) band, characteristic vibration mode of SBA-15.

### 5.1.2. PXRD

The membranes were also analysed by low-angle PXRD, in order to verify if the crystalline structure of the HPA@APTES-SBA-15 composites was maintained after incorporation in the PVA matrix. The obtained diffraction patterns are present in Figure 5.3.

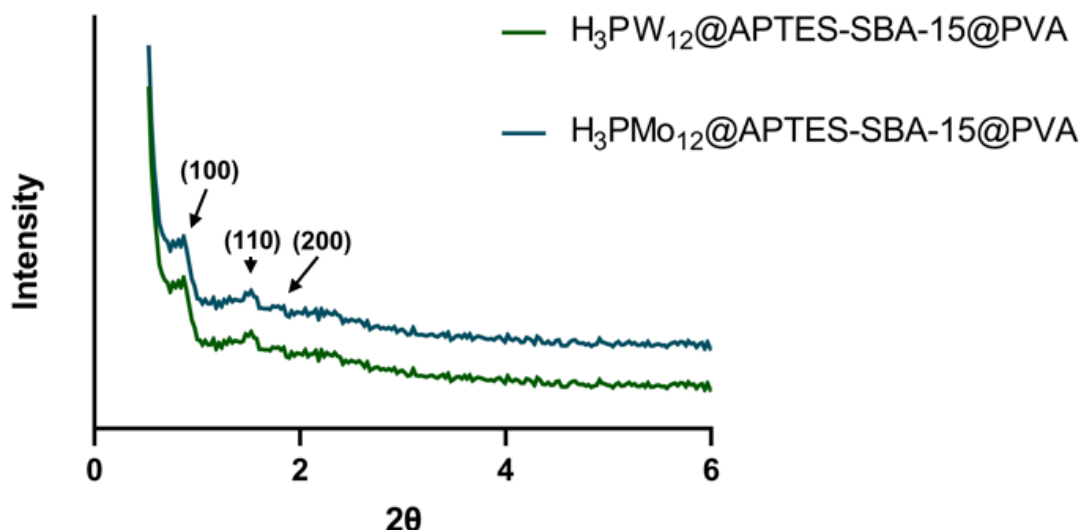


**Figure 5.3** – Diffraction pattern obtained for  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  (in green) and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$  (in blue).

The characteristic SBA-15 diffraction peaks were observed<sup>7, 9</sup>, confirming that the structure of the mesoporous silica maintained its crystallinity after incorporation into the polymeric PVA matrix. Similarly, to SBA-15, the (100) plane is very clearly observed since it is the most intense peak. The peaks for (110) and (200) planes were observed less clearly than for the powdered HPA@APTES-SBA-15 composites (Figure 3.6, chapter 3). This difference must be due to PVA interference, since the composite particles are involved by the polymeric matrix, instead of their isolated powder form.

### 5.1.3. SEM-EDS

The morphology and the composition of the composite membranes were analysed through SEM-EDS, and the results can be observed in Figure 5.4 and 5.5. Additional SEM characterization results are shown in Attachments section (Figure 8.5 and 8.6).

Both membranes exhibited a uniform surface without any apparent deformation. SEM images obtained at an ampliation of 10000x (images on the further right) demonstrate the appearance of agglomerates formed by elongated structures (characteristic of APTES-SBA-15 silica <sup>10, 11</sup>) confirming the presence of the HPA@APTES-SBA-15 composites inside the matrix.

Furthermore, the silica composite seems to be uniformly spread through the entirety of the PVA membrane. This was confirmed by elemental composition analysis (Figure 8.5 and 8.6 in Attachments section), where the lighter dots correspond to the composite (containing heavier elements present in HPA compounds and in the APTES-SBA-15 support), and the darker surrounding area is attributed to the PVA matrix.

EDS spectra obtained for both membranes confirm the presence of HPA, W for  $H_3PW_{12}@APTES-SBA-15@PVA$  and Mo for  $H_3PMo_{12}@APTES-SBA-15@PVA$ , and the presence of the Si peak, relative to APTES-SBA-15. It can be seen that the W and Mo peaks are much less intense than the C and O peaks, since the amount of HPAs in the composite membrane is low, when compared to the amount of PVA polymeric material.

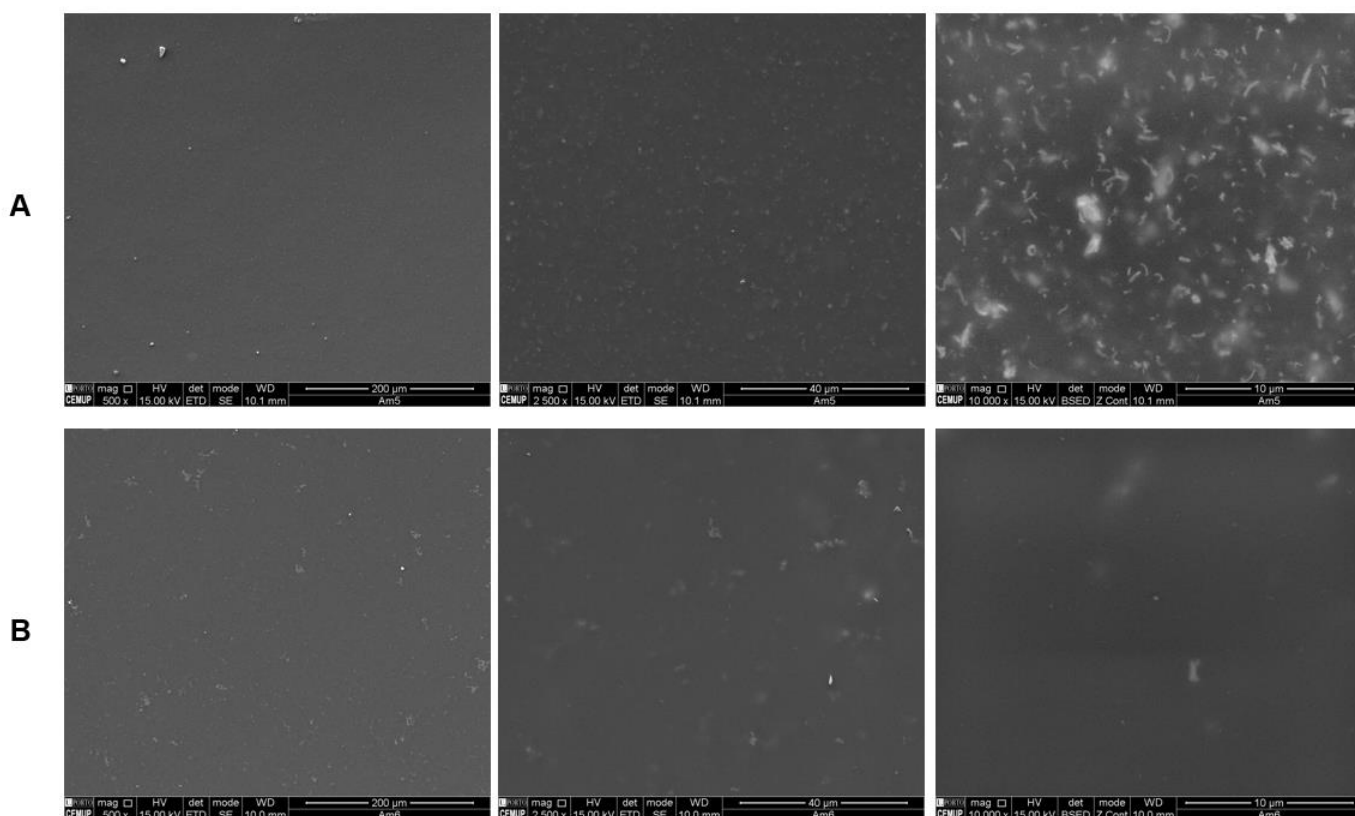


**Figure 5.4** – SEM images obtained for A)  $H_3PW_{12}@APTES-SBA-15@PVA$  and B)  $H_3PMo_{12}@APTES-SBA-15@PVA$ .

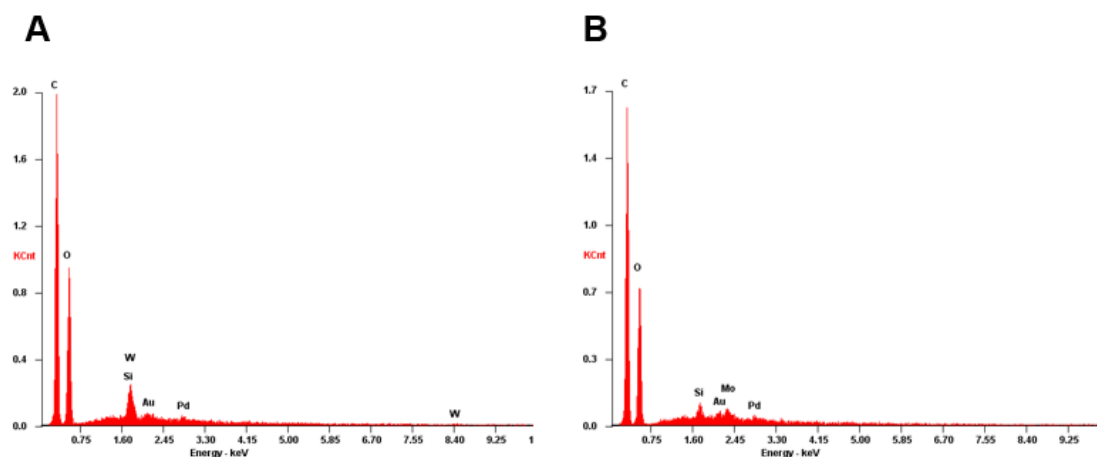


**Figure 5.5** – EDS spectra obtained for A)  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  and B)  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$ .

#### 5.1.4. ICP-OES

The quantification of HPA incorporated in each membrane was evaluated through ICP-OES analysis of W in  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  and Mo in  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$ . The results obtained can be observed in Table 5.4. The loading of HPA for each membrane was determined from the values of W or Mo per grams of membrane.

For the  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  membrane, it was obtained a loading of 16  $\mu\text{mol}$  of  $\text{H}_3\text{PW}_{12}$  per g of membrane and for the  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$  membrane, it was obtained a loading of 15  $\mu\text{mol}$  of  $\text{H}_3\text{PMo}_{12}$  per g of membrane.

**Table 5.4** – ICP-OES results and the quantity of HPAs loading for each composite membrane, where X corresponds to W in  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  and Mo in  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$ .

| Material                                            | $m_X$<br>(g / kg of membrane) | $n_{\text{HPA}}$<br>( $\mu\text{mol}$ / g of membrane) |
|-----------------------------------------------------|-------------------------------|--------------------------------------------------------|
| $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  | 35.9                          | 16                                                     |
| $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$ | 16.9                          | 15                                                     |

### 5.1.5. Potentiometric titration

Potentiometric titration was used to quantify the acidity of the two composite membranes:  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$ . A certain amount of each composite membrane was stirred in a NaCl 2M solution, with NaCl acting as the exchange cation. Then the resulting solutions were titrated, using NaOH (0.025M) as the titrant.

The results obtained can be observed in Table 5.5, where the acidity of the catalyst was posteriorly calculated.

**Table 5.5** - Potentiometric measurements obtained for the two composite membranes, followed by calculation of acidity.

| Materials                                           | pH   | V (NaOH)<br>(mL) | Acidity<br>(mmol $\text{H}^+$ /g) |
|-----------------------------------------------------|------|------------------|-----------------------------------|
| $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  | 5.43 | 0.115            | 0.192                             |
| $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$ | 4.05 | 0.223            | 0.372                             |

Similarly, to the results obtained in the previous chapters, the  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$  membrane showed the highest acidity value. In general, the results obtained were similar to those for  $\text{HPA@APTES-PVA}$  membranes.

### 5.2. Acetalization studies

The composite membranes were used as heterogeneous catalysts for glycerol acetalization, using the optimized experimental conditions already used in previous chapters: ratio of 1:15 glycerol/acetone, 0.373 mmol  $\text{H}^+$ /g of catalyst acidity, at 60 °C (optimized temperature for PVA catalytic membranes, chapter 4). Glycerol conversion was evaluated during 180 min by gas chromatography analysis.

The results for the catalytic efficiency of the composite membranes  $\text{HPA@SBA-15@PVA}$  are presented and discussed in section 5.2.2.

### 5.2.1. Catalyst configuration

The amount of each catalytic membrane used for glycerol acetalization reactions, containing the optimized acidity of 0.373 mmol H<sup>+</sup>/g was calculated. Results are presented in Table 5.6.

**Table 5.6** – The quantity of each catalytic membrane, HPA@APTES-SBA-15@PVA, to be used in glycerol acetalization reactions, maintaining the optimized catalyst acidity of 0.373 mmol H<sup>+</sup>/g.

| Material                                           | Material used (mg) |
|----------------------------------------------------|--------------------|
| H <sub>3</sub> PW <sub>12</sub> @APTES-SBA-15@PVA  | 29.212             |
| H <sub>3</sub> PMo <sub>12</sub> @APTES-SBA-15@PVA | 15.064             |

### 5.2.2. HPA@SBA-15@PVA catalytic performance

Acetalization of glycerol was performed using HPA@SBA-15@PVA composite membranes as one-piece heterogeneous catalysts. From these experiments, it was not possible to observe any conversion of glycerol, even after 180 min.

These results are similar to those obtained with HPA@APTES-PVA membranes in chapter 4, section 4.2.2. It was suggested that the presence of APTES could have prevented the HPA catalytic active centres from interacting with the reactional solution, since the HPA@PVA membranes without the APTES functional group showed to be highly catalytically active at 60 °C (chapter 4, section 4.2.3). The intention of using APTES functional group in silica or in membrane supports was to improve HPA immobilization, due to electrostatic interaction with the HPAs (Figure 1.15, chapter 1).<sup>12</sup> In the composite membranes HPA@APTES-SBA-15@PVA, APTES was impregnated on the surface of the SBA-15 support, and its interaction with HPAs active centres was probably responsible for the absence of catalytic activity, when the composites were impregnated into the PVA polymeric matrix.

Furthermore, in these composite membranes, the HPA active centres were not freely distributed in the PVA matrix (as is the case of the HPA@PVA membranes, discussed in chapter 4), but anchored to the silica surface, what turns more difficult the contact of

HPAs with the reaction solution. As such, the exposure of HPA in composite membranes was much more limited than in the HPA@PVA membranes or the HPA@APTES-SBA-15 composites.

As future work, this problem will be investigated, initially by preparing membranes with porosity, in order to increase the interaction between the substrate and the acidic sites immobilized. For PVA membranes, porosity can be formed by various strategies: i) different preparation methods, ii) use of pore-inducing agents or iii) application of membrane cross-linking.<sup>13</sup> Furthermore, composite membranes will also be prepared using other suitable polymeric materials or/and using other functional groups to replace APTES. As such, it would be interesting to study all these different aspects and evaluate their influence on the performance of the membranes as catalysts glycerol in acetalization reactions.

### 5.3. Final remarks

In this chapter, the preparation and characterization of composite membranes HPA@APTES-SBA-15@PVA was performed. The successful preparation of  $\text{H}_3\text{PW}_{12}$ @APTES-SBA-15@PVA and  $\text{H}_3\text{PMo}_{12}$ @APTES-SBA-15@PVA membranes was confirmed by various characterization techniques. These membranes were then applied in glycerol acetalization reactions, as one-piece heterogeneous catalysts.

Unfortunately, HPA@APTES-SBA-15@PVA membranes showed absence of catalytic activity at 60 °C, since no glycerol conversion was observed, even after 180 min of reaction, and possible reasons for this inactivity were described. These can be related to the lower accessibility of the HPA active centres, causing lower permeability of the membrane, and limiting the interaction with the reactional solution. Or even, by the presence of a strong interaction between the HPAs with APTES, under a polymeric PVA supporting environment.

While the results obtained were not satisfactory, various future strategies were assigned to solve this problem. These involve the creation of membrane porosity, that hopefully can allow the successful application of this type of catalysts in glycerol conversion.

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## 6. Experimental Section

## 6.1. Materials, reagents and solvents

All the materials, reagents and solvents used in this work were purchased and used as received, without any treatments.

The solid supports and composites were prepared using Pluronic P123 (Sigma-Aldrich), tetraethoxysilane (TEOS, Sigma-Aldrich), hydrochloric acid (HCl, Sigma-Aldrich), anhydrous toluene (Sigma-Aldrich, 99.8%), 3-aminopropyltriethoxysilane (APTES, Sigma-Aldrich, 98%), ethanol (Honeywell, 99.8%), phosphotungstic acid ( $\text{H}_3\text{PW}_{12}$ , Sigma-Aldrich), phosphomolybdic acid ( $\text{H}_3\text{PMo}_{12}$ , Sigma-Aldrich), silicotungstic acid ( $\text{H}_4\text{SiW}_{12}$ , Sigma-Aldrich), acetonitrile (Carlo Erba Reagents) and polyvinyl alcohol (PVA, Sigma-Aldrich, Mw 60000).

Material characterization techniques were accomplished using sodium hydroxide (NaOH, Pronalab), sodium chloride (NaCl) and deuterated acetonitrile ( $\text{CD}_3\text{CN}$ , Euriso-Top, 99.8%).

The acetalization reactions recurred to the use of acetone (Honeywell, 99.5%), glycerol (VWR Chemicals) and methanol (Fisher Chemical, 99.9%).

## 6.2. Preparation of mesoporous silicas

### 6.2.1. SBA-15

The SBA-15 solid support was prepared through a hydrothermal synthesis procedure, adapted from literature <sup>1</sup>. Pluronic P123 (1 g) was dissolved in HCl 2M (30 mL) and deionised water (7.5 mL), under constant stirring. Then, TEOS (2.4 mL) was added dropwise, and the mixture was left under constant stirring at 40 °C, for 24 h. Next, the obtained mixture was placed in Teflon autoclaves, and suffered heat treatment at 100 °C for another 24 h. After cooling, the mixture was filtered and washed with ethanol. Finally, the obtained solid was calcinated at 550 °C for 5 h, with a heating ramp of 1 °C/min. The final SBA-15 support was obtained.

### 6.2.2. APTES-SBA-15

The SBA-15 silica was functionalized following a post-grafting methodology, adapted from literature <sup>1</sup>. SBA-15 (1 g) was activated for 2 h at 100 °C (under vacuum, 175 mbar). Then, it was dispersed in anhydrous toluene (60 mL) and APTES (0.7 mL). The mixture was placed in a  $\text{N}_2$  atmosphere, under constant stirring at 90 °C for 24 h. After cooling, the mixture was filtered and washed with hot toluene and ethanol. Finally it was dried at 80 °C for 2 h (under vacuum, 200 mbar). The final APTES-SBA-15 support was obtained.

### 6.2.3. HPA@APTES-SBA-15 composites

Both  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$  composites were prepared following an impregnation technique, adapted from literature <sup>2</sup>. APTES-SBA-15 support (0.3 g) was dispersed in acetonitrile (12 mL), under constant stirring, followed by addition of the HPA ( $\text{H}_3\text{PW}_{12}$  or  $\text{H}_3\text{PMo}_{12}$ , 0.9 g). The mixture was left under constant stirring for 72 h, at room temperature. Then, it was filtered and washed with acetonitrile and ethanol. Finally, the obtained material was left to dry in a desiccator over silica gel.

## 6.3. Preparation of membranes

### 6.3.1. HPA@PVA

HPA@PVA membranes were prepared according to a method adapted from literature <sup>3</sup>. Two types of HPA@PVA membranes were obtained: i) Type I membranes (HPA@PVA membranes prepared with APTES) and ii) Type II membranes (HPA@PVA membranes prepared without APTES).

Type I membranes: PVA (0.5 g) was dissolved in deionised water (5 mL). The mixture was left under constant stirring at 90 °C for 4 h. Then, HPA ( $\text{H}_3\text{PW}_{12}$  or  $\text{H}_3\text{PMo}_{12}$ , 0.25 g) was added, and left under constant stirring for 24 h, at room temperature. Next, APTES (0.2 mL) was added dropwise to the mixture, continuing the stirring at room temperature for 5 h. Finally, the mixture was poured in a Petri dish and left to dry.

Type II membranes: PVA (0.5 g) was dissolved in deionised water (5 mL). The mixture was left under constant stirring at 90 °C for 4 h. Then, HPA ( $\text{H}_3\text{PW}_{12}$  or  $\text{H}_3\text{PMo}_{12}$ , 0.25 g) was added, and left under constant stirring for 24 h, at room temperature. Finally, the mixture was poured in a Petri dish and left to dry.

### 6.3.2. HPA@APTES-SBA-15@PVA

$\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15@PVA}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15@PVA}$  membranes were prepared by an adaptation from literature <sup>3</sup>. PVA (0.5 g) was dissolved in deionised water (4 mL), and left under constant stirring at 90 °C, for 4 h. HPA@APTES-SBA-15 composites (0.05 g) were dispersed in deionised water (1 mL) under sonication and added to the PVA. The obtained mixture was left under stirring for 24 h, at room temperature. Finally, the mixture was poured in a Petri dish and left to dry.

## 6.4. Characterization techniques and instrumentation

### 6.4.1. FTIR-ATR

Infrared spectra of all the obtained materials were obtained using a Perkin Elmer Spectrum BX spectrophotometer, with ATR system. The spectra were recorded using a wavenumber range between 400 and 4000  $\text{cm}^{-1}$ , with a resolution of 4  $\text{cm}^{-1}$  and using 64 scans.

### 6.4.2. PXRD

Powder X-Ray diffraction patterns of the mesoporous silica materials were obtained at room temperature, using a Rigaku Geigerflex diffractometer, with a Cu radiation source ( $\lambda_1 = 1.5405980 \text{ \AA}$ ;  $\lambda_2 = 1.5444260 \text{ \AA}$ ;  $\lambda_2/\lambda_1 = 0.500$ ) and a Bragg-Brentano configuration  $\theta/2\theta$  (45 kV, 40 mA). The data was collected using a step-counting method (step  $0.026^\circ$ ), in continuous mode, in the low angle range ( $0.5^\circ$  to  $19.9^\circ$ ).

Analyses were performed in the University of Aveiro – CICECO.

### 6.4.3. Zeta Potential

The mesoporous silica materials (1 mg) were suspended in ultrapure Millipore water (2 mL), under sonication. The zeta potential ( $\zeta$ ) was obtained using a Malvern Panalytical Zetasizer Nano ZS spectrometer, at room temperature.

### 6.4.4. SEM-EDS

The SEM samples were prepared by dispersing the materials in a carbon tape, and coated with a thin Au/Pd film, through sputtering.

The SEM images and EDS spectra were collected using a FEI Quanta 400 FEG ESEM electron microscope, with a EDAX Genesis X4M energy dispersive X-Ray spectrometer, operating at 15 kV.

Analyses were performed in CEMUP – *Centro de Materiais da Universidade do Porto*.

### 6.4.5. ICP-OES

The amount of HPAs immobilized in both silica and membrane materials was quantified using a Varian 820-MS spectrometer, through the quantification of the amount of molybdenum (Mo) and tungsten (W) present in the materials.

Analyses were performed in the University of Santiago de Compostela, Spain.

#### 6.4.6. Elemental Analysis

Elemental analyses of C, N and H in the functionalized APTES-SBA-15 material were obtained using a Leco CHNS-932 elemental analyser. These analyses allowed the quantification of the APTES functional group on the surface of the silica support material.

Analyses were performed in the University of Santiago de Compostela, Spain.

#### 6.4.7. $^{31}\text{P}$ NMR

The occurrence of HPA leaching from the catalytic materials used in acetalization reactions was studied through  $^{31}\text{P}$  NMR analysis. The reactional solution was removed at the end of the catalytic cycle, and approximately 10% (V/V) of deuterated acetonitrile ( $\text{CD}_3\text{CN}$ ) was added.  $^{31}\text{P}$  NMR spectra were obtained using a Nuclear BRUKER AVANCE III 400 MHz, 9.4 Tesla digital spectrometer.

Analyses were performed in CEMUP – Centro de Materiais da Universidade do Porto.

#### 6.4.8. Potentiometric titration

Determination of the acidity of the catalysts was possible through potentiometric titration measurement, an experimental procedure adapted from literature <sup>4</sup>.

Using NaCl as the cation-exchange agent, solutions containing the catalyst and NaCl were prepared and left at constant stirring for 24 h, at room temperature.

The preparation of the solutions was adjusted according with the amount of catalyst available for analysis. Measurements with HPA were prepared using 25 mg of HPA and 25 mL of NaCl 2M. Analysis with silica composites, membranes and membrane composites were prepared by dispersing 15 mg of each in 15 mL of NaCl 2M.

Then, acid base titrations were performed in an TitraLab AT1000 Series instrument, using NaOH (0.025 M) as the base. Calibration of the equipment took place using standard buffer solutions with pH of 1.679, 4.00, 7.00 and 10.00.

### 6.5. Acetalization studies

#### 6.5.1. Instrumentation

The study of glycerol acetalization was possible through the use of a Varian CP-3380 gas chromatograph, with a Suprawax-280 capillary column (30 m length, 0.25 mm internal diameter and 0.25  $\mu\text{m}$  film thickness). Hydrogen was used as the carrier gas, with a flow rate of 55  $\text{cm}^3\cdot\text{s}^{-1}$ .

### 6.5.2. Gas chromatography method

The GC analysis method is summarized in Table 6.1, resulting in a total run time of 9.5 min. Glycerol conversion results were obtained through the integration of the peaks obtained from glycerol, solketal and acetal.

**Table 6.1** – Used method for GC analysis, applied in glycerol acetalization reactions.

| Rate<br>(°C/min) | Temperature<br>(°C) | Total time<br>(min) |
|------------------|---------------------|---------------------|
| initial          | 100                 | 0                   |
| 20               | 150                 | 2.50                |
| 20               | 200                 | 5.00                |
| 20               | 250                 | 9.50                |

### 6.5.3. Reactional system setup

Glycerol acetalization reactions proceeded in catalytic reactors immersed in paraffin baths, with constant stirring and temperature. The reactor was filled with 120  $\mu\text{L}$  of glycerol and 1.88 mL of acetone, and left under agitation for 10 min, in order to homogenize the solution. The miscibility between glycerol and acetone was not complete after these 10 min, but a homogeneous phase was observed during the reaction.

Then, the catalyst was added, and glycerol conversion evaluated, as seen in Figure 6.1. The final reaction times and the temperatures used to investigate the catalytic performance of all catalysts are resumed in Table 6.2.

The glycerol conversion was evaluated through the periodical analysis of the reactional solution, taking 20  $\mu\text{L}$ , and adding it in a vial with 60  $\mu\text{L}$  of the internal standard prepared (methanol).

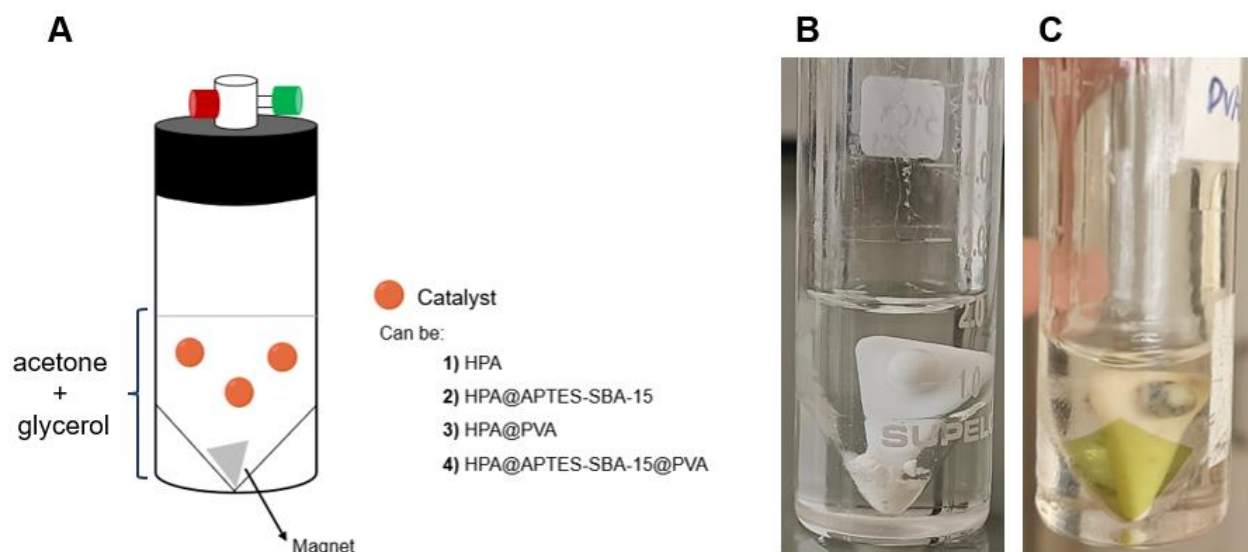


**Figure 6.1** – A) Experimental setup for glycerol acetalization reactions. B) Reactor used in glycerol acetalization reactions, using HPA@SBA-15 catalysts. C) Reactor used in glycerol acetalization reactions using HPA@PVA catalytic membranes.

**Table 6.2** – Final reaction times and temperatures used to investigate the catalytic performance of the different catalysts, in glycerol acetalization reactions.

| Catalyst             | Reaction time (min) | Reaction temperature (°C) |
|----------------------|---------------------|---------------------------|
| HPA                  | 60, 120             | 25, 60                    |
| HPA@APTES-SBA-15     | 120                 | 25, 60                    |
| HPA@APTES-PVA        | 180                 | 25, 60                    |
| HPA@PVA              | 180                 | 25, 60                    |
| HPA@APTES-SBA-15@PVA | 180                 | 60                        |

#### 6.5.4. Catalyst reutilization

For catalyst reutilization studies, a catalytic reactor with 120  $\mu\text{L}$  of glycerol, 1.880 mL of acetone and the catalyst were placed at constant stirring and temperature. After the 1<sup>st</sup> cycle, the reactional solution (containing unreacted glycerol, acetone and dissolved products solketal and acetal) was removed, the solid catalyst was left in the reactor, and a new batch of acetone and glycerol was placed in the reactor to run a new catalytic cycle. The process is repeated, as exemplified in Figure 6.2.

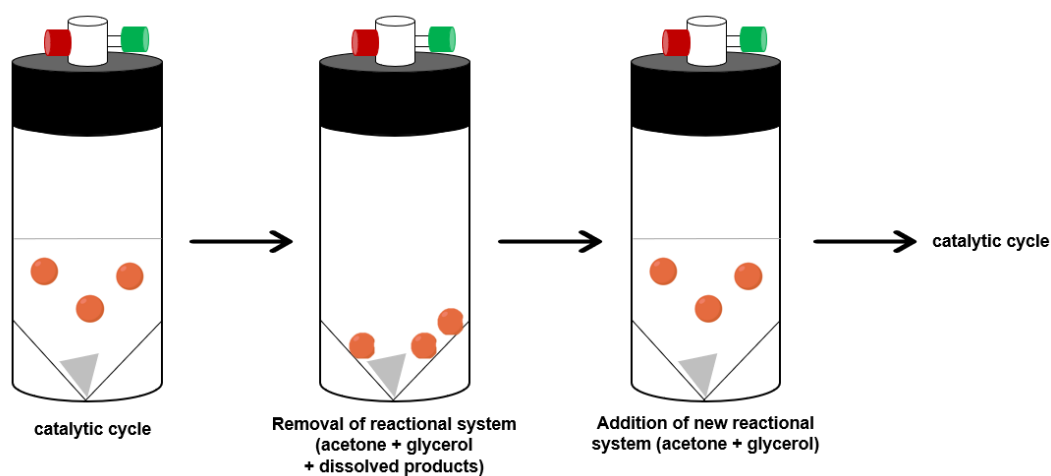


**Figure 6.2** – Scheme of the experimental setup for catalyst reutilization studies.

#### 6.5.5. Catalyst recycling

For catalyst recycling studies, a catalytic reactor with 120  $\mu\text{L}$  of glycerol, 1.88 mL of acetone and the catalyst were placed at constant stirring and temperature. After the 1<sup>st</sup> cycle, the entire reactional solution was removed, and the solid catalyst was washed, and then dried and weighed. Then, a new batch of glycerol and acetone was added, with adjusted amounts in order to maintain the same experimental conditions as the previous reaction cycles. A new catalytic cycle begins, and the process was repeated, as seen in Figure 6.3.

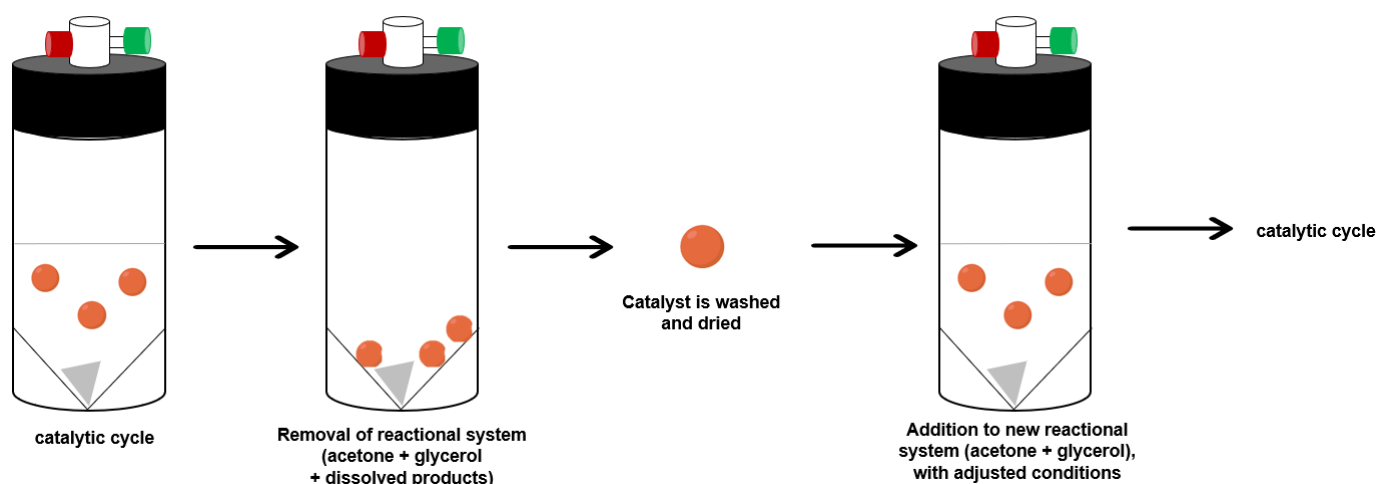


**Figure 6.3** - Scheme of the experimental setup for catalyst recycling studies.

## 6.6. References

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## **7. Conclusion and Future Perspectives**

The increasing environmental consciousness has led to the implementation of a plethora of legislations, designed to reduce and/or completely eliminate greenhouse gas emissions until 2050. As such, it is increasingly important to find new energy sources, that provide alternatives to fossil fuels. Biodiesel has distinguished itself as a non-toxic and biodegradable fuel, and its economic interest has exponentially increased in the past years. This fuel is originated from the transesterification reaction of triglycerides. An important obstacle associated to this industry is the large amount of glycerol produced as by-product. In order to improve the sustainability of the biodiesel production, there has been increasing interest in glycerol valorisation strategies, as is the case of acetalization. Acetalization of glycerol occurs in the presence of ketones (acting as the substrate), originating solketal as one of the reaction products. Solketal is an environmentally friendly compound, widely used as a fuel additive., promoting the Circular Economy in the biodiesel sector, by its use in the final valorised commercial biodiesel.

One of the main factors for successful glycerol acetalization reactions is the correct choice of catalyst, where polyoxometalates (also known as heteropolyacids, HPAs) have distinguished themselves due to their outstanding acidic characteristics. The immobilization of HPAs in solid supports, such as mesoporous silicas and polymeric materials, has allowed their application as heterogeneous catalysts in glycerol acetalization reactions, while improving their recuperation and recycling.

Therefore, the main objective of this dissertation was the development of novel catalysts for glycerol conversion, based on the heterogenization of HPAs in solid supports (SBA-15 and PVA), and to study their catalytic efficiency in glycerol acetalization reactions with acetone, under sustainable conditions. As such, four different catalysts were prepared and investigated: homogeneous HPAs, the heterogeneous powder HPAs@APTES-SBA-15, and the heterogenous one-piece HPAs@PVA and HPAs@APTES-SBA-15@PVA.

Firstly, three different HPAs ( $H_3PW_{12}$ ,  $H_3PMo_{12}$  and  $H_4SiW_{12}$ ) were used as homogeneous catalysts in glycerol acetalization, obtaining very positive results of glycerol conversion and solketal selectivity. Catalyst efficiency followed the trend of  $H_3PW_{12} > H_3PMo_{12} > H_4SiW_{12}$ , with  $H_3PW_{12}$  exhibiting the best catalytic performance with 97% conversion and 98% selectivity, after only 30 min at 25 °C. Higher glycerol conversions with HPA catalysts were obtained at the optimized experimental conditions of 25 °C and catalyst acidity of 0.373 mmol  $H^+$ /g. While the conversion results were very satisfactory, reusing or recycling the catalyst was not possible. The lack of catalyst

recycling is the biggest flaw of homogeneous catalysts, establishing the need for HPA heterogenization.

Heterogeneous catalysts based in powder mesoporous silicas (HPAs@APTES-SBA-15) were prepared and applied in glycerol acetalization reactions. Solid support SBA-15, functionalized support APTES-SBA-15 and composites,  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$ , were obtained and characterized by zeta potential, elemental analysis, FTIR-ATR, PXRD, SEM-EDS and ICP-OES, which confirmed their successful preparation. Then, the composites were applied in acetalization reactions, obtaining the following trend for catalyst efficiency:  $\text{H}_3\text{PW}_{12}\text{@APTES-SBA-15}$  (97% of glycerol conversion after 60 min at 25 °C) >  $\text{H}_3\text{PMo}_{12}\text{@APTES-SBA-15}$  (28% of glycerol conversion after 60 min at 25 °C). Catalyst stability tests were performed with the best performing catalyst, for both reutilization and recycling reactions. In both cases, a loss of catalytic activity was observed, caused by leaching of HPA from the solid support which decreased the catalyst acidity. The occurrence of leaching was confirmed by ICP-OES analysis after catalytic use, where it was observed a decrease in HPA loading in the composite.

Heterogeneous catalysts based in one-piece polymeric membranes (HPA@PVA) were prepared and applied in glycerol acetalization reactions. Type I membranes ( $\text{H}_3\text{PW}_{12}\text{@APTES-PVA}$  and  $\text{H}_3\text{PMo}_{12}\text{@APTES-PVA}$ ) and type II membranes ( $\text{H}_3\text{PW}_{12}\text{@PVA}$  and  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ ) were obtained and characterized by FTIR-ATR, SEM-EDS and ICP-OES, confirming their successful preparation. Type I and II membranes present different morphologies. In the first case, agglomerations of HPAs inside the polymeric matrix were observed, and in the latter case, HPAs were freely dispersed in the polymeric matrix. The catalytic efficiency of type I membranes was investigated, obtaining no glycerol conversion. The application of type II membranes to acetalization reactions resulted in higher conversion at 60 °C. As such, high conversion results (95% after 60 min for  $\text{H}_3\text{PW}_{12}\text{@PVA}$  and 95% after 120 min for  $\text{H}_3\text{PMo}_{12}\text{@PVA}$ ) were observed, with  $\text{H}_3\text{PW}_{12}\text{@PVA}$  being applied for ten consecutive reusing cycles without loss of activity. The results obtained solidified the choice of PVA as a successful polymeric material to impregnate active HPAs, allowing the development of catalytically active HPAs membranes, without occurrence of leaching (as confirmed by characterization after catalytic use).

Finally, a possible strategy to solve HPA@APTES-SBA-15 leaching occurrence was adopted, by the incorporation of these powder composites inside a PVA polymeric matrix. As such, one-piece heterogeneous catalysts based in composite polymeric

membranes (HPAs@APTES-SBA-15@PVA) were prepared and applied in glycerol acetalization reactions. The  $\text{H}_3\text{PW}_{12}\text{O}_{40}\text{@APTES-SBA-15@PVA}$  and  $\text{H}_3\text{PMo}_{12}\text{O}_{40}\text{@APTES-SBA-15@PVA}$  composite membranes were characterized by FTIR-ATR, PXRD, SEM-EDS and ICP-OES. The preparation was successful, with the structural integrity of the SBA-15 composites maintained after incorporation. These membranes were applied in acetalization reactions, demonstrating no catalytic activity. This lack of activity was probably caused by the inability of the HPA active centres to interact with the reactional solution, due to lower permeability of the membrane or strong electrostatic interactions between HPA and APTES functional group present in the composites.

Therefore, the main objectives of this thesis work were accomplished. The work here developed opened a new line of work in the area of glycerol acetalization by using one-piece catalytic membranes. Novel catalytic membranes were successfully prepared and used, producing a high yield of solketal, under a solvent-free system. In particular, HPA@PVA catalysts obtained very promising results, with possible scale-up potential.

The future projects of this work are mostly focused on the last chapter, with the objective of developing catalytically active composite membranes, solving leaching of active species to the reactional system, while simultaneously improving the handling of powder catalysts. As such, a few factors can be investigated, in order to understand their influence in the membrane stability and catalytic efficiency: i) creation of membrane porosity, through cross-linking or addition of porosity agents, ii) effect of the interaction between PVA and other functional groups that can be used in silica functionalization and iii) development of new catalytic membranes, using other polymeric materials.

## **8. Attachments**

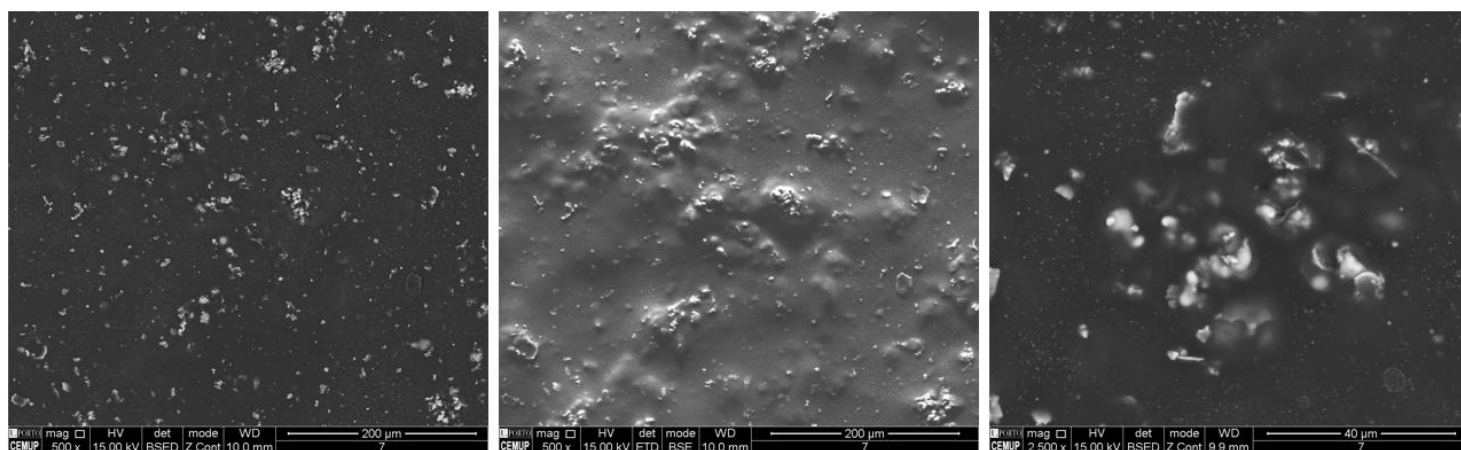


**Figure 8.1** – SEM images obtained for  $H_3PW_{12}@APTES-PVA$ , at different ampliations.

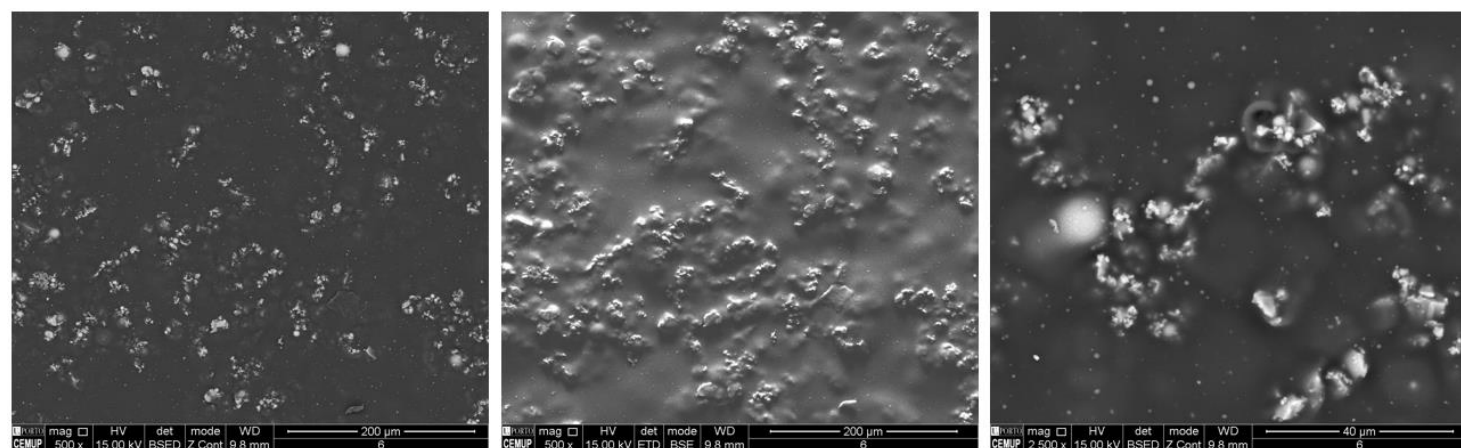


**Figure 8.2** – SEM images obtained for  $H_3PMo_{12}@APTES-PVA$ , at different ampliations.

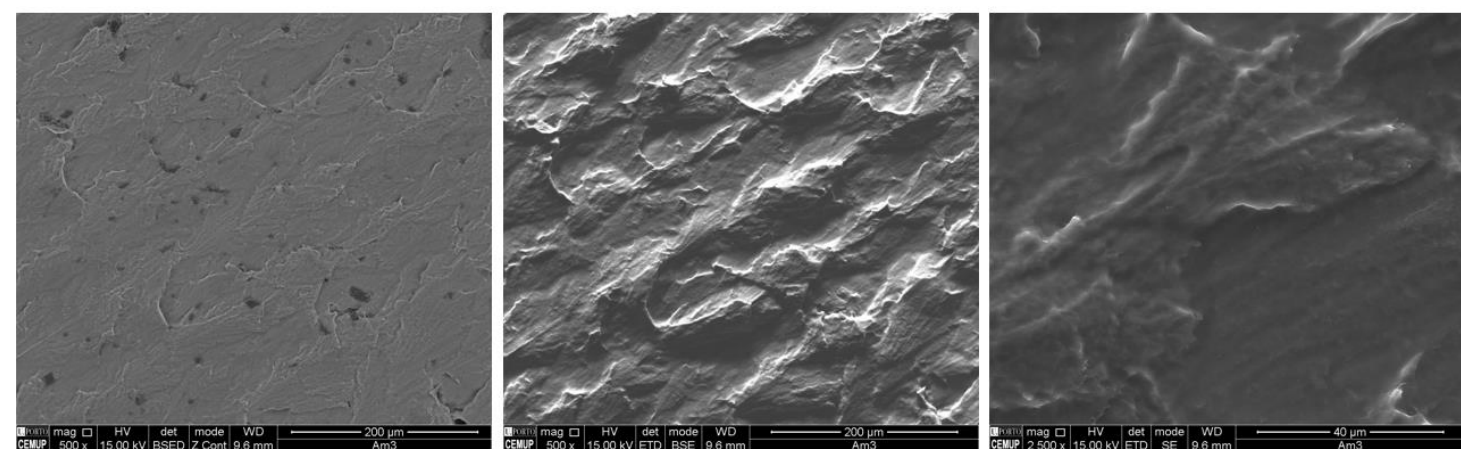


**Figure 8.3** – SEM images obtained for  $H_3PW_{12}@PVA$ , at different ampliations.

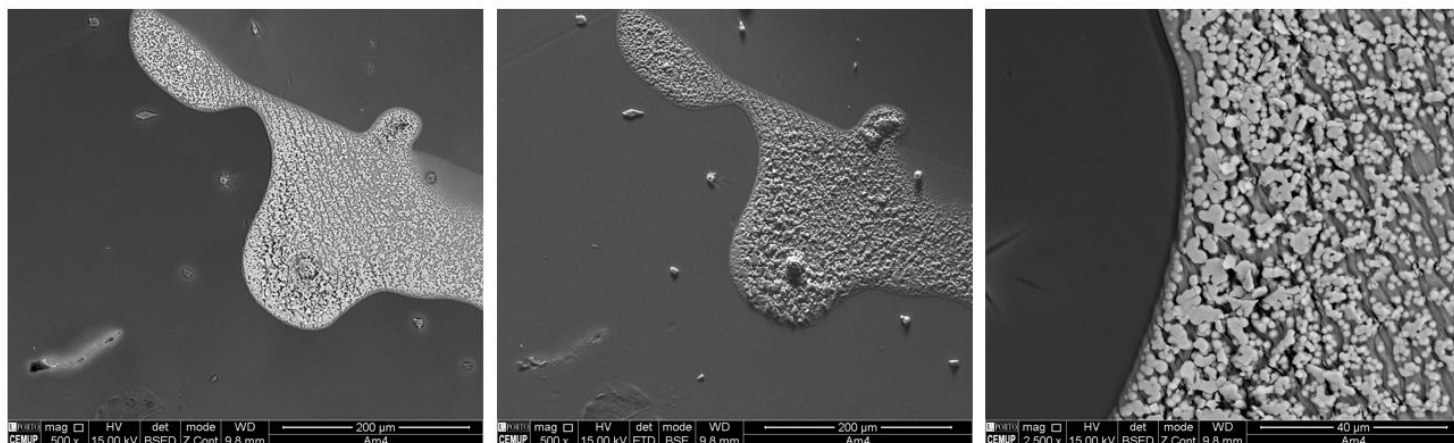


**Figure 8.4** – SEM images obtained for  $H_3PMo_{12}@PVA$ , at different ampliations.

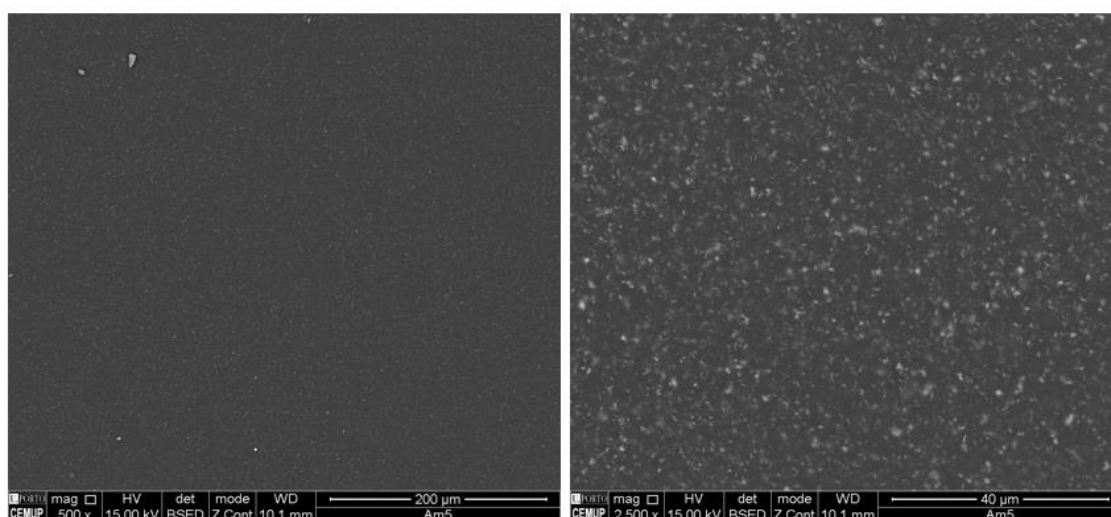


**Figure 8.5** – SEM images obtained for  $H_3PW_{12}@APTES-SBA-15@PVA$ , at different ampliations.

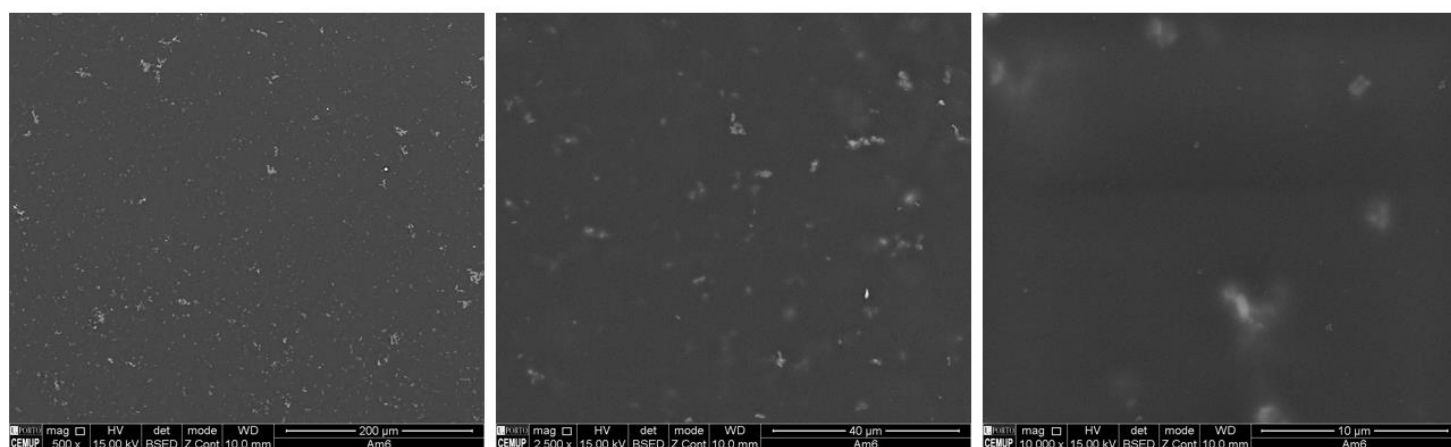


**Figure 8.6** – SEM images obtained for  $H_3PMo_{12}@APTES-SBA-15@PVA$ , at different ampliations.