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CATALYST DEVELOPMENT TO PRODUCE SYNTHETIC FUELS USING THE FISCHER- TROPSCH REACTION

TOWARDS CLEAN AND SUSTAINABLE FUELS

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using the Fischer-Tropsch reaction***

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Abstract

The scope of this work was to investigate the effect of Si addition to alumina-supported Re-promoted cobalt catalysts for syncrude production via Fischer-Tropsch synthesis. To accomplish this, several bifunctional catalysts, *i.e.* containing active sites for chain growth and hydrogenation/dehydrogenation reactions, and acid sites for simultaneous hydrocracking/isomerization, were prepared, characterized, and tested.

The catalytic tests were carried out in a fixed-bed reactor for 28 h under the optimal operating conditions, determined with a parametric study (493 K, 20 bar, H₂/CO ratio of 2, and GHSV of 2.67 m³·kg_{cat}⁻¹·h⁻¹). It was verified that an increase in Si enhances organics specific yield while lowering waxes. Moreover, Si doping reduces cobalt-time yield, C₅₊ selectivity, and olefin production while improving C₅-C₂₀ selectivity and isomers formation due to isomerization and waxes hydrocracking. These two processes strongly depend on catalyst acid site concentration, which, in agreement with what was verified by NH₃ temperature-programmed desorption, is likely to reach its maximum concentration for a 30 wt.% Si content. A long-period study on Co-Re/Siral-30 was also conducted, but no significant differences were found up to 75 h on stream, indicating excellent catalytic stability.

Since Co-Re/Siral-30 seemed to present the desired characteristics regarding product distribution, it should be thoroughly investigated to improve its properties for further application in a NetMIX reactor.

Keywords: Fischer-Tropsch synthesis, Cobalt catalyst, Si-doped alumina, Brønsted acid sites

Resumo

O objetivo deste trabalho centrou-se no estudo do efeito da adição de Si a um catalisador de cobalto suportado em alumina, usando Re como promotor, para a produção de crude sintético através da reação de Fischer-Tropsch. Para tal, vários catalisadores bifuncionais, *i.e.*, contendo sítios ativos para produção de hidrocarbonetos de cadeia longa e para reações de hidrogenação/desidrogenação, e sítios ácidos para hidrocraqueamento/isomerização, foram preparados, caracterizados e testados.

Os testes catalíticos foram realizados num reator de leito fixo durante 28 h, utilizando-se as condições de operação ótimas obtidas através de um estudo paramétrico (493 K, 20 bar, razão H_2/CO de 2 e GHSV de $2.67\text{ m}^3\cdot\text{kg}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$). Foi verificado que um aumento da quantidade de Si leva a um maior rendimento de orgânicos, ao mesmo tempo que diminui a fração de ceras. Além disso, ocorre uma redução do *cobalt-time yield*, seletividade para C_{5+} e da produção de olefinas, e um aumento da seletividade para C_5-C_{20} e da formação de isômeros devido à ocorrência de isomerização e hidrocraqueamento. Ambos os processos são fortemente dependentes dos sítios ácidos do catalisador, o que, de acordo com o verificado através de dessorção de NH_3 a temperatura programada, atinge uma concentração máxima para um conteúdo de 30 wt.% Si. Um estudo de longa duração foi realizado para o catalisador Co-Re/Siral-30, onde se confirmou a ausência de variações significativas até 75 h de reação, indicando excelente estabilidade catalítica.

Uma vez que o catalisador Co-Re/Siral-30 aparenta possuir as características desejadas relativamente à distribuição de produtos, este deverá ser detalhadamente investigado, de forma a possibilitar a melhoria das suas propriedades para uma futura aplicação num reator NetMIX.

Palavras-chave: síntese de Fischer-Tropsch, catalisador de Cobalto, alumina dopada com Si, sítios ácidos de Brønsted

Declaration

I hereby declare, under the word of honor, that this work is original and that all non-original contributions are indicated and due reference is given to the author and source



July 4th, 2022

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Notation and Glossary

C_{iso}/C_n	Iso-paraffin-to-paraffin ratio	
C_{ole}/C_n	Olefin-to-paraffin ratio	
$d_{av\ pore}$	Average pore diameter	nm
d_{Co}	Co average particle size	nm
F	Mass flow	$\text{mol}\cdot\text{h}^{-1}$
n	Carbon number	
P	Pressure	mPa
r_p	Pore radius	m
S_{C_j}	Selectivity to component C_j	
U_{NH_3}	NH_3 uptake	$\mu\text{mol}\cdot\text{g}^{-1}$
v	Volume of He displaced by a given sample	cm^3
v'	Volume of He displaced by the materials and pores of a solid	cm^3
V_p	Total pores volume	$\text{cm}^3\cdot\text{g}^{-1}$
w	Weight	g
W_n	Product weight fraction	
X	Conversion	
y	Loading	
Y_n	Product mole fraction	

Greek Letters

α	Chain growth probability	
γ	Surface tension at the liquid-gas interface	$\text{mN}\cdot\text{m}^{-1}$
θ	Wetting angle	°
ρ_s	True density	$\text{g}\cdot\text{cm}^3$
ρ_g	Apparent density	$\text{g}\cdot\text{cm}^3$
ϵ	Porosity	

Indexes

cat	Catalyst
i	CO ; CO_2 ; CH_4
in	Inlet
j	CO_2 ; CH_4
k	Carbon number ($k=2-20$)

org Organic

out Outlet

List of Acronyms

ASF Anderson-Schulz-Flory

BAS Brønsted acid sites

BtL Biomass-to-liquid

CoLAB Collaborative laboratory

CtL Coal-to-liquid

CTY Cobalt-time yield $\text{mol}_{\text{Co}} \cdot \text{g}_{\text{Co}}^{-1} \cdot \text{s}^{-1}$

DSC Differential scanning calorimetry

EDS Energy dispersive spectroscopy

FCC Face-centered cubic

FT Fischer-Tropsch

FTS Fischer-Tropsch synthesis

GC Gas chromatograph

GHSV Gas hourly space velocity $\text{m}^3 \cdot \text{kg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$

GtL Gas-to-liquid

HAADF High-angle annular dark-field

HC Hydrocarbons

HCP Hexagonal close-packed

HPV High pore volume

HTFT High-temperature Fischer-Tropsch

ICP Inductively coupled plasma

IST *Instituto Superior Técnico*

IWI Incipient wetness impregnation

LAS Lewis acid sites

LHHW Langmuir-Hinshelwood-Hougen-Watson

LPG Liquefied petroleum gas

LTFT Low-temperature Fischer-Tropsch

MAE Microactivity Effi

MM Molar mass $\text{g} \cdot \text{mol}^{-1}$

MSI Metal-support interaction

OES Optical emission spectroscopy

PA Peak area

PD	Product distribution	
PIDS	Polarization intensity differential scattering	
PSD	Particle size distribution	
R&D	Research and development	
STEM	Scanning transmission electronic microscopy	
TCD	Thermal conductivity detector	
TEM	Transmission electron microscopy	
TGA	Thermogravimetric analysis	
TOF	Turnover frequency	s^{-1}
TOS	Time on stream	h
TPD	Temperature programmed desorption	
TPR	Temperature programmed reduction	
XtL	X-to-liquid	
WGS	Water-Gas shift	
WL	Weight loss	
WtL	Waste-to-liquid	

1 Introduction

1.1 Framing and presentation of the work

At the ending stages of World War II, many in the United States of America feared petroleum shortages, and, in the 1970s, a four-fold increase in petroleum price prompted a massive investigation by petroleum companies' research laboratories of coal-to-oil processes, particularly the Fischer-Tropsch synthesis, FTS [1]. FTS was devised in 1926 by Franz Fischer and Hans Tropsch and consists of syngas, a mixture of CO and H₂, conversion into a wide spectrum of hydrocarbons, HC (C₁-C₁₀₀), that include liquefied petroleum gas (LPG), gasoline, jet fuel, diesel, and waxes [2]-[6]. It is noteworthy that the FT products constitute syncrude and not ready-to-use synthetic fuels, since the products need to undergo an upgrading stage to meet the industry requirements. However, for the sake of simplification, during this dissertation the carbon ranges C₅-C₁₁, C₁₂-C₁₅ and C₁₂-C₂₀ will be referred to as gasoline, jet fuel, and diesel, respectively.

The Fischer-Tropsch (FT) process is part of X-to-liquid (XtL) technologies, specifically gas-to-liquid (GtL), which comprises the conversion of gaseous carbon-containing sources to liquid fuels. Coal-to-liquid (CtL), biomass-to-liquid (BtL) and waste-to-liquid (WtL) are also included in XtL technologies [3], [5], [7]. XtL processes research and development, R&D, has been rising in recent decades, owing mostly to the following factors: i) global warming, caused mainly by fossil fuel consumption [3], [5]; ii) population increase and, consequently, higher demand for energy resources, with a 56% increase in the world's energy consumption expected by 2040 [5]; iii) increase in recently discovered natural gas fields; and iv) environmental obligations for CO₂-neutral fuels production [6].

FTS is seen as a good alternative approach for the production of synthetic fuels [8] since it is a promising clean technology, with the products showing high cetane number (up to 75), higher energy density than gas-phase fuels such as H₂ and being sulfur- and aromatic-free [3]-[6], [9], which could result in significant reductions in SO_x and NO_x emissions [2]. Despite its benefits, the global GtL market fell from 5.3 billion€ in 2019 to 3.9 billion€ in 2020, due to the negative impact of COVID-19 pandemic. Nonetheless, it is expected a growth in the upcoming years, with the market reaching 5 billion€ by 2027 [10].

Regardless of the carbon source that is used as raw material, the capital cost for the production of purified syngas constitutes 60-70% of the whole plant complex, while the FT section accounts for *ca.* 20% and the downstream refinery for only 10% [4], [5], [11]. However, the viability of a FT process is always determined by crude oil's price since the cost of a synthetically produced

fuel will have to compete with the latter. Despite market's instability, the future of FTS looks promising, as the cost of crude-oil technology has skyrocketed [6].

In 1938, there were nine industrial factories in operation, with $6.6 \times 10^5 \text{ t} \cdot \text{year}^{-1}$ of total capacity [12]. Several industries and projects are now being developed for the generation of more sustainable fuels. The Sasol facility in South Africa, with a daily production of $2.7 \times 10^7 \text{ L}$ and Pearl GtL in Qatar, with a daily production of $2.2 \times 10^7 \text{ L}$, are two of the largest plants. Furthermore, sustainable aviation fuel-oriented installations intend to produce over $3 \times 10^8 \text{ L}$ of FT liquid products by 2025 [13].

Because FTS is a catalytic reaction and presents a wide range of HC, the investigation of a catalyst design that can improve its efficiency and selectivity towards specific fractions becomes of great importance [14]. Specifically, the aim for bifunctional catalysts, that contain both active sites for chain growth and acid sites for hydrocracking and isomerization is of the most relevance since it would allow for a one-stage FT process, which is more financially viable than its two-stage counterpart [15].

Investigation regarding bifunctional catalysts has been growing in recent decades, with zeolites-supported catalysts being the ones closer to reach industrial application. Despite their high capability in providing acid sites, zeolites possess diffusional limitations and high deactivation due to coke formation [15]. Hence, this dissertation intends to study silica-doped alumina supports, a different and less-study alternative to zeolites, and clarify silicon effect on the bifunctional catalysts performance.

1.2 CoLAB Net4CO₂ presentation

The collaborative laboratory (CoLAB) Net4CO₂ - *Network for a sustainable CO₂ economy* is a non-profit private R&D institution founded in 2019 with the primary purpose of creating innovative CO₂-based processes and products in order to generate a circular CO₂ economy. For that, CoLAB Net4CO₂ research is focused on three key areas: i) sustainable and efficient CO₂ capture and separation; ii) production of synthetic fuels for CO₂ and CH₄ reuse; and iii) H₂ production with zero CO₂ emissions [16].

This research aims to contribute to the second field, *i.e.*, synthetic fuels production via FTS, by analyzing and comprehending the evolution of catalytic performance.

1.3 Contribution of the author to the work

The work carried out in partnership with CoLAB Net4CO₂ provided two significant contributions. Firstly, a detailed parametric test was conducted to establish the optimal operating conditions for the Fischer-Tropsch reaction. Secondly, a very important contribution was given to the

development and compilation of a dataset of catalytic results, which will be extremely useful in the future development of a NetMIX-based unit, capable of carrying out the production of syncrude through Fischer-Tropsch. For that, the influence of catalyst design and formulation (support doping, promoter effect) on the product distribution, PD, was studied through the preparation, characterization, and testing of single-catalysts containing dual functionalities, *i.e.*, capable of not only growing hydrocarbons from light gas molecules (*e.g.*, syngas), but also inducing cracking of long hydrocarbon chains, especially waxes (C_{21+}), through the incorporation of acidic sites on the support.

1.4 Organization of the dissertation

This report is divided into several chapters and sub-chapters, beginning with Chapter 1, which introduces this dissertation. It includes an overview of the connection between the petroleum industry and global warming, as well as an approach to XtL technologies, including FTS, as a potential solution to the problem. Moreover, it also covers the author's main contributions to the host association, CoLAB Net4CO₂, as well as a brief presentation of the latter.

Chapter 2 covers the current state of the art for FTS, including its primary reactions, mechanisms, and product distribution. Furthermore, it includes the operating conditions, specifically temperature, pressure, H₂/CO ratio, and gas hourly space velocity (GHSV), as well as the appropriate reactors for FTS use. Finally, a detailed analysis of the active metals, supports, and promoters used in the FT reaction is included.

The approaches for catalyst preparation and testing are explained in Chapter 3. First, the support properties, catalyst preparation, and experimental setup are described in detail. Then, there is an insight into the support and catalyst characterization methods used during the dissertation. The chapter concludes with an elucidation of the experimental setup where the catalytic tests were performed during this work, and on the selectivity assessments of both gas and liquid products.

Chapter 4 details the main results of this work. First, the properties of the supports and synthesized catalysts are discussed, covering the results obtained during the characterization of these materials. A parametric study of a prepared Co-Re/Al₂O₃ catalyst, used as reference, is then described, where the influence of temperature, pressure, and GHSV is examined. Moreover, the promoter's impact on product distribution is assessed. Then, using the operating conditions earlier determined, the catalytic performance of the catalysts is outlined, with a special emphasis on product distribution. Finally, the influence of a high pore volume support on FTS is studied, and the performance of the best catalyst is evaluated during a long period time on stream, TOS.

Chapter 5 presents the main findings drawn from the work developed, as well as some perspectives for future efforts.

Finally, Chapter 6 closes with an overview of the completed work.

2 Context and State of the art

FTS is a polymerization reaction that takes place on the surface of the catalyst [5], [17]. This synthesis involves CO hydrogenation to produce mostly n-paraffins (or alkanes) and α -olefins (or alkenes) [18], as shown in Eq. 2.1 and Eq. 2.2, respectively. Parallel to these reactions, the synthesis of oxygenated products (particularly alcohols, aldehydes, acids, ketones, and carbonyls) as byproducts may occur, following, e.g., Eq. 2.3 and Eq. 2.4 [5], [19].



^a ΔH is dependent on the products formed

This synthesis results in methane (C_1), LPG (C_2 - C_4), gasoline (C_5 - C_{11}), jet fuel (C_{12} - C_{15}), diesel (C_{12} - C_{20}), and wax (C_{21+}) production [5], [6], [19], [20], with C_{5+} HC being the most desirable products. Methane production is undesirable since it is a low-value product whose formation implies the absence of more profitable HC [5], [19], [20]. Waxes can be hydrocracked to form gasoline and jet fuel, which can be, thereafter, used as a transportation fuel. Furthermore, FTS products can be used as feedstock for the manufacturing of ethylene and propylene, lubricating oil, polishes, among others [6]. In addition to these main reactions, FTS can undergo hydrogenation of olefins to secondary paraffins, isomerization of alkanes (which will be discussed in detail in Section 2.4.2), dehydration of alcohols, and disproportionation of CO (Boudouard equilibrium). Moreover, Water Gas Shift (WGS) reaction (Eq. 2.5) also occurs [3], [5], [20].



Usually, a higher H_2/CO ratio displaces the equilibrium towards H_2O formation, whereas a lower H_2/CO ratio leads to CO_2 and H_2 production [5]. Hence, this reaction is particularly attractive to adjust the H_2/CO ratio in the feed [20]. It is worth noting that the water effects are independent from its source, with the formation of water from WGS reaction or its addition to the feedstock having the same effect [3].

Regarding the FT kinetics, the elevated number of species involved, along with the complexity of FT reactions and mechanisms, complicate the description of this parameter, with additional research on the subject being needed. As a result, the kinetic models may differ depending on the source, despite a Langmuir-Hinshelwood-Hougen-Watson (LHHW) type being usually applied [21].

2.1 FTS mechanism

Due to a wide range of products, FTS mechanism is complex [3], [6] and centers on three main steps: i) reaction initiation, ii) chain growth, and iii) chain termination [3]. The underlying FTS mechanism is still not quite well understood. For instance, there is not a consensus about the nature of the active site for the CO dissociation [11], [17], [18]. Two approaches have been proposed to explain this mechanism, namely CO insertion chain growth and carbide mechanism [3], [5], represented in Figure 2.1a and b, respectively.

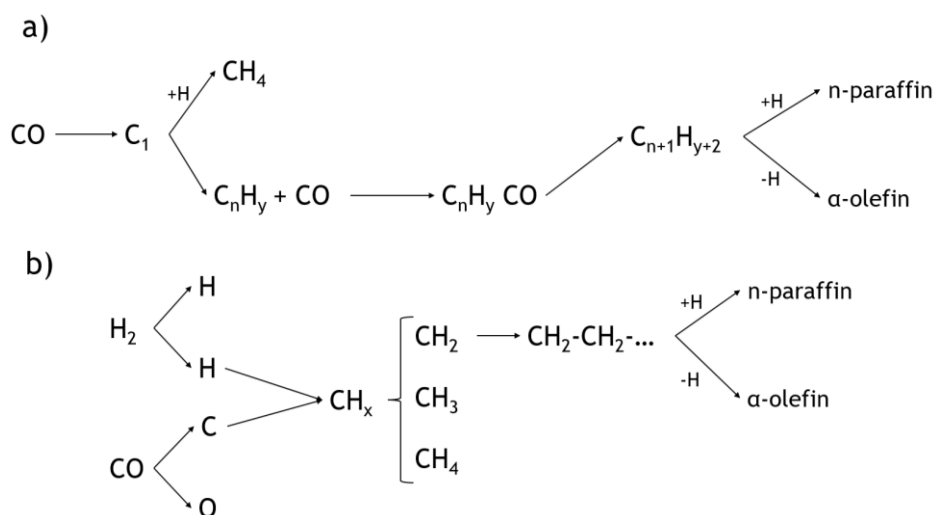


Figure 2.1: FT reaction scheme according to a) CO insertion chain growth mechanism, and b) carbide mechanism.

Adapted from [3].

In the CO insertion chain growth mechanism (Figure 2.1a), CO is first adsorbed on the catalyst surface, where it is dissociated, either directly or assisted by hydrogen, forming C_1 . This step originates the chain initiation. The dissociated CO is then hydrogenated, forming a CH_x molecule. Subsequently, another CO molecule is injected into the previously yielded CH_x . This gives rise to the chain growth, where a C-O bond splits, resulting in C_2H_y species. This continues indefinitely until the chain is terminated. This last step can take place whenever, forming an n-paraffin or an α -olefin, depending on whether there is an H introduction or removal, as can be confirmed from Eq. 2.1 and Eq. 2.2, respectively [3].

In contrast to the latter mechanism, where CO was the initiating monomer, in the carbide mechanism (Figure 2.1b), the initiating monomer is methylene, CH_2 . In order for that to occur, H_2 and CO are first adsorbed and dissociated on the surface of the catalyst. Then, C and H form a new bond, being able to yield a range of CH_x molecules, such as CH_2 , CH_3 , and CH_4 . The generated CH_2 species are inserted into the alkyl species, kicking off the chain propagation process. Finally, chain termination occurs as a result of a CH_3 or H addition, forming a paraffin, or due to an H removal, forming an olefin [3], [6]. Aside from the fact that it fails to explain the production of branched isomers and oxygenated products [6], this mechanism seems to be

the predominant one [17]. Nonetheless, there is a general scientific agreement that multiple monomers take part in chain growth reaction [6].

2.2 Product distribution, PD

PD in FTS varies extensively depending on a variety of factors [5], [11], [19].

Chain growth probability, α , represents, as the name implies, the probability of chain prolongation against chain termination in FT products [17]. In ideal circumstances, α would be chain length independent and would follow the Anderson-Schulz-Flory (ASF) arithmetical distribution [4], [11], [17]. Even so, the distribution calculations show a good fit with the observed results [4], [11], with only three types of deviations found from the ideal ASF distribution: experimental CH_4 selectivity is higher, C_2 and C_3 selectivities are lower and, in the case of low-temperature FT (LTFT) processes, α is larger for higher carbon numbers. However, the use of bifunctional catalysts can alter the PD due to the occurrence of secondary reactions [15], [21], hence breaking the ASF distribution. Chain growth probability is a function of the rates of propagation and termination, and it is related with the product weight fraction, W_n , and the carbon number, n , as represented by Eq. 2.6. Moreover, it can also be correlated with the product mole fraction, Y_n , as denoted in Eq. 2.7 [22]. Figure 2.2 depicts W_n as a function of α according to n.

$$W_n/n = (1 - \alpha)^2 \cdot \alpha^{n-1} \quad \text{Eq. 2.6}$$

$$Y_n = \alpha^{n-1} \cdot (1 - \alpha) \quad \text{Eq. 2.7}$$

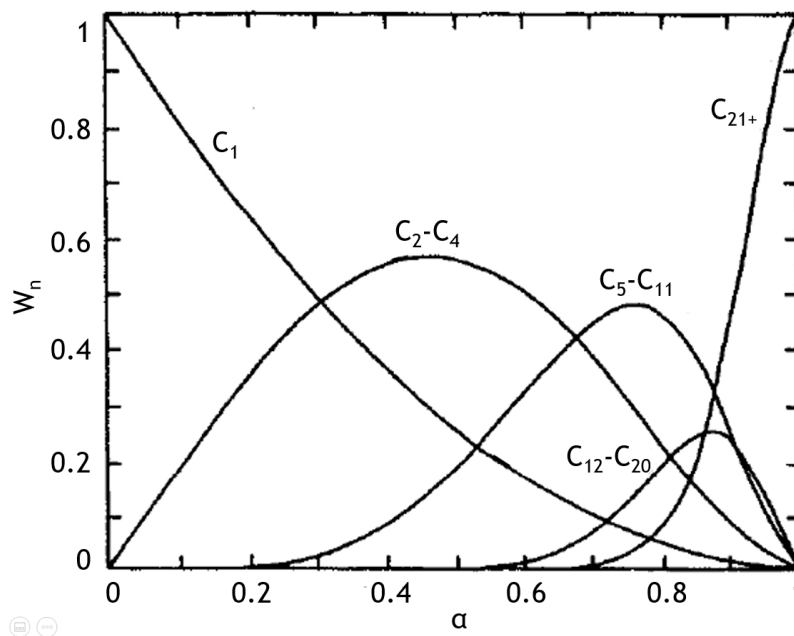


Figure 2.2: Hydrocarbon selectivity for various fractions as a function of α for the ideal ASF distribution. Adapted from [23].

The maximum selectivities for CH₄, LPG, gasoline, and diesel are 100 %, 56 %, 47 %, and 25 %, respectively. Because the primary selectivities for gasoline and diesel fuel are low, secondary conversion of FT products is critical [17].

2.3 Process conditions and reactor design

The operating conditions, such as temperature, pressure, feedstock composition, and GHSV, as well as the configuration of the reactor, strongly affect the CO conversion and PD [20]. In Table 2.1 it can be seen a qualitative overview of these variables in various parameters, namely α , olefin-to-paraffin ratio (C_{ole}/C_n), methane selectivity, and CO conversion [7], [21].

Table 2.1: Influence of operating conditions on product distribution [7], [21].

Increase in	α	C_{ole}/C_n	CH ₄ selectivity	CO conversion
Temperature	↘	↘	↗	↗
Pressure	↗	↕	↘	↗
H ₂ /CO ratio	↘	↘	↗	↗
GHSV	↕	↗	↘	↘

↗ increase, ↘ decrease, ↕ contradictory reports/complex relationship

Temperature

FTS can operate in two distinct modes, low-temperature FT (LTFT, between ca. 473-523 K) and high-temperature FT (HTFT, between ca. 593-648 K), with the former being the predominant FT technology developed in recent decades [24]. Because FTS is extremely sensitive to small temperature changes [20], an increase in temperature results in a higher CO conversion. However, it also results in a decrease in α , hence, a higher methane selectivity, higher carbon deposition (which leads to catalyst deactivation), and an increase in byproducts formation [4], [15], [17], [20].

Pressure

Pressure influences not just catalyst activity but also PD. For FTS conditions, the pressure used is around 20-30 bar since increasing pressure up to 2 bar leads to higher CO conversion, C₅₊ selectivity, and α [4], [25]. If higher pressures were used, the temperature would also have to rise to inhibit water condensation since this could improve catalyst deactivation, and, as previously stated, there would be a change in PD to lighter species, which is not desirable. Furthermore, and specifically in trickle and fixed-bed reactors, the outcome of a high increase in pressure would be a temperature increase along the reactor, which is not advisable due to

heat-transfer limitations. Nevertheless, the effect of reactor pressure is not as pronounced as the remaining operating conditions [20].

H₂/CO ratio

Syngas is expensive, hence, improving its conversion is of extreme importance [11]. As a result, syngas composition, namely its impurities and H₂/CO ratio, is critical in the FTS reaction. Impurities can speed up catalyst deactivation, while the H₂/CO ratio controls CO conversion. CO conversion increases with an increase in H₂/CO ratio, being the most sensitive for a ratio between 1 and 2. Additionally, there is an increase in CH₄ selectivity and a decrease in that of C₅₊ [20], since a higher H₂ partial pressure leads to an increase in paraffin formation, while a lower CO partial pressure results in a lower α , which would, thus, result in a shift in selectivity towards lighter products [11]. However, the conclusions must be taken carefully, as it appears to be an oversimplification to assume that an increase in the H₂/CO ratio leads to a shift in C₅₊ and CH₄ selectivities, given that the presence of CO₂ and H₂O also affects these parameters, specifically via WGS reaction [11]. Co-based catalysts present a low WGS activity, whereby feedstock requires an H₂/CO ratio of ≈ 2.1 to reduce deactivation by coke formation [4], [11], [20].

GHSV

Overall, an increase in GHSV reduces CO conversion [20], [26]. Moreover, it leads to a slight decrease in C₅₊ selectivity in Co supported in TiO₂, Al₂O₃, and SiC and to an increase in Co supported in SiO₂ [20], a decrease in CH₄ selectivity, and an increase in C_{ole}/C_n ratio [6].

Reactor design

The presence of three phases in the reactor could complicate its design [3], [11]. However, the capability of handling the heat of the reaction must be the key factor in selecting the reactor configuration [3]. FT reaction is highly exothermic, and the reaction heat needs to be quickly removed to avoid a temperature increase [4], [11]. For this reason, the reactor design is typically similar to industrial heat exchangers, employing an external coolant to keep the reaction at the desired temperature [20].

Slurry bubble columns, fixed-bed, and fluidized-bed reactors are the most implemented in the FT process [3]. While the former two are mostly used in LTFT processes, targeting waxes production, the latter is largely applied in HTFT processes since the reaction must occur in the gas phase, aiming at low molecular weight HC production [3], [11], [17].

2.4 FT catalysts

The FT viability is determined by the catalyst lifetime, activity, and selectivity towards C_{5+} HC [11]. These, in turn, depend on the chemical composition of the catalyst, as well as its physical properties [3]. A catalyst typically consists of a support as the main component, an active metal phase, and a promoter [19].

Catalyst deactivation is something that needs to be considered since it takes place by means of a decrease in the number of active sites, which, in turn, leads to a decrease in the FT reaction rate. There is currently no general agreement about the main phenomena that result in catalyst deactivation, although few occurrences have been described in the literature, including carbon deposition (coke), reoxidation of the active metal phase, metal sintering, and catalyst attrition [6], [7], [20], [27].

2.4.1 Active metal phase

All group VIII metals of the periodic table of elements have enough activity to convert CO to HC [3], [24], although only Fe-, Ni-, Co-, and Ru-based catalysts are capable of acting as a catalyst in FT reaction [4], [5], [17], with an approximate relative cost of 1:200:520:150 000, respectively [28]-[31].

Ruthenium is one of the most active catalysts for FTS. However, because it is a very scarce metal, it is exceedingly cost, making it industrially unappealing. Nickel is not of interest for FTS since, despite its high activity, it has an extremely high CH_4 selectivity [3]-[5], [11], [17], [18]. Iron-based catalysts present excellent activity for WGS reaction [5], [17], [32] and low CH_4 selectivity even at high temperatures, making them ideal for the HTFT process [17], [20].

Cobalt is the best choice for GtL technologies [9], [19] since it offers the following benefits: i) no water inhibition; ii) high selectivity for long-chain HC, with an α that can reach 0.95; iii) low selectivity for oxygenated products; iv) high activity for the LTFT process; v) high activity for CO dissociation [15]; vi) low deactivation rate; and vii) extended life span (about 5 years on stream compared to 6 months in the case of Fe) [5], [8], [17], [19], [33]. However, due to its cost, supports like Al_2O_3 and SiO_2 are widely used to increase Co dispersion in the support surface [3], [4], [11].

Co loading is a parameter that impacts FTS and is commonly reported in the 10-30 wt.% range [11], with some studies claiming that metal loading promotes C_{5+} selectivity [3], [20]. Furthermore, Co particle size has a strong impact on FT reaction, as shown in Figure 2.3. Turnover frequency, TOF, *i.e.*, the number of catalytic cycles in each site per second, increases with particle size, remaining constant for particles larger than 6-8 nm [3], [5], [24], whose variation can relate to the increase in CO-covered sites [3], [34].

Regarding C_{5+} selectivity, it typically increases with Co particle size up to 7-9 nm, stabilizing for bigger particles [18], [33]. This phenomenon might be explained by an increase in bridge-type adsorbed CO on large Co particles, since they show more flat surfaces and, hence, promote this type of bonding. Smaller Co particles, on the other hand, have more edges, resulting in linear bonds. CO activation is most likely the rate limiting step when Co-based catalysts are employed, and the bridge-type CO presents higher activity than the linear one due to its weaker C-O bond, whereby the dissociation between C and O is improved [3], [35], [36]. In terms of CH_4 , its formation is promoted over smaller Co particles due to the high H_2 coverage presented [3], [18], [34]. Moreover, because small Co particles are more exposed, they are easily oxidized by water, contributing to an increase in CH_4 selectivity and a reduction on that of C_{5+} [6], [7], [18].

Finally, it is well documented that particles smaller than 4 nm have a faster cobalt-time yield (CTY) drop than particles bigger than 15 nm [37]. Smaller particles present higher surface area, which boosts CTY. However, when particle size is too small, corner and edges sites dominate over flat ones, which reduces CTY; thus, there is an optimal particle size [18].

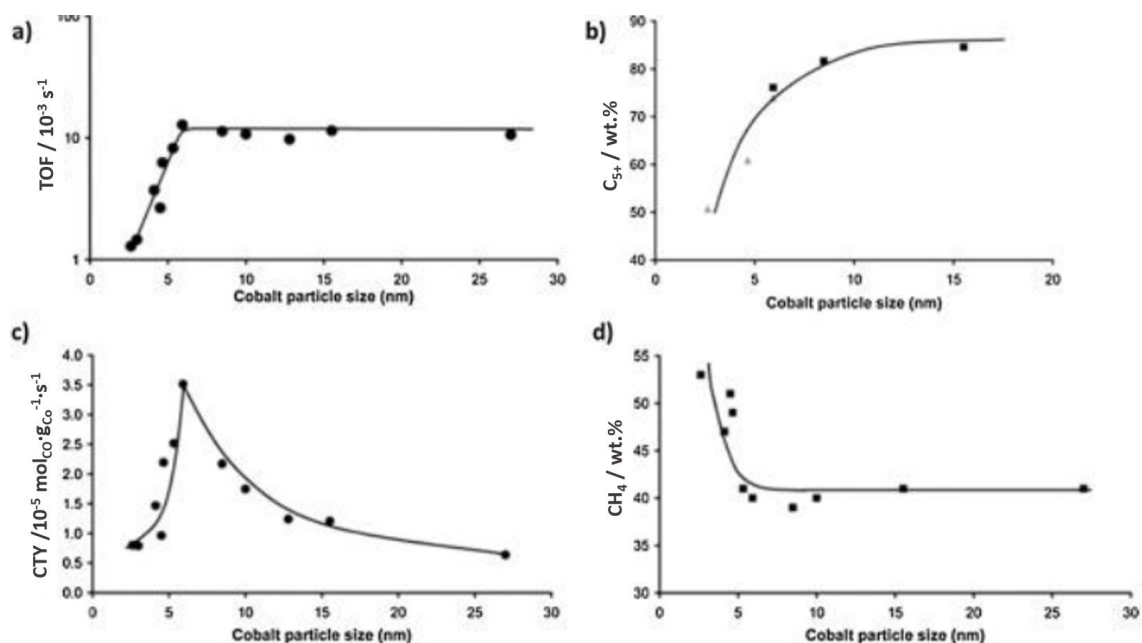


Figure 2.3: Influence of cobalt particle size on a) TOF, b) C_{5+} selectivity, c) CTY and d) CH_4 selectivity [34].

The crystal structure of the active metal is another aspect that influences FTS activity and selectivity, since different crystal phases exhibit diverse morphologies and surface topologies, resulting in distinct catalyst selectivities [18]. In the case of Co-based catalysts, the crystal structure can be hexagonal close-packed (HCP, Figure 2.4a) or face-centered cubic (FCC, Figure 2.4b). Under ambient conditions, the bulk of the catalyst acquires an HCP structure, changing to FCC when the temperature rises to 673 K [2], [18]. This structural shift might occur under milder conditions for smaller Co particles, with FCC being the main phase for particles lower than 20 nm and HCP the dominant structure for particles larger than 40 nm. When HCP is the

dominant phase, cobalt catalysts demonstrate higher activity, CO conversion rates, TOF, and lower CH₄ selectivity when compared with FCC [18].

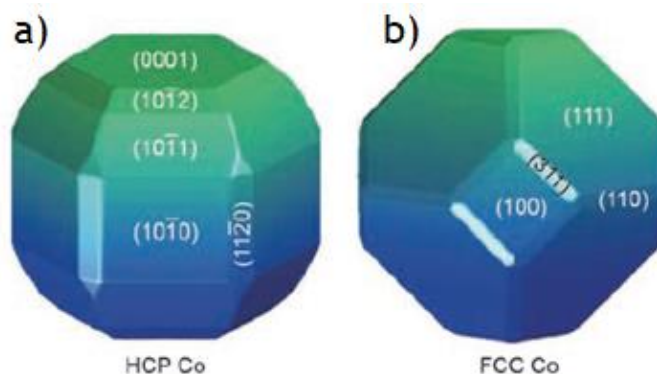


Figure 2.4: Cobalt crystal structure: a) HCP, and b) FCC [18].

2.4.2 Support material

The active phase is often supported, which improves catalytic activity due to an increase in the specific surface area, resulting in high metal dispersions, and, thus, enhancing the FTS reaction rate [20], [24], [38]. Furthermore, the support material itself can have an impact on FTS, with its properties influencing the metal-support interaction (MSI), crystallite size and structure, metal dispersion, mass transfer, mechanical and chemical strength, and thermal stability [3], [5], [12]. Thereafter, it is critical to take notice of the support surface area, as well as its pore properties for product diffusion [3], [39].

Diffusion limitations arise as a result of product formation in FTS. The products block the catalyst pores, limiting the diffusion of both products and reactants, and affecting the reaction rate. Given that the H₂ diffusion rate is higher than CO due to its size, the dissolution and diffusion of reactants into the catalyst pores generate higher H₂ concentrations and, therefore, a higher H₂/CO ratio, hence leading to the chain termination step, which decreases selectivity for long-chain HC and increases that of methane [3], [5]. Co catalysts with pore sizes of *ca.* 20-50 nm and 100-1000 nm show lower diffusion constraints than larger pore sizes (about 1-3 mm), with a decrease in diffusion restrictions with increasing pore size, since there is an improvement in the compounds' transportation between the active sites [3].

There are a variety of supports that have been studied throughout the years, as is the case of carbon-based materials, TiO₂, zeolites, Al₂O₃, and SiO₂, with the latter two being the most commonly employed for Co-based catalysts [5].

Al₂O₃ presents superb mechanical properties, elevated resistance to attrition, and adjustable pore structure, making it a widely used support for Co-based catalysts [3], [24]. Nevertheless, the presence of alumina can increase MSI, leading to catalyst deactivation and reducing the number of active sites [3], [6], [24]. Once formed, metal-oxide complexes are difficult to

reduce at FTS temperatures, and, therefore, they are inactive under FT conditions, leading to a loss in catalytic activity [38].

Alumina shows multiple phases, such as γ -, α -, θ - and δ - Al_2O_3 , which will affect the PD during FTS [3]. In fact, for identical Co particle sizes, the C_{5+} selectivity is dependent on the phase and pore size of Al_2O_3 , with α - Al_2O_3 supported catalysts being the ones that exhibit the highest selectivity [35]. Despite a higher MSI with γ - Al_2O_3 , this phase is the most extensively applied due to a greater mechanical, thermal, and hydrothermal stability, relatively high surface area, good sintering resistance, and enhanced metal dispersion attained [35], [40], [41]. At high temperatures (923-1373 K), the structure collapses and additional alumina phases, like α - Al_2O_3 , are developed, potentially leading to catalyst deactivation [41].

Regarding SiO_2 , this support presents an elevated surface area and surface/mass ratio, low density, narrow pore size distribution, and an ordered pore structure, hence being a popular support for Co-based catalysts. These characteristics improve metal dispersion, reducibility, catalytic activity, and thermal stability [3], [5]. When compared with alumina, silica shows weaker MSI, which increases reducibility and the number of active sites by improving Co dispersion [3], [24]. Silica surface accommodates a considerable number of silanol groups, SiOH , which can affect the catalyst's PD and reduction capabilities [3].

Although the support of a catalyst is usually inactive for a given reaction, in FTS it can provide acid sites, allowing for a one-stage process [15]. Silica-doped alumina supports have received considerable attention in recent decades since doping can enhance the properties of these two materials. The addition of SiO_2 to Al_2O_3 improves the total acidity, porosity, metal dispersion and reducibility, surface area, thermal and hydrothermal stability of the support, and lowers the MSI [15], [42]. This reduces catalyst deactivation and extends its lifespan while increasing its activity [3].

Acidity of silica-doped alumina

While alumina presents weak Lewis acid sites (LAS), an electron acceptor, and Brønsted acid sites (BAS), a proton donor, silica shows stronger acidity, ergo its addition to Al_2O_3 increases the formation of hydroxyl groups, which, in turn, leads to the formation of strong BAS (Figure 2.5a), whereas the replacement of Si^{4+} ions with Al^{3+} in the tetrahedral lattice sites leads to higher LAS due to the formation of aluminosilicate phases (Figure 2.5b) [3], [40], [43], [44].

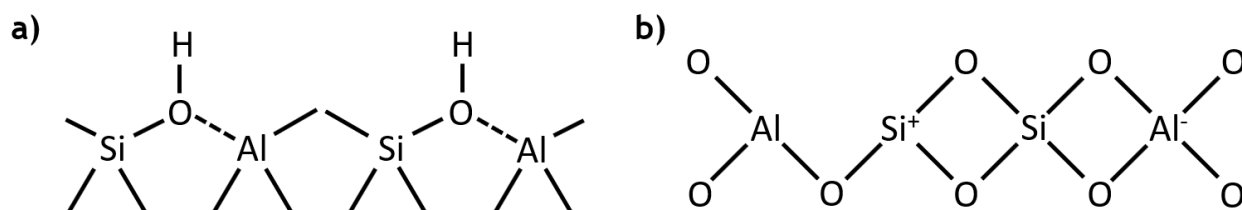


Figure 2.5: a) Brønsted acid sites [45] and b) Lewis acid sites [15] in a silica-doped alumina support.

The presence of acid sites, specially Brønsted ones [15], leads to hydrocracking, where at least one C-C bond is broken and the remaining free valencies are occupied by hydrogen, producing lighter HC than the reactant, and isomerization, where a rearrangement occurs for an iso-paraffin production. The most accepted hydrocracking/isomerization mechanism is depicted in Figure 2.6.

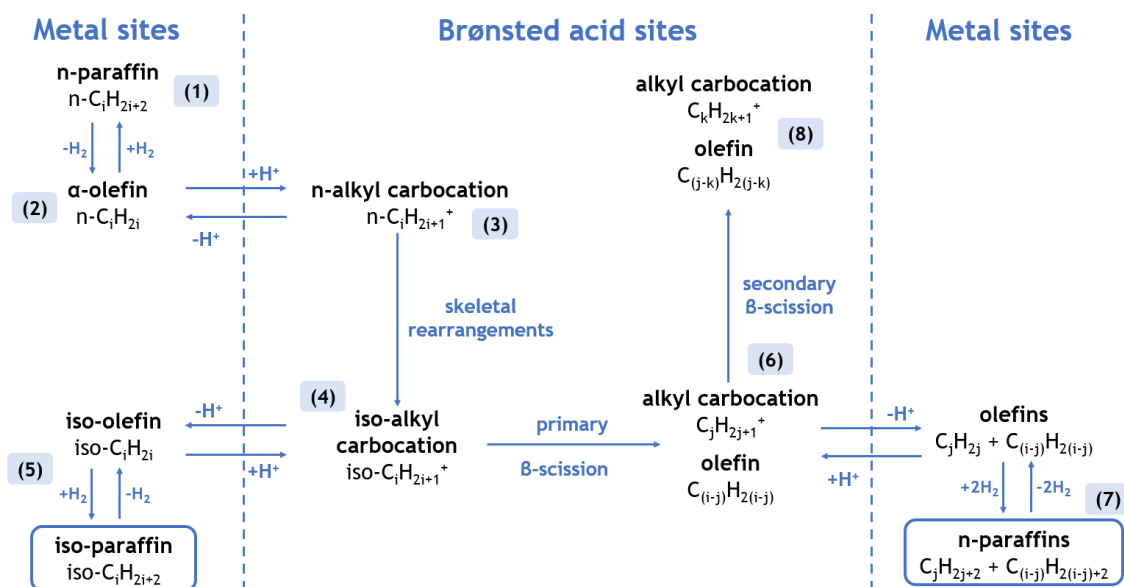


Figure 2.6: Mechanism of isomerization and hydrocracking on a bifunctional catalyst. Adapted from [46].

According to this mechanism, an n-paraffin formed on a metal site (step 1) is dehydrogenated to form an α -olefin (step 2), which is thereafter diffused to the Brønsted acid sites, where it is protonated to secondary alkyl carbenium ion (or carbocation), $n\text{-C}_i\text{H}_{2i+1}^+$ (step 3). These ions are reactive intermediates and do not undergo β -scission since this would implicate the formation of primary carbocations, such as CH_3^+ and C_2H_5^+ , which are extremely energetically unstable compounds. Thus, the n-carbocation suffers skeletal rearrangement, forming an iso-carbocation, $\text{iso-C}_i\text{H}_{2i+1}^+$ (step 4). If the desorption from the acid sites is efficient, the iso-carbocation diffuses to the metal sites, where it is hydrogenated to form an iso-paraffin (step 5); on the contrary, it can undergo β -scission, where there is rupture of C-C bonds, forming a smaller-chain n-carbocation, as well as an olefin (step 6) [46]-[48].

If the lighter n-carbocation here produced have at least 12 carbons in its chain, this product can proceed via two different routes. In the case of a rapidly product desorption, the ion will desorb to the metal sites, where it will be hydrogenated to form an n-paraffin (step 7). On the contrary, if the product desorption is not fast enough, the n-carbocation will form smaller ions through secondary β -scission, thus forming lighter paraffins (step 8) [46].

Hence, this acidity enhancement, which is proportional to the increase in Si/Al ratio [43], [49], lowers wax and long-chain HC production due to the high activity of the acid sites to hydrocracking, whilst increasing isoparaffins production due to isomerization [3], [6], [24],

[44], which leads to a high-quality fuel production due to an increase of the octane number [15] and of the fuels cold-flow properties [47]. Hence, the enormous advantage of silica-doped alumina is related with the direct synthesis of high-quality syncrude with controlled PD.

Nonetheless, it is noteworthy that the accessibility to the acid sites appears to be a more critical parameter in achieving one-stage FT process than acid concentration and strength [3], [15]. Moreover, metal and acid sites should be well balanced for a proper optimization of the bifunctional catalyst since abundant acid sites increase coke deposition and lead to secondary hydrocracking of the primarily formed C₅-C₂₀ HC, while too low acidic catalysts will not be capable of producing syncrude and isomers in acceptable amounts [47], [48], [50].

Daniell *et al.* (2000) [40] studied the influence of silicon addition to alumina on the surface acidity of the support. They concluded that even the addition of only 1.5 wt.% Si increased BAS strength, being the samples with a Si loading of 30-40 wt.% the ones that displayed the strongest BAS among all the range, while loadings higher than 40 wt.% showed no BAS of interest due to an encapsulation of the surface. Regarding LAS, all the samples up to 90 wt.% Si exhibited Lewis acidity. Hence, a silica-doped alumina support, with an optimal Si loading, can function as a bifunctional catalyst, containing active sites (namely Fe, Co, Ni or Ru) for chain growth and hydrogenation/dehydrogenation and, simultaneously, acid sites for hydrocracking and isomerization [6].

2.4.3 Promoters

A small amount of promoter is typically introduced into a Co-based catalyst [26], since it lowers the activation temperature, increases C₅₊ selectivity and activity (by reducing the formation of non-reducible cobalt oxides [3], [14], [24], [32], [33], [51]), and improves catalyst stability, which extends catalyst lifetime [20]. Nevertheless, promoter addition is not an assurance of a better catalyst [32] since it might lead to faster deactivation [52].

Promoters can be applied with different functions, *e.g.*, structural modifiers or stabilizers, and can be of various types, including transition metal oxides, alkali and alkaline earth metals, and noble metals [3]. Noble metals are the most commonly used promoters for Co-based catalysts [20], with Re being the most applied [3]. These promoters enhance hydrogen spillover, which improves CoO reduction through a shift in MSI [3], [33], [53], [54], increase Co dispersion and reducibility [3], [8], [14], [32], [33], [51], and prevent coke deposition [3], [32], although they can also block Co active sites if in higher amounts. Therefore, only a small load (about 0.1-0.5 wt. %) of promoter is added to the catalyst [3].

2.4.4 Catalyst preparation

The catalyst preparation method can influence the particle size, surface area and morphology of the catalyst [6], with the primary purpose being the production of stable cobalt-metal

surface sites [55]. For the development of a supported metal FT catalyst, the usual steps followed are outlined in Figure 2.7 [9].

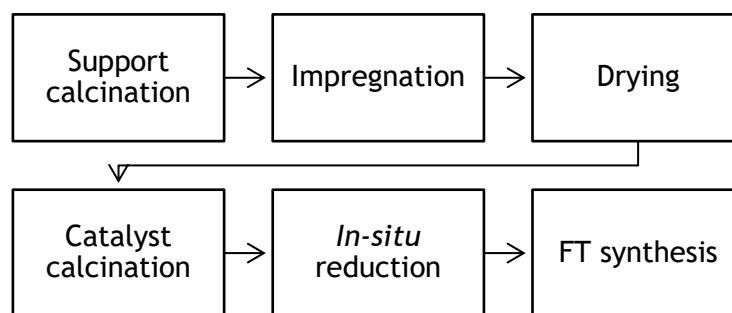


Figure 2.7: Steps for the preparation of a supported metal FT catalyst.

There are several methods available for the preparation of supported Co catalysts, the most common of which being incipient wetness impregnation (IWI). In this approach, Co precursor is added dropwise to the dried support under vacuum. Due to capillary suction, the solution is drawn into the pores of the support, filling them completely. MSI is relatively weak immediately after IWI, allowing for a redistribution of the active phase over the support surface during drying and calcination [24]. The Co precursor used can reduce catalytic performance due to its influence in MSI and Co dispersion [3], [12]. According to the literature, cobalt nitrate appears to be the ideal choice since it exhibits the highest degree of reduction, and average Co particle size, resulting in improved catalytic performance, with higher C₅₊ selectivity [3], [5], [56].

Catalytic performance is strongly influenced not only by the preparation method but by catalyst pretreatments as well [24]. Calcination is used to breakdown cobalt salt, in order to obtain supported cobalt oxide. Although high calcination temperatures (≈ 773 K) appear to increase Co stability and Co HCP phase fraction in the reduced catalyst, lower temperatures enhance CO conversion, catalytic activity, while decreasing CH₄ selectivity and cobalt-silica oxides formation [27]. Moreover, high calcination temperatures lead to the partial substitution of Co³⁺ ions by Al³⁺ in the matrix, which hinders Co reducibility [55] and, at temperatures above 573 K, silica migration occurs, which gives rise to more significant losses of surface area [38]. Notwithstanding, the effect of calcination conditions is poorly described in literature [9].

Reduction is also a crucial step in catalyst preparation since it reduces inactive cobalt oxide to active metallic cobalt, whereafter it remains in its metallic form under FT conditions. Cobalt is reduced from Co₃O₄ to CoO and, then, to Co⁰, as shown by Eq. 2.8 and Eq. 2.9, respectively [12], [24], [32]. Throughout this stage, the temperature must be kept below 623 K, since higher temperatures promote cobalt sintering and complicate Co diffusion into the support [24].



3 Materials and Methods

Because the support can have a strong impact on catalytic performance, the main purpose of this work was to evaluate the influence of Si doping over an alumina support on Co deposition and FT performance. To achieve this, a set of supports with varying silica loadings were used to support a Re-promoted cobalt catalyst. Furthermore, a parametric study on temperature, pressure, and GHSV, along with a study on promoter and pore volume influence and their effect on CO conversion was also carried out.

In this chapter, the properties of the supports employed are firstly presented. Then, the experimental procedure for catalyst synthesis is supplied, followed by the methodologies used for catalyst characterization, as well as the associated equipment and analytical conditions. Finally, a description of the catalytic tests and of the experimental setup is also provided.

3.1 Support characteristics

The catalysts used for this study were Co-based catalysts. To study the influence of silica-doped alumina catalyst, several Siral-x supports were evaluated, where x represents the silica weight fraction in the support. For reference, a boehmite with 0 wt.% Si (Pural) support was also tested on a catalyst. The supports were kindly supplied free of charge by Sasol and present the characteristics specified in Table 3.1, indicated by the supplier [57], where HPV stands for high pore volume.

Table 3.1: Chemical and physical properties of the tested Siral samples [57].

Chemical and physical properties	Siral-5	Siral-30	Siral-40	Siral-40 HPV
$\text{Al}_2\text{O}_3/\text{SiO}_2$ / wt. %	95.1 / 4.9	70.1 / 29.9	60.1 / 39.9	61.7 / 38.3
BET surface area / $\text{m}^2\cdot\text{g}^{-1}$	267	484	498	452

3.2 Catalyst synthesis

The catalysts were prepared using IWI. The supports were calcined at 823 K for 4 h (in case of alumina-based supports, to remove any organic components) or 5 h (in case of silica-doped alumina supports, to stabilize the material), with a heating ramp of $2\text{ K}\cdot\text{min}^{-1}$. Then, the calcined supports were sonicated at a constant temperature of 298 K (adding ice when needed to prevent heating) and under vacuum for 15 min. Afterwards, an aqueous solution of cobalt(II) nitrate hexahydrate, $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (Labbox, 99 %) and perrhenic acid, HReO_4 (Acro Organics, 99.99%) were added dropwise until the pores were filled. The necessary volume to entirely fill the pores was determined using a similar approach to what was stated, using water instead of Co and Re solutions. A scheme of the experimental setup is depicted in Figure 3.1 and the

quantities added of Co can be verified in Section 4.1.2. Given that the drying step is of extreme importance since the quick evaporation of the solvent can be responsible for an accumulation of metal species outside the pores, the catalysts were slowly dried in a muffle furnace using the following program: 313 K for 16 h, 323 K for 8 h, 333 K for 16 h, 343 K for 4 h and, lastly, 353 K for 2 h. Then, the catalysts were calcined at 673 K for 6 h, with $1.5 \text{ K} \cdot \text{min}^{-1}$ heating ramp. Finally, the calcined samples were reduced for 10 h in $30 \text{ mL} \cdot \text{min}^{-1} \text{ H}_2$ at 623 K, and a heating rate of $2 \text{ K} \cdot \text{min}^{-1}$.

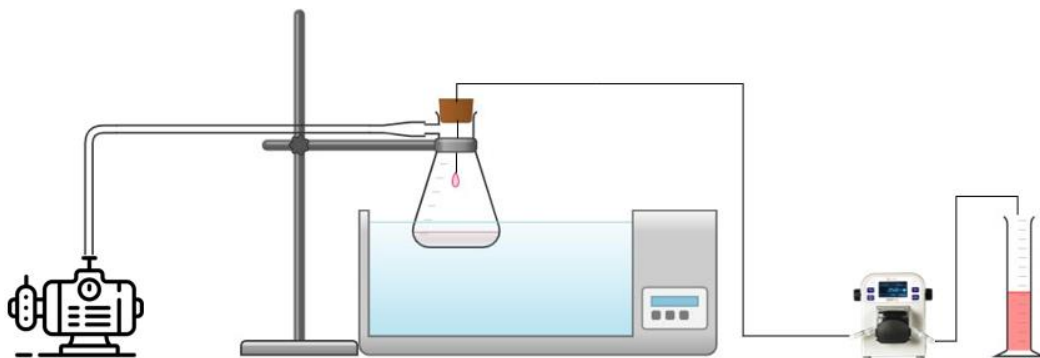


Figure 3.1: Experimental setup of catalysts preparation.

3.3 Characterization methods

Both the supports and the catalyst were characterized. It was used NH_3 temperature-programmed desorption (NH_3 -TPD), Hg porosimetry, He pycnometry and thermogravimetric analysis and differential scanning calorimetry (TGA/DSC) for the characterization of the supports, while the catalysts were characterized using inductively coupled plasma optical emission spectroscopy (ICP-OES), H_2 temperature-programmed reduction (H_2 -TPR), and scanning transmission electronic microscopy (STEM).

3.3.1 NH_3 -TPD

TPD is a method that can be applied to the study of the acidity (TPD of basic probe molecules, like NH_3) or basicity (TPD of acid probe molecules, such as CO_2) of various solids [58]. In NH_3 -TPD, NH_3 is adsorbed on the surface of the material, whereafter He is used to remove the chemically adsorbed NH_3 fraction. However, NH_3 can have chemical and physical adsorption, whereby a cleaning step for physisorbed NH_3 removal is needed. Afterwards, the analysis is performed while increasing the temperature so that more NH_3 is removed from the material. The chemisorbed NH_3 can be directly correlated with the peak area, PA, using the calibration curve described in Eq. 3.1, where U_{NH_3} corresponds to NH_3 uptake, in μmol per mass of support, w_{sample} , in g.

$$U_{\text{NH}_3} = \frac{PA \times 26.2 \times 10^{-3}}{w_{\text{sample}}} \quad \text{Eq. 3.1}$$

The analyses of the acidity of the supports prepared were performed in a unit developed at *Instituto Superior Técnico*, IST. 150 mg of sample were pretreated in He for 1 h at 623 K, after ramping at 5 K·min⁻¹. The materials were then saturated with 15% NH₃ in He for another hour at 398 K. Later, it was performed a cleaning step for the physisorbed NH₃ removal, which lasted for an hour at 423 K. Finally, the analysis *per se* was performed with 20 mL·min⁻¹ of He, with a temperature range between 423 K and 1023 K, and with a 10 K·min⁻¹ ramping rate. NH₃ desorption was detected using a thermal conductivity detector, TCD.

3.3.2 Hg porosimetry

Mercury porosimetry is a method widely used to analyze macroporosity and the wider part of mesoporosity. The technique is based on the penetration of mercury into the pores as a function of the applied pressure. It can cover pores ranging from 7.5 nm (at the usual high pressure of 200 MPa) to 15 µm (at atmospheric pressure). Nevertheless, this method can be quite destructive and only applies to uniformly cylindrical pores, representing poorly a real solid [58].

In practice, the sample is degassed in an oven at standardized conditions, being then subjected to a low pressure followed by a high pressure. The pressure is raised in stages and the liquid penetrates a pore with a radius r_p , in m, under a pressure P , in mPa, given by Washburn's equation, Eq. 3.2, where γ is the surface tension at the liquid-gas interface (480 mN·m⁻¹) and θ is the wetting angle of the liquid with the material (140°) [58].

$$P = \frac{-2 \cdot \gamma \cdot \cos\theta}{r_p} \quad \text{Eq. 3.2}$$

This measure allows for the estimation of the distribution of pores and total surface area [58] and it was performed using a Quantachrome Poremaster 60.

3.3.3 He pycnometry

Helium pycnometry is a complement to Hg porosimetry and is applied for the determination of true density, ρ_s (ratio between the mass of a solid and the volume of the material), and apparent density, ρ_g (ratio between the mass of a solid and the volume of the material and the void), both in g·cm³ of a porous solid. True and apparent density are calculated as shown in Eq. 3.3 and Eq. 3.4, respectively, where v (cm³) is the volume of He displaced by a given sample mass, m (g), and v' (cm³) is the volume of displaced by the materials and pores of a solid as a whole [58].

$$\rho_s = \frac{m}{v} \quad \text{Eq. 3.3}$$

$$\rho_g = \frac{m}{v'} \quad \text{Eq. 3.4}$$

This determination allows for the deduction of the total pores volume, V_p ($\text{cm}^3 \cdot \text{g}^{-1}$), and the porosity, ε , from Eq. 3.5 and Eq. 3.6, respectively [58].

$$V_p = \frac{1}{\rho_g} - \frac{1}{\rho_s} \quad \text{Eq. 3.5}$$

$$\varepsilon = 1 - \frac{\rho_g}{\rho_s} \quad \text{Eq. 3.6}$$

The He pycnometer unit used was developed at the Chemical Engineering Department of Faculty of Engineering of University of Porto (DEQ, FEUP).

3.3.4 TGA/DSC

TGA/DSC is a method that analyzes the mass variation of a given sample with temperature in a controlled atmosphere [59], [60]. This environment is often inert so that the material reacts exclusively to temperature during decomposition [59]. Weight loss, WL, and heat flow during the temperature increase can provide information on a wide range of physical and chemical reactions, such as absorption, desorption, decomposition, oxidation, reduction, or thermal stability [60]. Moreover, the first derivative of the TGA curve gives important information regarding the WL rate [59].

TGA/DSC was performed by IST in a SETSYS Evolution analyzer at a temperature range of 298-1073 K and a heating ramping rate of $10 \text{ K} \cdot \text{min}^{-1}$. The samples were heated under $30 \text{ mL} \cdot \text{min}^{-1}$ air flow.

3.3.5 ICP-OES

ICP-OES is a method employed for the qualitatively and quantitatively assessment of several elements [58] that was used, in this project, for the determination of the Co loading in each catalyst. This procedure entails converting a liquid sample into an aerosol of thin droplets via nebulization, which is then introduced into the core of the plasma through an Ar flow. Therefore, catalysts must be previously converted into liquids by acid digestion [58].

The samples were digested in a HCl solution, using a START D Microwave Digestion System, at 493 K for 15 min, and with a heating rate of $11 \text{ K} \cdot \text{min}^{-1}$, while measurements were taken with an iCAP 7400 ICP-OES Analyzer. The analyses were carried out at 318 K, with a sample injection volume of 10 mL. The calibration curve was plotted given the ICP multi-element standard solution IV provided by Merck (Ref. 111355), with concentrations ranging between 5 and 10000 ppb.

3.3.6 H_2 -TPR

H_2 -TPR is a technique used for the determination of the catalyst reducibility and the degree of oxidation of the active phase [58]. In this method, H_2 consumption is measured while the

catalyst is heated with a linear temperature rate [24], [58]. The interaction between H₂ and the catalyst leads to the reduction of different species, providing information about the catalyst redox properties [24].

The TPR profiles were computed using an Altamira AMI-200 chemisorption analyzer. 80 mg of sample were heated at a ramping rate of 10 K·min⁻¹ from 298 K to 1173 K. Simultaneously, a flow of 30 mL·min⁻¹ with 5 % H₂ in Ar was fed over the sample, allowing for H₂ consumption measurement with a TCD.

3.3.7 STEM

STEM is a method rather similar to transmission electron microscopy (TEM), which provides information about catalyst particle size, crystal morphology, and surface defects [6], [61] that was employed, in the present study, for the determination of cobalt particle size. This method operates at ultra-high vacuum (so that no collisions between the high energy electrons and air molecules occur [61]) and at room temperature, with atomic level resolution [24]. The electrons signal is quantified as a function of its position over the sample, yielding a detailed picture of the catalyst [61]. Nonetheless, the accuracy given by this method is highly reliant on the sample preparation and on the number of images taken since it is a local technique, thus not allowing for a global perspective of the material in analysis [24], [61], [62].

STEM and HAADF-STEM (high-angle annular dark-field STEM) observations were taken using a Hitachi HD2 700 B electron microscope operating at 200 kV. The samples were prepared by ultrasonic dispersion in an ethanol solution, and the suspensions were dropped on a copper carbon-coated grid. A mapping of Co distribution was performed using energy dispersive spectroscopy (EDS).

3.4 Catalytic tests

The catalytic tests were conducted in a bench-scale fixed-bed down-flow stainless steel SS316 reactor (Microactivity Effi, MAE, from PID Eng&Tech), with 306 mm height and 9.1 mm internal diameter. MAE's process control diagram is depicted in Figure 3.2. H₂, CO and N₂ (as an internal standard for gas chromatography) are fed to the top of the reactor and pass through the catalyst bed, which is placed on a 20 µm porosity sintered metal plate. After the FT reaction occurs, the products are routed via a wax trap at 403 K to condensate C₂₁₊ compounds. Then, at 288 K, the water and organic phase are condensed and after separated. Finally, the organic phase is collected for further offline analysis, while the gas phase is analyzed online using a gas chromatograph (GC). For all tests, a given mass of catalyst was placed in the reactor and silicon carbide was added until the sample volume reached 3 mL, as this reduces the occurrence of hot spots during the reaction due to its high thermal conductivity [63]. Since SiC should occupied at least 50 % of the total volume, the amount of catalyst added varied between 250, 500, or

750 mg due to their different apparent densities. The reactants were fed to MAE at 493 K, 20 bar, H_2/CO ratio of 2, and GHSV of $2.67\text{ m}^3\cdot\text{kg}_{\text{cat}}^{-1}\cdot\text{h}^{-1}$.

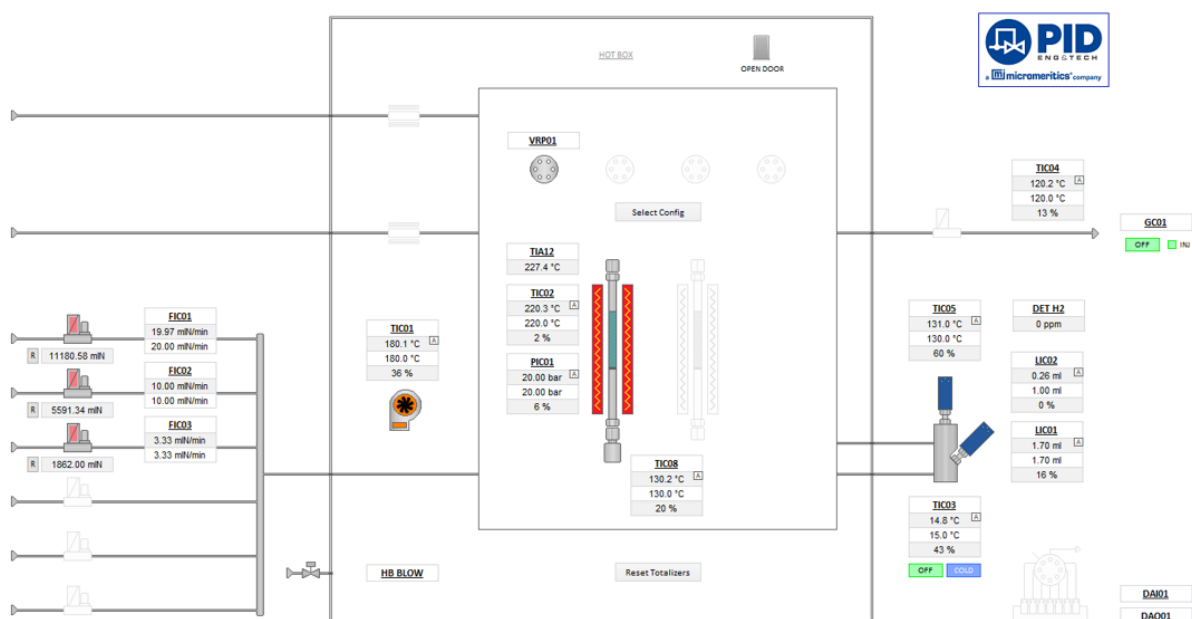


Figure 3.2: MAE's process control diagram.

3.4.1 Selectivity analyses

The gaseous products were examined online using a YL6500 (YL instrument CO. LTD) GC, fitted with two columns and a TCD, using He as the carrier gas. While the first column (VP-Molesieve with 30 m length, 0.53 mm internal diameter, and 15 μm film thickness) allowed for the separation of permanent gases, the second column (GS-GasPro, with 60m length, and 0.32 mm internal diameter) separated C_2 - C_6 HC. The peaks were calibrated using VGM-1 and VGM-3 certified standards, provided by MESA Specialty Gases & Equipment. The liquid products were analyzed offline using a Supelcowax 10 capillary GC column with 30m length, 0.32 mm internal diameter, and 0.25 μm film thickness, equipped with a FID and using He as the carrier gas. The peaks were calibrated using a C_5 - C_8 n-paraffin mix analytical standard and a C_7 - C_{30} saturated alkanes certified reference material, both provided by Sigma-Aldrich (Refs. 47100 and 49451-U, respectively). Moreover, a mix of C_7 n-paraffin, iso-paraffin and α -olefin, supplied by IST, was employed to establish the n-paraffin, α -olefin, isomers, and other olefins peaks sequence. Finally, the solid products, namely the waxes, were weighted in order to close the mass balance. The temperature program for both gaseous and liquid products analysis is depicted in Figure 3.3a and b, respectively.

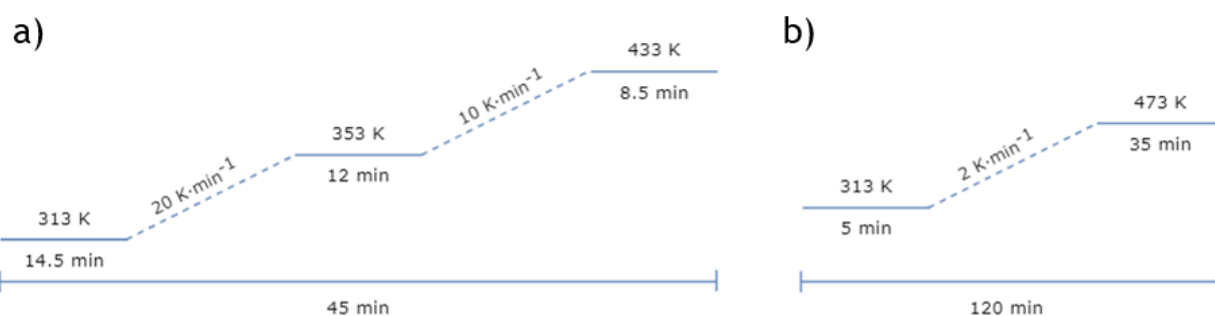


Figure 3.3: Temperature program for the GC analysis of a) gaseous and b) liquid products.

The amount of CO, CO₂ and CH₄, $F_{out,i}$, in mol·h⁻¹, where $i=CO$; CO₂; CH₄, was calculated using the calibration curves previously determined [64]. Moreover, the concentration of gaseous C₂-C₆ HC was deduced using the calibration curves plotted given the analyzed standards. All these curves are presented in Appendix A.1.

CO conversion, X_{CO} , in %, was obtained through the ratio between the residual amount of CO consumed, $F_{in,CO} - F_{out,CO}$, to the initial quantity of CO, $F_{in,CO}$, both in mol·h⁻¹, as exemplified in Eq. 3.7 [36], [65].

$$X_{CO} = \frac{F_{in,CO} - F_{out,CO}}{F_{in,CO}} \times 100 \quad \text{Eq. 3.7}$$

X_{CO} was, afterwards, normalized by Co loading in each catalyst so that a direct comparison could be made. This normalization is usually named cobalt-time yield, CTY, in mol_{CO}·g_{Co}⁻¹·s⁻¹, following Eq. 3.8, where w_{cat} is the catalyst weight, in g, $F_{in,CO}$ is the initial quantity of CO, in mol·s⁻¹, and y_{Co} is the Co loading, in wt.% [65].

$$CTY = \frac{F_{in,CO} \cdot X_{CO}}{w_{cat} \cdot y_{Co}} \quad \text{Eq. 3.8}$$

CO₂ and CH₄ selectivity, S_j , in %, where $j=CO_2$; CH₄, was obtained by dividing the quantity of the component in the outlet of the reactor, F_j , by the amount of CO consumed, as presented in Eq. 3.9 [36], [65].

$$S_{C_j} = \frac{n \cdot F_j}{F_{in,CO} - F_{out,CO}} \quad \text{Eq. 3.9}$$

Furthermore, C₂-C₂₀ selectivity, S_k , in %, where $k=2, 3, \dots, 20$ was calculated using Eq. 3.10, where TOS is the time on stream, in h, MM is the molar mass of the compound, in g·mol⁻¹, and w_{org} is the total weight of the organic fraction, in g.

$$S_k = \frac{w_{org}}{TOS} \times \frac{W_n}{MM} \times \frac{n}{F_{in,CO}} \quad \text{Eq. 3.10}$$

Finally, C_{21+} selectivity, $S_{C_{21+}}$, in %, was calculated as follows (Eq. 3.11) [36].

$$S_{C_{21+}} = 1 - (S_{CO_2} + S_{CH_4} + S_{C_2-C_{20}}) \quad \text{Eq. 3.11}$$

The amount of paraffins and olefins was estimated directly from the chromatograms. In the case of the liquid chromatogram and according to the standards used, the larger peak corresponds to n-paraffin and the second larger to α -olefin. The first peak, as well as the intermediate peaks between n-paraffin and α -olefin, correspond to iso-paraffins. Finally, the last peaks are secondary olefins. The peak distribution is exemplified in Figure 3.4 for C_9 . Regarding the gaseous products, all the paraffins and olefins order was obtained using the standards used.

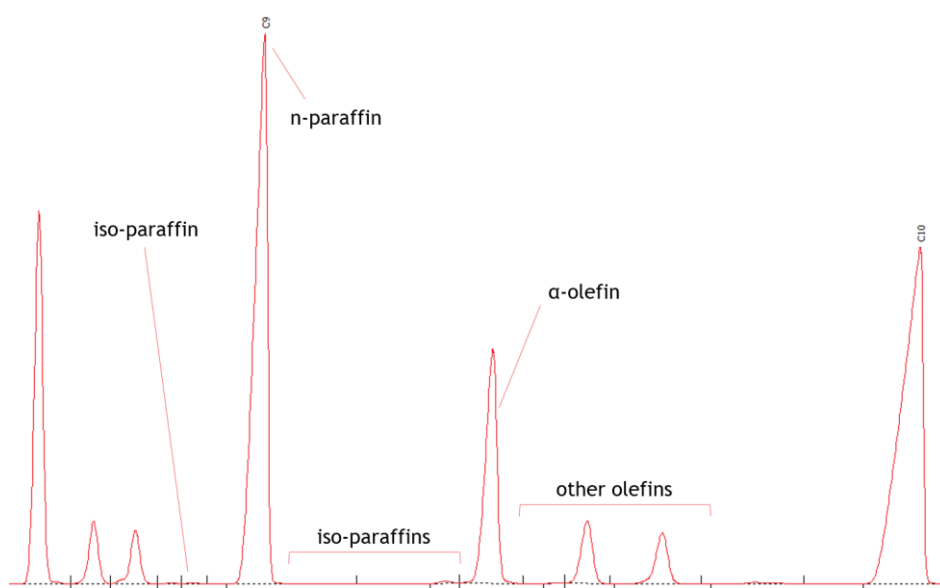


Figure 3.4: Representative image of the order of the peaks for C_9 compound.

The probability of chain growth was calculated using the logarithm of Eq. 2.6, indicated in Eq. 3.12 [6], taking into account only the linearity zone of each reaction, as exemplified in Appendix A.2. However, since the value calculated for chain growth probability only includes gaseous and liquid products (hence excluding waxes), it is not representative of the real value and product distribution and, thus, it will not be presented in the results that follow.

$$\log \frac{W_n}{n} = n \cdot \log \alpha + \log \frac{(1 - \alpha)^2}{\alpha} \quad \text{Eq. 3.12}$$

4 Results and discussion

Altogether, seven catalysts with different properties were prepared in this work. An alumina-supported catalyst was prepared and used as a reference. This catalyst was used to determine the best operating conditions by carrying out a detailed parametric study and to evaluate the influence of Re as a Co-catalyst promoter. In order to study the effect of Si doping on the alumina support, several boehmite-based materials containing different amounts of Si were tested. In this chapter, the characterization results obtained from the methods outlined in Section 3.3 will be presented and discussed. Moreover, the parametric study and the promoter influence on both CO conversion and PD will be analyzed in detail. Finally, the influence of Si-doped alumina supports on catalytic performance will be investigated, along with the influence of pore volume.

4.1 Properties of the supports and synthesized Co-based catalysts

In order to determine how the Si doping and Re promotion influence the catalytic performance, the prepared catalysts and supports were characterized using a variety of techniques previously described in Section 3.3. In this chapter, the results obtained with the characterization methods will be presented and discussed in detail.

4.1.1 Characterization of the supports

The supports were characterized by Hg porosimetry, He pycnometry and NH_3 -TPD. The results obtained via He pycnometry (ϵ), Hg porosimetry (V_p , in $\text{cm}^3 \cdot \text{g}^{-1}$, and average pore diameter, $d_{\text{av pore}}$, in nm), and NH_3 -TPD (U_{NH_3} , in $\mu\text{mol} \cdot \text{g}^{-1}$) are summarized in Table 4.1. The curves regarding NH_3 -TPD can be found in Appendix B.2.

Table 4.1: Results obtained for ϵ , V_p , in $\text{cm}^3 \cdot \text{g}^{-1}$, $d_{\text{av pore}}$, in nm, and U_{NH_3} , in $\mu\text{mol} \cdot \text{g}^{-1}$.

	Al_2O_3	Pural	Siral-5	Siral-30	Siral-40	Siral-40 HPV
ϵ	0.73	0.70	0.70	0.79	0.81	0.90
$V_p / \text{cm}^3 \cdot \text{g}^{-1}$	0.90	0.81	0.73	1.90	1.72	3.66
$d_{\text{av pore}} / \text{nm}$	40.6	11.0	19.5	25.9	63.9	182
$U_{\text{NH}_3} / \mu\text{mol} \cdot \text{g}^{-1}$	149	146	77	241	-	-

As visible, there is a rise in porosity, pore volume and size with increasing Si loading, with Siral-40 HPV, as the name indicates, the one that displayed the highest porosity of all. This improvement was already anticipated since an enhancement in these characteristics was observed in silica-doped alumina supports when compared to alumina [41], [42].

Pore size is a crucial parameter since it can affect Co particle size. Supports with narrow pores will result in the deposition of smaller Co particles which are hardly reduced, thus limiting

catalytic performance [6], [36], [66]. Larger pores, on the other hand, lead to a decrease in the amount of Co active sites, which also results in a loss of performance. Consequently, pore size should be in the ideal range of 6-10 nm [6], [36], which is not the case with the catalysts under consideration; hence, there is space to improve catalytic performance employing the analyzed supports.

The strong BAS concentration was determined quantitatively analyzing the second peak of NH_3 -TPD spectra (Table 4.1). It is important to notice that only this peak was analyzed since, at lower temperatures, NH_3 desorption could be due to both desorption from structural defects (related to weak LAS) and to physisorbed NH_3 , which would alter the results. According to the literature, increasing Si/Al ratio enhances acid concentration [43], [44], [49], with no big differences in acidic concentration expected for Si additions below 10 % [40]. Thus, it was expected a rise in U_{NH_3} in the order $\text{Al}_2\text{O}_3 \approx \text{Pural} < \text{Siral-5} < \text{Siral-30}$; instead, it is verified that 5 % silica addition results in a decrease in BAS concentration. This drop could be related to the analysis and thus, it should be repeated to ensure its reproducibility. Despite Siral-40 acid concentration has not been determined, it is assumed that its value would be somewhat similar to Siral-30, according to the information conveyed by the supplier. Additionally, according to Daniell *et al.* (2000) [40], the samples Siral-30 and Siral-40 are the ones that displayed the strongest BAS among all the 0-100 wt.% Si range. This occurs because, when 30 wt.% of Si is added to alumina, the surface of the support transitions from three phases (alumina, silica, and aluminosilicate) to only two (silica and aluminosilicate). The number of exposed aluminosilicate sites, which present the highest acidity, reaches a maximum with Siral-40 [40]. However, when 40 wt.% Si is added, the alumina surface is encapsulated by Si species, which reduces acidity [40], [67]. One can suggest that this occurs due to a decrease of Si^{4+} on alumina sites, along with a lower accessibility of the reactants to the acid sites already created. Thus, an assessment of Siral-40 acidity is needed for further conclusions.

Since Siral-30 could be the one presenting the highest acidity and, thus, the higher FT activity towards gasoline and jet fuel production, its weight loss was measured using TGA/DSC analysis. Pural WL was also measured for comparison. The TGA/DSC spectra of the two supports are depicted in Figure 4.1. According to the available data, a unique decomposition peak between 340-465 K is observed, which is related to the evaporation of physically adsorbed water [41], [68]. DSC also exhibits a single exothermic peak at 380-390 K related to water removal from the supports [68]. Furthermore, a small peak seems to appear at 890 K for Siral-30, which might be due to particle agglomeration. Regarding stability, Pural support presents a higher decomposition temperature (380 K compared to 372 K of Siral-30), which is indicative of a higher thermal stability. Despite the fact that Si doping is reported to enhance the support's thermal stability [41], the higher stability observed with Pural may be attributed to its pore size, as

smaller pores have been shown to improve stability [69]. Nonetheless, the temperature difference between the two supports is lower than 10 K, hence no major conclusion can be drawn on this subject. Moreover, WL did not stabilize completely but rather continues to increase despite the low rate. This might be the result of a system rearrangement and some particle agglomeration. The materials present a total overall WL of *ca.* 12.3% and 16.0% and attain stability (WL<1%) at 720 and 770 K for Pural and Siral-30, respectively. Thus, it is assumed that a calcination temperature of 823 K was sufficient for full stability of all the materials tested in this dissertation.

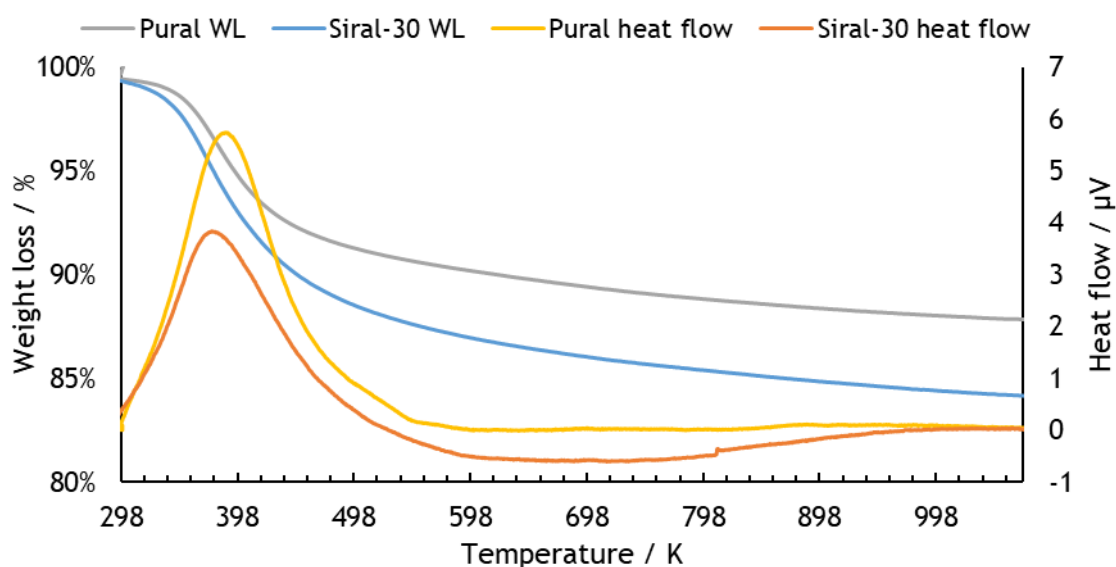


Figure 4.1: TGA/DSC spectra of Pural and Siral-30 supports.

4.1.2 Characterization of the catalysts

Regarding the catalysts, their characterization was performed using ICP-OES for the determination of Co loading, STEM for the measurements of the Co particle size, and H₂-TPR for the determination of catalyst reducibility. In Table 4.2 it is possible to verify Co loading, in wt.%, and Co average particle size, d_{Co} , in nm.

Table 4.2: Co loading, in wt.%, and particle size, in nm, of the prepared catalysts.

Catalyst	Co loading ^a / wt.%	d_{Co} ^b / nm
Co-Re/Al ₂ O ₃	7.56	9.7
Co-Re/Pural	6.46	8.0
Co-Re/Siral-5	6.88	-
Co-Re/Siral-30	7.50	7.6
Co-Re/Siral-40	6.96	-
Co-Re/Siral-40 HPV	8.69	-
Co/Al ₂ O ₃	6.82	-

^aMeasured by ICP-OES; ^bMeasured by STEM

The goal of the work was the addition of 10wt.% Co to each catalyst. However, the real loading was somewhat lower, which could be related to an inaccurate measurement of the necessary volume to fill the pores. Moreover, if the pore volume of the support is not sufficiently high, one impregnation might not be enough to achieve the desired Co loading [34]. Hence, to be able to do a direct comparison between the prepared catalysts, CO conversion was normalized by the Co content in each sample, which is known by CTY.

Moreover, Co particle size were studied using STEM analysis. A TEM image of Co-Re/Siral-30 catalyst is depicted in Figure 4.2a, where Co particles correspond to dark spots, while Figure 4.2b uses HAADF-STEM, where the cobalt particles (in white) are better identified. The red square shows an example of a Co particle in each image. STEM and HAADF-STEM imaging of the Co-Re/ Al_2O_3 and Co-Re/Pural catalysts were obtained as well and can be found in Appendix B.3, which includes an EDS mapping of a particle zone to verify the Co distribution.

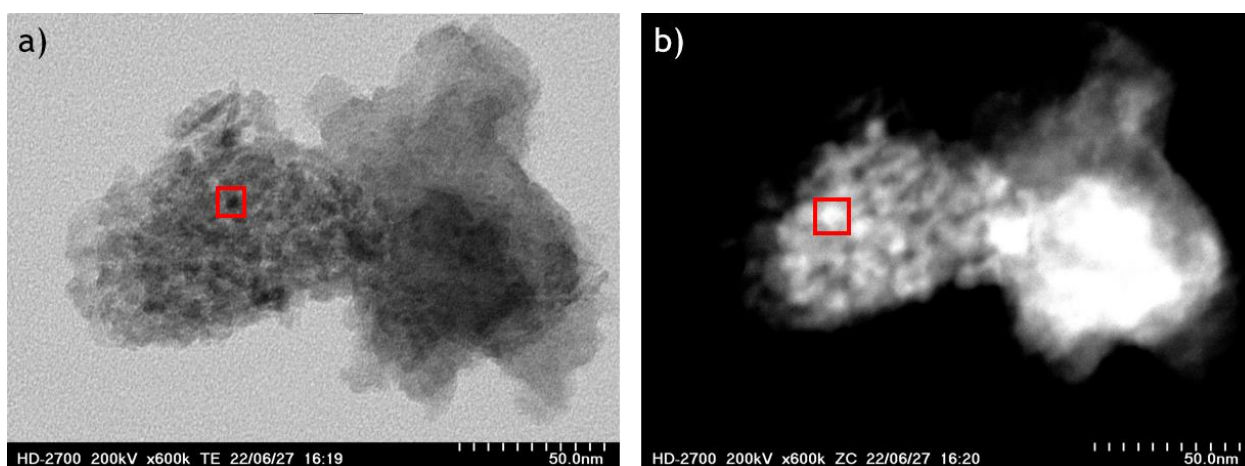


Figure 4.2: Co-Re/Siral-30 catalyst analysis by a) TEM and b) HAADF-STEM.

By analyzing Figure 4.2, one can see that cobalt was successfully impregnated in the support. The same conclusion can be drawn for Co-Re/ Al_2O_3 and Co-Re/Pural catalysts and it is expected that the remaining materials follow the same pathway, despite the need to perform an analysis of them as well. Moreover, it is confirmed that an overall good Co dispersion was attained, despite some clusters also being present. Concerning Co particle size, samples Co-Re/ Al_2O_3 , Co-Re/Pural, and Co-Re/Siral-30 yielded 9.7 ± 3.9 nm, 8.0 ± 2.4 nm and 7.6 ± 3.2 nm, respectively. Notwithstanding the values obtained being rather similar, they were estimated from under 100 particles, which, although providing a general idea, are not enough to give a statistically significant particle size distribution. Nonetheless, it is believed that the particle size of the catalysts is within the optimal range of ca. 6-10 nm.

FTS reduction behavior can be influenced by a variety of factors, including support composition, metal precursor and loading, promoters, and catalyst preparation method [42]. To study the influence of the support composition on Co reducibility, H_2 -TPR method was performed. The

curves obtained for Co-Re/Pural, Co-Re/Siral-5, Co-Re/Siral-30, Co-Re/Siral-40, and Co-Re/Siral-40 HPV are given in Figure 4.3.

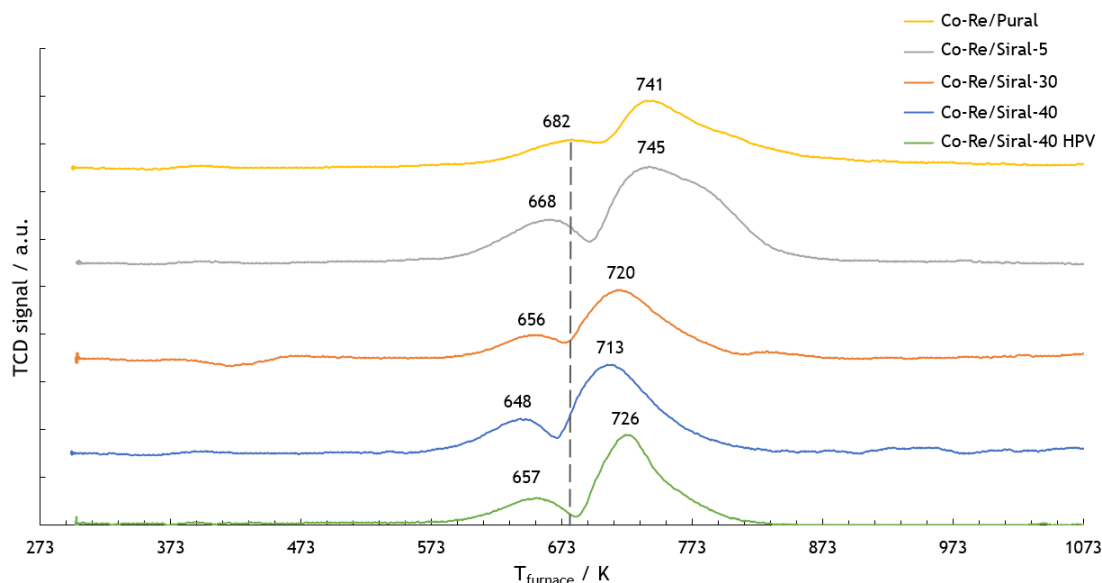


Figure 4.3: H_2 -TPR curves of Co-Re/Pural, Co-Re/Siral-5, Co-Re/Siral-30, Co-Re/Siral-40, and Co-Re/Siral-40 HPV.

Analyzing Figure 4.3, the presence of two broad peaks and a first small peak at *ca.* 395 K can be seen. This peak is probably related to the decomposition of residual undecomposed cobalt nitrate species in H_2 that remained during calcination stage [12], [42]. The first large peak occurs at 648–682 K and is usually attributed to the two-step reduction $Co_3O_4 \rightarrow CoO \rightarrow Co^0$ [44], [52], [70]. This reduction can be observed as one or two peaks, depending on whether the reduction sequence is sufficiently resolved or not [51], [71].

Regarding the second peak, between 713–745 K, it is usually assigned to the reduction of cobalt species interacting with the support [8], [12], [44], [63], [70]. Moreover, this peak presents a shoulder in the Co-Re/Pural and Co-Re/Siral-5, which could be due to the existence of mixed cobalt oxides, such as cobalt silicate and cobalt aluminate, with different degrees of interaction with the support [54], [70] as a function of cluster size, since smaller Co particles present greater interactions with the support and, hence, are reduced at higher temperatures [54]. In the samples with higher amounts of silica, namely 30 and 40 wt.%, this shoulder presents as an individual peak, around 830–880 K, which can be a result of Co particles inside the inner pores of silicon support, which require higher temperatures for reduction [3].

From these results, the degree of reducibility follows the order Co-Re/Siral-40 > Co-Re/Siral-30 $\approx$ Co-Re/Siral-40 HPV > Co-Re/Siral-5 > Co-Re/Pural. This shows that the silicon doping shifts the reduction peaks to lower temperatures, which is indicative of a decrease in MSI [42], [63] and, hence, a decrease in the formation of hardly reducible cobalt oxide phases [12], [63]. Furthermore, and despite the fact that it is not readily apparent, an increase in pore volume could be affecting Co reducibility as well.

Moreover, an H_2 -TPR analysis of $Co-Re/Al_2O_3$ and Co/Al_2O_3 was performed to check the promoter influence on Co reducibility. Both profiles can be visualized in Figure 4.4.

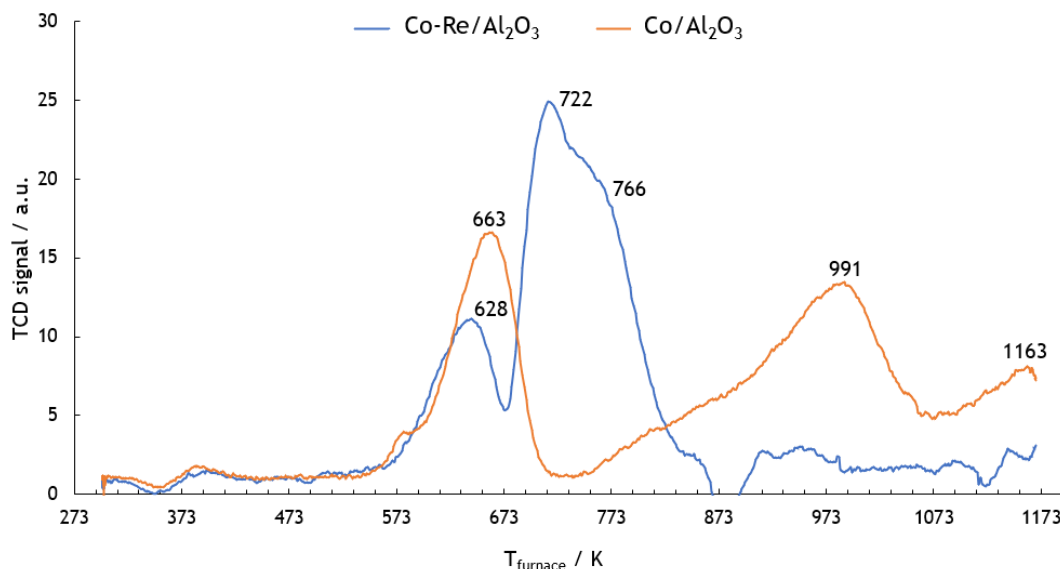


Figure 4.4: H_2 -TPR profiles of $Co-Re/Al_2O_3$ and Co/Al_2O_3 .

As is noticeable, the low-temperature peaks are not affected by the presence of Re, with only small differences visible between the promoted and unpromoted catalysts. Re reduction peak usually falls in *ca.* 720 K [8], [51], which can explain the lack of effect of Re on the low-temperature peak since it does not present yet in the reduced state. Regarding the high-temperature peak, there is a shift from 991 K to 722 K with Re addition, along with a shortening of its tailing, confirming the influence of the promoter on Co reducibility [8], [15], [33]. Moreover, it is probable that this peak is overlapping with the Re-reduction peak [32], [51]. Finally, the unpromoted catalyst shows a peak at 1163 K, which is related to the reduction of cobalt-aluminate oxides, which presents at a much lower temperature in the Re-promoted catalyst.

4.2 Catalytic performance

As stated before, the reactants were fed to the MAE unit at a constant temperature, pressure, and flow rate. In Appendix C.1 the evolution of these parameters along with the reaction may be observed, as well as the evolution of the liquids' formation (specifically, water and hydrocarbons) with TOS.

4.2.1 Parametric study of the $Co-Re/Al_2O_3$ base catalyst

The aim was to work under optimal operating conditions, targeting an approximate 40-50 % conversion rate since higher rates enhance WGS reaction and frequently result in catalyst oxidation due to H_2O and CO_2 production [6], [22]. Therefore, a parametric study was performed

on Co-Re/Al₂O₃ base catalyst so that an evaluation of the operating conditions could be made. The data obtained for each parametric study can be found in Appendix C.2.

Pressure

The reaction performance was studied at different pressure levels, ranging from 5 to 30 bar, in order to explore its impact on FTS. In Figure 4.5 it can be seen CO conversion, in %, as a function of pressure, in bar, whose values resulted from a TOS of 4 h.

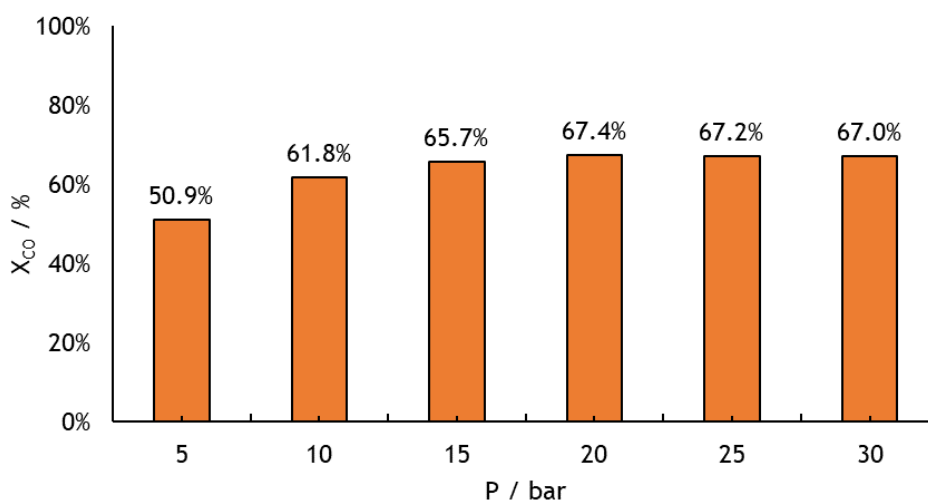


Figure 4.5: CO conversion, in %, as a function of P, in bar for a Co-Re/Al₂O₃ catalyst. Reaction conditions: GHSV of 2.67 m³·kg_{cat}⁻¹·h⁻¹, 493 K and H₂/CO ratio of 2.

As expected, there is an increase in CO conversion with pressure up to 20 bar, with the main increase occurring between 5 and 10 bar. Above 20 bar the conversion is rather similar, with only a 0.4 % variance. As a result, it can be inferred that 20 bar seems to be a reasonable pressure value for the reaction to operate at. Nonetheless, and as previously noted, the pressure effect on CO conversion is less pronounced, with a variation of only 16.1 % between 5 and 30 bar.

Temperature

To investigate the influence of temperature in FTS, the reaction performance was examined at various temperatures, ranging from 463 to 513 K (approximately LTFT range). In Figure 4.6 it can be seen CO conversion, in %, as a function of temperature, in K, whose values resulted from a TOS of 4 h.

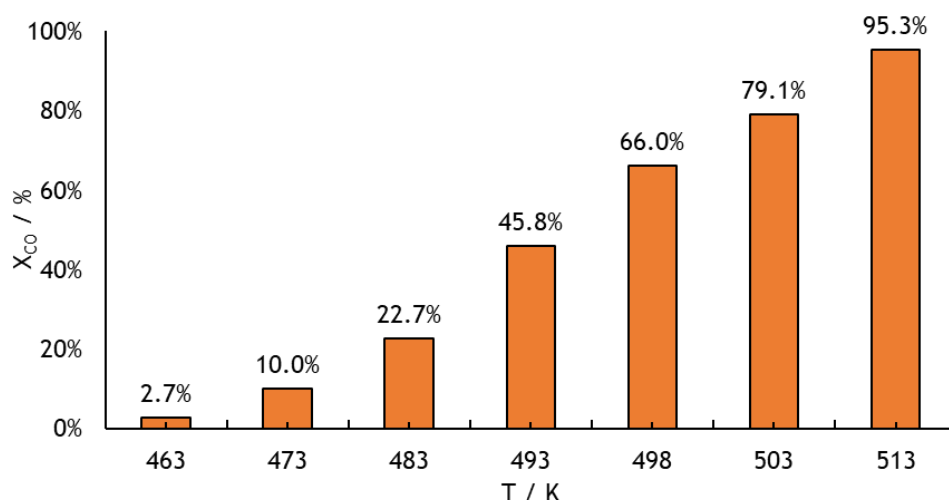


Figure 4.6: CO conversion, in %, as a function of T, in K for a Co-Re/Al₂O₃ catalyst. Reaction conditions: GHSV of 2.67 m³·kg_{cat}⁻¹·h⁻¹, 20 bar and H₂/CO ratio of 2.

As predicted, an increase in temperature causes a nearly proportionate increase in CO conversion, with the latter varying *ca.* 93 %, showing a strong FTS sensitivity to temperature. As previously stated, the goal was to work at a 50% conversion, hence, 493 K appears to be the best temperature choice, presenting a conversion rate of 45.8 %. Furthermore, the activation energy was determined considering the LTFT process (473-513 K), and a reasonable linear correlation was found, for which a value of 119.1 kJ·mol⁻¹ was attained (see Appendix C.3). This is in good agreement with the literature, with reported values that fall in the range of 67-129 kJ·mol⁻¹ for Co-based catalysts [23], [32], [72].

GHSV

To study the influence of GHSV in FTS, the reaction performance was analyzed at 1.33, 2.00, 2.67, 4.00, 5.33, and 6.67 m³·kg_{cat}⁻¹·h⁻¹. Figure 4.7 depicts CO conversion, in %, as a function of GHSV, in m³·kg_{cat}⁻¹·h⁻¹, whose data derived from a TOS of 4 h.

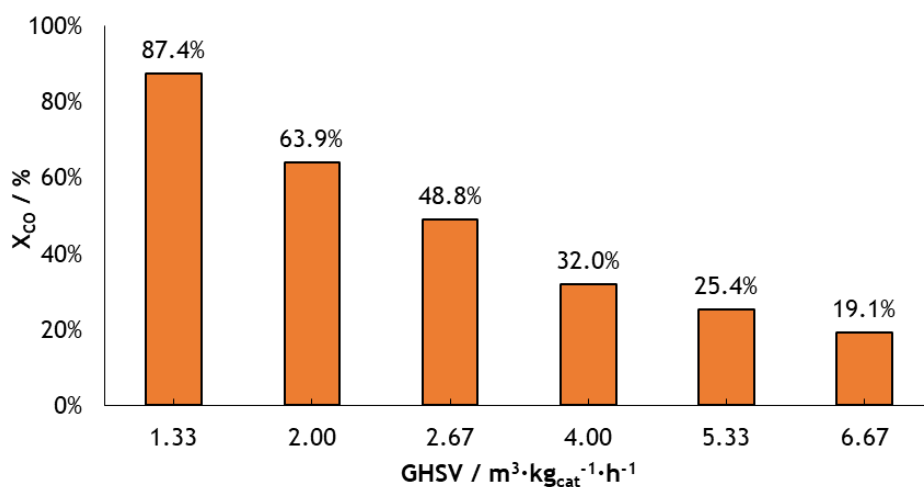


Figure 4.7: CO conversion, in %, as a function of GHSV, in m³·kg_{cat}⁻¹·h⁻¹ for a Co-Re/Al₂O₃ catalyst. Reaction conditions: 20 bar, 493 K, and H₂/CO ratio of 2.

As can be evaluated, CO conversion decreases with GHSV since an increase in the latter leads to a shorter contact period between the syngas and the catalyst, and hence, to a lower activity. The chosen GHSV value was $2.67 \text{ m}^3 \cdot \text{kg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, since it presented a conversion of 48.8%.

4.2.2 Promoter influence on FTS

A study was conducted on a $\text{Co}/\text{Al}_2\text{O}_3$ catalyst to evaluate Re influence on CO conversion, as well as in PD. The findings for CTY, as well as CO_2 , CH_4 , $\text{C}_2\text{-C}_4$, and C_{5+} selectivities for an un-promoted and Re-promoted Al_2O_3 -supported Co catalyst are summarized in Table 4.3. Figure 4.8 shows $\text{C}_1\text{-C}_{20}$ selectivities for both catalysts in greater detail.

Table 4.3: CTY, and CO_2 , CH_4 , $\text{C}_2\text{-C}_4$, and C_{5+} selectivities for an un-promoted and Re-promoted Co catalyst.

Catalyst	CTY / $10^5 \text{ mol}_{\text{CO}} \cdot \text{g}_{\text{Co}}^{-1} \cdot \text{s}^{-1}$	Selectivity / %			
		CO_2	CH_4	$\text{C}_2\text{-C}_4$	C_{5+}
$\text{Co}/\text{Al}_2\text{O}_3$	4.31	0.3	6.0	0.3	93.5
$\text{Co-Re}/\text{Al}_2\text{O}_3$	6.29	0.4	4.6	0.5	94.5

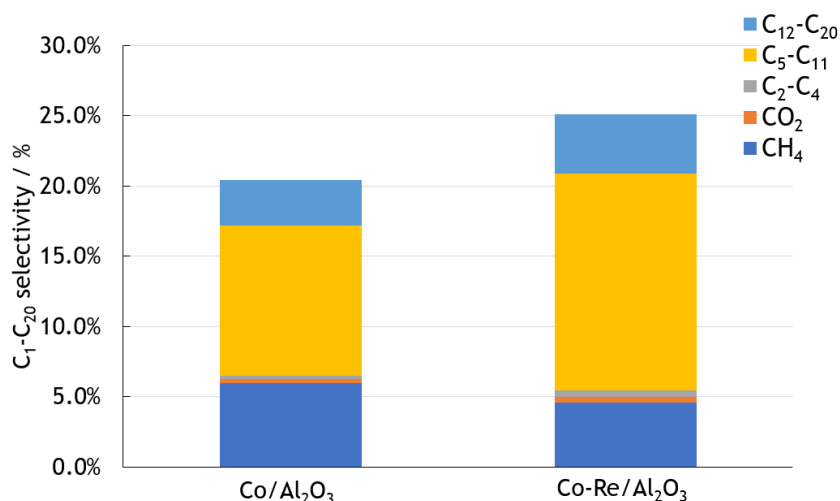


Figure 4.8: $\text{C}_1\text{-C}_{20}$ selectivities for an un-promoted and Re-promoted Al_2O_3 -supported Co catalyst.

Analyzing the data, it is clear that Re addition causes a high increase in CTY, which is consistent with the literature [27], [32], [33]. This occurs because the increase in FT activity following Re addition is often due to a proportionate increase in Co dispersion [33].

Moreover, despite no noticeable difference in C_{5+} selectivity, there is an increase in gasoline and jet fuel fractions with Re addition. Furthermore, CH_4 selectivity decreased, while that of CO_2 increased by about 50% on the Re-promoted catalyst. This can be explained by the high proneness of Re for CO adsorption, which, according to Eq. 2.5, results in CO_2 production [8]. However, there is no consensus on the Re effect on selectivity, with some authors describing a minor effect [8], [33], [73], [74], or no effect at all [9], [32], [75]-[77]. Nonetheless, it has been reported that PD is remarkably sensitive to the operating conditions and CO conversion

level and, because the increase in C_{5+} selectivity is quite low, distinguishing Re influence on selectivity from experimental mistakes can be demanding [33].

Concerning productivity, Table 4.4 depicts the effect of Re addition on waxes, water and organics specific yield, as well as in $C_{olefin}/C_{n-paraffin}$ (C_{ole}/C_n) and $C_{iso-paraffin}/C_{n-paraffin}$ (C_{iso}/C_n) ratios, while Figure 4.9 presents the C_5 - C_{20} product distribution for the two catalysts tested.

Table 4.4: Waxes, water and organics specific yield, C_{ole}/C_n and C_{iso}/C_n ratios for an un-promoted and Re-promoted Co catalyst.

Catalyst	Specific yield / $g_{product} \cdot g_{Co}^{-1}$			C_{ole}/C_n	C_{iso}/C_n
	Waxes	Water	Organics		
Co/ Al_2O_3	24.7	70.0	13.0	0.68	0.02
Co-Re/ Al_2O_3	83.6	85.6	19.5	0.66	0.03

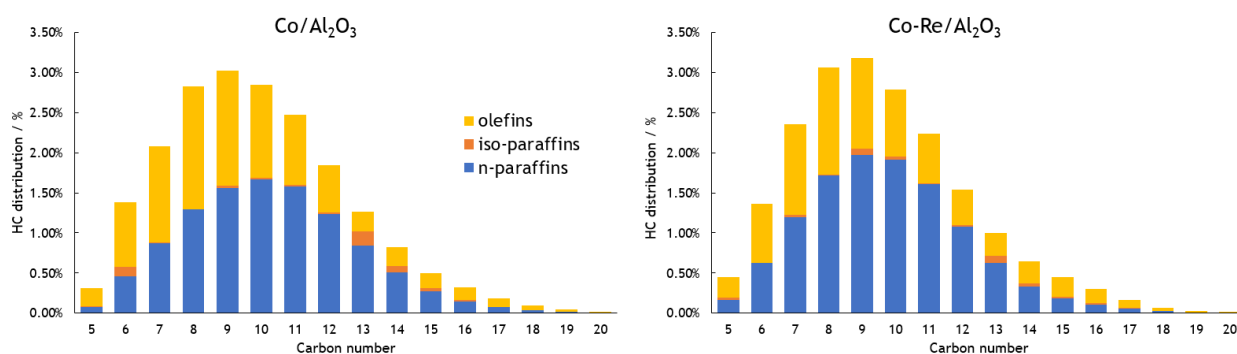


Figure 4.9: C_5 - C_{20} HC distribution for an un-promoted and Re-promoted Al_2O_3 -supported Co catalyst.

As noticeable, addition of Re results in more than a three-fold increase in waxes yield, along with a 33% increase in that of organics. Additionally, regarding PD, one can deduce that Re has no effect since, according to Figure 4.9, no perceptible difference can be found; thus, it can be concluded that, despite the lack of variation in C_{5+} selectivity, its production is considerably enhanced.

4.2.3 Catalytic performance of Co-Re/Siral-x

To study the influence of a silica-doped alumina support on FTS, three supports with three different Si loadings were tested: 5, 30, and 40wt.%. Moreover, Co-Re/Pural was also tested as a reference. The results concerning CTY, and CO_2 , CH_4 , C_2 - C_4 and C_{5+} selectivities for the catalysts are presented in Table 4.5, while Figure 4.10 depicts C_1 - C_{20} selectivities.

Table 4.5: CTY, and CO₂, CH₄, C₂-C₄, and C₅₊ selectivities for a Co-Re/Pural, Co-Re/Siral-5, Co-Re/Siral-30, and Co-Re/Siral-40 catalyst.

Catalyst	CTY / 10 ⁵ mol _{Co} ·g _{Co} ⁻¹ ·s ⁻¹	Selectivity / %			
		CO ₂	CH ₄	C ₂ -C ₄	C ₅₊
Co-Re/Pural	5.02	0.4	4.6	0.5	94.5
Co-Re/Siral-5	5.66	0.3	4.6	0.4	94.7
Co-Re/Siral-30	3.92	0.2	6.9	0.6	92.3
Co-Re/Siral-40	4.62	0.2	7.7	0.5	91.7

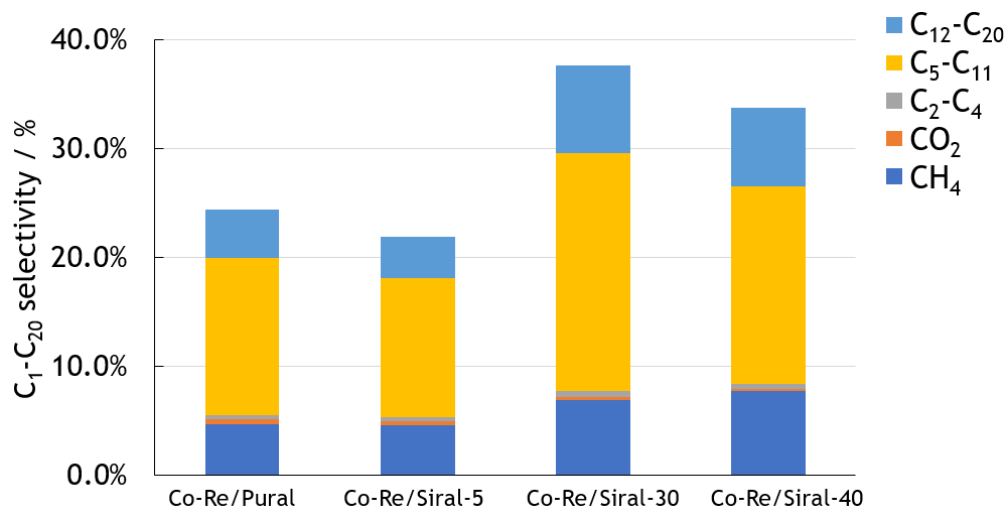


Figure 4.10: C₁-C₂₀ selectivities for a Co-Re/Pural, Co-Re/Siral-5, Co-Re/Siral-30 and Co-Re/Siral-40 catalyst.

According to the data, there are no major differences for the sample containing 5 % Si, which was predicted since low additions of silicon do not significantly modify BAS and LAS strength of the support when compared to Pural itself [40]. However, when 30 % or 40 % of Si is added to the support, it is possible to see a slight decrease in CTY. C₅₊ selectivity follows the same pathway, which is consistent with what was expected since Si acidity increases waxes hydrocracking, resulting in the formation of lighter HC. This is supported by Figure 4.10, which shows an increase in C₅-C₁₁ and C₁₂-C₂₀ selectivities, with Co-Re/Siral-30 exhibiting the highest selectivity for gasoline, jet fuel, and diesel fractions (29.9 % compared with 25.5 % of Co-Re/Siral-40, 18.9 % of Co-Re/Pural, and 16.5 % of Co-Re/Siral-5). CO₂ selectivity decreases owing to an increase in metallic cobalt over oxide phases, since, while metallic Co is active to CO dissociation, the oxide phases adsorb CO and lead to a higher WGS rate, and hence to an increase in CO₂ selectivity [78]. The fact that this selectivity is low in all the tested catalysts indicates a good Co reducibility [12]. Moreover, CH₄ selectivity increases up to 7.7 % with Si loading due to an increase of hydrocracking to lighter carbons.

The yield of waxes, water and organics was also studied. Table 4.6 displays these data, as well as C_{ole}/C_n and C_{iso}/C_n ratios. To complete, Figure 4.11 presents C₅-C₂₀ HC distribution for the four tested catalysts.

Table 4.6: Waxes, water and organics specific yield, C_{ole}/C_n and C_{iso}/C_n ratios for a Co-Re/Pural, Co-Re/Siral-5, Co-Re/Siral-30, and Co-Re/Siral-40 catalyst.

Catalyst	Specific yield / $g_{product} \cdot g_{Co}^{-1}$			C_{ole}/C_n	C_{iso}/C_n
	Waxes	Water	Organics		
Co-Re/Pural	24.1	90.0	15.9	1.11	0.06
Co-Re/Siral-5	83.3	70.7	15.5	0.83	0.04
Co-Re/Siral-30	5.4	98.8	24.5	0.63	0.10
Co-Re/Siral-40	5.3	100.6	22.0	0.42	0.09

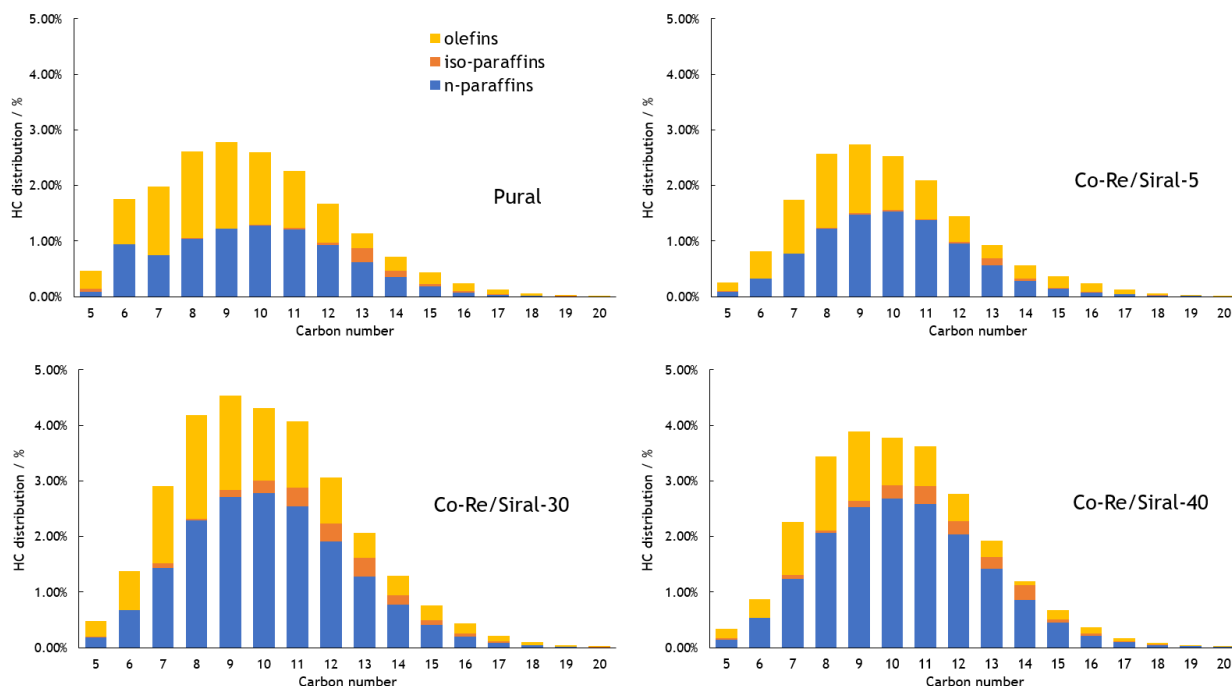


Figure 4.11: C_5 - C_{20} HC distribution for a Co-Re/Pural, Co-Re/Siral-5, Co-Re/Siral-30, and Co-Re/Siral-40 catalyst.

Regarding waxes yield, it is possible to understand that it decreases for the catalysts with Siral-30 and Siral-40 supports, which is consistent with what was previously mentioned. The increase in waxes yield with Co-Re/Siral-5 compared with Co-Re/Pural is in agreement with NH_3 -TPD analysis, which showed that a 5 % Si addition leads to a two-fold decrease in strong BAS. This result might be related to the calcination process of the samples and thus, to their thermal stability; nonetheless, further research on this topic is needed. Organics specific yield reaches its maximum with the catalyst prepared with Siral-30, while water presents a high yield for all catalysts as a result of WGS reaction, which, in Co catalysts, uses nearly all of the oxygen present from CO dissociation for water production [15].

In terms of product distribution, there is a noticeable increase in C_5 - C_{20} HC fraction. Furthermore, as the amount of Si increases, the C_{ole}/C_n ratio decreases, and more isomers are produced. All these results are in good agreement with those reported in the literature, which suggests that the rates of isomerization and hydrocracking are highly reliant on BAS concentration [43]. Thus, one can infer that acidic sites achieve their peak with Siral-30 support

rather than Siral-40, despite further research being required to establish any type of conclusion in this matter.

4.2.4 Long-period TOS study of Co-Re/Siral-30 catalyst

Since Co-Re/Siral-30 appears to present the desired characteristics regarding product yields and PD, a long-term study was conducted to assess its catalytic performance after 25, 50, and 75 h of TOS. The results regarding CTY, and CO₂, CH₄, C₂-C₄ and C₅⁺ selectivities are shown in Table 4.7, while Figure 4.12 provides C₁-C₂₀ selectivities after 25, 50 and 75 h on stream.

Table 4.7: CTY, and CO₂, CH₄, C₂-C₄, and C₅⁺ selectivities for the Co-Re/Siral-30 catalyst after a TOS of 25, 50 and 75 h.

TOS	CTY / 10 ⁵ mol _{CO} ·g _{Co} ⁻¹ ·s ⁻¹	Selectivity / %			
		CO ₂	CH ₄	C ₂ -C ₄	C ₅ ⁺
0-25 h	4.52	0.2	7.0	0.4	92.3
25-50 h	4.23	0.2	7.6	0.4	91.8
50-75 h	3.85	0.2	7.8	0.3	91.7

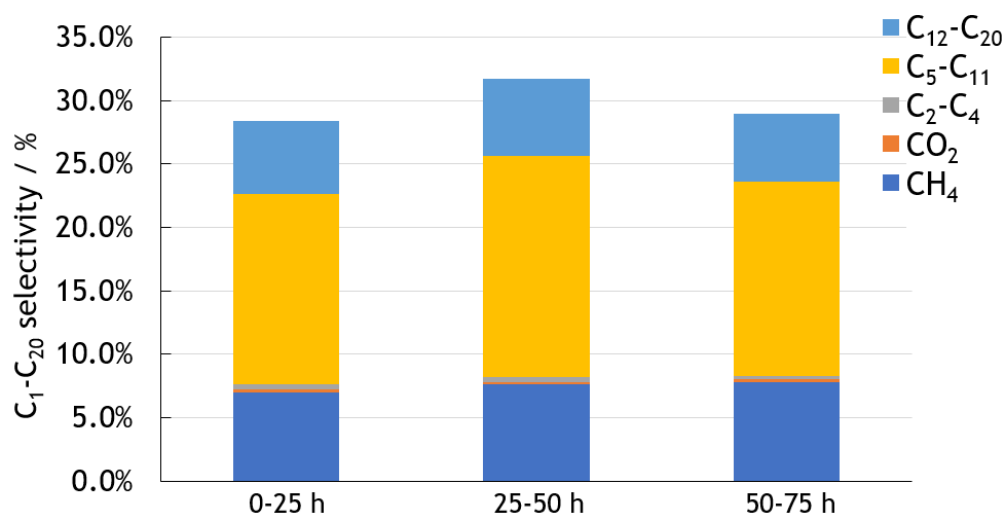


Figure 4.12: C₁-C₂₀ selectivities for the Co-Re/Siral-30 catalyst after a TOS of 25, 50 and 75 h.

Regarding CTY, a minor deactivation of the catalyst may result in a predicted reduction with TOS. Concerning selectivity, there is an enhancement of CH₄ formation and a reduction in C₅⁺ selectivity, while CO₂ and C₂-C₄ remain relatively unchanged. In terms of C₅-C₂₀ selectivity, it is possible to verify that it reaches its peak between a TOS of 25-50 h, which is a result of catalyst stabilization.

To verify what has been mentioned, waxes, water, and organics specific yield, as well as C_{ole}/C_n and C_{iso}/C_n ratios have been measured. These results can be verified in Table 4.8, while Figure 4.13 depicts product distribution after 25, 50 and 75 h on stream.

Table 4.8: Waxes, water and specific yield, C_{ole}/C_n and C_{iso}/C_n ratios for the Co-Re/Siral-30 catalyst after a TOS of 25, 50 and 75 h.

TOS	Specific yield / $g_{product} \cdot g_{Co}^{-1}$			C_{ole}/C_n	C_{iso}/C_n
	Waxes ^a	Water	Organics		
0-25 h		85.7	17.4	0.56	0.06
25-50 h	50.9	76.8	16.9	0.60	0.09
50-75 h		77.1	14.7	0.61	0.08

^aDue to equipment limitations, waxes could only be recovered at the end of the reaction.

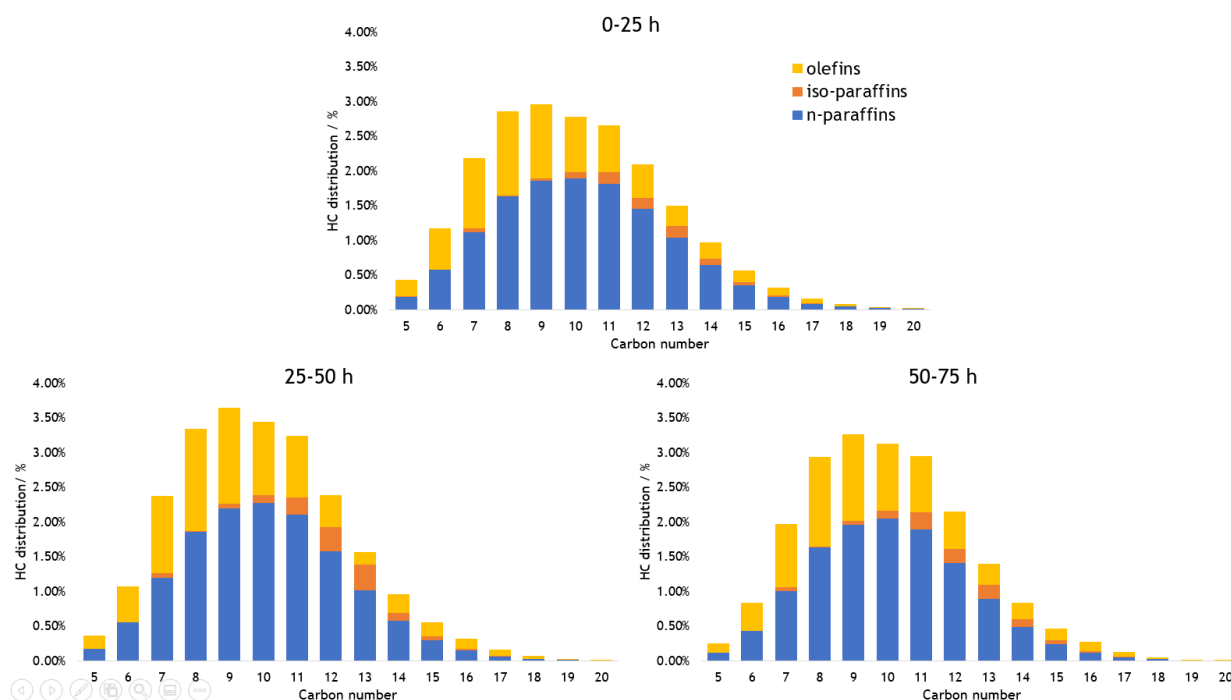


Figure 4.13: C_5 - C_{20} HC distribution for the Co-Re/Siral-30 catalyst after 25, 50 and 75 h.

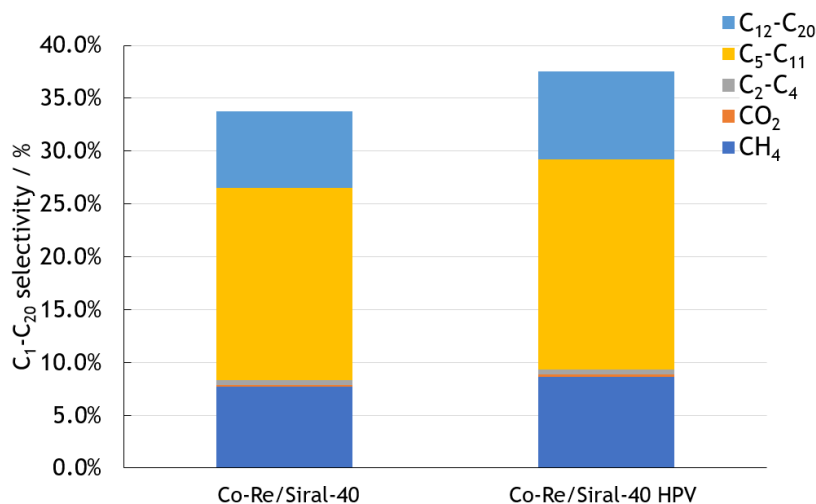
Concerning the specific yields, a decrease with TOS can be noticed, which was expected. Even though waxes could not be recovered until the end of the reaction due to equipment limitations, it is believed that its yield would follow the same tendency. Finally, there is an increase in both C_{ole}/C_n and C_{iso}/C_n ratios until 50h on stream, above which the values stabilize, demonstrating a high stability of the catalyst.

4.2.5 Pore volume influence for Co-Re/Siral-40 catalyst

A small study on the pore volume influence on FTS was carried out as well. For that, a Co-Re/Siral-40 HPV was analyzed and compared to a reference catalyst, Co-Re/Siral-40. The results regarding CTY, and CO_2 , CH_4 , C_2 - C_4 , and C_{5+} selectivities for the HPV and the reference catalyst are displayed in Table 4.9, whereas Figure 4.14 shows C_1 - C_{20} selectivities.

Table 4.9: CTY, and CO₂, CH₄, C₂-C₄, and C₅₊ selectivities for the Co-Re/Siral-40 and Co-Re/Siral-40 HPV catalysts.

Catalyst	CTY / 10 ⁵ mol _{Co} ·g _{Co} ⁻¹ ·s ⁻¹	Selectivity / %			
		CO ₂	CH ₄	C ₂ -C ₄	C ₅₊
Co-Re/Siral-40	4.62	0.2	7.7	0.5	91.7
Co-Re/Siral-40 HPV	4.27	0.2	8.7	0.5	90.7

Figure 4.14: C₁-C₂₀ selectivities for the Co-Re/Siral-40 and Co-Re/Siral-40 HPV catalysts.

Analyzing Table 4.9, it is possible to see that increasing pore volume and size leads to a decrease in CTY. However, no significant differences can be found regarding CO₂, CH₄ and C₂-C₄ selectivities. Despite C₅₊ selectivity has the same absolute value, its range slightly differs since, as the volume of the pores increases, selectivity shifts towards C₅-C₂₀ range.

To evaluate the pore effect on PD, waxes, water and organics specific yields were analyzed, together with C_{ole}/C_n and C_{iso}/C_n ratios, as well as the PD between C₅-C₂₀ HC range. These results can be found in Table 4.10 and Figure 4.15, respectively.

Table 4.10: Waxes, water and organics specific yield, C_{ole}/C_n and C_{iso}/C_n ratios for the Co-Re/Siral-40 and Co-Re/Siral-40 HPV catalysts.

Catalyst	Specific yield / g _{product} ·g _{Co} ⁻¹			C _{ole} /C _n	C _{iso} /C _n
	Waxes	Water	Organics		
Co-Re/Siral-40	5.3	100.6	22.0	0.42	0.09
Co-Re/Siral-40 HPV	8.9	103.5	26.8	0.68	0.24

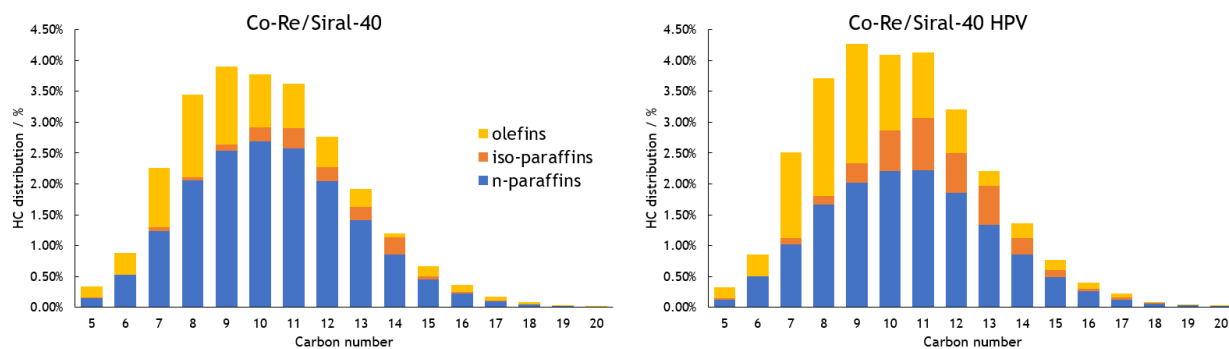


Figure 4.15: C₅-C₂₀ HC distribution for the Co-Re/Siral-40 and Co-Re/Siral-40 HPV catalysts.

The major differences between the two catalysts resides in PD rather than selectivity. Regarding specific yields, all three products have increased, with wax seeing the greatest enhancement (68% increase), despite the high activity for hydrocracking with increasing pore volume. Moreover, both C_{ole}/C_n and C_{iso}/C_n ratios are enhanced, which was also expected since larger pore sizes and volume contribute to longer residence times inside the catalyst and, thus, to an enhancement in isomerization for isoalkanes synthesis [3], [39]. Regardless of what has been observed, this study requires a deeper insight for further and more general conclusions since only the impact of the pores on Siral-40 was investigated.

5 Conclusion

The aim of this work was centered on the study of the influence of Si addition to an alumina-supported and Re-promoted cobalt catalyst on the Fischer-Tropsch synthesis (FTS) performance. For that, a variety of boehmite-based materials were tested with varying Si loading (Co-Re/Pural, Co-Re/Siral-5, Co-Re/Siral-30, and Co-Re/Siral-40, with 0, 5, 30, and 40 wt.% Si, respectively), along with a high pore volume support catalyst (Co-Re/Siral-40 HPV) and an unpromoted and Re-promoted alumina-based catalysts (Co/Al₂O₃ and Co-Re/Al₂O₃).

The best operating conditions for FTS operating in a fixed-bed reactor were determined by carrying out a detailed parametric study on pressure, temperature, and GHSV. Pressure was varied between 5 and 30 bar, and only a slight influence on CO conversion was detected. Temperature, on the other hand, was varied between 463 and 513 K, which corresponds to a CO conversion variation from *ca.* 3 % to 95 %, respectively, which is indicative of the large influence that temperature has on FTS. Finally, GHSV was varied between 1.33 and 6.67 m³·kg_{cat}⁻¹·h⁻¹, and a decrease was seen in CO conversion rate from about 87 % to 19 %. Since the goal was to maintain a conversion of 40-50 %, the operating conditions were chosen as follows: pressure of 20 bar, temperature of 493 K, GHSV of 2.67 m³·kg_{cat}⁻¹·h⁻¹, and H₂/CO ratio of 2.

A study conducted on a Co/Al₂O₃ catalyst to evaluate Re influence in cobalt-time yield (CTY) and in product distribution (PD) was also performed. This study showed that, since Re increases Co dispersion, a higher CTY is yielded. Moreover, specific yields demonstrated a three-fold increase in waxes yield, along with a 33 % increase in that of organics.

From the analyses of the boehmite-based catalysts, no major differences for the catalyst with 5 wt.% Si were found. In contrast, when 30 or 40 wt.% of Si is added to the boehmite support, organics specific yield is enhanced while that of waxes decreases. Si doping also reduces C₅₊ selectivity and olefin production, while increasing C₅-C₂₀ selectivity. This occurs due to an enhancement of catalytic acid sites concentration (Brønsted acid sites in particular) with the Si/Al ratio. A higher acidity lowers wax and long-chain hydrocarbons production due to an enhancement of hydrocracking activity. Besides this shift in PD, more isomers are produced since higher acidity increases the rate of isomerization. These two processes are strongly dependent on the acidic sites of the catalyst, which seems to reach its peak for the Co-Re/Siral-30 sample. Thus, a long-period time on stream (TOS) study was performed, where PD and selectivity were evaluated after 25, 50 and 75 h on stream. It was found a minor decrease in CTY and C₅₊ selectivity with TOS due to a small catalyst deactivation, indicating excellent catalytic stability.

Finally, a small study on pore volume was performed using Co-Re/Siral-40 and Co-Re/Siral-40 HPV, being found a 68 % increase in waxes specific yield and an enhancement of isomers formation. However, no major difference was observed regarding selectivity.

As future work perspectives, it is advised a STEM analysis for the determination of Co particle size for the remaining samples, since this is a parameter that can highly influence catalytic performance, along with a TGA/DSC analysis to confirm the thermal stability of the materials for the whole Si range.

The major objective of this work was to perceive Si influence on alumina-supported catalysts. It was demonstrated a better performance and a PD towards gasoline and jet fuel fraction when Co-Re/Siral-30 catalyst was employed, which one can assume that it is due to the highest acidity demonstrated. Nonetheless, Co-Re/Siral-40 acidity concentration was not measured, which should be a future matter of study to further confirm the results here obtained. More specifically, a pyridine adsorption/desorption followed by FTIR analysis should be performed in all samples to quantify the amount of Brønsted and Lewis acid sites. Moreover, a range of boehmite-based supports with Si loading between 5 % and 30 % should also be analyzed so that a potential tendency with Si addition, and thus intermediate acidities could be clearer. Finally, efforts should be directed towards the analysis of both the aqueous phase and waxes to identify and quantify other reaction products, which would in turn clarify mechanistic aspects of side reactions taking place during the main FT reaction.

This work will facilitate further research on acidity of silicon and its influence on FT performance at CoLAB Net4CO₂. Moreover, it is anticipated that this study could provide the necessary tools for future enhancement of the Siral-30 support, and thus, of its FT performance in NetMIX microreactors.

6 Assessment of the work done

6.1 Objectives Achieved

The main objective of this dissertation was to prepare single catalysts containing dual functionalities. This was successfully achieved using a boehmite-based support doped with different amounts of Si (Siral- x , where x corresponds to the weight fraction of doped Si and has the value of 0, 5, 30 and 40 wt.%) to deposit Co-Re metals and studying their influence over both the catalytic activity and product distribution during the FT reaction.

The FT reactions with the catalysts described above were carried out using the best operating conditions for fixed-bed reactors, which were identified after a detailed parametric study where the influence of pressure, temperature and GHSV was successfully evaluated.

The results obtained in this dissertation will provide an important contribution towards the catalytic performance of NetMIX-based reactors currently being developed at CoLAB Net4CO₂.

6.2 Other Work Carried Out

Aside from the work herein described, a study on the influence of the alumina support particle size was carried out as well, using ball-milling. Alumina samples, which consist of 50 μm diameter, were ball-milled varying the mass of sample, milling time and revolutions per minute, being thereafter evaluated its influence on particle size using Beckman Coulter LS230 and scanning electron microscopy.

The sample with the desired particle size distribution was, then, subjected to a catalytic test and its performance (CTY, specific yield and product selectivity and distribution) was compared with the reference and with a 100 nm diameter alumina.

6.3 Final Assessment

I believe that the research conducted during this dissertation is extremely valuable to CoLAB Net4CO₂ since it provides a deeper knowledge of silica-doped alumina supports and their application on FTS, which has received little attention in the literature. This work established a baseline for comparison with previously tested zeolites catalysts and provided CoLAB Net4CO₂ with the means to continue the research on acidity and its impact on catalytic performance for future application on a NetMIX-based unit. From a personal level, this work was extremely enriching since it gave one the opportunity to work on the field of cleaner and sustainable fuels production, while demonstrating that, despite the challenge of studying a topic that is not fully developed, it is possible to get closer to carbon neutrality.

7 References

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Appendix A - Selectivity analyses

A.1 CO, CO₂, CH₄, gaseous C₂-C₆, and liquids C₆-C₃₀ calibration curves

CO calibration curve

$$F_{out,CO} = \frac{F_{in,N_2}}{(1 - 0.96621 \times PA_{CO}^{1+0.01907})(1 + 0.98798 \times PA_{CO}^{1+0.01907})} \times \frac{0.96621 \times PA_{CO}^{1+0.01907}}{(1 + 0.98798 \times PA_{CO}^{1+0.01907})}$$

CO₂ calibration curve

$$F_{out,CO_2} = \frac{F_{in,N_2}}{1 - 0.76534 \times PA_{CO_2}} \times 0.76534 \times PA_{CO_2}$$

CH₄ calibration curve

$$F_{out,CH_4} = \frac{F_{in,N_2}}{1 - 0.92681 \times PA_{CH_4}} \times 0.92681 \times PA_{CH_4}$$

Gaseous C₂-C₆ calibrations curves

$$[C_2] = 0.8086 \times PA$$

$$[C_4] = 0.5269 \times PA$$

$$[C_5] = 0.4609 \times PA$$

$$[C_6] = 0.5097 \times PA$$

Where [C_i] corresponds to the C_i (i=2, 4, 5, 6) concentration, in ppm, and PA stands for the peak area of the component normalized by N₂ peak area.

Liquid C₆-C₃₀ calibrations curves

$$[C_6] = 0.0785 \times area$$

$$[C_7] = 0.0785 \times area$$

$$[C_8] = 0.0771 \times area$$

$$[C_9] = 0.0747 \times area$$

$$[C_{10}] = 0.0741 \times area$$

$$[C_{11}] = 0.0744 \times area$$

$$[C_{12}] = 0.0701 \times area$$

$$[C_{13}] = 0.0672 \times area$$

$$[C_{14}] = 0.0644 \times area$$

$$[C_{15}] = 0.0607 \times area$$

$$[C_{16}] = 0.0552 \times area$$

$$[C_{17}] = 0.0453 \times area$$

$$[C_{18}] = 0.034 \times area$$

$$[C_{19}] = 0.0245 \times area$$

$$[C_{20}] = 0.0175 \times area$$

$$[C_{21}] = 0.0137 \times area$$

$$[C_{22}] = 0.00950 \times area$$

$$[C_{23}] = 0.00745 \times area$$

$$[C_{24}] = 0.00694 \times area$$

$$[C_{25}] = 0.00603 \times area$$

$$[C_{26}] = 0.00530 \times \text{area}$$

$$[C_{27}] = 0.00443 \times \text{area}$$

$$[C_{28}] = 0.00496 \times \text{area}$$

$$[C_{29}] = 0.00432 \times \text{area}$$

$$[C_{30}] = 0.00432 \times \text{area}$$

Where $[C_j]$ corresponds to the C_j ($j=6, 7, \dots, 30$) concentration, in ppm, and area stands for the peak area of the component.

A.2 Chain growth probability calculation

For example, for Co-Re/ Al_2O_3 and Co-Re/Siral-30:

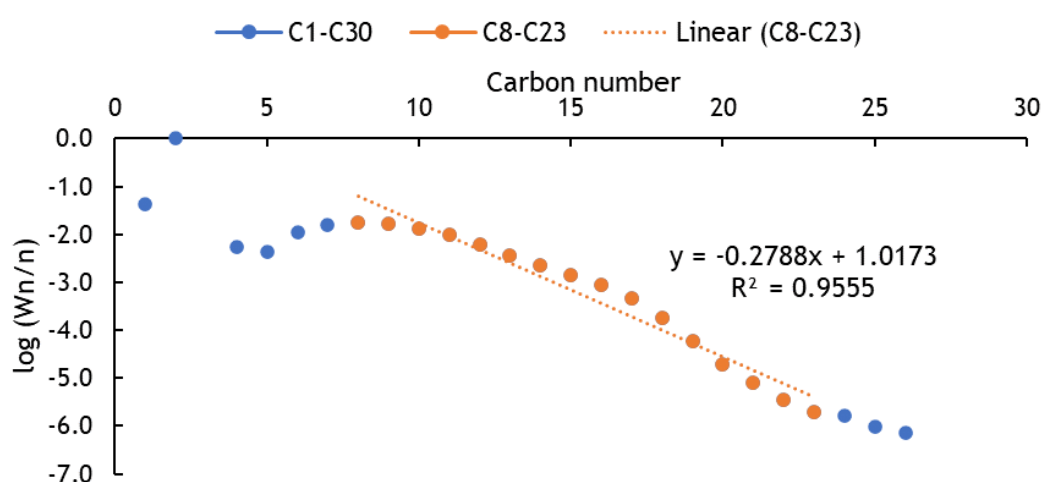


Figure A.1: $\log(Wn/n)$ as a function of carbon number for a Co-Re/ Al_2O_3 catalyst C_1 - C_{30} and C_8 - C_{23} HC distribution.

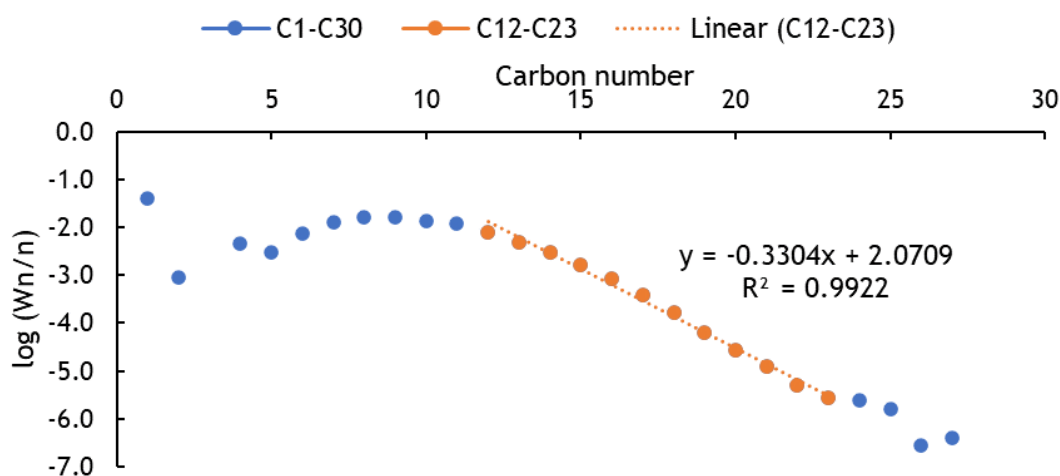


Figure A.2: $\log(Wn/n)$ as a function of carbon number for a Co-Re/Siral-30 catalyst C_1 - C_{30} and C_{12} - C_{23} HC distribution.

Appendix B - Characterization methods

B.1 Polarization intensity differential scattering, PIDS

Polarization intensity differential scattering, PIDS, is a technique that allows for the determination of particle size between 0.04 and 0.4 μm . This method is used in conjunction with laser diffraction that analyzes particles with diameters ranging from 0.4 to 2000 μm . These approaches are employed simultaneously since smaller particles present identical shapes and intensities of light scattering patterns, making laser diffraction measurements less accurate. On the other side, PIDS exhibits different scattering patterns and fine structures, allowing for the correct determination of PSD [79]. For the measurements, the supports were diluted in water and the analysis *per se* was carried out using a Beckman Coulter LS230. The results regarding the particle size of the supports can be found in Table B.1.

Table B.1: Particle size distribution and average diameter, in μm , for Pural, Siral-5, Siral-30, Siral-40 and Siral-40 HPV supports.

	Pural	Siral-5	Siral-30	Siral-40	Siral-40 HPV
Particle size < 10 μm / %	1.94	10.3	3.80	4.03	6.13
Particle size < 25 μm / %	4.61	32.1	9.28	12.3	10.9
Particle size < 50 μm / %	14.1	54.9	21.0	26.5	19.6
Particle size < 75 μm / %	35.1	76.2	36.0	40.0	32.4
Particle size < 90 μm / %	64.5	96.7	50.0	51.5	44.9
d_{average} / μm	24.4	58.9	24.5	27.4	22.9

B.2 NH_3 -TPD

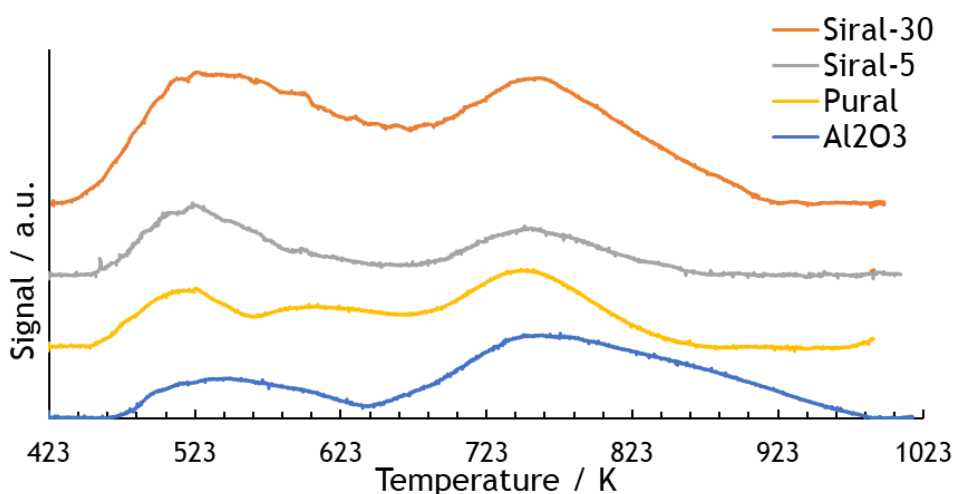


Figure B.1: NH_3 -TPD spectra for Al_2O_3 , Pural, Siral-5, and Siral-30 supports.

B.3 STEM

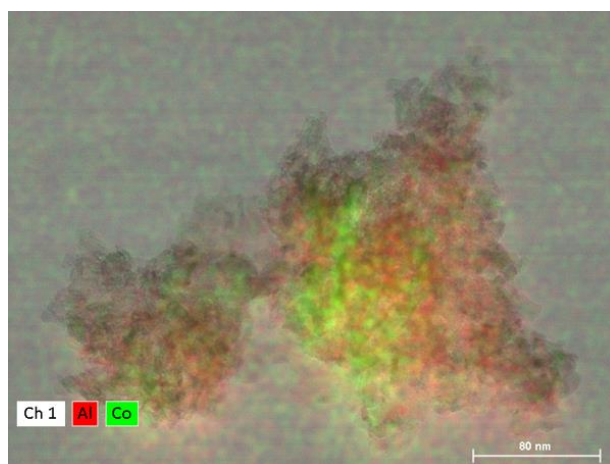


Figure B.2: EDS mapping of alumina (in red) and cobalt zones (in green).

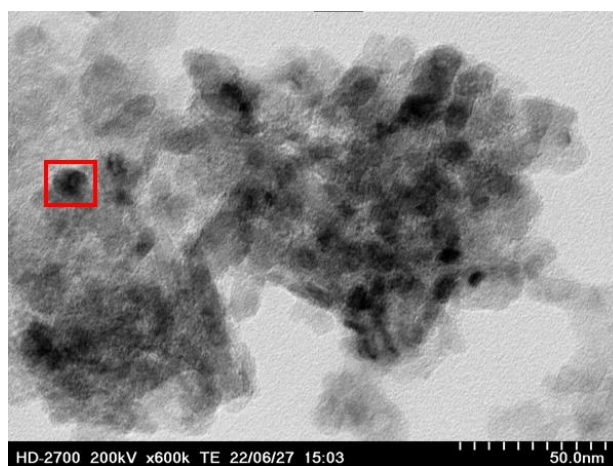


Figure B.3: Al_2O_3 catalyst analysis by TEM.

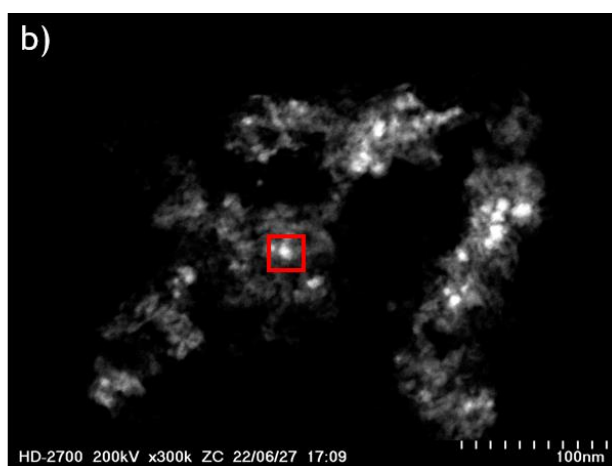
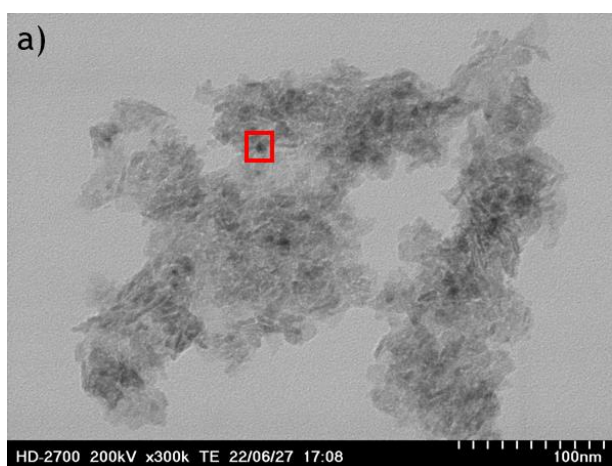


Figure B.4: Co-Re/Pural catalyst analysis by a) TEM and b) HAADF-STEM.

Appendix C - Catalytic performance

C.1 Reaction parameters

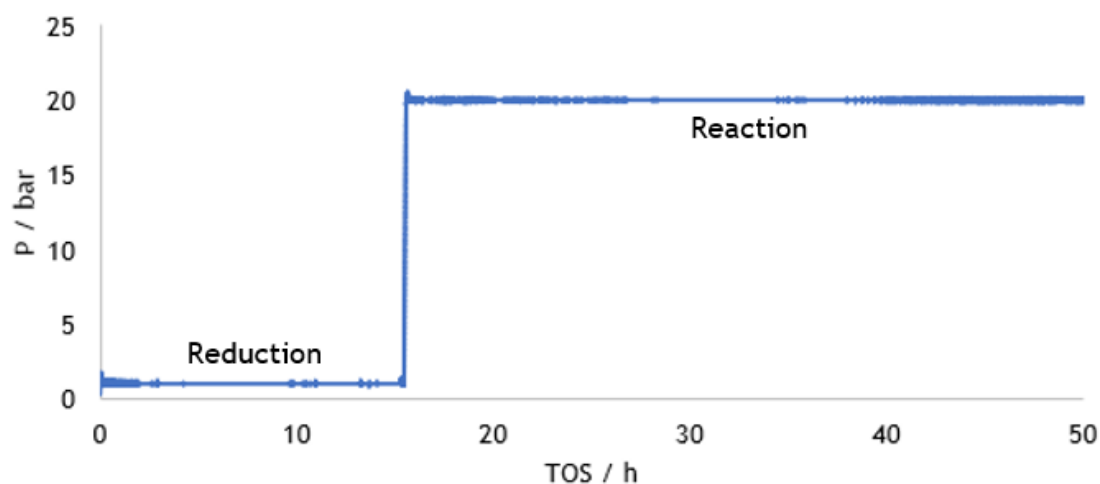


Figure C.1: Pressure evolution, in bar, with reduction and following reaction TOS.

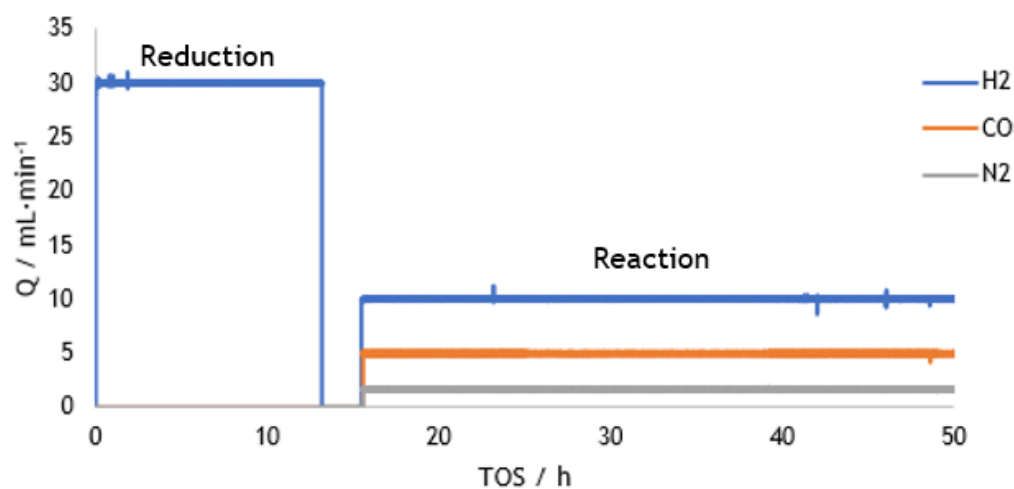


Figure C.2: H₂, CO and N₂ flow rates evolution, in mL·min⁻¹, with reduction and following reaction TOS, in h.

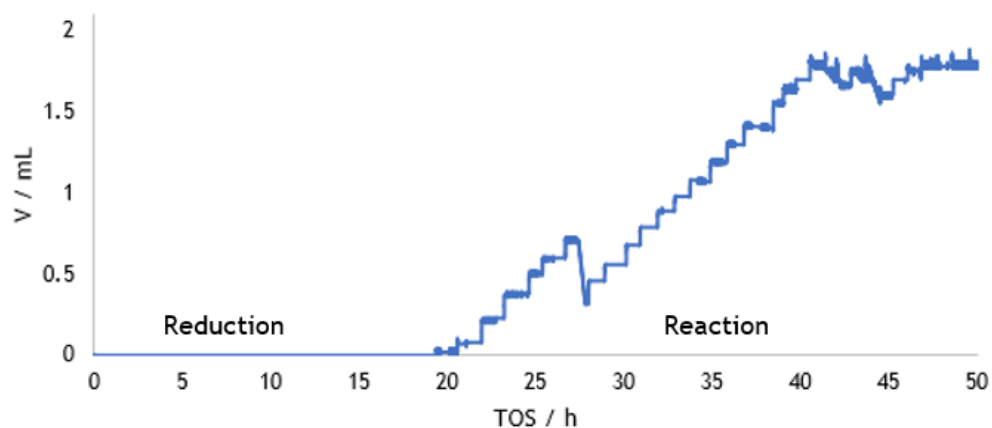


Figure C.3: Volume of liquid (water and organics) produced, in mL, during reaction TOS, in h.

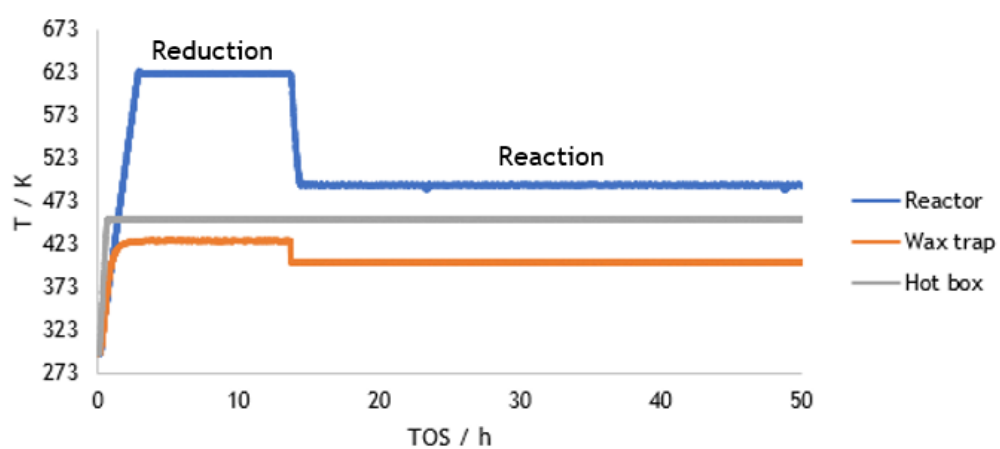


Figure C.4: Reactor, wax trap and hot box temperature evolution, in K, with reduction and following reaction TOS, in h.

C.2 Parametric study

In Table C.1 it is depicted the values of GHSV, pressure (P), and temperature (T) for the parametric study performed, where the values in green indicate the variable that is being studied, whereas the value in bold indicate the chosen value for the following catalytic tests.

Table C.1: GHSV, in $\text{m}^3 \cdot \text{kg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$, pressure, in bar, temperature, in K, and respective CO conversion, in %, for the parametric study performed.

GHSV / $\text{m}^3 \cdot \text{kg}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$	P / bar	T / K	X _{CO} / %
1.33	20	493	87.4
2.00	20	493	63.9
2.67	20	493	48.8
4.00	20	493	32.0
5.33	20	493	25.4
6.67	20	493	19.1
2.67	5	493	50.9
2.67	10	493	61.8
2.67	15	493	65.7
2.67	20	493	67.4
2.67	25	493	67.2
2.67	30	493	67.0
2.67	20	463	2.70
2.67	20	473	10.0
2.67	20	483	22.7
2.67	20	493	45.8
2.67	20	498	66.0
2.67	20	503	79.1
2.67	20	513	95.3

C.3 Activation energy

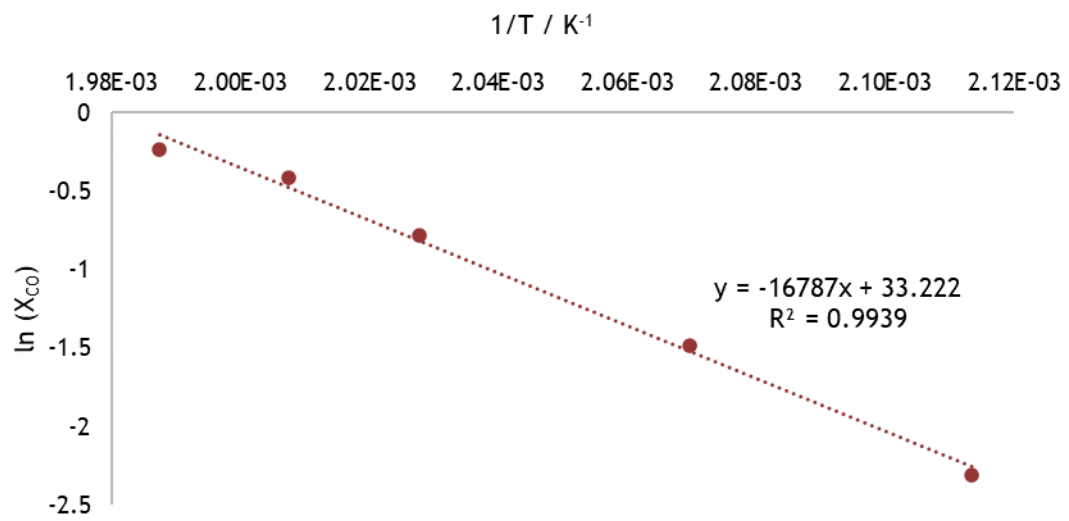


Figure C.5: $\ln(X_{Co})$ as a function of $1/T$, in K^{-1} .