Innovative preparation of catalysts by aerosol route for the Fischer – Tropsch synthesis

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Abstract – Usually Fischer – Tropsch (FT) catalysts are obtained through the deposition of cobalt active phase onto the support. This oxide support is normally obtained by a spray – drying synthetic pathway. The present work aims the synthesis and characterization of FT catalyst through spray-drying pathway.

Silica and alumina based solids were investigated. It was found a very high dispersion of cobalt leading to a high molecular interaction between the cobalt precursor and inorganic molecular precursor. Therefore, it was confirmed the existence of cobalt silicates or aluminates. In order to weaken Co and carrier atoms interactions, several preparation parameters were modified, like modifying pH of the atomizing solution to induce electrostatic attraction or repulsion of Co and Si or Al precursors in the initial solution. Better results regarding the cobalt accessibility and reducibility were achieved for a more acidic media. Nevertheless, it was still noticed the presence of cobalt silicates or aluminates.

A more exhaustive study should be done concerning synthesis parameters for both alumina and silica carriers. Furthermore, the loading of a promoter metal should be tried in order to improve the cobalt reducibility.

Keywords: Fischer – Tropsch catalysts, spray – drying, aerosol, cobalt, silica, alumina.

1. Introduction

The FT process was proposed by Hans Fischer and Franz Tropsch in 1925. This process converts a mixture of hydrogen and carbon monoxide, usually called synthesis gas (or syngas), into a hydrocarbon mixture. This mixture is mainly composed by paraffins, olefins and oxygenated compounds (mainly alcohols) with water. This process allows the production of methane (C\textsubscript{1}), petroleum gas (C\textsubscript{2}-C\textsubscript{4}), gasoline (C\textsubscript{5}-C\textsubscript{11}), diesel and jet fuel (C\textsubscript{12}-C\textsubscript{20}) and wax (C\textsubscript{21}+) and this latter being subsequently valorized into smaller molecules (diesel and gasoline) through hydrocracking.

The main goal of this work is the synthesis of a FT catalyst, in one step, by the spray – drying process. This synthesis pathway accomplishes a reduction in the number of steps required to synthetize an usual FT catalyst. To do that, two solutions should be prepared: the first one contains an inorganic molecular precursor, acidified water and a cobalt precursor; the second one contains a surfactant, ethanol and acidified water. These solutions should be mixed and the resulting solution is spray – dried. The obtained powder should be dried, calcinated and reduced in order to form the active phase. Moreover, as referred in the bibliographic study, the aerosol process can form mesostructured materials, however it is not the aim of this work, as the FT process does not requires mesostructured catalysts. The priority is to have a mesoporous catalyst.

1.1. Fischer – Tropsch catalysts

The FT catalysts are composed by an oxide support, a metallic active phase and sometimes metal and/or oxide promoters. The following paragraphs will described these topics.

1.1.1. Active phase

For FT applications only Fe-, Co-, Ni- and Ru-based catalysts have a satisfactory activity. Due to the low availability of Ru, and consequently its high price, Ru-based catalysts are not used.

Ni catalysts have a high hydrogenolysis capability and hence, produce large amounts of methane. Concerning Fe- and Co-based catalysts, despite the higher cost of cobalt catalysts, the latter presents a higher activity and longer life than Fe-based catalysts. Indeed, cobalt is the most active metal for long chain hydrocarbons. However, cobalt based catalysts are very sensitive to temperature changes, thus a small increase in temperature could lead to a high production of methane. [1] [2]
More in detail, cobalt catalysts have a higher resistance to deactivation than iron based catalysts. In addition, the WGS reaction has higher activity on Fe-based than on Co-based catalysts, thus it slows the reaction rate on Fe-catalysts.

This study will be focused on Co-based catalysts, due to their stability, higher activity and higher hydrocarbon productivity. These catalysts are considered an optimal choice for long-chain hydrocarbons production in the LTFT process. [3]

1.1.2. Supports

Concerning the support material, it is crucial to assure the stabilization of the Co particles in order to provide a good catalyst activity. Changing the support's surface, structure and pore size could lead to an improved metal dispersion, reducibility and the diffusion coefficients of reactants and products. As previously mentioned, Al₂O₃ and SiO₂, are the most used catalyst supports due to their high surface, and strong mechanical strength. [4]

The following paragraphs will describe the most often supports used in the FT process.

Silica – Supported catalysts: a better cobalt reducibility is achieved in this type of support due to a relatively weak interaction between the support and cobalt. However, the cobalt dispersion is much lower in silica-supported catalysts than the one achieved with alumina-supported catalysts.

Alumina – Supported catalysts: alumina has been one of the mostly used supports for cobalt FT catalysts. There are formed small cobalt crystallites due to strong interactions between cobalt oxides with this support. Cobalt reducibility is one of the most important problems of alumina-supported cobalt FT catalysts. However, promotion with noble metals can improve cobalt reducibility.

1.1.3. Metals and oxide promoters

According to the literature [2], cobalt-based catalysts are composed by an oxide support, metal and oxide promoters. Khodakov et al. [3] reported that the metal promoters are normally Pt, Ru, Ir and Re, which are described as “reduction promoters” that will result in an ease of cobalt reduction and an enhancement in the cobalt dispersion.

1.1.4. Usual catalyst preparation methods

The choice of the deposition method of the active phase will strongly influence the catalytic activity of the final catalyst. The following paragraphs will address the most usual preparation method to prepare cobalt-based catalysts for FT synthesis: impregnation method.

The preparation of cobalt-based FT catalysts includes the following steps [3]:

1) Synthesis of the catalyst support

Normally the supports used in the FT process are obtained through the spray-drying of a solution which contains inorganic precursors of the oxide support.

2) Preparation of cobalt precursors, and possibly promoters

3) Cobalt precursors dispersion onto the catalyst support

The purpose of dispersing the active phase, cobalt in this study, is to spread it along the porous support and to create metal clusters. [3] Moreover, it is necessary to generate a significant concentration of stable cobalt metal surface sites, and this depends on the size of cobalt particles as well as their reducibility. Incipient wetness impregnation is the most common method for preparing cobalt-based catalysts for the FT synthesis. This method consists on preparing a solution of a cobalt salt which is contacted to a dry porous support.

After being contacted, the solution is aspirated by capillary forces within the support pores. The incipient occurs when all pores of the support are filled with the liquid and there is no excess of moisture. At the moment right after impregnation, the interactions between the metal precursor and the support are relatively weak, which allows the redistribution of the active phase over the support during drying and calcination steps.

The distribution of Co²⁺ cations depends on the support charge, whether it is silica, alumina or titania. For each material, there are different points of zero charge (PZC), which correspond to the pH at which the positive and negative charges on the surface are equal and cancel. Therefore, at a pH below the PZC, the oxides surface is positively charged, and at a pH higher than PZC the oxides surface is negatively charged. Hence, if the impregnation solution has a pH below PZC, repulsion between the support surface and Co²⁺ ions will lead to a nonhomogeneous distribution of Co²⁺ ions. On the other hand, if the impregnation solution has pH above the PZC, Co²⁺ ions will be homogeneously distributed. [3] In a first approximation this last statement is correct. However, at a pH of 12-13, Co in water is not in the
usual form (Co2+), it is in the form of Co(OH)42-, thus repulsion would occur.

4) Post-treatment: drying and calcination.

5) Reducing treatments

The activation is the last step on the catalyst preparation. This operation involves a thermal treatment at high temperatures and it occurs usually under a hydrogen flow.

The reduction mechanism is generally assumed to occur in two steps, which are showed in the following equations. The first step, (Eq. 1), usually takes place at low temperatures, 100-350°C, and (Eq. 2) normally takes place at 400-600°C. [3]

\[
\begin{align*}
\text{Co}_3\text{O}_4 + \text{H}_2 & \rightarrow 3\text{CoO} + \text{H}_2\text{O} \quad \text{(Eq. 1)} \\
3\text{CoO} + 3\text{H}_2 & \rightarrow 3\text{Co} + 3\text{H}_2\text{O} \quad \text{(Eq. 2)}
\end{align*}
\]

According to Petru and co-worker [5], the metal particle size is a determinant factor in the reduction process of oxidized cobalt catalysts. Moreover, high reduction temperatures (>400°C) can lead to sintering cobalt particles. [3]

1.2. One-pot synthesis: Incorporation of the metallic phase on a mesoporous oxide matrix

In order to produce silica or alumina it is needed a precursor, such as Tetraethyl Orthosilicate (TEOS) (Si(OCH₂CH₃)₄), or aluminum chloride hexahydrate AlCl₃·6H₂O, respectively. One can note that metal alkoxides are popular precursors as they will lead to more pure solids than if a salt was used, and also because it is easier to control the kinetics of hydrolysis and condensation reactions. In the following equations is described the mechanism to synthesize silica. The reaction proceeds first through hydrolysis which is the hydrolysis of alkoxy groups. Once reactive hydroxy groups are formed, the generation of oligomers and polymers occurs via polycondensation reactions.

The sol-gel chemistry allows the synthesis of a large variety of amorphous or crystalline solids, with very different porosities, and in particular it can form mesoporous materials. As the condensation happens at ambient temperature, it is possible to add organic molecules in the reaction media, which will create a mesostructure. [6]

To explain what occurs during the synthesis of mesostructured materials, two mechanisms were proposed, depending on the surfactant concentration (c): True Liquid Crystal templating (TLC) and cooperative self-assembly mechanism.

The first one refers to the situation where c>CMC (Critical Micelle Concentration (CMC): above this surfactant concentration micelles are spontaneously formed), hence micelles soon begin to form. After, hydrolysis and condensation reactions of inorganic precursors take place around this template.

If c=CMC, the cooperative self-assembly mechanism takes place, where several processes occur simultaneously, such as hydrolysis and condensation reactions of the inorganic species, the self-assembly of the surfactant and the interaction between these two phase.

1.2.1. Mesostructured materials: synthesis techniques

**Spray-drying**

The spray-drying method is a sub-process of the evaporation technique, where a limpid solution (in fact it is a colloidal solution, as hydrolysis and condensation reactions have already begun some oligomers will be in solution) is transformed into a dry powder.

The aerosol technique presents many benefits when compared to the precipitation methods. It is a continuous process (the time between a droplet and a dry solid is between 1 to 4 seconds), it can be easily scaled-up to industrial scale, and, lastly, it allows a perfect control of the chemical composition of the final solid due to the existence of non volatile components that once were present in the atomization solution.

Therefore, this process permits the formation of materials that were not possible to be generated through the usual preparation methods, due to the fast evaporation that the precursors are obliged to co-arrange inside the matrix under a metastable state. Another benefit in using this method is the small amount of waste that is generated, in terms of energy, it is only needed to treat the gas that is released.

There are several spray-drying techniques, all related with the mechanical destabilization of the solution/atmosphere interface. The liquid feed can be atomized by several nozzles types depending on the required droplet size and this colloidal dispersion of liquid droplets in a gas is usually called “aerosol”. [6]

As one can see in Figure 1, firstly a very diluted solution is pumped to the nozzle. Furthermore, the aerosol is generated where liquid droplets are carried by the vector gas. Concerning the drying
step, the solvent evaporation allows the material’s structuration through a mechanism of autoassembly which is induced by the solvent evaporation. The evaporation driving force is the difference between \((P_0 - P_S)\), where \(P_S\) is the vapor pressure at the droplet surface and \(P_0\) is the saturation pressure. Therefore, when \(P_0 = P_S\) the evaporation process stops. After solids that are smaller than what is required are sent to an air filter, and the solids that meet the specifications are recovered in a collector.

Moreover, the non volatile species are responsible for the polarity fluctuation and the viscosity change in the droplet depth profile. Hence, the diffusion of volatile species inside the particles through the solid/gas interface, has an important role in the particles’ structure. Therefore, parameters related with this diffusion process, such as droplet size, residence time in the chamber, concentration, the carrier gas relative pressures in volatile species, temperature and flux, must be controlled.

Figure 1 - Spray - Dryer (Büchi B 290) working principle and material’s structuration mechanism. Adapted from [6]

2. Experimental Work

The catalysts prepared in this study are cobalt based catalysts either on silica or alumina matrix and they were obtained through spray-drying performed with an ultrasonic nozzle.

Several supports and cobalt catalysts were produced, and concerning the latter, all of them have 15 wt.% of cobalt regarding the total mass of catalyst.

2.1. Preparation Methods

The materials were obtained through a solution referred as “atomization solution”. The preparation of this solution requires several steps, the first one being the hydrolysis of the matrix precursors. After that, a surfactant solution (which will induce the mesostructuration), and a solution of the metallic precursors are prepared. Finally, these three solutions should be mixed and afterwards atomized in a Büchi B-290 spray – dryer. One should note that the atomization solution should be limpid to the eye during all the atomization period (without any precipitation or gelification phenomenon).

Solutions nature

The atomization solution results from the mixture of two solutions: an inorganic solution and an organic solution.

- **Inorganic solution**: is a mixture of a silica or alumina precursor and acidified water, and if a catalyst is synthesized, it will also contain a solution of the metallic precursor.
- **Organic solution**: is a mixture of surfactant (Pluronic®P123 (PEO20-PPO70-PEO20), where PEO stands for polyethylene oxide and PPO stands for polypropylene oxide), ethanol and acidified water.

One should note that the water in both solutions can be acidified with a solution of HCl or HNO₃.

In order to synthesize a catalyst, a metallic precursor solution has been added to the atomization solution. The metallic precursor solution used in this study was cobalt nitrate solution in water \((\text{Co(NO}_3\text{)}_2\) with 13.4% of Co, with a solution density of 1.48). Usually, the cobalt nitrate solution is added to the inorganic solution just before atomization starts. Furthermore, the organic solution remains equal as described in the supports. The only difference is in the inorganic solution that accomplishes the addition of the cobalt nitrate solution. Catalysts with 15 wt.% of cobalt, concerning the final catalyst mass, were produced.

The main objective is the transformation of a solution, which contains reagents of the desired product, into solid spherical elementary particles that were dried through an atomization process (evaporation). The following paragraphs describe the main steps of the spray drying process.

1) **Solution pumping**: The equipment responsible for the solution pumping is a
peristaltic pump. This pump is responsible for feeding the solution to the nozzle.

2) Aerosol generation: The aerosol is generated through a nozzle where the solution is mixed with a vector gas. The diameter reduction in the outlet of the nozzle combined with the vector gas flux allows the formation of small droplets that are carried by the gas. This vector gas is chosen according the desired atmosphere, for instance, it can be an inert gas if an inert atmosphere is required. There are different kinds of energy used to disperse the liquid feed into fine droplets.

- Two fluid nozzles: The energy required for atomization is provided by a rapid ejection of the spray gas, which was previously mixed with the liquid feed within the nozzle. It is more suitable for a laboratory scale, due to its low pressure consumption, low particle velocity and thus shorter required length in the spray chamber. The droplets produced by this kind of nozzle range from 5 - 30 µm.

- Ultrasonic nozzles: The droplet size is controlled by the frequency at which the nozzle vibrates, and by the surface tension and density of the liquid being atomized. One can note, that the higher the frequency, the smaller the median droplet size. Moreover, there is no need to use air pressure, the liquid is pumped to the nozzle vibrating surface. The produced droplets range from 2 - 100 µm.

There are other type of nozzles, such as rotary disks and pressure nozzles, however they are more suitable for an industrial scale, and because of that they are not mentioned in this report. In this study, an ultrasonic nozzle was chosen instead of a two fluid nozzle (the nozzle often used in the laboratory scale), because the size of the produced elementary particles is more appropriate for the final application of these catalysts (FT synthesis).

3) Aerosol evaporation: The liquid droplets have to be in contact with a hot gas, which allows the evaporation of the solvents and the droplets transportation. Therefore, the inlet temperature corresponds to the temperature of this heated vector gas. This temperature needs to be controlled which is detailed described in the spray – drier parameters.

At the end, the dried particle surface temperature approximates the temperature of the surrounding gas, as it is described later (spray – drier parameters).

4) Powder collection: is done through a cyclone that confers the particles separation by size. Based on inertial forces, the particles flow to the cyclone wall and are separated from the gas as a downwards strain. The smaller particles are sent to an air filter while the particles with a larger diameter are collected in the vessel under the cyclone.

In Table 1 it is a full description of all synthesized catalysts. All of them were produced through an ultrasonic nozzle and for all the samples the molar ratio between (EtOH:H2O) was 0.06, and all of them were synthetized using Pluronic® P123 as surfactant.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Matrix/Inorganic Precursor</th>
<th>pH: (HCl/HNO3)</th>
<th>Post – Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>JFR016</td>
<td>Silica/TEOS</td>
<td>2; HCl</td>
<td>Calcination at 350°C</td>
</tr>
<tr>
<td>JFR019</td>
<td>1; HNO3</td>
<td></td>
<td>Calcination at 400°C</td>
</tr>
<tr>
<td>JFR021</td>
<td>2; HNO3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JFR022</td>
<td>3; HNO3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>JFR024</td>
<td>Alumina/AlCl3·6H2O</td>
<td>2; HNO3</td>
<td></td>
</tr>
<tr>
<td>JFR037</td>
<td>Alumina/Al(NO3)3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. Results and Discussion

Generic remarks

On one hand, alumina matrix is the most used support in the FT synthesis. On the other hand, there is more information in the literature concerning silica sol – gel chemistry and also IFPEN has a vast experience in synthetizing silica based materials through the aerosol process. Therefore, a more detailed study was performed on silica matrixes.

Supports were firstly tried to produce instead of trying to produce directly a catalyst, in order to know if it was possible to synthesize it and also to characterize the elementary particles obtained through the ultrasonic nozzle, which has never been used at IFPEN.

3.1. Silica

Moreover, before having all the analysis results, a part of JFR016 (before being dried or calcinated)
was reduced under hydrogen flow, and tested in a FT catalytic test unit (slurry reactor). After 16 hours, there was no activity, in another words, there were no products formation. As there were no other catalytic tests in this work, no setup or reaction condition are presented here.

Therefore, two main hypotheses were proposed for the catalyst lack of activity: first, the presence of chlorine could affect the catalyst activity, and second, it could exist a strong interaction between the silica precursor and the cobalt precursor, consequently affecting the cobalt dispersion. In the following paragraphs is described in detail each hypothesis.

1) Presence of chlorine in the catalyst

The presence of chlorine in FT catalysts has showed a significant decrease in activity. This lack of activity could be due to the poising of several surface sites by Cl atoms. This could be related with the chlorine strong electronegativity, which prevents the CO dissociation on the catalyst. Moreover, it was found that the effect of chlorine atoms on the catalyst was slowly reversible. In order to prevent this effect HCl was replaced for HNO₃ in the initial solution. The following paragraphs describe the effect of HNO₃, either on the supports and catalysts.

The results revealed that using HCl (JFR016) or HNO₃ (JFR021) does not have influence in the cobalt reducibility. However, as previously stated, the presence of Cl atoms can affect negatively the activity of the catalysts in the FT synthesis. Thus, from now on, all the catalysts were synthesized with HNO₃ in the initial solution.

2) Strong interaction between the silica precursor and the cobalt precursor

Hardly reducible cobalt species were formed, which supports the hypothesis of a strong interaction between silica precursor and the cobalt precursor. These oxides (cobalt silicates) are often amorphous, which makes it harder to characterize those using conventional techniques, such as XRD. A low cobalt content and a high surface area favor the formation of hardly reducible oxides. Mixed cobalt – silicium or aluminum oxides can be formed during the catalysts preparation, oxidative and reductive pretreatments, and in the course of FT reaction.

In order to change the interaction between silica precursor (TEOS) and the cobalt precursor (cobalt nitrate), were made three solutions at different pH. The formed oligomers are mainly linear and easily condensable in an acid media (0<pH<2) and ramified in a less acid media (pH>2). The silica PZC is approximately at pH=2, hence a solution was made approximately at a pH=PZC (as in the usual procedure), and the other two at a pH above and below the PZC. Consequently, changing the pH of the solution would affect the size and the dispersion of the cobalt particles. Atomizing a solution with a pH below the PZC provides a silica surface positively charged, hence repulsion will occur between Co²⁺ ions and the surface leading to a “non – homogenous distribution” (creating perhaps cobalt domains and hence larger particles of cobalt species). On the other hand, atomizing a solution with a pH above the PZC provides a silica surface negatively charged, and the Co²⁺ ions will be “homogenous distributed”. Consequently, the following samples were prepared: pH=1 (JFR019), pH=2 (JFR021) and pH=3 (JFR022).

- **Textural properties**

Hereby is described the pH influence on the textural properties. In Figure 2 it is described the nitrogen adsorption – desorption isotherms for the three samples (JFR019, JFR021 and JFR022), and JFR016 is only represented as a reference (this solid was synthesized through an atomization solution which contained HCl and present a pH approximately of 2).
In Table 2 it is summarized the surface area (BET surface), porous volume and pore diameter for the previous samples.

<table>
<thead>
<tr>
<th>Reference</th>
<th>BET surface (m²/g)</th>
<th>Porous volume (mL/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JFR016</td>
<td>164</td>
<td>0.26</td>
<td>6.5</td>
</tr>
<tr>
<td>JFR019 (pH = 1)</td>
<td>338</td>
<td>0.38</td>
<td>5.2</td>
</tr>
<tr>
<td>JFR021 (pH = 2)</td>
<td>345</td>
<td>0.46</td>
<td>7.1</td>
</tr>
<tr>
<td>JFR022 (pH = 3)</td>
<td>258</td>
<td>0.35</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Concerning the isotherms shape, one can see that JFR019 (pH = 1) is slightly different from the others. JFR019 presents a hysteresis loop with more vertical lines, indicating the existence of a more organized solid, which is confirmed by TEM analysis, further presented. The shape of JFR021 (pH = 2) presents a hysteresis loop with more straight lines than JFR022 (pH = 3), but less pronounced than JFR019.

All the three samples (JFR019, JFR021 and JFR022) present different porous size distributions. This is due to different interactions between the surfactant and the inorganic species induced by the different pH.

JFR019 and JFR021 present higher surfaces areas than JFR022 due to a higher mesoporosity, as JFR021 presents a higher porous volume, and, JFR022 presents a slightly higher porous volume, but a much smaller pore diameter.

Therefore, it is possible to conclude that regarding the textural properties, atomizing solutions with different pH leads to solids with different properties.

- Organization of the porosity of the silica matrix
- In order to study the influence of the pH on the mesoporosity, low angles XRD analysis was performed.

As one can see in Figure 3, for the sample JFR022 (pH = 3) there is no long distance organization. While for JFR019 (pH = 1) and for JFR021 (pH = 2), it was confirmed the existence of a mesostructured organization.

This can be explained, since a higher condensation rate is expected at pH = 1 and pH = 3. However, JFR019 (pH = 1) is more organized than JFR022 (pH = 3) due to a better interaction between the surfactant and the inorganic molecular precursor, as for each pH, the silica surface is differently charged.

The mesoporosity was also confirmed by TEM analyses, which are described later on.

Furthermore, one can conclude that the pH of the atomized solution has influenced in the mesostructure process, as it was expected.

![Figure 3 - Low angles XRD patterns for JFR019, JFR021 and JFR022.](image)

- Cobalt reducibility

The cobalt reducibility as well as accessibility was studied by TPR analysis. In Figure 4, it is the TPR profile for JFR019, JFR021 and JFR022 after calcination. It is important to refer that JFR019 after calcination was black, which is the characteristic color of cobalt oxide (CoO), whereas JFR021 and JFR022 were violet after the same post – treatment.

![Figure 4 - TPR profile for JFR019, JFR021 and JFR022.](image)

As one can see in Figure 4, for JFR019 there is a first peak at 375°C and a second peak at 816°C. As the first peak is at a higher temperature than usual, it could correspond to the reduction of Co₃O₄→CoO and/or to the decomposition of residual NOₓ groups (endothermic reaction). These NOₓ groups are due to the cobalt precursor solution (cobalt nitrate) and the HNO₃ used to acidify the solution, because JFR019 is the more acidic solution so the more NO₃⁻ concentrated. [3] If one
decomposes the second peak, a part of it might correspond to the $\text{CoO} \rightarrow \text{Co}^\circ$ reduction. And the majority of this peak, as it happens at an elevated temperature may suggest, once more, the existence of cobalt silicates which are due to a strong interaction between the support and cobalt oxide. Regarding JFR021 it shows two peaks at 842°C and 899°C, and, JFR022 presents one peak at 825°C. These peaks may only suggest again the existence of cobalt silicates due to a strong interaction between silica and cobalt oxide.

A XRD analysis was performed in order to characterize the crystalline cobalt oxide phases present in the three catalysts. The XRD analysis revealed for JFR019 a small peak of cobalt oxide ($\text{Co}_3\text{O}_4$) which is in agreement with the TPR analysis. These particles were measured at 36.8° (2θ) and they have a size of 22 nm. Moreover, for all the three samples it was found a peak of metallic cobalt and this was not expected since the samples were only calcinated, and not reduced. It was expected after the conclusions taken by the TPR, which revealed the possible existence of cobalt silicates, to found a peak of cobalt silicates in the XRD diagrams. The absence of this peak may be justified by the cobalt silicates being amorphous, thus does not appear on the XRD diagrams. Therefore, a XPS analysis was performed in JFR019 (which presented a first peak in TPR and a peak of $\text{Co}_3\text{O}_4$ in XRD), and in JFR021. This analysis was not done in JFR022 since it present very similar results to the ones of JFR021. The results from XPS are summarized in Table 3, which describe in which form is the cobalt.

### Table 3 - Results from XPS analysis for JFR019 and JFR021.

<table>
<thead>
<tr>
<th>Reference</th>
<th>$\text{Co}^{2+}$</th>
<th>$\text{Co}_3\text{O}_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>JFR019</td>
<td>55.3%</td>
<td>44.7%</td>
</tr>
<tr>
<td>JFR021</td>
<td>100%</td>
<td>-</td>
</tr>
</tbody>
</table>

The results from XPS analysis, confirmed the existence of cobalt oxide in JFR019, and it reveals the existence of $\text{Co}^{2+}$ in both samples. XPS analysis is only able to specify that there is a specie in the catalyst that presents an oxidation state of $\text{Co}^{2+}$, but it could most likely be cobalt silicates.

Furthermore, it is interesting to note that no $\text{Co}^\circ$ was observed by XPS.

- **Organization of the porosity of the silica matrix and cobalt dispersion**

In order to study with more detail the silica mesoporosity and the cobalt phase, TEM analysis were performed. The following pictures show TEM micrographs for the previous three samples.

![Figure 5 - TEM micrographs for the support of JFR019.](image1)

Regarding the silica matrix, as one can see in Figure 5, the porous have a worm-like shape. Also, TEM showed that the pore size was approximately 5 nm, what is in agreement with the value taken from $\text{N}_2$ adsorption-desorption isotherm.

![Figure 6 - TEM micrographs for metallic phase of JFR019.](image2)

The metallic phase (Figure 6) is present in the form of particles which are heterogeneously distributed and ultra – dispersed onto the matrix. Moreover, there are zones where cobalt particles were not visible. However EDS analysis showed that Co is also present. Images in a dark – field mode did not show any diffraction, what makes possible to conclude that cobalt, in these zones, is in an amorphous form. Besides that, cobalt was found in two crystalline forms: cobalt oxide ($\text{Co}_3\text{O}_4$) and metallic cobalt ($\text{Co}^\circ$). Concerning the samples JFR021 and JFR022 (Figure 7), globally they present the same morphology. The oxide matrix presents a mesoporous domain as expected, and the structuration was still happening, leading to a worm – like structure. The metallic phase was present in an ultra-dispersed form, and, as seen in JFR019, it was found an amorphous phase rich in cobalt.
3.2. Alumina

Some initial trials were performed using AlCl₃ as inorganic precursor, but to avoid Cl atoms, aluminum nitrate was used instead.

Study of Al(NO₃)₃ as inorganic precursor

In the following paragraphs it is described the synthesis of cobalt catalysts on an alumina matrix, with 15 wt%, concerning the final catalyst mass.

- Textural properties

In Figure 8 is described the nitrogen adsorption – desorption isotherms for JFR037 and JFR024. One should note that the latter is only represented as a reference, as the inorganic precursor is the only difference between the both samples.

In Table 4 it is summarized the surface area (BET surface), the porous volume and the pore diameter for all the previous samples.

<table>
<thead>
<tr>
<th>Reference</th>
<th>BET surface (m²)</th>
<th>Porous volume (mL/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>JFR024</td>
<td>121</td>
<td>0.19</td>
<td>1.8</td>
</tr>
<tr>
<td>JFR037</td>
<td>32</td>
<td>0.11</td>
<td>12</td>
</tr>
</tbody>
</table>

Comparing the isotherms shape it is possible to affirm that JFR037 is not mesostructured, however a low angles XRD and TEM analysis should be performed to confirm this.

Concerning the differences in the pore diameter and in the surface area, a more detailed study on should be performed in order to justify these differences, but it seems that with Al(NO₃)₃ the organic molecule (surfactant) plays a role in building the porosity as it is wider than with AlCl₃ precursor.

The increase in the pore diameter is positive, as the produced hydrocarbons chains would be desorbed from the catalyst more easily. However, the porous volume it is not satisfactory for the FT process, hence a more detailed study should be done to improve the textural properties.

- Cobalt reducibility

The cobalt reducibility as well as accessibility was studied by TPR analysis. In Figure 9 it is the TPR profile for JFR037 and JFR024. It is important to refer that after calcination, both samples were black, which is the characteristic color of cobalt oxide (Co₃O₄), instead of violet for JFR024.
As one can see, in Figure 9, the TPR profile for the samples obtained with Al(NO$_3$)$_3$ as inorganic precursor have changed significantly.

If one decomposes the peaks of JFR037 it is found a first peak around 415°C, a second peak at 615°C and finally a third peak at 895°C.

For JFR037 sample the first peak likelihood corresponds to Co$_3$O$_4$→CoO reduction, whereas the second peak may correspond to CoO→Co° reduction. Concerning the first peak, one can note that it is at a more elevated temperature than usual, which might be explained through the decomposition of residual NO$_x$ groups (exothermic reaction). This group exists due to the presence of NO$_3$ in the inorganic precursor, cobalt precursor and acidified water.

Finally, JFR037 presents a third peak that probably correspond to the existence of cobalt aluminates. To confirm this, a more detailed characterization should be performed.

4. Conclusion and future work

The aim of this work is the synthesis of active FT catalysts by spray – drying. At this point, is not possible to conclude if the synthetized solids are catalysts, as they were not catalytic tested. It is only possible to affirm that it was possible to synthetize, by spray – drying, solids with a cobalt loading of 15 wt.% onto a silica and alumina matrix.

Concerning the solids synthetized onto a silica matrix, it was noticed that all of them present very good textural properties for final application in the FT process. Nevertheless, the existence of cobalt silicates was observed, due to high cobalt dispersion that lead to a strong interaction between the inorganic precursor (TEOS) and cobalt. Therefore in order to reduce this interaction the pH of the atomization solution was changed. Only at pH = 1 better results were achieved, as there was a reduction of Co$_3$O$_4$ →Co°. However, it was noticed the formation of cobalt silicates. Nevertheless, a more detailed study should be done, to really evaluate which parameter could change the interaction between silica and cobalt. Also, it should be understood the presence of metallic cobalt in samples that were not reduce. Depending on the catalytic tests results, it should be understood where the cobalt nanoparticles are located on the support and it could be tried the loading of a promoter metal in order to see if the cobalt reducibility was improved.

Moreover, concerning the solids synthetized onto an alumina matrix, it was noticed that the textural properties are not satisfactory for the application in FT process. In solids produced with aluminum chloride, as inorganic precursor, it was notice the existence of cobalt aluminates. Another aluminum precursor, aluminum nitrate, was tested: the cobalt reducibility was improved since there was a reduction of Co$_3$O$_4$ →Co° but, there were still cobalt aluminates. Though, concerning alumina matrixes a more detailed study should be performed in order to improve the textural properties and also to completely understand several differences that were reported in the results chapter.

5. References

[9] F. Colbeau-Justin, Design de nouveaux catalyseurs par incorporation d’hétéropolyanion dans une matrice mésosstructurée, 2012;