Synthesis and Evaluation of Bifunctional Catalysts
For Biofuels Production

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Engenharia Química

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Setembro de 2009
All truths are easy to understand once they are discovered; the point is to discover them.

Galileo Galilei
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Obrigado.
Abstract

The increase in world consumption of middle distillates, in addition to the necessity of reduction of greenhouse gases emissions into the atmosphere, becomes crucial the investment in clean and cost-effective processes for the production of diesel. An example of these processes is the Fischer-Tropsch process, which uses synthesis gas from natural gas (GTL) or biomass (BTL) to produce fuels. The hydrocracking of FT waxes gives a high in middle distillates, thus the demand for hydrocracking catalysts with high performance has been intensified over the past few decades.

One of the catalysts with better performance in hydrocracking of FT wax is USY, when non-supported presents drawbacks in mechanical strength (resulting in loss of catalyst) and even high pressure drops. The use of these catalysts in supported-type is of utmost importance, however the most common supports (silica or alumina) have major disadvantages, including its high chemical reactivity. The use of SiC as a catalyst support has been studied in recent years due to its high thermal conductivity, high mechanical strength and being an inert.

In this work, it was studied the feasibility of the synthesis of zeolite Y supported on SiC, evaluating the catalyst by various characterization techniques such as XRD analysis, specific surface area by N₂ adsorption, SEM, NMR, TPD and ICP-MS, proving the synthesis viability.

Several steaming tests of HY zeolite (non-supported type) were carried out, in order to determine the optimal conditions for achieving a high Si/Al ration by removing Al atoms from the framework. After finding the right conditions, the steaming was applied to the zeolite supported on SiC.

The harsh conditions that the steaming was carried out, taking into account the amount of supported zeolite (ca. 6 wt.%), led to the destruction of zeolite structure, being observed by XRD.

In order to test the catalyst, and because it was not possible to synthesize USY/SiC as originally planned, it was made the deposition of Pt on HY/SiC. Pt-HY/SiC catalyst was tested in catalytic isomerization of n-heptane (catalytic testing in IFP), demonstrating its good performance in the tasks for which it was synthesized.

Keywords: Zeolite USY, SiC, hydrocracking, Fischer-Tropsch waxes
Resumo

O aumento do consumo mundial de destilados médios, em conjunto com a necessidade de redução de emissões de gases de efeito de estufa para a atmosfera, torna fulcral o investimento em processos limpos e rentáveis para a produção de gasóleos. Um exemplo desses processos é o processo Fischer-Tropsch efectuado a partir de gás de síntese, proveniente de gás natural (GTL) ou biomassa (BTL). O hydrocracking das ceras provenientes do processo FT permite obter um elevado teor em destilados médios, pelo que a procura de catalisadores de hydrocracking com alto desempenho tem vindo a ser intensificada ao longo das últimas décadas.

Um dos catalisadores com melhor desempenho no hydrocracking das ceras de FT é o USY, que quando não suportado apresenta problemas de resistência mecânica (originando perdas de catalisador) e até mesmo elevadas perdas de carga. O uso de suportes neste tipo de catalisadores é de extrema importância, no entanto os suportes mais comuns (sílica ou alumina) apresentam grandes desvantagens, nomeadamente a sua elevada reactividade química. O uso de SiC como suporte de catalisadores tem vindo a ser estudado ao longo dos últimos anos, devido à elevada condutividade térmica, elevada resistência mecânica e pelo facto de ser inerte.

Neste trabalho estudou-se a viabilidade de síntese do zeólito Y suportado em SiC, avaliando o catalisador através de diversas técnicas de caracterização tais como DRX, análise de área específica por adsorção de N$_2$, SEM, RMN, TPD e ICP-MS, tendo-se comprovado a exequibilidade da síntese.

Foram efectuados diversos testes de steaming de zeólito HY (na forma não suportada), de modo a determinar quais as condições ideais para atingir uma elevada razão Si/Al por eliminação dos átomos de Al da rede. Após encontrar essas mesmas condições, foi aplicado o steaming ao zeólito na forma suportada.

As condições severas a que o steaming foi efectuado levaram à destruição da estrutura zeolítica, que foi possível constatar por DRX.

De modo a poder testar o catalisador, e devido ao facto de não ter sido possível sintetizar USY/SiC como inicialmente previsto, foi feita a deposição de Pt em HY/SiC. O catalisador do tipo Pt-HY/SiC foi utilizado no teste catalítico de isomerização da molécula-modelo n-heptano (IFP), comprovando-se o seu bom desempenho numa das tarefas para que foi concebido.

Palavras-Chave: Zeólito USY, SiC, hydrocracking, ceras Fischer-Tropsch
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<th>Description</th>
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<tbody>
<tr>
<td>AFS</td>
<td>Anderson-Flory-Schultz polymerization model</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmet-Teller</td>
</tr>
<tr>
<td>BTL</td>
<td>Biomass-to-Liquid</td>
</tr>
<tr>
<td>DHD</td>
<td>Dehydrogenation</td>
</tr>
<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
</tr>
<tr>
<td>EFAL</td>
<td>Extra-Framework Aluminum</td>
</tr>
<tr>
<td>FT</td>
<td>Fischer-Tropsch</td>
</tr>
<tr>
<td>GTL</td>
<td>Gas-to-Liquid</td>
</tr>
<tr>
<td>HD</td>
<td>Hydrogenation</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively Coupled Plasma Mass Spectrometry</td>
</tr>
<tr>
<td>LTFT</td>
<td>Low Temperature Fischer-Tropsch products</td>
</tr>
<tr>
<td>MAS</td>
<td>Magic Angle Spinning</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear Magnetic Resonance</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>STP</td>
<td>Standard Temperature and Pressure</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature Programmed Desorption</td>
</tr>
<tr>
<td>USY</td>
<td>Ultrastable Y</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
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</table>
1. Introduction

In the last decades the technical, social and economical scenario is favouring the Gas-to-Liquids and Biomass-to-Liquids tendency to produce synthetic fuels via Fischer-Tropsch (FT). Furthermore, due to the need of reducing the emission of greenhouse gases into the atmosphere, the production of cleaner fuels has lived a renewed interest. Therefore, the production of liquid fuels from various sources (coal, biomass, gas) via the FT process is one of the best ways to reduce those emissions. In particular, diesel fuels produced according to this process exhibit outstanding properties compared to diesel fuels derived from crude oil: very high cetane number (typically above 70), and virtually no sulfur, nitrogen, aromatics and metals, resulting in reduced emission of pollutants from the engine. Production of diesel fuels involves the catalytic hydrocracking of the heaviest part of the FT hydrocarbons. Alternatively, waxes produced by FT unit could be upgraded to lubricants base oil, the catalytic dewaxing route (which in addition to hydrocracking, also involves selective hydroisomerization in order to upgrade diesel properties: pour point, CFPP, etc.) to lubricants base oil becoming the preferred option compared to conventional solvent dewaxing. Both type of upgrading involve the use of bifunctional catalysts.

One of the most used heterogeneous catalysts in hydrocracking is USY. The ultrastabilization of zeolite Y is done by steaming or hydrothermal dealumination, which is a well-established procedure, commonly performed at a high partial pressure of steam and temperatures exceeding 500°C. New catalyst support materials are not frequently reported in the literature, with almost no new support materials being incorporated into commercial use since World War II. Obviously, many improved support materials have been introduced into catalytic processes but, today, the majority of commercial catalysts are still supported on alumina, silica or carbon, just as they were 50 years ago. All these support materials suffer drawbacks. The poor heat conductivity and the chemical reactivity of alumina and silica can induce a decrease in surface area and loss of active phase during operation. The weak oxidation resistance of carbon as support hinders its use for high-temperature oxidative reactions and the presence of a high microporosity can lead to mass transfer (diffusional) limitations. It is consequently of interest to discover and develop new support materials that can efficiently replace those cited above, mainly in terms of physical properties, avoiding the drawbacks linked to classical industrial supports. Silicon carbide (SiC) exhibits a high thermal conductivity, a high resistance towards oxidation, a high mechanical strength, a low specific weight, and chemical inertness; all
properties required for good heterogeneous catalyst support materials. Therefore, it’s of great interest to use SiC as a support for hydrocracking catalysts, as hydrocracking is commonly performed at severe conditions, which can destroy the catalyst. By using silicon carbide as a support for those catalysts, the catalyst is protected from destructive phenomenon.

Consequently, the main targets of this work are to perform the synthesis of Ultrastable Y zeolite, supported in silicon carbide, in order to test it in n-heptane hydroisomerization (which is performed at IFP-Lyon), after adding Pt to the composite structure. By various characterization methods such as XRD, SEM, NMR, et al., the catalysts will be analyzed in order to verify the feasibility of the synthesis and all the involved treatments. The catalytic test results will allow concluding if the desired composite is useful for hydrocracking of FT waxes for middle distillates production, in order to be used in further work.
2. Bibliography

2.1. Fischer-Tropsch Process and Hydrocracking

Fischer-Tropsch process was discovered at Kaiser Wilhelm Institute (Germany) in 1923 by Franz Fischer and Hans Tropsch. At that time the process found only limited commercial application.

In the past, only particular geopolitical situations favoured the realization of industrial plants to produce synthetic fuels and chemicals, starting from coal. It was the case of various German companies during World War II and for Sasol in South Africa during the period of the embargo.

Current Fischer-Tropsch GTL technology consists of three major sections (Fig. 2.1) centered on low temperature Fischer-Tropsch (LTFT) synthesis (200-250 °C), which correspond to the conversion of synthesis gas into wax by the Fischer-Tropsch process. The step of conversion of natural gas into synthesis gas (H₂/CO) by steam or oxygen/air based reforming, and the wax upgrading to synthetic crude by hydrocracking followed by separation into the end products have extensive commercial experience. Nevertheless their application to Fischer-Tropsch process needs an intensive integration activity to obtain the most cost-effective combination of these three technologies.

Figure 2.1 – GTL technology

FT waxes represent one of the most attractive hydrocracker feeds, alternative to the more traditional ones derived from crude oil. Besides the GTL technology, it is also possible to obtain waxes by FT process having as source biomass. Biomass, which is typically in a low density
form, must be collected and transported to a central processing facility so that it can be converted into a transportation fuel. The edible and non-edible part of biomass can be separated, and the non-edible fraction, after, can be converted into fuel. Although a number of other renewable options are available for sustainable electricity and heat production, such as solar, wind and hydroelectric, plant biomass is the only current renewable source of carbon that can be used directly for liquid fuels and chemicals. The first step in production of biofuels is to have a cheap abundant biomass feedstock. Lignocellulose (or cellulose) is the cheapest and most abundant source of biomass; another strategy is to use lignocellulosic biomass residues, such as agricultural, industrial and forest wastes. The schema that follows, presented in Figure 2.2, is representative of main strategies that biomass can undergoes to produce fuels.

![Figure 2.2 – Fuels production strategies from lignocellulosic biomass](image)

Biomass gasification is an old technology, and in the mid of 1940s was used in Europe. Biomass gasification is similar to coal gasification, but occurs at lower temperature because biomass is more reactive than coal. Biomass also contains potassium, sodium and other alkali that can cause slagging and fouling problems in conventional gasification equipment. A number of commercial biomass gasification units exist mainly to produce heat and electricity, and in the 1970s and 1980s about 40 worldwide companies offered to build biomass gasification plants. Biomass gasification can include a complex combination of reactions in the solid, liquid and gas phases. Table 2.1 contains examples of gasification reactions.
Table 2.1 – Fundamental reactions and Enthalpy of selected cellulose gasification reactions

<table>
<thead>
<tr>
<th>classification</th>
<th>stoichiometry</th>
<th>enthalpy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrolysis</td>
<td>$\text{C}_6\text{H}_5\text{O}_5 \rightarrow 5\text{CO} + 5\text{H}_2 + \text{C}$</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_6\text{H}_5\text{O}_5 \rightarrow 5\text{CO} + \text{CH}_4 + 3\text{H}_2$</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td>$\text{C}_6\text{H}_5\text{O}_5 \rightarrow 5\text{CO} + \text{CO}_2 + 3\text{CH}_4 + \text{H}_2$</td>
<td>-142</td>
</tr>
<tr>
<td>partial oxidation</td>
<td>$\text{Cu}_2\text{O}_2 + \frac{3}{2}\text{O}_2 \rightarrow 3\text{CO} + 5\text{H}_2$</td>
<td>71</td>
</tr>
<tr>
<td>steam gasification</td>
<td>$\text{Cu}_2\text{O}_2 + \text{O}_2 \rightarrow 3\text{CO} + \text{CO}_2 + 5\text{H}_2$</td>
<td>-213</td>
</tr>
<tr>
<td></td>
<td>$\text{Cu}_2\text{O}_2 + 5\text{O}_2 \rightarrow 6\text{CO} + 8\text{H}_2$</td>
<td>-776</td>
</tr>
<tr>
<td></td>
<td>$\text{Cu}_2\text{O}_2 + \text{H}_2\text{O} \rightarrow 6\text{CO} + 6\text{H}_2$</td>
<td>310</td>
</tr>
<tr>
<td>water-gas shift</td>
<td>$\text{Cu}_2\text{O}_2 + 3\text{H}_2\text{O} \rightarrow 4\text{CO} + 2\text{CO}_2 + 8\text{H}_2$</td>
<td>230</td>
</tr>
<tr>
<td>methanation</td>
<td>$\text{Cu}_2\text{O}_2 + 7\text{H}_2\text{O} \rightarrow 6\text{CO} + 12\text{H}_2$</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$</td>
<td>-41</td>
</tr>
<tr>
<td></td>
<td>$\text{CO} + 3\text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$</td>
<td>-206</td>
</tr>
</tbody>
</table>

*Adapted from Klass*

The syngas is used for production of fuels and chemicals. Many industrial routes for utilization of syngas exist such as production of H\(_2\) by the water gas shift reaction (WGS), alkanes by FT synthesis, methanol by methanol synthesis and methanol-derived fuels, isobutene by isosynthesis and ethanol by fermentation. Figure 2.3 shows routes for transportation fuels and chemicals production from syn-gas.

![Figure 2.3 – Pathways for fuel production from syn-gas](image)

Fischer-Tropsch reaction produces hydrocarbons starting from H\(_2\) and CO, according to the general equation:

$$n(\text{CO} + 2\text{H}_2) \rightarrow - (\text{CH}_2)_n - + n\text{H}_2\text{O}$$
As a matter of fact, not only paraffins are produced, indeed many different reactions occur simultaneously:

**Synthesis of paraffins:**
\[ nCO + (2n + 1)H_2 \rightarrow C_nH_{2n+2} + nH_2O \]

**Synthesis of olefins:**
\[ nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \]

**Synthesis of oxygenates:**
\[ nCO + 2nH_2 \rightarrow C_nH_{2n+1}OH + (n - 1)H_2O \]

**Water gas shift reaction:**
\[ CO + H_2O \rightarrow CO_2 + H_2 \]

**Coke formation:**
\[ H_2 + CO \rightarrow C + H_2O \]

### 2.1.1. Low Temperature Fischer-Tropsch Products (LTFT)

The low temperature Fischer-Tropsch synthesis is based on the R&D advancement for both catalyst and reactor technology. Catalyst and reactor selection influence the various characteristics of the Fischer-Tropsch process such as the thermal efficiency, heat removal, product selectivity and operating costs.¹

Whatever the catalysts and reaction conditions, the Fischer-Tropsch reaction produces normal aliphatic hydrocarbon chains with a range of carbon numbers. The carbon number distribution of the products follows the Anderson – Flory – Schultz (AFS) polymerization model. According to the AFS model, the carbon number distribution of the products is a function of the chain growth probability \( \alpha \) at the surface of the catalyst (Fig. 2.4).

With such kinetics, the selective synthesis of a product with a narrow range of chain lengths is not possible, except for methane if \( \alpha \) equals 0 or for infinite chain length if \( \alpha \) equals 1. Assuming ideal AFS kinetics, the maximum straight run middle distillates yield (typically the C\(_{10}\) – C\(_{20}\) cut) achievable is about 40 wt% (Fig. 2.5).
$n$-paraffins and $n$-olefins are the main products of the LTFT synthesis but side-products like oxygenates and branched compounds can also be obtained. LTFT products are virtually free of nitrogen and sulfur compounds.

![Diagram](image1)

**Figure 2.4** – FT products formation according to AFS model

![Diagram](image2)

**Figure 2.5** – Product composition (wt%) against chain growth probability assuming ideal AFS kinetics

### 2.1.2. The Hydrocracking of Fischer-Tropsch Products

Hydrocracking should selectively convert the heavy paraffins into middle distillates. It should minimize cracking of the middle distillates already present in the feedstock, if any. Moreover, it should favor the production of isomerized middle distillates in order to improve the cold flow properties.
The hydrocracking catalysts always contain a hydrogenation/dehydrogenation (HD/DHD) function provided by one or more metals or one or more sulfides and an acidic function of the Brönsted type. Compared to conventional hydrocracking of petroleum-based feedstocks, high conversion of the FT feedstock can be obtained under mild hydrocracking conditions thanks to the high chemical reactivity of heavy paraffin molecules and the absence of strong catalyst contaminants like sulfur or nitrogen compounds (Table 2.2). 2

<table>
<thead>
<tr>
<th></th>
<th>Conventional Hydrocracking</th>
<th>Mild Hydrocracking</th>
<th>FT Waxes Hydrocracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (MPa)</td>
<td>10 – 20</td>
<td>5 – 8</td>
<td>3.5 – 7</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>623 – 703</td>
<td>653 – 713</td>
<td>597 – 645</td>
</tr>
<tr>
<td>$\text{H}_2$/Feedstock (m$^3$/m$^3$)</td>
<td>800 – 2000</td>
<td>400 – 800</td>
<td>500 – 1800</td>
</tr>
<tr>
<td>LHSV (h$^{-1}$)</td>
<td>0.2 – 2</td>
<td>0.2 – 2</td>
<td>0.5 – 3</td>
</tr>
<tr>
<td>Reactor Technology</td>
<td>Trickle bed</td>
<td>Trickle bed</td>
<td>Trickle bed</td>
</tr>
<tr>
<td>Conversion (%)</td>
<td>70 – 100</td>
<td>20 – 40</td>
<td>20 – 100</td>
</tr>
</tbody>
</table>

2.1.3. Hydrocracking Mechanisms

For proper functioning the HD/DHD site requires the presence of hydrogen gas. After adsorption on the HD/DHD site, the $n$-paraffin is dehydrogenated to a corresponding $n$-olefin. The $n$-olefin diffuses to a Brönsted acidic site to be protonated and transformed to a carbocation. The carbocation can be isomerized into an isocarbocation and/or cracked to produce a lighter olefin and lighter carbocation. After deprotonation, the various olefinic products diffuse back to an HD/DHD site and are hydrogenated. Finally, hydrogenated products are desorbed from the catalyst (Figure 2.6). 2

The formation of cracked products generally involves two successive reaction steps: the hydroisomerization step and the actual hydrocracking step.

Two types of mechanisms rule the hydroisomerization step:

- Type A isomerization: the branching degree of the carbocation is not modified but branching undergo positional changes via alkyl and hydride shift, for example:

![Diagram of hydroisomerization](image)
Figure 2.6 – Bifunctional mechanism for hydroisomerization and hydrocracking of a normal paraffin

- Type B isomerization: the branching degree of the carbocation is increased or decreased via the formation of cyclic carbonium ion intermediates, like the protonated cyclopropane (PCP):

Several studies demonstrated that the A type isomerization is much faster than the B type isomerization. Consequently, on bifunctional catalysts that do not exhibit molecular shape selectivity, positional isomer fractions tend to be distributed according to their internal thermodynamic equilibria.

The hydrocracking step occurs via the scission of the carbon–carbon bond in β position of the positively charged carbon atom of the carbocation, a process called β-scission. It results in the formation of a smaller carbocation and an olefin.

The carbocation chemistry is of particular relevance for the hydrocracking of LTFT wax since the middle distillates produced will be branched as illustrated in figure 2.7. The product inherently will exhibit improved cold flow properties. Evidently, primary cracked products can undergo some hydroisomerization depending on reaction severity. As a consequence the third requirement of the hydrocracking stage can be met.
There are many reports on the relative reactivity of \( n \)-paraffins towards cracking. The reactivity increases with the chain length and with the increasing number of possible scission reactions. When LTFT waxes are processed on a bifunctional hydrocracking catalyst, process conditions can be tuned in order to achieve significant hydrocracking of the heavy part of the feed (say C\(_{20+}\) paraffin) and to minimize the cracking of the lighter part of the feed and especially the middle distillates. As a consequence, the second requirement of the hydrocracking stage could also be fulfilled.

### 2.1.4. “Ideal” Hydrocracking Catalyst

In order to fulfill the first requirement of the hydrocracking stage, the formulation of the hydrocracking catalyst is of course of prime importance. As middle distillates are the targeted hydrocracked products, successive cracking of the primary cracked products should be minimized, therefore:

- The reaction rate should not be limited by olefins transport, so the two catalytic functions must be at short mutual distance in order to respect the Weisz’s intimacy criterion;
- The hydro/dehydrogenation function should be strong enough to balance the acidic function in order to feed the acid sites with a maximal amount of intermediate alkenes (limited by thermodynamics) and quickly hydrogenate the cracked alkene intermediates.

In such catalyst, the hydro/dehydrogenation reactions are quasi equilibrium and the limiting step of the reaction takes place on the acid function (Figure 2.6). The key features of ideal hydrocracking of long chain \( n \)-paraffins are:
- Low reaction temperature,
- The possibility of high selectivities for isomerization,
- The possibility of pure primary cracking.

The ideal hydrocracking catalyst is the catalyst for which primary cracking occurs up to the highest conversion. It should be emphasized that the occurrence of ideal hydrocracking is not only related to the catalyst formulation, but also depends on the operating conditions. Ideal hydrocracking can be predicted assuming the following hypotheses based on the reaction mechanisms already discussed:
- Only pure primary cracking is allowed,
- C₁ and C₂ cannot be formed,
- Equal molar amounts of fragments between C₄ to C₁₉ are formed,
- Molar amounts of C₃ and C₂₀ are half from molar amounts to fragments between C₄ and C₁₉.

Figure 2.8 depicts this theoretical molar carbon number distribution of cracked products for the ideal hydrocracking of tricosane. It appears that on a weight basis, typical selectivity in middle distillates as high as 79% can be obtained. Therefore, if the production of heavy paraffins in the Fischer-Tropsch unit is combined with an ideal hydrocracking of these paraffins in an hydrocracking unit working in a full conversion mode, middle distillates yields around 80% could be obtained. Interesting to note is that this value is about twice that of the maximum middle distillates yield than could be produced with a Fischer-Tropsch unit alone (see Fig. 2.5).

![Figure 2.8 – Theoretical molar carbon number distribution of cracked products for the ideal hydrocracking of tricosane](image)
2.1.5. LTFT Waxes Hydrocracking Catalysts Formulations

Like for catalysts designed for hydrocracking of conventional petroleum feedstocks, the following metals could be used as HD/DHD function: noble metals (Pt, Pd), and non-noble transition metals from group VI A (Mo, W) and group VIII A (Co, Ni). Transition metals from group VI A and VIII A are usually applied as sulfides (Ni-W, Ni-Mo, Co-Mo).

From a practical point of view, the HD/DHD function also plays a key role when the catalyst stability is considered. A strong hydrogenating function will hydrogenate coke precursors like polynuclear aromatics formed by dehydrocyclisation of paraffins and, therefore, improve catalyst life cycle. Indeed, for the hydroconversion of n-decane at atmospheric pressure on Pt-HY catalysts, it was observed that increasing the ratio of accessible platinum sites to strong acid sites markedly improved the catalysts stability (Fig. 2.9).²

![Figure 2.9](image)

**Figure 2.9** – Ratio of the final to initial activities (A_f/A_0) of Pt-HY catalysts during n-decane hydroconversion as a function of the ratio of accessible platinum sites to strong acid sites (n_p/n_a)²

In an ideal catalyst the rate determining step of the reaction occurs on the Brønsted acid sites. Various factors can adversely affect the selectivity of the cracking of a wax molecule to middle distillates, like secondary cracking and cracking near the end of the chain. Schematically, the possibility of secondary cracking will increase an increased average residence time of olefinic intermediates in the vicinity of acid sites. Therefore, any diffusional limitation or confinement effect resulting in a too strong adsorption of the intermediates should be minimized. Reducing the acid site density and maintaining a constant hydrogenating power should also retard secondary cracking. Preferential cracking near the end of the chain can occur if the long chain paraffin penetrates only with its end into a pore of the solid catalyst.
There are several published findings about middle distillates production via LTFT waxes hydrocracking. In a general way, it can be deduced from the published results that high middle distillates yields can be obtained using solid acids with weak or medium acid strength, like silica-aluminas, silicated aluminas or polyoxocation pillared montmorillonite. Such observations are quite expected since with these solid acids the overcracking of olefinic intermediates can be minimized. In the field of conventional petroleum feedstocks hydrocracking, it is also well known that amorphous silica-alumina based catalysts are less active than zeolite based catalysts but are more suited to maximize the middle distillates production. It was recently claimed that the addition of very small amounts of USY zeolite to amorphous silica-alumina could strongly improve the activity of the catalyst for waxes hydrocracking without significant middle distillates selectivity loss. Hydrocracking of LTFT waxes is a valuable option for the production of high quality middle distillates. A proper choice of operating conditions and catalyst formulation enables the occurrence of ideal hydrocracking. Under the ideal hydrocracking conditions, the production of middle distillates can be maximized.

2.2. Dealuminated Zeolites

One of the best ways to control acidity of zeolite catalysts and thus their activity, stability and selectivity, is to modify the framework Si/Al ratio. Hydrothermal steaming is the most commonly used method for adjusting the framework Si/Al ratio as it leads to replacement of a part of the framework aluminum (Al\(^{IV}\)) by silicon. Parts of the structure which provide the silicon for this substitution may be destroyed, forming mesopores partially filled with amorphous debris. The nature of the extra-framework aluminum (EFAL) formed during steaming has been the subject of much research, and several candidate forms have been proposed with Al present as cations (Al\(^{III}\), AlO\(^{+}\), Al(OH)\(^{+}\), Al(OH)\(^{2+}\)) or as neutral or polymerized forms (AlO(OH), Al(OH)\(_{3}\), Al\(_{2}\)O\(_{3}\)). In the \(^{27}\)Al MAS NMR spectra of hydrated samples, pentacoordinated and octahedrally coordinated extra-framework aluminum species are indicated by signals at ca. 30 and 0 ppm, respectively. The presence of large amounts of EFAL has detrimental effect on catalytic and transport properties so that it is usual to extract the aluminum by subsequent chemical attack. Mineral acid attack to remove the EFAL is common industrial practice, but other agents have been proposed such as ammonium hexafluorosilicate (AHFS) and ethylenediaminetetraacetic acid (EDTA).
2.2.1. Ultrastable Y Zeolite

USY zeolite is the most used zeolite for hydrocracking application. The catalytic properties of ultrastable Y (USY) are directly influenced by the zeolite destruction which occurs during formation of USY and during subsequent hydrothermal treatment. \(^5\) Dealumination of zeolites by steaming requires an activation of the framework by introduction of protons (over the decomposition of the NH\(_4^+\) modification by heating). \(^6\)

The formation of ultrastable FAU materials may be viewed as a two-step process in which calcination of the ammonium (or H) from the Y-zeolite at \(T \geq 500 \, ^\circ C\), \(P_{H_2O} \approx 1 \, atm\), for more than 2 hours, first leads to the expulsion of Al atoms from the framework T-sites as indicated in fig. 2.11. In the second step, the vacancies created by aluminum expulsion from the lattice during hydrothermal treatment are, to a great extent, refilled by silicon atoms migrating from the collapsed portions of the crystal. If this “healing” did not occur, the entire zeolite crystal would collapse. The resulting restructured FAU material, commonly known as ultrastable Y or USY, displays a contracted unit cell size and increasing hydrothermal stability as framework Si/Al increases. A typical reduction in unit cell dimension is from 24.70 Å for the starting zeolite Y to 24.56 Å for the product USY. Increasingly severe steam treatments result in a higher level of dealumination, a more contracted unit cell, and an increasing level of crystalline zeolite destruction. \(^5\)

Prior sorption studies indicate that entire sodalite units, or β-cages, are destroyed during hydrothermal dealumination, leading to the formation of a secondary pore system or mesoporosity in the range of 5-50 nm, in addition to the zeolite micropores. These regions of zeolite destruction comprise the silica for “healing” the tetrahedral vacancies left by hydrothermal dealumination. As shown schematically in fig. 2.10, the collapse of sodalite units, or even assemblies of them, generates mesoporosity and simultaneously provides the source of Si atoms for “healing”. \(^5\)

![Figure 2.10](image)

Figure 2.10 – Schematic representation of formation of ultrastable Y materials. Expulsion of Al atoms from framework T-sites. \(^5\)
2.3. Silicon Carbide (SiC)

In the past, zeolite/SiC composites have been successfully prepared. 7, 8, 9, 10, 11 Silicon carbide has superior mechanical and thermal properties which, coupled to chemical inertness, avoids several of the problems inherent in the use of commercial oxide and carbon based supports and catalysts.

Silicon carbide (SiC) exhibits a high thermal conductivity, a high resistance towards oxidation, a high mechanical strength, a low specific weight, and chemical inertness (Table 2.3); all properties required for good heterogeneous catalyst support materials. 3

<table>
<thead>
<tr>
<th>Table 2.3 – Silicon Carbide physical properties 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity (W.m⁻¹.K⁻¹)</td>
</tr>
<tr>
<td>Thermal expansion coefficient between 100 and 500 K (10⁻⁶.K⁻¹)</td>
</tr>
<tr>
<td>Thermal expansion coefficient between 0 and 1000 K (10⁻⁶.K⁻¹)</td>
</tr>
<tr>
<td>Dielectric constant at 1 MHz</td>
</tr>
<tr>
<td>Density (g.cm⁻³)</td>
</tr>
<tr>
<td>Sintering temperature (K)</td>
</tr>
<tr>
<td>Young’s modulus (10¹² dyn.m⁻²)</td>
</tr>
</tbody>
</table>
In general, commercial heterogeneous catalysts are biphasic, being composed of a support material and one or more active phase component(s). The support provides a porous framework with pore diameter distribution permitting access to the active sites for the reactants and free exit for the products. Large macroscopic pores, or voids, are necessary to ease the traffic of the gaseous or liquid molecules of the reactants and the products, or, in more technical terms, to avoid diffusional limitations that could be detrimental to the activity and selectivity, and result in pressure drops in the catalytic reactor which could dramatically affect the process operation. The design of the shape of the macropores and/or their modelization is an important field of research for catalyst and catalyst support developers. Materials with high meso- and micro-porosity and in turn, high surface area, also play an important role. They usually help to increase the dispersion of the active phase(s) by rendering more difficult its sintering or aggregation. This dispersion is not only due to the presence of the meso- and micro-pores, but also to chemical and/or electronic interactions between the support and the active phase. Sometimes, this chemical interaction can be a serious drawback as solid-solid reactions can take place between the support and the active phase, eventually destroying the specificity of the catalyst. Nevertheless, dispersion is important because it increases the activity of the catalyst by increasing the number of accessible active sites without increasing the amount of the expensive (precious metals or complex chemicals) active phase.

Another important property of the support is its mechanical strength. In large industrial reactors, the collapse of the structure (catalyst bed) under its own weight should obviously be avoided because it will result in a severe and not easily corrected pressure drop. Mechanical strength is also required when the catalytic system is submitted to vibrations (car exhaust systems for instance) or to a very high gas liquid flow velocity (natural gas reforming, energy generation via natural gas combustion involving catalytic processes). Generally, mechanical strength is reinforced by a specific design of the macroscopic shape of the catalyst, i.e., pellets, extrudates, spheres, monoliths, etc. Reducing attrition by improving the mechanical properties of the catalyst (support), however, remains the best remedy to this problem. ³

The properties of the support attached to its thermal resistance and its thermal conductivity were the subject of only few investigations in the past. Research on the thermal stability of catalyst supports became significant when automotive exhaust catalysts were introduced and, more recently, because of the development of catalytically assisted combustion related to the minimization of NOx production – these reactions running at temperatures generally higher than the limit of stability of conventional pure alumina or silica. Studies taking directly into
account the thermal with the exception of classical chemical engineering studies dealing, for instance, with the design of adiabatic reactors.

The high thermal conductivity of SiC, comparing to other classical supports (Table 2.4), allows a uniform temperature in the catalyst bed, particularly by strongly decreasing the surface temperature at steady-state.

Finally, the support itself can affect the catalytic properties of the catalyst by adding chemical functionalities such as acid, basic or electron donating/withdrawing properties.  

Table 2.4 – Thermal conductivities of SiC and classical supports

<table>
<thead>
<tr>
<th>Support</th>
<th>Thermal Conductivity (W.mol⁻¹.K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>0.015 – 1</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1 – 8</td>
</tr>
<tr>
<td>SiC</td>
<td>146 – 270</td>
</tr>
</tbody>
</table>
3. Experimental Section

3.1. Characterization Techniques

3.1.1. XRD

X-ray diffraction is a versatile, non-destructive technique that reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials.

A crystal lattice is a regular three-dimensional distribution (cubic, rhombic, etc.) of atoms in space. These are arranged so that they form a series of parallel planes separated from another by a distance $d$, which varies according to the nature of the material. For any crystal, planes exist in a number of different orientations, each with its own specific $d$-spacing.

When a monochromatic X-ray beam with wavelength $\lambda$ is projected onto a crystalline material at an angle $\theta$, diffraction occurs only when distance traveled by the rays reflected form successive planes differs by a complete number $n$ of wavelengths. By varying the angle $\theta$, the Bragg's Law (equation 3.1) conditions are satisfied by different $d$-spacings in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns. 

\[ n\lambda = 2d(hkl) \sin \theta \]  
(equation 3.1)

Where:

$n$ is an integer determined by the order given

$\lambda$ is the wavelength of X-rays, and moving electrons, protons and neutrons

$d$ is the spacing between the planes in the atomic lattice

$\theta$ is the angle between the incident ray and the scattering planes.

In this work, all the catalysts were analyzed by XRD and their diffractograms were obtained using a diffractometer Bruker AXS D8 Advance, using a wavelength of $\lambda = 1.5418 \text{ Å}$.
3.1.2. BET

For measuring the specific surface area of the samples, the used method was the BET isotherm theory, by doing nitrogen gas adsorption and desorption. For each sample, the outgassing was done at 300 °C over night, to be sure that the water inside the pores was completely removed due to the fact of the Y zeolite being very hydrophilic.

3.1.3. NH$_3$-TPD

TPD analysis were performed to check the types of acidity of the zeolites. Temperature-Programmed Desorption (TPD) is one of the most widely used and flexible techniques for characterizing the acid sites on oxide surfaces. There are three types of molecular probes commonly used for characterizing acid sites using TPD: ammonia, non-reactive vapors and reactive vapors.

TPD of ammonia (NH$_3$) is a widely used method for characterization of site densities in solid acids due to the simplicity of the technique. Ammonia often overestimates the quantity of acid sites. Its smaller molecular size allows ammonia to penetrate into all pores of the solid where larger molecules commonly found in cracking and hydrocracking reactions only have access to large micropores and mesopores.

Also, ammonia is a very basic molecule which is capable of titrating weak acid sites which may not contribute to the activity of catalysts. The strongly polar adsorbed ammonia is also capable of adsorbing additional ammonia from the gas phase. The analysis involves heating a sample while contained in a vacuum and simultaneously detecting the residual gas (NH$_3$) in the vacuum by means of mass analyzer. As the temperature rises, certain absorbed species will have enough energy to escape and will be detected as a rise in pressure for a certain mass.

On temperature programmed desorption analysis, as the temperature rises and a particular species is able to desorb from the surface, the pressure will rise. As the temperature rises still further the amount of the species on the surface will reduce causing the pressure to drop again. This results in a peak in the pressure versus time plot. The temperature of the peak maximum provides information on the binding energy of the bound species.
In this work, all the catalysts were analyzed following this three steps:
1 – Heat from room temperature to 500°C (15°C/min) under He, then a plateau during 4 hours, after that return to room temperature
2 – Heat from room temperature to 150°C at 10°C/min under He/NH$_3$ (1.5%), then a plateau for 1 hour and return to room temperature
3 – From room temperature to 700°C under He (15°C/min), plateau for 1 hour and then return to room temperature

3.1.4. SEM

SEM stands for scanning electron microscope. The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. It also has much higher resolution than traditional microscopes, because it uses electromagnets rather than lenses, allowing having much more control in the degree of magnification.

A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample.

Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image. In Fig. 3.1 is represented the functioning of SEM.

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**Figure 3.1 – Schematic representation of SEM functioning**

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Because the SEM utilizes vacuum conditions and uses electrons to form an image, special preparations must be done to the sample. All water must be removed from the samples because the water would vaporize in the vacuum. All metals are conductive and require no preparation before being used. All non-metals need to be made conductive by covering the sample with a thin layer of conductive material. This is done by using a device called a "sputter coater". The sputter coater uses an electric field and argon gas. Therefore, the sample was placed in a small chamber that was at a vacuum. Argon gas and an electric field cause an electron to be removed from the argon, making the atoms positively charged. The argon ions then become attracted to a negatively charged gold foil. The argon ions knock gold atoms from the surface of the gold foil. These gold atoms fall and settle onto the surface of the sample producing a thin gold coating.\textsuperscript{15}

\subsection*{3.1.5. TEM}

Transmission Electron Microscopy (TEM) is a technique used for analyzing the morphology, crystallographic structure, and even composition of a specimen. TEM provides a much higher spatial resolution than SEM, and can facilitate the analysis of features at atomic scale (in the range of a few nanometers) using electron beam energies in the range of 60 to 350 keV. Unlike the SEM which relies on dislodged or reflected electrons from the specimen to form an image, the TEM collects the electrons that are transmitted through the specimen. Like the SEM, a TEM uses an electron gun to produce the primary beam of electrons that will be focused by lenses and apertures into a very thin, coherent beam. This beam is then controlled to strike the specimen. A portion of this beam gets transmitted to the other side of the specimen, is collected, and processed to form the image.

For crystalline materials, the specimen diffracts the incident electron beam, producing local diffraction intensity variations that can be translated into contrast to form an image. For amorphous materials, contrast is achieved by variations in electron scattering as the electrons traverse the chemical and physical differences within the specimen. The greatest consideration when performing TEM analysis is sample preparation. The quality of sample preparation contributes greatly to whether the micrograph will be good or not, so analysts are required to exercise the necessary diligence in preparing the sample for TEM analysis.\textsuperscript{16}
3.1.6. ICP-MS

For elemental analysis, the technique used was ICP-MS (Inductively Coupled Plasma – Mass Spectrometry). A plasma is a gas that contains a sufficient concentration of ions and electrons to make the gas electrically conductive. The plasmas used in spectrochemical analysis are essentially electrically neutral, with each positive charge on an ion balanced by a free electron. In these plasmas the positive ions are almost all singly-charged and there are few negative ions, so there are nearly equal amounts of ions and electrons in each unit volume of plasma.

An inductively coupled plasma (ICP) for spectrometry is sustained in a torch that consists of three concentric tubes, usually made of quartz. The end of this torch is placed inside an induction coil supplied with a radio-frequency electric current. A flow of argon gas (usually 14 to 18 liters per minute) is introduced between the two outermost tubes of the torch and an electrical spark is applied for a short time to introduce free electrons into the gas stream. These electrons interact with the radio-frequency magnetic field of the induction coil and are accelerated first in one direction, then the other, as the field changes at high frequency (usually 27.12 million cycles per second). The accelerated electrons collide with argon atoms, and sometimes a collision causes an argon atom to part with one of its electrons. The released electron is in turn accelerated by the rapidly-changing magnetic field. The process continues until the rate of release of new electron in collisions is balanced by the rate of recombination of electrons with argon ions (atoms that have lost an electron). This produces a “fireball” that consists mostly of argon atoms with a rather small fraction of free electrons and argon ions. The temperature of the plasma is very high, of the order of 10 000 K.

The ICP can be retained in the quartz torch because the flow of gas between the two outermost tubes keeps the plasma away from the walls of the torch. A second flow of argon (around 1 liter per minute) is usually introduced between the central tube and the intermediate tube to keep the plasma away from the end of the central tube. A third flow (again usually around 1 liter per minute) of gas is introduced into the central tube of the torch. This gas flow passes through the centre of the plasma, where it forms a channel that is cooler than the surrounding plasma, but still much hotter than a chemical flame. Samples to be analyzed are introduced into this central channel, usually as a mist of liquid formed by passing the liquid sample into a nebulizer.
As a droplet of nebulized sample enters the central channel of the ICP, it evaporates and any solids that were dissolved in the liquid vaporize and then break down into atoms. At the temperatures prevailing in the plasma a significant proportion of the atoms of many chemical elements are ionized, each atom losing its most loosely-bound electron to form a singly charged ion.

The ions from the plasma are extracted through a series of cones into a mass spectrometer. The ions are separated on the basis of their mass-to-charge ration and a detector receives an ion signal proportional to the concentration.\textsuperscript{17}

3.1.7. Titration $H_2$-$O_2$

By $H_2/O_2$ titration, the dispersion of the metal over the support is obtained. The analysis was realized on a Micrometrics Autochem II. The chemisorption $H_2/O_2$ provides an evaluation of the available metal surface compared to the total amount of introduced metal. The platinum form the catalyst is reduced under pure hydrogen and oxygen flow is carried to the catalyst: the volume of oxygen adsorbed is directly related to the number of platinum atoms on the surface of crystallites. The involved reaction between platinum and oxygen can be written as shown on equation 3.2.

$$Pt_s + \frac{3}{4}O_2 \rightarrow Pt_s - O + \frac{1}{2}H_2O$$

(equation 3.2)

The analysis is carried out by calcination under air for 2 hours at 530°C, and then the temperature is lowered to 35°C. Helium is purged at 35°C and then it’s made a reduction at 450°C for 2 hours with $H_2$. After that the temperature is dropped to 35°C, He is purged and $O_2$ titration is done at 35°C.
3.2. Catalyst Preparation
3.3. Catalytic Testing
4. Results and Discussion

4.1. Catalysts Characterization
4.2. Catalytic Test
5. Conclusion
References


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Appendices

A) Synthesis of BEA/SiC

The behavior of zeolites supported on silicon carbide was also extended to BETA zeolite, in order to apply on Friedel-Crafts reaction, a procedure which is being studied at LMSPC. The synthesis of BETA zeolite was done following the procedure suggested by Winé:

1. Dissolve 10.17 g of TEOH and 3.91 g of Aerosil® 200 on 7.23 g of H₂O at 50 °C
2. At the same time, dissolve 0.067 g of Al powder on 6.14 g of TEOH at 50 °C
3. After complete dissolution, mix both solutions at room temperature
4. The solution is left ageing for 1 h under stirring
5. 5 g of SiC extrudates are added to the mixture
6. Zeolite crystallization is performed in a autoclave at 140 °C for 24 h

After the synthesis procedure, the composite was analyzed by XRD, BET and SEM. The XRD pattern for the bulk zeolite is shown on Figure A.1, where are visible two large peaks corresponding to BETA zeolite. The fact of peaks being large indicates that the zeolite is not well crystallized, however it confirms that the synthesis is correct.

![Figure A.1 – XRD pattern for the synthesized BETA bulk zeolite](image-url)
In figure A.2 it’s shown the XRD pattern for the BEA/SiC composite. There’s visible the appearance of two peaks corresponding to BETA zeolite, as seen in Fig. A.1, one between 5° and 10° 2θ and the other between 10° and 15° 2θ. At around 35.5° and 41° 2θ there are two peaks corresponding to SiC material.

![Figure A.2 – XRD pattern for the synthesized BEA/SiC composite](image)

Fig. A.3 displays scanning electron microscopy images of the BEA zeolite. The inset shows that the BETA crystals morphology is totally different from Y crystals. Even though, it seems that the crystals are condensed, possibly due to sinterization. In Figure A.4 are shown the SEM images for BEA/SiC composite, on which we can see that the supported crystals have a different morphology of those from bulk zeolite, with a crystallite size of ca. 40 nm.
Figure A.3 – SEM images of the bulk BEA zeolite.  
Inset: low magnification images

Figure A.4 – SEM images of the BEA/SiC composite.  
Inset: low magnification images