Hydrotreating of synthetic fuels with bulk and supported Ni-Mo(W) sulfide catalysts.

by

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Abstract

Energy sources form fossil fuels are the most largely used ones, and even with the development of alternative energy sources their predominance is not reducing. In addition, light crude oil reserves are depleting and the heavier ones with higher amount of impurities (S, N containing components) have to be transformed. Thus, in order to compensate this increment and fulfill quality requirements on intermediates and products highly active and selective hydrotreating catalysts have to be developed. On this matter supported and unsupported Ni(Co) W(Mo) sulphide catalysts have been largely studied. However, further research in this matter is needed to accomplish a fully understanding of their catalytic activity and performance during hydrotreating processes.

This work addresses the usage of six bulk catalysts in the parallel hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) reactions of the model components quinoline (Q), o-propylaniline (OPA), and dibenzothiophene (DBT) as well as five supported catalyst in the hydrodearomatization (HDA) of phenanthrene (Phe). The unsupported catalyst were tested in order to study the influence of DBT in Q/OPA HDN and vice versa. On the other hand the supported catalyst were tested in order to study the influence of the amount of Ni in the HDA activity of Phe.

The overall mechanism for the OPA HDN stated in literature by Prins\textsuperscript{20} for the isolated Q HDN over NiMo catalysts supported on Al\textsubscript{2}O\textsubscript{3} as well as the DBT HDS stated by Chianelli \textit{et al} work well with the four different feedstocks tested, and it is related to the results obtained in all the cases. On the other hand, the hydrogenation of phenanthrene occurred via two pathways described by Beltamone \textit{et al}\textsuperscript{50}.

It was found that all catalysts are active for both Q/OPA HDN and DBT HDS, while the trend of increasing/decreasing activities with the increasing of temperature was different depending the HDN model compound selected. In addition, there were considerable differences between the results with the feedstocks containing OPA. In the case of the later there is appreciated an increase in the general conversion with the increase of temperatures, while for Q feeds an increase in temperature produces a decrease in the amount of Q converted. The activity rank of the catalysts in the HDN reactions shows that catalyst synthesized following the patent of Soled \textit{et al}\textsuperscript{9} at room temperature and the one formed by precipitation of thiometallates with H\textsubscript{2}S according to Yi \textit{et al}\textsuperscript{10} under hydrothermal conditions are the most active ones, no matter if OPA or Q are converted. On the other hand, the addition of Ni favors the conversion of phenanthrene.
However there is an optimum point (around 2.5 % Ni). Higher or lower concentrations showed a lower amount of phenanthrene converted in further components. The rates of both pathways increase linearly with the concentration, although with different slopes.
## Acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Significance</th>
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<tbody>
<tr>
<td><strong>General acronyms</strong></td>
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</tr>
<tr>
<td>HDM</td>
<td>Hydrodemetallization</td>
</tr>
<tr>
<td>HDN</td>
<td>Hydrodenitrogenation</td>
</tr>
<tr>
<td>HDO</td>
<td>Hydrodeoxygenation</td>
</tr>
<tr>
<td>HDS</td>
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</tr>
<tr>
<td>HDT</td>
<td>Hydrotreating</td>
</tr>
<tr>
<td>HDA</td>
<td>Hydrodearomatization</td>
</tr>
<tr>
<td>DDN</td>
<td>Direct denitrogenation pathway</td>
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<td>HT</td>
<td>Hydrothermal Synthesis</td>
</tr>
<tr>
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### Other compounds

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</tr>
<tr>
<td>TD</td>
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<td>Decalin</td>
<td>Decahydroronaphthalene</td>
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### Analytical methods

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</tr>
<tr>
<td>FID</td>
<td>Flame ionization detector</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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### Symbols

<table>
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<tr>
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<td>$S_i$</td>
<td>Selectivity of component $i$</td>
</tr>
<tr>
<td>$X_i$</td>
<td>Conversion of component $i$</td>
</tr>
<tr>
<td>$Y_i$</td>
<td>Yield of component $i$</td>
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Chapter 1: Introduction

1.1 Motivation

The development of the human lifestyle has been impacting the climate in our planet for the last couple of centuries. On this matter, the predominant fossil energy sources have played an important role. The emission of greenhouse gases, main product from the generation of energy from fossil sources, has increased, and it is well known as one of the most important causes of global warming. Thus, international community pays more attention to all the efforts that are carried out to reduce the production of these negative components. On this behalf, some technologies have been developed in the field of alternative energies, but it does not seem that these sources will overcome the predominant importance of fossil fuels (As is showed in figure 1). \(^1\), \(^2\), \(^3\)

![Figure 1. World energy consumption in million tons of oil equivalent per year.](image)

In addition, light oil sources are depleting, so unconventional crude oil ones (generally with higher amounts of S, N, O, metals and aromatic compounds) have to be treated in order to fulfill the different quality requirements and decrease the amount of harmful and undesired products. To fulfill these necessities crude oil has to be transformed into transportable fuels with different...
characteristics, for specific needs. These processes of transformation consist in the separation of the different fractions, the removal of certain heteroatoms, and the breakage of some bonds; consequently, the production of components (kerosene, gasoline, diesel, etc.) characterized for their highly energetic content, facility of transport, and less amount of highly harmful combustion products. 4,5

The treatment to remove impurities is known as hydrotreating. A general concept that involves the reactions of hydrogen with a feedstock that produces compounds without undesired heteroatoms. Specifically the removal of N, S, O, metals, and the hydration of aromatic rings. Hidrotreating processes are carried out in different feedstocks and in different stages of the refining processes. Commonly, hydrotreating is carried out in separated units that are located in different locations in a refinery. A simplified and general scheme of these possible locations is showed in figure 2. 6

![Figure 2. Simplified flow scheme of an oil refinery with possible locations of hydrotreating](image)

Summarizing, the increase of fossil sources consumption and the imbalance of impurity content in crude oil encourage the development of better and more efficient hydrotreating processes. This means the synthesis of more active and selective catalysts, as well as an intense study of these materials in order to prevent poisoning of catalysts but also to obtain a high level of hydrotreating. 7
1.2 Scope of the thesis

The objective of this work is to study the activity of various bulk and supported sulphide catalysts in different hydrotreating processes. The catalysts used were synthesized previously using different pathways. The unsupported catalysts were prepared using the methods described by: the patent of Maesen et al. \(^8\), the patent of Soled et al. \(^9\), and a precipitation method of thiometallates with \(\text{H}_2\text{S}\) according to Yi et al. \(^10\). The supported catalysts used in the hydrogenation reactions were synthesized using incipient wetness impregnation of \(\gamma\)-\(\text{Al}_2\text{O}_3\).

In the case of the six bulk catalysts, they were tested in simultaneous hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) reactions. For the nitrogen removal reactions, two different model compounds were used: O-propylaniline (OPA) and Quinoline (Q). Meanwhile, dibenzothiophene (DBT) was used as the only component for testing the HDS activity. On the other hand, the supported catalysts were used to carry out hydrodearomatization (HDA) reactions.

In this particular case the compound used was phenanthrene (Phe).

The HDN/HDS reactions were temperature dependent, and the values used were: 310, 330, 350, and 370 °C. For these reactions the space time considered was always constant and just the influence of the temperature was studied. In the case of the hydrogenation reactions, they were space time dependent. The results of the HDN/HDS experiments will be used to study the OPA and Q HDN, and DBT HDS mechanisms, while the HDA reactions to test the Phe hydrogenation.

Concluding results about the activity of the different catalysts and the influence of the presence of other compounds (HDS/HDN reaction) or the amount of Ni in the catalysts (HDA reactions) was studied.
Chapter 2: Literature review

2.1 Catalysts

2.1.1 Catalyst selection and synthesis

The industrial process known as hydrotreating or hydroprocessing of crude oil is a very old industrial application. This process, that is designed to change the molecular weight of the feed treated (due to the removal of heteroatoms or double bonds), is carried out with a catalyst in the presence of hydrogen at temperatures ranging from 200 to 450 °C and pressures between 5 and 300 bar. One of the components that plays a major role in this procedure is the catalyst, which constituents have hardly changed during the past 70 years. In industry the preferred catalysts are alumina (specially γ-Al₂O₃) supported transition metal sulphides (TMS), especially Co, Ni, Mo, and W ones due to their favorable chemical, physical, and mechanical properties, activity response and availability. Many studies have been carried out to determine the activity of many TMS based on their activity in HDS. The results showed a volcano plot according to the Sabatier principle. It means that the higher activity is related with the intermediate bond strength between the metal and sulfur.¹¹-¹³ A plot which contains information of certain metals is showed in figure 3.

![Figure 3](image-url)

**Figure 3.** Dependence of the activity on the strength of the metal - sulfur bond. ¹¹
As it is showed, the most active transition metals are Ru, Rh, Ir and Os. However, they are not the ones used in industrial applications due to their high price that results in a high cost/benefit ratio. Other metals like Mo, Ni, and Co are more economical and present a reasonable activity that make them the most suitable in production facilities.\textsuperscript{13}

The catalysts used are TMS, and the reason why sulphur containing species are used in HDS, HDN and HDA is mainly their great resistance against poisoning\textsuperscript{15}. Additionally, the presence of nickel or cobalt as promoter for the catalysts has showed an increase in the activity. While nickel promoted molybdenum catalysts are more effective in HDN, promotion with cobalt conducts to a higher HDS activity\textsuperscript{13}. The maximum promotion effect can be gotten at very well defined Ni or Co concentrations. This effect is related to the arrangement of Ni or Co atoms at the perimeter of Mo\textsubscript{S}\textsubscript{2} slabs (the promoter atoms that replace Mo atoms). However, many details of the nature and effect of promotion on structure and performance of Mo\textsubscript{S}\textsubscript{2} are still unknown, even when there is an agreement regarding the active form of the catalyst and some related catalytic phenomena.\textsuperscript{16-19}

In order to disperse the catalytic material and increase the accessibility to the active sites, in industry the catalysts are commonly supported on $\gamma$-alumina. This support also helps to stabilize the catalyst. However, the primary catalytic properties are based on the catalytic sites, so the support plays only a subordinate role. In fact, due to an interaction active site-support the activity is reduced in these catalysts.\textsuperscript{20}

The pore size distribution is another important characteristic of any hydrotreating catalyst. This pore size distribution has to be appropriate for the mixture that is being treated. HDS and HDN catalysts normally have a surface area between 150 and 250 m\textsuperscript{2}/g and a narrow pore-size distribution, where 75% of the total pore volume is in pores having diameters from 7 to 13 nm\textsuperscript{21}. “The pore volume is typically lower than 0.7 cm\textsuperscript{3}/g in order to have a sufficient activity per reactor volume”.\textsuperscript{12} In addition, some mechanical properties such as side crushing strength, bulk crushing strength, or abrasion are necessary to prevent catalyst beds in commercial reactors from collapsing under their own weight or increasing the pressure drop over the catalyst bed. In fact, those mechanical properties help to make the regeneration and reuse processes easier to carry out.\textsuperscript{22, 23}

Regarding the synthesis of bi and trimetallic catalysts (containing Ni, W, and Mo), countless different methods have been proposed. Some examples are: incipient wetness impregnation, solution reactions\textsuperscript{24}, thermal decomposition of thiosalts\textsuperscript{11} as well as hydrothermal and solvothermal processes\textsuperscript{25}. Within this list of methods, some lead to the formation of directly sulphided materials, while others to oxides that have to be sulphided before being used in the
reaction. This sulphidation is commonly performed with a mixture of hydrogen and one or more sulphur containing compounds like H₂S or dimethyl-disulphide (DMDS). After the sulphidation, Mo and W form a layered hexagonal structure coordinated trigonal prismatic by six sulphur atoms. The rotation of the layers between each other is 60° and they are shifted, so a metal atom is placed over/under a sulfur atom in the adjacent layers. In the meantime, nickel is in the form of Ni₃S₂ crystallites or as atoms replacing Mo or W on the edges of the MoS₂/WS₂ slabs. This is known as Ni-Mo-S phase. For supported catalysts on alumina, Ni might diffuse into the alumina phase, where they form octahedral or tetrahedral sites, resulting in a spinel structure.

### 2.1.2 Supported catalysts

In industrial hydrotreating the catalytic processes are in general performed with sulphides of molybdenum/tungsten with cobalt or nickel, supported on γ-Al₂O₃. These catalyst supports are in general porous materials that permit a high loading of highly dispersed metal particles. This is particularly useful when the particles of the active phase need to be synthesized in such a way that they are as small as possible.

One of the critical points that has to be considered when supported catalysts are studied is the interaction of Mo/W oxides with the alumina support. It has been discussed by many authors, and many interactions complex have been showed. These interactions are important due to their influence in the catalytic activity of the final product, and they are present in both oxidized and sulphided forms. It is difficult to determine the specific effects of this interactions, but it has been hardly explained that the amount and characteristic of them depend on the synthesis method. Preparing the support base and adding the metal sites can be done in many ways, but sometimes the preparation of catalysts starts from previously shaped supports. These particular supports are attractive because a support with optimal properties can be selected before and the characteristics of this matrix will not depend on other factors.

It is largely accepted that MoS₂/WS₂-like structures resembling dispersed platelets are found in the sulphided supported catalysts. Images obtained with electron microscopy have revealed that single and stacked Mo(W)S₂ slabs, with dimensions and degree of stacking being dependent on sulphidation conditions, are present in sulphided Mo(W)/Al₂O₃-catalysts.
2.1.3 Unsupported catalysts

On the other hand, unsupported catalysts, known also as bulk catalysts, are not supported in any component and have higher concentration of active metals than their supported counterparts. However, the dispersion might not be extraordinary, and there is also the possibility of finding a big concentration of inactive crystalline compounds on its structure. In these compounds the catalysts – support interactions and the interference of the support are not present in the evaluation of their performance, so it is easier to get a detailed vision on structure - activity relations as well as on the properties of the catalytic material by the usage of different analytical techniques. In addition, Topsøe et al indicated, that by the suppression of the interactions between the Co(Ni)-Mo-S structure and the alumina support, the resulting catalyst should have an improved intrinsic activity. This characteristic together with the higher density of active sites provides certain advantages to this type of catalysts over their supported equivalent. However, it also presents some disadvantages. First of all, not all the active sites are accessible, so the ratio activity/active metal content is directly affected. Additionally, the higher content of metal play a primary role in the increasing of the final cost of the catalytic component.

2.1.4 Active sites

It is known as active site the portion of the catalyst where molecules are adsorbed and a chemical reaction undergoes. The identification of this active phase through different physical-chemical techniques, the proposal of a model, and a better understanding of the dynamics of the transformation of the catalysts are some key parameters to improve them.

There have been innumerable reports where the characteristics of active sites of the most used hydrotreating catalysts have been described. For example, one study conducted by Daage and Chianelli, in 1994, aimed to understand the relation between the morphology of crystallites and their catalytic properties. For MoS₂ catalysts, they introduced the so called rim-edge site model, in which two different active sites (rim and edge) are distinguished based on their location on the MoS₂ slab (Figure 4). They used the results obtained after the HDS reaction of DBT, and the characterization of the catalysts used to show that the ratio of selectivities of desulfurization to hydrogenation was proportional to the stacking degree. This suggested that the rim sites could be considered active for both hydrogenation and desulfurization while the edge sites are only active in desulfurization. However, they saw that due to a more complicated process of removal...
of sulfur the basal sites are consider inactive. This last affirmation was verified running a HDS reaction where a catalyst, with rim and edges inactive sites, evidenced a high inactivity. \textsuperscript{33}

Another research conducted in 1992 by Ho \textit{et al} give us an idea about how the rim-edge site model can explain HDN and HDS catalytical processes. In that experiment a feed, containing sulfur as well as nitrogen molecules, was treated in catalysts with single layers of MoS\textsubscript{2} supported on small pyrrhotite crystals. A high selectivity towards HDN was observed while HDS was rather low. Since HDN is favored by hydrogenation active catalysts this results support the rim-edge model.\textsuperscript{34}

Figure 4. Rim/edge model of a MoS\textsubscript{2} catalytic particle

Regarding the function of Ni as a promoter and its beneficial effect on the hydrotreating activity many models have been proposed, but currently one model is mainly accepted. The so called Ni-Mo-S (Co-Mo-S) phase model that is described with Ni (Co) located on the edges of the MoS\textsubscript{2} layered crystallites where the Ni (Co) atoms are connected over four sulfur atoms with the slab, as displayed in figure 5. Depending on the partial pressure of H\textsubscript{2}S a fifth sulphur atom can be attached. \textsuperscript{20,32}

Figure 5. Proposed structure of the Ni-Mo-S phase.\textsuperscript{20}
It was observed that a small amount of Co(Ni) produces a Co-Mo-S phase which strongly increases the activity in thiophene HDS, but when a high amount of Co$_9$S$_8$ is formed it is possible to reach a lower HDS activity. Thus, the formation of the Co-Mo-S (Ni-Mo-S) was responsible for the increasing activity trough promotion. It has been proposed, that the positive impact of the promotion of Mo(W)S$_2$ with Ni (Co) on HDS can be explained because a sulfur atom between a Ni (Co) atom and a Mo (W) atom is less strongly bounded in comparison to a sulphur atom between two molybdenum atoms.\textsuperscript{33-35}

It is important to mention that currently some investigations have been conducted trying to determine if Ni (Co) acts just as a promoter and Mo (W) atoms are really the active sites, or if the Co (Ni) compounds act as active sites themselves. To prove this, Co and Ni sulphides supported on carbon, to reduce the interaction Co(Ni) - support, were studied in HDS reactions. The results showed that these components have a higher activity that MoS$_2$/C catalysts. Suggesting that the Ni or Co phases could be the catalysts and not the promoters. This can be explained analyzing the pretreatment of Co(Ni) before the sulphidation and the high interaction of these atoms with alumina supports. Due to this high interaction, Co (Ni) are not sulphided and consequently it is impossible for them to contribute to the HDS activity.\textsuperscript{20, 36}

2.2 Hydrodenitrogenation (HDN)

2.2.1 Nitrogen compounds in crude oil

Hydrotreating processes involve the consumption of hydrogen, from external sources majorly, to produce hydrogenolysis and hydrogenation reactions that generate a reduction of the molecular weight of the original feedstock. On this matter hydrodenitrogenation focuses on the elimination of nitrogen that is present in different compounds in diverse crude oil feedstocks. The elimination of this heteroatom will guarantee a less amount of NO$_x$ components after the combustion of the resulting fuel.\textsuperscript{37}

The compounds that can be found are mostly polycyclic aromatic nitrogen components like: quinoline (Q), indole, acridine, indole, and carbazole; additionally, nitrogen monocycles as: pyridine and pyrrole. Depending on the single electron of the nitrogen and his role on the aromatic rings there are two kinds of components: basic and non-basic. In the basic aromatics cycles the free electron pair of the nitrogen atom is not part of the aromatic system, conferring basicity to the components. On the other hand, the free electron pair is integrated into the aromatic system on the
non-basic ones. As a consequence, it is expected that the initial contact with the catalyst will be different for both types. On the basic components the interaction will be favored via the nitrogen atom while for the non-basic ones it will be done over the aromatic system. The components classified in these two groups are showed in the table 1.

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic aromatic rings</td>
<td>Pyridine</td>
<td><img src="image" alt="Pyridine" /></td>
</tr>
<tr>
<td></td>
<td>Quinoline</td>
<td><img src="image" alt="Quinoline" /></td>
</tr>
<tr>
<td></td>
<td>Acridine</td>
<td><img src="image" alt="Acridine" /></td>
</tr>
<tr>
<td>Non-basic aromatic rings</td>
<td>Pyrrole</td>
<td><img src="image" alt="Pyrrole" /></td>
</tr>
<tr>
<td></td>
<td>Indole</td>
<td><img src="image" alt="Indole" /></td>
</tr>
<tr>
<td></td>
<td>Carbazole</td>
<td><img src="image" alt="Carbazole" /></td>
</tr>
</tbody>
</table>

2.2.2 HDN mechanism of Quinoline

The HDN of polycyclic aromatic nitrogen compounds is more difficult than the removal from aliphatic compounds. However, when quinoline is chosen as model component to perform HDN studies the undesired and unexpected interactions are not present. Additionally, because of
the bicyclic nature of quinoline, containing both a carbocyclic and a heterocyclic six-membered ring, the two supposed elementary steps of the HDN reaction can be studied. While decahydroquinoline (DHQ) is the key intermediate of one pathway, ortho-propylaniline (OPA) is the main intermediate of the other one. 20, 38, 39

The mechanism of quinoline HDN over NiMo/Al2O3 was described by Satterfield et al. 39 That mechanism is based in the fact that the C-N bond is too strong to break, so in both pathways the process begins with the hydrogenation of the aromatic ring that contains the N component, followed by a ring opening elimination to produce an amine, arylamine or cyclohexylamine. In the OPA pathway the heterocycle in Q is hydrogenated to 1, 2, 3 4-tetrahydroquinoline (14THQ) before the ring is opened and forms OPA. Meanwhile, in the DHQ lane, this component is formed from the complete hydrogenation of both rings in the Q structure. We can obtain DHQ through 5, 6, 7, 8-tetrahydroquinoline (58THQ) or through the 14THQ intermediate. This two pathways can be competitive and even if the HDN of quinoline more likely will be done via the 14THQ –OPA, sometimes DHQ adsorbs more strongly than aniline like components, suppressing the rate of OPA and reducing it. Figure 6 shows a scheme of the mechanism proposed for HDN of quinoline.

Figure 6. Mechanism (based on the one proposed by Satterfield) for HDN of quinoline 39

Regarding the optimal conditions to carry out this process, it is known that the hydrogenations of the carbocycles of Q and 14THQ are slow at temperatures below 623 K (350 ºC), low H2 pressures and high H2S/H2 ratios. However, the temperature has to be controlled because thermodynamically the equilibrium can move to the aromatics side at high temperatures.20
2.2.3 HDN mechanism of OPA

As it was described the mechanism of HDN of quinoline is complex and leads to some equilibriums that make the understanding of the conversion more difficult. For that reason, either DHQ or OPA are frequently selected as model compounds. If OPA is picked up, two further pathways are possible to achieve the final objective of separating N in form of NH₃. The first pathway via a direct denitrogenation (DDN) of OPA forming propylbenzene (PB), and the second one that starts with the hydrogenation (HYDN) of OPA to propylcyclohexylamine (PCHA), then the transformation of PCHA into propylcyclohexane (PCH) either by hydrogenolysis of the C-N bond or over the intermediate propylcyclohexene (PCHE). PCHE can form PCH or PB through both hydrogenation and dehydrogenation paths respectively. However, the dehydrogenation pathway is insignificant due to inhibitive adsorption of OPA and because the adsorption constants of PCHE and PB are negligible compared to those of OPA. The simplified mechanism for OPA is showed in figure 7.

![Figure 7. Mechanism proposed by Prins for HDN of quinoline. Just the OPA pathway is displayed.](image_url)

2.2.4 Kinetics of HDN

As it was set HDN processes are important in industry, but currently the knowledge available about the kinetics involved is limited. A better understanding of this particular will enable the interpretation of the influence of the reaction conditions, the reaction mechanism, the properties of the catalyst and its preparation. Presently, all the kinetic analysis that we perform are based on a series of assumptions that reduce the applicability of the modeling results obtained. For example, DDN and HYDN are carried out in different active sites, so to simplify the analysis many authors assume that they take place in the same sites. Another common supposition is to say that
If the modeling is done with representative compounds like OPA, some considerations can be made at the moment of modeling the system. First of all, PCHA can be considered a compound that is always found in low amounts and omitted in the kinetic results. On the other hand, PCHE has to be treated mathematically as a primary product and the reaction from it to PB and vice versa should be neglected as soon as OPA is present because of the competitive adsorption of OPA. Finally, it has to be reflected that the adsorption constants of PCH, PB and PCHE are negligible in comparison to the ones of OPA and NH₃, the other major products.²⁰

2.3 Hydrodesulfurization (HDS)

2.3.1 Sulfur compounds in crude oil

Hydrodesulfurization focuses on the elimination of sulfur that is present in different compounds in diverse crude oil feedstocks. The elimination of this heteroatom will guarantee a lower amount of SOₓ compounds (main cause of acid rain) after the combustion process of the resulting fuel.³⁷

Mercaptans, sulphides, disulphides and derivates of thiophene are the sulphur containing components that are found in crude oil (Some examples of these are showed in table 2; Error! No se encuentra el origen de la referencia.). The stability of this compounds is due to the arrangement at molecular level that determines how easy is to remove the sulphur atoms. In fact, a C-S bond cleavage becomes more difficult with the grade of the steric interference of the sulphur atom. Thus, to facilitate the conversion, a saturation of the aromatic system can be favored releasing the steric limitation of the ring system.⁴⁰
Table 2. Structures of sulfur containing compounds that can be found in fossil fuels.

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercaptans</td>
<td>Aliphatic</td>
<td>R-SH</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>Sulfides</td>
<td>Hydrogen sulfide</td>
<td>H2S</td>
</tr>
<tr>
<td></td>
<td>Aliphatic</td>
<td>R-S-R</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>Disulfides</td>
<td>Aliphatic</td>
<td>R-S-S-R</td>
</tr>
<tr>
<td></td>
<td>Aromatic</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>Thiophenes</td>
<td></td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td></td>
<td>Benzothiophene</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td></td>
<td>Thiphene</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td></td>
<td>Dibenzothiophene</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td></td>
<td>4,6-Dimethyldibenzothiophene</td>
<td><img src="image" alt="structure" /></td>
</tr>
</tbody>
</table>
2.3.2 HDS mechanism of DBT

There is a big variety of sulphur containing compounds that are present in crude oil. From this variety, benzothiophene, dibenzothiophene (DBT) and derivates are frequently selected model components for the study of HDS reactions and catalysts. In particular, DBT is not only representative for sulphides but also is converted slowly. This makes it easier to follow the intermediates of the reaction and to determine the mechanism in an easier way. In this matter Houalla et al in 1978 detailed the mechanism of the DBT HDS on CoMo/γ-Al2O3 (Showed in figure 8). Similarly to the HDN of OPA, there are two different pathways. In the first one phenylcyclohexane (PhCH) is formed via the intermediate 1, 2, 3, 4-tetrahydrodibenzothiophene (Hyd-DBT). In this route one of the six-rings of DBT is hydrogenated before the removal of the sulfur, either by elimination or hydrogenolysis. This path is a called HYDS due to the first hydrogenation step. On the other hand, the second pathway proceeds over the intermediate biphenyl which is formed by hydrogenolysis of the rather weak C-S bonds in DBT. The intermediate could be further hydrogenated to PhCH, but this reaction is rather slow. Because of the direct removal of the sulfur atom, this pathway is call direct desulfurization (DDS).

![Figure 8. Mechanism proposed by Houalla et al for HDS of DBT](image)

2.3.3 Kinetics of HDS

As same as with HDN reactions, a better understanding of the kinetics is possible when some assumptions are done during the studies. In this particular case, it is commonly presumed that DDS and HYDS take place in the same active sites. Another common assumption that is that the
reaction is a 1st order one, so all the calculations are based on the equations for this kind of reactions.41

Houalla et al showed that the conversion of dibenzothiophene in sulphide catalysts produces principally biphenyl (BiPh). This means that sulphide catalysts are highly selective for DDS, but some HYDS also occurs. The later would occur with the formation of Hyd-DBT as primary product of the pathway. Regarding the BiPh reaction towards PhCH, it is commonly too slow, so it can be neglected and not added it in the reaction network. PhCH is considered the final product from the HYDS route, even though some bicyclohexyl (BiCH) can be formed. Additionally, the selectivity for DDS vs. HYDS is different when a Ni-Mo or a Ni-W catalyst is used instead of the typical Co-Mo. The conversion is usually about three times higher with a Ni-Mo (W) catalyst than with a Co-Mo(W) catalyst.41

2.4 Parallel HDN/HDS

Hydrotreating is a global concept that involves the elimination of various heteroatoms or multiple bounds in aromatics. The feeds that are treated contain a mixture of components that have to be processed in certain order that guarantees the maximum efficiency and minimizes the complex interaction between the different components. Hydrodenitrogenation (HDN) occurs simultaneously with hydrodesulfurization (HDS), hydrodeoxygenation (HDO), hydrodearomatization (HDA) and hydrodemetallization (HDM). The extent of the mutual effects depends on the origin of the feed, type of catalyst, and operating conditions. Specifically, industrial crude oil feedstocks are characterized by the presence of both sulphur and nitrogen containing components. Thus, model feedstocks containing a model component of each group can be studied in order to determine the influence of S or N containing components on HDN or HDS processes. In particular, HDN has been the focus of attention because N removal is required to accomplish the required level of S components in the final products. When nitrogen is not removed, its compounds would inhibit HDS and other reactions because of their preferential adsorption on catalytically active Lewis acids sites. The presence of these inhibiting species, even at low concentrations, can change the catalytic activity and its influence has to be kept in mind.42, 43, 44
2.5 Hydrogenation of aromatic compounds (HDA)

2.5.1 Aromatic compounds in crude oil

Polycyclic aromatic hydrocarbons from fossil sources are a class of organic compounds comprised of two or more fused benzene rings with different structural arrangements. These components have earned considerable attention due to their display of a variety of toxic effects (from nontoxic to extremely toxic) and the necessity of getting fuels that are cleaner and easier to transport. In this matter the hydrogenation of the aromatic compounds (HAD) plays an important role in any refinery. In a fuel there are several kinds of aromatic compounds that have to be hydrogenated and are commonly classified from the number of aromatic rings that are attached. For catalytic studies are considered polycyclic aromatic hydrocarbons from 1 to 3 aromatic rings combined in different ways. Among triaromatics, two fused rings structures, phenanthrenes and anthracenes, within the diaromatics naphthalene and its derivatives, and the mono aromatic benzene and its derivatives are commonly present. These components and their structures are showed in table 3.

<table>
<thead>
<tr>
<th>Type</th>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>One ring</td>
<td>Tetralin</td>
<td><img src="image1" alt="Tetralin" /></td>
</tr>
<tr>
<td>Two rings</td>
<td>Naphthalene</td>
<td><img src="image2" alt="Naphthalene" /></td>
</tr>
<tr>
<td></td>
<td>Anthracene</td>
<td><img src="image3" alt="Anthracene" /></td>
</tr>
<tr>
<td>Three rings</td>
<td>Phenanthrene</td>
<td><img src="image4" alt="Phenanthrene" /></td>
</tr>
<tr>
<td></td>
<td>Phenyl-Naphthalene</td>
<td><img src="image5" alt="Phenyl-Naphthalene" /></td>
</tr>
</tbody>
</table>
2.5.2 Phenanthrene HDA mechanism

Some investigations have been carried out in order to determine and propose reliable mechanisms of HDA of several components. In particular, tetralin, naphthalene and phenanthrene are commonly chosen as model compounds because of the difference in the amount of aromatic rings.\textsuperscript{48, 49, 50} When a three ring component is going to be studied, phenanthrene is the common choice. On this matter Beltamone \textit{et al.}\textsuperscript{50} proposed a mechanism (Figure 9) with two different pathways and a sequential hydrogenation of the aromatic rings one by one. In detail, the first hydrogenation can be carried out in one of the external rings, as well as the ring located in the center of the phenanthrene structure. If the central ring is hydrogenated dihydro-phenanthrene (DiHPhe) will be formed, but if an external ring is dearomatized the product of the first hydrogenation will be tetrahydro-phenathrene (TetHPhe). The subsequent ring that will be hydrogenated, in both pathways, will be an external ring. Leading to the formation of Asym-octahydro-phenanthre (\textit{asymOHPhe}) from DiHPhe and \textit{sym-octahydro-phenanthrene} (\textit{symOHPhe}) from TetHPhe. Finally, the last hydrogenation will lead to a single compound, perhydro-phenanthre (perHPhe), from both lanes. The interconversions from DiHPhe to TetHPhe and TetHPhe to \textit{asymOHPhe} have been largely discussed. According to some studies\textsuperscript{49, 50, 52, 53} the former can be neglected while the second one has to be considered and included in the mechanism. It is important to mention that all the reactions are reversible.\textsuperscript{49, 50}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure9.png}
\caption{Mechanism (based on the one proposed by Beltamone \textit{et al.}) for HDA of Phenanthrene\textsuperscript{50}}
\end{figure}
2.5.3 Kinetics of HDA

In this particular mechanism the assumptions made in order to facilitate the kinetic analysis were: it behaves like a 1\textsuperscript{st} order reaction, and the rate-limiting step corresponds to the surface reaction. This second assumption is consider true for approximately the 75\% of the heterogeneous reactions.\textsuperscript{50, 51, 52}

In the case of polycondensed ring aromatic hydrocarbons, like phenanthrene, the first-ring hydrogenation is most favored kinetically. The rates of hydrogenation of subsequent rings tend to become lower; consequently, the last hydrogenation step occurs at very low rate in comparison with the first stage. Additionally, in TetHPhe and \textit{asymOHPhe} it has been observed that the terminal ring is hydrogenated before the central ring. This could be explained with the difficulty of accessing the central ring due to steric reasons.\textsuperscript{50, 52}

2.6 Analytical methods

2.6.1 Raman spectroscopy

Raman spectroscopy is an analytical technique used to test the vibrational and rotational states in molecules, which can be excellent guides to a component structure and general chemical composition. To perform this analysis the sample is irradiated with a laser in the visible, near infrared or near ultraviolet range. Due to this beam, photons are scattered either elastically or inelastically by the sample molecules. In the former process, also called Rayleigh scattering, the photon is scattered changing neither the photon’s energy nor the molecule’s energy state. On the other hand, when inelastic scattering takes place, we talk about the Raman Effect. In this case an absorbed photon is re-emitted with lower energy. This generates a difference in energy between the excitation and scattered photons that corresponds to the energy required to excite a molecule to a higher vibrational mode.\textsuperscript{54, 55}

The Raman interaction leads to two possible outcomes. First of all, the one known as Stokes Raman Scattering, where the material absorbs energy and the emitted photon has a lower energy than the absorbed photon. On the other hand, the material can lose energy and the emitted photon will have a higher energy than the absorbed photon. This is known as Anti-Stokes shift in Raman spectrum. The probability of finding Stokes scattering is higher than for anti-Stokes scattering due to the highest occupation of the higher states.\textsuperscript{55} Figure 10 shows the different kinds of scattering and explains the main differences between them.
2.6.2 X-ray diffraction (XRD)

X-Ray diffraction is an analytical technique that describes the elastic scattering of X-ray photons by atoms in ordered structures like crystals. The X-rays used penetrate solids, so it is possible to get information about the structure of the component. This technique is based on the principle known as Bragg’s law (Equation 1). This condition occurs when electromagnetic radiation or subatomic particle waves, with wavelength of the same the distances between lattice planes, are incident upon a crystalline sample. These beams are scattered by the atoms in the system, and undergo constructive interference in accordance to Bragg's law. The waves (wavelength $\lambda$) are scattered from lattice planes separated by the interplanar distance $d$ with an angle $\theta$. The path length of each wave is equal to an integer ($n$) multiple of the wavelength.\(^{56,57}\) This scattering can be visualized in figure 11.

\textit{Equation 1.} Bragg’s law: \hspace{1em} 2d \sin \theta = n \lambda

Every organized structure presents different constructive interference according to the incidence angle of the beam. This footprint (diffractogram obtained) allows us to determine which kind of crystal we are analyzing. For example, crystallites consisting of more lattice planes lead to sharper corresponding reflections in the diffractogram. The width of a signal is further

Figure 10. Rayleigh, Stokes and anti-Stokes scattering. \(^{55}\)
depending on the used wavelength and instrumental parameters (e.g. slit width, sharpness of X-ray beam). This correlation is given by the Scherrer equation (Equation 2).\textsuperscript{57,58}

\textbf{Equation 2. Scherrer equation:} \[ \Delta(2\theta) = \frac{K\lambda}{L \cos \theta} \]

The full width at half maximum ($\Delta(2\theta)$) of the reflex is depending on the Scherrer shape factor ($K$), the X ray wavelength ($\lambda$), the dimension of the crystallite perpendicular to the lattice planes ($L$) and the angle of incidence ($2\theta$). The Scherrer equation is valid for crystals from 10 – 100 nm.\textsuperscript{58}

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{scherrer_equation_diagram.png}
\caption{Scattering of x-ray beams (wavelength $\lambda$) on lattice planes (Distance $d$ between planes). The angle of incidence is $\theta$.\textsuperscript{56}}
\end{figure}
Chapter 3: Experimental part

3.1 HDN/HDS reactions

The kinetic studies of the hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) were carried out in a continuous flow fixed bed reactor. Quinoline (Q), ortho-propylaniline (OPA) and dibenzothiophene (DBT) were employed as model components. The first two for HDN and the last one for HDS. There were 2 types of reactions with every nitrogen-containing compound (Q and OPA): reactions where just HDN was studied and reactions with simultaneous HDN and HDS processes. In the former, dimethyl-disulphide (DMDS) was added to the mixture with the purpose of keeping the catalysts sulphided, but the DMDS decomposition was not studied. All catalysts were examined in temperature dependent measurements at 4 different temperatures (310, 330, 350 and 370 ºC). The space time was kept constant, and the reaction followed the same sequence for all the 6 catalysts studied.

3.1.1 Set-up configuration

Figure 12 displays the set-up configuration, including the bed reactor, in which all kinetics measurements were carried out. The reactor was made of stainless steel while the interior (that is in contact with all the reactants) was glass lined in order to avoid poisoning and corrosion issues that could affect the measurements. The reactor was placed inside a concentric oven whose temperature is regulated via an Eurotherm Temperature Control Unit. This unit allowed to set the different temperature programs required to perform the reactions.

The gas feeds were transported from the source by means of high pressure mass flow meters (MFC, Bronkhorst) regulated by the program Flow DDE (V4, 41). The liquid feeds were delivered to the reactor though a HPLC pump (Shimadzu LC-20AD). The reactants (gas and liquid) were mixed before the reactor inlet while after the outlet the liquid and gas effluent phases were separated. When it was required, liquid samples were collected via a 16 port sampling valve controlled by the computer program Agilent VEE 80. If sampling was not required, both liquid and gas products were directed to a washing bottle that contained a NaOH solution to neutralize the pH of the mixture before disposing it. The pressure generated by the liquid and gas phases was not close to the desired one, so N₂ was supplied to a back pressure regulator (BPR) to cover the demand and control the pressure inside the reactor.
3.1.2 Catalyst preparation

The HDN/HDS activities of six different catalysts were compared. These catalysts were synthetized using the following three methods: the patent of Maesen et al\textsuperscript{8}, the patent of Soled et al\textsuperscript{9}, and a precipitation method of thiometallates with H\textsubscript{2}S according to Yi et al\textsuperscript{10}. There were 2 catalysts synthetized with every method. One using the normal procedure and one using a hydrothermal (HT) treatment. The difference between these two procedures was that the reactor used to produce the HT catalysts was a pressurized one. A list of the names assigned to the catalysts as well as the method used to synthetize them is showed in table 4.

When a catalyst had been synthesized, it was compacted into a self-supported wafer by applying a pressure between 250 and 500 MPa for approximately 10 seconds with a manual hydraulic press. Afterwards, the wafer was crushed and sieved to obtain pellets with a diameter between 150 µm and 250 µm. This material with the desired size was then loaded in the reactor in the way that is showed in figure 13. 50 mg of catalyst pellets were diluted with 1000 mg silicium
carbide (SiC, 355-500 µm). This solid mixture was encapsulated between two layers of pure SiC and supported with glass wool.

Table 4. Names assigned to the catalysts according to the synthesis method used

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Catalyst name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maesen <em>et al</em> patent</td>
<td>WMoNia</td>
</tr>
<tr>
<td></td>
<td>WMoNiaHT</td>
</tr>
<tr>
<td>Soled <em>et al</em> patent</td>
<td>WMoNib</td>
</tr>
<tr>
<td></td>
<td>WMoNibHT</td>
</tr>
<tr>
<td>Precipitation of thiometallates with H₂S according to Yi <em>et al</em></td>
<td>WMoNis</td>
</tr>
<tr>
<td></td>
<td>WMoNisHT</td>
</tr>
</tbody>
</table>

Figure 13 Schematic cross section of the reactor filled with catalytic material

### 3.1.3 Liquid feed preparation

In these reactions 4 different liquid feedstocks, whose compositions are showed in table 5, were used. These feeds consisted mainly of a mixture of tetradecane (TD) with hexadecane (HD) as solvent, small quantities of OPA or Q (1000 ppm N) as nitrogen-containing compound, and DBT (500 ppm S) or DMDS (1000 ppm s) as sulphur-containing or sulphidation compound. The idea of these compositions was to simulate an industrial diesel fuel feedstock, as well as got enough data to compare the influence of the different components in the mechanism of reaction of the other ones.
Table 5. Feedstocks compositions for all HDN/HDS reactions

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Component</th>
<th>Weight percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q + DMDS</td>
<td>Q</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>DMDS</td>
<td>0.14</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>93.99</td>
</tr>
<tr>
<td></td>
<td>HD</td>
<td>4.95</td>
</tr>
<tr>
<td>Q + DBT</td>
<td>Q</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>DBT</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>93.86</td>
</tr>
<tr>
<td></td>
<td>HD</td>
<td>4.94</td>
</tr>
<tr>
<td>OPA + DMDS</td>
<td>OPA</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>DMDS</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>93.95</td>
</tr>
<tr>
<td></td>
<td>HD</td>
<td>4.94</td>
</tr>
<tr>
<td>OPA + DBT</td>
<td>OPA</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>DBT</td>
<td>0.28</td>
</tr>
<tr>
<td></td>
<td>TD</td>
<td>93.82</td>
</tr>
<tr>
<td></td>
<td>HD</td>
<td>4.94</td>
</tr>
</tbody>
</table>

3.1.4 Measurements

All the six catalysts were previously prepared (in form of oxides) and set in the reactor. Then, they were sulphided in situ before the reaction\(^\text{12}\). To do so it was used a gas mixture of 10% hydrogen sulphide (\(\text{H}_2\text{S}\)) diluted in hydrogen (\(\text{H}_2\)) with a flow rate of 40mL/min at 1.8 MPa at 400 °C for 12 hours. The temperature went from room temperature to 400 °C with a constant rate of 5 °C/min. After that, the reactor was cooled to room temperature and the gas flow was changed to pure \(\text{H}_2\). Then, when the system was stable, the first set of reaction parameters was applied. All the reactions were performed with a pressure of 5.0 ± 0.2 MPa and maintained throughout the whole experiment. All reactions were performed in a constant excess of hydrogen (Flow rate: \(\text{liquid feed/} \text{hydrogen} = 1/300\)).

Temperature dependent measurements were carried out at four different temperatures at a constant space time for each catalyst (\(65 \text{ h} \times \text{g}_{\text{cat}} / \text{mol}_{\text{Q/QPA}}\) and \(625 \text{ h} \times \text{g}_{\text{cat}} / \text{mol}_{\text{DBT}}\)). The 4 experiments were conducted sequentially and in the same way for the 6 catalysts. The temperature program for all the experiments is shown in Figure 14. The change of temperatures was always done in half an hour, so the ramp was not always constant due to the different gaps between temperatures.
Figure 14. Graphic representation of the temperature program used in the HDN/HDS reactions

The sampling and other reaction parameters were the same for the six catalyst studied. A description of them is showed in table 6.

Table 6. Parameters used during the HDN/HDS reactions. The sequential order can be read from top to bottom

<table>
<thead>
<tr>
<th>Feed</th>
<th>Temperature [°C]</th>
<th>Sampling interval [h]</th>
<th>Samples taken</th>
<th>Liquid feed flow rate [ml/min]</th>
<th>H₂ flow rate [ml/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPA/Q</td>
<td>350</td>
<td>4.0</td>
<td>10</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>DBT</td>
<td>330</td>
<td>4.0</td>
<td>3</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>4.0</td>
<td>3</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>4.0</td>
<td>3</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>1.0</td>
<td>7</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>OPA</td>
<td>350</td>
<td>2.5</td>
<td>17</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>DMDS</td>
<td>330</td>
<td>1.5</td>
<td>5</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>1.5</td>
<td>4</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>1.5</td>
<td>4</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>1.5</td>
<td>4</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>Q</td>
<td>350</td>
<td>4.0</td>
<td>17</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td>DMDS</td>
<td>330</td>
<td>4.0</td>
<td>5</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>310</td>
<td>4.0</td>
<td>4</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>370</td>
<td>4.0</td>
<td>4</td>
<td>0.1</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>4.0</td>
<td>4</td>
<td>0.1</td>
<td>30</td>
</tr>
</tbody>
</table>
3.1.5 Product analysis with off-line gas chromatography (GC)

The liquid samples collected with the 16 port valve were analyzed off line by gas chromatography (GC). The GC instrument used (HP 6890) was equipped with a flame ionization detector (FID) and a DB-17 capillary column (60 m, Agilent, 0.25 mm i. d., 0.25 μm film thickness). The temperature program used in order to achieve the desired separation of the products is showed in figure 15.

**Figure 15:** Temperature program used in the GC measurements of the HDN/HDS reactions

The products detected during these measurements and their corresponding retention times are summarized in appendix 1 (figure 15). The concentrations of the components are calculated based on their corresponding peak areas with a calibration executed prior to measurement. For all reactions all employed reactants and products could be determined. The product distribution was calculated on the basis of all detected organic compounds in the sample and the calculation of the mol percentage of every compound in the mixture. That percentage was defined in this work as yield $Y_x$. The conversion $X_x$ of the reactant $x$ (Q, OPA, and DBT) was calculated based on the total amount of mols converted $C_{conv}$ (calculated from the addition of the mols of all the products formed from a specific reactant) over the initial concentration of the reactant $C_o$ in the feed.

$$\text{Equation 3: } X_x = \frac{C_{conv(x)}}{C_{o(x)}} \cdot 100\%, \%$$

Selectivities were also calculated as the percentage of the mols of $x$ product over the total amount of moles produced. In this case the remnant reactant is not considered for the calculation.
3.2 Hydrogenation reactions

The kinetic studies of the hydrodearomatization (HDA) were carried out in a continuous flow fixed bed reactor. Phenanthrene (Phe) was employed as model component. All catalysts were examined in space time dependent measurements at 2 different temperatures. The reaction followed the same sequence for all the five catalysts studied.

3.2.1 Set-up configuration

Figure 16 displays the set-up configuration, including the bed reactor, in which all kinetics measurements were carried out. The set-up used was very similar to the one used for the HDN/HDS reactions with a change in the liquid pump. In this case a Gilson 307, pump head 5SC was used. The sampling method use was the same as well as the configuration.

![Diagram of reaction flow sheet for HDN/HDS reactions](image)

Figure 16. Reaction flow sheet for HDN/HDS reactions

3.2.2 Catalyst preparation

The HDA activities of five different catalysts were compared. All the catalysts were synthetized previously using incipient wetness impregnation of γ-Al₂O₃, but the composition was
different. The Ni content of every catalyst varied and this characteristic was the one used to name them. These assigned name scan be seen in table 7.

<table>
<thead>
<tr>
<th>Percentage of Ni (%)</th>
<th>Catalyst name</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>WS&lt;sub&gt;2/γ&lt;/sub&gt;Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
</tr>
<tr>
<td>2.5</td>
<td>Ni(2.5)WS&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>5.0</td>
<td>Ni(5.0)WS&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>8.0</td>
<td>Ni(8.0)WS&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>11.0</td>
<td>Ni(11.0)WS&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
</tbody>
</table>

The procedure used to prepare the pellets was the same as the one used in the HDN/HDS reaction, but the final size of the catalyst was between 250 μm and 355 μm. The packing procedure and order was almost the same with the exception of the size of the SiC used. In this case 2 different sizes were used. In contact with the glass wool there was always SiC from 150 to 250 μm, while the one used to mix the catalyst and complete the bed was 63-90 μm. Figure 17 shows the way that the reactor was filled.

![Figure 17. Schematic cross section of the reactor filled with catalytic material](image)

### 3.2.3 Feed preparation

In these reactions the same liquid feedstock, whose composition is showed in table 8, was used. This feed consisted mainly on decalin (decahydro-naphthalene) as solvent, tetradecane (TD) as
internal standard, small quantities of phenanthrene (Phe) as model compound, and DMDS as sulphidation compound. The idea of this composition was to simulate an industrial diesel fuel feedstock, as well as got enough data to compare the influence of the amount of Ni in the mechanism of reaction.

<table>
<thead>
<tr>
<th>Component</th>
<th>Weight percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quinoline</td>
<td>0.92</td>
</tr>
<tr>
<td>DMDS</td>
<td>0.14</td>
</tr>
<tr>
<td>TD</td>
<td>93.99</td>
</tr>
<tr>
<td>HD</td>
<td>4.95</td>
</tr>
</tbody>
</table>

**Table 8. Feedstock composition for all HDA reactions**

3.2.4 Measurements

All the five catalysts were previously prepared (in form of oxides) and set in the reactor. Then, they were sulphided in situ before the reaction. The sulphidation was very similar to the one used with the HDN/HDS catalyst, but the pressure was 2.0 MPa, and it was carried out just for 8 hours. Then when the system was stable, the first set of reaction parameters was applied. All the reactions were performed with a pressure of 6.0 ± 0.2 MPa and maintained throughout the whole experiment.

Measurements were carried out at two different temperatures (300 and 360 °C) and at six different space times. The 8 experiments were conducted sequentially and in the same way for the five catalysts. The sampling and other reaction parameters were also the same and a description of them is showed in table 9.

**Table 9. Parameters used during the HDA reactions. The sequential order can be read from top to bottom**
<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>Sampling interval [h]</th>
<th>Samples taken</th>
<th>Liquid feed flow rate [ml/h]</th>
<th>H₂ flow rate [ml/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>360</td>
<td>2.00</td>
<td>12</td>
<td>9.0</td>
<td>45.0</td>
</tr>
<tr>
<td>300</td>
<td>1.00</td>
<td>8</td>
<td>6.0</td>
<td>30.0</td>
</tr>
<tr>
<td>300</td>
<td>2.00</td>
<td>7</td>
<td>7.2</td>
<td>36.0</td>
</tr>
<tr>
<td>300</td>
<td>0.59</td>
<td>5</td>
<td>12.0</td>
<td>60.0</td>
</tr>
<tr>
<td>300</td>
<td>0.59</td>
<td>5</td>
<td>15.0</td>
<td>75.0</td>
</tr>
<tr>
<td>300</td>
<td>0.59</td>
<td>5</td>
<td>18.0</td>
<td>90.0</td>
</tr>
<tr>
<td>300</td>
<td>1.25</td>
<td>6</td>
<td>9.0</td>
<td>45.0</td>
</tr>
<tr>
<td>360</td>
<td>1.25</td>
<td>6</td>
<td>9.0</td>
<td>45.0</td>
</tr>
</tbody>
</table>

### 3.2.5 Product analysis with off-line gas chromatography (GC)

As same as in the case of the HDN/HDS reactions the liquid samples were collected with a 16 port valve and analyzed off line by gas chromatography (GC). The GC instrument used (Shimadzu GC-2010) was equipped with a 50 m HP-1 column and a flame ionization detector (FID).

The products detected during these measurements and their corresponding retention times are summarized in appendix 2. The concentrations of the components are calculated based on their corresponding peak areas with a calibration executed. All the calculations performed were the same ones used in the HDN/HDS reactions, and the same parameters evaluated.

### 3.3 Catalyst characterization

#### 3.3.1 Raman spectroscopy

The HDN/HDS catalyst were tested after the reaction with the objective of having a look of its structure at the end of the reactions. Raman measurements were carried out by a Renishaw Raman Spectrometer (Type 1000). The instrument was equipped with a CCD detector and a microscope (Leica microscope DM LM) while an Ar-laser with a wavelength of 514 nm was used as excitation source. Prior to the measurements the system was calibrated with a Si (111) crystal. Measurements of at least five positions were conducted in order to have coherent and representative results. Spectra were obtained in a range of 100 cm⁻¹ to 4000 cm⁻¹.
Chapter 4: Results and discussion

As it was described in chapter 3, four different feeds were analyzed in order to get a better understanding of the HDN and HDS of quinoline (Q) and dibenzothiophene (DBT) respectively. These feedstocks are: Q, Q + DBT, OPA, and OPA + DBT. Every mixture was feed to a batch reactor, at the same conditions, just varying the catalyst. The data obtained was recorded and the results gave us a better understanding of the kinetics of some HDN and HDS reactions, as well as the influence of the sulphur component (DBT) on the HDN activity.

In regard to the HDA reactions, the feedstocks analyzed had always the same components that are described in 3.2.

4.1 Kinetics of Quinoline HDN without the presence of DBT

The HDN activities of the six catalysts described in the experimental part (WMoNia, WMoNiaHT, WMoNib, WMoNibHT, WMoNis, and WMoNisHT) were evaluated. These reactions were carried out with feeds containing quinoline (Q) without the presence of any sulfur component. In this way, it was possible to evaluate the conversion of Q alone without any interference of another competitive component. All the reactions were carried out keeping the space time constant, but using four different temperatures (310, 330, 350, and 370 ºC). Thus, the kinetic data (conversions, selectivities and yields) were used to determine the overall activity of every catalysts at different temperatures, as well as make a comparison between the behaviors of the different results. A general view of the conversion of Q on time and at different temperatures is showed in the figure 18.

With the objective of testing a possible deactivation of the catalyst, this and all the following reactions (HDN and HDS) were run at 350 ºC as first and last steps. It is seen that the catalysts stay active during the time of reaction. In general, there are some minimum changes in the values of less than 1%. The exception is the catalyst WMoNibHT that shows a big decrease of around 15 % at the end of the first cycle at 350 ºC. This decrease can be endorsed to a sulphidation problem at this point of the experiment, a sudden increase on the reactor’s temperature or a change in any flow. All of these possible explanations are based on an undesired change of conditions at the end of one reaction, in one catalyst, and cannot been considered the general behavior. On the other hand, if we examine the conversions during the first 4 hours, it is possible to see an increase in the conversions of all the catalysts. This suggests that at the beginning of the reaction the catalysts were not completely or correctly sulphided, so the reactions reached the steady state after
this period of time. Because a steady state was observed and maintained before switching to the
next temperature, it is assumed that no excessive deactivation occurred. This is further confirmed
by the observation, that a nearly the carbon mass balance is nearly close (Coke formation >5%).

Figure 18. Quinoline conversion (%) against time on stream (h) at 350, 330, 310 and 370 °C for the catalysts (From
top to bottom): WMoNia, WMoNiaHT, WMoNib, WMoNibHT, WMoNis, WMoNisHT. Q feedstocks.
The results of the average conversation of Q at every temperature studied is showed in the figure 19.

**Figure 19.** Conversion of Q as a function of temperature. Q feedstocks without any sulphur component

It is seen that the higher the temperature, the lower the conversion of quinoline. However, there is one exception to this trend, the WMoNis catalyst. This catalyst presents the lowest conversion of Q and shows a different trend (increasing the conversion with the increase of temperature). This is clearly the one with the lowest activity for HDN, which means that its morphology does not favor the elimination of nitrogen in Q. A ranking of the catalysts according to their Q activity is showed in table 4.1 (T= 330 °C used for comparison purposes).

**Table 10.** Relative ranking of catalysts regarding the conversion of Q without the presence of DBT at 330 °C
The catalysts “s” are clearly the extreme cases. While the one developed with the hydrothermal (HT) method is the most active one at any temperature, the one synthesized without using this method is the slowest. Catalysts “b” are the most similar between each other. The conversions are very alike and follow the same trend. On the other hand, catalysts “a” have a behavior that differs from the other four. While catalysts “s” and “b” prepared using the hydrothermal method are more active, in the case of catalysts “a” the one prepared in the conventional way is the most active.

To understand the HDN of Q is needed to understand the mechanism of it. How the molecule of Q is sequentially converted. Prins\textsuperscript{30} suggested a mechanism with two major pathways (DHQ and OPA as main intermediates) that are detailed in section 2.2.2. He suggests that because of the fast hydrogenation of the heterocyclic ring, and the formation of a very reactive intermediate (\textit{o}-propenylaniline) in the OPA path way, this route should be the predominant one. However, due to a higher adsorption ratio of DHQ with respect to OPA, DHQ plays also an important role in the mechanism. In our specific case, the selectivities of OPA (Figure 20) are higher than the ones of DHQ for all the catalysts. This indicates that the first part of the mechanism proposed is valid for the six catalysts, and that reactions through both path ways took place. It also means that the OPA pathway is preferred over the DHQ one. However, the selectivity of the second one cannot be neglected. Regarding the difference between the six catalysts studied. It is showed that the catalyst WMoNib has the highest selectivities in both pathways, while both catalysts “s” are the worse.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{selectivities.png}
\caption{OPA and DHQ selectivities as a function of temperature. Q feedstocks without any sulfur component.}
\end{figure}
The selectivities of the main products of the reaction were analyzed. The ones that do not present N on their structures (PCH and PB), can be seen in figure 21. They show that the catalyst WMoNib is by far the most active among all the catalyst studied. In both pathways, HYDN and DDN, the most important products (PCH and PB) are produced preferentially by this catalyst. Catalysts “a” have a similar behaviour and are the second ones in both pathways. Catalyst WMoNibHT is the next one with less selectivity than the “a” ones. Finally the catalysts “s” present the lowest selectivities among all the catalysts studied. This, together with the low selectivities of OPA and DHQ showed before, suggests that the active sites of these catalysts are saturated with the components produced before OPA and DHQ (14THQ and 58THQ), so the reaction cannot go forward and produce the components of interest. The case of the catalyst WMoNisHT is the best example of this. The general conversion of Q with these catalysts is the highest, but the selectivities of OPA, DHQ, PCH and PB are really low. On the other hand, the yield and selectivity of 14THQ (showed in the appendix IV) are the highest within all the catalysts. It means that the catalyst is very active and hydrogenates the heterocyclic ring really fast, but then due to desorption problems or blockage of active sites, the further reactions do not take place at the same rate.

Then the yields of some main and intermediate products (OPA, DHQ, PCH, and PB) of the Q HDN are compared (Figure 22). The yields follow the same general trend for all catalysts, indicating that the mechanism is the same. The catalyst WMoNis is the only one which deviates from the general trend of the other five. The yields remain almost constant and increase slightly.
at higher temperature. On the other hand, for the other catalysts the graphs show the same trend as the selectivities and conversion of Q. PCH and PB, which are produced from OPA, show a decrease in yields at higher conversions (lower temperatures). The shapes of the curves of these products prove that PCH and PB are main products and not secondary components. On the other side DHQ graph shows that these product is a clear intermediate, and that it is further converted in OPA.

Figure 22. OPA, DHQ, PCH, and PB selectivities as a function XQ. Q feedstocks without any sulfur component

The analysis of the two different routes for the hydrogenation of HDN will be done when the reaction where OPA is the starter material are examined. The data of the other intermediates for these reaction is set in Appendix IV.
4.2 Kinetics of simultaneous Quinoline HDN and DBT HDS

The simultaneous HDN and HDS activities of the six catalysts described in the experimental part (WMoNia, WMoNiaHT, WMoNib, WMoNibHT, WMoNis, and WMoNisHT) were also evaluated in feeds containing quinoline (Q) and dibenzothiophene (DBT). In this way, and comparing these results with the ones obtained and detailed in 4.1, it was possible to determine how the presence of DBT affects the overall HDN activity of the catalysts, as well as to have a better understanding of the HDS of DBT at different temperatures with different catalysts. The temperature conditions were the same as the ones used in the HDN reactions of pure Q (constant space time constant, four different temperatures: 310, 330, 350, and 370 ºC).

Regarding the deactivation testing (figure 23), it is seen that almost all the catalysts stay active during the time of reaction. In general, there are some minimum conversion changes in the values of less than 1%. The exception is the catalyst WMoNisHT that shows a big decrease of around 10% at the end of the reaction. This decrease can be endorsed to a sulphidation problem at the end of the experiment, a sudden increase on the reactor’s temperature or a change in any flow. All of these possible explanations are based on an undesired change of conditions at the end of one reaction, in one catalyst, and cannot been considered the general behavior. On the other hand, if we examine the conversions during the first 4 hours, it is possible to see a change in the conversions for all the catalysts. This suggests that at the beginning of the reaction there was a difference in the reaction rate and after some time the steady state was reached. Because steady state was observed and maintained before switching to the next temperature, it is assumed that no excessive deactivation occurred. This is further confirmed by the observation, that a nearly the carbon mass balance is nearly close (coke formation <5%).

The results of the average conversion of Q at every temperature studied are showed in figure 24. It is seen that the higher the temperature, the lower the conversion of quinoline. This trend is exactly the same as the one watched with the feedstock without the presence of DBT. So, it is clear that the existence or not of this component doesn’t affect the dependency of the conversion with temperature. The order of activities is showed in table 11.
Figure 23. Quinoline conversion (%) against time on stream (h) at 350, 330, 310 and 370 °C for the catalysts (From top to bottom): WMoNia, WMoNiaHT, WMoNib, WMoNibHT, WMoNis, WMoNisHT. Q + DBT feedstocks.
Table 11. Relative ranking of catalysts regarding the conversion of Q with the presence of DBT at 330 °C

<table>
<thead>
<tr>
<th>Conversion [%]</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WMoNisHT</td>
</tr>
<tr>
<td></td>
<td>WMoNia</td>
</tr>
<tr>
<td></td>
<td>WMoNibHT</td>
</tr>
<tr>
<td></td>
<td>WMoNib</td>
</tr>
<tr>
<td></td>
<td>WMoNiaHT</td>
</tr>
<tr>
<td></td>
<td>WMoNis</td>
</tr>
</tbody>
</table>

To understand the influence of DBT in the HDN of Q is needed to understand the differences between the results obtained with a feed containing this compound and one without it. First of all, it is important to analyze the influence of this component in the two hydrogenation pathways (DHQ and OPA). In our specific case, the selectivities of OPA (figure 25) and the selectivities of DHQ are different and it is not possible to see a trend. At lower temperatures (310 °C and 330 °C) the selectivities of OPA are smaller, but as soon as we increase the temperature the behavior is the same as the one that we could see in the reaction without DBT (higher selectivity of OPA that DHQ). This indicates that DBT influences the HDN process since the beginning of it. At lower temperature the DBT reaction is slower, and the DBT molecule is more easily adsorbed.
than the Q one. Consequently, the active sites are full of DBT molecules, so the further steps of the HDN are carried out at a slower rate.

Regarding the differences between these results and the ones with the feedstock without DBT, the differences in values and trends are different for each catalyst. For the OPA pathway, catalysts WMoNib, WMoNis, and WMoNisHT (at high temperatures 350 and 370 °C) present a similar behavior regardless the presence of DBT. Unrelated to the temperature of reaction, selectivities of OPA are always higher when DBT is present in the feed. In this case this could be related to a higher DBT conversion rate of this catalyst at every temperature. This will produce more H₂S free in the reactor that helps to keep more sulphidic active sites available, and in consequence and enhancement of the HDN activity. It is discarded and accumulation of OPA due to a slower production of PCH and PB in the feeds with DBT. As it will be explained, this is not the case.

On the other hand, the DHQ selectivities are always enhanced by the presence of DBT, with the exception of the catalysts WMoNisHT that behaves in the same way with both kinds of feeds. This could be due to the constant sulphidation produce by the HDS of DBT and the fact that DHQ is more easily adsorbed than OPA in the active sites. Regarding the difference between the six catalysts studied. It is showed that the catalyst WMoNib has the highest selectivities and favors
the OPA pathway, while the catalysts “a” favor the DHQ pathway. In both pathways both catalysts “s” are the worse.

![Figure 26. PCH and PB selectivities as a function of temperature. Q + DBT feedstocks](image)

Regarding the selectivities of the main products of the reaction (PCH and PB), can be seen in figure 26, as well as the feedstocks without DBT. The order of activity is the same as the one with the feedstocks without HDS for both pathways. The influence of the presence of DBT in the selectivities of these products, it is clearly positive in terms of formation of nitrogen-free components. In both pathways (DDN and HYDN) the presence of DBT enhance the removal of N. This could happen due to the higher sulphidation and the higher production of OPA and DHQ that are further converted in these final products.

The yields of some main an intermediate products (OPA, DHQ, PCH, and PB) as a function of the Q conversion are showed in figure 27. The differences and the similarities follow the same trends that the graphs that show the selectivities.
Figure 27. OPA, DHQ, PCH, and PB selectivities as a function of XQ + DBT feedstocks.

About the DBT reactions, the conversions obtained with all the 6 catalysts are showed in figure 28, as well as the ranking from the most active to the least active one in table 12. Catalyst WMoNib is the most active, followed by the WMoNibHT. It is a trend here that both catalyst “b” are the ones who converted more DBT (closer to a 100 % conversion at high temperatures), while the catalyst “s” are the worst. Catalyst WMoNis is so inactive that even at the highest temperature evaluated (370 ºC) the conversion is very close to 10 %. This higher conversion at higher temperature could be due to the higher reaction rates at higher temperatures.
Table 12. Relative ranking of catalysts regarding the conversion of DBT with the presence of Q at 330 ºC

| Catalyst          | Conversion [%] |
|-------------------|----------------|----------------|
| WMoNib            |                |
| WMoNibHT          |                |
| WMoNiaHT          |                |
| WMoNia            |                |
| WMoNis            |                |
| WMoNisHT          |                |
| WMoNia            |                |

Figure 28. Conversion of DBT as a function of temperature. Q + DBT feedstocks

Regarding the main products that can be obtained throughout the two pathways explained by Houalla\textsuperscript{41} (PhCH and BiPh), selectivities and yields are showed in figure 29. The products found do not differ from the product distribution found in literature. BiPh, Hyd-DBT and PhCH are observed, so the mechanism proposed for the DBT conversion, proceeding in parallel to the Q conversion, does not vary from the proposed mechanism for isolated DBT conversion over MoS\textsubscript{2} given in literature by Chianelli \textit{et al} \textsuperscript{27}. They propose that DBT is converted via hydrogenation (HYDS) to PhCH and via hydrogenolysis (DDS) to BiPh. On the HYDS pathway, Hyd-DBT can be found as primary product.
Figure 29. PhCH and BiPh selectivities as a function of T and yields as a function of XQ. Q + DBT feedstocks

The reason for the smaller selectivities and yields in the HYDS pathway in comparison with the DDS one is probably due to the competitive adsorption of Q and its byproducts on the HYDS active sites. A similar observation was made by Nagai et al.\textsuperscript{60,61} and recently by Ho et al.\textsuperscript{62} The second shows the inhibition of DBT conversion on a sulphided CoMo/Al\textsubscript{2}O\textsubscript{3}–SiO\textsubscript{2} catalyst by 3-ethylcarbazole (3ECBZ) and modeling of its effect on the HYDS and DDS pathways. The study shows a strong affinity of 3-ethylcarbazole inhibiting the HYDS active sites whereas the DDS active sites are less affected. However, with increasing of HDN conversion the inhibition of the HYDS active sites is assumed to be reduced because the competitive adsorption is reduced. In particular, for this case at higher Q conversions the HYDS should be faster due to a reduction of
the competitive adsorption. However, this is not the case of these reactions because some derivatives from the HDN of Q are competitive too and can be adsorbed in the active sites. This means that no matter how we change the Q conversion rates, these changes will not affect the HDS process. The change in selectivities and yields is due to a change in temperature and the modification for the active phase, not due to a change in the rate of Q HDN.

Other important kinetic results that were obtained are the activation energies and Arrhenius plots. They are showed in the table 13 and figure 30.

![Figure 30. Arrhenius plots for the HDS of DBT. Q + DBT feedstocks](image)

**Table 13** Activation energies for the HDS of DBT with the presence of Q

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation energy (kJ/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMoNia</td>
<td>88.3</td>
</tr>
<tr>
<td>WMoNiaHT</td>
<td>107.3</td>
</tr>
<tr>
<td>WMoNib</td>
<td>108.1</td>
</tr>
<tr>
<td>WMoNibHT</td>
<td>117.1</td>
</tr>
<tr>
<td>WMoNis</td>
<td>34.4</td>
</tr>
<tr>
<td>WMoNisHT</td>
<td>113.8</td>
</tr>
</tbody>
</table>

The Arrhenius plots show the rate of DDS pathway, while the table shows the values of the activation energies for the 1st order like reaction. The results obtained showed the same trend that was observed with the conversions and the dependence of the reaction with temperature. It
also showed that the catalyst WMoNis is the least active one and that the catalyst “b” are the ones that convert higher amounts of DBT.

4.3 Kinetics of OPA HDN without the presence of DBT

The HDN activities of the six catalysts described in the experimental part (WMoNia, WMoNiaHT, WMoNib, WMoNibHT, WMoNis, and WMoNisHT) were also evaluated with ortho-propylaniline (OPA) as a model component for HDN. As well as with the Q feedstocks mixtures with and without DBT were studied. In this way it was possible to evaluate the conversion of OPA alone without any interference of another competitive component, as well as to study the HDN mechanism of Q in a more detailed way using one of the most important intermediates. All the reactions were carried out in the same way as the ones with Q and the same kind of kinetic data analyzed. A general view of the conversion of OPA on time and at different temperatures is showed in the figure 31.

As same as with the Q feedstocks all the reactions were run at 350 ºC as first and last steps. It is seen that the catalysts stay active during the time of reaction. In this case there are some minimum changes in the values of less than 1%. There is one point in catalyst WMoNis that is not aligned with the other ones at 350 ºC. This change could be endorsed to a mistake in the sampling procedure or the result of some external contamination. Both explanations are based on that one of the samples was altered by an external source and happened just in one catalyst, so it cannot be considered the general behavior. On the other hand, if we examine the conversions during the first 2.5 hours, it is possible to see a change in the conversions of all the catalysts. This suggests that at the beginning of the reaction the catalysts were not completely or correctly sulphided, so the reactions reached the steady state after this period of time. Because steady state was observed and maintained before switching to the next temperature, it is assumed that no excessive deactivation occurred. This is further confirmed by the observation, that the carbon mass balance is nearly close (Coke formation <5%).
Figure 31. OPA conversion (%) against time on stream (h) at 350, 330, 310 and 370 °C for the catalysts (From top to bottom): WMoNia, WMoNiaHT, WMoNib, WMoNibHT, WMoNis, WMoNisHT. OPA feedstocks without DBT.

The results of the average conversation of OPA as a function of temperature are showed in the figure 32.
It is seen that the higher the temperature, the higher the conversion of OPA. This trend can be appreciated for the six catalysts and there is not any deviation from it. Similarly to the Q experiments, catalyst WMoNis is the one that clearly shows the lowest activity for HDN. This means that its morphology and structure does not favor an efficient removal of N. A ranking of the catalysts according to their OPA activity is showed in table 14 (T= 330 ºC used for comparison purposes).

Table 14. Relative ranking of catalysts regarding the conversion of OPA without the presence of DBT at 330 ºC

<table>
<thead>
<tr>
<th>Conversion [%]</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WMoNib</td>
</tr>
<tr>
<td></td>
<td>WMoNisHT</td>
</tr>
<tr>
<td></td>
<td>WMoNiaHT</td>
</tr>
<tr>
<td></td>
<td>WMoNibHT</td>
</tr>
<tr>
<td></td>
<td>WMoNia</td>
</tr>
<tr>
<td></td>
<td>WMoNis</td>
</tr>
</tbody>
</table>

Catalyst WMoNib and WMoNisHT are clearly the most active ones. It is even possible to get conversions close to 100 % with them. Catalysts WMoNiaHT and WMoNibHT are the next in the list. With them it is possible to reach conversions even close to 70 %. With the exception
of the “b” products catalysts prepared using the hydrothermal (HT) process are more active than the ones that are prepared without applying this treatment.

![Graphs showing selectivities and yields of four products as a function of temperature.](image)

**Figure 33.** PCH, PB, PCHE and, PCHA selectivities as a function of temperature. OPA feedstocks without DBT

In order to understand how OPA is sequentially converted and then study its influence in the general Q mechanism, figures 33 and 34 show the selectivities and yields of the four products of the HDN conversion of this model molecule. They show that the catalyst WMoNib is the most active among all the catalyst studied. In both pathways, HYDN and DDN, the most important products are produced preferentially by this catalyst. Catalysts WMoNisHT as well as WMoNiaHT, and WMoNibHT have a similar behaviour and are the second ones in both pathways.
Finally the catalysts WMoNia and WMoNis present the lowest selectivities among all the catalysts studied. This trend is comparable with the ones got from the general conversion and their interdependence suggest that there is no competitive adsorption of on the active sites, so the catalysts that convert more OPA produce more final products and the intermediate ones do not block the active sites and are converted at high rate, especially at higher temperatures. Additionally, the evolution of the curves give evidence that PCHA as well as PCHE are intermediates whereas PB and PCH are final products.

![Graphs showing yields of PCH, PB, PCHE, and PCHA](image)

**Figure 34.** PCH, PB, PCHE and PCHA yields as function of $X_{\text{OPA}}$. OPA feedstocks without DBT
In order to confirm the mechanism and pathways proposed in literature the relations between the reactants, the intermediates, and the products have to be examined more in detail. On this matter, the relation between yields and conversions were analyzed. These results together with the selectivities presented before indicate a complex reaction (even tough simpler than the complete Q network). PB appears as primary product, while PCHA and PCHE are intermediates. PCH is a secondary product. Consequently, two parallel pathways take place (OPA to products PB and PCH) as it is set by Prins\textsuperscript{20}. It means, sequential reactions from OPA to PCHA and PCHE and then to the final products PB and PCH as well as the direct denitrogenation from OPA to PB (DDN). A strong correlation between the degradation of PCHE and the formation of PCH can be observed over the whole conversion range. This indicates that PCHE is an intermediate product in the HYD pathway. However, a direct reaction step from OPA to PCHE does not look possible and accurate from the chemical point of view (combined hydrogenation and denitrogenation), so an intermediate in this network is needed. On this matter, a route from OPA over PCHA to PCHE is chemically consistent. The first step from OPA to PCHA is well understood, since the hydrogenation capacity of unsupported trimetallic catalysts (W, Mo, Ni) is known\textsuperscript{63}. The second step (PCHA to PCHE) can be done through a Hoffman elimination as is proposed by Prins\textsuperscript{64}.

Other important kinetic results that were obtained are the activation energies and Arrhenius plots for both pathways, HYDN and DDN. They are showed in the table 15 and figure 35.

![Figure 35. Arrhenius plots for the HDN of OPA. HYDN and DDN pathways. OPA feedstocks without any DBT](image-url)
Table 15. Activation energies for the HDN of OPA without the presence of DBT

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation energy HYDN (kJ/gmol)</th>
<th>Activation energy DDN (kJ/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMoNia</td>
<td>148.3</td>
<td>164.4</td>
</tr>
<tr>
<td>WMoNiaHT</td>
<td>145.6</td>
<td>197.7</td>
</tr>
<tr>
<td>WMoNib</td>
<td>136.4</td>
<td>142.1</td>
</tr>
<tr>
<td>WMoNibHT</td>
<td>133.1</td>
<td>149.1</td>
</tr>
<tr>
<td>WMoNis</td>
<td>138.7</td>
<td>167.3</td>
</tr>
<tr>
<td>WMoNisHT</td>
<td>197.4</td>
<td>226.5</td>
</tr>
</tbody>
</table>

The Arrhenius plots show the rate of DDN and HYDN pathways, so the temperature dependency of the conversion of OPA, while the table shows the values of the activation energies for the 1st order like reaction. The results obtained showed the same trend that was observed with the conversions, selectivities and yields. It also showed that the catalyst WMoNis is the least active one and that the catalyst WMoNib is the one that converts higher amounts of OPA. The results can be seen also as a support of the fact that the HYDN is more favored for all the catalyst than the DDN path.

4.4 Kinetics of simultaneous OPA HDN and DBT HDS

The simultaneous HDN and HDS of OPA and DBT respectively were also evaluated. These reactions were carried out in parallel with feeds containing OPA and DBT. In this way, and comparing these results with the ones obtained and detailed in 4.2 and 4.3, it was possible to determine how the presence of DBT affects the overall HDN activity of the catalysts, the effect of different nitrogen-containing compounds in the DBT HDS, and a better understanding of the HDS of DBT at different temperatures with different catalysts. The temperature conditions were the same as the ones already described (constant space time constant, four different temperatures: 310, 330, 350, and 370 ºC).

The results from the time on stream plots (figure 36) show that almost all the catalysts stay active during the time of reaction. In general, there are some minimum changes in the values of less than 1%. The exception is the catalyst WMoNis that shows a big increase of around 10% at the end of the reaction. This can be endorsed to an undesired change of conditions at the end of one reaction, in one catalyst, and cannot been considered the general behavior. On the other hand, if we examine the conversions during the first 4 hours, it is possible to see a change in the conversions for all the catalysts. This suggests that at the beginning of the reaction there was a
difference in the reaction rate and after some time the steady state is reached. Because steady state was observed and maintained before switching to the next temperature, it is assumed that no excessive deactivation occurred. This is further confirmed by the observation, that a nearly the carbon mass balance is nearly close (Coke formation <5%).

Figure 36. OPA conversion (%) against time on stream (h) at 350, 330, 310 and 370 °C for the catalysts (From top to bottom): WMoNia, WMoNiaHT, WMoNib, WMoNibHT, WMoNis, WMoNisHT. OPA + DBT feedstocks
The results of the average conversion of OPA as a function of temperature is showed in figure 37. It is seen that the higher the temperature, the higher the conversion of OPA. This trend is exactly the same as the one watched with the feedstock without the presence of DBT. So, it is clear that the existence or not of this component doesn’t affect the dependency of the conversion with temperature. The order of activity is showed in table 16.

![Figure 37. Conversion of OPA as a function of temperature. OPA+DBT feedstocks](image)

**Table 16.** Relative ranking of catalysts regarding the conversion of OPA + DBT feedstocks at 330 ºC

<table>
<thead>
<tr>
<th>Conversion [%]</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WMoNib</td>
</tr>
<tr>
<td></td>
<td>WMoNisHT</td>
</tr>
<tr>
<td></td>
<td>WMoNibHT</td>
</tr>
<tr>
<td></td>
<td>WMoNiaHT</td>
</tr>
<tr>
<td></td>
<td>WMoNia</td>
</tr>
<tr>
<td></td>
<td>WMoNis</td>
</tr>
</tbody>
</table>

To understand the influence of DBT in the HDN of OPA is needed to know the differences between the results obtained with a feed containing this compound and one without it. Catalyst WMoNib and WMoNisHT are clearly the most active ones. It is even possible to get conversions close to 100 % with them. Catalysts WMoNiaHT and WMoNibHT are the next in the list with
conversions close to 80 %. With the exception of products “b” catalysts prepared using the hydrothermal (HT) process are more active than the ones that are prepared without applying this treatment. The influence of DBT is clear. All the conversions, for all the six catalysts at every temperature are higher than the ones got when the feeds do not have DBT. As same as with the Q feeds, DBT enhances the HDN process and convert more OPA (Q) into a different derivative. It is clear that even if there is competitive adsorption, the continuous sulphidation that the catalysts have because of the fast reaction of DBT, increases the rate of HDN, no matter which catalyst is involved in the process.

Figure 38. PCH, PB, PCHE and, PCHA selectivities as a function of temperature. OPA+ DBT feedstocks
In order to understand how OPA is sequentially converted and then study the influence of DBT in its transformation figures 38 and 39 have been done. They show the selectivities and yields of the four products of the HDN conversion of OPA. They show that the catalyst WMoNib is the most active among all the catalyst studied. In both pathways, HYDN and DDN, the most important products are formed preferentially by this catalyst. Catalyst WMoNisHT as well as WMoNiaHT, and WMoNibHT have a similar behaviour and are the second ones in both pathways. Finally the catalysts WMoNia and WMoNis present the lowest selectivities among all the catalysts studied. These trends are comparable with the ones got from the general conversion. Their interdependence suggests that there is not competitive adsorption on the active sites, so the catalysts that convert more OPA produce more final products. It means that the intermediate compounds do not block the active sites and are converted at high rate, especially at higher temperatures. Additionally, the evolution of the curves give evidence that PCHA as well as PCHE are intermediates whereas PB and PCH are final products.

As well as in the pure OPA feeds, to prove the mechanism and pathways proposed in literature the relations between the reactants, the intermediates, and the products have to be examined more in detail. On this matter, the relation between yields and conversions were analyzed. The same two pathways observed previously (OPA to products PB and PCH) take place. It means sequential reactions from OPA to PCHA and PCHE and then to the final products PB and PCH as well as the direct denitrogenation from OPA to PB (DDN). A strong correlation between the degradation of PCHE and the formation of PCH is observed over the whole conversion range. This indicates that PCHE is an intermediate product in the HYD pathway. However, a direct reaction step from OPA to PCHE does not look possible and accurate from the chemical point of view (combined hydrogenation and denitrogenation), so an intermediate in this network is needed. On this matter, a route from OPA over PCHA to PCHE is chemically consistent. The first step from OPA to PCHA is well understood, since the hydrogenation capacity of unsupported trimetallic catalysts (W, Mo, Ni) is known\textsuperscript{63}. The second step (PCHA to PCHE) can be done through a Hoffman elimination as is proposed by Prins\textsuperscript{64}.

Even if the presence of DBT improves the general conversion of OPA, as well as the selectivities and yields of the main products (PCH and PB), the trends are similar in both experiments carried out with OPA. The HYDN pathways is preferred and the amount of PCH formed at the end is bigger than the amount of PB formed for the six catalysts studied.
Other important kinetic results that were obtained are the activation energies and Arrhenius plots for both pathways, HYDN and DDN. They are showed in the table 17 and figure 40.
Figure 40. Arrhenius plots for the HDN of OPA. HYDN and DDN pathways. OPA + DBT feedstocks.

Table 17. Activation energies for the HDN of OPA. OPA + DBT feedstocks

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation energy HYDN (kJ/gmol)</th>
<th>Activation energy DDN (kJ/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMoNia</td>
<td>138.9</td>
<td>160.6</td>
</tr>
<tr>
<td>WMoNiaHT</td>
<td>168.2</td>
<td>192.4</td>
</tr>
<tr>
<td>WMoNib</td>
<td>141.7</td>
<td>191.7</td>
</tr>
<tr>
<td>WMoNibHT</td>
<td>136.4</td>
<td>179.4</td>
</tr>
<tr>
<td>WMoNis</td>
<td>100.0</td>
<td>139.7</td>
</tr>
<tr>
<td>WMoNisHT</td>
<td>129.3</td>
<td>173.5</td>
</tr>
</tbody>
</table>

The Arrhenius plots show the rate of DDN and HYDN pathways, so the temperature dependency of the conversion of OPA, while the table shows the values of the activation energies for the 1st order like reaction. The results obtained showed the same trend that was observed with conversions, selectivities and yields. It also showed that the catalyst WMoNis is the least active one and that the catalyst WMoNib is the one that converts higher amounts of OPA. The results can be seen also as a support of the fact that the HYDN is more favored for all the catalyst than the DDN path.

Regarding the DBT reactions, the conversions obtained with all the 6 catalysts are showed in figure 41, as well as the ranking form the most active to the least active ones in table 18. Catalyst WMoNib is the most active, followed by the WMoNibHT. These ones converted a higher amount of DBT (closer to a 100 % conversion at high temperatures). Catalyst WMoNiaHT is the less
active one. This higher conversion at higher temperature could be due to the increase of the active phase during the reaction.

On the other hand, if we compare these results with the ones obtained with the Q + DBT experiments, there are notable differences. Even though in both experiments the catalysts “b” are the most active ones, the rest of the ranking is different in the case of the OPA feeds. In this case the catalysts “s” show a higher activity that in the presence of Q and the catalyst WMoNiaHT shows a decrease on it. These difference in the catalysts could be due to the difference in the adsorptions of the Q and OPA molecule in the active sites.

Table 18. Relative ranking of catalysts regarding the conversion of DBT with the presence of OPA at 330 ºC

<table>
<thead>
<tr>
<th>Conversion [%]</th>
<th>Catalyst</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>WMoNib</td>
</tr>
<tr>
<td></td>
<td>WMoNibHT</td>
</tr>
<tr>
<td></td>
<td>WMoNisHT</td>
</tr>
<tr>
<td></td>
<td>WMoNia</td>
</tr>
<tr>
<td></td>
<td>WMoNis</td>
</tr>
<tr>
<td></td>
<td>WMoNiaHT</td>
</tr>
</tbody>
</table>

Figure 41. Conversion of DBT as a function of temperature. OPA + DBT feedstocks
Regarding the main products that can be obtained throughout the 2 pathways explained by Houalla\textsuperscript{41} (PhCH and BiPh), selectivities and yields are showed in figures 42. The products found do not differ from the product distribution found in literature and in the feedstocks with Q instead of OPA. BiPh, Hyd-DBT and PhCH are observed, so the mechanism proposed for the DBT conversion, proceeding in parallel to the OPA conversion, does not vary from the proposed one for isolated DBT conversion over MoS\textsubscript{2} given in literature by Chianelli \textit{et al.}\textsuperscript{27}. They propose that DBT is converted via hydrogenation (HYDS) to PhCH and via hydrogenolysis (DDS) to BiPh. On the HYDS pathway, Hyd-DBT can be found as primary product.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure42.png}
\caption{PhCH and BiPh selectivities as a function of T and yields as a function of X_{Q}. Q + DBT feedstocks}
\end{figure}
The reason for the smaller selectivities and yields in the HYDS pathway in comparison with the DDS one is probably due to the competitive adsorption of OPA and its byproducts on the HYDS active sites. Similar observations that the ones made with the Q feedstocks due to the similar results obtained.

Other important kinetic results that were obtained are the activation energies and Arrhenius plots. They are showed in the table 19 and figure 43.

![Figure 43. Arrhenius plots for the HDS of DBT. OPA + DBT feedstocks](image)

**Table 19. Activation energies of the DBT HDS with the presence of OPA**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Activation energy (kJ/gmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WMoNia</td>
<td>100.5</td>
</tr>
<tr>
<td>WMoNiaHT</td>
<td>92.6</td>
</tr>
<tr>
<td>WMoNib</td>
<td>92.5</td>
</tr>
<tr>
<td>WMoNibHT</td>
<td>91.4</td>
</tr>
<tr>
<td>WMoNis</td>
<td>122.2</td>
</tr>
<tr>
<td>WMoNisHT</td>
<td>107.9</td>
</tr>
</tbody>
</table>

The Arrhenius plots show the rate of DDS pathway, so the temperature dependency of the conversion of DBT. While the table shows the values of the activation energies for the 1st order like reaction. The results obtained showed the same trend that was observed with the conversions and the dependence of the reaction with temperature. It also showed that the catalyst WMoNia is the least active one and that the catalyst “b” are the ones with convert higher amounts of DBT.
4.5 **Summary of HDN/HDS reactions**

With the purpose of study the HDN and HDS catalytic activity of six different catalysts, 4 different feedstocks were used. Three catalysts were prepared in a conventional way by synthesis routes at ambient pressure and increased temperature, while the other 3 under hydrothermal conditions (HT catalysts). All catalyst were sulphided in situ with an H₂S/H₂ mixture at the same conditions. The 4 feedstocks used Q and OPA as nitrogen-containing-model compounds, while DBT was used as a model compound to study the HDS activity. Additionally, when DBT was not added in the mixtures, DMDS was used with the objective of keeping the catalyst sulphided during the reaction and avoiding bigger errors in the results obtained. The mechanisms studied where Q HDN, OPA HDN, and simultaneous OPA/Q HDN with DBT HDS.

Temperature dependent activity tests were conducted with the 6 catalysts in order to examine the mechanism of both reactions. The overall mechanism for the OPA HDN stated in literature by Prins\textsuperscript{30} for the isolated Q HDN over NiMo catalysts supported on Al₂O₃ works well with 4 different feedstocks tested, and it is related to the results obtained in all the cases. The DBT HDS results obtained in both systems that contain this compound are in concordance with the results expected following the mechanism stated in literature for the isolated DBT HDS over MoS₂ by Houalla\textsuperscript{41}. Moreover, it was found that all catalysts are active for both Q/OPA HDN and DBT HDS, while the trend of increasing/decreasing activities with the increasing of temperature were different depending the HDN model compound selected. The results suggest that for all catalysts the mechanism and the active sites are similar for each the OPA/Q HDN and the DBT HDS.

The differences found between the results with the feedstocks containing OPA and Q are considerable. First of all, for OPA mixtures it is appreciated an increase in the general conversion with the increase of temperatures, while for Q feeds an increase in temperature produces a decrease in the amount of Q converted. This is related to the differences in structure between Q and OPA and the way that these molecules are adsorbed in the active sites. This difference is observable in 5 of the 6 catalysts, being the catalyst WMoNi the only exception. In this particular, Q and OPA HDN have similar behavior with changes in temperature. This could be explained due to the low catalytic activity that this particular material shows. Additionally, the influence of DBT in the OPA/Q HDN is observable in both cases. No matter which nitrogen-containing compound is used as HDN model, the presence of DBT will always increase the conversions and selectivities of the main products in the different mechanisms. This is associated to the higher sulphidation of the catalysts due to the higher reaction rates for DBT HDS in comparison with both HDN processes.
In the particular case of Q it is also related to the higher production of OPA and DHQ that are further converted in PCHA and PB. Finally, there were also differences between the HDS of DBT according to the nitrogen-containing compound uses to test the HDN activity. Q and OPA influence this conversion in a different way and different results were found. This is again related to the differences in structure and adsorption of OPA and Q.

4.6 Kinetics of Phenanthrene HDA

The HDA activities of the 5 catalysts described in the experimental part (WS₂/γAl₂O₃, Ni(2.5)WS₂, Ni(5.0)WS₂, Ni(8.0)WS₂, Ni(11.0)WS₂) were evaluated. These reactions were carried out with feeds containing Phenanthrene (Phe) as a multiaromatic model component. All the reactions were carried out using 6 different space time values, at constant temperature. However, experiments at a different temperature were performed at the beginning and end of the reaction with the objective of testing if whether or not the reaction reached a steady state. Thus, the kinetic data (conversions, selectivities and yields) were used to determine the overall activity of all catalysts at different space times, as well as make a comparison between the behavior of the different materials, and the influence of the amount of Ni present in the overall activity.

A general view of the conversion of Phe on time and at different space times is showed in the figure 44. First of all, with the objective of testing a possible deactivation of the catalyst, all the reactions were carried out at 360 ºC as first and last steps. It is seen that the catalysts stay active during the time of reaction. In general, there are some minimum changes in the values of less than 3%. However, for all the catalyst it is seen that the first conversion at 360 ºC is always above the average, it means that the time between samples was not enough to stabilize the conditions and get accurate results. All the data look congruent with the exception of the last point at 360 ºC in the catalyst Ni(2.5)WS₂. It is seen a big decrease to 0% that can be endorsed to a sudden decrease on the reactor’s temperature. This is an undesired change of conditions at the end of one reaction, in one catalyst, and cannot been considered the general behavior. Because steady state was observed and maintained before switching to the next temperature and/or space time, it is assumed that no excessive deactivation occurred. This is further confirmed by the observation, that the carbon mass balance is nearly close (coke formation <5%).
Figure 44. Phe conversion (%) against time on stream (h) at different space times. Temperature 360 and 300 °C. Catalysts (from top to bottom): WS_{2}/γAl_{2}O_{3}, Ni(2.5)WS_{2}, Ni(5)WS_{2}, Ni(8)WS_{2}, Ni(11)WS_{2}.

The results of the Phe conversion as a function of space time is showed in the figure 45. First of all, it is seen that the addition of Ni significantly increased the rate of phenanthrene.
hydrogenation. In fact, at 90 h·g\textsubscript{cat}/mol\textsubscript{Phe} the conversion of phenanthrene reached 9.8\% on WS\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3}, and triples on Ni(2.5)WS\textsubscript{2} (31.6\%). Precisely this is the catalyst that reaches the highest conversion of 25.4\% at 90 h·g\textsubscript{cat}/mol\textsubscript{Phe}. It is clear that that there is an optimum Ni\% that guarantees the highest conversion rate. At the same space time, increasing further the concentration of Ni decreased the conversion to 27.1\% and 25.4\% for Ni(5.0)WS\textsubscript{2} and Ni(8.0)WS\textsubscript{2}, respectively.

The mechanism proposed by Beltamone \textit{et al}\textsuperscript{50} shows sequential hydrogenation pathways with intermediates that could be found. It means that ring opening and multiple hydrogenolysis were not detected. The products observed were 9,10-dihydrophenanthrene (DiHPhe), 1,2,3,4-tetrahydrophenanthrene (TetHPhe), 1,2,3,4,5,6,7,8-octahydrophenanthrene (symOHPhe) and 1,2,3,4,4a,9,10,10a-octahydrophenanthrene (asymOHPhe). The fully hydrogenated product, Perhydrophenanthrene (PerHPhe), was a special case. There were some peaks in the GC analysis that can be related to this compound, but generally the selectivities and yields were so small that can be neglected.

\begin{center}
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Diagram.png}
\caption{Conversion of OPA as a function of temperature. OPA feedstocks without DBT}
\end{figure}
\end{center}

Regarding the formation rates and hydrogenation, they depend dramatically on the presence of Ni. Figure 46 shows the selectivities observed for the five catalyst studied. Particularly, in the case of WS\textsubscript{2}/γ-Al\textsubscript{2}O\textsubscript{3} only DiHPhe and TetHPhe are formed. The selectivities for the further hydrogenation are too close to 0\% at any apace time. On the other hand, with
catalysts Ni(x)WS$_2$ the deeper hydrogenated products, $sym$OHphe and $asym$OHphe were also produced.

\[ \text{Figure 46. Selectivities of the products formed after the HDA of Phe as functions of space time} \]

The yields observed on all the catalysts are presented as a function of phenanthrene conversion in figure 47. DiHPhe and TetHPhe were primary products indicating that the products were directly formed from phenanthrene. On WS$_2$/γ-Al$_2$O$_3$, the selectivity to DiHPhe and TetHPhe remained constant at 90 and 10 %, respectively, in the studied range of conversion. The products $sym$ and $asym$OHphe (just present on Ni(x)WS$_2$ catalysts) were regarded as secondary products.
based on the yield vs. conversion plots. These plot as well as the ones displaying selectivities show that in every case the SymOHPhe pathway is preferred over the asymOHPhe one.

![Yield vs. Conversion Plots](image)

**Figure 47.** Yields of the products formed after the HDA of Phe as functions of Phe conversion

The angular shape formed by the three rings in phenanthrene creates two electron sextets at the corners of the molecule, leaving a single double bond with high reactivity at the middle ring. This most reactive bond of the molecule is in the 9, 10-position. When a hydrogenation is performed, there are two explanations about the mechanism of reaction. First of all, Ishihara et al.\(^65\) suggest that DiHPhe is the only primary product, and that it reacts further to either TetHPhe or asymOHPhe. On the other hand, Beltamone et al.\(^50\) and Girgis and Gates\(^66\) defined two primary
Phe HDA products, DiHPhe and TetHPhe, the latter being hydrogenated toward sym- and asymOHPhe. A disagreement exist between this authors on whether DiHPhe reacts to asymOHPhe or is only in equilibrium with Phe. The actual reaction network is likely to depend on the particular reaction conditions, as hydrogenation steps may be reversible on sulfide catalysts (in contrast to the irreversible C-S or C-N ruptures). Consequently, the analysis of the obtained data is required in order to develop the reaction network. Firstly, DiHPhe and TetHPhe were both identified as primary hydrogenated products from the yield vs conversion graphs. Secondly, sym and asymOHPhe showed an extrapolated initial selectivity equal to zero, so they are secondary products. Additionally, the selectivity to both primary products decreased steadily with increasing phenanthrene conversion that implied that both compounds were involved in secondary reactions. Also, the decrease of TetHPhe selectivity is very similar to the increase of symOHPhe selectivity that means that under our reaction conditions Phe is hydrogenated in the two parallel reaction pathways described by Beltamone et al. 50

The hydrogenation of phenanthrene on catalysts with varying Ni concentrations showed a maximum in activity on Ni(2.5)WS₂ with a Ni/(W+Ni) ratio of 0.25. This optimum is close to the maximum HDS and HDN activity on supported Ni-promoted Mo(W)S₂ catalysts reported at Ni/(Mo(W)+Ni) ratios of 0.3-0.4 67-71. We also observed that Ni promotion has a dramatic effect on the selectivity of the hydrogenation of Phe, as for HDS and HDN. It means that adding Ni to the catalyst WS₂/γ-Al₂O₃ increased the concentration of active sites and increased the activity.

4.7 Characterization of post-reaction catalysts

After the HDN/HDS reaction all the catalysts were analyzed using Raman spectroscopy with a wavenumber range from 100 to 4000 cm⁻¹. These spectra are showed in figure 48. The Raman spectra of the six catalysts show very similar signals, even though they are not well defined probably due to a band overlapping. Only WMoNiSHT shows an additional signal at 1775 cm⁻¹, but it is considered an impurity. To determine the characteristics of these signals it is necessary to compare them with the peaks found in literature (table 20). On this matter, the region with the lowest shift (1300 – 4000 cm⁻¹) shows peaks related to the synthesis of the catalysts and it analysis is not very useful. A small signal at 3470 cm⁻¹ is found that can be assigned to an O-H stretch vibration. Similar values have been reported for the hydroxide stretch vibration in nickel hydroxide. The position of the signal at 1650 cm⁻¹ is characteristic for the stretching vibration of C=C double bonds. On the other hand, the other region (100 – 1300 cm⁻¹) is more relevant in our
particular case. It contains: molybdate ions in the region 900 – 800 cm\(^{-1}\) (stretch vibrations) and 400 – 275 cm\(^{-1}\) (bend vibrations)\(^{74}\) and tungstates\(^{75}\) in the range of 1000 – 600 cm\(^{-1}\) (stretch vibrations) and 400 – 200 cm\(^{-1}\) (bend vibrations).

**Figure 48.** Raman spectra of catalysts after reaction. The spectra are shifted vertically for better visualization. Catalysts ((From top to bottom): WMoNia, WMoNiaHT, WMoNib, WMoNibHT, WMoNis, WMoNisHT.
<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raman shift (cm(^{-1}))</td>
<td>Raman shift (cm(^{-1}))</td>
</tr>
<tr>
<td>3470</td>
<td>3580</td>
</tr>
<tr>
<td>1650</td>
<td>1666</td>
</tr>
<tr>
<td>949</td>
<td>950</td>
</tr>
<tr>
<td>830-870</td>
<td>850, 857</td>
</tr>
<tr>
<td>750-770</td>
<td>766</td>
</tr>
<tr>
<td>530</td>
<td>544</td>
</tr>
<tr>
<td>414-401</td>
<td>420, 408</td>
</tr>
<tr>
<td>377</td>
<td>383</td>
</tr>
<tr>
<td>350</td>
<td>350</td>
</tr>
<tr>
<td>150-170</td>
<td>174</td>
</tr>
</tbody>
</table>

It is possible to see some bands that can be related to the catalyst in the oxide form or to some synthesis precursor. In fact, the oxide signals (500 to 100 cm\(^{-1}\)) are the biggest ones in all the catalysts that means that not all the oxide precursors were sulphided. The signals for WS\(_2\) and MoS\(_2\) are relatively intense in all the catalysts, which indicates a rearrangement of the crystallites during reaction resulting in crystallites with a higher short range order. Since during the reaction deep reduction and further sulphidation of the components is expected, this is an indication that the signals arise from sulphided metals.
Chapter 5: Conclusions

5.1 HDN/HDS reactions

In this section six different Ni-promoted WMoS$_2$ catalysts were tested in the OPA/Q HDN and the DBT HDS. Three different patents where used to synthesize the catalysts as well as two different synthesis routes (ambient and hydrothermal conditions). Catalytic experiments were performed in continuous model (packed bed reactor) at 4 different temperatures (310, 330, 350 and 370 °C) and 5.0 MPa total pressure.

The overall mechanism for the OPA HDN stated in literature by Prins$^{20}$ for the isolated Q HDN over NiMo catalysts supported on Al$_2$O$_3$ works well with 4 different feedstocks tested, and it is related to the results obtained in all the cases. As it was set in literature, Q has a bicyclic nature containing both a carbocyclic and a heterocyclic six-membered rings. The latter one is hydrogenated faster than the former and produces a very reactive intermediate ($\alpha$-propenylaniline) that should be the predominant one. However, due to a higher adsorption ratio of DHQ (the second route product) with respect to OPA, DHQ is also formed. We could see that Q follows both pathways, but the OPA one is preferred in every case.

In the case of OPA, its transformation follows the two described pathways in the HDN net (direct denitrogenation of OPA forming PB and direct hydrogenation to PCHA followed by its transformation of into PCHE and finally PCH). The obtained results support the fact that the HYDN is more favored than the DDN path in the 4 different feedstocks analyzed.

The DBT HDS is in concordance with the results expected following the mechanism stated in literature for the isolated DBT HDS over MoS$_2$ by Houalla$^{41}$. This mechanism is described in two different pathways: direct desulfurization (DDS) forming BiPh and direct hydrogenation (HYDS) to PhCH with Hyd-DBT as intermediate. The products found do not differ from the product distribution found in literature, so the mechanism proposed for the DBT conversion, proceeding in parallel to the OPA/Q conversion, does not vary from the proposed mechanism for isolated DBT conversion over MoS$_2$ given in literature by Chianelli et al$^{27}$.

It was found that all catalysts are active for both Q/OPA HDN and DBT HDS, while the trend of increasing/decreasing activities with the increasing of temperature were different depending the HDN model compound selected. The results suggest that for all catalysts the mechanism and the active sites are similar for each the OPA/Q HDN and the DBT HDS.

The differences found between the results with the feedstocks containing OPA and Q are considerable. First of all, for OPA mixtures it is appreciated an increase in the general conversion
with the increase of temperatures, while for Q feeds an increase in temperature produces a decrease in the amount of Q converted. This difference is observable in five out of six catalysts, being the catalyst WMoNi the only exception.

The activity ranking of the catalysts in the HDN reactions shows that catalysts WMoNi and WMoNiHT are the most active ones, no matter if OPA or Q are converted. There is just an exception in the Q + DMDS feedstock where catalyst WMoNi and WMoNiHT are converted in more than WMoNi, but the gap is not considerable so WMoNi is still considered one of the best. For the DBT HDS it is also clear that both catalyst b are the most active ones and the ones that convert more DBT.

The influence of DBT in the OPA/Q HDN is observable in both cases. No matter which nitrogen-containing compound is used as HDN model, the presence of DBT will always increase the conversions and selectivities of the main products in the different mechanisms. On the other hand, there were observed differences between the HDS of DBT according to the nitrogen-containing compound used to test the HDN activity. Q and OPA influence this conversion in a different way and different results were found. In the case of OPA feedstocks the conversion of DBT is always higher that in the case of the Q feedstocks.

The post reaction test of the six catalysts showed that the oxide precursors were sulphided and that the products after reaction are still active due to the presence of a sulphidic phase.

5.2 HDA reactions

A series of Ni-promoted WS2/γ-Al2O3, with different concentrations of Ni, were tested in the phenanthrene HDA. The content of W was constant (22 w/w %) and the loading of Ni was varied from 0 to 11 w/w %. Catalytic experiments were performed in continuous mode (packed bed reactor) at 300 °C and 6.0 MPa total pressure.

The hydrogenation of phenanthrene occurred via two pathways (as described in literature). The first one that leads to the production of → 1,2,3,4,5,6,7,8-octahydrophenanthrene (symOHPhe) from the hydrogenation of phenanthrene (Phe) with 9,10-dihydrophenanthrene (DiHPhe) as intermediate. The second the formation of 1,2,3,4,4a,9,10,10a-octahydrophenanthrene via 1,2,3,4-tetrahydrophenanthrene (TetHPhe). In the non-promoted reactions (catalyst MoS2/γ-Al2O3) symOHPhe and asymOHPhe are not observed. The addition of Ni increases the rate of both hydrogenation routes. However, in all the cases the first pathway is more favored (selectivity in the first one almost the double of the second one on
Ni-containing catalysts). The activity for the Phe HDA correlates with the concentration of exposed Ni atoms. This enhancement is not directly proportional to the amount of Ni. There is an optimum point (2.5 % of Ni), activities below and over this point are smaller.
References

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   Chemosphere. 2011. 82. 573–580
   5677
   2008, 47, 7161-7166
   12264−12269


Table I. GC retention times for organic compounds in HDN/HDS reactions

<table>
<thead>
<tr>
<th>Name</th>
<th>M (g/gmol)</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl-disulphide (DMDS)</td>
<td>94.24</td>
<td>5.85</td>
</tr>
<tr>
<td>Propylcyclohexane (PCH)</td>
<td>126.24</td>
<td>6.4</td>
</tr>
<tr>
<td>3-Propylcyclohexene</td>
<td>124.20</td>
<td>7.44</td>
</tr>
<tr>
<td>Propyliden-cyclohexene</td>
<td>124.20</td>
<td>7.57</td>
</tr>
<tr>
<td>1-Propylcyclohexene</td>
<td>124.20</td>
<td>7.69</td>
</tr>
<tr>
<td>Propylbenzene (PB)</td>
<td>120.20</td>
<td>8.34</td>
</tr>
<tr>
<td>Propylcyclohexylamine (PCHA)</td>
<td>141.24</td>
<td>10.6 and 10.9</td>
</tr>
<tr>
<td>Trans-decahydroquinoline (DHQ)</td>
<td>153.26</td>
<td>11.70-11.80</td>
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<tr>
<td>Cis-decahydroquinoline (DHQ)</td>
<td>153.26</td>
<td>12.52</td>
</tr>
<tr>
<td>Tetradecane (TD)</td>
<td>198.20</td>
<td>14.67</td>
</tr>
<tr>
<td>1,2,3,4tetrahydroquinoline (14THQ)</td>
<td>133.21</td>
<td>14.96 - 15.00</td>
</tr>
<tr>
<td>Ortho-propylaniline (OPA)</td>
<td>135.21</td>
<td>15.77</td>
</tr>
<tr>
<td>Phenylcyclohexane</td>
<td>160.26</td>
<td>16.53</td>
</tr>
<tr>
<td>Quinoline (Q)</td>
<td></td>
<td>16.80</td>
</tr>
<tr>
<td>Hexadecane (HD)</td>
<td>226.44</td>
<td>18.91</td>
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<tr>
<td>1,2,3,4tetrahydroquinoline (14THQ)</td>
<td>133.21</td>
<td>19.53 – 19.60</td>
</tr>
<tr>
<td>Biphenyl (BiPh)</td>
<td>154.21</td>
<td>19.71 - 19.75</td>
</tr>
<tr>
<td>Hyd-DBT ()</td>
<td></td>
<td>25.14 – 25.20</td>
</tr>
<tr>
<td>Dibenzothiophene (DBT)</td>
<td>184.26</td>
<td>25.62</td>
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### Appendix II

**Table ii.** GC retention times for organic compounds in HDA reactions

<table>
<thead>
<tr>
<th>Name</th>
<th>M (g/gmol)</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetradecane (TD)</td>
<td>198.20</td>
<td>10.30</td>
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<tr>
<td>Perhydrophenanthrene (PerHPhe)</td>
<td>192.35</td>
<td>13.90, 14.60, 17.70, and 23.10</td>
</tr>
<tr>
<td>1,2,3,4,4a,9,10,10a-octahydrophenanthrene (asymOHPhe)</td>
<td>186.30</td>
<td>18.30</td>
</tr>
<tr>
<td>9,10-dihydrophenanthrene (DiHPhe)</td>
<td>182.27</td>
<td>22.60</td>
</tr>
<tr>
<td>1,2,3,4,5,6,7,8-octahydrophenanthrene (symOHPhe)</td>
<td>186.30</td>
<td>24.60</td>
</tr>
<tr>
<td>1,2,3,4-tetrahydrophenanthrene (TetHPhe)</td>
<td>182.27</td>
<td>26.20</td>
</tr>
<tr>
<td>Phenanthrene (Phe)</td>
<td>178.23</td>
<td>27.80</td>
</tr>
</tbody>
</table>
Appendix III

Table iii. EA and BET of the catalysts used in HDA

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>W (w/w %)</th>
<th>Ni (w/w %)</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WS$_2$/γAl$_2$O$_3$</td>
<td>21,9</td>
<td>-</td>
<td>140</td>
<td>0,45</td>
</tr>
<tr>
<td>Ni(2.5)WS$_2$</td>
<td>20,2</td>
<td>2,2</td>
<td>140</td>
<td>0,44</td>
</tr>
<tr>
<td>Ni(5.0)WS$_2$</td>
<td>20,4</td>
<td>4,5</td>
<td>140</td>
<td>0,42</td>
</tr>
<tr>
<td>Ni(8.0)WS$_2$</td>
<td>19,9</td>
<td>7,8</td>
<td>140</td>
<td>0,37</td>
</tr>
<tr>
<td>Ni(11.0)WS$_2$</td>
<td>17,2</td>
<td>11,1</td>
<td>140</td>
<td>0,36</td>
</tr>
</tbody>
</table>
Appendix IV

Figure i. 14THQ, 58THQ, PCHE and PCHA selectivities as a function of temperature. Q feedstocks without any sulfur component.
Figure ii. 14THQ, 58THQ, PCHE and PCHA yields as a function of $X_Q$. Q feedstocks without any sulfur component
**APPENDIX V**

*Figure iii. 14THQ, 58THQ, PCHE and PCHA selectivities as a function of temperature. Q + DBT feedstocks*
Figure iv. 14THQ, 58THQ, PCHE and PCHA yields as a function of $X_0$. Q + DBT feedstocks