Preparation and Evaluation of Sulfided NiMo/\(\gamma\)-Al\(_2\)O\(_3\) Hydrotreating Catalysts

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Abstract

Four nickel-molybdenum catalysts were synthesized on γ-alumina with higher surface area and on NiMo catalyst was prepared using γ-alumina with lower surface area. Catalysts with higher-surface-area support were prepared by coimpregnation, sequential impregnation and adding phosphorous. Theses catalysts were calcined at 500 °C. Effect of higher calcination temperature was investigated by preparation of one catalyst calcined at 700 °C. Catalysts were thoroughly characterized via four characterization techniques. The hydrotreating activity of three catalysts was carried out in a micro reactor at high pressure and three different temperature with Nynas vacuum middle distillate. Prior to the test, sulfiding was carried out to activate the catalysts. Hydrotreated-oil samples as products were analyzed to evaluate the activity and conversion of the catalyst. Also, the spent catalysts were characterized to evaluate the surface area characteristics and deactivation of catalysts. Addition of phosphorous to NiMo/γ-Al₂O₃ improved the interaction between the metals and the support as well as reduced the coke formation as observed in scanning electron microscopy micrographs.
Contents

Contents iv
List of Figures v
List of Tables vi

1 Introduction 3
  1.1 Setting the stage ........................................... 3
  1.2 Goal and scope of the thesis ............................. 4

2 Hydrotreating process 5

3 Hydrotreating catalysts 7
  3.1 Catalysts selection ........................................ 7
  3.2 Catalysts characterization ................................... 8
    3.2.1 Catalyst structure ..................................... 8
    3.2.2 Characterization techniques ........................... 13
  3.3 Catalysts preparation procedures ......................... 15
    3.3.1 Impregnation ............................................ 15
    3.3.2 Metal loading .......................................... 17
    3.3.3 Calcination temperature ............................... 18
    3.3.4 Promoters ................................................ 19

4 Experimental 23
  4.1 Catalyst preparation ....................................... 23
  4.2 Characterization ........................................... 24
  4.3 Activity Tests ............................................. 25

5 Results and discussion 29
  5.1 Catalysts characterization ............................... 29
  5.2 Catalytic activity ......................................... 38

6 Conclusions and further Work 45

Bibliography 47
List of Figures

1.1 Simplified block flow diagram for Nynas refinery . . . . . . . . . . . . . 4
3.1 HDS activity as a function of pore size for different feeds. Adapted from [1]
   First feed: Californian GO, Second feed: Californian VGO,
   and Third feed: Arabian HVGO. . . . . . . . . . . . . . . . . . . . . . . 8
3.2 Catalysts components and their key role to the hydroprocessing catalyst:
   a concept of acid-based supported catalyst. Adapted from [2]. . . . . . 9
3.3 Effect of calcination temperature on HDS activity. Adapted from [3]. . . 19
3.4 Calcination temperature and promoter contents relation, and its impact
   on activity. Adapted from [4] . . . . . . . . . . . . . . . . . . . . . . . 20
4.1 Unit schematic flow diagram . . . . . . . . . . . . . . . . . . . . . . . . 25
4.2 Conditions for activity test for catalysts . . . . . . . . . . . . . . . . . 26
4.3 Packing for the micro reactor . . . . . . . . . . . . . . . . . . . . . . . . 27
5.1 $N_2$ adsorption-desorption isotherms . . . . . . . . . . . . . . . . . 30
5.2 XRD of fresh catalysts . . . . . . . . . . . . . . . . . . . . . . . . . . . . 32
5.3 TPR profile of fresh catalysts . . . . . . . . . . . . . . . . . . . . . . . . 33
5.4 SEM micrographs for fresh catalysts . . . . . . . . . . . . . . . . . . . . 36
5.5 SEM micrographs for spent catalysts . . . . . . . . . . . . . . . . . . . . 37
5.6 Formation of whiskers in SEM micrographs for spent catalysts . . . . . 38
5.7 Catalysts Ageing Trend at $T_{base}$ and $x$ bar . . . . . . . . . . . . . 39
5.8 Process yield for hydrotreated oils . . . . . . . . . . . . . . . . . . . . . 39
5.9 Aromatics, nitrogen and sulfur contents in products . . . . . . . . . . . 41
5.10 HDA, HDN AND HDS activity rate constants and conversions . . . . 42
5.11 Color, density and viscosity in products . . . . . . . . . . . . . . . . . 43
List of Tables

2.1 Feedstocks and Products for Hydrotreating Unit, adopted from [5] . . . . 5
3.1 Typical example for impregnation methods . . . . . . . . . . . . . . . . 16
4.1 Summary of prepared catalysts. . . . . . . . . . . . . . . . . . . . . . . . 24
5.1 Textural properties of support and catalysts. . . . . . . . . . . . . . . . 29
5.2 Compositions for catalysts obtained from SEM-EDX . . . . . . . . . . 34
5.3 Products characteristics during a two-day process . . . . . . . . . . . . 40
# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
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<tr>
<td>$C_a$</td>
<td>%</td>
<td>Aromatics content</td>
</tr>
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<td>$C_p$</td>
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<td>$C_n$</td>
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<td>Naphthenic content</td>
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<td>$P$</td>
<td>bar</td>
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<td>$P_0$</td>
<td>bar</td>
<td>Saturation pressure</td>
</tr>
<tr>
<td>$x$</td>
<td>–</td>
<td>Ratio of Partial pressure to saturation pressure</td>
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<td>$V$</td>
<td>ml</td>
<td>Adsorbed volume at partial pressure</td>
</tr>
<tr>
<td>$V_m$</td>
<td>ml</td>
<td>Adsorbed volume at monolayer coverage</td>
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<tr>
<td>$c$</td>
<td>–</td>
<td>Constant</td>
</tr>
<tr>
<td>$B$</td>
<td>–</td>
<td>Peak width</td>
</tr>
<tr>
<td>$d$</td>
<td>–</td>
<td>Crystallite size</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>–</td>
<td>X-ray wavelength</td>
</tr>
<tr>
<td>$\Theta$</td>
<td>–</td>
<td>Diffraction angle</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>–</td>
<td>Shape constant</td>
</tr>
<tr>
<td>$LHSV$</td>
<td>$h^{-1}$</td>
<td>Liquid hourly space velocity</td>
</tr>
<tr>
<td>$k_{HDA}$</td>
<td>$h^{-1}$</td>
<td>Activity rate constant for hydrodearomatization</td>
</tr>
<tr>
<td>$k_{HDN}$</td>
<td>$h^{-1}$</td>
<td>Activity rate constant for hydrodenitrogenization</td>
</tr>
<tr>
<td>$k_{HDS}$</td>
<td>$ppm^{-0.5}h^{-1}$</td>
<td>Activity rate constant for hydrodesulfurization</td>
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<td>$A_F$</td>
<td>wt.%</td>
<td>Aromatics content in feed of the micro reactor</td>
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<tr>
<td>$A_P$</td>
<td>wt.%</td>
<td>Aromatics content in product of the micro reactor</td>
</tr>
<tr>
<td>$N_F$</td>
<td>ppm</td>
<td>Nitrogen content in feed of the micro reactor</td>
</tr>
<tr>
<td>$N_P$</td>
<td>ppm</td>
<td>Nitrogen content in product of the micro reactor</td>
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<td>$S_F$</td>
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<td>Sulfur content in feed of the micro reactor</td>
</tr>
<tr>
<td>$S_P$</td>
<td>ppm</td>
<td>Sulfur content in product of the micro reactor</td>
</tr>
<tr>
<td>$V_{am}$</td>
<td>ml</td>
<td>Volume of sample</td>
</tr>
<tr>
<td>$V_F$</td>
<td>ml</td>
<td>Volume of the consumed oil (as the feed)</td>
</tr>
<tr>
<td>$T_m$</td>
<td>°C</td>
<td>Reduction temperature</td>
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Chapter 1

Introduction

1.1 Setting the stage

In recent years, environmental legislations on the sulfur content in transport fuels has brought about the need for ultra low sulfur fuels. In addition, as a response to the growing global energy demand as well as decreasing the quality of crude oils due to the pattern of changing the sources into heavy and extra-heavy, interests in heavy and extra-heavy crude oils have been increasing. These factors have positioned hydrotreating process to be the center of improvement. This process covers both the pretreatment (heavy and extra-heavy crude oils hydrotreating before distillation) and post treatment (hydrotreating of products). Although hydrotreating process has been applied for many years, it still requires more modifications to satisfy the new demands. The main problems in hydroprocessing are (i) the limitations for pore diffusion which prevent the access of large molecules to the active sites, and (ii) rapid catalyst deactivation by coke and metal deposition. In order to tackle these two problems at the same time, bi-functional catalysts are required. Such a catalyst should have a support with sufficient pore diameter to improve metal deposition and pore diffusion, enough acidity to efficiently crack the large molecules, and optimum dispersion of active metals [6].

Nynas Refinery process is different from a typical oil refinery with production of transport fuels as main products. Figure 1.1 illustrates a simplified block flow diagram of Nynas Refinery. Vacuum distillation middle cuts are processed in hydrotreating units to mainly reduce aromatics, nitrogen and sulfur contents to meet the products specifications. Nynas products range includes bitumen, transformer oil, base oil and other oils such as oils for adhesives, printing inks, etc. In general, these products are characterized by their naphthenic hydrocarbons content. The mineral oil aromatic content plays an important role to meet the required products specifications. Sulfur content is not the main concern for this product. However, many products with different specifications are produced in this refinery and the priority for each one may differ.

Bearing above into consideration, proper catalysts for Nynas hydrotreating pro-
cess should remove the aromatic, nitrogen and sulfur contents to satisfy products characteristics and, at the same time, be enough flexible for a range of feed. In addition, operating conditions in which the catalysts give the highest activity are very important as they affect the energy consumption of the process. Since the most focus of researches is on fuel treatment, almost all the experiments reported in literatures have concentrated on sulfur and nitrogen removal. Therefore, conducting an experiment to evaluate the behavior of different catalysts on Nynas various feedstocks helps the company to have a better understanding of the catalysts behavior and a cleverer selection approach in the market.

1.2 Goal and scope of the thesis

The aim is to provide an overview of the effect of hydrotreating catalysts at different operating conditions. This includes a literature review, evaluating and selecting of the most proper methods for catalyst preparation and modification, making a number of catalysts, characterizing, and testing. However, due to time span of this thesis, five catalysts were made and characterized, but only three of them were tested in Nynas micro-reactor with one feed.

Catalysts preparation and characterization were done at KTH laboratories in chemical engineering department, SEM-EDX at electron microscopy laboratory at KTH-Kista, and activity tests and products characterization are performed at the laboratory of Process Technology department Nynas Refinery.
Chapter 2

Hydrotreating process

Hydrotreating is a multi functional process to reduce the content of sulfur, nitrogen, oxygen, metals and aromatics in products of a typical refinery as well as improving cetane number, smoking point and the density. The feed of this process includes different distillate range from naphtha to atmospheric residue. Increasing the amount of contaminants leads to more difficult and severe upgrading; i.e. heavier feeds leads to increasing severity, and accordingly the consumption of hydrogen and catalyst. The aim of hydrotreating process is to catalytically convert distillation fractions to commercial products which are adversely affected by the environmental legislations for clean products as well as increasing demand [2,7]. Table 2.1 shows some possible feeds and products for a typical hydrotreater unit [5]. Researches and companies owning the know-how of hydrotreating processes have been putting their effort to innovatively enhance the process and its catalysts [2,7].

Table 2.1: Feedstocks and Products for Hydrotreating Unit, adopted from [5].

<table>
<thead>
<tr>
<th>Feed</th>
<th>Product</th>
</tr>
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<tbody>
<tr>
<td>Naphtha</td>
<td>Catalytic Reformer Feed</td>
</tr>
<tr>
<td>Straight-run Light Gas Oil</td>
<td>Kerosene, Jet Fuel</td>
</tr>
<tr>
<td>Straight-run Heavy Gas Oil</td>
<td>Diesel Fuel</td>
</tr>
<tr>
<td>Atmospheric Residue</td>
<td>Lube base Stock, Low Sulfur Lube Oil, RFCC Feed</td>
</tr>
<tr>
<td>Vacuum Gas Oil</td>
<td>FCC Feed, Lube base Stock</td>
</tr>
<tr>
<td>Vacuum Residue</td>
<td>RFCC Feed</td>
</tr>
<tr>
<td>FCC Light Cycle Oil</td>
<td>Blend Stock for Diesel, Fuel Oil</td>
</tr>
<tr>
<td>FCC Heavy Cycle Oil</td>
<td>Blend Stock for Fuel Oil</td>
</tr>
<tr>
<td>Visbreaker Gas Oil</td>
<td>Blend Stock for Diesel, Fuel Oil</td>
</tr>
<tr>
<td>Coaker Gasoil</td>
<td>FCC Feed</td>
</tr>
<tr>
<td>Deasphalted Oil</td>
<td>Lube base Stock, FCC Feed</td>
</tr>
</tbody>
</table>

Various processes for hydrotreating have been developed by different companies like Shell, UOP, Axens, Halder Topsøe, Texaco, etc. [8]. Commercial units have em-
ployed a broad ranges of operating conditions due to feed characteristics. Different type of reactors, i.e. fixed or moving bed, ebullated or slurry bed, needed to be selected to satisfy the process requirements. In addition, this process requires catalyst to efficiently transfer hydrogen to reactant molecules. The process also generally is affected by the design of the catalytic reactor and its internals in particular. In order to reach to a high-performance-hydrotreating unit, feed type requires to be matched with the reactor and catalyst which in turn resulted in minimizing the catalyst deactivation rate [2,7].
Chapter 3

Hydrotreating catalysts

3.1 Catalysts selection

Several parameters play important roles in catalyst selection for hydrotreating such as catalyst life, activity toward side reactions (unwanted or desired), pressure drop, ease of activation, regeneration and price. Moreover, for certain applications, using a combination of different catalyst types in one reactor may be the optimum solution. In general, a detailed study of the specific situation is required to select catalyst [1].

In hydrotreating catalyst the most common combinations of active elements are CoMo, NiMo and NiW supported on alumina, silica-alumina, silica, zeolites, and magnesia, with surface areas of 100 to 300 m$^2$/g [1,9]. Catalyst selection is based on the application and desired activity/selectivity. CoMo catalysts are excellent for HDS while showing less activity in HDN and HDA. On the other hand, NiMo catalysts show high activity in HDN and HDA. As a result, this type of catalysts are often preferred for treating unsaturated feeds. Selectivity of heteroatom removal versus hydrogenation can be increased for alumina-supported catalysts by addition of phosphorous which is described in Section 3.4.2. NiW catalysts, in comparison with CoMo and NiMo, have the highest activity for HDA at low hydrogen sulfide partial pressures [1,10].

Diffusion in the catalyst pores in hydrotreating often influence reaction rates. Thus, choosing proper catalyst particle size and shape, and pore system geometry is important. This is especially true in hydrotreating of heavier feeds, where the reactions may be limited by diffusion of reactants and products in and out the pore system. Hence, for processing residue, small catalyst particles with relatively large pores which expose significant external surface area are preferred [1]. There is a tendency in processing heavy feeds for bed plugging because of deposits (likely consisting of V and Ni sulfides, debris, iron compounds, coke and NaCl) on the exterior of the catalyst particles. The particulates settle in the voids between the catalyst particles at the inlet of fixed-bed reactors. Thus, bed plugging is especially serious at this point. In order to effectively tackle the bed-plugging problem, catalysts in the form of large rings should be used or bed grading should be adopted [1].
The effect of pore size on hydrotreating has been considered in several literature reports (e.g. [1]) and an optimum pore size is reported [11]. Topsøe et al. [1] showed that the optimum pore size increases with increasing pressure and particle size. Also, feed and process conditions can affect the optimum pore size. Smaller pores make the activity become limited by diffusion, while larger pores give less active surface area. Figure 3.1 illustrates these features for a light feed (the first one), a heavier feed (the second one) and a heavy feed (the third one).

![Figure 3.1: HDS activity as a function of pore size for different feeds. Adapted from [1]
First feed: Californian GO, Second feed: Californian VGO, and Third feed: Arabian HVGO.](image)

3.2 Catalysts characterization

3.2.1 Catalyst structure

The structure of hydrotreating catalysts consists of two main components: active site and support. Stanislaus et al. [2] provided a general classification of catalyst components and their key elements as illustrated in Figure 3.2.
3.2. Catalysts Characterization

Figure 3.2: Catalysts components and their key role to the hydroprocessing catalyst: a concept of acid-based supported catalyst. Adapted from [2].

3.2.1.1 Active Site

It is commonly assumed that the catalytically active sites in either promoted or non-promoted hydrotreating catalyst are the molybdenum atoms at the surfaces of the molybdenum sulfide (MoS$_2$) crystallites, with at least one sulfur vacancy at a site to allow the reacting molecule to bond chemically to the molybdenum atom [1,12]. These crystallites have a layer lattice, and the sulfur-sulfur interaction between successive MoS$_2$ layers is weak [13]. Crystals grow as platelets with relatively large dimensions parallel to the basal sulfur planes as well as small dimensions perpendicular to the basal plane. It is suggested that the edges of the MoS$_2$ platelets are bonded to the surface of the support by Mo-O-Al bonds [12,13].

Coordinatively Unsaturated Sites (CUS) or sulfur ion vacancies are resulted from removing the corner and edges of sulfur ions in MoS$_2$ under hydroprocessing conditions [2]. Sulfur atoms in the basal planes of MoS$_2$ are much more difficult to remove than sulfur atoms at edges and corners. Hence, exposed molybdenum atoms are predominantly present at edges and corners resulting in catalysis occurrence at MoS$_2$ edges and corners rather than on the basal plane. This also was confirmed by results of a study in which a single crystal of MoS$_2$, with a high basal plane to edge surface area ratio, was found to have a low HDS activity [14]. Its activity increased after the sulfur atoms were sputtered away from the basal plane and exposed to the molybdenum atoms. Another study showed that exposure of the
MoS$_2$ nano-particles to hydrogen led to creation of sulfur vacancies. Such vacancies at the MoS$_2$ edge were supposed to be the active sites for HDS [15]. Thus, in case of non-promoted catalyst, basal plane are inactive in molecules adsorption and are not probably important in hydrotrating reactions [2].

In case of promoted catalyst, metal sulfide, e.g. MoS$_2$, is decorated by promoters, e.g. Ni(Co). This gives more active CUS and accordingly improves the rate of hydrogen activation [16]. The effect of adding promoters in increasing HDS and HDN [2] has been explained through different models which four of them have been more in center of attention: Monolayer Model [17–20], Intercalation Model [21,22], Contact Synergy Model [23–25], and Co-Mo-S Model [1,26]. As among these models, Co-Mo-S model has been broadly accepted [1,2], a brief description is provided as follows.

Topsøe et al. [26–33] applied in-situ Mössbauer spectroscopy, extended X-ray absorption spectroscopy, and infrared spectroscopy studies to directly observe a Co-Mo-S phase in CoMo catalyst. This enabled them to provide a detailed structural description of this catalyst and a new explanation for the promotion. The building blocks of Co-Mo(Ni)-S structures are small MoS$_2$ nano-catalysts with cobalt (or nickel) promoter atoms [2]. These atoms are located at the edges of MoS$_2$ layers in the same plane of molybdenum atoms [1,2,26]. HDS activity was found to have a linear correlation with the relative amount of cobalt atoms present as Co-Mo-S phase [2].

The structure of Co-Mo-S is not a single, bulk phase with a fixed overall Co:Mo:S stoichiometry. Instead, it should be regarded as a family of structures with a wide range of cobalt concentrations (from pure MoS$_2$ up to essentially full coverage of the MoS$_2$ edges by cobalt). The cobalt atoms in Co-Mo-S may not all have identical properties because of the effects of different edge-site geometries [34,35], Co-Co interactions [30,31], and changes in sulfur coordination [36]. Cobalt and neighboring molybdenum atoms interactions have been evidenced by both magnetic susceptibility [1] and ESR [37] measurements. In this context, it was noticeable that the standard molar free enthalpy calculation of formation of slabs of MoS$_2$ indicated that the edge location (decoration) of promoters increased the slabs stability [1].

Studies on the correlation between structure and activity of these catalyst systems resulted in the identification of two types of Co-Mo-S structures. One type shows substantially higher activity than the other one. Based on the the low and high activity forms of Co-Mo-S, the terms Type I and Type II were chosen respectively [2]. Depending on preparation and activation parameters, type of support, presence of additives, metal loading, etc., both single and multiple slab Co-Mo-S structures have been observed. For the catalyst supported on alumina, Type I Co-Mo-S (i.e. single slab structures) interact strongly with the support, maybe via Mo-O-Al linkages at the edges [1]. According to Stanislaus et al. [2], the Type I structures are incompletely sulfided and have some remaining Mo-O-Al linkages to the support. The presence of these linkages is related to the interaction occurring in the calcination state between molybdenum and surface alumina hydroxyl groups which leads to oxygen bridged mono-layer type structure that are difficult to sulfide
In contrast, the interactions between Type-II Co-Mo-S (i.e. multiple slab form) and the support are small and they are fully sulfided [1,2]. In this type, the underlying MoS$_2$ are less dispersible. It consists of multiple slabs which are not linked with the support [2]. Other studies [38,39] showed that the degree of staking in MoS$_2$ and Co-Mo-S structures can be controlled by carefully controlling support properties and preparation parameters. Also, the formation of small stable single slabs of MoS$_2$ on alumina supports have been achieved. These have a high dispersion of MoS$_2$ which can accommodate more cobalt atoms to form higher active single slab Type II Co-Mo-S structures [2].

In summary, Type II structures are higher activity forms of Co-Mo-S than Type I. However, in 2009, Okamoto et al. [40,41] reported the results of their experiment on preparation of CoMo/SiO$_2$ catalyst sulfided with 10 % H$_2$S/He and forming extraordinary active Co-Mo-S (higher than Type II) on SiO$_2$ regardless of the precursor of Mo. They call it Type III Co-Mo-S structures. It should be noted that catalytic activity is mostly connected to the presence of promoters in Co-Mo-S. This structure is also observed to be true for type of promoted catalysts i.e. Fe-Mo-S, Ni-Mo-S, Co-W-S Ni-W-S and Fe-W-S [1].

3.2.1.2 Support

Active compounds, i.e. mixed sulfides of molybdenum and cobalt or nickel as Ni(Co)-Mo-S phases, in hydrotreating catalyst are supported on a carrier (support) which generally affect catalytic properties for both promoted and non-promoted types [1,2]. The carrier provides mechanical strength to the catalyst as well as high surface area to maximize active phase dispersion [2]. Generally alumina exerts stronger interactions with the active phases compared to silica, carbon, or titania for instance. The strong support interactions are very important as they are responsible for the fact that highly dispersed MoS$_2$ structures can easily be prepared and remain stable during operation. However, these strong interactions in alumina-supported catalysts have negative sides as they are probably responsible for the formation of the relatively less active Type I Ni(Co)-Mo-S. For some other supports (e.g. silica), the support and the active phases interactions are quite weak. This mainly leads to influence on the activity via changes in dispersion and phase distribution [1].

The support effect has been studied from different angles. Topsøe et al. [1,42] pointed out the dependency of catalytic activity upon form, orientation and growth of MoS$_2$ species on the support site. Sakashita et al. [43–45] studied the effects of surface orientation and crystallinity of the support. They showed the dependency of the catalytic activity and selectivity of MoS$_2$ catalysts on the microstructures of MoS$_2$ clusters that were affected by the surface orientation of gamma alumina. They concluded that the gamma-alumina support surface properties are important factors in controlling the catalytic functionality of MoS$_2$-based catalysts. Also, based on their results, controlling the microstructure of MoS$_2$ clusters by tailoring the sur-
face orientation of alumina supports is possible. In other experiments [46,47] the impact of pH of the impregnating solution, alumina phase, particle size and textural properties of Al$_2$O$_3$ supports on HDS, HDN amd HDA were studied. Their results showed that both the textural properties and hydrotreating activity of the nickel-molybdenum catalysts supported on two alumina phases are noticeably different while evaluating with a real feedstock. The behavioral differences of the catalysts appear to have their origin in the different support crystal size that was used during the catalysts and alumina phase preparation. This could modify the concentration and distribution of the surface hydroxyl groups and enhance the catalytic activity. They also reported that the link between particle size of the alumina support, NiMo oxide catalysts, and NiMoS catalyst was important to determine the changes of the active sites after calcining and sulfiding. The results revealed that the catalytic activity of HDS, HDN and HDA depends on the particle size of the support and on the NiMo species metallic particle size. In addition, the catalyst with a smaller particle size gave the maximum reaction rates for all three processes.

The effect of the surface characteristics of support on its interaction with metal and its correlation with hydrodesulfurization activity and CoMo selectivity by several characterization methods have been investigated [48]. It showed that alumina support with higher crystallinity and fewer hydroxyl groups resulted in a more moderate interaction with metal. This enhanced Mo sulfidation and caused a higher stacking number and longer average slab length for the CoMo catalyst. Also, it stimulated more Co-Mo-S structures, giving rise to higher HDS activity and selectivity. In a new approach in the evaluation of the support effect, Ninh et al. [49] proposed a preparation method that might be more efficient than the classic co-impregnation method. They selected the interaction of acetylacetonate complex directly onto supported MoS$_2$. Then supported MoS$_2$ was prepared on different type of support and Ni(ACAC)$_2$ used to achieve MoS$_2$ promotion in refluxing methanol. The results showed that the Ni-Mo-S sites on different type of catalysts had almost the same intrinsic activities, suggesting that active sites quality would not be very affected by the support nature.

Among the available developed supports for hydrotreating catalyst, gamma alumina (γ-Al$_2$O$_3$) has been widely applied in hydrotreating [1,2,16]. This broad application is due to its reasonably high surface area and porosity, high thermal stability, excellent mechanical strength, containing acidic and basic sites, very good morphology and low cost [1,2,50,51]. In addition, as mentioned by Breysse et al. [52], broad knowledge availability of γ-alumina is another reason for its widely usage. Nevertheless, several studies have been carried out on other types of catalyst such as carbon, silica, silica-alumina, zeolites, titanium, zirconia, and magnesia. Topsoe et al. [1] reviewed the work’s regarding different supports as well as Breysse et al [52] who provided an overview on the various support interactions for hydrotreating catalysts. The latter showed that many different aspects such as electronic properties modifications or the active site morphology, bifunctional reactions with acidic sites, absence or presence of linkage between the support and the sulfide site need to be considered in study of the support effect.
In recent years, hydrothermal treatment (HTT) has been introduced as an alternative method for the modification of $\gamma$-Al$_2$O$_3$ support [50,53–58]. Stanislaus et al. [54] conducted a series of experiments to develop the understanding of the mechanism of pore widening in $\gamma$-Al$_2$O$_3$ supports under hydrothermal conditions. Their results showed that pore enlargement occurred because of rehydration of $\gamma$-Al$_2$O$_3$ and its transformation to well-crystallized boehmite. A wide pore NiMo/$\gamma$-Al$_2$O$_3$ prepared by the hydrotreating procedure showed exceptionally high activity for hydrodemetal- lization and asphaltene conversion reactions in vacuum residue hydroprocessing.

Xiang et al. [55] studied the impact of HTT on Ni/Al$_2$O$_3$ catalyst and reported that the method was effective to reach high activity. Another study [57] was carried out on the same catalyst regarding structureal and textural evolution of Ni/Al$_2$O$_3$ catalyst under HTT. Li et al. [50] performed HTT on $\gamma$-Al$_2$O$_3$ at 140 °C for 1-24 hours. This resulted in the formation of plate-like $\gamma$-AlOOH nano-crystallites with different morphologies, which linked closely to the surface acidity of the corresponding support. Reaction time rise in the period of 1-2 hours led to increasing of the specific surface area, OH surface and $\gamma$-Al$_2$O$_3$ acidity, especially the weak acidity. However, extending hydrothermal reaction time brought about the decrease of specific surface area, OH surface and total acidity of $\gamma$-Al$_2$O$_3$ because of the growth of the surface crystallites.

### 3.2.2 Characterization techniques

Process optimization and development require a better understanding of catalysts. In addition, the emergence of new material with catalytic properties and peculiar characteristics, and development in technology and computer have led to a considerable growth in techniques for catalyst characterization [59]. These techniques help to understand the relationship among physical, chemical and catalytic properties; clarifying deactivation causes, designing regeneration procedures, and selecting catalyst properties to minimize such deactivation. Other beneficial of these techniques includes establishing physical and chemical properties for catalyst marketing, reactor design, modeling, and process optimization; and ensuring quality control in catalyst manufacturing [60].

**Morphology and physical properties.** Important properties of catalysts are surface area, pore size and pore volume since they are responsible to define the measure of catalysts internal surface available to accommodate active sites, accessibility of active sites to reactants and the extent to which transport of products from the catalyst surface to the bulk fluid is facilitated [60]. For most heterogeneous catalysts, porosity occurs through the preparation methods, e.g. by drying or calcining precipitates of hydrous oxides [59,60]. The size and number of pores determine the internal surface area which is usually flavored to be high (high density of small pore sizes) to maximize the dispersion [60]. The pore sizes classification is usually considered as micropores ($\phi < 2$ nm), mesopores ($2 < \phi < 50$ nm) and macropores ($50$ nm $< \phi$). Morphological parameters play an important role to understand the evolution of catalysts during preparation step. This is helpful to enhance preparation
methods to reach the desired results [59].

Nitrogen adsorption at its boiling point (77 K) is the most common technique for determining catalyst morphology [59, 60]. This technique determines the absorbed volume of \( \text{N}_2 \) versus its relative pressure (i.e. adsorption isotherm). Depending on which suitable evaluation method (e.g. BET, t-plot, BJH, etc.) the data is analyzed, different properties such as catalyst total surface area, pore size and volume are determined [59].

Brunauer, Emmett and Teller (BET) is a very common evaluation method which describes the relationship between the volume absorbed at a given partial pressure and the volume adsorbed at monolayer coverage. Equation 3.1 in which \( x = P/P_0 \), \( P \) is the \( \text{N}_2 \) partial pressure, \( P_0 \) the saturation pressure at the temperature of the experiment, \( V \) the volume adsorbed at \( P \), \( V_m \) the volume adsorbed at monolayer coverage, and \( c \) is a constant [60].

\[
\frac{x}{V(1-x)} = \frac{1 + (c-1)x}{cV_m}
\]

Electron microscopy is a powerful tool that frequently used for direct observing of shape, size, chemical structure, surface texture, and crystallite size, over a broad range of size resolution ranging from atomic dimensions to several hundred microns. Two quantitative methods are Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM), which provides a direct view of the catalyst under study [59, 60].

The electron beam focused on the sample is scanned in SEM by a set of deflection coils. TEM involves electron analysis focused and transmitted through a thin sample on a conducting grid to form high resolution images of the specimen. TEM is used to determine crystallite size and size distribution for supported metals, e.g. for sintering of supported Ni and Pt catalysts. The modern High Resolution Transmission Electron Microscope (HRTEM) is a useful tool to study nanostructure of nanophase materials with the possibility of seeing molecular layers and surface layers [60].

**Surface properties** Probably, the first characterization technique applied to catalysts was infrared spectroscopy (IR) which continues to be one of the most widely used in studies on catalysts and surfaces [60]. This technique can be used to determine adsorbed species and/or adsorbed reaction intermediates and their structures on well-dispersed catalysts and surfaces, and give sign of active sites chemistry on catalyst surfaces during preparation and reaction, i.e. acidity, oxidation state, and sit molecularity [59, 60]. Nevertheless, IR spectroscopy suffers from two limitations: low frequency region cannot be used due to the skeleton vibrations of the solid, and non-resistance of most IR transparent materials to water or other liquids [59].

Raman Spectroscopy (RS) analyzes the intensity of Raman scattering of monochromatic light as a function of the scattered light frequency [60]. The same detailed molecular structure information as IR spectroscopy obtained from RS; however, the limitations in IR are covered in RS as it allows detection of low frequency vibrations [59, 60].
Temperature Program Desorption (TPD) is applied to study various adsorption states, their binding energies, their surface concentrations, and their desorption kinetics. These studies are carried out through measurement of the rate of desorption adsorbed molecules as a function of linear temperature ramp [60].

Since most catalysts are crystalline solids, diffraction of an X-ray beam as a function of the angle of the incident beam results in evaluation of the crystalline nature, their concentration in the solid and their size [59,60]. X-Ray Diffraction (XRD) also can be applied for both qualitative and quantitative chemical phase analyses [60]. In an XRD diffractogram, peak width is inversely related to the crystallite size of a given phase. Thus the width of the peak can be related to the crystallite size. Based on Scherrer equation 3.2, the width, $B$, relates to half-peak height of an XRD line because of a specific crystalline plane to the size of the crystallites, $d$. $\lambda$ is the X-ray wavelength, $\Theta$ the diffraction angle, and $\kappa$ is the shape constant usually equals to 1 (assumption for spherical particle).

$$
B = \frac{\kappa \lambda}{d \cos \Theta}
$$

Nuclear Magnetic Resonance (NMR) can be useful in study of the bonding and mobility of different kinds of adsorbed hydrogen species on noble metal catalysts, carbon deposits structure responsible for poisoning of catalysts during CO hydrogenation, kinetics of exchange reactions between physisorbed and chemisorbed molecules, reactions of short-lived transition metal complexes on oxide catalysts, and structures of adsorbed molecules [60].

### 3.3 Catalysts preparation procedures

Different preparation methods have been applied e.g. molecular designed dispersion method [61], sol-gel method [62], unconventional slurry impregnation or solvent assisted spreading method [63], sequential and simultaneous equilibrium deposition filtration (EDF) technique, successive or simultaneous dry impregnations, successive or simultaneous wet impregnations [64], equilibrium adsorption (EA) method [65,66], equilibrium deposition filtration (EDF) [67], sequential and simultaneous incipient wetness (pore filling [1]) impregnation [68–71]. Based on the literature review of this study, the most common method is impregnation which will be described hereafter. Catalytic activity and selectivity, and catalyst structure and morphology are dependent on preparation procedure [1]. Such dependency mainly include the effect of impregnation procedure, metal loading, calcination temperature and activation [1].

#### 3.3.1 Impregnation

Impregnation deposits the catalyst active elements, i.e. Mo and Ni(Co), on the surface of the support. Therefore, impregnation has a key role in impacting on the active phase structure and dispersion [2]. Hence, modification of the impregnation
procedures has been targeted in order to prepare high-active catalysts. A brief explanation of different impregnation methods is provided as follows.

**Successive / one-batch – Sequential / Coimpregnation.** Metals (e.g. Mo and Ni) can be added to the support in two ways. An aqueous solution of Ni (as promoter) and Mo is added to the support (e.g. $\gamma$-Al$_2$O$_3$). This method is called coimpregnation (simultaneous impregnation). In the other method (sequential), an aqueous solution of each metal is prepared separately and added to the support apart from each other. Either of these methods also can be done in two different ways. In coimpregnation, the metals solution can be added at once which called one batch. In contrast, in successive method, first an adequate amount of the solution (e.g. based on the pore volume of the support) is added to the support. After drying, another batch of the solution is added and dried. This step is repeated as many times as required to reach to the desired concentration of metals in the catalyst. The same concept is also applicable for the sequential method. To give a better understanding of these methods, a typical example is given in Table 3.1.

<table>
<thead>
<tr>
<th>Coimpregnation</th>
<th>Sequential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni and Mo simultaneously</td>
<td>Ni first, Mo next</td>
</tr>
<tr>
<td>One batch</td>
<td>Aqueous solution of Ni and Mo is added to $\gamma$-Al$_2$O$_3$ following by drying.</td>
</tr>
<tr>
<td>Step 1 Adequate amount of aqueous solution of Ni and Mo is added to $\gamma$-Al$_2$O$_3$ following by drying.</td>
<td>Adequate amount of aqueous solution of Ni is added to $\gamma$-Al$_2$O$_3$ following by drying.</td>
</tr>
<tr>
<td>Successive Step 2 Adequate amount of aqueous solution of Ni and Mo is added to NiMo / $\gamma$-Al$_2$O$_3$ following by drying.</td>
<td>Adequate amount of aqueous solution of Ni is added to NiMo / $\gamma$-Al$_2$O$_3$ following by drying.</td>
</tr>
<tr>
<td>Step 3 Step 2 is repeated until reaching the final concentration of Ni and Mo in the catalyst.</td>
<td>Step 2 is repeated until reaching the final concentration of Ni in the catalyst.</td>
</tr>
</tbody>
</table>

The order of incorporation of the active phases strongly influences the dispersion and distribution of the metal phases and their textural properties [70]. Typically, introducing molybdenum before promoter results in more active catalyst since different precursor structures formed [1,70]. In this case, the molybdenum dispersion improves during the second step of nickel impregnation, and nickel is more accessible to form some Ni-Mo-O interaction species after molybdenum partial hydrolysis, leading to increased activity [70]. On the contrary, promoter introduction at first leading to predominant formation of the inactive $\text{Ni}_3(\text{Co}_3)\text{O}_4$ precursors.
Upon addition of Mo, these precursors are not transformed to Ni(Co)-Mo-O structures [31, 72]. In addition, the results of a study by Salerno et al. [70] showed that the incorporation of Ni before Mo leads to badly dispersed and separated active nickel and molybdenum phases. Its reason is that the major part of Ni occupy ion exchange positions into the octahedral layers of the clay, being non-reduced and sulfided. That is why they observed poor HDS and HDN activities. However, a higher catalytic activity was reported [70] obtained from preparing the NiMo catalysts by co-impregnation. Simultaneous presence of nickel favors even more the dispersion of molybdenum and the formation of Ni-Mo-O interaction phase on the support surface, which is the catalyst precursor of the Ni-Mo-S active phase for hydrotrating reactions. Significant enhancement in catalyst activity is reached by adding promoter in successive steps instead of in one batch [71, 73] due to a reduction in formation of unwanted Ni₃(Co₃)O₄ [1].

3.3.2 Metal loading

The structures and their relative proportion in sulfided both promoted and non-promoted molybdenum catalysts depends on the loading of both molybdenum and promoter (cobalt or nickel). Metals loading is therefore one of the essential parameters in optimizing commercial hydrotreating catalysts. In industrial applications, the metal loadings are usually governed by the desire to achieve as high activity as possible with as small amounts of the expensive metals as possible. Hence, wasting metals in undesirable low activity phases should be avoided. Topsøe et al. [1] introduced typical amount of molybdenum loading as about 8 to 15 wt. % which is corresponded to approximately a monolayer coverage for an alumina support with a typical surface area of about 250 m²/g. If the molybdenum exceeds this level or alumina with low surface area is used, separate MoO₃ entities are formed. This results in bulk-like MoS₂ phases upon sulfiding. The promoter loading depends on the molybdenum level and type of hydrotreating application. Thus, optimized loading is obtained from experience. Topsøe et al. stated that the promoter concentration usually amounts to about 1 to 5 wt. %, giving a promoter-molybdenum atomic ratio of 0.1 to 1.0. As they concluded from the results of other works using different characterization techniques to study this subject, catalysts with low molybdenum loading are more difficult to be sulfided than high-loading catalysts. Topsøe et al. suggested that it is possible that decreasing molybdenum loading increases the relative proportion of oxygen bonds between MoS₂ species and the alumina surface [1]. Their suggestion is in line with results of the XPS studies of Li et al. [74] indicating the presence of Mo₅⁺ in a significantly lower concentration in addition to Mo₄⁺ (MoS₂). Topsøe et al. [1] also mentioned that the alumina coverage by molybdenum species increases linearly with the molybdenum loading up to a certain limit. Above this limit, the coverage is leveled off suggesting growth of bulk-like MoS₂ structures. Further rise in molybdenum loading decrease the edge dispersion of the MoS₂ and therby the activity. Consequently, the ratios of promoter oxide to molybdenum and oxygen to molybdenum decreased (as a result of a decrease in
MoS$_2$ edge dispersion).

Using high promoter concentrations gives a tendency of formation of separate promoter phases (e.g. Co$_3$O$_4$) [1]. Topsøe et al. [33] conducted IR studies of NO adsorbed on sulfided NiMo/Al$_2$O$_3$ and CoMo/Al$_2$O$_3$ catalysts and showed that an increase in the intensity of the bands associated with NO adsorption on promoter atoms. The formation of increasing amounts of Ni(Co)-Mo-S was also obvious by a decrease in the intensity of the bands associated with adsorption on molybdenum edge atoms because of covering/blocking of molybdenum edge sites.

### 3.3.3 Calcination temperature

The effect of increasing calcination temperature above 500-600 °C showed a decrease in catalytic activity [3, 75, 76]. Stanislaus and Al-Dolama [77] showed that high-temperature calcination leads to volatilization of molybdenum salts. Results of calcining NiMo/Al$_2$O$_3$ at 800 and 900 °C resulted in 50% and 85% drop in molybdenum content, respectively. Calcining CoMo/Al$_2$O$_3$ at the same temperatures produced molybdenum loss of 27% and 43% respectively. In another study, Stanislaus et al. [3] investigated what changes in the catalysts occurred when high calcination temperature was applied and if these changes were advantageous to hydrotreating activity. Studies (e.g. [78, 79]) have suggested that the catalytically active phase in NiMo/γ-Al$_2$O$_3$ and CoMo/γ-Al$_2$O$_3$ was produced from an intimate mixture of octahedrally coordinated promoter with octahedrally coordinated molybdenum attached to the surface. Based on these studies, the amounts of these species depended on catalyst loading and on calcination conditions. According to Zingg et al. [78], the most of the octahedrally coordinated species were produced at calcination temperature of 500 °C with a loading of about 16% MoO$_3$. While increasing the temperature to 700 °C decreased the surface area. The relative amount of tetrahedrally coordinated molybdenum and the promoter increased [78, 79] and Al$_2$(MoO$_4$)$_3$ (an interaction species between MoO$_3$ and the surface) was formed [78, 80].

Volatilization of molybdenum and an increase in the effective promoter to molybdenum ratio is reported at calcination temperatures above 700 °C. Both the increased temperature and the reduced molybdenum content favored the formation of tetrahedrally coordinated molybdenum, tetrahedrally coordinated promoter, and aluminates. Also, it resulted in more diffusion of the promoter into the bulk [78]. Consequently, the activity declines rapidly as shown in Figure 3.3 [3]. The varying chemistry of nickel and cobalt induced changes at different calcination temperature. Greegor et al. [79] showed that nickel had a higher octahedral site preference than cobalt but both octahedrally and tetrahedrally coordinated nickel are formed at low nickel loading. Moné also introduced nickel aluminate as a partly inverse spinel in which the nickel ions occupied both tetrahedral and octahedral holes, opposite to cobalt aluminate, which is a normal spinel [81, 82]. Nickel aluminate was found to be formed at temperatures as low as 650 °C [79, 82, 83]. Therefore, NiO amount available to form an intimate mixture with molybdate was reduced and, above calcinatin temperature of 650 °C, the behavior of the catalyst could be expected to
be closer to that of Mo/γ-Al₂O₃ [78]. In line with this, the molybdenum volatilization was greater [77], the molybdenum dispersion was less and polymolybdates were observed on the surface [78] by increasing the calcination temperature.

Scheffer et al. [4] also showed the effect of increasing the calcination temperature on the activity was dependent on the promoter content (Figure 3.4). Their results revealed that the effect of a change in calcination temperature depended strongly on the promoter content. They showed that as the calcination temperature was raised, a sharp drop in activity for catalysts with a low Co content was observed, but a slight rise in activity was seen at high cobalt content. At intermediate Co loadings the impact of increasing the calcination temperature was not so strong.

### 3.3.4 Promoters

Adding a material as a third elements to hydrotreating catalysts are investigated in many studies as endeavors to reach higher active catalysts or selectivity [1]. Some works performed on catalysts supported by γ-Al₂O₃ showed that adding some materials such as fluoride [84], boron [9, 85–87], phosphorus [88–95], etc. can increase the surface acidity, resulting in an increase in the hydrotreating activities. The reason for this improvement in catalytic activities may be resulted from the variation in metal-support interactions [2, 96, 97]. This in turn, may affect the morphology and dispersion of the active components. The support and impregnated
metals interactions strongly affect both the active phase formation and the dispersion on the surface of the support. Recently, the most common material as modifier in hydrotreating process has been phosphorous [1, 2]. As reported by literatures, phosphorous doping modifies both hydrodenitrogenation [85, 98, 99] and hydrodesulfurization [100–102]. Nevertheless, when it comes to NiMo/γ-Al₂O₃, phosphorous promotes specially the activity of HDN rather than HDS [2, 85, 89, 103, 104]. In addition, it improves dispersion of active metal salts, reduce the interaction between oxides of Mo and Ni as precursors, modifies the acid sites or forms new active phase, increases MoS₂ stacking and forms bigger MoS₂ slabs [2, 85, 89, 105–107].

Hence, study of the effect of phosphorous was considered in the scope of this thesis. As different preparation methods have been suggested in literature reports, in order to use the best method, some of them are reviewed as follows:

Lewis et al. [95] studied the effect of different phosphorous contents in three different procedures of preparation of NiMo/γ-Al₂O₃ on gas oil hydروprocessing. In the first series, they prepared the catalysts through one-batch coimpregnation. For the other two series, the catalysts were prepared based on sequential impregnation. The order of addition was ammonium heptamolybdate followed by nickel nitrate hexahydrate aqueous solution. The difference between the second and the third series was in sequence of phosphoric acid addition which was introduced to the support prior to the metals.

Ferdous et al. [9] firstly prepared a series of NiMo/γ-Al₂O₃ with different nickel and molybdenum concentrations using incipient wetness co-impregnation method.
and extruded NiMo/γ-Al₂O₃. Zhou et al. [88] prepared NiMoP catalysts with different phosphorous content using the same method but with different material (MoO₃ powder, nickel carbonate tetrahydrate and phosphoric acid). Xiang et al. [91] prepared different catalysts regarding the amount of phosphorous content through successive incipient wetness impregnation. Rayo et al. [108] prepared both possible P-doped: on support and on NiMo using simultaneous incipient wetness impregnation.
Chapter 4

Experimental

4.1 Catalyst preparation

Based on experimental results reported in literature, five catalysts were made. Two different commercial $\gamma$-$\text{Al}_2\text{O}_3$ supports with different surface areas were used. The first one with smaller surface area was Sasol Puralox NGa150 in powder form and the other one was Saint Gobain as pellet.

In order to prepare 20 g of each catalyst, 5.520 g ammonium heptamolybdate (Alfa Aesar (NH$_4$)$_6$Mo$_7$O$_{24}$ · 4 H$_2$O) and 3.468 g of nickel nitrate (Aldrich Ni(NO$_3$)$_2$ · 6 H$_2$O) was dissolved in ultra pure water. The target was to obtain a final content of 3 wt.% Ni and 15.0 wt.% Mo. To prepare NiMo/$\gamma$-$\text{Al}_2\text{O}_3$ catalyst via co-impregnation method, this solution was dropped on 16.30 g of support in three steps. After each step the catalyst was dried at 120 $^\circ$C for 4 hours, and after the last step, calcined at 500 $^\circ$C for 4 hours.

Alumina extruder was crushed and the above procedure was followed to prepare 40 g of the catalyst based on Saint Gobain alumina, NiMo/$\gamma$-$\text{Al}_2\text{O}_3$. However, only 20 g of this catalyst was calcined at 500 $^\circ$C for 4 hours. The other half of NiMo/$\gamma$-$\text{Al}_2\text{O}_3$ was calcined at 700 $^\circ$C for 4 hours and called NiMo/$\gamma$-$\text{Al}_2\text{O}_3$.$^{700}$.

The fourth catalyst, NiMo/$\gamma$-$\text{Al}_2\text{O}_3^{SEQ}$, was prepared through sequential impregnation by dropping a solution of 5.520 g ammonium heptamolybdate in adequate amount of water in two steps. Between each step the catalyst was dried at 120 $^\circ$C for 4 hours. The next sequence was dropping a solution of 3.468 g of nickel nitrate in adequate amount of water on the catalyst in two steps while in between it dried as the previous sequence condition and finally calcined at 500 $^\circ$C for 4 hours.

As discussed in section 3.3.4, phosphorus, as a secondary promoter in NiMo/$\gamma$-$\text{Al}_2\text{O}_3$ catalysts, enhances HDS and HDN [9]. For this reason, the last catalyst was made by adding phosphorous. Based on the result of Rayo et al. [108] (see also 3.3.4), adding phosphorous to the support was selected to make the last catalyst. 2.531 g of H$_3$PO$_4$ was dropped on 15.50 g of Saint Gobain alumina and dried and calcined at 120 $^\circ$C for 4 hours and 500 $^\circ$C for 4 hours repectively. Same procedure as mentioned above for the preparation of NiMo/$\gamma$-$\text{Al}_2\text{O}_3$ was followed and this catalyst named
NiMo/Pγ-Al₂O₃. The target was to have a concentration of phosphorous of 4 % in the final catalyst while keeping the same nickel and molybdenum concentrations in other catalysts (5 % and 15 % respectively).

A summary of prepared catalysts are given in Table 4.1. Only three of these five catalysts were tested in micro-reactor at Nynas (NiMo/γ-Al₂O₃, NiMo/Pγ-Al₂O₃ and NiMo/γ-Al₂O₃₁₅₀); hence, these three catalyst were pelletized, crashed and sieved to obtain particles with the range of 0.25 to 0.5 mm to avoid pressure drop in the reactor.s

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Preparation method</th>
<th>Calcination temperature, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/γ-Al₂O₃</td>
<td>Saint Gobain</td>
<td>Coimpregnation</td>
<td>500</td>
</tr>
<tr>
<td>NiMo/Pγ-Al₂O₃</td>
<td>Saint Gobain</td>
<td>Coimpregnation</td>
<td>500</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃₁₅₀</td>
<td>Sasol</td>
<td>Coimpregnation</td>
<td>500</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃₇₀₀</td>
<td>Saint Gobain</td>
<td>Coimpregnation</td>
<td>700</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃SEQ</td>
<td>Saint Gobain</td>
<td>Sequential impregna</td>
<td>500</td>
</tr>
</tbody>
</table>

### 4.2 Characterization

BET surface area (BET) of the oxide catalysts were measured in a Micromeritics ASAP 2000 equipment. The supports and catalysts were degassed at 473 K prior to the adsorption. X-ray powder diffraction was carried out in a Siemens D5000 diffractometer from 10 to 90 2θ at 2.5 degree⁻¹ scan rate. Temperature Programmed Reduction was conducted for catalysts using Micromeritics AutoChem 2910 up to 800 °C.

Spent catalysts were washed with gasoline and dried at room temperature for 24 hours. Then they were dried at 60 °C for 24 hours. The catalysts were sieved to separate SiC; however, NiMo/γ-Al₂O₃₁₅₀ was mixed with sand of the same size range. That was why separation of the catalyst from sand was not done. BET was performed for NiMo/γ-Al₂O₃ and NiMo/γ-Al₂O₃ while SEM was conducted for all spent catalysts.

The samples of hydrotreated oils were collected and analyzed. Samples were bubbled by nitrogen and filtered prior to characterization. Aromatic, paraffinic and napthenic contents were analyzed by ThermoFisher. Sulfur and nitrogen contents were measured by Antek 9000NS analyzer. Mettler Toledo DM40-RX40-SC30 density meter was applied to measure the density of products using 15 °C ASTM D4052 method. Products kinematic viscosity were determined by Herzog Multi-Range Viscometer (HVM 472). The color of products measured by spectrophotometric colorimeters Lovibond PFX195 Tintometer with ASTM D156.
4.3 Activity Tests

The measurements of the catalytic activity for the three above mentioned catalysts were carried out under steady-state operation in a high pressure fixed-bed up-flow micro reactor (Swagelok). A detailed scheme of this unit is shown in Figure 4.1. The reactor was made of stainless steel tube with the total length and internal diameter of 275 and 10 mm. The period of each test was about 15 days including waiting time for steady state (Figure 4.2).
For reactor loading, 5 ml of each catalyst was diluted with 4 ml silicon carbide of the mesh size of 0.2-0.5 mm and placed in the center of the reactor. The remaining volume of the reactor in both sides were identically filled as illustrated in Figure 4.3. After the reactor was purged with nitrogen and leak tested at room temperature, the catalyst was sulfided \textit{in situ} using the method presented by Eijsbouts et al. [39]. Sulfiding was conducted for 19 hours by a presulfiding oil in presence of hydrogen. This oil stream containing the required amount of di-tert-butyl disulfide to give a final composition of 3.7 wt.% sulfur in the oil. The reaction was carried out at a pressure of 45 bar with a liquid hourly space velocity (LHSV) of 3.0 h\(^{-1}\) and \(\text{H}_2/\text{oil}\) ratio of 200 at 150 °C for 3 hours then at 320 °C for 16 hours.

After sulfiding period, the feed (Nynas vacuum distillation) was introduced to the reactor and its temperature and pressure were set to \(T_{\text{base}}\) and \(x \text{ bar}\). \(\text{H}_2/\text{feed}\) ratio and LHSV were considered \(z\) and \(y \text{ h}^{-1}\) respectively. Ageing took 6 days and 3-4 samples taken for analyzing. Activity of the catalysts were investigated at three temperatures of \(T_{\text{base}}+20\), \(T_{\text{base}}\) and \(T_{\text{base}}-20\) for two days for each. After 12 hours of changing the temperature, 1-2 samples were taken for analysis.

The rate constant for HDA, HDN and HDS were determined by using Equations 4.1 to 4.3 [46,90]. \(k_{\text{HDA}}\) and \(k_{\text{HDN}}\) are the pseudo first order HDA and HDN kinetic constant (h\(^{-1}\)), respectively, and \(k_{\text{HDS}}\) is the pseudo 1.5 order HDS kinetic constant (ppm\(^{-0.5}\text{h}^{-1}\)). A, N and S in these equations stand for aromatics (wt.%), nitrogen and sulfur contents (ppm), respectively. The subscripts F and P represent feed and product, respectively. LHSV is the liquid hourly space velocity (h\(^{-1}\)) and n is the order of reaction.

\[
k_{\text{HDA}} = (LHSV)\ln\left(\frac{A_F}{A_P}\right)
\]  
\[4.1\]
4.3. ACTIVITY TESTS

Figure 4.3: Packing for the micro reactor

\[ k_{HDN} = (LHSV) \ln \left( \frac{N_F}{N_P} \right) \]  \hspace{1cm} (4.2)

\[ k_{HDS} = 0.2LHSV \left( \frac{1}{S_P^{1.5}} - \frac{1}{S_F^{1.5}} \right) \]  \hspace{1cm} (4.3)

Equation 4.4 to 4.6 was used to calculate conversions (%) and the yield of the process is calculated based on the total oil feed on-stream and the amount of the product as shown in Equation 4.7 where \( V_{sam} \) is the sample volume (ml) and \( V_F \) is the volume of the consumed feed (ml).

\[ Conversion = [1 - \frac{A_P}{A_F}] \times 100 \]  \hspace{1cm} (4.4)

\[ Conversion = [1 - \frac{N_P}{N_F}] \times 100 \]  \hspace{1cm} (4.5)

\[ Conversion = [1 - \frac{S_P}{S_F}] \times 100 \]  \hspace{1cm} (4.6)

\[ Yield = \left[ \frac{V_{sam}}{V_F} \right] \times 100 \]  \hspace{1cm} (4.7)
Chapter 5

Results and discussion

5.1 Catalysts characterization

The textural properties of supports, synthesized catalysts and two spent catalysts (NiMo/γ-Al₂O₃ and NiMo/Pγ-Al₂O₃) were detected by N₂-adsorption measurement. It can be seen in Figure 5.1 that the isotherms of NiMo/γ-Al₂O₃ fresh catalyst is type IV, suggesting the presence of large mesopores or macropores [51,109]. However, the isotherm shapes of other fresh catalysts are very close to type II but the quantity of adsorption increases rapidly when the relative pressure exceeds 0.9. This suggests that the adsorption process had two steps i.e. the porosity showed a bimodal distribution. Hence, it can be concluded that the other fresh catalysts also had large mesopores or macropores.

Table 5.1: Textural properties of support and catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-Al₂O₃⁷⁰⁰</td>
<td>149</td>
<td>0.475</td>
<td>127</td>
</tr>
<tr>
<td>γ-Al₂O₃⁷⁰⁰</td>
<td>227</td>
<td>0.705</td>
<td>124</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃</td>
<td>188</td>
<td>0.504</td>
<td>107</td>
</tr>
<tr>
<td>NiMo/Pγ-Al₂O₃</td>
<td>131</td>
<td>0.406</td>
<td>123</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃⁷⁰⁰</td>
<td>113</td>
<td>0.335</td>
<td>117</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃SEQ</td>
<td>189</td>
<td>0.511</td>
<td>107</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃⁷⁰⁰</td>
<td>126</td>
<td>0.515</td>
<td>162</td>
</tr>
<tr>
<td>Spent NiMo/γ-Al₂O₃</td>
<td>87</td>
<td>0.163</td>
<td>74</td>
</tr>
<tr>
<td>Spent NiMo/Pγ-Al₂O₃</td>
<td>85</td>
<td>0.193</td>
<td>90</td>
</tr>
</tbody>
</table>
Figure 5.1: $N_2$ adsorption-desorption isotherms

(a) Supports and catalysts

(b) Tested catalysts

(c) Non-tested catalysts
5.1. CATALYSTS CHARACTERIZATION

As can be observed in Table 5.1 and Figure 5.1a, the surface area of the supports decreased due to the metal loading during catalyst synthesis. NiMo/γ-Al₂O₃ decreased about 17% while this reduction for NiMo/γ-Al₂O₃ formed at 150 °C was 24%. NiMo/γ-Al₂O₃ formed at 700 °C showed the considerable reduction of 44% which caused because of higher calcination temperature.

Particle size, as reported by Ferdous et al. [9], increased by rising the calcination temperature to 500 °C but reduced when calcination temperature increased to 600 °C. As the applied calcination temperature for NiMo/γ-Al₂O₃ was 500 °C, it may be concluded that temperature of 500 °C is the optimal calcination temperature for nickel-molybdenum-alumina catalysts. At 500 °C, sintering, because of Al₂O₃ transformation by forming Al₂(MoO₄)₃, might have a role in increasing the particle size [9]. Decrease in particle size at higher temperature may be due to sublimation of MoO₃ as reported by Kasztelan et al. [110]. Phosphorous addition also caused a decrease of 42% maybe due to the blockage of micropores of the support by phosphates. Simillar results also reported by Jian and Prins [111] and Maity et al. [92]; however, Ferdous et al. reported no change in surface area for the catalyst with phosphorous [9]. Comparing the two catalysts synthesized through different co-impregnation procedures suggests that the applied methods had almost the same impact on the surface area (16.4% for NiMo/γ-Al₂O₃).

The results of the surface study on two spent catalysts (Table 5.1 and Figure 5.1) showed the surface area of NiMo/γ-Al₂O₃ and NiMo/Pγ-Al₂O₃ decreased by about 54 and 36% respectively. The pore volume and pore diameter of both catalysts also decreased significantly (>50%). These losses during hydrotreating process could be attributed to coke deposition [85] which led to significant catalyst deactivation by blocking the pores. As will be described hereafter while introducing SEM results, the coke formation for NiMo/γ-Al₂O₃ was more than the NiMo/Pγ-Al₂O₃ which confirmed the BET results.

X-ray diffraction spectra for the supports are displayed in figure 5.2a. The bottom spectrum of both supports patterns indicates three high peaks located at 38, 46 and 67°, which are γ-Al₂O₃ characteristic as also can be recognized in XRD of all catalysts as shown in Figure 5.2. In general, the crystallinity is poor as the peaks intensity are rather small, specially the alumina with a higher surface area showed a lower crystallization degree and a smaller average crystallite size. These are in line with other works e.g. [45, 112, 113]. In XRD of the catalysts prepared from these supports, fig 5.2b, two peaks in 23.5° and 27.3° are related to MoO₃ [70]. Here, as expected, also the previous pattern was followed and the catalyst with lower-surface-area support showed a relatively higher crystallinity as the peaks are sharper and have higher intensity. No nickel oxides characteristic reflection (43.5° and 63°) suggested that these compounds were amorphous or microcrystalline [114], or too disposal or too low contents. However, at higher calcination temperature, i.e. 700 °C, a peak appeared at 63°, as shown in Figure 5.2c. Calcination at higher temperature generally resulted in higher crystallization degree. The reflection of NiMo/γ-Al₂O₃ is closely akin to NiMo/γ-Al₂O₃ but with a higher intensity, Figure 5.2d.
CHAPTER 5. RESULTS AND DISCUSSION

32

(a) XRD of supports with different surface area

(b) XRD of NiMo/γ-Al₂O₃ with different surface areas of support

(c) NiMo/γ-Al₂O₃ calcined at 500 and 700 °C

(d) Impact of adding phosphorous on the support

(e) Difference between coimpregnation and sequential preparation methods

Figure 5.2: XRD of fresh catalysts
5.1. CATALYSTS CHARACTERIZATION

The impact of addition phosphorous can be observed in Figure 5.2e where the intensity of the both peaks of MoO$_3$ are considerably improved indicating that phosphorous improved the interaction between molybdenum and the support.

Temperature program reduction was performed to evaluate the effect of the methods of preparation on the reducibility of the catalysts and examine their impact on the structure of the active phase and on the interaction between the support and the active phase. Based on previous studies [9, 61, 115] the reduction of MoO$_3$ may be divided into two steps. The low-temperature reduction that can be related to the partial reduction (MoO$_{6}^{2+}$ to MoO$_{4}^{4+}$) of amorphous, highly defective, multilayered molybdenum oxides or hetropolymolybdates, which are generally accepted as the precursor of the type II Ni-Mo-S. The high-temperature reduction is comprised of tetrahedral molybdenum species including highly dispersed monolayered MoO$_3$, molybdenum oxides with deep reduction and the intermediate-reducible crystalline phases of orthorhombic MoO$_3$ and Al$_2$(MoO$_4$)$_3$ resulted from the strong reaction with the support [116–118]. Ranges of 500-650 °C and 800-950 °C are suggested in literatures [9, 61, 115, 119] for the low-temperature and high-temperature reduction, respectively.

As TPR was performed up to 800 °C in this experiment, no high-temperature reduction observed as shown in Figure 5.3. The low-temperature peaks are also between 550 and 700 °C. Higher reduction temperature in this experiment may be due to reduction of NiO. According to Brito and Laine [120, 121], bulk NiO reduced before 300 °C, but when it was supported on alumina, the peak appeared at 700 °C since nickel might perform a role of reduction promoter of the molybdenum. The reduction temperature, $T_m$, (shows the maximum temperature for H$_2$ consumption)

![Figure 5.3: TPR profile of fresh catalysts](image)
Table 5.2: Compositions for catalysts obtained from SEM-EDX

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Element</th>
<th>C</th>
<th>O</th>
<th>Al</th>
<th>S</th>
<th>P</th>
<th>Ni</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/γ-Al₂O₃</td>
<td>Site 1</td>
<td>0</td>
<td>48.82</td>
<td>32.16</td>
<td>0</td>
<td>0</td>
<td>3.66</td>
<td>15.36</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>0</td>
<td>44.87</td>
<td>37.33</td>
<td>0</td>
<td>0</td>
<td>1.27</td>
<td>16.53</td>
</tr>
<tr>
<td>NiMo/Pγ-Al₂O₃</td>
<td>Site 1</td>
<td>0</td>
<td>30.59</td>
<td>34.81</td>
<td>0</td>
<td>4.47</td>
<td>0</td>
<td>7.91</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>0</td>
<td>36.29</td>
<td>29.52</td>
<td>0</td>
<td>3.63</td>
<td>0</td>
<td>19.77</td>
</tr>
<tr>
<td>NiMo/γ-Al₂O₃¹⁵₀</td>
<td>Max.</td>
<td>0</td>
<td>45.52</td>
<td>33.22</td>
<td>0</td>
<td>0</td>
<td>6.35</td>
<td>21.69</td>
</tr>
<tr>
<td></td>
<td>Min.</td>
<td>0</td>
<td>39.49</td>
<td>28.23</td>
<td>0</td>
<td>0</td>
<td>5.15</td>
<td>16.81</td>
</tr>
<tr>
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<td>0</td>
<td>48.25</td>
<td>38.42</td>
<td>0</td>
<td>6.83</td>
<td>0</td>
<td>27.3</td>
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<tr>
<td></td>
<td>Site 2</td>
<td>0</td>
<td>28.87</td>
<td>29.31</td>
<td>0</td>
<td>0</td>
<td>5.41</td>
<td>12.65</td>
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<tr>
<td>Spent NiMo/γ-Al₂O₃</td>
<td>Site 1</td>
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<td>38.83</td>
<td>24.20</td>
<td>3.88</td>
<td>0</td>
<td>2.46</td>
<td>24.42</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
<td>9.97</td>
<td>49.06</td>
<td>20.97</td>
<td>8.17</td>
<td>0</td>
<td>3.96</td>
<td>7.88</td>
</tr>
<tr>
<td>Spent NiMo/Pγ-Al₂O₃</td>
<td>Site 1</td>
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<td>65.10</td>
<td>14.53</td>
<td>3.15</td>
<td>1.71</td>
<td>2.41</td>
<td>9.49</td>
</tr>
<tr>
<td></td>
<td>Site 2</td>
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<td>20.99</td>
<td>10.50</td>
<td>2.39</td>
<td>4.32</td>
<td>6.17</td>
</tr>
<tr>
<td>Spent NiMo/γ-Al₂O₃¹⁵₀</td>
<td></td>
<td>6.23</td>
<td>41.39</td>
<td>22.93</td>
<td>8.39</td>
<td>0.00</td>
<td>4.50</td>
<td>16.56</td>
</tr>
</tbody>
</table>

for NiMo/γ-Al₂O₃ is 672 °C which is higher than NiMo/γ-Al₂O₃⁷₀₀ (633 °C) due to higher calcination temperature. However, higher calcination temperature had no effect on the intensity which is in contrast with the results of Ferdous et al. [9] who showed that higher calcination temperature significantly decreased the intensity. It was reported that all nickel reduced under the Ni_I band [120] at calcination temperature lower than 600 °C. It is also reported that most of the nickel simultaneously reduced with molybdenum under the low-temperature reduction [75]. Nickel reducibility depends on the catalyst calcination temperature [9] as at calcination temperature over 600 °C, essentially all Ni reduces with Mo_{II} [75,120]. For NiMo/γ-Al₂O₃⁷₀₀ more time might be needed for complete nickel reduction.

NiMo/γ-Al₂O₃^{SEQ} showed the lowest T_m (589 °C) suggesting weaker interaction between nickel and support. The reduction temperature of NiMo/γ-Al₂O₃¹⁵₀ (677 °C) and its intensity are higher than NiMo/γ-Al₂O₃. This may indicate better interactions between the support and metals in the catalyst with lower surface area. The reduction temperature of the catalyst with phosphorous was 40 °C higher than NiMo/γ-Al₂O₃ which is similar to Zhou’s results (30 °C difference) [119]. The formed AlPO₄ phase on the support surface [122] inhibited the active component and the support interaction. This might result in larger active phase particles [9] and higher reduction temperature [123].

Scanning electron microscopy were used to study the surface morphology of fresh (except NiMo/γ-Al₂O₃⁷₀₀) and spent catalysts whereas EDX was applied to quantify the elemental composition of a single particle present on the surface of the catalysts. Three different approach were applied: analyzing a surface area of a selected site, measuring through a long line on a selected site and analyzing several short lines in a surface of a selected site. The results of these analyses are tabulated...
in Table 5.2 and the SEM micrographs are showed in Figure 5.2. The results (both those mentioned here and other EDX analyses not presented here) indicate that the theoretical composition is different with the targeted one. The reason can be the way of dropping metal solution on the support which resulted in a non-homogeneous dispersion or possible weighing error.

Ferdous et al. [9] mentioned that higher Mo content obtained from EDX indicated that molybdenum might have migrated and agglomerated more on the surface. However, as EDX analysis is based on the elemental analysis of selected particles on the surface of the catalyst, it has limitation in quantifying the composition of the catalyst surface. Figures 5.4c and 5.4d show SEM micrographs for NiMo/γ-Al₂O₃. Phosphorous addition to the catalyst gave irregular particle size and agglomeration as the presence of phosphorous in these particles confirmed by EDX analysis. This result also is reported by Ferdous et al. [9].

Sulfidation and precoking lead to formation of MoS₂ [124] and carbon deposition on the catalyst surface [9]. Comparing the micrographs and based on EDX analysis for fresh and spent NiMo/γ-Al₂O₃ and NiMo/γ-Al₂O₃[150] indicated reduction of particle size in both spent catalysts indicating the formation of MoS₂ as the result of sulfiding. In NiMo/Pγ-Al₂O₃ case, the particles size are mostly larger in spent catalyst (which had lower surface area, see 5.2) than the fresh one (Figures 5.4c and 5.4d) . As reported by Lopez [125], it may be concluded that size and number of MoS₂ species was increased on the catalyst surface due to adding phosphorous (see also section 3.3.4). Results of XRD, as discussed earlier above, confirmed this as well (see Figure 5.2e) since MoS₂ species were formed from MoO₃ during sulfiding. A few parts in this catalyst were seen that totally eroded away (Figure 5.6c) and consisted of about 80 wt.% Al₂O₃.

As observed in spent catalysts micrographs (Figure 5.6), some fibers were formed in three catalysts during the hydrotreating process. EDX analysis showed that these long fibers mostly had nickel (more than 60 wt.%) and sulfur (between 15 and 25 wt.%) indicating the deactivation of the catalyst by carbon (4 to 6 wt.%). This is the deactivation phenomenon that can occur for catalysts containing nickel. These fibers are called whiskers; however, they are usually carbon-based. The number of these whiskers were considerable lower in spent NiMo/Pγ-Al₂O₃ meaning lower deactivation for this catalyst due to the presence of P which interacts strongly with the support. Hence, it decreases the possibility of direct interacting of coke precursors with the support. This is in line with the study of Maity [92]. On the other hand, phosphorous reduces the number of strong acid sites of the catalyst [126] which facilitate the coke formation on the catalyst [92]. Thus, this can be another reason for lower deactivation for NiMo/Pγ-Al₂O₃.
Figure 5.4: SEM micrographs for fresh catalysts
5.1. CATALYSTS CHARACTERIZATION

Figure 5.5: SEM micrographs for spent catalysts
5.2 Catalytic activity

Under the conditions of the experiment, the catalysts were on streams for six days to show their initial activity loss; then steady activity was reached. As shown in Figure 5.7, the aromatic content increased during ageing mainly due to decreasing of active sites. All catalysts showed similar trends. The results of products analysis are summarized in Table 5.3. In addition, yield was calculated for each sample and plotted as shown in Figure 5.8. Unfortunately, the yield results are not exact due to the instrument low scale and very low flow rates.

One of the main factors for catalyst deactivation is coke deposition which may introduce important changes in the surface properties. The coke deposition as observed in SEM monographs (see Figure 5.6) can be formed firstly during the activation step (i.e. sulfiding) due to the sulfur sources; and then, during the hydrotreating process through secondary reactions (polyaromatics chain) [47]. In order to study the catalytic activity, based on measured data tabulated in Table 5.3, the contents of aromatics, nitrogen and sulfur in products at each test temperature are plotted as illustrated in Figure 5.9. Also, conversions and activity rate constants were calculated and plotted as shown in Figure 5.10.

HDA is inhibited by hydrogen sulfide produced from the HDS activity [127] as
5.2. CATALYTIC ACTIVITY

Figure 5.7: Catalysts Ageing Trend at $T_{\text{base}}$ and x bar

Figure 5.8: Process yield for hydrotreated oils
Table 5.3: Products characteristics during a two-day process

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Unit</th>
<th>$C_a$ %</th>
<th>$C_p$ %</th>
<th>$C_n$ %</th>
<th>Viscosity $\text{mm}^2/\text{s}$</th>
<th>Density $\text{g/cm}^3$</th>
<th>Sulfur ppm</th>
<th>Nitrogen ppm</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/γ-Al$_2$O$_3$</td>
<td>$T_{\text{base}}$-20</td>
<td>19.1</td>
<td>44.4</td>
<td>36.5</td>
<td>21.84</td>
<td>0.911</td>
<td>3,076</td>
<td>120</td>
<td>12</td>
</tr>
<tr>
<td>NiMo/γ-Al$_2$O$_3$</td>
<td>$T_{\text{base}}$</td>
<td>17.8</td>
<td>42.2</td>
<td>40.0</td>
<td>19.04</td>
<td>0.902</td>
<td>585</td>
<td>9</td>
<td>23</td>
</tr>
<tr>
<td>NiMo/γ-Al$_2$O$_3$</td>
<td>$T_{\text{base}}+20$</td>
<td>12.6</td>
<td>43.4</td>
<td>44.0</td>
<td>13.34</td>
<td>0.888</td>
<td>242</td>
<td>3</td>
<td>30</td>
</tr>
<tr>
<td>NiMo/Pγ-Al$_2$O$_3$</td>
<td>$T_{\text{base}}$-20</td>
<td>20.6</td>
<td>43.5</td>
<td>36.4</td>
<td>22.22</td>
<td>0.912</td>
<td>3,971</td>
<td>152</td>
<td>4</td>
</tr>
<tr>
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<td>42.7</td>
<td>39.0</td>
<td>18.32</td>
<td>0.902</td>
<td>818</td>
<td>10</td>
<td>23</td>
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<td>NiMo/Pγ-Al$_2$O$_3$</td>
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<td>11.0</td>
<td>44.3</td>
<td>44.7</td>
<td>11.22</td>
<td>0.884</td>
<td>368</td>
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<td>22.07</td>
<td>0.911</td>
<td>3413</td>
<td>129</td>
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<tr>
<td>NiMo/γ-Al$_2$O$_3$</td>
<td>$T_{\text{base}}$</td>
<td>18.5</td>
<td>42.6</td>
<td>39.0</td>
<td>19.37</td>
<td>0.903</td>
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<tr>
<td>NiMo/γ-Al$_2$O$_3$</td>
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<td>12.0</td>
<td>43.6</td>
<td>44.4</td>
<td>12.18</td>
<td>0.886</td>
<td>237</td>
<td>7</td>
<td>30</td>
</tr>
</tbody>
</table>

well as the three-ring aromatic compounds which considerably inhibit the hydrogenation of the two-ring aromatic and one-ring aromatic compounds [128]. On the other hand, aromatics and nitrogen require severer operating conditions for their elimination [47]. By analyzing the temperature range (Figure 5.10a), it can be observed that HDA was increased at higher temperatures. Unexpectedly, HDN activity trend was not similar to HDA as the HDN reaction takes place mainly through hydrogenation of the aromatic rings [111]. The reason might be related to the inhibition effect. A slight improvement at higher temperature in HDA and aromatics conversion for NiMo/Pγ-Al$_2$O$_3$ was observed (Figure 5.10a and 5.10b) maybe due to the fact that phosphorous induces either new or more active sites for the hydrogenation of aromatics [129]. A reason for this was explained by Jian and Prins [129] as it might be the replacement of a sulfur atom by a phosphorous atom in the nickel coordination. Phosphorous which is close to Ni-MoS$_2$ particles might be reduced to PH$_3$ by spilled over hydrogen atoms, which induces a P-S exchange reaction at the catalyst surface.

Sulfur removal in HDS may directly take place without hydrogenation of the associated aromatic ring, while removal of nitrogen happens through a complex sequence of reaction which involves aromatic ring hydrogenation followed by carbon-nitrogen bond breakage [85]. All catalysts showed similar HDS activity rate constant at low temperature (Figure 5.10c) but as the temperature was increased, the catalytic responses were enhanced, obtaining a better catalytic activity for NiMo/γ-Al$_2$O$_3$ and NiMo/γ-Al$_2$O$_3$ $150$. This could be attributed to the effect of adding phosphorous.

Nitrogen content mainly affects the color of products. As illustrated in Figure 5.11a, the results of color measurement are also in line with the theory. For instance, NiMo/Pγ-Al$_2$O$_3$ showed less brightness than the other catalysts at $T_{\text{base}}+20$ as it had also the highest nitrogen content among the others. At $T_{\text{base}}$ $^\circ\text{C}$ also the trend of the color and nitrogen content for all catalysts are the same. Density is highly affected by the aromatics content and as seen in Figure 5.11b, the results show similar trend. Comparing figures 5.9a and 5.11c showed that viscosity was also increased as the aromatic content was raised.
5.2. CATALYTIC ACTIVITY

(a) Aromatics content

(b) Nitrogen content

(c) Sulfur content

Figure 5.9: Aromatics, nitrogen and sulfur contents in products
CHAPTER 5. RESULTS AND DISCUSSION

Figure 5.10: HDA, HDN AND HDS activity rate constants and conversions
5.2. CATALYTIC ACTIVITY

(a) Color

(b) Density

(c) Viscosity

Figure 5.11: Color, density and viscosity in products
Chapter 6

Conclusions and further Work

The results of BET, XRD and TPR studies showed the effect of phosphorous on improvement of NiMo/γ-Al₂O₃ characteristics. Phosphorous addition to NiMo/γ-Al₂O₃ increased the number of accessible molybdenum sites on the surface due to higher dispersion. Regarding catalytic activity, NiMo/Pγ-Al₂O₃ enhanced HDA while it had negative impact on HDS and HDN. SEM micrographs showed a much less deactivation in spent NiMo/Pγ-Al₂O₃ indicating stability improvement. For NiMo/γ-Al₂O₃, the surface area loss was more due to the lower surface area of the support as seen in BET results. This catalyst performed much better at higher temperature, specially for HDS and HDN. However, SEM micrographs revealed higher deactivation for this catalyst compared to NiMo/γ-Al₂O₃. Although no activity test was carried out for NiMo/γ-Al₂O₃, it can be concluded that due to the severe surface area reduction and lower number of MoO₃, lower activity would be expected. Based on the results of BET, coimpregnation and sequential impregnation behaved similarly regarding the loss of surface area. However, TPR study showed the nickel in the catalyst impregnated sequentially had weaker interaction with the support in comparison with the catalyst prepared by coimpregnation.

The behavior of nickel-molybdenum supported on γ-alumina significantly depends on the preparation method, calcination temperature and promoter. Therefore, being familiar with the variety of these behaviors helps to select the right catalyst to obtain the desire product(s). It should be noted that other parameters e.g. feed type, operating conditions, sulfiding, promoter amount, etc. affect the catalyst behavior as well. Hence, the continuation of this study can be included the activity test for all prepared catalysts on different feed types and operating conditions. Also, applying characterization methods for sulfided catalysts is suggested to evaluate sulfiding effect on catalytic activity and find the optimum conditions. For the products that HDN and HDA are important, evaluating the effect of hydrothermal treatment of γ-alumina on the activity of NiMo/γ-Al₂O₃ and NiMo/Pγ-Al₂O₃ is suggested.
Bibliography


