Support and fluorination effects in hydrodenitrogenation over Ni-Mo hydrotreating catalysts

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Support and Fluorination Effects in Hydrodenitrogenation over Ni-Mo Hydrotreating Catalysts

A dissertation submitted to the Swiss Federal Institute of Technology Zurich

For the degree of Doctor of Technical Sciences

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Abstract

The effects of support and in-situ fluorination on hydrodenitrogenation have been studied under typical industrial conditions, i.e. 583 to 643 K and 5.0 MPa in a continuous microflow reactor over sulfided Ni-Mo catalysts supported on alumina and amorphous silica-alumina. The in-situ fluorination was performed after the sulfidation of catalysts with o-fluorotoluene at 643 K and 5.0 MPa. O-toluidine, methylcyclohexylamine were chosen as model nitrogen-containing compounds. The hydrogenation of methylcyclohexene, an important intermediate in the hydrodenitrogenation was studied to elucidate the effect on hydrogenation of olefins. Hydrogenation of toluene was also studied under the same conditions as in hydrodenitrogenation. Kinetic parameters were obtained by fitting Langmuir-Hinshelwood type equations with experimental data with the non-linear program Scientist®.

The oxidic Ni-Mo catalysts were characterized with magic-angle solid-state nuclear magnetic resonance spectra and temperature-programmed reduction to study the interaction between Mo and Ni species and the supports. The sulfided catalysts were further measured with transmission electron microscopy to study the degree of stacking of the MoS2 in these catalysts.

The hydrodenitrogenation of o-toluidine proceeds by two reaction pathways: path 1 is the hydrogenation to methylcyclohexylamine, followed by elimination forming methylcyclohexene, and subsequent hydrogenation to methylcyclohexane; path 2 is the direct hydrogenolysis to form toluene, which accounts for only 10% of the total conversion. A direct path from methylcyclohexylamine to methylcyclohexane may also exist, but it is not the main path for the hydrodenitrogenation of methylcyclohexylamine.

Higher hydrodenitrogenation activities were obtained with the silica-alumina-supported Ni-Mo catalysts than with their alumina-supported counterparts. A much stronger promotional effect was induced by the silica-alumina support in the hydrodenitrogenation activity of o-toluidine, an aromatic nitrogen-containing compound. Silica-alumina-supported catalysts also showed superior hydrogenation activity for toluene. However, the alumina-supported catalysts exhibited better hydrogenation activity and lower isomerization activity for cyclohexene than the silica-alumina-supported catalysts.
The *in-situ* fluorination enhanced the activities of all catalysts for the hydrodenitrogenation of methylcyclohexylamine, and to a larger extent for the hydrodenitrogenation of *o*-toluidine, and for the hydrogenation of toluene. Also, the isomerization of cyclohexene was promoted by the *in-situ* fluorination, whereas the hydrogenation of cyclohexene was not influenced.

Kinetic parameters confirmed that the promotional effects on the hydrodenitrogenation introduced by the silica-alumina support and by the *in-situ* fluorination are mainly caused by enhancing the (hydrogenation and) elimination path to form methylcyclohexene, and less by effects on the direct denitrogenation path from methylcyclohexylamine or from *o*-toluidine. The results for the hydrogenation of cyclohexene excluded the promotional effect of fluorination on the hydrogenation of olefins. Similar activation energies and heats of adsorption suggested that the intrinsic activity of the active sites for hydrodenitrogenation was not influenced by the support or by the *in-situ* fluorination, only the number of sites was increased, possibly by a higher degree of stacking of the MoS2 crystallites in the catalysts.

Based on the different effects of the support and the *in-situ* fluorination on the four model reactions, four kinds of active sites involved in the HDN of aromatic nitrogen-containing compounds were distinguished. The active site for the C(sp²)─N bond cleavage is highly unsaturated and accommodates aromatic amines in a flat adsorption mode. The site for the C(sp³)─N bond cleavage involves not only a surface vacancy, but also an acid site for the elimination, or a site to provide SH⁻ for nucleophilic substitution. Hydrogenation of aromatics is favored by higher stacking of the MoS2 slabs with more edge and corner sites, whereas the hydrogenation of olefins is favored on catalysts with better dispersion and lower stacking of MoS2 slabs.

On the silica-alumina support, Mo and Ni species adsorb preferentially on the alumina sites during impregnation. When the support contains a large amount of silica (less alumina), a lower metal dispersion is obtained because of the weaker interaction of Mo and Ni species with the support. Upon sulfidation, a higher stacking of MoS2 is then formed with the silica-alumina-supported catalysts. This is the reason for the much higher activities for the hydrogenation of aromatics and for the hydrodenitrogenation of aromatic nitrogen-containing compounds.
Zusammenfassung


Silica-Alumina erwies sich als der Träger, der zu aktiveren Ni-Mo–Entstickungskatalysatoren führte als Alumina. Silica-Alumina induzierte einen viel stärkeren

Die in-situ Fluoridierung erhöhte die Aktivität aller Katalysatoren für die Entstickung von Methylocyclohexylamin und in noch stärkeren Masse für die Entstickung von o-Toluidin und die Hydrierung von Toluol. Ausserdem wurde die Isomerisierung von Cyclohexen durch die in-situ Fluoridierung begünstigt, während die Hydrierung von Cyclohexen nicht beeinflusst wurde.


Olefinen auf Katalysatoren mit höherer Dispersion und geringerer Stacking von MoS₂-Platten bevorzugt.

Auf Silica-Alumina Trägern werden Mo und Ni während der Imprägnierung bevorzugt auf Aluminapartikeln adsorbiert. Wenn der Träger viel mehr Silica (und weniger Alumina) enthält, bekommt man aufgrund der schwächeren Wechselwirkungen zwischen Mo und Ni und dem Träger eine viel schlechtere Verteilung der Metallteilchen. Das führt während der Sulfidierung zu verstärktem MoS₂-stacking, wenn Silica-Alumina als Katalysatorträger verwendet wird. Das erklärt die viel höheren Aktivitäten für die Hydrierung von aromatischen Verbindungen und für die Entstickung von aromatischen stickstoffhaltigen Verbindungen.
Chapter 1
General Introduction

1.1 HYDROTREATING PROCESSES AND CATALYSTS

Hydroprocessing of commercial feeds has been extensively practiced in the petroleum industry and in the primary upgrading of heavy crudes and synthetic fuels. It is also an integral part of the production of liquid fuels from coal and biomass. The flowsheet of a modern petroleum refinery in Figure 1.1 indicates the frequent use of hydroprocessing processes (1). In the oil refining industry, hydroprocessing reactions (e.g., hydrogenation, hydrocracking, and removal of heteroatoms, such as S, N, O, and metals) are often classified according to the severity of the operation (Table 1.1). Hydrotreating is operated under relatively mild conditions. It refers to a variety of catalytic hydrogenation processes which saturate unsaturated hydrocarbons and remove S, N, O, and metals from various petroleum streams in a refinery. Accordingly, the reactions involved are named hydrodesulfurization (HDS), hydrode-nitrogenation (HDN), hydrodeoxygenation (HDO), hydrodemetallization (HDM), hydrogenation of aromatics (HDA), and hydrogenation of olefins. These processes usually imply only small changes in overall molecular structure, thus the boiling point of the oil fraction is hardly reduced, but hydrocracking reactions often occur simultaneously and may in fact be desired. Hydrocracking, on the other hand, not only removes N, S, and metals but also leads to cracking of hydrocarbons to give lighter products. Thus, (heavy) gas oil is cracked to give middle distillates. Hydrocracking is carried out under much more severe conditions than hydrotreating (2, 3). For instance, hydrocracking can be performed at 10 MPa and 673 K, whereas HDS is performed at 3 MPa and 623 K. Mild hydrocracking is a process variant which has recently become popular because the moderate conditions under which it is performed enable the use of existing hydrotreating reactors but still result in some conversion to lighter products. Thus, the operation and capital cost can be lowered substantially.
Hydrotreating ranks in importance with other large-scale petroleum refining processes (catalytic cracking and reforming). Its application is growing to meet several needs, including the protection of the catalysts used in downstream units of the refining process, the processing of heavier feeds, the production of high-performance lubricants, the introduction of cleaner burning fuels to lower the NO$_X$ and SO$_X$ emissions, and the possible future utilization of biomass through the
upgrading of pyrolytic bio-oils. Most oil streams in a refinery must be hydrotreated; consequently, hydrotreating is the largest application in industrial catalysis based on the amount of material processed per year. On the basis of the amount of catalyst sold per year in the world market, hydrotreating catalysts rank third after exhaust gas catalysts and fluid catalytic cracking catalysts (4).

Industrial hydrotreating catalysts usually contain molybdenum and cobalt or nickel, supported on $\gamma$-Al$_2$O$_3$ (5-8). Since oil fractions always contain S, different amount of H$_2$S is produced during the hydrotreating processes. Therefore, a metal or metal oxide that is introduced as catalyst would quickly become sulfided. In practice, one therefore sulfides supported metal oxides under controlled conditions before starting the hydrotreating process in order to obtain a stable operation. When supported alone on alumina, molybdenum sulfide has a much higher activity for the removal of S, N, and O atoms than cobalt or nickel sulfide. Therefore, molybdenum sulfide is traditionally considered to be the actual catalyst. Sulfided Co-Mo/Al$_2$O$_3$ and Ni-Mo/Al$_2$O$_3$, on the other hand, have substantially higher catalytic activities than Mo/Al$_2$O$_3$. Consequently, cobalt and nickel are referred to as promoters. Cobalt is used mainly as a promoter for sulfided Mo/Al$_2$O$_3$ in HDS, whereas nickel is the choice for HDN. In addition to molybdenum and cobalt or nickel, hydrotreating catalysts often contain additives incorporating elements such as phosphorus, boron, fluorine, or chlorine, which may influence the catalytic as well as the mechanical properties.

Hydrotreating catalysts originated in the 1920s when German researchers developed unsupported metal sulfide catalysts to liquify coal. However, it was not until the 1970s that the structures of these catalysts and mechanisms of their catalytic action began to be understood. It was established that under catalytic reaction conditions, most of the molybdenum in industrial hydrotreating catalysts is present as small MoS$_2$ particles in the pores of the $\gamma$-Al$_2$O$_3$ support. It was not until the 1980s that the location of the cobalt and the nickel promoter ions in the hydrotreating catalysts was more or less determined. The role of phosphate and fluorine additives is still under investigation. Supports other than $\gamma$-Al$_2$O$_3$ like amorphous silica-alumina, are also used in commercial units and their functions are topics of academic and industrial research.
1.2 CHEMISTRY OF HYDRODENITROGENATION

HDN is mainly used for lowering the nitrogen content in transportation fuels to diminish the emission of NO$_x$ from burning and preventing downstream acidic catalysts in refineries from being poisoned. At the same time, sulfur, metals, and unsaturated compounds are removed. Among hydrotreating reactions, HDN is receiving more and more attention, because of the increasing interest in converting petroleum residua, coal, shale, and tar sands, which contain higher concentration nitrogen, to liquid fuels. There are increasing demands for more clean and light fuels such as gasoline, kerosene, diesel and less heavier oils and also more stringent environmental regulations. Therefore, people need to process more heavy feedstocks such as vacuum gas oil (VGO), coker gas oil, and residue, and light cycle oil produced from VGO and residue, besides other sources of oils. This needs not only HDS, but also HDN. When processing heavier feedstocks, HDN is more important because the concentration of nitrogen-containing compounds in the heavier feedstocks is much higher than that in the straight run distillates. Usually the acidic catalysts such as those used for catalytic cracking (the most profitable process in a refinery) of the heavier feedstocks are easily poisoned by nitrogen-containing compounds and polyaromatics, especially the basic nitrogen-containing compounds. It is, therefore, necessary to perform HDN of the feeds to obtain a better product quality and distribution. Several reviews have summarized the process and catalysts for HDN (4, 6, 8-10). In order to develop new, effective HDN catalysts, further investigations on HDN processes and catalysts are still required. In the following sections, we will deal with the nitrogen-containing compounds in petroleum, their reaction networks, and the difficulties of HDN.

1.2.1 Nitrogen-Containing Compounds

Nitrogen-containing compounds in petroleum and coal-derived liquids are normally divided into two groups: heterocyclic and nonheterocyclic. Noncyclic nitrogen compounds such as aliphatic amines and nitriles are present in oil in small
amount and are easy to denitrogenate. Among nonheterocyclic nitrogen compounds, aniline derivatives are the most important ones in HDN because they are always formed in the HDN network of heterocyclic nitrogen compounds (see Section 1.2.2) and are more difficult to denitrogenate than aliphatic ones. They may also exist in relative large amount in coker and catalytic diesel distillates. Heterocyclic nitrogen-containing compounds are present in larger amount and more difficult to remove. They can be divided into basic and nonbasic compounds. Nonbasic compounds consist of five-membered heterocycles such as pyrrole, indole, carbazole, etc. The lone-pair electrons on the nitrogen atom of these compounds are delocalized around the aromatic ring and are not available for donation to acid sites on catalyst surfaces. Basic compounds include six-membered heterocycles such as pyridine, quinoline, acridine, etc. The lone-pair electrons on the nitrogen atom of these compounds, on the contrary, are not tied up in the π-cloud of the heterocyclic ring and are available for sharing with acid sites on catalyst surfaces. The saturated five-membered heterocycles, like indoline, are strongly basic, as aliphatic amines. Table 1.2 lists the various types of nitrogen-containing compounds (without alkyl substitution).

Table 1.2 Representative Nitrogen-Containing Compounds in Petroleum Crude, Shale Oil, and Coal-Derived Liquids

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nonheterocyclic compounds:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aniline</td>
<td>C₆H₅NH₂</td>
<td>![Aniline structure]</td>
</tr>
<tr>
<td>Pentyamine</td>
<td>C₅H₁₁NH₂</td>
<td>![Pentyamine structure]</td>
</tr>
<tr>
<td><strong>Nonbasic heterocyclic compounds:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrrole</td>
<td>C₄H₅N</td>
<td>![Pyrrole structure]</td>
</tr>
</tbody>
</table>
### Table 1.2 (continued)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indole</td>
<td>C(_8)H(_7)N</td>
<td><img src="image" alt="Indole Structure" /></td>
</tr>
<tr>
<td>Carbazole</td>
<td>C(_{12})H(_9)N</td>
<td><img src="image" alt="Carbazole Structure" /></td>
</tr>
<tr>
<td>Indoline</td>
<td>C(_8)H(_9)N</td>
<td><img src="image" alt="Indoline Structure" /></td>
</tr>
<tr>
<td>Acridine</td>
<td>C(_{13})H(_8)N</td>
<td><img src="image" alt="Acridine Structure" /></td>
</tr>
<tr>
<td>Benz((a))acridine</td>
<td>C(<em>{17})H(</em>{11})N</td>
<td><img src="image" alt="Benz(a)acridine Structure" /></td>
</tr>
<tr>
<td>Benz((c))acridine</td>
<td>C(<em>{17})H(</em>{11})N</td>
<td><img src="image" alt="Benz(c)acridine Structure" /></td>
</tr>
<tr>
<td>Dibenzo((c, h))acridine</td>
<td>C(<em>{21})H(</em>{13})N</td>
<td><img src="image" alt="Dibenzo(c, h)acridine Structure" /></td>
</tr>
</tbody>
</table>

**Basic heterocyclic compounds:**
1.2.2 Reactions and Reaction Networks

HDN involves hydrogenolysis of the C—N bonds in nitrogen-containing compounds to yield ammonia and the corresponding hydrocarbon. Under industrial conditions, HDN is always accompanied by other hydrotreating reactions such as hydrogenation of olefins, HDS, HDO, HDM, HDA, and hydrocracking, in addition to coking.

HDN of aromatic nitrogen-containing compounds occurs via a complex reaction network involving hydrogenation of the aromatic rings followed by C—N bond scission, in contrast to HDS which mainly involves direct scission of C—S bonds (Figure 1.2). The direct desulfurization path can be three orders of magnitude faster than the hydrogenation one (11). But HDN is less selective compared with HDS. Therefore, much more hydrogen is consumed and higher hydrogen pressure is required. In this section, we will discuss the reaction networks of different cyclic nitrogen-containing model compounds.

Figure 1.2 Reaction network for hydrodesulfurization of dibenzothiophene over Co-Mo/Al₂O₃ catalyts under elevated pressure (11).
General Introduction

1.2.2.1 Pyridine

Pyridine is often considered to be the simplest heterocyclic nitrogen compound and is often used as a model compound for comparing the HDN activity of catalysts and studying the HDN mechanism (12-16). The reaction scheme is shown in Figure 1.3.

![Figure 1.3 HDN network of pyridine over sulfided Ni-Mo/Al₂O₃ catalysts](image)

The HDN of pyridine usually proceeds via the hydrogenation of the pyridine ring to piperidine, followed by denitrogenation (17-21). The first hydrogenation of pyridine to piperidine is inferred to take place on sulfur-deficient sites of the metal sulfide surface since a negative effect of H₂S was observed on this step. This reaction is favored by hydrogen as well (19, 20, 22). The second step, ring-opening of piperidine and the following nitrogen-removal reaction, probably occur by elimination and lead to alkene intermediates. This reaction is favored by H₂S (19, 20, 22). At high H₂S partial pressure, 2-methyl-thiacyclopentane and thiacyclohexene were found as products (23, 24). The high H₂S concentration induced a nucleophilic substitution of the amino group of 5-aminopentene-1 by the SH group, and the resulting 5-thiopentene-1 reacted intramolecularly to give a five- and six-membered thiacycloalkane. The fact that these two molecules were observed in the HDN of pyridine, piperidine, and 5-aminopentene-1, but not in that of 1-pentylamine, strongly supports the mechanism shown in Figure 1.4. That ring opening and removal of nitrogen are promoted by H₂S suggests that these are elimination reactions and take place on relatively sulfur-rich sites on the metal sulfide surface.
Figure 1.4    Possible HDN mechanism of pyridine via SH nucleophilic substitution

Thermodynamics may play an important role in the HDN of aromatic heterocycles. In general, at higher temperatures the equilibrium between ring hydrogenation and dehydrogenation shifts to the dehydrogenation side leading to a decrease in the equilibrium concentration of the hydrogenated compound, and thus a decrease in nitrogen removal rate. Satterfield and Cocchetto (13) observed that under such a condition, the overall rate of pyridine HDN showed a maximum with increasing temperature. Therefore, the rate-determining step in the HDN of pyridine is changing with reaction conditions. At a temperature of 573 K and pressure of 3 MPa, the rate of hydrogenation of pyridine is about the same as that of the ring-opening of piperidine over NiMo, CoMo, and NiW catalysts (19, 22, 25, 26). H₂S may have a promoting as well as a poisoning effect on the HDN of pyridine under these conditions. At a low H₂S/H₂ ratio, pyridine hydrogenation to piperidine is not inhibited, but ring opening of piperidine by β-elimination is going slowly, thus leading to a low overall HDN conversion to C₅ hydrocarbons. Under such conditions, the effect of adding nickel to molybdenum is not very important for total HDN to give C₅ products (22). This observation has led some to conclude that nickel does not promote molybdenum in HDN as it does in HDS (27, 28). However, at higher H₂S/H₂ ratio, hydrogenation of pyridine to piperidine is retarded by H₂S, but ring opening is accelerated. Thus, even at a lower pyridine conversion, the yield of hydrocarbons increases (22). At an even higher H₂S/H₂ ratio, the negative effect of H₂S is
responsible for low conversions to piperidine and low HDN conversions. At lower hydrogen pressures and higher reaction temperatures, pyridine hydrogenation becomes rate determining, and H₂S becomes increasingly toxic. At higher hydrogen pressures and lower temperatures, H₂S acts as a promoter because the ring-opening reaction becomes rate determining. Under such conditions, nickel clearly promotes the HDN of pyridine.

During the HDN of pyridine and piperidine, a higher molecular weight product, N-pentylpiperidine is formed readily, especially when the partial pressure of intermediates (piperidine and pentylamine) is high. It is formed by the disproportionation of piperidine and pentylamine (12, 19, 29). Even though N-pentylpiperidine can be denitrogenated at high conversion of the reactant, this makes the HDN network of pyridine quite complicated to study.

1.2.2.2 Quinoline

Quinoline is used as a model compound because it contains a six-membered heterocyclic ring as well as a phenyl ring. All reactions involved in the HDN process are present in the HDN network of quinoline (9, 30-34) (Figure 1.5). Quinoline (Q) can be denitrogenated in two ways. One path is via o-propylaniline (OPA), and the other is via decahydroquinoline (DHQ). Since the C─N bond in the aromatic heterocycle is too strong to break, hydrogenation is necessary in both pathways. First, the heterocycle in quinoline is hydrogenated to 1,2,3,4-tetrahydroquinoline (THQ-1). This is a very fast reaction, and under most conditions, equilibrium is reached between Q and THQ-1 (30). Thereafter, ring opening of the heterocycle to OPA takes place via the highly reactive OPA intermediate. It should be expected that OPA undergoes denitrogenation just as aniline does (see Section 1.2.2.4) so that the HDN of Q would take place predominantly via OPA. However, this is not the case since competitive HDN studies of aniline and DHQ showed that DHQ adsorbs much more strongly than aniline and OPA (35). In the presence of DHQ, Q, or THQ-1, the rate of HDN of OPA is therefore suppressed (30, 36). At 643 K and 3 MPa, and in the
presence of H$_2$S, only about 40% of the HDN of Q takes place via the THQ-1 to OPA pathway (37).

In the second HDN pathway of quinoline, it is first fully hydrogenated to DHQ via the sequence THQ-1 $\rightarrow$ DHQ or 5,6,7,8-tetrahydroquinoline (THQ-5) $\rightarrow$ DHQ. The hydrogenations of the carbocycles of Q and THQ-1 are slow at temperatures below 623 K. A high conversion of Q to DHQ is promoted by a high hydrogen pressure and a low H$_2$S/H$_2$ ration. Furthermore, a sufficiently high temperature aids the conversion of Q to DHQ (kinetic effect), but not too high to induce thermodynamic limitations.
DHQ undergoes denitrogenation via ring-opening elimination to \( o \)-propenylcyclohexylamine, which is expected to have a large adsorption constant and a high rate of hydrogenation. HDN experiments carried out at high \( H_2 \) as well as high \( H_2S \) pressures provided evidence for the formation of \( o \)-propenylcyclohexylamine. As in the HDN of pyridine and piperidine, it was shown that a high \( H_2S \) pressure in the HDN of THQ-1 leads to the formation of five- and six-membered thiacycloalkane rings, in this case octahydro-2H-1-benzothiopyrane and octahydro-2-methylbenzo-thiophene (24). Under normal HDN conditions, however, \( o \)-propenylcyclohexylamine is quickly hydrogenated. The resulting \( o \)-propylcyclohexylamine is also highly reactive and has been observed only in low concentrations (38). It quickly reacts via NH\(_3\) elimination to give \( o \)-propenylcyclohexene, which mainly undergoes hydrogenation to propylcyclohexane, as long as a substantial amount of amine is present to inhibit its dehydrogenation to propylbenzene.

Since the DHQ pathway is usually more important for the removal of nitrogen from Q than the OPA pathway, the HDN of quinoline is similar to that of pyridine. Initially, total hydrogenation of the reactant takes place, followed by two consecutive C—N bond cleavages and, eventually, hydrogenation to give aliphatic products. \( H_2S \) promotes the HDN of quinoline at 623—643 K and 3—7 MPa (39, 40). This result demonstrates that hydrogenation is not rate determining. As in the case of pyridine, the kinetic situation is not simple. Both hydrogenation and C—N bond cleavage are slow, and the kinetics cannot be described by a model including a rate determining step. The effect of the \( H_2S \) partial pressure on the two pathways for the HDN of quinoline is different (40, 41). In the route from THQ-1 via OPA to \( o \)-propylcyclohexylamine, the C—N bond-breaking elimination is promoted by \( H_2S \), whereas the hydrogenation of OPA is inhibited by \( H_2S \). As a result, there is an accumulation of OPA with increasing \( H_2S \) pressure. In the route from Q via DHQ to \( o \)-propylcyclohexylamine, the hydrogenation of quinoline to give DHQ is suppressed by \( H_2S \), and the the C—N bond-breaking elimination of DHQ is promoted by \( H_2S \). Therefore, at increasing \( H_2S \) pressure, less DHQ is observed in the reaction mixture because it is produced at a lower rate and reacts at a higher rate.
1.2.2.3 Indole

Indole is comparable to quinoline in incorporating a carbocyclic as well as a heterocyclic ring. The heterocycle, however, is five-membered and less aromatic than the six-membered pyridine ring of quinoline. Therefore, the exclusive initial reaction in HDN is the hydrogenation of the heterocyclic ring to form indoline (2,3-dihydroindole). On the basis of a presumed analogy of the two reaction paths of THQ-1 to DHQ and OPA for the HDN of quinoline, one would expect that in the case of indole two paths are important as well—one proceeding via hydrogenation of indoline to octahydroindole (OHI) and the other via ring opening of indoline to o-ethylaniline (OEA). In contrast to the HDN of quinoline, however, it is generally assumed that the path via OEA is the main one for indole (19, 25, 42). Analogous to the conversion of aniline and OPA, the conversion of OEA takes place mainly via hydrogenation to o-ethylcyclohexylamine and subsequently to ethylcyclohexane and ethylcyclohexene (19, 42-44). On the other hand, it has been observed that indole and indoline strongly inhibit the conversion of aniline (and thus ethylaniline) (43), just as quinoline and THQ inhibit the conversion of propylaniline. This suggests that, as in the HDN network of indole, the totally hydrogenated OHI intermediate may be as important as OEA. Indications of such a contribution were observed by Zhang and Ozkan (45). In a recent study of six methyl-substituted indoles, Kim and Massoth (46) also considered the OHI route. The resulting analysis showed that this route is more important than the OEA route for Ni-Mo catalysts, whereas the reverse is true for Co-Mo catalysts (46). Apparently, the OHI route is more important on a Ni-Mo catalyst than on a Co-Mo catalyst because of the higher hydrogenation activity of the former (Figure 1.6).
1.2.2.4 Aniline

Hydrogenation of the aromatic ring is not only a prerequisite for the removal of the nitrogen atom from pyridine, quinoline, and indole, it is also important for the removal of the nitrogen atom from anilines. HDN of aniline occurs mainly via hydrogenation to give cyclohexylamine, which very quickly undergoes elimination of NH$_3$ to form cyclohexene (19, 47). Cyclohexene is then hydrogenated to cyclohexane. A small part of aniline, however, is directly transformed to benzene and ammonia, as observed for aniline and alkylanilines (25, 47-49). Because aniline adsorbs much more strongly than benzene on hydrogenation sites of the catalysts and expels benzene from these sites by competitive adsorption, hardly any cyclohexene is formed by hydrogenation of benzene as long as aniline is present (38). For the same reason, dehydrogenation of cyclohexene to benzene is important only at high conversions. Apart from very high conversions, the reaction network of the HDN of aniline can therefore be simply described by two parallel reactions. On the one hand, aniline
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1.2.3 Difficulties of HDN

HDN is typically more difficult than HDS. This can be partially explained by the relative bond strength as shown in Table 1.3 (50). The C≡N bond (615 kJ/mol) has a much higher energy than the C―N bond (308 kJ/mol), and the C―N bond is also stronger than the C―S bond (259 kJ/mol). That is why the aromatic nitrogen-containing compounds, especially the aromatic nitrogen-containing heterocycles must be saturated before they can be further denitrogenated, unless some materials with metallic properties such as metal carbides and nitrides are used as HDN catalysts.

Heavier feedstocks such as VGO, residue, light cycle oil from VGO and residue, and coal-derived liquids usually contain much higher concentration of nitrogen-containing compounds than straight-run streams. They are more complex in structure and more difficult to denitrogenate. For example, the pseudo-first-order rate constants for HDN decreased in the order: pyridine (20.9 min\(^{-1}\)) > quinoline (6.6 min\(^{-1}\)) > acridine (2.2 min\(^{-1}\)) > benz(a)acridine (1.0 min\(^{-1}\)) in a batch reactor at 640 K and 13.6
MPa over a sulfided Ni-Mo/Al₂O₃ catalyst (51). With increasing boiling point of the feeds, not only the nitrogen contents increase much faster, but also the size of molecules of these nitrogen-containing compounds increases, which reduces their accessibility to the catalyst surface.

<table>
<thead>
<tr>
<th>Bond</th>
<th>Energy, kJ/mol</th>
<th>Bond</th>
<th>Energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>H─H</td>
<td>436</td>
<td>N─H</td>
<td>391</td>
</tr>
<tr>
<td>C─H</td>
<td>413</td>
<td>C─N</td>
<td>308</td>
</tr>
<tr>
<td>C─C</td>
<td>348</td>
<td>C=N</td>
<td>615</td>
</tr>
<tr>
<td>C=C</td>
<td>614</td>
<td>C≡N</td>
<td>891</td>
</tr>
<tr>
<td>C≡C</td>
<td>839</td>
<td>C─S</td>
<td>259</td>
</tr>
<tr>
<td>C─O</td>
<td>358</td>
<td>C=S</td>
<td>577</td>
</tr>
<tr>
<td>C=O</td>
<td>799</td>
<td>S─H</td>
<td>347</td>
</tr>
</tbody>
</table>

During HDN processes, secondary nitrogen-containing compounds are formed, which could be more resistant to nitrogen removal than the original ones. Nitrogen-containing compounds often have a strong adsorption capacity on the catalyst surface. Self-inhibition by the high concentration of these compounds as well as the secondary compounds lead to a much lower HDN rate. Sometimes, much stronger adsorption can be expected, as that of DHQ in the HDN of quinoline. More severe catalyst deactivation is caused by the higher molecular weight-aromatic compounds in the feedstock. During HDN, coke is also formed, mainly by condensation of the basic nitrogen-containing compounds on Lewis acid sites of the catalyst.
1.3 HYDRODENITROGENATION CATALYSTS

1.3.1 Structure of Oxidic Catalysts

Conventional HDN catalysts are derived from HDS catalysts. That is, molybdenum and tungsten sulfides promoted with cobalt or nickel supported on alumina and silica-alumina. More common is the use of molybdenum (tungsten) and nickel. Even though tungsten is more expensive than molybdenum, it is used in HDN catalysts because it has a higher activity for aromatic saturation, which is usually the first step and indispensable in HDN.

Hydrotreating catalysts are usually prepared by a sequential pore volume impregnation procedure or by co-impregnation (5-8). In the former method, γ-Al₂O₃ support is first impregnated with an aqueous solution of ammonium heptamolybdate (NH₄)₆Mo₇O₂₄ or ammonium metatungstate (NH₄)₆W₁₂O₄₆H₂O, followed by drying and calcination in air. In a second step, the resulting material is further impregnated with an aqueous solution of nickel nitrate Ni(NO₃)₂ or cobalt nitrate Co(NO₃)₂ and then dried and calcined. Alternatively (and preferentially in the industry), all inorganic materials are coimpregnated in order to shorten the preparation procedure and lower the operation cost, and the resulting catalyst precursor is then dried and calcined.

Regarding the formation of surface structures, it is commonly accepted that molybdenum interacts in the calcined oxidic state with the hydroxyl groups on the Al₂O₃ surface, resulting in a monolayer structure (52, 53). This has been proved by a thermodynamic study (54), electron spin resonance (55), ¹H-NMR and chemisorption (56), EXAFS (57, 58), and infrared spectroscopy (59). In case of tungsten, isolated WO₄²⁻ or polytungstate species are formed on the Al₂O₃ surface, depending on the tungsten loading (60-62). The difference is that tungsten oxide has a stronger interaction with the Al₂O₃ support (63, 64), which leads to a lower sulfidability (65). When nickel or cobalt are introduced, they will inevitably interact with the Al₂O₃ support and form spinels.

Investigations also confirmed interactions between molybdenum and nickel or cobalt in the catalyst in the oxidic state. Thus, the order of impregnation and
calcination—first molybdenum and then nickel or cobalt or vice versa—plays an important role in the activity of the final sulfided catalyst. Catalysts in which the support is impregnated first with a solution containing molybdenum invariably have a higher activity. It has been suggested that the nickel or cobalt cations interact with the polymolybdate phase by forming a metal heteropolymolybdate (66, 67). Several publications deal with this project: For instance, the infrared absorption bands of NO adsorbed on Co-Mo/Al₂O₃ are shifted from those of NO on Co/Al₂O₃ (68), and Raman bands indicating polymeric molybdenum oxide species decrease in intensity with increasing the cobalt loading in an oxidic Co-Mo/Al₂O₃ catalyst (69). The results suggest that nickel or cobalt cations interact especially with the most polymeric molybdenum oxide species to form species in which nickel or cobalt and molybdenum interact. In this way the promoter cations stay at the surface and close to the molybdenum cations and are positioned to form the active Ni-Mo-S structure during sulfidation. Furthermore, the promoter ions interact to a lesser extent with the support and thus can be used more efficiently after sulfidation.

1.3.2 Structure of Sulfided Catalysts

Hydrotreating catalysts are used in the presence of sulfur. Therefore, they have to be sulfided to transform the oxidic metal species into their active sulfided states before reaction. Sulfidation can be performed in a mixture of H₂ with one or more sulfur-containing compounds such as H₂S, CS₂, dimethyl disulfide, thiophene, and even elemental sulfur. The oil fraction to be treated can be used for the sulfidation as well. The properties of the final sulfidic catalyst depend to a great extent on the calcination and sulfidation conditions. High-temperature calcination induces a strong interaction between molybdenum and nickel or cobalt cations and the alumina support. Consequently, it is difficult to transform the oxidic species into sulfides. Mössbauer spectroscopy of Co-Mo/Al₂O₃ catalysts showed that at increasingly high calcination temperatures, increasingly more of Co²⁺ ions are incorporated into the bulk of the alumina, forming a spinel (70). The higher the calcination temperature, the higher the sulfidation temperature needed to bring these cations back to the surface to
provide a high catalytic activity for hydrotreating. When the sulfidation temperature is too high, the metal sulfides sinter or do not form the catalytically active Co—Mo—S phase. Optimum calcination and sulfidation temperatures are in the range 673—773 K for Al₂O₃-supported catalysts (71).

The sulfidation mechanism was investigated by temperature-programmed sulfidation, in which the oxidic catalyst was heated in a flow of H₂S and H₂, and the consumption of H₂S and H₂ and the evolution of H₂O were measured continuously (72). It was found that H₂S is taken up and H₂O given out, even at room temperature, indicating a sulfur—oxygen exchange reaction. This conclusion was confirmed by Cattaneo and Prins (73) with quick extended X-ray absorption fine structure (QEXAFS) studies (Figure 1.8, phase 2), which also demonstrated that the Mo (VI) species containing both oxygen and sulfur transform into intermediate MoS₃-type species at temperatures between 520 and 570 K (Figure 1.8, phase 3). At higher temperatures, the MoS₃ is reduced to MoS₂ (Figure 1.8, Phase 4) with concomitant H₂ consumption and H₂S evolution. (72).

During sulfidation and hydrotreating catalysis, the conditions are highly reducing, and H₂S is always present; it follows from thermodynamics that molybdenum should be present in the form of MoS₂. Nevertheless, results obtained by X-ray photoelectron spectroscopy have shown that complete sulfidation of molybdenum, and especially of tungsten, is difficult. Apparently, some of the Mo(VI) ions interact so strongly with the Al₂O₃ support that they can be sulfided only at temperatures higher than 773 K. However, in the presence of nickel or cobalt cations, molybdenum and tungsten can be sulfided more easily. EXAFS molybdenum K-edge absorption spectra demonstrated that, in well-sulfided Mo/Al₂O₃ catalysts, the Mo—S and Mo—Mo distances are the same as in MoS₂ (57, 68); the only difference is that in the catalyst each molybdenum atom is surrounded, on average, by fewer than six molybdenum atoms, as for pure MoS₂. EXAFS is a bulk technique by means of which the environment of surface molybdenum atoms as well as that of molybdenum atoms in the interior of the MoS₂ particles is determined. Consequently, a coordination number lower than 6 indicates that the proportion of surface molybdenum atoms is substantial and that the MoS₂ particles on the support surface typically contain about 60 molybdenum atoms each (74, 75).
MoS$_2$ has a layer lattice, and the sulfur—sulfur interaction between successive MoS$_2$ layers is weak (van der Waals force). Crystals grow as platelets with relatively large dimensions parallel to the basal sulfur planes and small dimensions perpendicular to the basal planes. High-resolution transmission electron microscopy of model catalysts containing MoS$_2$ crystallites on planar Al$_2$O$_3$ showed that the MoS$_2$ crystallites occurred as platelets with a height-to-width ration between 0.4 and 0.7 (Figure 1.9). Investigations of model catalysts consisting of MoS$_2$ grown on $\gamma$-Al$_2$O$_3$ films on the surfaces of MgAl$_2$O$_4$ supports have shown that MoS$_2$ grows with its basal plane parallel to the (111) surface of $\gamma$-Al$_2$O$_3$ and perpendicular to the (100) $\gamma$-Al$_2$O$_3$ surface (76). This observation suggests that the edges of the MoS$_2$ platelets are bonded to the (100) surface of $\gamma$-Al$_2$O$_3$ by Mo—O—Al bonds (Figure 1.10).
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Figure 1.9  TEM imagine of a sulfided NiMo/Al₂O₃ catalyst.

Figure 1.10  Orientation of small MoS₂ particles on γ-Al₂O₃ surface
Nickel atoms may be present in three forms after sulfidation: as Ni$_3$S$_2$ crystallites on the support, as nickel atoms adsorbed on the edges of MoS$_2$ crystallites (the so-called Ni─Mo─S phase), and as nickel cations at octahedral or tetrahedral sites in the γ-Al$_2$O$_3$ lattice (Figure 1.11). Depending on the relative concentrations of nickel or cobalt and molybdenum and on the pretreatment conditions, a sulfided catalyst may contain a relatively large amount of either Ni$_3$S$_2$ or Co$_9$S$_8$ or the Ni─Mo─S (or Co─Mo─S) phase.

Several *in-situ* characterization techniques such as Mössbauer (70), infrared, and EXAFS confirmed the Ni─Mo─S (or Co─Mo─S) edge decoration model. The occurrence of nickel or cobalt adsorbed on the MoS$_2$ surface is unexpected from the point of view of thermodynamics, the most stable phases of nickel and cobalt under sulfiding conditions being Ni$_3$S$_2$ and Co$_9$S$_8$, respectively. Nevertheless, the infrared spectra of NO molecules adsorbed on sulfided Co-Mo/Al$_2$O$_3$ catalysts indicated that as the cobalt content increased at a fixed molybdenum content, the number of NO molecules adsorbed on cobalt sites increased and the number of NO molecules
adsorbed on molybdenum sites decreased (77). Cobalt atoms at edge-decoration sites cover molybdenum atoms and block adsorption of NO on these molybdenum atoms. The observed behavior is therefore in accordance with the edge-decoration location.

EXAFS studies showed that a nickel atom in a sulfided Ni-Mo catalyst supported on γ-Al₂O₃ or on carbon is surrounded by four or five sulfur atoms at a distance of 2.2 Å, by one or two molybdenum atoms at a distance of 2.8 Å, and by one nickel atom at a distance of 3.2 Å (78). These data are consistent with a model in which the nickel atoms are located at the MoS₂ edges in the molybdenum plane in a square pyramidal coordination. The nickel atoms are connected to the MoS₂ by four atoms, and depending on the H₂S partial pressure a fifth sulfur atom may be present in the apical position in front of the nickel atom (Figure 1.12). Recent density functional theory (DFT) calculations suggested a different edge-decoration model (79). Instead of substituting molybdenum atoms at the (1010) molybdenum edge, cobalt atoms were claimed to prefer to substitute molybdenum atoms at the (1010) sulfur edge. Other DFT calculations, however, indicated that these particular edge positions are an artifact of the too small MoS₂ clusters used to model MoS₂ in the calculations (80). DFT calculations with larger MoS₂ clusters showed that the most favorable location of the promoter atoms is the substitutional position at the molybdenum edge. The nickel and cobalt atoms extend, as it were, the MoS₂ lattice by taking up molybdenum positions (80). This conclusion is in good agreement with the EXAFS results (Figure 1.12).

Mössbauer data of Crajé et al. (81) showed that the cobalt quadrupole splitting in Co-Mo/Al₂O₃ varies continuously with the cobalt loading and sulfiding temperature, which was suggested to be a consequence of the increasing size and ordering of the cobalt sulfide particles at the MoS₂ edges (81). At very low cobalt loadings and after sulfiding at relatively low temperatures, all the cobalt atoms can be positioned around the MoS₂ edges and the catalytic activity initially increases with increasing Co/Mo ratio. If all the edge positions are occupied, then additional cobalt atoms must be located on top of the cobalt atoms that are already present or must be present separately as Co₉S₈ crystallites. High sulfiding temperatures also lead to growth of the cobalt sulfide species as a result of growth of the MoS₂ crystallites, and as a
consequence, a decrease in the MoS$_2$ edge area. Ultimately, relatively larger Co$_9$S$_8$ particles form, which are in contact with the MoS$_2$ particles. Since the Co$_9$S$_8$ particles have a low catalytic activity and cover the MoS$_2$ particles, the HDS activity of Co-Mo catalysts decreases at increasingly high Co/Mo ratios. Maximum activity is usually observed at a Co/Mo ratio of 0.3 to 0.5. This result implies that the MoS$_2$ particles present on the Al$_2$O$_3$ support must be so small that the ratio of the number of molybdenum edge atoms to the total number of molybdenum atoms is the same (i.e. 0.3–0.5) (82). Commercial catalysts usually have Co/Mo or Ni/Mo ratios slightly higher than 0.5, with molybdenum loadings of about 10 to 15 wt%.

Figure 1.12 Structure involving the nickel atoms in the Ni—Mo—S phase as determined by EXAFS (78). Big balls are sulfur; small black, nickel; small grey, molybdenum.

1.3.3 Nature of Active Sites

As can be seen from Section 1.2.2, different types of reactions are involved in HDN. Then the question is what are the active sites for these reactions. Are molybdenum sites the catalytically active sites, and if so, how are they promoted by nickel and cobalt, or do the nickel and cobalt atoms constitute new sites which are supported on and influenced by MoS$_2$?
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It was commonly assumed that the catalytically active sites in hydrotreating catalyst are the molybdenum atoms at the surfaces of the MoS$_2$ crystallites, with at least one sulfur vacancy at a site to allow the reacting molecule to bond chemically to the molybdenum atom (5-8). Since sulfur atoms in the basal planes of MoS$_2$ are much more difficult to remove than sulfur atoms at edges and corners, exposed molybdenum atoms are predominantly present at edges and corners. Catalysis therefore occurs at MoS$_2$ edges and corners rather than on basal plane, as verified by results of a surface-science study in which a MoS$_2$ single crystal, with high basal plane to edge surface area ratio, was found to have a low HDS activity. Its activity increased after the sulfur atoms were sputtered away from the basal plane and exposed to the molybdenum atoms (83). Scanning tunnelling microscopy was used recently to image MoS$_2$ nanoparticles on a gold surface (84). Most MoS$_2$ nanoparticles had triangular shapes rather than the hexagonal shapes observed by electron microscopy for MoS$_2$ crystallites on Al$_2$O$_3$. Exposure of the MoS$_2$ nanoparticles to hydrogen led to the creation of sulfur vacancies. Such vacancies at the MoS$_2$ edge are supposed to be the catalytically active sites for HDS.

Because the HDN and HDS activities of a MoS$_2$/Al$_2$O$_3$ catalyst both increase substantially with addition of nickel or cobalt, several explanations have been proposed for the promoting function of nickel and cobalt (5-8). The first model (85) was based on the monolayer structure of oxide precursor supported on γ-Al$_2$O$_3$ support (52, 86). The oxidic monolayer was formed through dehydration of the Al$_2$O$_3$ surface hydroxyl groups during calcination. During sulfidation, sulfur atoms replace the terminal oxygen atoms. The first layer contained only sulfur atoms, each bonded to a molybdenum atom of the second layer, these molybdenum atoms being bonded to two oxygen atoms also located in this layer. When a sulfur atom was removed by reduction (in H$_2$ flow) of Mo$^{5+}$ to Mo$^{3+}$, a vacancy was formed at the surface and became the preferential adsorption site of a sulfur (or nitrogen) atom in the organic gas phase. The presence of cobalt (or nickel) incorporated into underlaying layers of the Al$_2$O$_3$ support pushed up to the second layer aluminium ions (Al$^{3+}$) in tetrahedral sites, resulting in each atom of the sulfur from the first layer now being bonded to two molybdenum atoms. A sulfur vacancy now liberated two molybdenum atoms instead of one for the adsorption site, which would explain the higher activity of this
promoted catalyst. Since the sulfur anion is larger than the oxygen anion, sulfur uptake in the monolayer configuration can occur only to a limited extent, corresponding to a S/Mo ratio of less than unity (85). However, Massoth (87) observed ratios as high as 2.75, which is much higher than that required by the model. This model could not explain the role of promoters (cobalt or nickel) for unsupported catalysts, either.

The second model (82, 88) was derived from the structure of sulfides called intercalated solids. Nickel and cobalt can penetrate the van der Waals layers of the lamellar tungsten sulfide to occupy the octahedral symmetrical voids. Although the intercalation of nickel and cobalt to molybdenum sulfide might be difficult under catalytic conditions, Ni$^{2+}$ and Co$^{2+}$ could be located at the edges of the MoS$_2$ crystallites. For tungsten-based catalysts, the active sites were the exposed unsaturated W$^{3+}$ with different degrees of unsaturation. These sites were suitable for the adsorption of benzene and cyclohexene, called corner and edge sites, respectively (82). Therefore, the promoter atoms induce a surface reconstruction of the edges of the MoS$_2$ (or WS$_2$) layers, leading to a greater number of exposed molybdenum (or tungsten) atoms, and thus, to enhanced activity (82). However, infrared (77) and EXAFS (74, 78) investigations demonstrated that the molybdenum atoms were covered by the sulfur and the promoter atoms. Thus, if only the molybdenum atoms were active, the activity should decrease upon addition of nickel or cobalt atoms.

The third model (89, 90) was based on the observations that unsupported Co-Mo catalysts have only two phases: Co$_9$S$_8$ and MoS$_2$, and they interact with each other. Even a mechanical mixture of Co$_9$S$_8$ and MoS$_2$, when in close contact, can be rather active (91, 92). Delmon and co-workers believed that segregated cobalt sulfide is the promoter and that it supplies MoS$_2$ with hydrogen atoms. These “spilled-over” hydrogen atoms are inferred to create reduced centers on the MoS$_2$ surface, which are the catalytically active sites (89, 90). The Co$_9$S$_8$ would then have “remote control” over the MoS$_2$ surface. Combined Mössbauer spectroscopy and HDS activity studies demonstrated, however, that the promoter effect of cobalt is related to the cobalt atoms in the Co$-$Mo$-$S phase and not to the separate Co$_9$S$_8$ (93, 94). Small amounts of cobalt strongly increased the thiophene HDS activity and led preferentially to Co$-$Mo$-$S phase. Co$_9$S$_8$ formed only at higher cobalt loadings at which the activity
had already levelled off. The catalytic activity actually decreased when Co₈S₈ became
the dominant phase at high cobalt loadings.

A fourth model therefore attributed the promotion effect to the cobalt present in
the Co–Mo–S phase, based mainly on the in-situ emission Mössbauer spectroscopy
(93). Cobalt atoms are located at the edges of the MoS₂ crystallites (94, 95). A
significant contribution of separate Co₈S₈ was excluded (93, 94). This so-called
Co–Mo–S model (or Ni–Mo–S model for Ni-Mo catalysts) is currently the most
accepted one.

However, the Co–Mo–S model does not indicate whether the catalytic activity
arises from molybdenum promoted by the presence of cobalt or from the cobalt sites
themselves. Both cobalt and nickel sulfides, when supported on carbon, have higher
HDS activities than MoS₂/C (96). Therefore, it has been suggested that the cobalt in
the Co–Mo–S phase and nickel in the Ni–Mo–S phase might be the actual catalysts
and not the promoters. In the past, the idea that cobalt and nickel might be the
catalysts in sulfided Co-Mo and Ni-Mo systems was rejected because sulfided
Co/Al₂O₃ and Ni/Al₂O₃ had very low HDS activities. However, during the usual
pretreatment of Co/Al₂O₃ and Ni/Al₂O₃ (without molybdenum) catalysts, cobalt and
nickel cations interact strongly with the Al₂O₃ support. Therefore, during subsequent
sulfidation, the metal cations are not sulfided at all and do not contribute to the HDS
activity. Alternatively, severe sulfidation brings the metal cations back to the surface
but lowers their dispersions (by sintering), and thus lowers their activities.

Carbon-supported cobalt and nickel sulfide catalysts, when carefully prepared, are
indeed highly active. The activity of a sulfided Co-Mo/C catalyst, per cobalt atom,
correlated much better with the estimated number of surface cobalt atoms in a
sulfided Co/C catalyst than with the estimated number of edge molybdenum atoms in
a MoS₂/C catalyst (97). The observation that the hydrogenation activity of Co-Mo (or
Ni-Mo) catalysts resembles that of sulfided cobalt or nickel catalysts and is different
from that of supported MoS₂ is further evidence that cobalt and nickel are the catalytic
sites rather than molybdenum. As previously mentioned, infrared (77) and Mo-edge
EXAFS data (74, 78) showed that molybdenum in Co-Mo and Ni-Mo catalysts is
fully coordinated and not accessible to reactant molecules. The molybdenum therefore
can not be catalytically active. Although attempts to show direct proof of nickel or
cobalt as the actual catalytically active sites gave both positive and negative results by EXAFS data of catalysts adsorbed with selenophene (analog of thiophene) (98-101), it seems clear that the first reaction takes place on cobalt but not on molybdenum. Recent discussions of the catalytic sites have concentrated on a combined action of nickel (or cobalt) and molybdenum (79, 80, 102-104). In HDS, a sulfur-containing molecule is supposed to adsorb on a site with a sulfur vacancy and react to give a hydrocarbon molecule and a sulfur atom. This sulfur atom occupies the vacancy and must be removed by hydrogen before the catalytic cycle can start again. It has been pointed out that a sulfur atom between a nickel (or cobalt) and a molybdenum atom is less strongly bonded than a sulfur atom between two molybdenum atoms. Therefore, it can be more easily removed. This would explain the promoter effect of nickel and cobalt on molybdenum in HDS. If HDN were to occur analogously to HDS, a nitrogen atom should be taken up by the metal sulfide catalyst particles and later be removed by hydrogen in the same way. This seems less likely than the equivalent sulfur uptake and removal in HDS, and it is suggested that the sites used in HDN are different from those used in HDS. As shown in the foregoing section, C—S bond breaking is kinetically important in HDS, whereas the hydrogenation of N-containing aromatic rings is kinetically the most important step in HDN.

Now the question is how the metal atoms are situated at the catalyst surface and what is the structure of the catalytic sites. Therefore, we first consider the edges of pure and promoted MoS₂. Raybaud et al. reported DFT calculations representing the edge surface of unpromoted (80) and promoted MoS₂ (104). Two types of edges are present in stoichiometric, hexagonal MoS₂ particles (Figure 1.13). The (1010) edge is terminated by molybdenum atoms, and is therefore called the molybdenum edge; in contrast, sulfur atoms terminate the (1010) edge (sulfur edge). The local density functional calculations showed that addition of sulfur atoms to the molybdenum edge is an exothermic process for sulfur coverages up to 50% (80). Sulfur removal from the sulfur edge is endothermic. At low H₂S pressures in the gas phase, and thus at low H₂S/H₂ partial pressure ratios, the molybdenum atoms at the Mo edge have four nearest sulfur neighbors (Figure 1.13). At a high H₂S/H₂ ratio (≥0.01), the molybde-
num atoms have six nearest sulfur neighbors (Figure 1.14), where the extra sulfur atoms are in bridging positions between molybdenum edge atoms.

Figure 1.13 Stoichiometric, hexagonally shaped MoS$_2$ particle with 25 Å diameter and 40% molybdenum edge atoms. Large balls are sulfur atoms, small molybdenum atoms.

The most stable position for the cobalt promoter atoms was calculated to be at the edge, substituting as it were for the molybdenum atoms (104). The promoter decreased the equilibrium sulfur coverage of the edge from 50 to 0-17% for Co/Mo edge = 1, and it weakened the sulfur–metal bond. In a naive ionic model of the bonding in metal sulfides, this result makes sense because the charge on Co$^{2+}$ is lower than that on Mo$^{4+}$. The coordination of cobalt at the edge is almost identical to that of the molybdenum edge atoms in Figures 1.13 and 1.14, apart from shorter Co–S than Mo–S distances.
Figure 1.14 Energy-optimized structure representing the molybdenum atoms at the Mo-terminated edge of MoS$_2$ particles at 50% sulfur coverage (83). Black balls are molybdenum atoms, grey sulfur; the distances are in Angstroms.

The DFT calculations showed that the edge structure of MoS$_2$ and promoted MoS$_2$ can be substantially different from that of ideally cleaved MoS$_2$ slabs. The surface can relax and take up sulfur atoms, as was predicted years ago by Farragher (105). The molybdenum (or nickel or cobalt) structures presented in Figures 1.13 and 1.14 may represent the actual sites during catalysis. It is more likely, however, that some reorganization occurs before catalysis takes place. For instance, one could envisage that the bridging edge sulfur atoms in Figure 1.14 shift to non-bridging on-top positions, thus creating a vacancy at the cobalt, nickel, or molybdenum atoms at the edge. A reacting molecule can then adsorb with its sulfur atom (in HDS) or nitrogen atom (in HDN) on this vacancy. Such a reorganized site may be the site where elimination of NH$_3$ from a nitrogen-containing molecule takes place. Probably the
more open sites, with two or more vacancies, are the sites where aromatic molecules are hydrogenated. At such sites, the aromatic ring can be $\pi$ bonded to the exposed molybdenum, cobalt, or nickel atoms at the molybdenum edge, as in Figure 1.13.

In most publications, no distinction is made between the structures of nickel and cobalt. It is commonly assumed that both are situated at identical positions at the $\text{MoS}_2$ edge, in the $\text{Ni-Mo-S}$ and $\text{Co-Mo-S}$ structures. The DFT calculations of Raybaud et al. (104) suggest that the sulfur coverage of these sites is lower in the nickel case than in the cobalt case. Future theoretical studies may indicate whether this difference is sufficient to explain why Ni-Mo is the better hydrogenation, thus HDN catalyst and Co-Mo the better HDS catalyst.

1.4 DEVELOPMENT OF NEW HDN CATALYSTS

All efforts devoted in the research of HDN aim at developing more active and selective catalysts to achieve better performance of the HDN process. Although new catalytic materials have been synthesised and tested, the conventional Ni-Mo(W)/Al$_2$O$_3$ catalysts are still by far the most widely used HDN catalysts. With increasing demands to process heavier feeds, research is focusing on additives, supports, and materials other than the sulfides of molybdenum, tungsten, nickel and cobalt.

1.4.1 Effect of Additives

Many additives have been studied, including phosphorus, fluorine, boron, chlorine, zinc, magnesium, lithium, sodium, potassium, calcium, as well as rare-earth metals. Among them, phosphorus and fluorine received the most attention. Results obtained from industry and model compounds studies demonstrated a substantial promotional effect of phosphorus on HDN (106-111) but only a weak effect on HDS (107, 109, 112). Therefore, phosphorus is most commonly used in Ni-Mo/Al$_2$O$_3$ HDN catalysts. A promotional effect of phosphorus was also observed in the HDS and
HDN of gas oil, doped with pyridine, catalyzed by a W/Al₂O₃ catalyst (113). Phosphorus weakens not only the interaction between oxidic nickel or cobalt and the support (114, 115), but also the interaction of molybdenum or tungsten and the support, thus leads to a lower dispersion (116) and higher degree of stacking of MoS₂ (117) and WS₂ (112, 118). Another explanation is that during HDN reaction, some molybdenum and nickel phosphides were formed on the catalyst surface (49, 119, 120), which showed higher HDN activity than the corresponding sulfides (121-123).

Fluorine has also been used commercially as a promoter in HDN. Traditionally, fluorine was used as an additive to increase the acidity of catalysts thus to promote the cracking activity. But model compound results demonstrated that fluorine rather than molybdenum or nickel accounts for the cracking (124). The promotional effect of fluorine on HDN has been observed with Ni-Mo/Al₂O₃ (125) and Ni-W/Al₂O₃ (126-129) catalysts. The addition of fluorine to the Al₂O₃ support leads also to a weaker interaction between oxidic molybdenum and the support, which, in turn, causes a lower dispersion (106), but it may change with fluorine content (125). The fluorine effect has also been explained by an increase of the sulfidability of tungsten-based catalysts (126, 127, 131). However, after a careful check with catalysts prepared via ammonium tetrathiotungstate by different techniques, Sun and Prins (132, 133) found that sulfidation is not the main cause for the promotional effect of fluorine. There must be other reasons. Van Veen et al. suggested that fluorine (106) as well as phosphorus (134) favors the formation of the type II Ni—Mo—S phase instead of the type I Ni—Mo—S phase.

1.4.2 Effect of Support

The support plays an important role in hydrotreating catalysis. In addition to the commonly used γ-Al₂O₃, many other supports may induce better activity and selectivity in HDN. They may help improve the dispersion of active phases, weaken the interaction between the active component and the support, thus lead to a higher sulfidation degree, prevent the formation of nickel and cobalt spinel, thus increase the usage of nickel and cobalt metals, adjust the acidity of catalysts to reduce the
deactivation by coke formation. An extensive review about the effect of support on the activity and selectivity on Ni-Mo and Co-Mo catalysts was presented by Luck (135). Silica-alumina and zeolites are used commercially in hydrocracking catalysts. Ni-Mo supported on silica-alumina is a better HDN catalyst than conventional Ni-Mo on γ-Al₂O₃ and is used in the first reactor of a two-stage hydrocracking process (2). Minderhoud and van Veen (136) reported that a silica-alumina-supported NiMo catalyst showed higher HDN, hydrocracking, and hydrodearomatization, but a lower HDS activity than its Al₂O₃-supported counterpart. A similar detrimental effect of silica-alumina on the HDS activity was reported for Co-Mo and Ni-W catalysts (137-139). Ni-Mo or Ni-W supported on a zeolite such as USY is a good bifunctional hydrocracking catalyst that can be used in the second hydrocracking reactor (140). A physical mixture of Ni-Mo/Al₂O₃ with ruthenium sulfide on zeolite Y had a higher HDN activity (141), which was ascribed to the better hydrogenation of the nitrogen-containing aromatic reactants by RuS₂ and the better cleavage of the aliphatic C—N bond by Ni-MoS₂ (142).

Carbon can be a good support regarding the interaction between metals and the support (96, 143-146). Ni-Mo supported on carbon is less likely to be poisoned by basic nitrogen-containing compounds during HDS (147) and more resistant to coke formation (146). The higher activity of carbon-supported catalysts is attributed to the weaker interaction between the active metals and the support (144). This weaker interaction can also lead to a fully sulfidation of tungsten catalysts (148). The main drawbacks of activated carbon as a support are its low density, thus a low activity per unit volume of catalysts, its microporosity, and its low mechanical strength. These drawbacks, however, can be solved by using carbon black materials (149) or carbon-covered alumina (150), which combines the structural advantage of alumina and the surface properties of carbon.

Titania-supported catalysts showed higher activity than its Al₂O₃-supported counterpart on the basis of per mole of metal in the catalyst, but not on the basis of per gram of catalyst (151, 152). This is because titania usually has a low surface area of about 50 m²/g, which is four time less than alumina. Efforts have been devoted to combine the high surface area of alumina and the chemical properties of titania, and not only a higher intrinsic activity but also a higher activity per gram of catalyst was
achieved (153-158). However, these improvements were not so substantial as with silica-alumina. Other supports, such as Al-pillared montmorillonite (159), magnesia (160), or silica-ceria (161) were also reported to work for sulfided.

1.4 A ROADMAP FOR THIS DISSERTATION

As mentioned above, aniline derivatives are almost always present in the HDN network of heterocyclic compounds and can be present with high amount in some diesel distillates. Therefore, nitrogen removal of anilines is important for understanding the mechanism of C—N bond scission. During the HDN of o-toluidine, several reactions are involved in the HDN process, such as C(sp$^3$)—N bond cleavage, C(sp$^2$)—N bond cleavage, and hydrogenation of aromatics and olefins. Therefore, we have chosen o-toluidine as the main model compound for our study. Fluorine has been widely used as a promoter for HDN, and a new fluorination method like in-situ fluorination after sulfidation of the catalysts has been used in commercial units. Silica-alumina is one of the supports other than alumina applied in HDN and hydrocracking catalysts. The aim of this dissertation is to study the effects of supports and in-situ fluorination on the performance of HDN and on catalyst structure by kinetics and catalyst characterization.

HDN of o-toluidine proceeds via two pathways: one is the direct C(sp$^2$)—N bond cleavage to form toluene, the other is the hydrogenation of the phenyl ring to methylcyclohexylamine, followed by elimination of NH$_3$ to give methylcyclohexene, which is then hydrogenated to methylcyclohexane. Therefore, in Chapter 2 we will discuss the effects of support and fluorination on the hydrogenation of cyclohexene, an analog to methylcyclohexene. Alumina-supported Ni-Mo is superior to its silica-alumina-supported counterpart for the hydrogenation of olefins, whereas silica-alumina exhibits a much higher acidity and higher isomerization activity for cyclohexene to methylcyclopentene. Therefore, the hydrogenation of methylcyclopentene is also studied in order to obtain a detailed kinetics on Ni-Mo catalysts supported on silica-alumina. Langmuir-Hinshelwood expressions for the hydrogenation and isomerization of cyclohexene is obtained on all catalysts.
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Chapter 3 deals with the C(sp³)–N bond cleavage from methylcyclohexylamine. A kinetics study is conducted to elucidate the effects of support and fluorination on the elimination step. The direct C(sp³)–N bond cleavage from methylcyclohexylamine forming methylcyclohexane exists as a reaction parallel to elimination and less influenced by the support and the in-situ fluorination. Higher HDN activity is obtained with the ASA-support and with the in-situ fluorination, mainly by promoting the elimination path, not the direct reaction.

In Chapter 4, the HDN of o-toluidine is studied, which contains the C(sp²)–N bond cleavage and hydrogenation of the phenyl ring. Special attention is paid to the excellent promotional effects of silica-alumina and fluorination on the hydrogenation and HDN activity. A simplified kinetics scheme for the HDN of o-toluidine is presented. The much lower concentration of methylcyclohexylamine during the HDN of o-toluidine is explained by „hidden kinetics“.

Related to the foregoing chapters concerning the performance for the hydrogenation of olefins, the HDN of methylcyclohexylamine and o-toluidine, the effects of support and fluorination on the hydrogenation of toluene is studied in Chapter 5. Different active sites involved in the HDN of aromatic nitrogen-containing compounds are discussed. We are trying to figure out the nature of active sites for different reactions occurred in HDN.

Characterization of the catalysts is presented in Chapter 6. The evolution of the active phase from oxidic to sulfidic state is shown for the two kinds of supports. MAS-NMR is used to determine the adsorption of molybdenum on the supports. Weaker interaction between molybdenum and nickel species in the oxidic state is confirmed by temperature-programmed reduction for the silica-alumina-supported Ni-Mo catalyst. Transmission electron microscopy shows the higher degree of stacking of MoS₂ in the catalyst.
1.6 REFERENCES


General Introduction


General Introduction

Chapter 2

Hydrogenation of Cyclohexene

2.1 ABSTRACT

The effect of fluorine on the hydrogenation of cyclohexene over sulfided Ni-Mo catalysts supported on Al₂O₃ and amorphous silica-alumina (ASA) was studied at 5.0 MPa and between 583 and 623 K. Fluorination was performed in situ after sulfidation of the catalyst. The hydrogenation of cyclohexene produced mainly cyclohexane over the Al₂O₃-supported catalysts. On the ASA-supported catalysts, large amounts of the isomerization products methylcyclopentene and methylcyclopentane were formed in addition to the hydrogenation product cyclohexane. At the applied partial pressure of cyclohexene between 16 and 100 kPa, the hydrogenation is between zero and first order in the partial pressure of cyclohexene on all catalysts. The Al₂O₃-supported catalysts showed higher conversions of cyclohexene than their ASA-supported counterparts. Fluorination mainly enhances the isomerization of cyclohexene to methylcyclopentene. Kinetic parameters were obtained by fitting the kinetic data with Langmuir-Hinshelwood rate equations in a wide range of conversions. The unchanged activation energy and heat of adsorption for the hydrogenation of cyclohexene to cyclohexane indicate that the active sites for the hydrogenation are not influenced by in-situ fluorination. The activation energy for the isomerization of cyclohexene remained constant after fluorination. In-situ fluorination introduces more acid sites for the isomerization reaction over both the Al₂O₃- and ASA-supported catalysts.

2.2 INTRODUCTION

Fluorine is widely used as an additive in hydroprocessing catalysts. Its role in Al₂O₃ catalysts and Al₂O₃-supported catalysts has been reviewed by Ghosh and Kydd (1). Recent studies have furthered the understanding of the effect of fluorine in
Hydrogenation of Cyclohexene

Hydrogenation of cyclohexene (2-10). Fluorination is conventionally performed by impregnating the support with a fluoride salt, like NH₄F (see e.g. refs. 3, 4). After NH₄F impregnation, drying, and calcination, molybdenum and nickel salts are introduced as usual by impregnation. After a subsequent calcination, the resulting materials are sulfided in a stream of H₂S in H₂. The disadvantage of this method is that the dispersion of MoS₂ and Ni may be different in fluorine-containing and fluorine-free Ni-Mo catalysts. Thus, it is difficult to compare their catalytic properties. 

In-situ fluorination, after preparation of the Ni-Mo catalyst in the sulfidic form has been described in patents (see e.g. refs. 11, 12), but not in the open literature. Because the metal sulfides are prepared before fluorination in this method, the catalyst dispersion might not be influenced by the fluorination. In-situ fluorination may thus allow us to investigate the role of fluorine without having to deal with the complication of different dispersions of the metal sulfide phase in fluorine-free and fluorine-containing catalysts.

Therefore, we studied the effect of in-situ fluorination of sulfided Ni-Mo catalysts supported on γ-Al₂O₃ and amorphous silica-alumina (ASA) on hydrodenitrogenation (HDN). By comparing the kinetic parameters of the different catalysts, the effect of fluorination on the catalytic activity, reaction network, and the active sites can be determined. As model compound we chose o-toluidine because its HDN network contains all the reactions (hydrogenation of the aromatic ring, elimination, hydrogenation of the resulting olefin) that are essential for HDN. During the HDN of o-toluidine, the first intermediate o-methylcyclohexylamine (MCHA) is only present in minor amounts since its rate of formation is slow and its rate of elimination to the second intermediate methylcyclohexene (MCHE) is fast. MCHE reacts relatively slowly to methylcyclohexane (MCH) and is therefore always present in large amount (13).

The hydrogenations of cyclic olefins and aromatics are important reaction steps in industrial hydroprocessing and are efficiently performed over sulfide catalysts like Ni-Mo and Ni-W supported on Al₂O₃ and ASA (14, 15). The hydrogenation of cyclic olefins plays an important role in hydrodenitrogenation (HDN) and hydrodesulfurization (HDS) reaction networks and occurs on a different site on sulfide catalysts as the C—N and C—S bond cleavage reactions (16). Many studies have been devoted
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to the kinetics and to the mechanism of the hydrogenation of olefins over metallic catalysts (see e.g. refs. 17-19). Little attention has been paid, however, to the catalytic chemistry and kinetics of hydrogenation reactions over sulfide catalysts.

In order to study the detailed mechanism of the HDN reaction, it is necessary to study the kinetics of the hydrogenation of MCHE separately. Because of the similarity of cyclohexene (CHE) and MCHE, we used CHE as the model compound.

2.3 EXPERIMENTAL

The catalysts, containing 4 wt% Ni and 13 wt% Mo, were prepared by pore volume impregnation of γ-Al₂O₃ (Condea) and ASA (Shell) with aqueous solution of ammonium molybdate tetrahydrate (Fluka) and nickel nitrate hexahydrate (Fluka), followed by drying at 393 K overnight and calcination at 773 K for 4 h in air after each impregnation step. The resulting NiMo/Al₂O₃ catalyst had a pore volume of 0.42 ml·g⁻¹ and a surface area of 155 m²·g⁻¹ as determined by BET nitrogen adsorption. The NiMo/ASA catalyst had a pore volume of 0.43 ml·g⁻¹ and a surface area of 265 m²·g⁻¹. An amount of 0.02-0.05 g catalyst diluted with 8 g SiC was loaded in a continuous-flow fix-bed microreactor. After loading in the reactor, the catalyst was dried for 2 h at 673 K and then sulfided with a mixture of 10% H₂S in H₂ at 1.0 MPa. Sulfidation started from ambient temperature with a slow increase in 14 h to 643 K; the temperature was then maintained at 643 K for 2 h.

The in-situ fluorination was performed after the sulfidation step. The pressure was first increased to that of the reaction condition (5.0 MPa) with the sulfiding gas. After cooling the reactor to 473 K, a solution of 0.26 wt% α-fluorotoluene (Fluka) in n-decane (Fluka) was dosed to the reactor with a syringe pump (Isco 100D). The temperature was slowly raised to 643 K and kept for 48 h, while the sulfiding and fluorination gas was flowing through the reactor. The fluorine contents in the thus fluorinated catalysts was about 1 wt% determined by X-ray fluorescence absorption.

After activation, the temperature was adjusted to 623 K, and the sulfiding and fluorination gas was switched to pure hydrogen. Then a solution of CHE, octane
(solvent), n-heptane (HEP, internal standard), and dimethyl disulfide (to generate H$_2$S \textit{in situ}) (all from Fluka, without further treatment) was fed to the reactor with a high-pressure syringe pump (Isco 500D). The temperature range studied was between 583 and 623 K. Partial pressures at the reactor inlet were P$_{CHE}$ = 16, 60, or 100 kPa, P$_{HEP}$ = 0.1 kPa, P$_{H_2S}$ = 17.5 kPa, P$_{H_2}$ = 4.8 MPa, and octane as the balance. The liquid feed rate was varied between 0.039 and 0.50 ml·min$^{-1}$.

The reaction products were analysed by on-line gas chromatography on a Varian Star 3400 CX instrument equipped with a 30 m DB-5MS fused silica capillary column and a flame ionization detector. Kinetic data were obtained by varying the weight time and reactant initial partial pressure after stabilization for 20 h. Weight time was defined as $\tau = m_C/n_{\text{feed, total}}$, where $m_C$ denotes the catalyst weight and $n_{\text{feed, total}}$ the total molar flow fed to the reactor. The hydrogen flow rates were always changed in proportion to the liquid flow rates. No diffusion and transport limitations were detected under the conditions studied. This allowed us to model the reaction with a Langmuir-Hinshelwood mechanism by non-linear numeric fitting of the data with the SCIENTIST$^\text{®}$ programme from MicroMath Inc. The goodness-of-fit is indicated by the Model Selection Criterion (MSC) and is defined by the formula:

$$\text{MSC} = \ln \left( \frac{\sum_{i=1}^{n} w_i (Y_{\text{obs}, i} - \bar{Y}_{\text{obs}})^2}{\sum_{i=1}^{n} w_i (Y_{\text{obs}, i} - Y_{\text{cal}, i})^2} \right) - \frac{2p}{n},$$

where $\bar{Y}_{\text{obs}}$ is the weighted mean of the observed data $Y_{\text{obs}, i}$, $Y_{\text{cal}, i}$ are the calculated data, $p$ and $n$ are the number of parameters and the measured points in the model, respectively, and $w_i$ are the weights applied to the points. All the weight factors were taken to be equal to 1 in our fitting. The larger the value of MSC, the better is the fit.
2.4 RESULTS

2.4.1 Hydrogenation of CHE

The reaction network for the hydrogenation of CHE is shown in Figure 2.1. Over the Ni-Mo/Al₂O₃ catalyst, the main product of the hydrogenation of CHE was cyclohexane (CH), as shown in the product distribution versus weight time plot in Figure 2.2a. Two types of skelet-isomerization products were observed, i.e. methylcyclopentene (MCPE) and methylcyclopentane (MCP) which is formed by successive hydrogenation of MCPE. The conversion to these isomerization products was always less than 1% over Ni-Mo/Al₂O₃, but reached 15% for the fluorinated Ni-Mo/Al₂O₃ catalyst (F-Ni-Mo/Al₂O₃). A trace of cyclohexanethiol was detected at the lowest temperature used (583 K) over the fluorinated catalysts, in agreement with Van Gestel et al. who observed up to 10% cyclohexanethiol at 553 K and 4.0 MPa over a sulfided Ni-Mo/Al₂O₃ catalyst (20).

![Reaction scheme for the hydrogenation of cyclohexene (CHE) to cyclohexane (CH) and for the isomerization of CHE to methylcyclopentene (MCPE) and its subsequent hydrogenation to methylcyclo-pentane (MCP) over sulfided Ni-Mo/Al₂O₃ and Ni-Mo/ASA catalysts.](image)

Figure 2.1 Reaction scheme for the hydrogenation of cyclohexene (CHE) to cyclohexane (CH) and for the isomerization of CHE to methylcyclopentene (MCPE) and its subsequent hydrogenation to methylcyclo-pentane (MCP) over sulfided Ni-Mo/Al₂O₃ and Ni-Mo/ASA catalysts.
More isomerization products, MCPEs and MCP, were formed over the Ni-Mo/ASA catalyst than over the Ni-Mo/Al$_2$O$_3$ catalyst. Substantial amounts of 3-MCPE and 4-MCPE were detected in addition to 1-MCPE and MCP. The product distribution versus weight time plot for the Ni-Mo/ASA catalyst shows clearly that MCPE is an intermediate and that MCP is the final product (Figure 2.2b). After fluorination of the ASA-supported catalyst, the yield of isomerization products was even higher, and attributed up to 75% of the products. No cracking products were observed under our reaction conditions.

To study the active sites for the hydrogenation of CHE, pure CHE without dimethyl disulfide was fed to the reactor as well. In the absence of H$_2$S the hydrogenation of CHE was much faster than in the presence of H$_2$S (Figure 2.3). The strong inhibition effect of H$_2$S on the olefin hydrogenation indicates that the active sites for the hydrogenation of CHE are surface sites with low sulfur coordination, i.e. vacancies on which H$_2$S as well as an olefin can competitively adsorb. This is in agreement with earlier findings (2, 5, 21-23). Further evidence was provided by Hubaut et al. (24) by reducing MoS$_2$/Al$_2$O$_3$ catalysts at different temperatures. They obtained the best activity for the hydrogenation of olefins when a large number of anionic vacancies were created.
Figure 2.2 Product distribution during the hydrogenation of cyclohexene (CHE) to cyclohexane (CH) and the isomerization to methycyclopentene (MCPE) and methycyclopentane (MCP) at 623 K over a) Ni-Mo/Al₂O₃ and b) Ni-Mo/ASA.
Figure 2.3 Inhibition of H$_2$S on the hydrogenation of cyclohexene (CHE) over Ni-Mo/ASA at 623 K.

The plot of $-\ln(1-x)$ versus weight time shows that the hydrogenation of CHE is not a first-order reaction on Ni-Mo/Al$_2$O$_3$ catalysts at the initial partial pressures of CHE that we applied. Not only at 583 K, but even at 623 K the plot is not linear (Figure 2.4a). The same holds for the fluorinated catalyst (not shown) and for the Ni-Mo/ASA catalysts (Figure 2.4b). It is clear that under our reaction conditions the reaction is between first and zero order.
Figure 2.4 Plot of $-\ln (1-x_{\text{CHE}})$ versus weight time for the hydrogenation of cyclohexene (CHE) over a) Ni-Mo/Al$_2$O$_3$ and b) Ni-Mo/ASA.
The effect of the support on the hydrogenation of CHE is shown in Figure 2.5. The Al$_2$O$_3$-supported Ni-Mo catalyst has a higher conversion (hydrogenation, as well as total) than the ASA-supported catalyst. On the other hand, the yield of isomerization products (MCPEs + MCP) is higher on the ASA-support catalyst owing to its higher acidity.

Figure 2.5 Conversion of cyclohexene to cyclohexane (CH) and methylcyclo-pentene (MCPE) and methylcyclopentane (MCP) over Ni-Mo/Al$_2$O$_3$ (dashed lines) and Ni-Mo/ASA (solid lines) at 603 K.

The *in-situ* fluorination was performed after the metal compounds had been transformed to their sulfided states. The fluorination precursor $o$-fluorotoluene can be decomposed to HF and toluene over sulfided catalysts, while the toluene is not further hydrogenated under these conditions (33). The HF formed acts as the real fluorination agent.
Fluorination has a positive effect on the conversion of CHE over the Al$_2$O$_3$-supported catalyst as well as over its ASA-supported counterparts. A detailed analysis of the products shows, however, that this positive effect is not due to an increased hydrogenation. For both series of catalysts, the conversion to CH stays constant, only the isomerization to MCPE and MCP increases substantially after fluorination (Figures 2.6a and 2.6b). This is due to the higher acidity introduced into the catalysts by fluorination, which promotes the isomerization reaction.
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Figure 2.6 Fluorination effect on the conversion of 100 kPa cyclohexene to cyclohexane (CH), methylcyclopentene (MCPE), and methylcyclo-pentane (MCP) at 623 K over a) Ni-Mo/Al₂O₃ and b) Ni-Mo/ASA. Full lines for fluorinated catalysts, dashed lines for fluorine-free catalysts.
2.4.2 Hydrogenation of 1-Methylcyclopentene

When MCPE and MCP are present in large amounts on ASA-supported catalysts, it was impossible to obtain a good fit of the CHE reaction when leaving out the contribution from MCPEs and MCP. Therefore, we studied the hydrogenation of 1-MCPE separately to complete the whole reaction network of the CHE reaction (Figure 2.1). The reaction conditions for the hydrogenation of 1-MCPE were the same as those for the hydrogenation of CHE. The hydrogenation of 1-MCPE was studied at two initial partial pressures of 1-MCPE, 16 and 100 kPa. Only the Ni-Mo/ASA and F-Ni-Mo/ASA catalysts were studied, because the formation of MCPE and MCP in the conversion of CHE was only substantial over these catalysts.

When 1-MCPE was fed over Ni-Mo/ASA, the saturated product MCP was formed readily (Figure 2.7). In addition, substantial amounts of 3-MCPE and 4-MCPE were detected, indicating that isomerization (double bond shift) took place on the ASA-supported catalysts. The amount of CHE formed by skeletal isomerization of the MCPEs plus the CH formed by the successive hydrogenation of CHE was always less than 5%, even on the fluorinated Ni-Mo/ASA catalyst, which has the highest acidity. No cracking products, with carbon number below 6, were formed up to 673 K. These results indicate that the reverse reaction from MCPE to CHE can be neglected in the CHE reaction network (Figure 2.1).
The fast disappearance of 1-MCPE and evolution of 3-MCPE and 4-MCPE at short weight time (cf. Figure 2.7) suggest that 3-MCPE and 4-MCPE are intermediates in the conversion of 1-MCPE. The reaction scheme for 1-MCPE conversion is shown in Figure 2.8.
Figure 2.8 Reaction scheme for the conversion of 1-methylcyclopentene (1-MCPE) to 3-methylcyclopentene (3-MCPE) and 4-methylcyclopentene (4-MCPE), and then to methylcyclopentane (MCP) over Ni-Mo/ASA catalysts.
The isomerization of 1-MCPE to 3-MCPE and 4-MCPE occurs on the acid sites, while the hydrogenation of MCPE takes place on the hydrogenation sites. This reaction scheme gives a good fit of the reaction data (Figure 2.9).

![Figure 2.9](image)

Figure 2.9 A fit of the conversion of 100 kPa 1-methylcyclopentene (1-MCPE) to 3-methylcyclopentene (3-MCPE) and 4-methylcyclopentene (4-MCPE), and then to methylcyclopentane (MCP), including the route from 1-MCPE directly to MCP over F-Ni-Mo/ASA at 623 K. Lines are the fitted results and points are the experimental data.

Fitting based on this scheme generated large uncertainties in the kinetic parameters, but clearly demonstrated that the transformation of 1-MCPE to 3-MCPE and 4-MCPE is very fast. The enthalpy of reaction from 1-MCPE to 3-MCPE and 4-MCPE is about 8 and 7.5 kJ·mol⁻¹, respectively (38), and 1-MCPE isomerizes quickly to 3- and 4-MCPE under our reaction conditions. Because we are more interested in the parameters for the hydrogenation than for the isomerization of 1-MCPE, we decided to lump the three MCPE isomers together when fitting the hydrogenation.
reaction of 1-MCPE. Thus, the fitting of the kinetics of the hydrogenation of 1-MCPE was based on the Langmuir-Hinshelwood Equation (1):

\[
\frac{dP_{\text{MCP}}}{d\tau} = -\frac{dP_{\text{MCPE}}}{d\tau} = \frac{k_{\text{HM}}K_{\text{HM}}P_{\text{MCPE}}}{1 + K_{\text{HM}}P_{\text{MCPE}}}
\]

(1)

where \(k_{\text{HM}}\) and \(K_{\text{HM}}\) are the rate and adsorption equilibrium constants for MCPE on the hydrogenation sites, respectively, and \(P_{\text{MCPE}}\) is the sum of the partial pressures of the three MCPE isomers. As an example of the goodness of the fit, the experimental results and the fits of the hydrogenation of 16 and 100 kPa MCPE to MCP over F-Ni-Mo/ASA at 623 K are presented in Figure 2.10. The resulting parameters for the hydrogenation of 1-MCPE are shown in Table 2.1.

Figure 2.10  Fit of the hydrogenation of the sum of all methylcyclopentenes (MCPE) to methylcyclopentane (MCP) over F-Ni-Mo/ASA at 623 K. Lines are the fitted results and points are the experimental data.
Table 2.1  Fitted Parameters for MCPE Hydrogenation over Ni-Mo/ASA

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>k_HM (kPa·mol·g(^{-1})·min(^{-1}))</th>
<th>K_HM (kPa(^{-1}))</th>
<th>MSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Mo/ASA</td>
<td>4.5 (0.6)</td>
<td>0.023 (0.010)</td>
<td>5.2</td>
</tr>
<tr>
<td>603 K</td>
<td>10 (1.3)</td>
<td>0.017 (0.005)</td>
<td>5.7</td>
</tr>
<tr>
<td>623 K</td>
<td>31 (6.8)</td>
<td>0.008 (0.003)</td>
<td>5.1</td>
</tr>
<tr>
<td>F-Ni-Mo/ASA</td>
<td>2.7 (0.4)</td>
<td>0.013 (0.004)</td>
<td>8.3</td>
</tr>
<tr>
<td>603 K</td>
<td>8.4 (0.3)</td>
<td>0.010 (0.003)</td>
<td>6.4</td>
</tr>
<tr>
<td>623 K</td>
<td>27 (9.6)</td>
<td>0.006 (0.003)</td>
<td>5.4</td>
</tr>
</tbody>
</table>

a—Standard deviation in brackets.

2.4.3 Kinetics of the Hydrogenation of CHE

Kinetic modelling for the hydrogenation of CHE was performed based on the reaction scheme shown in Figure 2.1. Since MCPE and MCP were hardly detected over the Al\(_2\)O\(_3\)-supported catalyst, we did not consider the isomerization for the kinetic modelling for this catalyst and only Equation (2) was used:

\[
\frac{dP_{CHE}}{d\tau} = \frac{dP_{CH\text{E}H}}{d\tau} = \frac{k_H K_H P_{CHE}}{1 + K_H P_{CHE}}
\]

For the F-Ni-Mo/Al\(_2\)O\(_3\) catalyst at 623 K and for the Ni-Mo/ASA and F-Ni-Mo/ASA catalysts at all temperatures, MCPE and MCP were present in substantial amounts and we had to use the whole network. The back reaction from MCPE to CHE was not taken into account, since the results presented in the foregoing section showed that this reaction could be neglected under our conditions. There are different kinds of sites for the hydrogenation (H-sites) and isomerization (A-sites) of CHE.
Since MCPE and CHE can be adsorbed on both kinds of sites, equations (3) to (6) are obtained:

\[\frac{-dP_{\text{CHE}}}{d\tau} = \frac{k_{\text{H}}K_{\text{H}}P_{\text{CHE}}}{1 + K_{\text{H}}P_{\text{CHE}} + K_{\text{HM}}P_{\text{MCPE}}} + \frac{k_{\text{A}}K_{\text{A}}P_{\text{CHE}}}{1 + K_{\text{A}}P_{\text{CHE}} + K_{\text{A}}P_{\text{MCPE}}} \quad (3)\]

\[\frac{dP_{\text{CH}}}{d\tau} = \frac{k_{\text{H}}K_{\text{H}}P_{\text{CHE}}}{1 + K_{\text{H}}P_{\text{CHE}} + K_{\text{HM}}P_{\text{MCPE}}} \quad (4)\]

\[\frac{dP_{\text{MCPE}}}{d\tau} = \frac{k_{\text{A}}K_{\text{A}}P_{\text{CHE}}}{1 + K_{\text{A}}P_{\text{CHE}} + K_{\text{A}}P_{\text{MCPE}}} - \frac{k_{\text{HM}}K_{\text{HM}}P_{\text{MCPE}}}{1 + K_{\text{H}}P_{\text{CHE}} + K_{\text{HM}}P_{\text{MCPE}}} \quad (5)\]

\[\frac{dP_{\text{MCP}}}{d\tau} = \frac{k_{\text{HM}}K_{\text{HM}}P_{\text{MCPE}}}{1 + K_{\text{H}}P_{\text{CHE}} + K_{\text{HM}}P_{\text{MCPE}}} \quad (6)\]

In these equations, \(k_{\text{H}}, k_{\text{A}},\) and \(k_{\text{HM}}\) are the reaction rate constants for the CHE hydrogenation, CHE isomerization, and MCPEs (sum of three isomers) hydrogenation, respectively, while \(K_{\text{H}}, K_{\text{A}},\) and \(K_{\text{HM}}\) are the corresponding adsorption equilibrium constants. \(P_{\text{CH}}, P_{\text{CHE}}, P_{\text{MCPE}},\) and \(P_{\text{MCP}}\) are the partial pressures of CH, CHE, MCPEs, and MCP, respectively. We assume that the adsorption equilibrium constants of all MCPEs and CHE on the isomerization sites are equal. A separate experiment showed no influence of adding CH on the conversion of CHE. This indicates that MCP and CH are very weakly adsorbed on the hydrogenation and isomerization sites compared with MCPE and CHE. The values of the rate and adsorption equilibrium constants (\(k_{\text{HM}}\) and \(K_{\text{HM}}\)), determined in the previous section from the hydrogenation of 1-MCPE, were used in the fitting of the CHE results on the ASA-supported catalysts. The hydrogen partial pressure was always kept constant in our system and was, therefore, combined with the rate constant \(k\).

All reactions were performed at a total pressure of 5.0 MPa and a partial pressure of hydrogen at the reactor inlet of 4.8 MPa. The kinetic data were obtained after 20 h on stream when the catalyst had reached a stable activity at 623 K. No deactivation was observed during the experiments. Three initial partial pressures of CHE were
used at each temperature with varying weight times in order to achieve a wide range of CHE conversions. More than four weight times (liquid flow rates range from 0.025 to 0.5 ml-min⁻¹) were tested at each CHE initial partial pressure. The temperatures studied were 583, 603, and 623 K. Based on the thus obtained data, kinetic modelling was performed using the SCIENTIST® program. Reaction rate constants and adsorption constants for different reaction steps on various sites were obtained from the fitting, and are presented in Tables 2.2 and 2.3. An example of the fit is shown in Figure 2.11.

Figure 2.11 Fit of the hydrogenation of 100 and 60 kPa cyclohexene (CHE) to cyclohexane (CH) and isomerization to methylcyclopentenes (MCPE) and methylcyclopentane (MCP) over Ni-Mo/ASA at 603 K. Lines are the fitted results and points are the experimental data.
### Table 2.2  Fitted Parameters for CHE Hydrogenation over Ni-Mo/Al₂O₃ \(^a\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(k_H) kPa·mol·g(^{-1})·min(^{-1})</th>
<th>(K_H) kPa(^{-1})</th>
<th>MSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Mo/Al₂O₃</td>
<td>23 (1.1)</td>
<td>0.024 (0.002)</td>
<td>5.9</td>
</tr>
<tr>
<td>583 K</td>
<td>80 (7.0)</td>
<td>0.008 (0.001)</td>
<td>6.3</td>
</tr>
<tr>
<td>603 K</td>
<td>296 (69)</td>
<td>0.003 (0.001)</td>
<td>6.1</td>
</tr>
<tr>
<td>F-Ni-Mo/Al₂O₃</td>
<td>20 (1.7)</td>
<td>0.032 (0.007)</td>
<td>4.7</td>
</tr>
<tr>
<td>583 K</td>
<td>59 (9.4)</td>
<td>0.014 (0.004)</td>
<td>4.6</td>
</tr>
<tr>
<td>623 K</td>
<td>248 (91)</td>
<td>0.004 (0.002)</td>
<td>4.6</td>
</tr>
</tbody>
</table>

\(^a\)—Standard deviation in brackets.

### Table 2.3  Fitted Parameters for CHE Reactions over Ni-Mo/ASA \(^a\)

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(k_H) kPa·mol·g(^{-1})·min(^{-1})</th>
<th>(K_H) kPa(^{-1})</th>
<th>(k_A) kPa·mol·g(^{-1})·min(^{-1})</th>
<th>(K_A) kPa(^{-1})</th>
<th>MSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Mo/ASA</td>
<td>4.5 (0.4)</td>
<td>0.035 (0.009)</td>
<td>0.9 (0.2)</td>
<td>0.070 (0.090)</td>
<td>5.5</td>
</tr>
<tr>
<td>583 K</td>
<td>12 (1.2)</td>
<td>0.026 (0.006)</td>
<td>28 (11)</td>
<td>0.003 (0.003)</td>
<td>5.1</td>
</tr>
<tr>
<td>623 K</td>
<td>36 (1.8)</td>
<td>0.001 (0.001)</td>
<td>221 (31)</td>
<td>0.001 (0.001)</td>
<td>4.8</td>
</tr>
<tr>
<td>F-Ni-Mo/ASA</td>
<td>3.7 (0.2)</td>
<td>0.110 (0.034)</td>
<td>1.3 (0.4)</td>
<td>0.050 (0.050)</td>
<td>5.4</td>
</tr>
<tr>
<td>583 K</td>
<td>9.5 (0.7)</td>
<td>0.060 (0.018)</td>
<td>56 (14)</td>
<td>0.002 (0.001)</td>
<td>4.9</td>
</tr>
<tr>
<td>623 K</td>
<td>29 (1.6)</td>
<td>0.015 (0.009)</td>
<td>301 (38)</td>
<td>0.001 (0.001)</td>
<td>4.5</td>
</tr>
</tbody>
</table>

\(^a\)—Standard deviation in brackets.
2.5 DISCUSSION

Our results show that at a CHE initial partial pressure between 16 and 100 kPa, a H₂S partial pressure of 17.5 kPa and between 583 and 623 K, the hydrogenation is between zero and first order in CHE over sulfided NiMo catalysts. In the literature, first order kinetics has been reported for the hydrogenation of olefins over sulfided catalysts, but these results were obtained at much lower olefin partial pressures than in our experiments (16, 25, 26). Nag et al. (27) observed that the hydrogenation of CHE is zero order with respect to CHE (up to 18 kPa), and first order to hydrogen (up to 80 kPa) on a sulfided Ni-W/Al₂O₃ catalyst at atmospheric pressure and between 523 and 623 K. Günther (28) studied the kinetics of olefin hydrogenation over a WS₂-NiS catalyst. He found that in the hydrogenation of a mixture of olefins with boiling point between 323 and 423 K, the reaction is pseudo first order with respect to olefins and that the reaction rate is practically independent of the hydrogen pressure in the range 5 to 30 MPa. This agrees with observations by Heinemann et al. in a study of the hydrogenation of heptenes on a sulfided Co-Mo catalyst (29).

The ASA-supported catalysts have a much lower hydrogenation activity for olefins (factor between 5 and 9) than their Al₂O₃-supported counterparts (cf. Figure 2.5). This lower hydrogenation activity is in contrast to our observation that ASA-supported catalysts have a higher HDN activity than their Al₂O₃-supported counterparts (30). The decreased olefin hydrogenation on the ASA-supported catalyst may be due to the difference between the two supports. Although the ASA support has a higher surface area than Al₂O₃, part of it consists of SiO₂ domains, and the other part of Al₂O₃ domains. It has been reported that Al₂O₃ adsorbs Mo species stronger than silica, regardless of the pH used during preparation (31, 32). Consequently, more Mo will be accommodated on the alumina domains than on silica domains during catalyst preparation on ASA. Our ASA support contains only 25% Al₂O₃, however, on which most of the Mo species will adsorb. This leads to a lower dispersion of the metal sulfides on the ASA support and thus to a lower hydrogenation activity of CHE, especially when the metal loading is relatively high.

A promoting effect of fluorine on the conversion of olefins has been reported for Al₂O₃-supported Ni-Mo and Co-Mo catalysts in which the fluorine was introduced by
ex-situ fluorination (2, 5, 7). Ramirez et al. (5) showed that fluorine increased the activity for the hydrogenation of olefin and ascribed the promotion to the increased catalyst dispersion by fluorine incorporation. Papadopoulou et al. (34, 35) concluded that, during the activation process, fluorine ions hinder the reduction and/or sulfidation of Mo$^{\text{VI}}$ and the sulfidation of Ni$^{\text{II}}$ supported ions of the Ni-Mo/Al$_2$O$_3$ catalyst after ex-situ fluorination. Other studies proved just the opposite, that fluorine promotes the degree of sulfidation (3, 36). Van Veen et al. (37) explained the role of fluorination by a transformation of the partly sulfided Ni—Mo—S phase to the more active, fully sulfided Ni—Mo—S phase. After breaking the Mo—O—Al linkage with the support, the Ni—Mo—S phase interacts with the support only via van der Waals forces. This may lead to increased stacking of the MoS$_2$ slabs and thus to a better accessibility of the sites for the adsorbent and to a higher activity.

Our results demonstrate that in-situ fluorination does not influence the hydrogenation of olefins at all. In all cases the yield of CH did not change upon fluorination (Figure 2.6). Only the acid-catalyzed isomerization of CHE to MCPE was promoted substantially on the Al$_2$O$_3$-supported catalyst and slightly on the ASA-supported catalyst. Table 2.2 shows that the fluorination does not influence the hydrogenation rate constants very much over Ni-Mo/Al$_2$O$_3$. The equilibrium adsorption constants of CHE on the hydrogenation sites seem to increase after fluorination, which would mean a stronger adsorption of CHE on the fluorinated catalyst. As a result, the amount of CH formed in the system remains unchanged (Figure 2.6a). More isomerization products are formed with the fluorinated catalyst, leading to a smaller MSC in the model fitting (Table 2.2).

The reaction rate constants for the hydrogenation of CHE to CH over the ASA-supported catalysts decrease slightly after fluorination, while the adsorption equilibrium constants of CHE on the hydrogenation sites seem to increase with fluorination (Table 2.3), as in the case of the Al$_2$O$_3$-supported catalysts. Although the parameters for the isomerization were obtained with large standard deviations, it is nevertheless clear that the rate constants increase after fluorination, while the adsorption equilibrium constants of CHE on the acid sites remain more or less the same.
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From the results obtained at different temperatures, one can calculate the temperature dependence of the reaction rate and adsorption equilibrium constants. The activation energies of the hydrogenation reaction were calculated according to the Arrhenius plot of \( \ln k \) versus \( 1/T \) \( (k = k_0 e^{-E/RT}) \) for the \( \text{Al}_2\text{O}_3 \)-supported catalysts (Figure 2.12). Similarly, the heats of adsorption were obtained from \( K = K_0 e^{-\Delta H/RT} \) (Figure 2.13). Table 2.4 shows that the fluorinated Ni-Mo/\( \text{Al}_2\text{O}_3 \) catalyst has the same activation energy for the hydrogenation of CHE to CH as the Ni-Mo/\( \text{Al}_2\text{O}_3 \) catalyst. Also the heat of adsorption was found to be the same for the fluorinated and unfluorinated Ni-Mo/\( \text{Al}_2\text{O}_3 \) catalysts. Similar results were found for the Ni-Mo/ASA and the fluorinated Ni-Mo/ASA catalysts (Table 2.4). The activation energy for the isomerization reaction was not changed after fluorination. This suggests that the surface sites of Ni-Mo/ASA were not modified for the isomerization reaction after fluorination. The improved activity can be attributed to an increase in the number of acid sites introduced by the \textit{in-situ} fluorination, which caused by the higher electronegativity of fluorine linked to aluminium. This in turn enhances the isomerization reaction.

![Figure 2.12 Plot of ln k versus 1/T for the hydrogenation of cyclohexene over Ni-Mo/\text{Al}_2\text{O}_3 and F-Ni-Mo/\text{Al}_2\text{O}_3.](image-url)
Figure 2.13  Plot of $\ln K_H$ versus $1/T$ for the hydrogenation of cyclohexene over Ni-Mo/Al₂O₃ and F-Ni-Mo/Al₂O₃.

Table 2.4  Temperature Dependence of $k$ and $K^a$

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>NiMo/Al₂O₃</th>
<th>F-NiMo/Al₂O₃</th>
<th>NiMo/ASA</th>
<th>F-NiMo/ASA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_H$, kJ·mol⁻¹</td>
<td>193 (15)</td>
<td>190 (15)</td>
<td>157 (15)</td>
<td>155 (11)</td>
</tr>
<tr>
<td>$k_{H_0}$, kPa·mol·g⁻¹·min⁻¹</td>
<td>$4\times10^{18}$</td>
<td>$2\times10^{18}$</td>
<td>$5\times10^{14}$</td>
<td>$3\times10^{14}$</td>
</tr>
<tr>
<td>$-\Delta H_H$, kJ·mol⁻¹</td>
<td>157 (37)</td>
<td>157 (37)</td>
<td>100 (44)</td>
<td>150 (28)</td>
</tr>
<tr>
<td>$K_{H_0}$, kPa⁻¹</td>
<td>$2\times10^{-16}$</td>
<td>$3\times10^{-16}$</td>
<td>$4\times10^{-11}$</td>
<td>$5\times10^{-15}$</td>
</tr>
<tr>
<td>$E_A$, kJ·mol⁻¹</td>
<td>—</td>
<td>—</td>
<td>416 (30)</td>
<td>413 (30)</td>
</tr>
<tr>
<td>$k_{A_0}$, kPa·mol·g⁻¹·min⁻¹</td>
<td>—</td>
<td>—</td>
<td>$2\times10^{37}$</td>
<td>$2\times10^{37}$</td>
</tr>
</tbody>
</table>

*a—Standard deviation in brackets.

Our results show that in-situ fluorination hardly influences the properties of the sulfided Ni-Mo catalysts for the hydrogenation of olefins. That the sites stay the same is not surprising, since it is known that fluorine is positioned on the support and not
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on the metal sulfide (36). The fluorine on the support improves the acidity of the catalyst, which explains that its main effect on the reaction of CHE is on the isomerization and not on the hydrogenation. The fact that the hydrogenation activity is not influenced means that the number of sites did not change by in-situ fluorination. Promoted MoS$_2$ catalysts consist of two-dimensional MoS$_2$ particles with nickel atoms decorating the edges. Vacancies on the edges are supposed to be the active sites. It is actually assumed that the hydrogenation of olefins on MoS$_2$ and promoted MoS$_2$ is not structure sensitive, meaning that any vacancy will be active and that vacancies on the top platelets of a stack of Ni-MoS$_2$ particles are not more active than vacancies on the underlying ones. In that case, the insensitivity of the olefin hydrogenation to the presence of fluorine indicates that the in-situ fluorination did not change the size of the Ni-MoS$_2$ particles. It is then impossible, however, to draw any conclusion about a change in the degree of stacking of the Ni-MoS$_2$ platelets.

2.6 CONCLUSIONS

The hydrogenation of CHE takes place on sulfur-deficient sites of sulfided Ni-Mo catalysts. The Al$_2$O$_3$-supported catalysts exhibit a higher activity than their ASA-supported counterparts, which is probably due to the better dispersion of Mo on the Al$_2$O$_3$ support. Over Ni-Mo/ASA catalysts, the reaction network is different from Ni-Mo/Al$_2$O$_3$ catalysts and more isomerization products are formed. Lower rate constants and higher adsorption equilibrium constants for the hydrogenation of CHE were found for the fluorinated catalysts resulting in an unchanged conversion of CHE to CH. The activation energy for the isomerization stays constant. In-situ fluorination introduced more acid sites for the isomerization reaction over both the Al$_2$O$_3$- and ASA-supported sulfided Ni-Mo catalysts.
2.7 REFERENCES

   references therein.
   (1997).
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   283 (1999).
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Hydrogenation of Cyclohexene

Chapter 3
Hydrodenitrogenation of Methylcyclohexylamine

3.1 ABSTRACT

The effects of in-situ fluorination on the hydrodenitrogenation of methylcyclohexylamine have been studied at 583 to 623 K and 5.0 MPa in a continuous microflow reactor over sulfided and fluorinated sulfided Ni-Mo catalysts supported on alumina and silica-alumina. The silica-alumina-supported catalysts exhibit higher hydrodenitrogenation activity than their alumina-supported counterparts. In-situ fluorination promotes the hydrodenitrogenation activity by mainly enhancing the elimination of NH₃ from methylcyclohexylamine, while less effect is observed for the direct reaction of methylcyclohexylamine to methylcyclohexane. Kinetic parameters were obtained for the reaction network by fitting the experimental results with Langmuir-Hinshelwood equations. After fluorination, the reaction rate constants of all catalysts increase substantially for the elimination step, but only slightly for the direct reaction. The activation energies and the heat of adsorption are about the same over all catalysts. This indicates that the intrinsic activity of the active sites is not influenced by the in-situ fluorination and by the support, only the number of active sites for hydrodenitrogenation is increased by a change of the dispersion of the active phase.

3.2 INTRODUCTION

Removal of organic nitrogen-containing compounds from oil fractions is of paramount importance in modern refining industries, especially when heavier feedstocks, coal-derived distillates, and oil shale, which contain more nitrogen compounds than conventional feedstocks, are processed (1). Conventionally fluorinated hydroprocessing catalysts are used in refineries in the hydrofining of
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lubricant oils (2-4). With increasing demand for hydrotreating, fluorine is widely studied as an additive in hydrotreating and hydrocracking catalysts containing Mo and W supported on alumina, silica-alumina and zeolites. As many patents on the use of fluorine as a promoter in hydrotreating and hydrocracking demonstrate (5-20), even if ways of introducing fluorine are different, some refineries are using fluorinated catalysts for hydrotreating and hydrocracking, at least in some regions of the world. Several studies have furthered the understanding of the effect of fluorine in hydrotreating catalysts (21-35), but only a few dealt with HDN (22, 23, 25-28). The enhancement of the HDN activity by fluorine addition has been assigned to higher acidity, better dispersion, and higher chemisorption capacity for hydrogen. In most cases, fluorination is performed by impregnating the support with a fluoride salt, like NH₄F (see e.g. refs. 21, 28). After NH₄F impregnation, drying, and calcination, molybdenum and nickel are introduced as usual by impregnation. After a subsequent calcination, the resulting materials are sulfided in a stream of H₂S in H₂. The disadvantage of this method is that the dispersion of the resulting MoS₂ and Ni sulfides may be different in the fluorine-containing and fluorine-free Ni-Mo catalysts. Conclusions about the effect of fluorine are then difficult to make. In-situ fluorination, after preparation of the Ni-Mo catalysts in their sulfidic form, has been described in patents (see e.g. refs. 36, 37), but not in the open literature. Because in this method the metal sulfides are prepared before fluorination, the catalyst dispersion might not be influenced by the fluorination and this might allow one to draw firm conclusions about the effect of fluorine in HDN.

In previous work, we found that in-situ fluorination has a positive effect on the isomerization and no effect on the hydrogenation of cyclohexene (38). In this work, the effect of in situ fluorination of the sulfide Ni-Mo catalysts supported on Al₂O₃ and amorphous silica-alumina (ASA) supports was studied. By comparing the kinetic parameters of the different catalysts, the effect of fluorination and the support on the activity and reaction network can be discussed.

Ortho-toluidine is a convenient nitrogen-containing model compound to study the kinetics of the hydrodenitrogenation (HDN) reaction (39-41). The HDN of toluidine takes mainly place via hydrogenation to methylcyclohexylamine (MCHA). This MCHA then reacts to methylcyclohexene (MCHE) and methylcyclohexane (MCH).
Only traces of MCHA are detected as primary reaction intermediates in the HDN of \textit{ortho}-toluidine because its rate of formation is much slower than its rate of further reaction. MCHA has a strong inhibition effect on the HDN of \textit{ortho}-toluidine.

C(\textit{sp}^3)-N bond scission in MCHA can take place in two ways. The direct elimination of NH$_3$ from MCHA occurs by the removal of a hydrogen atom at the $\beta$-C atom relative to the amino group, followed by olefin saturation (42, 43). The other is the direct cleavage of the C-N bond in MCHA, which leads to MCH (39, 43-45). This complicates the kinetic modelling of the HDN network of \textit{ortho}-toluidine and makes it difficult to obtain reliable kinetic parameters. Therefore, it is necessary to study the HDN of MCHA first.

3.3 EXPERIMENTAL

The catalysts containing 4 wt\% Ni and 13 wt\% Mo were prepared by pore volume impregnation of the supports, $\gamma$-Al$_2$O$_3$ (Condea) and ASA containing 25 wt\% Al$_2$O$_3$ (prepared by the sol-gel method), with aqueous solutions of ammonium molybdate tetrahydrate (Fluka) and nickel nitrate hexahydrate (Fluka), followed by drying at 393 K overnight and calcination at 773 K in air after each impregnation step. The Ni-Mo/Al$_2$O$_3$ catalyst has a pore volume of 0.42 ml\cdot g$^{-1}$, a surface area of 155 m$^2\cdot$g$^{-1}$ by BET nitrogen adsorption. The Ni-Mo/ASA catalyst has a pore volume of 0.43 ml\cdot g$^{-1}$ and a surface area of 265 m$^2\cdot$g$^{-1}$. The HDN of MCHA was carried out over 0.02-0.05 g \textit{in-situ} fluorinated sulfided Ni-Mo/Al$_2$O$_3$ and Ni-Mo/ASA catalysts diluted with 8 g SiC in a high-pressure micro-reactor. The catalyst was dried for 2 h at 673 K and then sulfided with a mixture of 10\% H$_2$S in H$_2$ at 1.0 MPa. Sulfidation started from ambient temperature with a slow increase in 14 h to 643 K and maintained for 2 h.

\textit{In-situ} fluorination was performed after the sulfidation step. The pressure was first increased to reaction condition (5.0 MPa) with the sulfiding gas. When the temperature of the reactor had decreased to 473 K, a solution of 0.26 wt\% \textit{ortho}-fluorotoluene in octane was dosed to the reactor at a rate of 0.0016 ml/min with a syringe pump. The temperature was slowly raised to 643 K and kept for 48 h (total
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fluorination duration 55 h). The sulfiding gas was flowing through the reactor throughout the fluorination process. The final fluorine content on the catalysts was about 1 wt% as determined by X-ray fluorescence analysis.

After activation, the temperature was adjusted to 623 K, and the sulfiding gas was replaced by pure hydrogen. A solution of MCHA, cyclohexene (CHE), octane (solvent), n-heptane (internal standard), and dimethyldisulfide (to generate H$_2$S in situ) was fed to the reactor. Partial pressures at the reactor inlet were $P_{\text{MCHA}} = 2, 4, 14, 24, \text{and } 36 \text{ kPa}$, $P_{\text{CHE}} = 4 \text{ kPa}$, $P_{\text{H}_2\text{S}} = 17.5 \text{ kPa}$, $P_{\text{H}_2} = 4.8 \text{ MPa}$, and octane as the balance. CHE was added to the reactants in order to monitor the hydrogenation of olefin in the presence of MCHA. Preliminary experiments showed that CHE had no influence on the HDN of MCHA.

The reaction products were analysed by on-line gas chromatography (Varian Star 3400CX equipped with a 30 m DB-5MS fused silica capillary column and a flame ionization detector). All the kinetic data were obtained by varying weight time and reactant initial partial pressure after stabilization for 20 h on stream. Weight time was defined as $\tau = m_C/n_{\text{feed, total}}$, where $m_C$ denotes the catalyst weight and $n_{\text{feed, total}}$ the total molar flow fed to the reactor. The hydrogen flow rate was always changed in proportion to the liquid flow rate. No diffusion and transport limitations were detected under the conditions studied. This allowed us to model the reaction with a Langmuir-Hinshelwood mechanism assuming adsorption equilibrium for the HDN compounds. The program used for the non-linear numeric fitting was SCIENTIST® version 2.0 by MicroMath Inc.

3.4 RESULTS AND DISCUSSION

3.4.1 HDN Reaction Scheme of MCHA

The HDN network of MCHA is shown in Figure 3.1. Even though the HDN of amines is quite simple, there are still two reaction pathways: the elimination of NH$_3$ to MCHE, followed by hydrogenation to MCH (path 1), and the direct production of MCH (path 2). This direct reaction is generally considered to occur by exchange of
the NH₂ group by an SH group, followed by fast hydrogenolysis of the resulting ortho-methycyclohexylthiol to MCH and H₂S (39, 43-47). For simplicity, we will call this reaction the direct reaction.

Figure 3.1 Hydrodenitrogenation reaction network for methylcyclohexylamine (MCHA) over Ni-Mo/Al₂O₃ and Ni-Mo/ASA.

The product distribution versus weight time plot shows that MCHE and MCH are both formed at small weight time and thus are primary products. Nevertheless, MCHE reaches a maximum and the MCH curve bends upwards at larger weight time, indicating that MCH is also a product of MCHE (Figures 3.2a and 3.2b). A trace of the isomerization product ethylcyclopentane (ECP) was formed at high temperature and longer weight time. The formation of ECP was about equally low over Ni-Mo/ASA and fluorinated catalysts as over Ni-Mo/Al₂O₃. MCHE is present in the product with a relatively high concentration until a very high MCHA conversion is reached. This indicates a strong inhibition of MCHA on the hydrogenation of MCHE by competitive adsorption, which is confirmed by a comparison of the results obtained with a mixed feed of MCHA and CHE and with a pure CHE feed (Figure
3.3). With MCHA in the reaction mixture, isomerization of CHE to methylcyclopentane (MCP) did not take place.

Figure 3.2 Product distribution during the hydrodenitrogenation of 24 kPa methylcyclohexylamine (MCHA) at 623 K over a) Ni-Mo/Al₂O₃ and b) Ni-Mo/ASA catalysts.
Figure 3.3 Inhibition of methylcyclohexylamine (MCHA) on the hydrogenation of cyclohexene (CHE) at 623 K over Ni-Mo/Al₂O₃.

3.4.2 Support Effect

The conversions of MCHA and CHE over the two catalyst systems show that the ASA-supported catalyst has a slightly higher HDN activity and lower olefin hydrogenation activity than its Al₂O₃-supported counterpart (Figure 3.4). The latter conclusion is in agreement with our earlier findings of the effect of the support on the hydrogenation of pure CHE (38). Compared with Al₂O₃-supported catalysts, more MCHE is present in the products over ASA-supported catalysts, while the amount of MCH is almost the same (Figure 3.5a). The same holds for the fluorinated catalysts (Figure 3.5b). This means that the ASA support (with higher acidity) favors the elimination pathway of the HDN network. The direct reaction path either remains almost unchanged, or the ASA-supported catalyst has a lower hydrogenation activity than the Al₂O₃-supported catalyst. We will come back to this point when discussing
the kinetic results. The MCHE formed by the elimination path is hydrogenated relatively slowly, owing to the strong inhibition of MCHA in the system. Thus, the MCHE yield reaches high values. The formation of ECP is substantial only when almost all the MCHA has been converted.

Figure 3.4 Effect of the support on the hydrodenitrogenation of 14 kPa methylcyclohexylamine (MCHA) and the hydrogenation of 4 kPa cyclo-hexene (CHE) at 623 K over Ni-Mo/Al₂O₃ (full lines) and Ni-Mo/ASA (dashed lines).

Minderhoud and van Veen (48) reported that an ASA-supported Ni-Mo catalyst showed higher HDN, hydrocracking, and hydrodearomatization, but a lower hydrodesulfurization (HDS) activity than its Al₂O₃-supported counterpart. This indicates that the active centres for HDS and HDN are different. A similar detrimental effect of silica-alumina on the HDS activity was reported for Co-Mo and Ni-W catalysts (49-51). It was explained by the poorer dispersion of the molybdenum and tungsten phases on the silica-alumina support. Al₂O₃ and Al₂O₃-rich supports interact strongly with Mo or W oxide species due to the abundance of basic OH groups. SiO₂ and SiO₂-rich supports, on the other hand, promote agglomeration of Mo or W oxides because of a weak interaction (52). This is probably the case for our ASA support
which contains 75% SiO₂. However, an enhancement of the HDS activity over Ni-Mo/ASA was reported recently when 4-methyl, 6-ethyl dibenzothiophene was used as a model compound (53).
3.4.3 Fluorination Effect

After fluorination, the total HDN conversion of MCHA increases slightly, while the conversion of CHE hydrogenation stays constant (Figures 3.6a and 3.6b). This indicates that the hydrogenation of CHE occurs on a different site as the HDN of MCHA. A stronger promotion effect was observed with the ASA-supported catalysts than with their Al₂O₃-supported counterparts. The MCH and MCHE yields with and without fluorination are shown in Figures 3.7a and 3.7b. The MCHE yield increased after fluorination while the MCH yield was not changed substantially in the HDN of MCHA over both the Al₂O₃- and ASA-supported catalysts. This indicates that in-situ fluorination mainly promotes the elimination path in the HDN of MCHA (Figure 3.1).

Benitez et al. (22, 23) attributed the enhanced HDN activity of their ex-situ fluorinated W/Al₂O₃ and Ni-W/Al₂O₃ catalysts to changes in the morphology of the WS₂ crystallites (higher stackings and larger sizes), a higher surface acidity, and also a better sulfidation of the W oxidic phase which is promoted by the addition of fluoride to the alumina support, previously to the incorporation of the W precursor. Lewandowski and Sarbak studied the effect of fluorine of the hydrofining activity for a coal liquid over a Ni-Mo/Al₂O₃ catalyst (28). They concluded that the enhanced HDN activity was caused by the higher acidity (mainly the Brønsted acidity) induced by fluoride addition to the alumina support which promotes the C-N bond cleavage and also the resistance to coking. Van Veen et al. (25) explained the role of fluorination by a transformation of the partly sulfided Ni—Mo—S phase to the more active, fully sulfided Ni—Mo—S phase. After breaking the Mo-O-Al linkages with the support, the Ni—Mo—S phase interacts with the support only via van der Waals forces. This may lead to increased stacking of the MoS₂ slabs and thus to a better accessibility of the sites for the adsorbent and to a higher HDN activity.

Even though in all cases ECP was present in a small amount only, an increase after fluorination could be observed. This is mainly caused by the increase in acidity by fluorination which enhances the isomerization activity of the catalysts, as reported for the e-situ fluorination (27, 33, 54, 55).
Figure 3.6 Effect of fluorination on the hydronitrogenation of 14 kPa methylcyclohexylamine (MCHA) and the hydrogenation of 4 kPa cyclohexene (CHE) at 623 K over a) Ni-Mo/Al₂O₃ and b) Ni-Mo/ASA catalysts. Full lines for F-containing catalysts, dashed lines for F-free catalysts.
Figure 3.7 Effect of fluorination on the yields of methylcyclohexene (MCHE) and methylecyclohexane (MCH) during the hydrodenitrogenation of 14 kPa methylecyclohexylamine (MCHA) at 623 K over a) Ni-Mo/Al₂O₃ and b) Ni-Mo/ASA catalysts. Full lines for F-containing catalysts, dashed lines for F-free catalysts.
When using fluorinated catalysts, fluorine leaching takes place, but is not severe. For instance, a catalyst that originally contained 4.5 wt% of F, retained 2.5 wt% of F after one-year on-stream (8000 h) in a hydrotreating unit for diesel feed (private communication). At the same time, a corrosive test performed inside the reactor and in the downstream pipelines showed no influence on the materials of the reactor and pipelines. Furthermore, the possible effect of the leached fluorine on downstream catalysts like zeolites was negligible under severe conditions. For that reason, we did not measure the fluorine content after reaction. As judged from the above mentioned industrial case, we believe that within our three week experiments there is no substantial loss of fluorine and, thus, no influence on the performance of the catalysts.

3.4.4 Kinetics of the HDN of MCHA

Kinetic modelling was based on the reaction scheme shown in Figure 3.1. Since ECP was only detected at low concentrations at high MCHA conversion, it was not considered in the kinetic modelling. There are two different kinds of sites for the HDN of MCHA and hydrogenation of CHE. Assuming that the hydrogenation of MCHE takes place on the same sites as for CHE, which are different from the sites for the HDN of MCHA, we obtain the following Langmuir-Hinshelwood rate equations:

\[ \frac{dP_{\text{MCHE}}}{d\tau} = \frac{k_1 K_{\text{MCHE}} P_{\text{MCHE}}}{1 + K_{\text{MCHE}} P_{\text{MCHE}}} \]  \hspace{1cm} (1)

\[ \frac{dP_{\text{MCHAMCHA}}}{d\tau} = \frac{(k_1 + k_2) K_{\text{MCHAMCHA}} P_{\text{MCHAMCHA}}}{1 + K_{\text{MCHAMCHA}} P_{\text{MCHAMCHA}}} \]  \hspace{1cm} (2)

\[ \frac{dP_{\text{MCHE}}}{d\tau} = \frac{k_2 K_{\text{MCHE}} P_{\text{MCHE}}}{1 + K_{\text{MCHE}} P_{\text{MCHE}}} + \frac{k_3 K_{\text{MCHE}} P_{\text{MCHE}}}{1 + K_{\text{MCHE}} P_{\text{MCHE}}} \]  \hspace{1cm} (3)

where \( k_1 \) and \( k_2 \) are the reaction rate constants for the elimination and the direct reaction pathways, respectively, and \( k_3 \) is the reaction rate constant for the
hydrogenation of MCHE to MCH. $K_i$ and $K'_i$ are the adsorption equilibrium constants of compound $i$ on the HDN sites and hydrogenation sites, respectively. Here, we assume that the adsorption constants for the elimination and the direct reaction are the same since there are no significant changes in the selectivity of MCHE when changing the initial partial pressure of MCHA. The values of the rate and adsorption equilibrium constants for the hydrogenation of MCHE ($k_3$ and $K_{MCHE}$) were taken from the results of CHE hydrogenation in our previous study (38). The adsorption equilibrium constant of NH$_3$ was assumed to be zero, because it is one magnitude smaller than that of MCHA (56, 57).

All the reactions were performed at a total pressure of 5.0 MPa and a partial pressure of hydrogen at the reactor inlet of 4.8 MPa. All the kinetic data were obtained after 20 h on stream when the catalyst was stabilized at 623 K. No deactivation was observed during the experiments. Five initial partial pressures of MCHA were used at each temperature, and at each MCHA initial partial pressure more than five weight-times were tested. The temperatures studied were 583, 603, and 623 K. Based on the thus obtained data, kinetic modelling was performed with the SCIENTIST® program. The initial values for $k_1$ and $k_2$ were estimated from the initial conversions of MCHA at 36 kPa to MCHE and MCH, because at that high MCHA partial pressure the reactions can be approximated as being zero order and at low conversion the hydrogenation of MCHE can be neglected. Reaction rate constants for the two reaction pathways and adsorption equilibrium constants of MCHA on the HDN sites were obtained from the fitting of all data obtained at five initial partial pressures of MCHA, more than five weight times, and three temperatures as indicated above. The results are presented in Tables 3.1 and 3.2. Numbers in brackets indicate the standard deviations of the fitted parameters and MSC is the model selection criterion. The larger the value of MSC is, the better is the fit. The MSC is defined by the formula:

$$MSC = \ln \left( \frac{\sum_{i=1}^{n} w_i (Y_{o, i} - \bar{Y}_{o, i})^2}{\sum_{i=1}^{n} w_i (Y_{o, i} - Y_{c, i})^2} \right) - \frac{2p}{n}$$
where $\bar{Y}_{obs}$ is the weighted mean of the observed data $Y_{obs,j}$, $Y_{cal,j}$ is the calculated data, $p$ and $n$ are the number of parameters and measured points in the model, respectively, and $w_j$ is the weight factors applied to the points. All weight factors were put equal to one.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$K_{MCHA}$</th>
<th>$K'_{MCHA}$</th>
<th>MSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>583 K</td>
<td>0.27 (0.01)</td>
<td>0.12 (0.01)</td>
<td>0.45 (0.05)</td>
<td>8.7 (3.8)</td>
<td>7.9</td>
</tr>
<tr>
<td>603 K</td>
<td>0.94 (0.02)</td>
<td>0.22 (0.01)</td>
<td>0.24 (0.02)</td>
<td>1.2 (0.1)</td>
<td>7.3</td>
</tr>
<tr>
<td>623 K</td>
<td>3.15 (0.08)</td>
<td>0.69 (0.05)</td>
<td>0.17 (0.01)</td>
<td>0.9 (0.1)</td>
<td>6.2</td>
</tr>
<tr>
<td>F-NiMo/Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>583K</td>
<td>0.37 (0.01)</td>
<td>0.13 (0.01)</td>
<td>0.38 (0.04)</td>
<td>9.4 (2.2)</td>
<td>7.4</td>
</tr>
<tr>
<td>603 K</td>
<td>1.24 (0.03)</td>
<td>0.27 (0.02)</td>
<td>0.23 (0.03)</td>
<td>2.4 (0.3)</td>
<td>7.0</td>
</tr>
<tr>
<td>623 K</td>
<td>3.88 (0.12)</td>
<td>0.78 (0.05)</td>
<td>0.14 (0.01)</td>
<td>1.2 (0.2)</td>
<td>6.0</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$K_{MCHA}$</th>
<th>$K'_{MCHA}$</th>
<th>MSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMo/ASA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>583 K</td>
<td>0.33 (0.01)</td>
<td>0.08 (0.01)</td>
<td>0.60 (0.07)</td>
<td>8 (20)</td>
<td>8.3</td>
</tr>
<tr>
<td>603 K</td>
<td>1.20 (0.01)</td>
<td>0.16 (0.03)</td>
<td>0.39 (0.04)</td>
<td>0.7 (0.3)</td>
<td>7.2</td>
</tr>
<tr>
<td>623 K</td>
<td>3.85 (0.20)</td>
<td>0.39 (0.04)</td>
<td>0.26 (0.04)</td>
<td>0.1 (0.5)</td>
<td>6.2</td>
</tr>
<tr>
<td>F-NiMo/ASA</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>583 K</td>
<td>0.49 (0.01)</td>
<td>0.10 (0.01)</td>
<td>0.35 (0.02)</td>
<td>12 (4)</td>
<td>8.8</td>
</tr>
<tr>
<td>603 K</td>
<td>1.64 (0.01)</td>
<td>0.24 (0.02)</td>
<td>0.27 (0.01)</td>
<td>7 (2)</td>
<td>8.3</td>
</tr>
<tr>
<td>623 K</td>
<td>5.52 (0.17)</td>
<td>0.50 (0.09)</td>
<td>0.16 (0.02)</td>
<td>0.7 (0.1)</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Illustrative fits are shown in Figure 3.8. It is clear that MCHA has a strong inhibition on the hydrogenation of MCHE. The maximum of the MCHE intermediate is reached at different weight times at different MCHA partial pressures. When the conversion of MCHA is below 40%, the MCH yield varies linearly with weight time. Only when most of the MCHA has reacted away, an increase in the production rate of MCH is observed.

Figure 3.9 An illustration of the fit for the hydrodenitrogenation of 14, 24, and 36 kPa methylecyclohexylamine over F-Ni-Mo/ASA at 623 K. Lines are the fitted curves, points are the experimental data.
Over the Al₂O₃-supported catalysts, at all three temperatures studied, the HDN reaction rate constants for the elimination increased by about 30% after fluorination, while those for the direct reaction increased less (Table 3.1). The adsorption equilibrium constants of MCHA remained almost unchanged by fluorination.

For the ASA-supported catalysts, the HDN rate constants for the elimination increased by more than 40% after fluorination, while those for the direct reaction increased less (see Table 3.2). The ratio k₁/k₂ for the ASA-supported catalysts (with values between 4 to 11) was higher than that for the Al₂O₃-supported catalysts (between 2 to 5) at all temperatures. The adsorption equilibrium constants of MCHA on the HDN sites decreased after fluorination. Over all catalysts, the adsorption equilibrium constants of MCHA on the hydrogenation of MCHE are relative large compared with those on the HDN of MCHA itself, often with large errors. Because the majority of the kinetic data was obtained at MCHA conversion below 40%, the hydrogenation of MCHE to MCH plays only a minor role. As a consequence, uncertainties in k₃ in equations (2) and (3) and K'MCHA have almost no influence on the parameters k₁, k₂, and KMCHA, which are the main parameters of interest in our study.

With the Al₂O₃-supported as well as the ASA-supported catalysts, a weaker effect of fluorination was observed for the direct reaction than for the other reaction. This is caused by the different mechanisms of the two reactions. The direct reaction takes place via nucleophilic substitution of NH₂ by SH followed by C–S bond hydrogenolysis (46, 47). This is different from the other reaction via the β-Hofmann elimination of NH₃ from MCHA. The former reaction is mainly determined by the partial pressure of H₂S in the reactor and not by the fluorination.

The activation energies of the HDN reaction paths were calculated from the Arrhenius plots of lnk versus 1/T (Figure 3.9 and Table 3.3). Within the uncertainties of the measurements, the activation energies for path 1 and path 2 were independent of support and fluorination: about 180 kJ·mol⁻¹ for the elimination path and 130 kJ·mol⁻¹ for the direct path. This indicates that the catalytic sites on which MCHA react are the same for the Al₂O₃-supported as well as for the ASA-supported catalysts and are not influenced by the presence of fluorine. This confirms the general belief that fluorine is located on the support and not on the metal sulfide. The only effect of support and fluorine is to change the dispersion of the NiMo sulfide.
Fluorination as well as changing the support from Al₂O₃ to ASA increases the number of sites active in the HDN of MCHA. Fluorine and the ASA support have about the same positive influence on the elimination path (cf. Tables 3.1 and 3.2), while Ni-Mo on fluorinated ASA showed the largest k₁ values.

Figure 3.9 Plot of ln k versus 1/T for the hydrodenitrogenation of methylcyclohexylamine over Ni-Mo/ASA catalysts. Full lines for F-free catalysts, dashed lines for F-containing catalysts.

Table 3.3 Activation Energies and Pre-exponential Factors for the HDN of MCHA

<table>
<thead>
<tr>
<th></th>
<th>NiMo/Al₂O₃</th>
<th>F-NiMo/Al₂O₃</th>
<th>NiMo/ASA</th>
<th>F-NiMo/ASA</th>
</tr>
</thead>
<tbody>
<tr>
<td>E, kJ·mol⁻¹</td>
<td>Path 1</td>
<td>186 (8)</td>
<td>177 (6)</td>
<td>186 (6)</td>
</tr>
<tr>
<td></td>
<td>Path 2</td>
<td>132 (12)</td>
<td>135 (14)</td>
<td>118 (14)</td>
</tr>
<tr>
<td>A, kPa·mol·g⁻¹·min⁻¹</td>
<td>Path 1</td>
<td>1×10¹⁶</td>
<td>1×10¹⁶</td>
<td>1×10¹⁶</td>
</tr>
<tr>
<td></td>
<td>Path 2</td>
<td>3×10⁹</td>
<td>9×10⁹</td>
<td>3×10⁹</td>
</tr>
</tbody>
</table>
Like the activation energies, the heats of adsorption can be obtained from an Arrhenius plot of $\ln K$ versus $1/T$ (Figure 3.10 and Table 3.4). The heat of adsorption of MCHA on the catalytic sites for HDN over all catalysts are about the same, 60 kJ·mol$^{-1}$. This further confirms that the active sites for HDN of MCHA are not influenced by fluorination and the support, only the number of active sites increases after fluorination and with ASA support.

![Figure 3.10](image)

**Figure 3.10** Plot of $\ln K$ versus $1/T$ for the hydrodenitrogenation of methylcyclohexylamine over Ni-Mo/ASA catalysts. Full lines for F-free catalysts, dashed lines for F-containing catalysts.

**Table 3.4 Heat of Adsorption**

<table>
<thead>
<tr>
<th></th>
<th>NiMo/Al$_2$O$_3$</th>
<th>F-NiMo/Al$_2$O$_3$</th>
<th>NiMo/ASA</th>
<th>F-NiMo/ASA</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-\Delta H_{\text{ad}}$, kJ·mol$^{-1}$</td>
<td>77 (7)</td>
<td>75 (8)</td>
<td>63 (7)</td>
<td>59 (6)</td>
</tr>
<tr>
<td>$K_0$, kPa$^{-1}$</td>
<td>$6\times10^{-8}$</td>
<td>$7\times10^{-8}$</td>
<td>$1\times10^{-6}$</td>
<td>$2\times10^{-6}$</td>
</tr>
</tbody>
</table>
3.5 CONCLUSIONS

The HDN of MCHA proceeds via two pathways, the elimination of NH$_3$ followed by the hydrogenation of MCHE to MCH and the direct reaction to MCH. When a certain amount of MCHA is present in the reactor, the HDN of MCHA can be considered as parallel reactions. Fitting of the kinetic data with Langmuir-Hinshelwood rate equations showed that the higher HDN activity over ASA-supported Ni-Mo catalyst compared to the Al$_2$O$_3$-supported counterpart is due to the faster elimination of NH$_3$. The ASA support contributed nothing to the direct reaction.

The promoting effect of fluorination is stronger for the elimination step than for the direct reaction. The promotion effect of fluorination arises from the increase of the number of active sites for the HDN of MCHA, while the intrinsic activity remains the same.
3.6 REFERENCES

Hydrodenitrogenation of Methylcyclohexylamine


Chapter 4
Hydrodenitrogenation of ortho-Toluidine

4.1 ABSTRACT

The kinetics of the hydrodenitrogenation of o-toluidine has been studied between 603 and 643 K at 5.0 MPa in a continuous micro-flow reactor over sulfided and fluorinated sulfided Ni-Mo catalysts supported on alumina as well as silica-alumina. The silica-alumina-supported catalysts exhibited a higher hydrodenitrogenation activity than their alumina-supported counterparts. In-situ fluorination promoted the hydrodenitrogenation activity by mainly enhancing the activity for the saturation of the aromatic ring. Kinetic parameters for the reaction network were obtained by fitting the experimental results with Langmuir-Hinshelwood equations. The reaction rate constants of the alumina- as well as silica-alumina-supported Ni-Mo catalysts increase substantially after fluorination. The activation energies and the heats of adsorption are about the same over all catalysts. This indicates that the intrinsic activity of the active sites is not influenced by the in-situ fluorination and by the support, only the number of hydrodenitrogenation sites is increased by a higher stacking of MoS₂.

4.2 INTRODUCTION

Hydrodenitrogenation (HDN) is one of the key processes in oil refining. Its main purpose is to eliminate nitrogen from engine fuels and petroleum distillates in order to minimize NOₓ emission upon burning and to prevent downstream acidic catalysts from poisoning. With the increasing demands for upgrading heavy feed stocks, coal-derived liquids, and oil shale, as well as more stringent environmental regulations, better knowledge of HDN is needed to develop new catalysts and processes for the efficient removal of nitrogen (1). o-Toluidine is a convenient nitrogen-containing
model compound to study the mechanism and kinetics of HDN (2, 3). The HDN of toluidine takes mainly place via hydrogenation to methylcyclohexylamine (MCHA). This MCHA then reacts to methylcyclohexene (MCHE) and methylcyclohexane (MCH) (Figure 4.1). Only traces of MCHA are detected as primary reaction intermediates in the HDN of toluidine because its rate of formation is much slower than its rate of further reaction. Nevertheless, MCHA may have a strong inhibition effect on the HDN of toluidine. This complicates the kinetic modelling of the HDN network of toluidine and makes it difficult to obtain reliable kinetic parameters. Therefore, we have studied separately the HDN of MCHA (4) and the reaction of olefin hydrogenation (5). In this paper, we will describe the kinetics of the HDN of o-toluidine (o-methyl aniline, OMA).

Fluorine is widely used in hydrotreating catalysts. Several studies have furthered the understanding of the effect of fluorine in hydrotreating catalysts (6-20), but only a few dealt with HDN (7, 8, 10, 11). The enhancement of the HDN activity by fluorine addition has been assigned to the higher acidity of fluorine-containing catalysts, the better dispersion of the metals on the fluorine-modified supports, as well as the higher chemisorption capacity for hydrogen. In most cases, fluorination is performed by impregnating the support with a fluoride salt, like NH₄F (see e.g. refs. 6 and 13). After NH₄F impregnation, drying, and calcination, molybdenum and nickel are introduced as usual by impregnation. After a subsequent calcination, the resulting materials are sulfided in a stream of H₂S in H₂. Thus, in this method the dispersion of the resulting MoS₂ and Ni sulfides may be different in the fluorine-containing and fluorine-free Ni-Mo catalysts, caused by the different surface properties of these supports. Conclusions about the effect of fluorine are then difficult to make. In-situ fluorination, after preparation of the Ni-Mo catalysts in their sulfidic form, has been described in patents (see e.g. refs. 21 and 22), but not in the open literature. Because in this method the metal sulfides are prepared before fluorination, the surface properties of the support will not influence the catalyst dispersion. This might allow one to draw firm conclusions about the real chemical effect of fluorine in HDN, apart from any change in dispersion.

Amorphous silica-alumina (ASA) seems to be a promising support in hydroprocessing. Many studies and patents have described its use in aromatics
Chapter 4

hydrogenation (23-25), mild hydrocracking (26), hydrocracking (25, 27-29), HDS (24, 25, 29-35), and HDN (29, 36) using noble metal-based (23-25, 27, 28, 30, 32, 35, 36) and Mo- and W-based catalysts (26, 29, 31, 33-35). Better performances were reported for ASA-supported catalysts than for their conventional Al₂O₃-supported counterparts. Only a few studies dealt with HDN over Mo- and W-based catalysts. In previous studies over supported Ni-Mo catalysts, we already described that the ASA support substantially increased the activity for the HDN of MCHA (4) and lowered the rate of hydrogenation of olefins (5). The in-situ fluorination had a promoting effect on the HDN of MCHA and no effect on the hydrogenation of cyclohexene. In this chapter, the kinetics of the HDN of OMA was studied over sulfided and fluorinated Ni-Mo catalysts supported on Al₂O₃ and ASA. By comparing the kinetic parameters, the effects of in-situ fluorination and of the support on the HDN of the aromatic nitrogen-containing compound could be studied.

4.3 EXPERIMENTAL

Catalysts containing 4 wt% Ni and 13 wt% Mo supported on γ-Al₂O₃ (Condea) and amorphous silica-alumina (ASA, prepared by the sol-gel method, containing 25 wt% Al₂O₃) were prepared by sequential pore volume impregnation with aqueous solutions of ammonium molybdate tetrahydrate (Fluka) and nickel nitrate hexahydrate (Fluka) with Mo first, followed by drying overnight at 393 K and calcining at 773 K in air after each impregnation step. The Ni-Mo/Al₂O₃ catalyst had a pore volume of 0.42 ml·g⁻¹ and a surface area of 155 m²·g⁻¹ as measured by BET nitrogen adsorption. The Ni-Mo/ASA catalyst had a pore volume of 0.43 ml·g⁻¹ and a surface area of 265 m²·g⁻¹. The HDN reaction was carried out over 0.05 g (in-situ fluorinated) of a sulfided Ni-Mo/Al₂O₃ or Ni-Mo/ASA catalyst diluted with 8 g SiC to achieve plug-flow conditions in a high-pressure micro-reactor. The catalyst was first dried for 2 h at 673 K and then sulfided with a mixture of 10% H₂S in H₂ at 1.0 MPa. Sulfidation started from ambient temperature with a slow temperature increase in 14 h to 643 K and temperature was then maintained for 2 h. In-situ fluorination was performed with a solution of o-fluorotoluene in octane at 643 K while continuing the sulfidation (5,
The pressure was first increased to that of the reaction condition (5.0 MPa) with the sulfiding gas. After cooling the reactor to 473 K, a solution of 0.26 wt% \textit{o}-fluorotoluene (Fluka) in \textit{n}-decane (Fluka) was dosed to the reactor with a syringe pump (Isco 100D). The temperature was slowly raised to 643 K and kept for 48 h, while the sulfiding and fluorination gas was flowing through the reactor. The fluorine contents in the thus fluorinated catalysts was about 1 wt% determined by X-ray fluorescence absorption. The total amount of fluorine passed over the catalyst was 6% on the basis of catalyst weight. Because the retained F content was only 1%, the conversion of \textit{o}-fluorotoluene to HF and toluene was low. As a consequence, and because we used a microreactor containing only 50 mg catalyst, there will be no F gradient over the catalyst bed.

After activation, the pressure was kept at 5.0 MPa and the temperature at 643 K. A solution of \textit{o}-toluidine (OMA) and cyclohexene (CHE) in octane (with \textit{n}-heptane as the internal standard and dimethyldisulfide to generate H\textsubscript{2}S \textit{in situ}) was fed to the reactor. Partial pressures at the reactor inlet were $p_{\text{OMA}} = 2, 7, 10, \text{ or } 14 \text{ kPa}$, $p_{\text{CHE}} = 4 \text{ kPa}$, $p_{\text{H}_2\text{S}} = 17.5 \text{ kPa}$, $p_{\text{H}_2} = 4.8 \text{ MPa}$, and octane was the balance.

The reaction products were analyzed by on-line gas chromatography (Varian Star 3400CX equipped with a 30 m DB-5MS fused silica capillary column and a flame ionization detector). All kinetic data were obtained by varying the weight time and reactant initial partial pressure after stabilisation for 20 h. Weight time was defined as the catalyst weight divided by the total molar flow fed to the reactor. The hydrogen flow rates were always changed in proportion to the liquid flow rates. No diffusion and transport limitations were detected from conversion of OMA under the conditions studied. This allowed us to model the reaction with a Langmuir-Hinshelwood mechanism assuming adsorption equilibrium for the HDN compounds. The program we used for the non-linear numeric fitting was the SCIENTIST\textsuperscript{®} by MicroMath Inc.
4.4 RESULTS AND DISCUSSION

4.4.1 HDN Reaction Scheme of OMA

The HDN network of OMA is shown in Figure 4.1. There are two reaction pathways in the HDN of OMA over (fluorinated) sulfided Ni-Mo/Al₂O₃ and Ni-Mo/ASA catalysts: path 1 is the hydrogenation of OMA to MCHA, with further reaction to MCHE and MCH, and path 2 the direct hydrogenolysis of OMA to toluene. The formation of MCHE and MCH from OMA can be attributed to the hydrogenation of the phenyl ring to MCHA, followed by breaking of the C(sp³)–N bond by elimination of NH₃ and hydrogenation of the resulting MCHE to MCH. There is also a direct path from MCHA to MCH (2, 3). A small amount of ethylcyclopentane (ECP) is formed by isomerization of MCHE and subsequent hydrogenation. The formation of toluene indicates that a direct C(sp²)-N bond cleavage occurred, which accounted for about 10% of the total conversion.

Figure 4.1 Reaction network for the HDN of OMA over Ni-Mo/Al₂O₃ and Ni-Mo/ASA catalysts.
Hydrodenitrogenation of ortho-Toluidine

The product distribution versus weight time plot clearly shows that MCHE is an intermediate and MCH the final product (Figure 4.2). MCHE is formed at a relatively high concentration as long as the OMA concentration is reasonably high. This is similar to what happens during the HDN of MCHA (4), which indicates that a strong (competitive adsorption) inhibition of OMA and MCHA on the hydrogenation of MCHE takes place. This is also evident from a comparison of the CHE conversion obtained with a pure CHE feed at 623 K with that obtained with a mixed feed of CHE with either 14 kPa of OMA or 14 kPa of MCHA (Figure 4.3). Obviously, both OMA and MCHA substantially inhibit the hydrogenation of CHE, but MCHA is a stronger inhibitor than OMA.

Figure 4.2 Product distribution during the HDN of 7 kPa OMA at 643 K over F-Ni-Mo/ASA.
Figure 4.3 Inhibition of 14 kPa OMA and MCHA on the hydrogenation of 4 kPa CHE at 623 K over Ni-Mo/Al₂O₃ expressed by CHE conversion versus weight time.

No MCHA was observed under our conditions in the HDN of OMA, due to the fast reaction of MCHA to MCHE and NH₃. The MCHA intermediate reacts faster away than it diffuses out of the catalyst pores and is not detected at the exit of the reactor (3). Nevertheless, we can not exclude that the (low) concentration of MCHA in the pores of the catalyst has an inhibition effect on the HDN of OMA and on the hydrogenation of MCHE and CHE. MCHA could be detected in the HDN of OMA when a large amount of CHE was added to the reaction mixture (3). Direct proof of the inhibition effect of MCHA on the HDN of OMA was that, in the presence of 14 kPa MCHA, the HDN of OMA was strongly inhibited (Figure 4.4). Only after most of the MCHA had reacted away, did the HDN of OMA start. No increase in the formation of ECP was observed with Ni-Mo/ASA and fluorinated catalysts compared to Ni-Mo/Al₂O₃. When OMA or MCHA was present in the reaction mixture, no isomerization of CHE to methylcyclopentane (MCP) occurred.
4.4.2 Support Effect

From the conversion of OMA and CHE on the Ni-Mo catalysts supported on Al₂O₃ and ASA (Figure 4.5), it is clear that both the fluorine-free and the fluorine-containing ASA-supported catalysts have a higher HDN activity and a lower olefin hydrogenation activity than their Al₂O₃-supported counterparts. The higher activity for the hydrogenation of olefins over Al₂O₃-supported catalysts has been attributed to the higher dispersion of MoS₂ on the Al₂O₃ support (5). More MCHE and less MCH is produced over the ASA-supported catalyst than over the Al₂O₃-supported catalyst (Figure 4.6). This holds for the fluorinated catalysts as well (not shown here). The effect of the support on the selectivity of MCHE and MCH during the HDN of OMA was similar to that on the HDN of MCHA (4). As in the HDN of MCHA, the higher
selectivity of MCHE and lower selectivity of MCH in the HDN of OMA means that the formation of MCHE from MCHA was promoted, while its further hydrogenation to MCH was inhibited by the presence of the nitrogen-containing compounds. This trend is more obvious for the Ni-Mo/ASA than for the Ni-Mo/Al₂O₃ catalysts. The selectivity of ECP and toluene was hardly influenced by the support. We have noticed that the ASA-supported catalyst has a larger surface area than the Al₂O₃-supported catalyst. A higher dispersion of NiMoS might thus be expected. However, characterization results showed that owing to a weaker interaction between Ni, Mo and the ASA support, a lower dispersion and higher stacking of MoS₂ was obtained. The Ni and Mo species tend to adsorb preferentially on the alumina sites of the ASA support (37).

![Figure 4.5](image)

Figure 4.5  Effect of support on the HDN of 7 kPa OMA and the hydrogenation of 4 kPa CHE at 643 K over Ni-Mo/Al₂O₃ (dashed lines) and Ni-Mo/ASA (solid lines).
4.4.3 Fluorination Effect

After fluorination, the HDN conversion of OMA increased by a factor of two over both catalysts, while the conversion of CHE hydrogenation hardly changed for the Al₂O₃-supported catalyst and slightly increased for the ASA-supported catalyst (Figures 4.7a and 4.7b). This indicates that the hydrogenation of CHE occurs on a different kind of site as the HDN of OMA. The slight increase of the hydrogenation of CHE can not be attributed to the direct effect of fluorination, because fluorination has no influence on olefin hydrogenation (5). The effect observed in the present case must be due to the faster HDN reaction, which diminishes the inhibition of OMA (and the possibly formed MCHA) on the hydrogenation (c.f. Figure 4.3). The higher HDN activity might be attributed to a higher stacking of the MoS₂ after fluorination, which enhances the saturation of aromatic rings (34, 35, 38, 39), and in turn enhances the
HDN of aromatic nitrogen-containing compounds. The effect of fluorination was much stronger on the HDN of OMA than on the HDN of MCHA (4). This indicates that the rate-determining step in the HDN of OMA, the hydrogenation of the phenyl ring of OMA, is strongly promoted by the fluorination. The selectivity for MCHE was increased substantially with the fluorinated catalyst in the HDN of OMA, while the MCH selectivity decreased (Figure 4.8). This is caused by the strong inhibition of OMA (and MCHA) as well. Fluorination promotes the formation of MCHE, but not its further hydrogenation, and thus leads to an increased accumulation of MCHE. The selectivities for toluene and ECP did not depend on the presence of fluorine. The toluene selectivity was independent of the OMA conversion. The effect of water formed during sulfidation (fluorination) might be a possible driving force for the redispersion (higher stacking) of MoS₂ on ASA supports. However, we believe that the catalyst (50 mg) was already highly (at least 95%) sulfided after a long sulfidation process and maintaining 2 h at 370°C, especially for the ASA-supported catalyst in which the Ni and Mo interact much weaker with the support. Thus, the additional 48 h do not form much water during the \textit{in-situ} fluorination. Furthermore, in a study of a WS₂-based catalyst prepared by ammonium tetrathiotungstate, in which all the tungsten is already in the sulfidic form, the addition of fluorine still caused a higher stacking of WS₂ (40). Therefore, we exclude this possibility.
Figure 4.7 Effect of fluorination on the HDN of 7 kPa OMA and the hydrogenation of 4 kPa CHE at 643 K over a) Ni-Mo/Al₂O₃ and b) Ni-Mo/ASA (dashed lines for fluorine-free catalyst and solid lines for fluorinated catalyst).
Figure 4.8 Effect of fluorination on the selectivity to MCHE (▲), MCH (■), TOL (★), and ECP (♦) during the HDN of 7 kPa OMA at 643 K over fluorine-free Ni-Mo/ASA (dashed lines) and fluorinated Ni-Mo/ASA (solid lines).

4.4.4 HDN Kinetics of OMA

Kinetic modelling was based on the reaction scheme shown in Figure 4.1. Since MCHA was not detected when OMA was used as the reactant, we could not model the HDN of OMA with a reaction network including MCHA. Therefore, we assumed in the kinetic treatment that a direct pathway for the reactions from OMA to MCHE and MCH existed. Furthermore, we are mainly interested in HDN in this work, not in the hydrogenation of MCHE to MCH. Therefore we classify the reactions in two categories: first hydrogenation to MCHA followed by the formation of MCHE and MCH (noted as MC), and second the direct hydrogenolysis to toluene (noted as TOL). The small amount of ECP formed was included in MC. These two reactions take
place on the same kind of sites, thus we have the following Langmuir-Hinshelwood equations:

\[
\frac{dP_{MC}}{d\tau} = \frac{k_1K_{OMA}P_{OMA}}{1 + K_{OMA}P_{OMA}}
\]  \hspace{1cm} (1)

\[
\frac{dP_{TOL}}{d\tau} = \frac{k_2K_{OMA}P_{OMA}}{1 + K_{OMA}P_{OMA}}
\]  \hspace{1cm} (2)

and

\[
-\frac{dP_{OMA}}{d\tau} = \frac{dP_{MC}}{d\tau} + \frac{dP_{TOL}}{d\tau}
\]

where \(k_1\) and \(k_2\) are the reaction rate constants for the formation of MC (MC = MCHE + MCH + ECP) and TOL, respectively. \(K_{OMA}\) is the adsorption constant of OMA on the HDN sites. The adsorption constants of MCHE, MCH, ECP, and TOL were neglected because of the much stronger adsorption of OMA (3-5). The adsorption of NH\(_3\) is also very weak on these sites and was neglected (3, 41). \(P_i\) is the partial pressure of the components in the reactor.

All reactions were performed at a total pressure of 5.0 MPa and a partial pressure of hydrogen at the reactor inlet of 4.8 MPa. The kinetic data were obtained after 20 h on stream when the catalyst was stabilized at 643 K. No deactivation was observed during the experiments. Four initial partial pressures of OMA were used at each temperature, and at each OMA initial partial pressure more than five weight times were measured. The temperatures studied were 603, 623, and 643 K. Kinetic modelling was performed with the program SCIENTIST\textsuperscript{®} based on the kinetic data obtained at these five weight times, four OMA initial partial pressures, and three temperatures. The resulting reaction rate constants and adsorption constants for the different reaction steps are shown in Tables 4.1 and 4.2 (with standard deviation in brackets). The goodness-of-fit is indicated by the Model Selection Criterion (MSC) and is defined by the formula:
where $Y_{obr}$ is the weighted mean of the observed data $Y_{obs}$, $Y_{cal}$ are the calculated data, $p$ and $n$ are the number of parameters and the measured points in the model, respectively, and $w_i$ are the weights applied to the points. All the weight factors were taken to be equal to 1 in our fitting. The larger the value of MSC, the better is the fit. As an illustration of the fittings, the experimental results obtained at 643 K are compared with fits based on Equations (1) and (2) in Figure 4.9.

Figure 4.9 An illustration of the fit for the HDN of OMA over F-Ni-Mo/ASA at 643 K (lines are the fitted results and points are the experimental data).
Over the Al₂O₃-supported catalyst (Table 4.1), the HDN reaction rate constants for path 1 increased by a factor of about two after fluorination at all three temperatures studied, while those for path 2 showed an even greater promotion. However, hydrogenolysis only contributes about 10% to the total conversion. The adsorption equilibrium constant of OMA on the HDN sites did not change by fluorination.

### Table 4.1  Fitted Parameters for the HDN of OMA over Ni-Mo/Al₂O₃

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>k₁ (kPa·mol·g⁻¹·min⁻¹)</th>
<th>k₂ (kPa·mol·g⁻¹·min⁻¹)</th>
<th>K_{OMA} (kPa⁻¹)</th>
<th>MSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-Mo/Al₂O₃ 603 K</td>
<td>0.13 (0.006)</td>
<td>0.011 (0.003)</td>
<td>0.58 (0.13)</td>
<td>7.7</td>
</tr>
<tr>
<td>623 K</td>
<td>0.27 (0.003)</td>
<td>0.023 (0.002)</td>
<td>0.47 (0.05)</td>
<td>9.0</td>
</tr>
<tr>
<td>643 K</td>
<td>0.52 (0.004)</td>
<td>0.052 (0.004)</td>
<td>0.37 (0.03)</td>
<td>8.7</td>
</tr>
<tr>
<td>F-Ni-Mo/Al₂O₃ 603 K</td>
<td>0.25 (0.002)</td>
<td>0.025 (0.002)</td>
<td>0.60 (0.06)</td>
<td>8.9</td>
</tr>
<tr>
<td>623 K</td>
<td>0.56 (0.014)</td>
<td>0.061 (0.006)</td>
<td>0.46 (0.05)</td>
<td>6.7</td>
</tr>
<tr>
<td>643 K</td>
<td>1.14 (0.009)</td>
<td>0.154 (0.009)</td>
<td>0.36 (0.03)</td>
<td>6.4</td>
</tr>
</tbody>
</table>

For the ASA-supported catalyst (Table 4.2), the HDN rate constant increased 2.5 to 3 times for both reaction pathways after fluorination. The adsorption constant of OMA on the HDN sites is somewhat higher on the ASA-supported catalyst than on its Al₂O₃-supported counterpart. After fluorination the adsorption equilibrium constant decreased.
### Table 4.2  Fitted Parameters for the HDN of OMA over Ni-Mo/ASA

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$k_1$</th>
<th>$k_2$</th>
<th>$K_{OMA}$</th>
<th>MSC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kPa·mol·g⁻¹·min⁻¹</td>
<td>kPa·mol·g⁻¹·min⁻¹</td>
<td>kPa⁻¹</td>
<td></td>
</tr>
<tr>
<td>Ni-Mo/ASA 603 K</td>
<td>0.17 (0.003)</td>
<td>0.018 (0.003)</td>
<td>1.03 (0.10)</td>
<td>8.1</td>
</tr>
<tr>
<td>623 K</td>
<td>0.35 (0.004)</td>
<td>0.036 (0.004)</td>
<td>0.75 (0.12)</td>
<td>8.3</td>
</tr>
<tr>
<td>643 K</td>
<td>0.69 (0.008)</td>
<td>0.093 (0.008)</td>
<td>0.60 (0.11)</td>
<td>7.2</td>
</tr>
<tr>
<td>F-Ni-Mo/ASA 603 K</td>
<td>0.39 (0.007)</td>
<td>0.042 (0.007)</td>
<td>0.38 (0.05)</td>
<td>7.0</td>
</tr>
<tr>
<td>623 K</td>
<td>0.97 (0.010)</td>
<td>0.110 (0.010)</td>
<td>0.30 (0.03)</td>
<td>6.5</td>
</tr>
<tr>
<td>643 K</td>
<td>2.11 (0.017)</td>
<td>0.300 (0.015)</td>
<td>0.21 (0.02)</td>
<td>6.3</td>
</tr>
</tbody>
</table>

From the results obtained at different temperatures, the activation energies of the HDN reaction paths were calculated from the Arrhenius plot of $\ln k$ versus $1/T$ (Figure 4.10 and Table 4.3). There seems to be a slight increase of the activation energies with fluorination and with going from $\text{Al}_2\text{O}_3$-supported to ASA-supported Ni-Mo. However, these differences are insignificant within the uncertainties of the measurements. The pre-exponential factors increase by two order of magnitudes with fluorination. This indicates that only the number of the catalytic sites increased by fluorination, while the intrinsic activity of the sites remained unchanged. Since we did not fix the activation energies in our fitting, a compensation effect may exist in the system. Therefore, the two orders of magnitude difference in the pre-exponential factors do not mean that the reaction rates should be two orders of magnitude faster.
Figure 4.10  \( \ln k \) versus \( 1/T \) plot for the HDN of OMA over Ni-Mo/ASA (dashed lines for fluorine-free catalyst and solid lines for fluorinated catalyst).

### Table 4.3  Activation Energies and Heats of Adsorption for the HDN of OMA

<table>
<thead>
<tr>
<th></th>
<th>NiMo/Al₂O₃</th>
<th>F-NiMo/Al₂O₃</th>
<th>NiMo/ASA</th>
<th>F-NiMo/ASA</th>
</tr>
</thead>
<tbody>
<tr>
<td>E, kJ·mol⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>path 1</td>
<td>112 (9)</td>
<td>122 (14)</td>
<td>113 (16)</td>
<td>136 (8)</td>
</tr>
<tr>
<td>path 2</td>
<td>125 (25)</td>
<td>144 (16)</td>
<td>132 (18)</td>
<td>159 (25)</td>
</tr>
<tr>
<td>A, kPa·mol⁻¹·g⁻¹·min⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>path 1</td>
<td>6×10⁸</td>
<td>1×10¹⁰</td>
<td>1×10⁹</td>
<td>3×10¹¹</td>
</tr>
<tr>
<td>path 2</td>
<td>7×10⁸</td>
<td>8×10¹⁰</td>
<td>5×10⁹</td>
<td>2×10¹²</td>
</tr>
<tr>
<td>( -\Delta H_{ads} ), kJ·mol⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>36 (7)</td>
<td>41 (5)</td>
<td>44 (7)</td>
<td>48 (6)</td>
</tr>
<tr>
<td>( K_0 ), kPa⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4×10⁻⁴</td>
<td>2×10⁻⁴</td>
<td>2×10⁻⁴</td>
<td>3×10⁻⁵</td>
</tr>
</tbody>
</table>
Like the activation energies, the heats of adsorption can be obtained from the Arrhenius plot of $\ln K$ versus $1/T$ (Figure 4.11 and Table 4.3). The heat of adsorption of OMA on the catalytic sites for HDN showed no substantial difference between the fluorine-free catalysts and their fluorinated counterparts. This further confirms that fluorination mainly increases the number of active sites for HDN without altering the nature of the sites.

![Figure 4.11](image)

**Figure 4.11** $\ln K$ versus $1/T$ plot for the HDN of OMA over Ni-Mo/ASA (dashed lines for fluorine-free catalyst and solid lines for fluorinated catalyst).

The fact that hardly any MCHA is observed in the HDN of OMA suggests that the rate of reaction of MCHA is very much faster than its rate of formation. From the present results on the HDN of OMA and those obtained earlier on the HDN of MCHA (4), the ratios of the apparent rate constants $k' = kK/(1 + KP)$ for the HDN of 14 kPa OMA and for the HDN of 14 kPa MCHA to MCHE and MCH can be obtained. As Table 4.4 shows, the ratios of $k'_{\text{MCHA}}/k'_{\text{OMA}}$ range from 4.5 to 7.7 at 603 K and from
5.3 to 12 at 623 K. This indicates that the apparent rate constants do not differ enough to explain why no MCHA was observed in the HDN of OMA. For instance, considering the consecutive reaction

\[ \text{OMA} \xrightarrow{k'_{\text{OMA}}} \text{MCHA} \xrightarrow{k'_{\text{MCHA}}} \text{MCHE} + \text{MCH} \]

and assuming pseudo first-order reactions, the maximum concentration of MCHA is

\[ \left( \frac{\text{MCHA}}{\text{OMA}} \right)_{\text{max}} = \left( \frac{k'_{\text{OMA}}}{k'_{\text{MCHA}}} \right)^{k'_{\text{MCHA}}/(k'_{\text{MCHA}} - k'_{\text{OMA}})} \]

and the weight time for the maximum MCHA concentration is

\[ \tau_{\text{max}} = \ln \left( \frac{k'_{\text{OMA}}}{k'_{\text{MCHA}}} \right) / \left( k'_{\text{OMA}} - k'_{\text{MCHA}} \right) \]

At 603 and 623 K, the maximum MCHA concentration should then be between 7 to 14 mol\% of the initial OMA concentration, and the weight time for the maximum MCHA concentration should be between 1.3 and 2.6 min·g·mol\(^{-1}\) at 603 K, and below 1 min·g·mol\(^{-1}\) at 623 K for all catalysts. With a detection limit of at least 0.5 mol\%, we should have been able to detect these amounts of MCHA under our reaction conditions (\(\tau \geq 0.5\) min·g·mol\(^{-1}\)). Therefore, there must be other factors why we did not detect MCHA formed in the pores of the catalysts.

<table>
<thead>
<tr>
<th></th>
<th>Values of (k'<em>{\text{MCHA}} / k'</em>{\text{OMA}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni-Mo/Al(_2)O(_3)</td>
</tr>
<tr>
<td>603 K</td>
<td>7.7</td>
</tr>
<tr>
<td>623 K</td>
<td>12</td>
</tr>
</tbody>
</table>
A reason for the discrepancy between the ratio of the rate constants and the very low concentration of MCHA observed might be “hidden kinetics”. If during the HDN of OMA the reaction of MCHA at the catalyst surface is much faster than MCHA desorption, then equilibrium between MCHA at the catalyst surface and in the gas phase is not established. In that case, the expected partial pressure of MCHA cannot be estimated from a Langmuir-Hinshelwood equation. It is conceivable that this equilibrium is attained in the HDN reaction of MCHA itself, but not in that of OMA. During the HDN of MCHA, the basic MCHA molecule will adsorb in $\sigma$ mode with its free electron pair towards the surface. This configuration is not well suited for Hofmann elimination of the H atoms at the $\beta$ carbon atom, which in this $\sigma$ bonding configuration point away from the catalyst surface. On the other hand, during the HDN of OMA, the lone pair in OMA is conjugated with the aromatic ring and as a consequence, OMA is less basic as MCHA and can adsorb in $\pi$ mode on the metal sulfide surface. In this configuration, parallel to the surface, it can not only easily be hydrogenated to MCHA, but the resulting MCHA can easily undergo $\beta$-H elimination before desorption to the gas phase. This would explain why a measurement starting with MCHA comes up with a lower reaction rate for MCHA than that of a measurement starting with OMA.

### 4.5 CONCLUSIONS

Different pathways are involved in the HDN of OMA. The direct hydrogenolysis of the C(sp$^2$)-N bond accounts for 10% of the whole conversion, while the path via hydrogenation to MCHA, followed by NH$_3$ elimination, is the main HDN reaction mechanism.

The ASA-supported catalysts show a higher HDN activity of OMA than their Al$_2$O$_3$-supported counterparts. A much more pronounced HDN performance for the $in situ$ fluorinated catalysts was observed for the HDN of OMA than for MCHA. This is caused by the higher activity for the hydrogenation of aromatic ring involved in the HDN of OMA, induced by the higher stacking of MoS$_2$ in the ASA-supported catalysts.
Fluorination enhances the HDN activities of both the Al₂O₃- and the ASA-supported catalysts. Kinetic parameters indicate that the intrinsic activity of the active sites is not influenced, only the number of the HDN sites is increased.
4.6 REFERENCES

37. Qu, L., Zhang, W., Kooymen, P. J., and Prins, R., submitted to J. Catal. (JCAT-02/155(N)).


Chapter 5
Different Sites Involved in Hydrodenitrogenation

5.1 ABSTRACT

The different active sites involved in hydrodenitrogenation over supported sulfided Ni-Mo catalysts have been investigated with different model reactions such as the hydrodenitrogenation of methylcyclohexylamine and o-toluidine, and the hydrogenation of cyclohexene and toluene. By comparing the effects of silica-alumina support and in-situ fluorination on the activity of these reactions, at least four sites were distinguished in hydrodenitrogenation. The active site for the C(sp\(^2\))─N bond cleavage is highly unsaturated and accommodates aromatic amines in a flat adsorption mode. The site for the C(sp\(^3\))─N bond cleavage involves not only a surface vacancy, but also an acid site for the elimination, or a site to provide SH\(^-\) for nucleophilic substitution. Hydrogenation of aromatics is favored by high stacking of the MoS\(_2\) slabs with more edge and corner sites, whereas the hydrogenation of olefins is favored on catalysts with better dispersion and lower stacking of MoS\(_2\) slabs.

5.2 INTRODUCTION

Hydrodenitrogenation (HDN) is one of the most important reactions performed in the hydrotreating process in refineries. It is used for lowering the nitrogen content in transportation fuels to diminish the emission of NO\(_X\) from burning and for preventing acidic catalysts of downstream processes from being poisoned by base nitrogen compounds. The increasing demands in converting petroleum residua, coal, shale, and tar sands, which contain higher concentration nitrogen, to liquid fuels have stimulated researches in the chemistry of HDN. Several reviews have summarised the process and catalysts for HDN (1-4).
Active Sites in HDN

Compared with hydrodesulfurization (HDS), HDN received less attention. Many studies have focused on the preparation conditions of hydrotreating catalysts (5), effects of supports (6), and operating conditions like H₂S partial pressure (7-9). Key points are the structure and nature of active sites and their relations with reactivity. Once the nature of the active sites has been identified, we can work more effectively on the design and manufacture of catalysts used for HDN, which becomes more and more important nowadays with increasing environmental regulations. The structure and function of the catalyst and the promoter in HDS catalysts have been reviewed by Prins et al. (10). However, few attempts were ever made directly for the different sites in HDN. The nature of the active sites was assumed to be different for activating nitrogen compounds and hydrogen. The sites for nitrogen compounds are commonly accepted to be sulfur vacancies associated with exposed Mo atoms whose electronic and structural configurations are also influenced by the neighboring promoter metals. These coordinatively unsaturated sites (CUS) exist at the edges of MoS₂ slabs (2, 3, 5). Several models were proposed to explain the different performances of hydrotreating catalysts for HDS (5), to which HDN is analogous. Taking into account all possible configurations in the edge crystallographic planes of a MoS₂ slab, Kasztelan (11) proposed a number of potential sites in MoS₂-based catalysts. These sites are only hypothetical and further assignments to each of them are required. Recently theoretical calculations proved some of the sites in MoS₂-based systems (12-17). Acid sites are often assumed to be involved in HDN. Some authors even reported the direct participation of surface acid sites in the HDN reaction (18). However, we tend to classify the different active sites by their functions in the HDN network, which is more meaningful.

O-toluidine (o-methylaniline, OMA) is a convenient model compound to study the reaction mechanism and active sites involved in HDN. Alkyl anilines are present in crude oils and distillates and are the intermediates of most aromatic nitrogen-containing heterocyclic compounds. By studying the HDN of anilines, it is possible to elucidate hydrogenation and C(sp²)─N and C(sp³)─N bonds cleavage functions of a catalyst (8, 19-21). Three types of reactions were discussed in the HDN of aromatic nitrogen-containing compounds by Perot (22) from an overall point of view: hydrogenation of nitrogen-containing rings, hydrogenation of benzenic rings, and
C—N bond scission. In fact, there are more types of reactions involved in the HDN of an aromatic nitrogen-containing compound: hydrogenation of aromatics (including the nitrogen-containing phenyl rings), hydrogenation of olefins, aromatic C(sp²)—N bond cleavage, and aliphatic C(sp³)—N bond cleavage. At least three types of catalytic sites were proposed by Delmon et al. (23): hydrogenation, breaking of the C—N bond by hydrogenation (hydrogenolysis HDN), and rupture by acid catalysis (probably similar to β-elimination or, perhaps, nucleophilic substitution). In our laboratory, at least four different sites in HDN have been proposed by studying the effects of Ni and H₂S on the HDN performance of Mo/Al₂O₃ catalysts (24): sites active for C(sp³)—N bond cleavage, for C(sp²)—N bond cleavage, for the hydrogenation of olefins, and for the hydrogenation of phenyl rings. It has been confirmed by a differentiation of the adsorption equilibrium constants of different compounds on NiMo supported catalysts (25).

In this chapter, we further elucidate the nature of the active sites involved in HDN by studying different model reactions with Ni-Mo catalysts supported on alumina and silica-alumina supports, with and without fluorination. By comparing the effects of support and in-situ fluorination on different model reactions, combined with results from literature, the active sites for HDN are discussed.

5.3 EXPERIMENTAL

5.3.1 Catalysts

Preparation of the NiMo catalysts has been described in details elsewhere (26). They were prepared by successive pore volume impregnation (Mo first) with aqueous solutions containing the required amounts of ammonium molybdate tetrahydrate (Fluka) and nickel nitrate hexahydrate (Fluka). The final calcined catalysts contained 2.9 wt% Ni and 8.8 wt% Mo, as analyzed by AAS. The Al₂O₃-supported catalyst had a surface area of 202 m²·g⁻¹ and a pore volume of 0.33 ml·g⁻¹ with a narrow pore size distribution, at around 5.6 nm diameter, as determined by the BET N₂ adsorption. The
ASA-supported catalyst had a surface area of 296 m$^2$·g$^{-1}$ and a pore volume of 0.44 ml·g$^{-1}$ with a narrow pore size distribution at around 5.3 nm.

### 5.3.2 HDN of Methylcyclohexylamine

The procedure of the HDN of methylcyclohexylamine (MCHA) has been described in detail in (27). 0.05 g of catalyst was diluted with 8 g of SiC and loaded in the isothermal zone of a micro-reactor. The catalyst was first sulfided with a mixture of 10% H$_2$S in H$_2$ at 1.0 MPa. Sulfidation started from ambient temperature with a slow increase in 14 h to 643 K; the temperature was then maintained at 643 K for 2 h. The *in-situ* fluorination was performed after the sulfidation step. The pressure was first increased to that of the reaction condition (5.0 MPa) with the sulfiding gas. After cooling the reactor to 473 K, a solution of 0.26 wt% o-fluorotoluene (Fluka) in n-decane (Fluka) was dosed to the reactor with a syringe pump (Isco 100D). The temperature was slowly raised to 643 K and kept for 48 h, while the sulfiding and fluorination gas was flowing through the reactor. The fluorine contents in the thus fluorinated catalysts was about 1 wt% determined by X-ray fluorescence absorption.

After activation, the temperature was adjusted to 623 K, and the sulfiding and fluorination gas was switched to pure hydrogen. Then a solution of methylcyclohexylamine, octane (solvent), n-heptane (HEP, internal standard), and dimethyldisulfide (to generate H$_2$S *in situ*) (all from Fluka, without further treatment) was fed to the reactor with a high-pressure syringe pump (Isco 500D). Partial pressures at the reactor inlet were $P_{\text{MCHA}} = 14$ kPa, $P_{\text{HEP}} = 0.1$ kPa, $P_{\text{H}_2\text{S}} = 17.5$ kPa, $P_{\text{H}_2} = 4.8$ MPa, and octane as the balance. The reaction was performed at 623 K. Reaction products were analyzed by on-line chromatography with a capillary column. The conversion was controlled below 20% to allow a differential treatment of the reaction data. The activity of catalysts was expressed as apparent rate constant assuming a first-order reaction.
5.3.3 HDN of o-Toluidine

The activation procedure was the same as in the HDN of MCHA. The reaction was conducted at 623 K and 5.0 MPa. All other conditions were the same as in the HDN of MCHA except that the partial pressure of OMA at the reactor inlet was 7 kPa. The analysis and data processing were the same as described in Section 5.3.2.

5.3.4 Hydrogenation of Cyclohexene

The detailed procedure for the hydrogenation of olefins has been described in (28). For similarity to HDN reactions, the hydrogenation of cyclohexene (CHE) was also performed at 623 K and 5.0 MPa with a H$_2$S partial pressure of 17.5 kPa. The partial pressure of CHE at the reactor inlet was 16 kPa. The activities of the different catalysts were compared by the ratios of the apparent rate constants.

5.3.5 Hydrogenation of Toluene

The activation of the catalysts was the same as mentioned above. The hydrogenation of toluene was performed at 643 K and 5.0 MPa in the presence of H$_2$S. The partial pressures at the reactor inlet were $P_{\text{TOL}} = 4$ kPa, $P_{\text{HEP}} = 0.1$ kPa, $P_{\text{H}_2\text{S}} = 17.5$ kPa, $P_{\text{H}_2} = 4.8$ MPa, and octane as the balance. The main reaction product was methylcyclohexane (MCH), with a small amount of ethylcyclopentane (ECP) that was formed by the isomerisation of methylcyclohexene (MCHE) and further hydrogenation. Under the conditions studied, no methylcyclohexene (MCHE) was detected. The conversion of the reaction was controlled below 15% to allow a differential treatment of the data. The activity was expressed as the apparent first-order rate constant for the hydrogenation of toluene.
5.4 RESULTS

In the HDN of OMA, there are two reaction pathways over (fluorinated) sulfided Ni-Mo/Al$_2$O$_3$ and Ni-Mo/ASA catalysts: path 1 is the hydrogenation of OMA to MCHA, with further reaction to MCHE and MCH, and path 2 the direct hydrogenolysis of OMA to toluene (Figure 5.1). The formation of MCHE and MCH from OMA can be attributed to the hydrogenation of the phenyl ring to MCHA, followed by the breaking of the C(sp$^3$)$-\text{N}$ bond by elimination of NH$_3$ and hydrogenation of the resulting MCHE to MCH. There is also a direct path from MCHA to MCH (19-21, 27). A small amount of ECP was formed by isomerization of MCHE and its subsequent hydrogenation. The formation of toluene indicates that a direct C(sp$^3$)$-\text{N}$ bond cleavage occurred, which accounted for about 10% of the total conversion. From results of different model reactions in the following parts, further information can be provided concerning different sites involved in the HDN.

Figure 5.1 Reaction network for the HDN of \textit{o}-toluidine.
5.4.1 HDN of Methylcyclohexylamine

As has already been reported in (27), an ASA-supported Ni-Mo catalyst has a higher HDN activity for MCHA than Ni-Mo/Al₂O₃, meaning a promotional contribution from the ASA support. Fluorination increases the activity of both catalysts by 20 to 30%. In Figure 5.2, the relative activities of the different catalysts were normalised to that of Ni-Mo/Al₂O₃ catalyst (also for other reactions below). This reaction involves only the C(sp³)—N bond cleavage.

![Graph](image)

Figure 5.2 Comparison of activities for the HDN of methylcyclohexylamine.
5.4.2 HDN of o-Toluidine

For the HDN of OMA, the Ni-Mo/ASA catalyst exhibits 50% higher activity than its Al$_2$O$_3$-supported counterpart (Figure 5.3), which is much higher than for the HDN of MCHA. This suggests that the ASA support strongly promotes the hydrogenation pathway, because the direct C(sp$^2$)$\text{─N}$ bond cleavage only contributes 10% of the total conversion of OMA. Furthermore, after fluorination, the HDN activity increases two fold for the Ni-Mo/Al$_2$O$_3$ and 2.5 fold for the Ni-Mo/ASA. These promotions are much stronger for the HDN of OMA than for the HDN of MCHA. This indicates that both the ASA support and fluorination enhances the hydrogenation of the aromatic ring of OMA and in turn, promotes the HDN of OMA. The selectivity for toluene does not change with the support and fluorination, suggesting that the direction path is hardly influenced by the support and fluorination.

![Figure 5.3](image)

Figure 5.3 Comparison of activities for the HDN of o-toluidine.
5.4.3 Hydrogenation of Cyclohexene

Hydrogenation of olefin (MCHE), after the elimination of NH₃ from MCHA and OMA. Therefore, we performed separately the hydrogenation of CHE, which is similar to MCHE. Higher hydrogenation activity of olefin was observed on the Ni-Mo/Al₂O₃ catalyst than on the Ni-Mo/ASA catalyst (28). After fluorination, the conversion of CHE increased to a small extent (Figure 5.4). However, a careful check showed that the yield for the saturation of CHE to CH did not change. This indicates that fluorination does not influence the olefin hydrogenation. Only the isomerization of CHE was promoted by stronger acidity introduced by the *in-situ* fluorination (28).

Figure 5.4 Comparison of activities for the hydrogenation of cyclohexene.
5.4.4 Hydrogenation of Toluene

Toluene was used as a model compound for studying the hydrogenation activity of aromatics. As shown in Figure 5.5, much larger differences were observed for the hydrogenation of toluene with the four different catalysts. The ASA-supported catalyst showed two times higher activity than its Al$_2$O$_3$-supported counterpart. This is just opposite to the hydrogenation of olefins, in which the ASA-supported catalyst has a poor hydrogenation activity. After fluorination, furthermore, the hydrogenation activity for aromatics increased two fold on the Ni-Mo/Al$_2$O$_3$, and about 2.5 fold on the Ni-Mo/ASA catalyst, which is similar to the trend in the HDN of OMA. Therefore, the higher HDN activity for OMA on the Ni-Mo/ASA catalyst and the strong promotion by fluorination must be due to the outstanding hydrogenation activity of aromatics.

![Figure 5.5](image)  
**Figure 5.5** Comparison of activities for the hydrogenation of toluene.
5.5 DISCUSSION

Different effects of support and fluorination were observed for the various model reactions. The ASA support shows a promotional influence on the HDN of MCHA and OMA and on the hydrogenation of toluene, and a negative influence on the hydrogenation of CHE. Fluorination promotes the HDN of MCHA and OMA and the hydrogenation of aromatics, but hardly influences the hydrogenation of olefin. The promotion effect on the HDN of MCHA can be attributed to the enhancement of the elimination by the ASA support and fluorination. The strong effects of the ASA support and fluorination on the HDN of OMA are mainly due to the excellent hydrogenation activity for aromatics, which in turn promotes the HDN performance. The direct C(sp\(^2\))\text{─}N bond cleavage is not influenced by fluorination. This indicates that the sites for the cleavage of C(sp\(^2\))\text{─}N and C(sp\(^3\))\text{─}N bond are different. The different influence of the support and fluorination indicates that the hydrogenation of olefin and aromatics takes place on different sites.

5.5.1 Sites for C(sp\(^2\))\text{─}N Bond Cleavage

As observed in the HDN of OMA, toluene was always present in about 10\% in the products, which means that a direct C(sp\(^2\))\text{─}N bond cleavage occurs. In the past, this reaction was considered to be a direct hydrogenolysis of the C\text{─}N bond. However, this “direct hydrogenolysis” may proceed by partial hydrogenation of the aromatic ring, followed by nucleophilic substitution of the NH\(_2\) group with an SH group, then followed by C\text{─}S bond hydrogenolysis (29), which is much easier than hydrogenolysis of the C\text{─}N bond.

The C(sp\(^2\))\text{─}N bond cleavage from aromatic amines is inhibited by the presence of H\(_2\)S (8, 25), indicating a different mechanism as for the C(sp\(^3\))\text{─}N bond cleavage, which is promoted by H\(_2\)S. The direct hydrogenolysis of the aromatic C\text{─}N bond in the HDN of aniline (30, 31), o-toluidine (19-21), 2-propylaniline (32), and naphthylamine (33) has been observed by the direct formation of benzene, toluene, propylenes, and naphthalene, respectively. Moreau et al. (34) showed that, in a
series of substituted benzenes, hydride species realize a direct aromatic C–N bond cleavage by nucleophilic substitution. Jian and Prins (24, 25) proposed a direct hydrogenolysis of the C(sp\(^2\))–N bond. They reported a negative effect of Ni on this reaction and concluded that the hydrogenolysis requires highly unsaturated Mo atoms. Recently, van Gestel et al. (35) further proved the direct hydrogenolysis of the aromatic C–N bonds in the reaction of 2,6-dimethylaniline. Based on the negative effect of Co and Ni on the direct denitrogenation of Mo catalyst and infrared characterization, they proposed a mechanism for the direct denitrogenation in the absence of H\(_2\)S (Figure 5.6). The active sites for the direct denitrogenation are highly unsaturated Mo sites, with at least three adjacent Mo atoms. These sites are situated at the edge of the MoS\(_2\) slabs. They facilitate the adsorption of an aniline molecule parallel to the catalyst surface with both the nitrogen atom and aromatic ring. Upon addition of H\(_2\)S to the reactor, the direct denitrogenation activity diminishes readily, because the highly unsaturated edge sites are easily poisoned.

### 5.5.2 Sites for C(sp\(^3\))–N Bond Cleavage

There is no doubt for the existence of sites for the C(sp\(^3\))–N bond cleavage. The mechanism has been proved by \(\beta\)-elimination of NH\(_3\) from amines. Since the C(sp\(^3\))–N bond cleavage is promoted by H\(_2\)S, SH groups are supposed to be involved in the HDN of saturated amines. Nitrogen removal proceeds by Hofmann elimination after quaternization of the nitrogen atom by protonation on a Brønsted acid site (Figure 5.7). The protonated amine may alternatively undergo an S\(_N\)2 nucleophilic substitution by SH-, followed by the hydrogenolysis of the C–S bond (Figure 5.8) (21, 22, 36-41). When there are no hydrogen atoms on the \(\beta\) carbon atom and elimination is not possible, C–N bond breaking is still possible, as shown by Vivier et al. for benzylamine (42). Direct hydrogenolysis of a C(sp\(^3\))–N bond is more likely to occur than that of a C(sp\(^3\))–N bond, because a C(sp\(^3\))–N bond is weaker than a C(sp\(^3\))–N bond. Recently, Rota and Prins (43) have proved the direct hydrogenolysis of the C(sp\(^3\))–N bond.
Figure 5.6 Active sites and reaction mechanism for the direct denitrogenation of 2,6-dimethylaniline in the absence of H₂S (35).
Based on the effect of the Ni promoter and the mutual influence of HDS/HDN, Ozkan et al. (44) found similar trends in Al$_2$O$_3$-supported and unsupported Ni-Mo catalysts. They suggested that the intrinsic nature of the active sites is essentially independent of the support. This is in accordance with our results that the HDN of MCHA was not promoted to a large extent by the ASA support.

The presence of H$_2$S in the feed increases the activity for C(sp$^3$)$-\text{N}$ bond cleavage, while it decreases the activity for C(sp$^2$)$-\text{N}$ bond cleavage. The former is attributed to protonic sites and the later to anionic vacancies associated with Mo (45).

The nature of active sites for the C(sp$^3$)$-\text{N}$ bond cleavage have to be considered for the different reaction mechanisms such as $\beta$-elimination, nucleophilic substitution, and direct hydrogenolysis. In the $\beta$-elimination mechanism, an acid helps to quaternize the nitrogen atom, thereby creating a better leaving group, while a base promotes elimination by removal of a $\beta$-hydrogen (Figure 5.7). Therefore, only one site is needed to adsorb the aliphatic amine molecule. The acid can be from the support or from the metal sulfides.

For the nucleophilic substitution, the NH$_2$ group is first substituted by a SH group, then the C$-\text{S}$ bond (a weaker bond) undergoes hydrogenolysis on the catalyst surface, which is much easier than that of the C$-\text{N}$ bond (Figure 5.8). In this case, one site is required for the adsorption of amine molecule and another should be available for providing the SH group, probably through dissociatively adsorption of H$_2$S on a surface vacancy. The direct hydrogenolysis of the C$-\text{N}$ bond is much slower than the former two (3), and to a lesser extent (43) (Figure 5.9). Active sites for this reaction still need to be investigated.

![Figure 5.7](image-url)  
Proposed HDN mechanism via $\beta$-elimination
5.5.3 Sites for Hydrogenation of Aromatics

Outstanding activity for the hydrogenation of toluene was observed over the ASA-supported Ni-Mo catalyst (Figure 5.5). Fluorination greatly enhanced the hydrogenation activity of aromatics. In our TEM study of the sulfided catalysts (26), we found that the lengths of the MoS$_2$ slabs are about the same in the Al$_2$O$_3$- and ASA-supported catalysts. Only a higher stacking of MoS$_2$ was obtained with the ASA-supported catalyst. Therefore, the higher activity of the Ni-Mo catalyst supported on ASA can be attributed to more edge and corner sites of MoS$_2$ slabs in the sulfided Ni-Mo/ASA catalyst. Because, when the length of the MoS$_2$ slabs are the same, higher
stacking means more exposed edge and corner sites. Higher stacking of the MoS$_2$ slabs can accommodate more aromatic molecules with a flat adsorption mode in the Ni-Mo/ASA.

Dispersion of metal sulfides plays an important role in the hydrogenation of aromatics. In a study of Ni-W catalysts, Vradman and Landau obtained a six times higher activity in the hydrogenation of toluene over a SiO$_2$-supported catalyst with two times higher stacking of WS$_2$ slabs, compared with its Al$_2$O$_3$-supported counterpart (46). They attributed the high hydrogenation activity of the sulfided Ni-W/SiO$_2$ to the multi-layered WS$_2$ slabs which provided a higher density of multiply vacancies facilitating the $\pi$-complexation of the aromatic ring, which is the same explanation as in our study.

H$_2$S has a moderate inhibiting effect on the hydrogenation of aromatics (47-49). In a kinetic study with H$_2$S partial pressures varying in a wide range, Kasztelan and Guillaume (50) proposed a two-site model for the hydrogenation of aromatics. One site is an unsaturated Mo ion and the other stable is a sulfur ion acting as host of the proton generated by the heterolytic dissociative adsorption of hydrogen and hydrogen sulfide. They found that H$_2$S only has an inhibition effect at medium pressure, and no effect at very low and high H$_2$S partial pressures. In a recent study, Blanchin et al. (51) further confirmed that the heterolytic dissociation occurred on centers composed of an unsaturated Mo ion and a sulfur anion. The hydrogenation of toluene occurred through a heterolytic mechanism starting with a hydride addition followed by a proton addition. The proton addition was the rate-determining step. Whatever is the rate-determining step for the hydrogenation of aromatics, hydride addition or proton addition, it is always true that an aromatic ring adsorbs via a $\pi$-complex on the surface sites. These sites should be more open, with two vacancies. In order to have a higher hydrogenation activity for aromatics a catalyst must have more sites to accommodate the adsorption of reactants.

Hydrogenation of nitrogen-containing phenyl rings should occur via the same mechanism as aromatics. Many researchers have reached the conclusion that H$_2$S inhibits the hydrogenation of aromatic ring, but enhances the C─N bond breaking (52-54). However, Hanlon (55) observed that no effect of H$_2$S on the initial hydrogenation of pyridine to piperidine.
The excellent hydrogenation activity for aromatics on ASA-supported catalysts also indicates the potential use for producing low sulfur and low aromatic fuels in refineries.

5.5.4 Sites for Hydrogenation of Olefins

Sites for the hydrogenation of olefins seem to be different from those for the hydrogenation of aromatics. Al₂O₃-supported Ni-Mo exhibits higher activity for the hydrogenation of olefins than ASA-supported catalysts. This has been explained by a better dispersion of Ni and Mo on the Al₂O₃ support (28). A correlation has been reached between the dispersion of Mo oxides and the hydrogenation activity (56, 57). TEM measurement of the sulfided catalysts showed that more stacking occurred with ASA-supported catalyst than with Al₂O₃-supported catalyst (26). This means that the higher stacking of MoS₂ does not improve the hydrogenation of olefins, on the contrary, it lowered the activity. Different adsorption configurations of aromatics and olefins should be responsible for the different behavior of the hydrogenation activity with these two kinds of supports. On the ASA-supported catalyst, the toluene molecule adsorbs in a flat mode on the edges of the MoS₂ slabs, whereas the CHE molecule can only adsorb from the side.

The hydrogenation sites for olefins were proposed by Tanaka and Okuhara (58) to be triply coordinatively unsaturated Mo sites (CUS). These sites can be generated by treating the sulfided Mo catalyst under hydrogen at elevated temperature (59, 60). They were poisoned by H₂S at low temperature (58). At higher temperature, the hydrogenation sites were little affected by H₂S (61). At higher temperature (for typical HDS and HDN above 623 K), the H₂S molecule dissociatively adsorbs on CUS Mo sites in the following manner (62):

\[ \text{H}_2\text{S} \rightleftharpoons \text{H}_{\text{ads}} + \text{HS}_{\text{ads}} \]
Based on the results of the temperature-programmed desorption of adsorbed NO and the linear correlation between the number of the triply CUS Mo-sites on both the Al₂O₃- and TiO₂-supported Mo catalysts, catalytic cycles were proposed by Okamoto et al. (63) combining the hydrogenation of olefins at low and high temperatures and in the presence and absence of H₂S (Figure 5.10). The amount of the triply CUS is dependent on the metal loading and support because of the Mo-support interaction.

Figure 5.11  Plausible catalytic cycles for the hydrogenation of olefins over sulfided Mo-based catalysts (63).
This scheme can explain that hydrogenation of olefins can take place by dissociatively adsorbed H₂ or H₂S. In a Ni-containing catalyst, the active sites for hydrogenation can also be associated with the coordinatively unsaturated Ni sites formed via the removal of sulfur by hydrogen at temperatures used in commercial HDS/HDN operations, as proposed by Zhang et al. (64):

\[
\begin{align*}
\text{Ni} + \text{S}^2- & \quad \quad + \text{H}_2 \\
\text{Ni} & \quad \quad \quad \quad \quad \quad + \text{H}_2\text{S}
\end{align*}
\]

This kind of site should be much more active than the Mo sites. The deactivation of a Ni-Mo catalyst is directly related with the loss of active Ni sites. As pointed out by Prins (3), the reaction seems to take place preferentially on Ni and not Mo sites.

In our experiments, we found that H₂S has a strong inhibition on the hydrogenation of olefins (28), which is different from the results of Massoth and MuraliDhar (61). The fact that H₂S has a weaker inhibition on the hydrogenation of the phenyl ring than on the hydrogenation of olefins can be attributed to the higher reaction temperature for the hydrogenation of aromatics which promotes the dissociatively adsorption of H₂S on the CUS sites. However, the involvement of SH groups in olefin hydrogenation has been proposed in the case of Mo sulfides (65) and Mo complexes (66). Our results suggest a better catalyst for the hydrogenation of olefins must possess a better dispersion of metal (sulfides) on the support with less steric hindrance for the adsorption of olefin (especially the cyclic) molecules.
5.6 CONCLUSIONS

Based on the above results and discussion, we can conclude that there are at least four kinds of sites involved in the HDN of aromatic nitrogen-containing compounds: Sites for C(sp$^2$)─N bond cleavage should be highly coordinatively unsaturated, usually three vacancies together to accommodate the flat adsorption of the aromatic ring and the conjugated nitrogen atom. Sites for C(sp$^3$)─N bond cleavage require one vacancy and probably a neighbouring acid or SH group to conduct elimination or nucleophilic substitution. Hydrogenation of aromatics is favoured by more edge and corner sites, derived from higher stacking of MoS$_2$ slabs. Hydrogenation of olefins needs a catalyst with better dispersion.
5.7 REFERENCES

Chapter 6
Characterization of Catalysts
by MAS NMR, TPR, and TEM

6.1 ABSTRACT

$^1$H MAS NMR, $^1$H spin-echo MAS NMR with Al irradiation, $^{29}$Si MAS NMR, and $^1$H→$^{29}$Si CP MAS NMR were used to investigate the deposition of Mo and Ni species on the surface of alumina and silica-alumina. Mo and Ni species first occupy the alumina sites and then the silica sites. The results of temperature-programmed reduction show that the weaker interaction between the Mo and Ni species and the silica-alumina support leads to better reducibility of the metal oxides on silica-alumina than on Al$_2$O$_3$. Mo and Ni species also interact with each other. Transmission electron microscopy proved that, after sulfidation, higher stacks of MoS$_2$ are formed on the silica-alumina support than on the Al$_2$O$_3$ support. The higher stacking is responsible for the higher hydrodenitrogenation activity of the NiMoS catalysts supported on silica-alumina.

6.2 INTRODUCTION

Supported nickel-molybdenum catalysts are extensively used in hydrotreating, one of the most important processes in oil refining (1). These catalysts are usually prepared by depositing molybdenum and nickel oxides on the surface of oxodic supports such as alumina (Al$_2$O$_3$) and silica-alumina (SiO$_2$-Al$_2$O$_3$). The catalysts are used in the active, sulfided state, and the nature and properties of the oxide precursors largely determine the performance of the catalysts. Many studies focused on the nature and structure of the Mo species, and the results of studies employing many characterization techniques indicate that the presence of the promoter atoms does not greatly affect the state of the Mo species on the Al$_2$O$_3$ surface. Since Al$_2$O$_3$ is the
most commonly used support, most studies have focused on Mo oxides supported on Al₂O₃ (see, e.g. 2-7). Several studies dealt with SiO₂-supported Mo (8-15), whereas few studies dealt with SiO₂-Al₂O₃-supported systems (8, 9, 12, 16-18). It is generally accepted that Mo oxide on an Al₂O₃ support forms amorphous monolayers or “islands” on the Al₂O₃ at an Mo loading below 5 atoms/nm² owing to the strong interaction with the support (19, 20). The Mo species were identified as octahedrally or tetrahedrally coordinated (21, 22). On SiO₂ supports, the same octahedrally and tetrahedrally coordinated species are formed, in addition to bulk, orthorhombic MoO₃, even at very low Mo loadings (21, 23). However, less agreement was reached with respect to the silica-alumina-supported catalysts.

Solid-state NMR was used to characterize hydrotreating catalysts (4, 7, 24-31). Most studies concentrated on the Mo structure and the effect of additives by measuring the ²⁷Al, ⁹⁵Mo, and ³¹P NMR spectra. ¹H MAS NMR was used for the structural investigation of hydroxyl groups on Al₂O₃-supported Mo catalysts (4, 7, 26). However, ²⁹Si NMR was not used in hydrotreating catalysis, although one example was reported in a recent patent (32).

In previous studies (33, 34), we reported that the performance of NiMo catalysts supported on amorphous silica-alumina (ASA) is outstanding in hydrodenitrogenation but that a higher hydrogenation activity was found on Al₂O₃-supported catalysts. In the present study, we tried to understand the interaction of the Mo and Ni species with the support. Much attention was paid to the ASA-supported catalysts, and Al₂O₃-supported catalysts were studied for comparison. ¹H MAS NMR and ¹H spin-echo MAS NMR with Al irradiation were used to identify and monitor changes in the surface OH groups. ²⁹Si MAS NMR and ¹H→²⁹Si CP MAS NMR were used to characterize the evolution of the surface Si sites and, in turn, the Al sites. TPR was used to elucidate the phases of Mo and Ni species in the catalysts and TEM to study the MoS₂ stacking of the sulfided catalysts.
6.3 EXPERIMENTAL

6.3.1 Catalyst Preparation

Ni-Mo catalysts supported on alumina (Condea) and silica-alumina (Shell, containing 75 wt% SiO₂, prepared with the sol-gel method) were prepared by successive pore volume impregnation (Mo first) with aqueous solutions containing the appropriate amounts of ammonium molybdate tetrahydrate (Fluka) and nickel nitrate hexahydrate (Fluka). The impregnated materials were dried overnight in air at 393 K and further calcined at 773 K for 4 h after each impregnation step (heating rate 3 K·min⁻¹). The final catalysts contained 2.9 wt% Ni and 8.8 wt% Mo, as analyzed by AAS. The Al₂O₃-supported catalyst had a surface area of 202 m²·g⁻¹ and a pore volume of 0.33 ml·g⁻¹ with a narrow pore size distribution, at around 5.6 nm diameter, as determined by BET N₂ adsorption. The ASA-supported catalyst had a surface area of 296 m²·g⁻¹ and a pore volume of 0.44 ml·g⁻¹ with a narrow pore size distribution at around 5.3 nm.

6.3.2 MAS NMR Measurements

All the NMR spectra were obtained at 9.4 T on a Bruker AMX-400 spectrometer. ²⁹Si MAS NMR spectra were recorded at 79.5 MHz using a 2 µs (π/4) pulse with a 4 s recycle delay and 6000 scans. ¹H→²⁹Si CP/MAS NMR experiments were performed with a 4 s recycle delay, 8000 scans, and a contact time of 10 ms. All the ²⁹Si spectra were collected using 7-mm ZrO₂ rotors at a spinning rate of 5 kHz; chemical shifts were referenced to Q₈M₈ (cubic octamer silicic acid trimethylsilyl ester). Before the ¹H MAS NMR measurements, samples were dehydrated at 673 K and at a pressure below 10⁻² Pa for 15 h. ¹H MAS NMR spectra were recorded at 400.2 MHz by a spin-echo pulse sequence (π/2–τ–π–τ–acquire), where τ was set to one rotor period, and the excitation pulse length was 4.5 µs (π/2). ¹H{²⁷Al} spin-echo double resonance experiments were performed according to the method of van Eck et al. (35). In this experiment, a spin-echo pulse was applied to the ¹H channel and aluminium was
irradiated simultaneously during the first $\tau$ period. The $^{27}$Al irradiation field was about 60 kHz. All the $^1$H spectra were accumulated for 128 scans with a 10 s recycle delay and using 4-mm ZrO$_2$ rotors spun at 10 kHz. The chemical shifts were referenced to adamantane ($\delta=1.74$ ppm). The modified Winfit software Dmfit 98 was employed for deconvolution using Gaussian line shapes. The fitting errors for our spectra were estimated to be about 7\%.

6.3.3 Temperature-Programmed Reduction (TPR)

TPR measurements were conducted with a Micromeritics AutoChem 2910 Automated Catalyst Characterization System. About 0.2 g of sample were used for each measurement. A mixture of 4.8 vol\% H$_2$/Ar was introduced at 50 ml·min$^{-1}$ into the sample loop, and was also used as a reference gas. The sample was heated at a rate of 10 K·min$^{-1}$ to 1173 K and was maintained at this temperature for 30 minutes. The effluent gas was passed through a viscous solution of isopropanol, cooled by liquid N$_2$ to remove the water produced during reduction and analyzed with a Thermal Conductive Detector.

6.3.4 Transmission Electron Microscopy (TEM)

The catalysts were sulfided \textit{quasi in situ} in a mixture of 10 vol\% H$_2$S/H$_2$. The gas flow was kept at 150 ml·min$^{-1}$, while the catalyst was heated at a rate of 6 K·min$^{-1}$ to 623 K. The temperature was then kept at 623 K for 4 h. Subsequently, the sample was cooled to room temperature under flowing high-purity N$_2$. Then the sample was sealed in the reactor and transferred to a glovebox.

TEM measurements were performed using a Philips CM30T electron microscope with an LaB$_6$ filament as the source of electrons operated at 300 kV. Samples were mounted on a microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of the ground sample in n-hexane on the grid, followed by drying under ambient conditions, all in an Ar glovebox. The samples were transferred
to the microscope in a special vacuum-transfer sample holder under exclusion of air
(36).

At least 10 representative micrographs were taken for each catalyst in high-
resolution mode. Typically, the length (L) and number of the stacks (n) of at least 250
slabs were measured for each catalyst.

6.4 RESULTS AND DISCUSSION

6.4.1 MAS NMR

High-resolution $^1$H MAS NMR is a useful and straightforward tool for
characterizing the hydroxyl groups in alumina and zeolites. It can provide quantitative
information about the interaction between metal ions and hydroxyl groups on the
support without the difficulties associated with extinction coefficients that are
encountered in IR spectroscopy. Figure 6.1a illustrates the $^1$H MAS NMR spectra
obtained for the $\gamma$-Al$_2$O$_3$ support and the NiMo/Al$_2$O$_3$ catalyst. As expected, there
were two main peaks. The peak at 1.9 ppm is attributed to the acidic hydroxyl groups
on the alumina surface and the other at -0.2 ppm to the basic hydroxyl groups (7, 37,
38). When quantitative deconvolution of the spectrum, a broad shoulder at around 5.2
ppm can also be identified. It is ascribed to a small amount of physisorbed and
chemisorbed water on the alumina or silica-alumina surface (38). After impregnation
with Mo and Ni, the total number of hydroxyl groups on the alumina surface
decreased substantially, and the basic hydroxyls at -0.2 ppm were preferentially
reduced compared to the acidic hydroxyls at 1.9 ppm. It is agreed that Mo species
adsorb preferentially on the basic hydroxyl groups on Al$_2$O$_3$ support (7, 39). The
preferential disappearance of the basic hydroxyl groups at –0.2 ppm might also be due
to the paramagnetic Ni in the vicinity of hydroxyl groups. When we compare the
results obtained here with those from only Mo supported on Al$_2$O$_3$ (7, 39), however,
this possibility can be excluded. The basic hydroxyls are preferentially occupied, also
upon deposition of F and P on Al$_2$O$_3$ (4, 24).
In the case of ASA, an asymmetric signal was found in the NMR spectrum (Figure 6.1b). After deconvolution, three lines were obtained. As indicated above, the broad line at about 5.0 ppm can be assigned to trace amount of physisorbed and chemisorbed water on ASA (38). The peak at 1.7 ppm may be tentatively ascribed to surface silanol groups, while the peak at about 2.2 ppm may be attributed to OH groups attached to aluminium species or to another kind of hydrogen-bonded silanol group (40). To clarify this, $^1\text{H}$$^{27\text{Al}}$ spin-echo double resonance experiments were carried out, which is analogous to the dipolar dephasing experiment described by Fyfe et al. (41). Under strong aluminium irradiation during the spin-echo pulse sequence applied to the proton, the signal of the proton groups that are strongly coupled to aluminium will be significantly suppressed, while the other protons will be unaffected. Therefore, it offers the possibility of differentiating between the OH signals of species close to an aluminium atom and those of species, which are further away. As shown in the spectra of the ASA support (Figure 6.1b), the intensity of the peak at 2.2 ppm decreases with Al irradiation, while the peak at 1.7 ppm remains unchanged. Thus, we deduced that the peak at 2.2 ppm is the result of the hydroxyl protons associated with aluminium species, and that at 1.7 ppm should be assigned to the silanol protons.

A quantitative analysis showed that the ratio of the surface aluminium hydroxyl groups (AlOH) to silanol groups (SiOH) is 2.2 on the ASA support, whereas this ratio decreased to 0.5 for the NiMo/ASA catalyst. The surface AlOH groups decreased in intensity by 94% after impregnation with Mo and Ni species, while the SiOH groups decreased by 72%. This indicates that Ni and Mo species adsorb preferentially on the AlOH sites on the ASA support.
Figure 6.1 $^1$H MAS NMR spectra of supports and catalysts. a) Al$_2$O$_3$ support and Ni-Mo/Al$_2$O$_3$; b) ASA support and Ni-Mo/ASA.
The ASA support and the NiMo/ASA catalyst were further studied using $^{29}$Si MAS NMR and $^1$H→$^{29}$Si CP/MAS NMR (Figures 2a and 2b). After careful deconvolution of the $^{29}$Si MAS NMR spectra, four peaks were obtained quantitatively. The peaks at –112 and -108 ppm are ascribed to the Si(OSi)$_4$ and Si(OSi)$_3$(OAl) groups, respectively (42-44). The peaks at –100 and -86 ppm are ascribed to terminal silanol groups as in Si(OH)(OSi)$_3$ and Si(OH)$_2$(OSi)$_2$, respectively (45, 46). The assignment of the silanol groups is facilitated by the use of the $^1$H→$^{29}$Si cross-polarization technique (45, 47). As demonstrated in Figure 6.2, application of the CP technique selectively enhances the signals at –102 and -86 ppm of silicon atoms which are coupled with protons of hydroxyl groups by dipolar $^1$H—$^{29}$Si interaction. In comparing the spectra of the ASA support with the ASA-supported catalyst, a strong decrease in intensity was observed at –86 ppm and a slight decrease at -100 ppm. This indicates that Mo and Ni species interact with the silanol groups, and are adsorbed more easily on the geminal silanols.
Figure 6.2 $^{29}\text{Si}$ MAS NMR and $^{1}\text{H} \rightarrow ^{29}\text{Si}$ CP/MAS NMR spectra of a) ASA support and b) NiMo/ASA catalyst
6.4.2 TPR

The interactions between Mo and the supports were further studied by TPR. In order to evaluate the interaction between Ni and Mo species, catalysts containing only Ni or Mo were measured as well (Figures 6.3 and 6.4). Under the applied conditions, all the species can be reduced. For Ni/Al$_2$O$_3$ (Figure 6.3), the maximum reduction temperature is shown as a broad band centred between 640 to 800°C (for simplicity, the celcius degree instead of kelvin is used in this section), which is a higher temperature than for bulk NiO, which shows a single reduction peak at around 300°C (8). For Mo/Al$_2$O$_3$, two main peaks, one at 422°C and the other at 874°C, and a shoulder were observed at 710°C. The low-temperature peak can be assigned to the partial reduction (Mo$^{6+}$ → Mo$^{4+}$) of amorphous, highly defective, multilayered Mo oxides or heteropolymolybdates (octahedral Mo species) (12, 21, 48). The high-temperature peak at 874°C comprises the deep reduction of all Mo species, including highly dispersed tetrahedral Mo species. The peak at 710°C may be due to the intermediate-reducible crystalline phases of orthorhombic MoO$_3$ and Al$_2$(MoO$_4$)$_3$ (18, 48-50). After incorporation of Ni into Mo/Al$_2$O$_3$, the TPR profile shifted to lower temperature (cf. Ni-Mo/Al$_2$O$_3$ in Figure 6.3). Peaks were observed at 370, 593, and 830°C. By changing the Ni content and calcination temperature of the NiMo catalysts, the peak at 593°C was assigned to the reduction of Ni species (8). Both peaks for the Mo species shifted by 40 to 50°C to a lower temperature, indicating that the addition of Ni promoted the reducibility of Mo. At the same time, the reduction of the Ni species was promoted from 640 to 800°C for the reduction of Ni/Al$_2$O$_3$ to 593°C for the reduction of the Ni species in Ni-Mo/Al$_2$O$_3$. This suggests that there was an interaction between Ni and Mo species.

For Ni/ASA (Figure 6.4) the peak reduction temperature is 565°C, which is lower than for Ni/Al$_2$O$_3$, indicating a weaker interaction between Ni and the ASA support. The TPR spectrum for Mo/ASA shows two regions, a broad band with peaks at 460 and 539°C, and another band at 882°C. Compared with the spectrum of Mo/Al$_2$O$_3$ (Figure 6.3), there are more easily-reducible species in the Mo/ASA sample, suggesting that the interaction between the Mo species and the ASA support is weaker than that between the Mo species and the Al$_2$O$_3$ support. After adding Ni to the
Mo/ASA, the reduction peaks of the Mo species shifted to 402 and 802°C (cf. Ni-Mo/ASA in Figure 6.4). The major part of the Mo species was reduced at lower temperature. The reduction of Ni species was also promoted, showing a maximum at 530°C.

Figure 6.3 TPR patterns of Ni, Mo, and Ni-Mo supported on Al₂O₃.

Figure 6.3 TPR patterns of Ni, Mo, and Ni-Mo supported on Al₂O₃.
A comparison of the TPR spectra of the Ni-Mo catalysts supported on Al$_2$O$_3$ and ASA (Figures 6.3 and 6.4) showed that there are more easily-reducible Mo species in the ASA-supported catalyst than in the Al$_2$O$_3$-supported catalyst. The reduction peaks for both the Ni and Mo species shifted to lower temperature. This is in agreement with the results of Rajagopal et al. (12), who studied Mo catalysts supported on a series of silica-alumina of different composition. They found that the extent of reduction increases with SiO$_2$ content, reaching a maximum at the composition SiO$_2$:Al$_2$O$_3$ = 75:25 (wt%) for a fixed Mo loading. A relationship between reducibility and catalytic
activity was established for Mo-containing catalysts (19, 51, 52); this may, to some extent, explain the difference in activity caused by the different supports. The lower hydrogenation activity for cyclohexene over the Ni-Mo/ASA catalyst (33) may be related to the higher reduction temperature (402°C, the first peak for Ni-Mo/ASA in Figure 6.4) compared to the reduction temperature for Ni-Mo/Al2O3 (370°C in Figure 6.3). A relation between hydrodenitrogenation activity and reducibility has, however, not been reported.

We also checked for Mo oxide species by XRD, but no crystalline phases of Mo, Ni, or Al2(MoO4)3 were detected in the Al2O3- and ASA-supported catalysts. They are all amorphous, suggesting that, even though the interaction of Mo and Ni with ASA is weaker than with Al2O3, it is not weak enough to form crystalline phases. We can not rule out the formation of less crystalline MoO3, or Al2(MoO4)3, which can not be detected by XRD. This differs to the results of Massoth et al. (16) and Rajagopal et al. (18). They found proof of three-dimensional Mo species in catalysts with supports containing 75 wt% or more of SiO2 in their silica-alumina samples. One reason may be that they used a higher calcination temperature (540 to 550°C) and a longer calcination time for preparing their catalysts.

6.4.3 TEM

The TEM micrographs of the sulfided catalysts clearly show the edge planes of MoS2-like slabs oriented in line with or slightly tilted from the electron beam. Figure 6.5 shows a representative TEM micrograph of sulfided Ni-Mo/Al2O3. The slabs are homogeneously distributed over the Al2O3 surface. The MoS2-like structures are made up of small ordered sections, which are often bent on a longer scale, suggesting a strong interaction with the support surface. The number of stacking layers is between 1 and 2, with an average of 1.8 layers. The average slab length is calculated to be 48 Å. For Ni-Mo/ASA (Figure 6.6), the slabs tend not to be homogeneously distributed. Some nest-like stacks, in which several slabs are cross-linked, were observed in some of the micrographs. The stacks are higher than in the case of Al2O3 and can consist of
up to 6 layers. The average number of stacking is 2.6 layers and the average slab length is the same as in Ni-Mo/Al₂O₃.

Figure 6.5 TEM image of sulfided Ni-Mo/Al₂O₃.
Figure 6.6 TEM image of sulfided Ni-Mo/ASA.
From the distribution of MoS$_2$ stacking (Figure 6.7), higher stacking was observed for the ASA-supported catalyst than for its Al$_2$O$_3$-supported counterpart. About 35% of the distinguishable MoS$_2$ slabs in the Al$_2$O$_3$-supported catalyst are present as single layers, 50% as double layers, and 15% in three and four layers. For the ASA-supported catalyst, a relatively larger number of slabs present are stacked higher: fewer than 10% in single layers, 55% in double layers, 20% in three layers, and 15% in crystallites with between four to six layers. This confirms the weaker interaction between the ASA support and the Mo species. With higher stacking at the same slab length, there are more edge and corner sites on the ASA-supported catalysts than on the Al$_2$O$_3$-supported catalyst. In analog to the „rim-edge“ model proposed by Daage and Chianelli for HDS (53), hydrodenitrogenation may occur on the corner and edge sites and hydrogenation of phenyl ring only on the corner sites. The higher hydrodenitrogenation activity over the ASA-supported catalysts (34) suggests that the edge and corner sites are responsible for the hydrodenitrogenation reaction. The distribution of the slab lengths was broader for the ASA-supported catalyst than for its Al$_2$O$_3$-supported counterpart (Figure 6.8), in line with the more heterogeneous distribution of the slabs in the ASA-supported catalyst.
Figure 6.7  Stacking distribution (solid line, NiMo/Al₂O₃; dashes, NiMo/ASA).

Figure 6.8  Slab length distribution (solid line, Ni-Mo/Al₂O₃; dashes, Ni-Mo/ASA).
6.5 CONCLUSIONS

MAS NMR was used to study the structure of oxidic Ni-Mo catalysts supported on alumina and silica-alumina. Mo and Ni species on the ASA support preferentially adsorb on the alumina sites, but they can also be located on the silica sites after saturation of the alumina sites.

A weaker interaction of Mo and Ni species with the ASA support leads to a better reducibility of the Mo and Ni oxides than on the Al₂O₃ support. Interaction between Ni and Mo species also contributes to the reduction.

A lower dispersion of the Mo species in the oxidic state, due to the weaker interaction with the ASA support, is the cause of the higher stacking of MoS₂ in the sulfidic form. This in turn leads to a higher hydrodenitrogenation activity over the ASA-supported catalysts.
6.6 REFERENCES


Chapter 7

Concluding Remarks

7.1 CONCLUSIONS

In this thesis, the effects of support and fluorination on the HDN performance and catalyst structures have been studied. The following conclusions have been reached.

Two reaction pathways exist in the conversion of cyclohexene: the hydrogenation to cyclohexane, and the isomerization to methylcyclopentene followed by the hydrogenation to methylcyclopentane. The Al₂O₃-supported Ni-Mo catalysts showed higher activity for the hydrogenation of olefins, whereas the ASA-supported catalysts had stronger acidity and much higher isomerization activity. Strong inhibition by the presence of H₂S indicated that the hydrogenation of olefins takes place on sulfur-deficient sites (vacancies) of the catalyst surface. Under the applied conditions (typical for hydrotreating), i.e. 583 to 623 K and 5.0 MPa, the hydrogenation of cyclohexene is between zero and first order in the partial pressure of cyclohexene (between 16 and 100 kPa) on all catalysts. The in-situ fluorination only promotes the isomerization of cyclohexene to methylcyclopentene by introducing more acid sites for both the Al₂O₃- and the ASA-supported catalysts, whereas the hydrogenation of cyclohexene is not influenced. The kinetic results were fitted with Langmuir-Hinshelwood equations for the conversion of cyclohexene and kinetic parameters were obtained for all the reactions over all catalysts. The possible contribution of fluorination to the hydrogenation of methylcyclohexene to methylcyclohexane in the HDN of methylcyclohexylamine has been excluded.

HDN of methylcyclohexylamine goes via two pathways: the elimination of NH₃ to form methylcyclohexene followed by hydrogenation of methylcyclohexene to methylcyclohexane, and the direct C—N bond cleavage to form methylcyclohexane. Owing to the strong inhibition of methylcyclohexylamine on the hydrogenation of methylcyclohexene and the fact that the hydrogenation of olefins is not promoted by fluorination, the HDN of methylcyclohexylamine can be considered as two parallel
Concluding Remarks

reactions over all catalysts, when there is substantial amount of the reactant present in the reactor. The ASA-supported Ni-Mo catalysts showed higher HDN activity than their Al₂O₃-supported counterparts, mainly by enhancing the elimination path and contributing nothing to the direct reaction to methylcyclohexane. The in-situ fluorination promotes the HDN of methylcyclohexylamine in the same way. Kinetic parameters obtained by fitting experimental data with Langmuir-Hinshelwood equations suggest that the intrinsic activity of the active sites is not influenced by the support or by the in-situ fluorination, only the number of active sites is increased by a change of the dispersion of the active phase.

Two reaction pathways are responsible for the HDN of o-toluidine over Ni-Mo catalysts supported on Al₂O₃ and ASA: path 1 is the hydrogenation of o-toluidine to methylcyclohexylamine, with further reaction to methylcyclohexene and methylcyclohexane, and path 2 is the direct hydrogenolysis of o-toluidine to toluene. The second path only accounts for about 10% of the total conversion. The formation of methylcyclohexene and methylcyclohexane can be attributed to the hydrogenation of the phenyl ring to methylcyclohexylamine, followed by breaking of the C(sp³)–N bond by elimination of NH₃ and hydrogenation of the resulting methylcyclohexene to methylcyclohexane, as in the HDN of methylcyclohexylamine. The ASA-supported catalyst showed higher HDN activity than its Al₂O₃-supported counterpart, and a much stronger promotion by the ASA support was observed in the HDN of o-toluidine than in the HDN of methylcyclohexylamine. The in-situ fluorination enhanced the HDN of o-toluidine to a larger extent on both the Al₂O₃- and ASA-supported catalysts than the HDN of methylcyclohexylamine. In the presence of o-toluidine, the hydrogenation of olefins is not influenced by the in-situ fluorination. The higher HDN activity for o-toluidine may be explained by the better activity for the hydrogenation of the phenyl ring introduced by the ASA support and by the in-situ fluorination. The similar activation energies and heats of adsorption on all catalysts indicate that the intrinsic activity of the active sites is not influenced by the support or by the fluorination. The number of active sites may be increased by a higher stacking of MoS₂, which favors the hydrogenation of aromatics. The much lower concentration of methylcyclohexylamine detected in the HDN of o-toluidine can be explained by the
fast reaction rate of methylcyclohexylamine which is due to strong adsorption on the catalyst surface and no desorption before it undergoes further denitrogenation.

The higher activity for the hydrogenation of aromatics with the ASA support and the in-situ fluorination is further confirmed by the hydrogenation of toluene under typical hydrotreating conditions in the presence of H₂S. By analyzing the different effects of the support and the in-situ fluorination on the four model reactions, four kinds of active sites involved in the HDN of aromatic nitrogen-containing compounds were distinguished. The active site for the C(sp²)─N bond cleavage is highly unsaturated and accommodates aromatic amines in a flat adsorption mode. The site for the C(sp³)─N bond cleavage involves not only a surface vacancy, but also an acid site for the elimination, or a site to provide SH⁻ for nucleophilic substitution. Hydrogenation of aromatics is favored by higher stacking of the MoS₂ slabs with more edge and corner sites, whereas the hydrogenation of olefins is favored on catalysts with better dispersion and lower stacking of MoS₂ slabs.

MAS NMR results showed that during catalyst preparation, Mo and Ni species adsorb preferentially on the alumina sites of the ASA support. Therefore, with the ASA support containing only 25% Al₂O₃, a lower dispersion is obtained. Weaker interaction exist between Mo and Ni species and the ASA support, as indicated by a lower reduction temperature, than that with the Al₂O₃ support. Transmission electron microscopy of the sulfided catalysts showed a higher degree of stacking of the MoS₂ in the ASA-supported catalyst, which is responsible for the higher activity for the hydrogenation of aromatics, and thus the HDN of aromatic nitrogen-containing compounds, and the lower activity for the hydrogenation of olefins.

7.2 OUTLOOKS

ASA support is used in commercial hydrocracking processes. It shows potential applications in HDN and hydrogenation of aromatics. In-situ fluorination is an efficient way of producing catalysts used in processing lubricant feeds. Therefore, by combining the ASA support with the in-situ fluorination technique, catalysts with excellent HDN and hydrogenation of aromatics performances can be developed with
Concluding Remarks

conventional Ni-Mo components. A higher HDS activity for 4-methyl, 6-ethyl dibenzothiophene has been reported by with a Ni-Mo/ASA catalyst (1). Therefore, with the mesoporous structure and suitable acidity of the ASA support, it can also be used to prepare catalysts for deep HDS to produce low sulfur and low aromatics diesel fuels so as to meet the more stringent environmental regulations.

Alternatives may also exist for new HDN catalysts. Carbon support retains advantages such as a lower propensity for coke deposition, higher utility of the metal components and easy recovery of the metals, in addition to superior surface properties for higher activity, compared with the conventional $\gamma$-Al$_2$O$_3$ support. The drawbacks of the microporosity and weaker mechanical strength can be overcome by using carbon-covered alumina to exert the surface properties of carbon and the mechanical strength and pore structure of alumina (2-4). Carbon-covered alumina has shown good performance in hydroprocessing a gas oil (3, 4). Therefore, it can be used to prepare good HDN catalysts, even though a higher amount of additives like fluorine may be needed (3).

Although sulfides of molybdenum and tungsten are commonly used as the main components for hydrotreating catalysts, they are not the most most active ones for HDS and HDN. A systematical study of metal sulfides in HDN by Eijsbouts et al. (5-7) showed the different orders of activity for different reactions with same molar amount of transition metal sulfides supported on an active carbon. For the HDN of quinoline, in which hydrogenation is rate determining, the order follows: Ir > Os > Pt > Re > Rh > Pd, Ru > Mo > W. For the HDN of 2-propylaniline, in which hydrogenation is also rate determining, the order follows: Ir > Re > Os > Ru > Rh > Pt > Mo, W, Pd (7). For the HDN of DHQ, in which C¿N bond breaking through Hoffmann elimination is rate determining, the order is as follows: Ir > Os, Rh > Ru > Mo, Pt > Re > W (6). Ledoux and Djellouli (8) reported that among the second-row transition metal sulfides on activated carbon, Ru was better than Pd, Rh, and Mo for HDN of pyridine. Even Mo/C was better than a commercial Ni-Mo/Al$_2$O$_3$ HDN catalyst based on per mole of Mo. In a study of the simultaneous HDN of pyridine and HDS of thiophene with a series of transition metal sulfides, the order of activity was Ir > Pt > Rh > Ru > Pd (9). All these carbon-supported metal sulfides exhibited higher activity per mole of metal than conventional sulfided Ni-Mo/Al$_2$O$_3$ and Co-
Mo/Al\(_2\)O\(_3\) catalysts. There is no doubt that these transition metal sulfides are at least as good as Ni-Mo and Co-Mo catalysts. Thus, Ir/Al\(_2\)O\(_3\) catalyst is more active for HDN than a Ni-Mo/Al\(_2\)O\(_3\) catalyst per mole of metal and has a higher HDN/HDS selectivity (10). When used in industrial reactors, not only the molar activity is important, but also a high loading of metals should be attainable. The economic feasibility has to be considered as well.

Metal carbides and nitrides are potential catalysts in HDN. High surface-area Mo\(_2\)N and W\(_2\)N can be prepared by nitriding MoO\(_3\) and WO\(_3\), respectively, with ammonia (11) and Mo\(_2\)C by carbiding MoO\(_3\) with methane (12). Mo\(_2\)C and Mo\(_2\)N were highly active for the HDN of quinoline (13). Their activities were similar to a commercial sulfided Ni-Mo/Al\(_2\)O\(_3\) catalyst. In the absence of sulfur, Mo\(_2\)C showed a much higher selectivity for aromatic hydrocarbons than sulfided Ni-Mo/Al\(_2\)O\(_3\). This indicates that Mo\(_2\)C and Mo\(_2\)N can remove nitrogen from propylaniline directly by hydrogenolysis of the C—N bond, without having to hydrogenate the phenyl ring. When sulfur was added to the feed, however, the propylbenzene to propylcyclohexane ratio was much lower and more representative of a sulfided Ni-Mo/Al\(_2\)O\(_3\) catalyst. These results were confirmed by Lee et al. (14) and Abe et al. (15) with Mo\(_2\)N and Stanczyk et al. (16) with molybdenum and niobium oxynitrides. Better HDN performance in the absence of H\(_2\)S was reported with Mo\(_2\)N (17) and with a nitrided Ni-Mo/Al\(_2\)O\(_3\) catalyst (18) than a commercial sulfided Ni-Mo/Al\(_2\)O\(_3\) catalyst. However, under typical hydrotreating conditions, metal sulfides were readily formed at the catalyst surface, as detected by X-ray photoelectron spectroscopy, even if X-ray diffraction did not show any crystalline MoS\(_2\) (20, 21). Then, the carbides and nitrides behave as the sulfides in HDN. Therefore, molybdenum carbides and nitrides can only be used in cases with very low sulfur contents.
7.3 REFERENCES

Publications Related to This Project

Lianglong Qu, and Roel Prins
„Reaction Kinetics of the Hydrodenitrogenation of Methylcyclohexylamine over Fluorinated NiMoS/Al₂O₃ Catalysts“

Lianglong Qu, and Roel Prins
„Hydrogenation of Cyclohexene over *in Situ* Fluorinated NiMoS Catalysts Supported on Alumina and Silica-Alumina“

Lianglong Qu, and Roel Prins
„The Effects of *in Situ* Fluorination and Support on the Hydrodenitrogenation of Methylcyclohexylamine“

Lianglong Qu, Weiping Zhang, Patricia J. Kooymen, and Roel Prins
„MAS NMR, TPR, and TEM Studies of the Interaction of NiMo with Alumina and Silica-Alumina Supports“

Lianglong Qu, Martin Flechsenhar, and Roel Prins
„Kinetics of the Hydrodenitrogenation of o-Toluidine over Fluorinated NiMoS/Al₂O₃ and NiMoS/ASA Catalysts“
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Curriculum Vitae

Lianglong Qu
Born on 25 October 1965
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Sept. 1983-July 1987 Undergraduate study at the Department of Chemistry, Zhengzhou University, Henan, China

Bachelor of Science
Jan. 1987-July 1987 Pilot plant research on the synthesis of higher alcohols from syngas, Henan Fertilizer Plant, Henan, China

Sept. 1987-Jan. 1990 Post-graduate study at the Graduate School of China Petrochemical Corporation (SINOPEC), Beijing, China

Master in Engineering (Organic Chemical Engineering)

Jan. 1990-Aug. 1998 Assistant Engineer, Engineer (since 1991), and Senior Engineer (since 1997) at RIPP, SINOPEC, Beijing, China
Catalysts and processes R & D; Supervising catalysts scale-up, industrial production, and process performance in refineries and petrochemical complexes; Providing technical services to industries

Apr. 1995-Oct. 1995 Research Scientist at the Institut de Recherches sur la Catalyse (IRC), Centre National de la Recherche Scientifique (CNRS), Villeurbanne, France
Characterization of RuS2/SiO2 catalysts using FTIR (pyridine and CO adsorption), XRD, and XPS

Since Aug. 1998 Research assistant and doctoral thesis in the group of Prof. Dr. R. Prins at the Laboratory for Technical Chemistry, Federal Institute of Technology (ETH), Zurich, Switzerland
Kinetic study of hydrodenitrogenation over in-situ fluorinated NiMo catalysts supported on alumina and silica-alumina