Comparative study of alumina- and carbon-supported catalysts for hydrogenolysis and hydrogenation of model compounds and coal-derived liquids

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Comparative Study of Alumina- and Carbon-Supported Catalysts for Hydrogenolysis and Hydrogenation of Model Compounds and Coal-Derived Liquids

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Carbon- and alumina-supported Fe, Mo, Fe-Mo, and Co-Mo sulfide catalysts were compared for their ability to catalyze hydrotreating reactions such as dibenzothiophene hydrodesulfurization, quinoline hydrodenitrogenation, dibenzofuran hydrodeoxygenation, and hydrogenation of butenes, naphthalene, biphenyl, and coal extract. The temperature and pressure varied from 653 to 703 K and from 1 to 300 bar of H2, respectively. Below 50 bar of H2 the carbon-supported catalysts were more active for hydrogenolysis and hydrogenation than the alumina-supported ones. However, further H2 pressure increase was most effective for the latter catalysts. The activity differences between carbon- and alumina-supported catalysts are ascribed to differences in active phase-support interaction. Generally, iron sulfide was found less active than molybdenum sulfide, and iron sulfide also appeared to be less effective than cobalt sulfide in promoting molybdenum sulfide. However, the Fe-Mo sulfide showed the higher selectivity for hydrogenation relative to hydrodesulfurization. Carbon-supported iron sulfide (low-cost catalyst) had considerable activity for coal extract hydrogenation.

Introduction

It is anticipated that the shortage of clean and easy to handle petroleum feedstocks will become severe within the next decades. Large investments therefore will be spent in many countries with the ultimate objective of commercializing coal conversion processes, yielding gaseous and liquid fuels of a desired high purity (Meyers, 1981; Simoons, 1978). Liquids derived from coal need to be purified in order to reduce their content of heteroatoms (such as sulfur, nitrogen, and oxygen). It is a well-established fact that these constituents cause a substantial environment pollution. They are also known to have a harmful effect on the efficiency of the installations (such as power generation stations and internal combustion engines) to which they are applied. For the removal of the above contaminants, hydrotreating catalysts used in the oil-processing industry have so far been found to be most applicable. Numerous studies have been carried out in recent years dealing with the application of sulfide catalysts for coal hydroconversion reactions.

In general, two approaches to direct liquefaction can be distinguished. First, catalysts can be used, in combination with a suitable solvent, in a one-stage process, in which the coal is liquefied and simultaneously upgraded. This process (e.g., H-coal), however, requires not only a multifunctional catalyst, but presumably will effect a rapid deactivation of the catalyst applied. Second, clean-burning coal liquids can be produced in a two-stage process. During the first step the coal is thermally depolymerized, i.e., converted to soluble form, after which radical stabilization is required, for instance, with the aid of a disposable catalyst. In the second step the liquefied product may be upgraded by using catalysts that possess high hydrogenolysis activity. Alumina-supported Co-Mo and Ni-Mo catalysts are considered to be very active for the removal of heteroatoms from coal liquids, whereas radical stabilization is reported to be one of the catalytic properties of intrinsic mineral coal constituents like pyrite (Curtis et al., 1983; Guin et al., 1978; Brooks et al., 1983).

Despite the high activity of Co-Mo and Ni-Mo on alumina catalysts, there is a potential for applying a more inert material like carbon as a support for sulfide catalysts. Via application of carbon carriers one might meet some of the disadvantageous properties of alumina-supported catalysts, i.e., the high propensity for coke formation and heavy metal deposition causing a rapid deactivation. It has to be anticipated that commercially available carbon materials, such as carbon black, active carbon, and graphite, can also have some serious drawbacks, for instance, a poor mechanical strength (causing crushing when packed in an industrial reactor) and a high degree of microporosity (causing diffusion limitation in the case of large reactant molecules). However, as outlined by Walker (1978) and Vissers (1985), carbon carriers can be prepared that are not subject to these drawbacks. Promising results have recently been obtained with carbon-supported sulfide catalysts in terms of hydrodesulfurization and coal extract hydrogenation activity. The most advantageous properties of a carbon carrier are believed to be its low interaction toward a deposited active phase (providing a high active-phase efficiency), low cost (e.g., activated carbons), and high available surface area (to finely disperse the active phase), which may exceed 1000 m²/g. Due to these favorable features, when supported on carbon, the conventionally applied sulfides of cobalt–nickel–molybdenum have shown a remarkably higher activity for hydrodesulfurization (de Beer et al., 1981; Duchet et al., 1983).
In view of the complexity of this matter, we have chosen, as a first approach, to compare catalysts having similar metal contents on the basis of their activity per mass unit.

In view of the possible profit of low-cost catalysts for coal liquefaction reactions, attention is given to four aspects. In the first place, the properties of various carbons, of which, e.g., activated carbons are inexpensive compared to alumina, as a carrier material are checked and compared to those of aluminas under various conditions (1–300 bar, 623–703 K, batch and flow reactors). Second, the activity of iron sulfide catalysts is studied relative to that of molybdenum sulfides for a number of hydrotreating reactions, viz., thiophene and dibenzothiophene hydrodesulfurization (HDS), butene (olefin) hydrogenation (HYD), naphthalene and biphenyl (aromatic) HYD, quinoline hydrodenitrogenation (HDN), and dibenzofuran hydrodeoxygenation (HDO). In the third place, it was examined for the same set of reactions to what extent iron could replace cobalt as a promotor for molybdenum sulfide catalysts. Finally, some of the investigated catalysts were tested for their ability to hydrogenate a coal extract.

### Experimental Section

#### Catalyst Preparation and Composition

The properties of the support materials used in both commercial and laboratory-prepared catalysts are listed in Table I. The compositions of the catalysts examined are given in Table II, where the metal loading is shown as the weight percentage of metal oxide in the oxidic catalyst precursors. The laboratory samples were prepared by pore volume impregnation of the support with aqueous solutions of Co(NO$_3$)$_2$6H$_2$O (Merck, >99%), Fe(NO$_3$)$_3$9H$_2$O (Merck, >99%), and (NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O (Merck, >99%). Samples containing two different metals were prepared by a two-step impregnation procedure, in which the Mo phase was deposited first. After impregnation with ammonium heptamolybdate or cobalt nitrate solutions, the samples were dried at 383 K for 16 h. Samples impregnated with iron nitrate solution were dried at 293 K for 16 h in flowing air (100 cm$^3$/min), since it was reported before that drying at 383 K caused considerable active-phase sintering and consequently a lower catalytic activity (Groot et al., 1984). None of the catalysts was subjected to any further heat treatment or calcination procedure. Metal contents of the laboratory-prepared samples were checked by atomic absorption spectroscopy using a Perkin-Elmer 300 AAS spectrometer.

#### Presulfiding

Prior to each activity test, except coal extract hydrogenation, the catalyst was presulfided in situ in a mixture of 10 mol % H$_2$S (Matheson CP grade) in H$_2$ (flowrate 60 cm$^3$/min) at atmospheric pressure. Two different presulfiding procedures were followed: (a) linear increase of temperature from 293 to 673 K in 1 h and (b) linear increase of temperature from 293 to 673 K in 1 h, followed by 2 h at 673 K. The Fe/RX3 and Fe/EC-3.5 catalysts, when their thiophene HDS activity was examined, were presulfided according to the first procedure, while in all other experiments the catalyst was presulfided according to procedure b.

### Table I. Properties of Support Materials

<table>
<thead>
<tr>
<th>support</th>
<th>surface area, $S_{BET}$, m$^2$/g</th>
<th>pore vol, cm$^3$/g</th>
<th>notation used in this report</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma$-Al$_2$O$_3$ (Ketjen 000-1.5E)</td>
<td>170</td>
<td>0.64</td>
<td>Al$_2$O$_3$(K)</td>
</tr>
<tr>
<td>$\gamma$-Al$_2$O$_3$ (G-1, Poland) activated carbon (Norit RX3-extra)</td>
<td>260</td>
<td>0.24</td>
<td>Al$_2$O$_3$(G) RX3</td>
</tr>
<tr>
<td>activated carbon (Norit RX3)</td>
<td>1190</td>
<td>1.03</td>
<td>RX3</td>
</tr>
<tr>
<td>carbon black composite* (Ketjen EC-3.5)</td>
<td>950</td>
<td>0.75</td>
<td>ROX3</td>
</tr>
</tbody>
</table>

*Metal contents are given in the same sequence. Commercial sample.

### Table II. Catalyst Composition Given as wt % Metal in the Oxidic Catalyst Precursors

<table>
<thead>
<tr>
<th>support</th>
<th>metal phase</th>
<th>Co–Mo*</th>
<th>Fe–Mo*</th>
<th>Fe</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al$_2$O$_3$(K)</td>
<td>3.1</td>
<td>8.0b</td>
<td>2.8</td>
<td>8.0</td>
<td>6.4</td>
</tr>
<tr>
<td>Al$_2$O$_3$(G)</td>
<td>1.3</td>
<td>11.2b</td>
<td>2.8</td>
<td>8.0</td>
<td>5.0</td>
</tr>
<tr>
<td>RX3</td>
<td>3.1</td>
<td>8.0</td>
<td>2.8</td>
<td>8.0</td>
<td>5.0</td>
</tr>
<tr>
<td>ROX3</td>
<td>2.1</td>
<td>6.7</td>
<td>2.6</td>
<td>7.9</td>
<td>5.2</td>
</tr>
<tr>
<td>Ec-3.5</td>
<td>1.2</td>
<td>6.7</td>
<td>2.6</td>
<td>7.9</td>
<td>5.2</td>
</tr>
</tbody>
</table>

*Metal contents are given in the same sequence. Commercial sample.

### Table III. Reactions Applied for Catalytic Activity Measurements

<table>
<thead>
<tr>
<th>notation</th>
<th>type of reactor</th>
<th>operating pressure, bar</th>
<th>operating temp, K</th>
<th>reactor diam or vol</th>
<th>presulfiding</th>
<th>sampling</th>
<th>mixing</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>flow</td>
<td>1</td>
<td>673</td>
<td>0.8 cm</td>
<td>in situ</td>
<td>periodically</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>batch</td>
<td>35–70</td>
<td>623–685</td>
<td>20 cm$^2$</td>
<td>in situ</td>
<td>at end of run</td>
<td>vibration</td>
</tr>
<tr>
<td>III</td>
<td>batch</td>
<td>15–140</td>
<td>883</td>
<td>1000 cm$^3$</td>
<td>in situ</td>
<td>periodically</td>
<td>rotation (800 rpm)</td>
</tr>
<tr>
<td>IV</td>
<td>batch</td>
<td>300</td>
<td>703</td>
<td>200 cm$^3$</td>
<td>in situ</td>
<td>at end of run</td>
<td>shaking (100 min$^{-1}$)</td>
</tr>
</tbody>
</table>

*The catalyst particle size was 0.5–0.85 mm.
Catalytic Reactors. Catalytic activity measurements were carried out in four different reactors, the main characteristics of which are given in Table III. Reactor I consisted of a flow-through quartz reactor in which 200 mg of catalyst was presulfided and subsequently tested without intermediate flushing or temperature change. The reaction products are analyzed by means of an on-line gas chromatograph. The experimental error was found to be less than 2%.

In reactor II, which will be described by Tajik et al., 12.5 mg of catalyst was presulfided in situ. Next, the reactor was cooled to room temperature (approximately 7 K/min), after which the reactant mixture (2.0 cm³) was introduced to the main vessel. Then the mixture was agitated by vibration of a closed capillary in which a rod was rotated (1500 rpm). The operating temperature and pressure were established as fast as possible in order to minimize preambulatory effects. After reaction the reactor was cooled to room temperature (approximately 84 K/min) and opened to air. The reaction products were analyzed by gas chromatography. The experiments were carried out in duplicate, yielding conversion levels with an accuracy of approximately 3%.

In reactor III, 2.0 g of catalyst was presulfided in situ. While the reactor was kept at the maximum sulfiding temperature, the reaction mixture (180 cm³) was fed into the autoclave under hydrogen pressure. Then mixing was brought about by magnetic stirring, and hydrogen was added to attain operating pressure. Liquid samples were taken periodically and were analyzed by gas chromatography. The experimental error amounted to about 3%.

In reactor IV only measurements on coal extract hydrogenation were carried out. The reactor was filled with a slurry containing 5.0 g of catalyst and 10.0 g of feed, whose composition is given in the next section. Since the catalyst could not be presulfided, 2.53 g of CS₂ (Merck, 99%) was added to the reaction mixture to provide a sufficient H₂S partial pressure. Hydrogen was added to a pressure of 125 bar, after which the vessel was heated to the desired temperature. The reactor was then shaken mechanically at a frequency of 100 periods per minute. After reaction the autoclave was cooled to ambient temperature and opened to air. According to a method described elsewhere (Stolarski et al., 1981), a mass balance was drafted for various solubility fractions (see next section). All experiments were carried out in duplicate with an accuracy of about 5%.

Catalytic Activity Measurements. A set of eight test reactions was applied to determine the catalytic activities.

a. Thiophene HDS. Thiophene was desulfurized to butenes and butane in reactor I (1 bar, 673 K). The reactant feed consisted of 6.2 mol % thiophene (Merck, >99%) in H₂ (flowrate 50 cm³/min). Assuming a first-order reaction rate in thiophene (Lee and Butt, 1977), the reaction rate constant k_HDS (expressed as m³ of feed/(kg of catalyst)-s) is calculated after a 2-h runtime.

b. Butene HYD. Being a consecutive reaction of thiophene HDS, butene HYD activities were determined under conditions identical with those of the thiophene HDS activities. Since we consider the reaction of the various butenes (1-butene, trans-2-butene, and cis-2-butene) to butene to be first order in butene, the reaction rate constant k_HYD (m³ of feed/(kg of catalyst)-s) is calculated after a 2-h run.

c. Dibenzothiophene (DBT) HDS. The reaction mechanism of dibenzothiophene (Aldrich, 99%) HDS has been the subject of thorough investigation (Singhal et al., 1981; Kwart et al., 1980; Broderick and Gates, 1981; Houalla et al., 1980). The main reaction pathway is believed to proceed via initial C-S bond scission, although the side route via partially hydrogenated dibenzothiophene intermediates may not be totally excluded (Broderick and Gates, 1981). Biphenyl (BP; Fluka, >99%), cyclohexylbenzene (CHB; Aldrich, 99%), and dicyclohexyl (DCH; Aldrich, 99%) were found to be the main reaction products. HDS conversions were calculated according to % HDS = (BP + CHB + DCH)/(BP + CHB + DCH + DBT).

In reactor II experiments were carried out for 4 h at 50 bar of H₂ and 653 K. The feed consisted of 50 mg of DBT dissolved in 1.5 g of n-dodecane. Carbon disulfide (6.3 × 10⁻³ g), which is rapidly converted to H₂S and CH₃ in a hydrogen atmosphere, was added to the reaction mixture. Although H₂S is also produced during the HDS of DBT (maximum 0.27 mol of H₂S), CS₂ with a maximum production of 0.16 mol of H₂S was fed to the mixture. In order to maintain a sufficiently high H₂S partial pressure in the reactor (to keep the catalyst in the sulfided state), the same amount of CS₂ was added to the mixture in the HDO, HDN, and aromatic HYD reactions.

In reactor III dibenzothiophene HDS was carried out at 683 K, while the pressure was varied between 15 and 140 bar of H₂. The reaction mixture fed to the reactor contained 6.0 g of DBT, 0.63 g of CS₂, and 180.0 g of n-dodecane (Merck, 99%). The conversions reported in this paper were calculated after 1 h of reaction time.

d. Dibenzo furan (DBF) HDO. An approximate reaction network for the HDO of dibenzofuran (Aldrich, 99%) has recently been proposed by Krishnamurthy et al. (1981). In the present reaction mixture BP and CHB were identified as the main reaction products. HDO conversions were calculated by % HDO = (BP + CHB)/(BP + CHB + DBF). The activity measurements were carried out in reactor II under the same conditions as the HDS of DBT (i.e., 50 bar of H₂, 653 K, 4-h reaction time). Correspondingly, the feed consisted of 50 × 10⁻³ g of DBF and 6.3 × 10⁻³ g of CS₂ dissolved in 1.5 g of n-dodecane.

e. Quinoline (Q) HDN. Extensive effort has been devoted by several investigators to the elucidation of the reaction network for the HDN of quinoline (Aldrich, 99%), for example, Satterfield and Cocchetto (1981), Satterfield and Carter (1981), Miller and Hineman (1984), and Schulz (1979). It is now generally accepted that prior to the C-N bond fission the nitrogen-containing ring has to be hydrogenated. Propylbenzene (PB; Aldrich, 99%), propylcyclohexane (PCH; Aldrich, 99%), and 1,2,3,4-tetrahydroquinoline (THQ; Aldrich, 99%) were identified as the main reaction products. HDN conversion was determined by % HDN = (PB + PCH)/ (PB + PCH + THQ + Q). In accordance with the HDS and HDO model reactions, the HDN of Q was carried out in reactor II at 653 K of 50 bar of H₂ for 4 h by using a reaction mixture that contained 50 × 10⁻³ g of Q, 6.3 × 10⁻³ g of CS₂, and 1.5 g of n-dodecane.

f. Biphenyl (BP) HYD. In agreement with the HDS of DBT, which takes place via BP formation, the reaction products present after the HYD of BP are CHB and DCH. Biphenyl HYD levels were calculated by % HYD = (CHB + DCH)/(CHB + DCH + BP). Biphenyl HYD experiments were carried out in reactor II by using a mixture of 50 × 10⁻³ g of BP, 6.3 × 10⁻³ g of CS₂, and 1.5 g of n-dodecane. The conditions used were 653 K, 70 bar of H₂, 4 h of reaction time.

g. Naphthalene (NL) HYD. Naphthalene (Fluka, 99%) is primarily hydrogenated to tetralin (TL; Merck, 99%) and next to decalin (DL; Merck, 99%) under high conditions.
the active phase. Iron and molybdenum sulfide catalysts
supports, of which the RX3 type yields the best catalysts.
carrier results in lower activities for sulfided iron and co-
more pronounced when iron rather than molybdenum is
between carbon- and alumina-supported samples is much
negligible HDS activity and that the carbon-supported
gaseous products (G).

Results
Thiophene HDS and Butene HYD. In Figure 1 the
reaction rate constants \( k_{\text{HDS}} \) and \( k_{\text{HYD}} \) are presented for
the entire series of catalyst examined as well as for the
blank supports. In order to compare the relative activities,
the \( k_{\text{HYD}}/k_{\text{HDS}} \) ratios are also included in the figure.

Figure 1a clearly shows that the blank supports have a
negligible HDS activity and that the carbon-supported
catalysts have a much higher activity for thiophene HDS
than the alumina-supported catalysts, for both the pro-
and nonpromoted systems. The difference between carbon-
and alumina-supported compounds is much more pronounced when iron rather than molybdenum is the active phase. Iron and molybdenum sulfide catalysts possess comparable activities on the same carbon support. Provided that the same supports are used, sulfided Co–Mo catalysts are much more active for HDS than Fe–Mo systems. In fact, for the Fe–Mo catalysts, very little promoting action is observed. The carbon composite carrier results in lower activities for sulfided iron and co-
butene HYD and thiophene HDS.

no \( k_{\text{HYD}}/k_{\text{HDS}} \) ratios can be obtained for the blank
supports and for \( \text{Fe}(6.4)/\text{Al}_2\text{O}_3(\text{K}) \), due to their negligible
HDS activities. However, it appears from Figure 1, parts
b and c, that sulfided Fe–Mo and Mo catalysts show a high
selectivity for butene HYS compared to Co–Mo and Fe
catalysts. The sulfided Co–Mo catalyst supported on
\( \text{Al}_2\text{O}_3(\text{G}) \) also shows a significantly higher selectivity to
HYS than that on \( \text{Al}_2\text{O}_3(\text{K}) \), which has a correspondingly
lower Mo-to-Co ratio. Thus, whereas addition of Co to a
Mo catalyst especially results in an enhanced HDS activity,
iron favors the HYS activity of Mo catalysts.

Dibenzothiophene HDS, Dibenzofuran HDO, and Quinoline HDN, at 50 bar of \( \text{H}_2 \). The conversion levels for HYS, HDO, and HDN model compound reactions are given in Figure 2 for various catalysts and the corre-
spending support materials. It should be noted that these
activity data are obtained under different reaction condi-
tions (type of reactor, temperature, and pressure) than the
activities for thiophene HYS.

a. Dibenzothiophene HYS. The HYS activity of
alumina-supported catalysts relative to those of carbon-

<table>
<thead>
<tr>
<th>Coal Extract Composition* and HYD Conversions after 2 h of Reaction at 703 K and 300 bar of ( \text{H}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>feed composition</td>
</tr>
<tr>
<td>blank</td>
</tr>
<tr>
<td>RX3</td>
</tr>
<tr>
<td>( \text{Fe}(5.0)/\text{RX3} )</td>
</tr>
<tr>
<td>( \text{Co}(3.1)-\text{Mo}(8.0)/\text{RX3} )</td>
</tr>
<tr>
<td>( \text{Co}(3.1)-\text{Mo}(8.0)/\text{Al}_2\text{O}_3(\text{K}) )</td>
</tr>
<tr>
<td>( \text{Co}(1.3)-\text{Mo}(11.2)/\text{Al}_2\text{O}_3(\text{G}) )</td>
</tr>
</tbody>
</table>

*Composition of feed and product is expressed in weight percentages.
supported catalysts is clearly enhanced at higher hydrogen pressure as follows from a comparison between Figures 1a and 2a. Co-Mo, Mo, and Fe catalysts have only slightly higher activities for DBT HDS when supported on carbon rather than on alumina, while the Fe-Mo catalysts are far more active on carbon than on alumina. Furthermore, Mo catalysts have a much higher activity than Fe catalysts. It is noted that it is difficult to discriminate between the various promoted systems, which have conversions near 100%. However, the promotional actions of Fe and Co on Mo catalysts seem to be similar when a carbon support is used. The Fe-Mo/Al₂O₃(K), however, has even less activity than Mo/Al₂O₃(K).

b. Dibenzofuran HDO. From the lower conversions obtained for HDO in comparison to HDS for the catalysts as well as for the blank supports, it appears that the oxygen can be less easily removed than sulfur from corresponding organic molecules under the conditions applied. As can be seen from Figure 2b, there are clearly differences between carbon- and alumina-supported catalysts, the carbon-supported ones giving the higher activities for all types of active phases. Among the nonpromoted systems molybdenum sulfides yield high conversions compared to iron sulfides, which appear to be essentially inactive for quinoline HDN. Whereas Mo-based catalysts have clearly enhanced HDN activity after addition of cobalt, iron seems to poison them when either carbon or alumina is employed as a support.

d. Quinoline HDN. A fair estimation concerning the ease of nitrogen removal compared to oxygen and sulfur removal cannot be made on the basis of the reactions studied, due to the differences in organic structure of the N-, S-, and O-containing model compounds employed. Conversions yielded in the blank HDN experiments are in between those for HDS of DBT (higher) and for HDO of DBF (lower). Differences obtained for quinoline HDN (Figure 2c) between carbon- and alumina-supported catalysts are apparent, though less pronounced than those observed for dibenzofuran HDO. Among the nonpromoted systems molybdenum sulfides yield high conversions compared to iron sulfides, which appear to be essentially inactive for quinoline HDN. Whereas Mo-based catalysts have clearly enhanced HDN activity after addition of cobalt, iron seems to poison them when either carbon or alumina is employed as a support.

Dibenzothiophene HDS at Various H₂ Pressures. Dibenzothiophene HDS conversions, determined after 30 min of reaction time for Co(3.1)-Mo(8.0)/Al₂O₃(K) and Co(2.1)-Mo(6.7)/ROX₃ catalysts, are shown as a function of hydrogen pressure in Figure 3. For comparison the HDS conversion of Co(2.6)-Mo(7.9)/EC-C3.5 at 140 bar of H₂ is presented in the same figure.

Obviously, sulfided alumina- and carbon-supported Co-Mo catalysts behave differently with increasing hydrogen pressure. Whereas the activity of Co(2.1)-Mo(6.7)/ROX₃ only increases by about 50% from 35 to 140 bar, the activity of Co(3.1)-Mo(8.0)/Al₂O₃(K) is considerably enhanced at increasing H₂ pressure. It is clear from the figure that both catalysts have a similar activity at about 50 bar of H₂. Furthermore, the activity of the composite carbon-supported catalyst is approximately equal to that of the active carbon-supported one at high hydrogen pressure.

In Figure 4 a typical HDS conversion vs. reaction time curve for a Co-Mo/Al₂O₃ catalyst is shown. In addition, corresponding figures for Fe(6.4)/Al₂O₃(K) and Fe(5.0)/
RX3 are given. The thermal background conversion had appeared to be negligible.

From Figure 4 it is clear that both sulfided iron catalysts possess a much lower HDS activity at 140 bar of H₂ than Co(3.1)-Mo(8.0)/Al₂O₃(K). Therefore, the reaction catalyzed by iron sulfide catalysts starts very slowly, whereas Co–Mo catalysts yield a substantial DBT conversion within the first minutes. The conversions as a function of reaction time obtained by alumina- and carbon-supported iron sulfide catalysts are more or less equal. Figures 3 and 4 suggest that the point of equal activity for alumina- and carbon-supported iron sulfides lies at much higher H₂ pressure than that for Co–Mo catalysts.

**Biphenyl and Naphthalene HYD.** Optimum conditions for the HYD of biphenyl were determined by testing the Co(2.1)-Mo(6.7)/ROX3 catalyst at various temperatures and pressures as shown in Figure 5. From the figure it can be seen that biphenyl aromatic ring HYD has a strong pressure and a moderate temperature dependency. The highest conversion is obtained at high H₂ pressure and relatively low temperature, which is consistent with thermodynamic predictions and with literature data for the hydrogenation of other aromatic ring compounds (de Vlieger et al., 1984; Gates et al., 1979).

Biphenyl and naphthalene HYD conversions, determined after 4 h of reaction at 653 K and 70 bar of H₂, are presented in Figure 6.

Considerable differences are observed between carbon- and alumina-supported catalysts for the hydrogenation of biphenyl, despite the high hydrogen pressure. The unpromoted systems yield much lower conversions than the promoted ones. Among them, however, Mo catalysts are more active than iron catalysts. Furthermore, cobalt appears to be a better promoter for Mo catalysts than iron, at least on carbon. It is noteworthy that Co(2.1)-Mo(6.7)/ROX3 is more active for aromatic ring hydrogenation than Fe(2.8)-Mo(8.0)/RX3, while the latter is the better olefin (butene) HYD catalyst (Figure 1b).

It is evident from a comparison of parts a and b of Figure 6 that under the conditions applied naphthalene is much easier to hydrogenate than biphenyl, as predicted by thermodynamics. For the simple iron and molybdenum catalysts a clearly higher activity for hydrogenation of naphthalene is noticed for the carbon-supported systems than for the alumina-supported ones. Among these, Mo catalysts are the more active. Due to the high conversion levels obtained with all promoted catalysts, no fair comparison can be made among them. Nevertheless, it seems that the promoting action of both cobalt and iron on molybdenum sulfide catalysts is small.

**Coal Extract HYD.** In Table IV results are presented for coal extract hydrogenation experiments using various alunina- and carbon-supported catalysts, the pure carbon support, and blank run.

One of the more interesting results is the high conversion level obtained with Fe(5.0)/RX3. Although this is lower than those of the alumina-supported catalysts, the activity of Fe(5.0)/RX3 appears to be considerably higher than that yielded by Co(3.1)-Mo(8.0)/RX3. Among the alumina-supported catalysts the one produced by Ketjen is the more active; both, however, are much more effective than the corresponding carbon-supported sample. From the blank runs it is clear that some conversion of the heaviest fractions already can be obtained without addition of catalyst.

**Discussion**

**Alumina- vs. Carbon-Supported Catalysts.** All of the hydrotreating reactions studied, i.e., sulfur, oxygen, and nitrogen removal and hydrogenation, are catalyzed by both alumina- and carbon-supported sulfide catalysts. The application of carbon substrates is particularly advantageous at relatively low hydrogen pressures, while alumina-supported catalysts generally are the more active at high pressures. However, the hydrogen pressure at which both supports yield similar activities is dependent upon the metal components and the type of reaction.

Most of these features, we believe, are caused by differences in the interaction between the metal component and the support. Due to their being relatively inert, carbon substrates do not interact strongly with the active material (Jung et al., 1982). The alumina surface, however, possesses high concentrations of surface hydroxyl groups, which can serve as relatively strong chemisorption sites for the metal components during the preparation procedure (Wang and Hall, 1982). The metal ions, which are,
especially after calcination of the catalyst precursor (like in commercial alumina-supported catalysts), strongly bonded to the alumina surface, may be less readily reduced than when supported on carbon (Garten and Ollis, 1974). Although partial exchange of sulfur for oxygen may occur at our maximum sulfiding temperature (675 K), as shown by Arnolde et al. (1985) for calcined Mo/Al₂O₃ catalysts, an insufficiently sulfided catalyst will result in a correspondingly low activity.

Uncalcedined alumina-supported catalysts are less hampered by active phase-support interaction since Fe/Al₂O₃, not subjected to any heat treatment, was reported to be completely sulfided under the present sulfiding conditions (Groot, 1984). However, catalysts that are not heat treated can be essentially deactivated by deposition of elemental sulfur upon the active phase. Especially anionic remainders of the initially employed metal salt, which contain large amounts of oxygen (e.g., nitrate), can be responsible for producing an excess of elemental sulfur by oxidation of H₂S (Groot, 1984). When the elemental sulfur formed cannot readily be rehydrogenated to H₂S under the sulfiding conditions applied, the active sulfide phase will remain covered by the sulfur and show a poor catalytic activity. On a carbon surface the oxygen-containing components will be less strongly adsorbed and may be converted into volatile compounds prior to reacting with H₂S.

It is clear from the data obtained for the HDS of thiophene and the subsequent HYD of butene that carbon-supported catalysts are more active than those on alumina when the reaction is carried out at atmospheric pressure. Prior to the other HDO, HDS, HDN, and HYD model reactions the catalyst sulfiding procedure is carried out at atmospheric pressure. Consequently, the calcined alumina-supported catalysts may be insufficiently converted into their active sulfide form, as they were before the thiophene HDS test. An increase in hydrogen pressure should facilitate the reduction of strongly bonded metal ions. Moreover, coke formation on alumina catalysts will be suppressed at elevated hydrogen pressures. In the case of uncalcined alumina-supported catalysts, the elemental sulfur formed during the low-pressure sulfiding step will be more readily hydrogenated with increasing hydrogen pressure. The results presented in the former section indeed concur with these assumptions. Increasing the hydrogen pressure enhances the activity of the alumina catalysts but has much less effect upon the activity of the carbon-supported catalysts. The above, of course, would imply that alumina-supported catalysts operating at low hydrogen pressure can be activated by means of a high-pressure presulfidation.

Obviously, the nature of the active material also determines the differences between alumina- and carbon-supported catalysts at low hydrogen pressure. Thiophene HDS data obtained for carbon-supported catalysts (Figure 1a), for example, show that iron sulfide is more active than molybdenum sulfide. The corresponding (uncalcined) alumina-supported samples, however, show that sulfided iron on alumina catalysts are essentially inactive for the same reaction, whereas sulfided molybdenum on alumina possesses a reasonable activity. This can be explained as follows. Fe/Al₂O₃ catalysts produce a considerable amount of elemental sulfur during the sulfiding procedure, probably without being able to sufficiently rehydrogenate the sulfur deposited on the (potentially active) iron sulfide phase at atmospheric pressure. On sulfided Mo/Al₂O₃ catalysts, however, the excess of elemental sulfur is readily converted into H₂S during the sulfiding procedure, resulting in a more or less free accessible molybdenum sulfide phase. Hence, it is not surprising that the hydrogen pressures at which alumina- and carbon-supported catalysts show an equal activity differ significantly for molybdenum and iron sulfide. While the pressure at which alumina- and carbon-supported molybdenum sulfides yield equal conversions for HDS of DBT presumably lies slightly above 50 bar of H₂ (Figure 2a), the corresponding pressure for iron sulfides is about 140 bar of H₂ (Figures 2a and 4).

From the above it is clear that employing carbon as a carrier material for sulfide catalysts yields the most benefit compared to alumina at relatively low hydrogen pressures. This behavior is more pronounced when a metal component is applied, which interacts strongly with an alumina surface. Because of the disadvantages of alumina supports (expensive, high hydrogen pressure required, high coking propensity), carbon-supported catalysts (lower bulk density) might gain economical significance when their activity (per unit of volume) at low hydrogen pressure is large enough compared to alumina-supported ones.

Sulfided Fe vs. Mo Catalysts. While Fe/RX₃ is more active for thiophene HDS than Mo/RX₃, all of the other model reactions studied are more favorably catalyzed by molybdenum-containing rather than by iron-containing catalysts. When the reaction is carried out at elevated pressures, Mo/Al₂O₃ is also a better catalyst than Fe/RX₃, although the former contains double the amount of active phase. Moreover, iron-based catalysts yield negligible HDO and HDN conversions.

Very little has been published about carbon-supported sulfide catalysts. Bridgewater et al. (1982) found that sulfided alumina- and charcoal-supported Mo catalysts had similar activities for thiophene HDS at 625 K and atmospheric pressure. However, they prereduced the Mo/C catalyst, which presumably resulted in a MoO₂ phase that is difficult to sulfide. Very high activities, on the other hand, are claimed by Gavis and Jones (1981), who reported MoS₂/C to be superior to Co–Mo/γ-Al₂O₃ for coal extract hydrogenation. As far as we know, no studies have been reported on carbon-supported iron sulfides. Iron sulfides have been the subject of extensive investigation (Weisser and Landa, 1979), as they are present in coal as the main intrinsic catalytic component. In this respect, iron sulfides are known to possess some activity for hydrogenation reactions and for the removal of heteroatoms from coal (Curtis et al., 1983; Guin et al., 1978; Brooks et al., 1983; Mazzocco et al., 1981). Work in which unsupported iron sulfide was added to coal (Stohl, 1983; Garg and Givens, 1983; Derbyshire et al., 1981) also revealed that the overall S, N, and O content was lowered by the catalytic action of iron sulfide. These studies, however, did not clarify the intrinsic catalytic functionalities of iron sulfides. Model compound studies with iron sulfides in hydrogenolysis reactions are also reported (Brooks et al., 1983; Thomas et al., 1982; Montano and Bommannavar, 1983), although no consensus exists to what extent iron sulfides are catalytically active. The model compound studies cited, however, were carried out on unsupported iron sulfides having a relatively low surface area. From our experiments it was evidently proved that HDS and HYD are catalyzed by iron sulfides, preferably dispersed on a relatively inert support, which is in clear contradiction with the findings reported by Montano and Bommannavar (1983), who firmly exclude HDS functionality. Although negligible HDN and HDO conversions were noticed, it may be worthwhile to investigate these functions of iron sulfide at increased hydrogen pressure.

In conclusion it may be said that, although Mo-based catalysts are generally more active than Fe-based ones,
sulfided iron on carbon catalysts have rather promising activities for HDS and HYD under moderate conditions. Hence, carbon-supported iron sulfides might be useful as low-cost disposable catalysts.

**Sulfided Fe–Mo vs. Co–Mo Catalysts.** A comparison of Fe-Mo and Co-Mo catalysts shows that, on the same support, Co-Mo catalysts are the more active for thiophene HDS, dibenzofuran HDO, quinoline HDN, and biphenyl HYD. Similar activities of Co-Mo and Fe-Mo catalysts are observed for dibenzo[ghi]fluoranthene HDS (except Fe-Mo/Al₂O₃, which has a low activity compared to Co-Mo/Al₂O₃) and naphthalene HYD. The selectivity of Fe-Mo catalysts toward butene HYD is rather poor compared to thiophene HDS; however, it is much higher than that of Co-Mo catalysts. Although the application of Fe-Mo catalysts to hydrotreating reactions has not been widely investigated, they have been studied by Thakur et al. (1979). They found that unsupported Fe-Mo catalysts are about 2 times less active than Co-Mo catalysts for thiophene HDS; the activity for cyclohexene HYD was reported to be about similar for both systems. Considering the differences between supported and unsupported catalysts with regard to differences in preparation, active surface area, etc., our results are consistent with those of Thakur.

Generally, sulfided Fe-Mo/RX₃ has an activity comparable to that of the commercial Co-Mo/Al₂O₃ catalysts for all reactions studied. Although Fe-Mo/RX₃ possesses a high selectivity for butene (olefin) HYD compared to Co-Mo/Al₂O₃, this advantage is not found for the HYD of aromatics. Quinoline HDN, which is considered to proceed via aromatic ring hydrogenation (Satterfield and Cocchetto, 1981; Rollmann, 1977), is less catalyzed by Fe-Mo/RX₃ than by Co-Mo/Al₂O₃(K). However, carbon-supported Fe-Mo sulfide catalysts might be promising catalysts for coal hydroliquefaction reactions, since high HYD activity is required at the beginning of the process as the high aromatics present in coal have to be hydrogenated and as the coal radicals formed need to be stabilized by rapid hydrogenation, therewith avoiding retrograde polymerization reactions. Moreover, Fe-Mo catalysts can be relatively inexpensive since iron is used instead of cobalt, and the carriers employed, especially activated carbons, are less expensive than alumina.

**Coal Extract Hydrogenation.** A factor, which will highly influence the catalytic conversion of coal extracts or feedstocks containing similar large molecules, is the catalyst pore size distribution. Since both of the alumina-supported catalysts possess a favorable pore size distribution with an average pore diameter between 5 and 16 nm, no significant diffusion limitations may be anticipated. In fact, Co(3.1)-Mo(8.0)/Al₂O₃(K), which yields a higher conversion than Co(1.3)-Mo(11.2)/Al₂O₃(G), also has the wider pores. Both carbon-supported catalysts, however, have the disadvantage of having more than 50% of the pore volume contained in micropores, with a diameter below 1.2 nm. These pores, of course, are hardly accessible for reactants of the same molecular size. So, it may not be very surprising that the Co(3.1)-Mo(8.0)/RX₃ catalyst shows a low activity for coal extract HYD compared to alumina-supported catalysts. On the other hand, the Fe(5.0)/RX₃ catalyst appears to be rather active, although the same microporous active carbon was used as a carrier material. This unexpected high activity, however, might be explained by the fact that the iron phase is deposited predominantly on or near the outer surface of the support grains (Groot, 1984), while a more uniform distribution of Co-Mo on the same support might be expected [Mo is introduced as anionic species, for which sufficient anchorage sites on the carbon surface are available (Vissers et al., 1983)]. Consequently, most of the active iron-containing phase will be available for adsorption of reactant molecules and hence may provide a reasonable activity. Fortunately, some of the hydrotreating reactions involved in coal extract HYD occur relatively easily, such as the HYD of polyaromatics, and can be accomplished by a moderately active catalyst like iron sulfide.

**Conclusions**

Carbon-supported sulfide catalysts are much more active than those supported on alumina for HDS, HDO, HDN, and HYD model reactions when a relatively low hydrogen pressure (below 50 bar of H₂) is employed. At higher hydrogen pressures, however, alumina-supported catalysts become more active. The difference in activity between carbon- and alumina-supported metal sulfides at low hydrogen pressure increases as (a) less reactive compounds are studied (i.e., the model reactions studied may be ranked in the following order of decreasing reactivity: HDS ≅ naphthalene HYD > HDN > HDO ≅ biphenyl HYD) and (b) the interaction between the active-phase precursor and the alumina support increases (in the case of calcined catalyst precursors) or, as in uncalcined catalysts, the active sulfide phase is a better catalyst for the hydrogenation of elemental sulfur formed during the presulfiding pretreatment (e.g., Mo > Fe).

Cobalt sulfide is a better promoter for molybdenum sulfide than iron sulfide. Iron sulfide promoted molybdenum sulfide catalysts, however, have a much higher selectivity for HYD relative to HDS. For nonpromoted catalysts, except for thiophene HDS, in which Fe/C catalysts are better than Mo/C, the latter are more active for the other model reactions.

Carbon-supported sulfide catalysts may thus be economically attractive compared to the conventional alumina-supported ones for application in a coal liquefaction process at relatively low hydrogen pressure. Obviously, the same applies to heavy oil and bitumen upgrading. Moreover, the catalyst itself, probably also being less sensitive to coking compared to ones on alumina, is inexpensive when an activated carbon is used as carrier for an active phase in which iron may take part. Application of iron sulfide is favored by its promising activity for coal extract hydrogenation. Iron sulfide in combination with molybdenum sulfide possesses a high selectivity for hydrogenation, which might facilitate radical stabilization in the primary coal liquefaction step.

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**Registry No.** DBT, 132-65-0; DBF, 132-64-9; Q, 91-22-5; BP, 92-52-4; NL, 91-20-3; Fe, 7439-89-6; Mo, 7439-98-7; C, 7440-44-0. Cobalt sulfide, 12653-56-4. Carbon-supported sulfide catalysts are much more active than those supported on alumina for HDS, HDO, HDN, and HYD model reactions when a relatively low hydrogen pressure (below 50 bar of H₂) is employed. At higher hydrogen pressures, however, alumina-supported catalysts become more active. The difference in activity between carbon- and alumina-supported metal sulfides at low hydrogen pressure increases as (a) less reactive compounds are studied (i.e., the model reactions studied may be ranked in the following order of decreasing reactivity: HDS ≅ naphthalene HYD > HDN > HDO ≅ biphenyl HYD) and (b) the interaction between the active-phase precursor and the alumina support increases (in the case of calcined catalyst precursors) or, as in uncalcined catalysts, the active sulfide phase is a better catalyst for the hydrogenation of elemental sulfur formed during the presulfiding pretreatment (e.g., Mo > Fe).

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Role of Nickel Crystallite in Nickel Zeolite Catalysts: n-Hexane Isomerization

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The isomerization of n-hexane has been studied in the presence of excess hydrogen at 643 K in a flow reactor over NiCa-Y (nickel calcium Y type faujasite) and NiM (nickel hydrogen mordenite) catalysts. Catalysts were prepared by ion exchange, and nickel concentration was varied from 1 to 5 wt%. Nickel crystallite size distribution was affected with the degree of nickel exchange and the type of parent cation present in the zeolite. NiCa-Y containing 1.86 wt% nickel exhibited maximum isomerization activity and selectivity. NiM catalysts showed lower conversion and activity compared to NiCa-Y catalysts because of higher acidity and the presence of deactivation, and their usage requires severe pretreatment of feedstocks. The noble-metal-loaded acid zeolites are free from this drawback and can be operated at relatively low temperatures (Kouwenhoven, 1971). Pt and Pd supported over faujasite type Y and mordenite in decationized alkaline earth and rare earth exchanged forms exhibited excellent isomerization activity and selectivity in a number of cases (Rabo, 1961, 1965; Lanewalla, 1967; Voorhies, 1968). A number of extensive reviews on isomerization of C5 or C6 paraffins using bifunctional catalysts are reported (Minachev, 1969; Bolton, 1970; Hopper, 1972; Ribeiro, 1980).

Introduction

Isomerization of n-paraffins is an industrially important octane-upgrading process. Various bifunctional catalysts containing noble metals like Pt and Pd over various supports such as silica-alumina, chlorinated alumina, and crystalline aluminosilicates (zeolites) have been widely studied and proven to possess high isomerization selectivity (Weisz, 1983). Thermodynamic consideration of isomerization reactions reveals that the lower the reaction temperature the greater the increase in octane number (Kouwenhoven, 1975; Bolton, 1976), and thus chlorinated alumina base catalysts, which can be operated at lower temperatures (383–453 K), are found to be the best bifunctional catalysts. However, these catalysts represent potential corrosion problems and are susceptible to deactivation, and their usage requires severe pretreatment of feedstocks. The noble-metal-loaded acid zeolites are free from this drawback and can be operated at relatively low temperatures (Kouwenhoven, 1971). Pt and Pd supported over faujasite type Y and mordenite in decationized alkaline earth and rare earth exchanged forms exhibited excellent isomerization activity and selectivity in a number of cases (Rabo, 1961, 1965; Lanewalla, 1967; Voorhies, 1968; Beecher, 1966; Minachev, 1969; Bolton, 1970; Hopper, 1972; Ribeiro, 1980).

A few studies using nickel zeolites have been reported in the literature (Koradia, 1980; Law, 1980; Rubenstein, 1986; 4321/186/1225-0530@1.50/0 © 1986 American Chemical Society