Hydrocracking of n-decane over zeolite-supported metal sulfide catalysts. 2. Zeolite Y-supported Ni and Ni-Mo sulfides

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Hydrocracking of n-Decane over Zeolite-Supported Metal Sulfide Catalysts. 2. Zeolite Y-Supported Ni and Ni–Mo Sulfides

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For zeolite Y-supported nickel sulfide catalysts the influence of the metal sulfide dispersion on the hydrocracking properties for n-decane is examined. In order to obtain different nickel sulfide distributions (inside or outside the zeolite structure) and dispersions, the preparation method (impregnation of CaY or ion exchange of NaY), sulfidation procedure (direct sulfidation or sulfidation after drying), and metal loading are varied. A higher nickel sulfide surface (as measured by dynamic oxygen chemisorption) results in a strong increase of the n-decane conversion, but this is not accompanied by an improvement of the catalytic properties toward ideal hydrocracking. Additionally, some zeolite Y-supported Ni–Mo sulfide catalysts (varying in preparation method and sulfidation procedure) are tested for the hydroconversion of n-decane. However, no promoter effect could be observed. The activity of the bimetallic sulfide catalysts is always almost equal to that of the most active monometallic sulfide constituent.

Introduction

Hydrocracking is one of the major processes for the conversion of heavy oil fractions (large high boiling molecules) into more valuable clean low boiling products (Bolton, 1976; Ward, 1983). For this process bifunctional catalysts with both a hydrogenation–dehydrogenation and a cracking function are needed. Typical examples of these types of catalysts are noble metals (Pt, Pd) supported by acidic zeolites. Weitkamp et al. (Schulz and Weitkamp, 1972; Weitkamp, 1982) and Jacobs et al. (Jacobs et al., 1982, 1984; Martens et al., 1986; Jacobs and Martens, 1991) examined the reaction mechanism for the hydrocracking of higher paraffins over these types of catalysts extensively.

However, modern hydrocracking catalysts are required to have a flexible product selectivity combined with a high activity and a high resistance against heteroatom (S, N, O) containing molecules. These requirements can be met by combining a zeolite with a sulfidic hydrogenation catalyst. In part 1 of this study (Welters et al., 1995) several CaY-supported transition metal sulfide (Fe, Co, Ni, Mo, Ru, Rh, Pd, W, Re, Ir, and Pt) catalysts prepared by impregnation are compared on their hydrocracking properties. The CaY-supported Rh and Ir sulfide catalysts show almost ideal hydrocracking behavior (high conversions combined with a high product selectivity for isomerization of n-decane and almost no secondary cracking (Jacobs and Martens, 1991)). The lowest conversions are measured for the Fe, Co, and Ni sulfide catalysts. These catalysts show no isomerization of n-decane and a high degree of secondary cracking, indicating that the hydrocracking properties are far from ideal (Jacobs and Martens, 1991). For zeolite Y-supported nickel sulfide catalysts, Welters et al. (1994a) have shown that both the preparation method (impregnation of CaY or ion exchange of NaY) and the sulfidation procedure (direct sulfidation or sulfidation after drying) can influence the dispersion and distribution of the sulfide phase (inside or outside the zeolite pores) and consequently the thiophene hydrodesulfurization activity of these catalysts. Especially sulfdation after drying can result in a strong increase of nickel sulfide dispersion and catalytic activity. On the basis of their findings one may assume that also for hydrocracking catalysts improvement of the metal sulfide dispersion results in a higher conversion and/or catalytic properties more close to ideal hydrocracking (Jacobs and Martens, 1991). In order to verify this assumption, the influence of the metal sulfide dispersion on the hydrocracking properties is examined by studying the hydroconversion of n-decane at moderate pressure (3.0 MPa) for zeolite-supported nickel sulfide catalysts.

In commercial hydrocracking catalysts usually Mo or W sulfide promoted by Ni or Co sulfide is used. Combination of these metal sulfides results in very active hydrotreating catalysts, due to the presence of a so-called CoMoS or NiMoS phase (Topsoe and Clausen, 1984; Prins et al., 1989). Possibly, a CoMoS or NiMoS phase can also be prepared on an acidic zeolite support. Hydrocracking catalysts consisting of a zeolite-supported CoMoS or NiMoS phase might show a substantially higher hydrocracking activity than the single metal sulfide catalysts. Several studies (Cid et al., 1985, 1987; Davidova et al., 1986; Leglise et al., 1988; Kovacheva et al., 1991; Laniecki and Zmierczak, 1991) have been performed to investigate the promoter effect on sulfided zeolite-supported bimetallic Co–Mo or Ni–Mo catalysts. In some of them a promoter effect is reported, for instance by Cid et al. (1987) and Laniecki and Zmierczak (1991) for thiophene hydrodesulfurization (HDS) and by Leglise et al. (1988) for benzene hydrogenation at medium high pressure. However, the general picture is that the promoter effects, if present at all, are very small. In the present study it is attempted to obtain a synergetic effect between Mo and Ni sulfide in zeolite-supported sulfided Ni–Mo catalysts in order to achieve a better balance between the (de)hydrogenation and the acidic function for hydrocracking of n-decane.
Experimental Section

Catalyst Preparation. The CaY support (Ca$_{2}$Na$_{8}$\((\text{AlO})_9\text{SiO}_2\text{H}_2\text{O}\) is prepared from a NaY (Na$_{8}$\((\text{AlO})_9\text{SiO}_2\text{Na}_2\text{H}_2\text{O}\); PQ, CBV-100) zeolite by ion exchange with aqueous CaCl$_2$ solutions followed by washing until Cl$^-$ free. CaY-supported catalysts containing 4 and 8 wt % Ni are prepared by pore volume impregnation with aqueous solutions of Ni(NO$_3$)$_2$. After impregnation, the catalysts are dried in static air at 383 K for 16 h, followed by calcination in static air at 673 K for 2 h.

NiNaY zeolites containing 4 and 8 wt % Ni are prepared by ion exchange with NiCl$_2$ aqueous solutions. After filtration, the zeolite is washed until Cl$^-$ free and dried at 383 K for 16 h in static air. The impregnation and ion exchange type catalysts are denoted as Ni(x)/CaY and Ni(x)NaY, respectively, with x representing the weight percentage nickel (determined by atomic absorption spectroscopy and calculated on the basis of the water-free zeolite).

One bimetallic catalyst is prepared by pore volume impregnation with an ammonium heptamolybdate (AHM) solution of appropriate concentration on Ni(8)-NaY zeolite (Mo(7)/Ni(8)NaY, the catalyst contains 7 wt % Mo). A second Ni-Mo catalyst is prepared by consecutive impregnation of CaY with an AHM solution and a Ni(NO$_3$)$_2$ solution (Ni(8)/Mo(7)/CaY). After each impregnation step the catalyst is dried in static air at 383 K (16 h) and calcined at 673 K (2 h).

All samples are stored in a desiccator over a saturated CaCl$_2$ solution. Prior to catalytic testing the powders are pressed, ground, and sieved to obtain a particle size fraction between 125 and 425 $\mu$m.

Hydrocracking of n-Decane. All hydrocracking experiments are performed in a microflow reactor containing about 0.5 g of dry catalyst mixed with 5 g of SiC (particle size 0.5 mm) at a total pressure of 3.0 MPa. Prior to reaction the catalysts are sulfided at 673 K (6 K min$^{-1}$ from room temperature to 673 K, 2 h at 673 K) in a 10% H$_2$S in H$_2$ flow of 100 std cm$^3$ min$^{-1}$ at 3.0 MPa pressure (standard sulfidation). In previous work it is shown that the presence of water during sulfidation strongly influences the nickel sulfide dispersion. Prior to sulfidation experiments are first sulfided in a higher dispersion (Welters et al., 1994a). Therefore, in some cases sulfidation is preceded by in situ drying at 673 K (heating rate 6 K min$^{-1}$) in a He flow. At this temperature the flow is switched to a 10% H$_2$S/H$_2$ flow (100 std cm$^3$ min$^{-1}$) and the catalyst is sulfided for 2 h at atmospheric pressure (dry sulfidation). The sulfidation pretreatment is given in parentheses after the catalyst notation. Standard sulfidation and dry sulfidation are abbreviated to (st sulf) and (dry sulf), respectively.

During reaction a H$_2$S/H$_2$ gas flow is led over the catalysts (total flow 1250 std cm$^3$ min$^{-1}$, H$_2$S:H$_2$ = 1:1250). Liquid n-decane is pumped into the system where it is immediately evaporated and mixed with the H$_2$S/H$_2$ gas flow (liquid flow rate of 50 $\mu$L min$^{-1}$, molar ratio n-decane:H$_2$ = 1:200; W/F = 0.37 gcat. h g$_{n}$-decane$^{-1}$). Gas samples are taken at the reactor exit and analyzed with an on line gas chromatograph equipped with a UCON LB 550 X capillary column. The products with one or two carbon atoms cannot be separated by this analysis, and for the comparison of product selectivities they are therefore treated as a lumped fraction referred to as C1–C2.

Subsequently, the reaction temperature is decreased in steps of approximately 20 K, holding the temperature at each step until the conversion is stable. In this way the n-decane conversion is measured as a function of temperature. At the end of each run the temperature was increased to 673 K to examine the deactivation of the catalyst during the entire activity test. This deactivation never exceeds 3 conversion %.

Catalyst Characterization. Thermogravimetric analysis (TGA) is used to determine the coke content of the spent nickel sulfide catalysts (oxygenation in a 20% O$_2$/He flow, Setaram TG 85 balance). Because the oxidation of the coke deposits and the metal sulfide phase cannot be separated, the measured weight loss is corrected for the weight loss due to the oxidation of the nickel sulfide, assuming the presence of Ni$_3$S$_2$.

Dynamic oxygen chemisorption (DOC) measurements are used to determine the relative nickel sulfide dispersion (Bachelier et al., 1980, 1982, 1984; Bouwens et al., 1994). Two different sulfidation procedures are used: (I) the “dry sulf” type samples are directly sulfided in the DOC reactor using the atmospheric pressure procedure described in the previous section; (II) the “st sulf” type samples are first sulfided ex situ using the high pressure procedure described in the previous section. Subsequently, they are sulfided in the DOC reactor at atmospheric pressure. Control measurements showed that the air contact and the resulfidation have no measurable influence on the nickel sulfide dispersion. After sulfidation the catalysts are flushed for 1 h at 673 K in He (O$_2$ and H$_2$O levels lower than 1 ppm) to remove adsorbed H$_2$S, and then cooled to 333 K, at which temperature the oxygen chemisorption is performed. At this temperature the support does not chemisorb oxygen. According to Bachelier et al. (1980, 1982, 1984) side reactions (SO$_2$ and COS formation) are avoided, and the oxygen is adsorbed irreversibly on the sulfide catalyst. Pulses of 5% O$_2$ in He are injected in the carrier gas flow and passed over the catalyst sample and a thermal conductivity detector. When effluent peaks are increased to a constant size (less than 1% difference between two successive peaks), the total O$_2$ uptake is calculated.

Results

In Figure 1 the conversion of Ni(4)/CaY (st sulf) is compared with that of Ni(4)NaY (st sulf). The catalysts
the product distributions at the same conversion (about Figure 1). In the case of the impregnated Ni(x)/CaY being observed for the ion exchanged type Catalysts (see Catalysts do not show ideal hydrocracking behavior, the nickel loading does not have (4)NaY (dry sulf). 

Table 2. Coke Contents of Spent Nickel Sulfide Catalysts

<table>
<thead>
<tr>
<th>catalyst</th>
<th>wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(4)CaY (st sulf)</td>
<td>15.8</td>
</tr>
<tr>
<td>Ni(4)NaY (st sulf)</td>
<td>15.4</td>
</tr>
<tr>
<td>Ni(4)CaY (dry sulf)</td>
<td>14.4</td>
</tr>
<tr>
<td>Ni(4)NaY (dry sulf)</td>
<td>13.3</td>
</tr>
<tr>
<td>Ni(8)NaY (dry sulf)</td>
<td>11.1</td>
</tr>
</tbody>
</table>

a The formation of C8 and C9 has not been observed. b Moles of cracked products (NCx) per mole of n-decane cracked (NC10).

Table 3. Dynamic Oxygen Chemisorption on Nickel Sulfide Catalysts with Different Preparation and Sulfidation Conditions (mmol of O2 Chemisorbed per kg of Catalyst)

<table>
<thead>
<tr>
<th>catalyst</th>
<th>standard sulfidation</th>
<th>drying before sulfidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(4)CaY</td>
<td>14</td>
<td>23</td>
</tr>
<tr>
<td>Ni(8)/CaY</td>
<td>-</td>
<td>26</td>
</tr>
<tr>
<td>Ni(4)NaY</td>
<td>13</td>
<td>51</td>
</tr>
<tr>
<td>Ni(8)NaY</td>
<td>-</td>
<td>66</td>
</tr>
</tbody>
</table>

appear to have a similarly low conversion. An increase of the nickel loading to 8 wt % does not result in a significant change of the hydrocracking properties either for Ni(8)/CaY (st sulf) or for Ni(8)/NaY (st sulf) (the results of these activity measurements are not shown). When dry sulfidation is applied, the catalysts become much more active, with the strongest increase in activity being observed for the ion exchanged type catalysts (see Figure 1). In the case of the impregnated Ni(x)/CaY (dry sulf) samples an increase of the nickel content to 8 wt % does not influence the n-decane conversion (Ni(8)/CaY (dry sulf) is therefore not shown). In contrast herewith, Ni(8)/NaY (dry sulf) shows a clearly higher activity than Ni(4)/NaY (dry sulf).

In Table 1 the product distributions of the Ni catalysts shown in Figure 1 are given. None of the catalysts shows any isomerization of n-decane. Comparison of the product distributions at the same conversion (about 15%) suggests that the improved activity for dry sulfided catalysts leads to less secondary cracking, as the number of cracked products per cracked molecule of decane decreases (Table 1, last column), especially for the ion exchanged catalysts. However, as these catalysts do not show ideal hydrocracking behavior, the product distribution is not only dependent on the conversion, but also on the reaction temperature (Steinjäger et al., 1981). When the product selectivities are compared at almost the same reaction temperature (about 660 K), the degree of secondary cracking for the dry sulfided catalysts appears to be as high as or even higher than for the standard sulfided catalysts. Apparently, the dry sulfidation does not result in a significantly lower degree of secondary cracking. Also the nickel loading does not have a strong effect on the product selectivities, not even for Ni(8)/NaY (dry sulf), despite its clearly higher conversion compared to Ni(4)/NaY (dry sulf).

In Table 2 the coke contents of various spent nickel sulfide catalysts are given. On all catalysts a high amount of coke is deposited during the activity test. The amount decreases if the catalysts are dried prior to sulfidation. Also the increase in nickel loading on Ni(4)/NaY (dry sulf) leads to a decrease in coke deposition. The amounts of oxygen chemisorbed on the catalysts as determined by DOC are presented in Table 3. This amount is a measure for the relative nickel sulfide surface area. Both standard sulfided catalysts (Ni(4)/CaY and Ni(4)NaY) show a similar O2 chemisorption. Interestingly, the quantities of chemisorbed oxygen are low compared to the values reported earlier (Welters et al., 1994a) for the same type of catalysts sulfided at 0.1 MPa instead of 3.0 MPa. Due to the lower space velocity during the sulfidation at 3.0 MPa (57 versus 4 min⁻¹ at 673 K), the water adsorbed on the zeolite is removed more slowly than during sulfidation at 0.1 MPa. Therefore, higher amounts of water will be present during the sulfidation process and consequently more sintering of the nickel sulfide phase will occur (Welters et al., 1994a). As a result, catalysts sulfided at 3.0 MPa will have a lower nickel sulfide dispersion than those sulfided at 0.1 MPa.

The oxygen uptake increases if the catalysts are dried before sulfidation. The increase is strongest for the ion exchanged sample. The 4 and 8 wt % Ni containing Ni(x)/CaY (dry sulf) samples adsorb similar amounts of O2, indicating a comparable sulfide surface area in spite of the different nickel contents. Ni(8)/NaY (dry sulf) shows an increase in oxygen chemisorption compared to Ni(4)/NaY (dry sulf). However, the increase is not proportional to the increase in nickel loading; indicating that the nickel sulfide dispersion in Ni(8)/NaY (dry sulf) is lower than in Ni(4)/NaY (dry sulf). Possibly, an improvement of the hydrocracking activity can also be obtained by the use of bimetallic catalysts. The presence of both Ni and Mo may generate a synergetic effect (Topsøe and Clausen, 1984; Prins et al., 1989) resulting in a stronger hydrogenation function, and, consequently, in higher conversions and/or ideal hydrocracking behavior (Welters et al., 1995). Figure 2 shows the n-decane conversions for several zeolite Y-supported Ni-Mo catalysts. For comparison also the activity of a sulfided Mo(7)/CaY sample is included (Welters et al., 1995). The n-decane conversion of Ni(8)/Mo(7)/CaY (dry sulf) is almost equal to that of sulfided Mo(7)/CaY. For both catalysts the sulfidation pretreatment is found to have no influence on the hydrocracking properties. Therefore, only the results of the dry sulfided catalysts are included. Mo(7)/Ni(8)/NaY (st sulf) shows a catalytic activity similar to that of the sulfided Mo(7)/CaY catalyst. Mo(7)/Ni(8)/NaY (dry sulf) has the highest n-decane conversion, which is comparable to that of Ni(8)/NaY (dry sulf) shown in Figure 1.
Table 4. Product Selectivities of the Ni–Mo Catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv (reaction temp. [K])</th>
<th>C1–C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C10</th>
<th>NCx/NC10&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(7)/CaY (dry sulf)</td>
<td>13% (699)</td>
<td>3.9</td>
<td>21.3</td>
<td>64.1</td>
<td>60.9</td>
<td>46.9</td>
<td>9.3</td>
<td>2.5</td>
<td>2.12</td>
</tr>
<tr>
<td>Ni(4)/Mo(7)/CaY (dry sulf)</td>
<td>16% (684)</td>
<td>2.6</td>
<td>18.0</td>
<td>60.6</td>
<td>61.9</td>
<td>50.6</td>
<td>10.3</td>
<td>2.2</td>
<td>2.09</td>
</tr>
<tr>
<td>Mo(7)/Ni(8)/NaY (st sulf)</td>
<td>20% (681)</td>
<td>2.6</td>
<td>21.8</td>
<td>62.9</td>
<td>60.5</td>
<td>47.7</td>
<td>9.2</td>
<td>1.4</td>
<td>2.10</td>
</tr>
<tr>
<td>Mo(7)/Ni(8)/NaY (dry sulf)</td>
<td>14% (671)</td>
<td>0</td>
<td>18.8</td>
<td>63.2</td>
<td>64.1</td>
<td>51.7</td>
<td>8.4</td>
<td>0</td>
<td>2.06</td>
</tr>
</tbody>
</table>

<sup>a</sup> The formation of C8 and C9 has not been observed. <sup>b</sup> Moles of cracked products (NCx) per mole of n-decane cracked (NC10).
water during the sulfidation of a Mo(7)/CaY catalyst apparently has no influence on the metal sulfide dispersion. Also for Ni(8)/Mo(7)/CaY the sulfidation method has no influence on the catalytic activity. Its activity is almost equal to that of Mo(7)/CaY, indicating that on Ni(8)/Mo(7)/CaY no synergetic effect between the nickel and the molybdenum sulfide phase is present. The activity of the latter catalyst is almost entirely determined by the Mo(7)/CaY part, which is in agreement with the fact that Ni(8)/CaY is far less active than Mo(7)/CaY.

The same applies to Mo(7)/Ni(8)NaY (st. sulf). Again the activity is comparable to the Mo(7)/CaY, and no synergetic effect is present. The activity of Mo(7)/Ni(8)NaY (dry sulf) is comparable to that of Ni(8)NaY. On Mo(7)/Ni(8)NaY (dry sulf) the Ni(8)NaY part of the catalyst is more active than the Mo component, and consequently the conversion will be determined by the Ni part of the catalyst. Clearly, on none of these catalysts a synergetic effect is present.

The absence of a synergetic effect may be due to the fact that a very large part of both sulfide phases (Ni and Mo) are located at the exterior of the zeolite particles (Welters et al., 1995). Due to the low external zeolite surface area large molybdenum and nickel sulfide crystals are formed, which will hamper the formation of a NiMoS phase. Even if some NiMoS is formed on the outside of the zeolite particles, its influence on the hydrocracking reaction will probably be very low, as the metal sulfides on the exterior cannot prevent the deposition of coke in the channels of the zeolite. If all metal sulfides (including NiMoS) are located on the outside of the zeolite particles, after coking only a few acid sites will remain available for cracking reactions, and the activity of the catalysts will be very low. However, a small part of the metal sulfides are located in the zeolite pores (Welters et al., 1994a,b). These internal metal sulfides are probably responsible for a large part of the catalytic activity. More acid sites remain free of coke deposits and are available for hydrocracking reactions. Apart from the above it is doubtful whether it is possible to form a NiMoS phase in the narrow pores of a zeolite. This phase consists of nickel ions located at the edges of small MoS2 slabs (Topsoe and Clausen, 1984; Prins et al., 1989). It is reasonable to assume that these structures require more space than available in the supercages of a zeolite. Most likely, only single metal sulfide phases will be formed in the zeolite pores, explaining why for each bimetallic catalyst the conversion is determined by the most active single metal sulfide component.

In a few papers synergetic effects are claimed for thiophene HDS (Cid et al., 1987; Laniecki and Zmierczak, 1991) and benzene hydrogenation (Leglise et al., 1988) over zeolite Y-supported Co-Mo and Ni-Mo catalysts. These promoter effects are however very small. In some cases (Cid et al., 1987; Laniecki and Zmierczak, 1991), the activity of the bimetallic catalysts is hardly higher than the combined activity of the monometallic catalysts. The promoter effect observed by Leglise et al. (1988) may also be explained by the formation of a NiMoS phase in the somewhat larger voids and defects usually present in stabilized Y zeolites (Leglise et al., 1988).

In order to prepare zeolite Y-supported Ni-Mo or Co-Mo sulfide catalysts with a significant promoter effect, other preparation routes have to be used, in which small bimetallic metal sulfide clusters with stronger hydrogenation properties are prepared in the supercages of the zeolite. The structure of these clusters must be different from the NiMoS phase, as Ni sulfide decorated MoS2 crystals probably cannot be formed in the pores of a zeolite.

Conclusions

Drying of zeolite Y-supported Ni catalysts prior to sulfidation results in a higher nickel sulfide dispersion, and consequently less coke formation and a substantial improvement of the hydrocracking conversion. A larger part of the zeolite pores and thus more acid sites are available for reactions leading to higher hydrocracking conversions. However, as both the nickel dispersion and the number of acid sites increase, the catalytic properties are not improved toward ideal hydrocracking.

For none of the zeolite-supported Ni-Mo sulfide catalysts can a promoter effect be observed. In all cases the activity is similar to that of the most active single metal sulfide catalyst. Most likely, the zeolite pores are too small to allow the formation of a MoS2-supported nickel sulfide phase (NiMoS) in the supercages.

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Literature Cited


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