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The Hydroisomerization Activity of Nickel-Substituted Mica Montmorillonite Clay

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Three-layer sheet aluminosilicates, when exchanged into the acidic form, are far less active as hydroisomerization catalysts than zeolites having a comparable surface proton density. However, introducing Ni$^{2+}$ or Co$^{2+}$ into the octahedral positions of the Al$^{3+}$ layer in synthetic beidellite results in hydroisomerization catalysts of an activity similar to that of a zeolite. From pyridine poisoning experiments and FT/IR measurements it can be concluded that this increased activity stems from the increased acidity of the resulting NiSMM (Ni-synthetic mica montmorillonite) clay, due to reduction of Ni.

By intercalating the clay with aluminium oligomers "pillared" clays of enhanced surface area have been synthesized. The increase in catalytic activity with enhanced basal surface area indicates that the acidic sites are located in the basal plane of the synthetic clay particles.

There has been renewed interest in catalytically active clays since the report by Swift and Black (1) to the effect that replacement of octahedrally coordinated aluminium ions by nickel or cobalt in synthetic smectite clays, as done by Granquist (2), results in a new type of catalyst, called nickel- (or cobalt-) substituted mica montmorillonite (Ni(Co)SMM), which is very active in the isomerization and cracking of hydrocarbons.

Its activity is comparable to that of zeolites, but - because of its layered structure - it does not contain the small micropores of the zeolite. Thus this catalyst is a potential alternative to zeolites in cases where effects due to pore diffusion have to be avoided.

Earlier novel clay-like systems consisting of silica-alumino-silica layers (2:1 layers) with unit cell composition (3):

$$[(Al_{4})_{octa} (Al_{x}Si_{x-x})_{tetra} O_{20} (OH,F)_{4}]^{3-} x NH_{4}^+ H_2O$$

with $x$ about 1.5 were synthesized, which had a much lower activity.
The alumina layer, in which the aluminium ions are in octahedral positions, is sandwiched between two silica layers with the tetrahedral silicon ions partly replaced by aluminium ions, giving a net negative charge to the 2:1 layers. Since these systems contain both mica-like (non-waterswellable) and montmorillonite-like layers, they have been called synthetic mica montmorillonite, SMM (4). After deammoniation the resulting proton gives SMM its acidic properties.

Much attention has been given to the highly active Ni-substituted mica montmorillonite (Ni-SMM) clays. The activities of noble-metal-impregnated synthetic clays for the isomerization of pentane are compared in Table I. Pd-Ni-SMM in its protonic form has been pre-reduced at 350 °C.

Table I. Comparison of the activities of some clays

<table>
<thead>
<tr>
<th>Clay</th>
<th>Temp. (°C)</th>
<th>Conversion</th>
<th>$k_{350}$ $(°C)c$</th>
<th>g·g⁻¹·h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hectorite-H$^a$</td>
<td>403</td>
<td>2</td>
<td>$2 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Beidellite-H$^a$</td>
<td>265</td>
<td>2</td>
<td>$8 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Ni-SMM-H$^a$</td>
<td>250</td>
<td>55</td>
<td>2.133</td>
<td></td>
</tr>
<tr>
<td>Zeolite</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mordenite-H$^b$</td>
<td>260</td>
<td>55</td>
<td>0.73</td>
<td></td>
</tr>
</tbody>
</table>

Stoichiometry: Hectorite-H

(Si₅)(Mg₅.22Li₀.48)O₂(H₂O)₂.5F₁.5

Stoichiometry: Beidellite-H

(Si₅.78Al₂.22)Al₄O₂(H₂O)₂.5F₁.5

Stoichiometry: Ni-SMM-H

(Si₅.26Al₂.74)(Al₁.32Mg₄.02)O₂(H₂O)₂.5F₁.5

Stoichiometry: Mordenite-H

(Si₂O₂/Al₂O₃ ≈ 17)

$^a$ %w Pd: 0.7; surface area 150 m²/g; WHSV = 2 g·g⁻¹·h⁻¹; H₂/C₅ = 1.25.

$^b$ %w Pd: 0.5; LHSV = 1 ml·ml⁻¹·h⁻¹; H₂/C₅ = 1.81.

$c$ Calculated rate of C₅ conversion at 250 °C; $k_{cat} = 25$ kcal/mol.

The clays used all belong to the class of smectites. Except for the Ni-SMM clay their activities are appreciably smaller than those of the zeolites.

The nickel replacement of Al³⁺ ions in the octahedral layers occurs by hydrothermal treatment of a clay reaction mixture in which part of the aluminium ions are replaced by Ni²⁺ ions. It has been found that the nickel ions in the resulting clay occupy octahedral positions, two aluminium ions being replaced by three nickel ions, one nickel ion occupying an originally empty octahedral hole.

Therefore, this new material is a mixed dioctahedral-trioctahedral synthetic clay, in which the relative amount of trioctahedral layers is directly related to the percentage nickel in the finished material.
So far, no satisfactory explanation of its high catalytic activity has been given. An experiment with Ni\(^{2+}\) exchanged on SMM resulted in a very poor hydroisomerization catalyst, which indicated that the high catalytic activity is due to the presence of Ni\(^{2+}\) in the clay lattice. However, it was found that the catalyst is only active after reduction of part of its nickel.

XRD experiments indicate weak lines due to reduced metallic nickel. The catalytic activity is enhanced by impregnation of the catalyst with a noble metal which has been found to catalyze the reduction of lattice nickel ions (5).

Work by Burch (6) and Sohn and Ozaki (7, 8) indicates that higher dispersed nickel may enter into a special kind of interaction with silica, leading to a high isomerization activity.

Heinerman et al. (5) found a relation between the amount of reduced nickel and the pentane isomerization rate, which suggests a metal-catalyzed reaction.

However, ammonia adsorption experiments in our laboratories (5) demonstrated an enhanced acidity after reduction (Figure 1). So a dual function mechanism (9, 10), in which metal sites are responsible for the (de)hydrogenation of (alkanes) alkenes and acid sites isomerize the alkenes via a carbocation mechanism, may also explain the high isomerization activity.

With the aid of selective pyridine-poisoning experiments, we will show that isomerization of alkanes over NiSMM is a bifunctionally catalyzed reaction.

The formation of acidic and metallic sites has been investigated in detail at pressures of 2 to 5 Torr (0.3-0.6 kPa) after in-situ reduction of catalyst samples and by FT-IR investigation of pyridine adsorption as a function of temperature. The amounts of hydrogen chemisorbed proved to be pressure-independent under these conditions.

The paper will be concluded with a discussion of crosslinking experiments of NiSMM samples with alumina oligomers.

Experimental

Catalysts

The NiSMM catalysts used were of the following global composition, as found from elemental analysis:

\[(\text{Al}_{1.1} \text{Ni}_{4.4})\text{octa}(\text{Si}_{6.6} \text{Al}_{1.4})\text{tetra} \text{O}_{20}(\text{OH})_3 \text{.2F}_0.8(\text{NH}_4)_1.4\].

We used the same synthesis procedure as detailed by Heinerman et al. (5).

A typical reaction mixture used for the preparation of SMM consisted of 88 g SiO\(_2\)/Al\(_2\)O\(_3\) (25 % Al\(_2\)O\(_3\)), 67.2 g Al(isoprop)_3, 9.1 g NH\(_4\)F, and some water. About 120 g of white product was obtained after hydrothermal treatment (16 h at 300 °C) and XRD confirmed that the product thus formed was pure synthetic beidellite. Since beidellite is NiSMM without Ni\(^{2+}\), it can also be described as synthetic mica montmorillonite (SMM). The composition of the clay was:

\[(\text{Al}_{1.4})\text{octa}(\text{Si}_{7.3} \text{Al}_{0.7})\text{tetra} \text{O}_{20}(\text{OH})_3 \text{.2F}_0.9(\text{NH}_4)_0.7\]

By replacing part of the Al\(^{3+}\) by Ni\(^{2+}\) in the synthesis mixture and following the same procedure a NiSMM clay was obtained containing Ni in the octahedral layer. Pt or Pd was exchanged onto the catalysts, using the tetramine chloride complexes.
Figure 1. FT/IR spectra of NH₃ adsorbed onto NiSMM
bottom: unreduced
middle: reduced
top: after removal of zero-valent nickel
NiSMM was outgassed at 540 °C. Ammonia was adsorbed at 170 °C, followed by evacuation at 180 °C (bottom).
Then ammonia was removed by outgassing at 540 °C. After reduction in flowing hydrogen at 440 °C, ammonia was adsorbed as described above (middle).
Then the NiSMM pellet was outgassed at 540 °C and the reduced nickel removed by reaction with CO at about 120 °C. After outgassing at 540 °C ammonia was adsorbed as described above (top).
The samples were dried at 120 °C and calcined for 0.5 h at
540 °C, prior to reduction in flowing hydrogen at temperatures from
350 to 450 °C.

The XRD pattern displayed in Figure 2 clearly demonstrates the
layered structure of the material obtained. This is confirmed by
transmission electronmicroscopic studies (21).

Isomerization Experiments

The catalytic experiments were performed in a conventional microflow
reactor, using a few grams of 30–80 mesh catalyst particles. The
reaction products were analyzed on-line by GLC with a 100-m squalane
capillary column.

Infrared Experiments

Infrared spectra of pyridine adsorbed onto Pd-NiSMM and Pd-SMM were
recorded at room temperature with a Digilab FTS 15 C Fourier trans­
form infrared spectrometer.

Hydrogen Chemisorption

The chemisorption of hydrogen was studied in a volumetric apparatus
at room temperature and pressures of 2 to 5 Torr (0.3-0.6 kPa) after
in-situ reduction of the catalyst samples. The amounts of hydrogen
chemisorbed proved to be pressure-independent under these conditions.

Results

Hydroisomerization of Paraffins

In this section we present experimental evidence for a bifunctional
alkane isomerization mechanism obtained by selective poisoning of
the acidic sites of Pd-NiSMM with pyridine, which was pulse-injected
into the liquid hydrocarbon feed stream. The possibility of addi­
tional poisoning of the metallic sites was checked by studying the
hydrogenation of benzene and the isomerization and ring opening of
methylcyclopentane (MCP).

The isomerization of n-hexane at 250 °C, 26 bar, a H₂/hydrocar­
bon (HC) molar ratio of 22.4, and a WHSV of 3.3 g·g⁻¹·h⁻¹ over fresh
Pd-NiSMM led to a conversion of 56 %, almost without cracking. This
isomerization activity was totally and irreversibly destroyed after
injection of about 10²¹ molecules pyridine per g Pd-NiSMM. Benzene
hydrogenation over the poisoned catalyst (260 °C, 26 bar, H₂/HC = 25)
showed that the hydrogenation function of the catalyst was still
active enough to hydrogenate benzene totally to cyclohexane, indica­
ting that the metallic sites had only been partially poisoned, if at
all.

Since benzene hydrogenation was still in equilibrium over
pyridine-poisoned NiSMM, we studied the conversion of MCP to deter­
mine the effect of pyridine on the acidic and metal sites. Under the
conditions chosen, the main reaction of MCP is isomerization to
cyclohexane (CH). In addition, MCP can undergo ring opening, which
may proceed either acid-catalyzed or metal-catalyzed. A distinction between these mechanisms can easily be made, since acid-catalyzed ring opening of MCP leads to the selective formation of n-hexane (11), while metal-catalyzed ring opening of MCP leads either to the formation of mainly methylpentanes (MP) or to a statistical cleavage of all ring bonds, depending on the metal and the state of the metal (12).

The reactions of MCP at about 300 °C are displayed in Figure 3. The initial CH/(CH-MCP) ratio shown indicates that equilibrium isomerization conversion is obtained. The second class of products found are about 4 % hexanes, resulting from ring opening. The n-hexane/isohexanes ratio found is 0.4. Since this agrees neither with acid-catalyzed nor with metal-catalyzed ring opening, it indicates a secondary isomerization of the primarily formed ring opening products or a contribution of both mechanisms. Isomerization is totally and irreversibly poisoned by means of several pyridine pulses, while ring opening goes through a minimum and reaches the former level again when poisoning is discontinued. The ratio of 2-MP/3-MP/n-hexane is now 10:8:1, which is similar to the ratio reported in the literature for metal-catalyzed ring opening of MCP over Ni (13, 14). Therefore, it is concluded that MCP ring opening over NiSMM is catalyzed by the metal sites, which are reversibly poisoned by pyridine, while isomerization is catalyzed by the acidic sites, which are irreversibly poisoned by pyridine. Figure 4 neatly shows the reproducibility of the reversible poisoning of the metal-catalyzed MCP ring opening over NiSMM. Having shown the importance of the acidic sites of NiSMM for isomerization and in view of the previous finding that metal sites are also required for alkane isomerization over NiSMM (5), we conclude that this reaction follows a bifunctional mechanism.

The Acidic Sites

FT/IR measurements of adsorbed NH₃ on NiSMM catalysts have shown that the number of sites, most probably Brønsted sites, increases due to Ni reduction (5). This suggests that the newly formed acidic sites are responsible for the increased activity of NiSMM compared with e.g., beidellite, in which no Ni²⁺ is substituted for Al³⁺ in the octahedral sites. The newly formed sites should then be highly acidic. In order to verify this statement we have studied the thermal desorption of pyridine from Pd-NiSMM before and after reduction, by means of FT/IR spectroscopy. For comparison, the same study was made with Pd-exchanged synthetic beidellite.

After admission of pyridine and pumping at 20 °C, the catalysts contained pyridine bound to Brønsted sites (NH bending mode at 1550 cm⁻¹) and to Lewis sites (ring vibrations at 1613 cm⁻¹); see Figure 5. The relative amounts of pyridine desorbed by pumping at 150, 250, and 400 °C are given in Figure 6. The desorption was almost complete at 400 °C. The desorption temperature of pyridine can be regarded as a measure of the acid strength of the clay.

In-situ reduction (16 h at 350 °C) of the sample increases the number of free (3750 cm⁻¹) and associated (around 3550 cm⁻¹) hydroxyl groups. Pyridine adsorption gives a spectrum (see Figure 5), which shows five times (case B) as many Brønsted sites as before
Figure 2. XRD of nickel-substituted mica montmorillonite (NiSMM) prepared according to the procedure detailed in ref. 2.

Figure 3. Effect of pyridine on the conversion of MCP. WHSV: 2 g/l.h.
RING OPENING, %w

$T = 306 \, ^\circ C$
$P = 27 \, \text{bar}$
$H_2/HC \approx 20$

Figure 4. Effect of pyridine on the conversion of MCP, second pyridine pulse.

LEWIS SITES

BRÖNSTED SITES

Figure 5. Fourier transform infrared spectra of pyridine adsorbed before (B) and after (A) reduction of Pd-NiSMM.
reduction (case A). The number of Lewis sites does not change much. A shift of a part of the 1613 cm\(^{-1}\) band to higher wave numbers may indicate an increase of the strength of the Lewis sites. The desorption experiments show that the newly formed Brønsted sites are indeed strongly acidic, since they adsorb pyridine at higher temperatures (see Figure 6).

The Lewis and Brønsted acidities of Pd-beidellite do not change at all during the reduction treatment. This means that (a) the water formed during Pd reduction does not disturb the balance between Lewis and Brønsted sites, and (b) no new Brønsted sites are formed during reduction of Pd. This implies that after calcination Pd is no longer located in exchange positions and is already metallic.

The number and the average strength of the Brønsted sites are lower for Pd-beidellite than for reduced Pd-NiSMM (Figure 7). Pd-NiSMM contains 15 times as many strong Brønsted sites (defined as sites which adsorb pyridine above 250 °C) as Pd-beidellite. We have measured the activity of Pd-beidellite, too. At 250 °C and 30 bar pressure (\(\text{H}_2/\text{HC} = 1.25\); WHSV = 2 g.l\(^{-1}\).h\(^{-1}\)) we obtained a n-pentane conversion of 18%; 0.9% was converted to iso-pentane. This corresponds to a \(k_{\text{isom}}\) of about 1 g.g\(^{-1}\).h\(^{-1}\). Thus the measured isomerization activities qualitatively in agreement with the number of Brønsted sites which adsorb pyridine above 250 °C.

We conclude that most of the highly acidic Brønsted sites which are responsible for the high isomerization activity of NiSMM are formed during the reduction of Ni\(^{2+}\) in the octahedral layer of the NiSMM clay.

The Metal Function

The metallic sites of NiSMM are formed by reduction of octahedral lattice Ni\(^{2+}\) and of additional Pt or Pd exchanged onto or impregnated on the catalyst prior to calcination and reduction. Pt and Pd are known to catalyze the reduction of Ni\(^{2+}\) (1). Without Pt or Pd, Ni\(^{2+}\) can be reduced above 380 °C. The amounts of reduced Ni have been assessed by X-ray diffraction (5). For metal- and bifunctionally catalyzed reactions it is essential to know the dispersion and surface area of the metal.

TEM shows that after 16 h reduction at 440 °C Ni crystallites of sizes from 5 to 15 nm are formed. Hydrogen chemisorption reveals that 0.14 % Ni\(^2\) per gram catalyst adsorbs H\(_2\).

With Pd- or Pt-containing catalysts the problem arises how to discriminate between reduced Ni and the reduced metal. Temperature-programmed reduction experiments (5) have shown that Pd is reduced around 80 °C. Reduction of Ni starts at 200 to 300 °C. Reoxidation and rereduction point to a possible Pd-Ni alloy formation. We have studied Pd-NiSMM and Pt-NiSMM samples after reduction at 350 and 450 °C by TEM combined with electron microprobe analysis. Metal crystallites with a maximum diameter of 20 nm are formed. Part of them contain Pd and Pt, respectively. Because of the background of lattice Ni\(^{2+}\), reduced Ni is difficult to distinguish by this technique. Since, moreover, large metal crystallites are observed from which no Pd or Pt signal is obtained at all, it seems reasonable to assume that these crystallites are reduced Ni. The presence of alloys cannot be ruled out.

We have also tried to discriminate between reduced Ni and Pd or
Figure 6. Amount of pyridine desorbed as a function of temperature for reduced (shaded bars) and unreduced Pd-NiSMM (nonshaded bars).

Figure 7. Amount of pyridine desorbed from reduced Pd-NiSMM catalysts relative to Pd-SMM.
Pt by hydrogen chemisorption. Since Ni reduction is slow compared with the reduction of Pd or Pt, we related the amount of H₂ chemisorbed after 1 h reduction at 350 °C to the H/Pt or H/Pd molar ratio. Pd-beidellite as reference shows that Pd reduction is then complete. The measured H/Pt and H/Pd ratios are rather low and range from 0.13 to 0.5, depending on the history of the catalyst (Table II). After prolonged reduction the H₂ chemisorption capacity of the catalysts increases due to Ni reduction. After 16 h reduction at 350 °C, the standard reduction procedure, a substantial part of the metal surface area consists of reduced Ni. The relative contribution of Ni and Pt or Pd to the metal activity of the catalysts further depends on the intrinsic activity of the various metals under the given reaction conditions.

Table II. H₂ chemisorption

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Pd-NiSMM</th>
<th>Pd-NiSMM</th>
<th>Pd-SMM</th>
<th>Pd-SMM</th>
<th>Pt-NiSMM</th>
<th>Pt-NiSMM</th>
</tr>
</thead>
<tbody>
<tr>
<td>%w Pd/pt</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.73</td>
<td>0.73</td>
</tr>
<tr>
<td>Reduction treatment</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 h 120 °C</td>
<td>4.8</td>
<td>4.4</td>
<td>1.5</td>
<td>17.1c</td>
<td>5.3</td>
<td>8.9</td>
</tr>
<tr>
<td>1 h 350 °C</td>
<td>24.2</td>
<td>10.2</td>
<td>15.9</td>
<td>15.6</td>
<td>22.9</td>
<td></td>
</tr>
<tr>
<td>16 h 350 °C</td>
<td>15.9</td>
<td>0.13</td>
<td>0.5</td>
<td>0.16</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>+2 h 450 °C</td>
<td>15.9</td>
<td>0.13</td>
<td>0.5</td>
<td>0.16</td>
<td>0.5</td>
<td>0.6</td>
</tr>
<tr>
<td>H/Me ratio</td>
<td>0.13</td>
<td>0.5</td>
<td>0.16</td>
<td>0.5</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

a Exchange onto dried catalyst.

b Exchange onto calcined catalyst.
c 0.3 h: 16.9 µmol/g cat.
d See text.

Balance between Metal and Acid Functions

In the section on hydroisomerization we have shown that paraffin isomerization over Pd-NiSMM is a bifunctionally catalyzed reaction. The metal and acid functions of the catalyst were characterized in the subsequent sections. For optimization of a bifunctional catalyst it is necessary to know whether the activity is limited by one of the catalytic functions.

It has been shown that over NiSMM without Pd or Pt the rate of n-pentane isomerization depends on the metal function (5). Pt-NiSMM and Pd-NiSMM catalysts are only about 2-5 times more active than pure reduced NiSMM (5), so it is questionable whether the mere addition of Pt or Pd is sufficient to optimize the acidic properties of NiSMM.

Since metallic and acidic sites are both created during reduction of NiSMM, it is very difficult to measure exclusively the influence of the metal function on the bifunctional activity of the catalyst.

For the catalysts listed in Table II we found a correlation
between the H₂ adsorption capacity after 16 h reduction at 350 °C and the activity for n-pentane isomerization after the same reduction procedure (Figure 8). On the basis of this observation one cannot decide whether this increase in activity is due to the increased number of metal sites available or to an increased number of strongly acidic sites formed after prolonged Ni reduction, or both. Therefore it is necessary to have an independent measure of the balance between the metal and the acid function of a bifunctional catalyst.

Such an independent measure is the selectivity of bifunctionally catalyzed consecutive reactions, e.g., the isomerization followed by hydrocracking of n-decane. By model calculations one can show that for a bifunctional catalyst limited in the acid function, the selectivity for the intermediate product is high and does not change upon variation of the activity of the metal function. Large changes in selectivity because of such variations are expected for catalysts where neither the metal function nor the acidic function is rate-limiting. If a bifunctional catalyst is really limited in the metal function, this limitation is accompanied by a very low selectivity for intermediate products.

In Figure 9 the yield of iso-decane is plotted against the conversion of n-decane over NiSMM reduced at 450 °C (Ni₈₀ = 0.13 %), a 0.7 %w Pd-NiSMM and a 0.7 %w Pt-NiSMM reduced at 400 °C. The maximum yield of isodecanes is 45 % over NiSMM 60 % over Pd-NiSMM, and reaches the very high value of 80 % over Pt-NiSMM. The large differences in selectivity show that on these bifunctional catalysts the balance between metal and acidic activity is changed and no rate-limiting step exists (13). Perhaps the specific Pt-NiSMM sample tested is close to an ideal bifunctional catalyst with sufficient metal activity to balance the high acidic activity of NiSMM.

These results imply that improvement of both the metal function and the acidic function may lead to the formation of more active catalysts.

Crosslinking experiments with NiSMM clays

Swelling clays can be crosslinked (16-20) with inorganic metal hydroxide oligomers to yield thermally stable, pillared clays with properties reminiscent of zeolites.

We applied this technique to the pillaring of NiSMM, in order to determine the location of the catalytically active sites. If these are located in the basal plane, an enhanced hydroisomerization activity is expected. The NiSMM material prepared according to Swift and Black's (1) procedures turns out not to be water-swellable. An analysis of the energetics of swelling (Figure 10) shows two regions where clays are expected to be non-swellable. One region is found at high Al₄₄/Si₄₄ ratios, where the negative charges on the layers stabilize the cations between the layers better than the solvation energy of water, the other is found at low Al₄₄/Si₄₄ ratios where the number of cations per layer area is so low that the attractive Van de Waals energy per unit layer area is larger than the gain of solvation energy.

We prepared water-swellable NiSMM by choosing the Si/Al/Ni ratio in the synthesis mixture such that enough, but not too much Al
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REACTION CONDITIONS:
250 °C, \( p = 30 \) bar
\( \frac{H_2}{H_2+CH_4}: 1.25 \)
WHSV: 2 g/l h

Figure 8. \( \text{cisom} \) as a function of \( H_2 \) adsorption.

Iso-DECANE YIELD

\( p \) = 30 bar
\( \frac{H_2}{CH_4} = 30 \)
WHSV = 2 g/l h
TEMP = 200 - 270 °C

Figure 9. Yield of iso-decanes versus n-decane conversion for various NiSMM catalysts.
Figure 10. Energetics of swelling.
is in a tetrahedral coordination. Good results are found for
$\text{Al}_{\text{tetra}}/\text{Si}_{\text{tetra}}$ ratios between 0.15 and 0.3.

Crosslinking of such a NiSMM clay with a solution of a hydroxy-
alumina oligomer in H$_2$O leads to considerable catalytic enhancement
(sample 1, Table III). The table shows the first-order rate con-
stant, $k$, for catalysis, before and after crosslinking. For sample
1 we used as crosslinking agent a hydroxy-aluminium oligomeric solu-
tion, made by refluxing metallic aluminium in 1 M HCl for 8 h and
ageing this solution for at least 10 days. Crosslinking took place
by stirring a slurry of the clay with this solution at 70 °C for
20 h. We used a ratio of 6 mmol Al/g clay in the mixture. The
Brunauer-Emmett-Teller surface area of the clay after calcination at
350 °C had increased from 170 to 230 m$^2$/g.

Table III. Hydroisomerization of n-pentane at 250 °C,
using samples reduced at 343 °C$^a$

<table>
<thead>
<tr>
<th>Pd-Ni-SMM sample</th>
<th>X.R.D.$^c$</th>
<th>$k$ ($\text{g}.\text{g}^{-1}.\text{h}^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before cross-</td>
<td>1.26</td>
<td>2.5</td>
</tr>
<tr>
<td>linking (1)$^d$</td>
<td>1.73</td>
<td>3.6</td>
</tr>
<tr>
<td>(2)$^e$</td>
<td>1.26 1.96</td>
<td>0.3</td>
</tr>
</tbody>
</table>

$^a$ weighted hourly space velocity = 2 g. g$^{-1}$. h$^{-1}$;
$H_2/\text{feed} = 1.25 \text{ mol/mol}$;
$P(H_2) = 30 \text{ bar}$;

$^b$ stoichiometry of Pd-Ni-SMM: tetrahedral Si$_{6.72}$ Al$_{1.28}$
octahedral Al$_{1.62}$ Ni$_{3.57}$

c 001 reflection, nm, after drying at 110 °C
d crosslinked with Al oligomer
e crosslinked with Si-Al oligomer

The X-ray diffraction (X.R.D.) peak corresponding to a repeat
distance of 1.26 nm for the non-crosslinked sample had been com-
pletely replaced by the peak corresponding to the expanded lattice with a
repeat distance of 1.73 nm.

Completely different results were obtained with a NiSMM sample
treated with a solution containing a silica-alumina oligomer. Cross-
linking was carried out at a pH of 4.8, using a solution prepared by
refluxing a mixture of chlorohydrol and a sodium silicate solution
for 24 h.

With X.R.D., only a weak signal of the basal spacing of the
expanded structure was detected, whereas the original 001 reflection
at 1.26 nm was still present. The surface area of the sample
treated as such had now decreased to 125 m$^2$/g.

Transmission electron micrographs (21) show a significant
amount of agglomeration in the basal direction in the product cross-
linked with the silica oligomer solution. This probably is the
cause of the decrease in total surface area observed after treatment
with the silica-alumina oligomer solution. The much larger decrease
in catalytic activity (sample 2, Table III) indicates that the major-
ity of the catalytically active sites are located in the lateral layers or the edges of lateral and basal planes.

The cause of agglomeration is basically the same as that which induces pillaring of the clays. The positively charged oligomers exchange with the surface cations. In this particular case the charge of the oligomers is such that it is not only compensated by the negative charge in the surface layers of one crystallite, but can also exchange with charge of another surface.

Discussion and Conclusions

The isomerization of n-alkanes over NiSMM is a bifunctional reaction, i.e., both the metal sites and the acid sites are involved in the reaction mechanism.

The high activity of this catalyst can be ascribed to Brønsted sites of high acidity, which are mainly formed during reduction of lattice nickel. The acidic activity of NiSMM is so strong that, even with 0.7% Pd or Pt on the catalyst, effects due to too low a metal activity on the bifunctional activity and selectivity cannot be excluded.

Since fluorine is contained in NiSMM prepared by the conventional procedure, one may suspect it to be responsible for the enhanced acidity.

However, an experiment with NiSMM prepared without fluorine gave the same enhancement after nickel reduction, so that fluorine cannot be responsible for the increased acidity.

Elsewhere (22) a model for the highly acidic sites is discussed that is supported by electrostatic potential calculations. According to that model the activity is due to generation of protons coordinated to oxygen ions that connect the silicon-containing tetrahedra with aluminium-containing octahedra. Such sites, however, can only contribute to catalysis at lateral planes, at lattice dislocations in the basal plane or at the edges of the lateral and basal planes.

The dislocations have been observed by TEM and are partially generated because of nickel reduction. The presence of dislocations in the basal planes may induce some dependence of the catalytic activity on the basal-plane surface area.

At present, rearrangement of silica tetrahedra and alumina octahedra into zeolite-type tetrahedra in the basal plane cannot be excluded.

Literature Cited


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