

## The Catalytic Activity of Nickel-Substituted Mica Montmorillonite

J. J. L. HEINERMAN, I. L. C. FRERIKS, J. GAAF, G. T. POTT, AND J. G. F. COOLEGEM

*Koninklijke Shell Laboratorium Amsterdam (Shell Research B.V.), Badhuisweg 3, 1031 CM Amsterdam, The Netherlands*

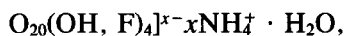
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Nickel-substituted mica montmorillonite (NiSMM) is of particular interest as a catalyst for the hydroisomerization and hydrocracking of paraffins. An important pretreatment step of this catalyst is its reduction in hydrogen. Temperature-programmed reduction and X-ray diffraction show that palladium promotes the formation of zero-valent nickel. Infrared spectra of ammonia adsorbed onto NiSMM reveal that the reduction step also increases the number of acid sites. Removal of metallic nickel from reduced NiSMM (not containing palladium) by carbon monoxide destroys the pentane hydroisomerization activity, while leaving the number of acid sites unchanged. Apparently, the acid sites alone are not capable of isomerizing pentane, the presence of a metal function being necessary.

### INTRODUCTION

Natural clays have been used in the past as catalyst base materials for such processes as catalytic cracking. Later, amorphous silica-alumina and zeolite catalysts were developed, which showed improved activities and selectivities (1). More recently, there has been a renewed interest in catalytically active clays, instigated mainly by the finding of Granquist that the hydrothermal synthesis of some clay-like silicates (2) gives catalysts which show a better cracking activity than commercial silica-alumina catalysts (3, 4).

These novel clay-like systems consist of silica-alumina-silica layers (2:1 layers) with the unit cell composition (2, 5-7)



where  $x$  is about 1.5. The alumina layer, in which the aluminum ions are in octahedral coordination, is sandwiched between two silica layers with the tetrahedral silicon ions partly replaced by aluminum ions, giving a net negative charge to the 2:1 layers. Since these systems contain both mica- and montmorillonite-like layers they have been

called synthetic mica montmorillonite (SMM) (6). After deamination the resulting proton gives SMM its acidic properties.

After the first disclosure of the catalytic applications of SMM by Capell and Granquist (3), it was found that SMM-based catalysts containing a hydrogenation component could be used in hydrofining and hydrocracking processes (8). Such SMM catalysts are also active for isomerization reactions (9, 10), e.g., the hydroisomerization of pentane (11). It was found that incorporation of cobalt and especially nickel into the SMM structure dramatically improves the activity for the hydrocracking and hydroisomerization of light straight-chain paraffins (12). The preparation of such catalysts has been described by Granquist (13); it consists essentially of replacing part of the aluminum ions in the reaction mixture by other metal ions, after which the hydrothermal treatment leads to the desired metal-substituted SMM. Much attention has been given to the synthesis of nickel-substituted SMM and it was stated that the nickel ions occupy octahedral positions, two aluminum ions being replaced by three nickel ions, where one nickel ion occupies an originally empty octahedral hole

(13, 14). 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.

Several catalytic applications of NiSMM and CoSMM have been reported. These include hydroisomerization and hydrocracking (12, 15), oligomerization of olefins (16), and hydrotreating (17).

The origin of the high activities found for NiSMM catalysts is unknown; mainly the reason why incorporation of nickel into the SMM lattice leads to enhanced activities is not understood.

In the hydroisomerization of pentane and hexane, NiSMM is first loaded with a hydrogenation component such as palladium, and then calcined at about 540°C and reduced in flowing hydrogen at about 340°C. Without a hydrogenation component a good activity can be obtained by performing the reduction at 450°C (18). It can be speculated that at 450°C some nickel is reduced, thus becoming a hydrogenating component itself. Concerning a possible nickel reduction, Swift (14) stated that the rate of nickel reduction in NiSMM does not become appreciable until 425°C, while Cole (19) found no nickel reduction at all at temperatures up to 600°C.

The aim of our experimental work is to provide more insight into the changes that occur during the reduction treatment of NiSMM and to find out which of these are of importance for the pentane hydroisomerization activity.

## EXPERIMENTAL

### A. Synthesis of the Catalysts

*PdNiSMM 503.* Sodium silicate solution, 42.0 g (27–29 wt% SiO<sub>2</sub>), was dispersed in 450 ml deionized water. This dispersion was exchanged three times with Amberlite IR 120-H cation resin. Next, 30.0 g nickel acetate (Ni(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> · 4H<sub>2</sub>O) dissolved in 150 ml water was added with stirring to the silica dispersion. Then 28.2 g aluminum iso-

propylate and 0.9 g ammonium fluoride were added with stirring. The resulting slurry was heated with stirring to remove some water, until the volume was about 350 ml. Six milliliters of aqueous ammonia (25% NH<sub>3</sub>) was then added and half of the slurry was transferred to a glass container in a stainless-steel pressure vessel without a stirring device. The temperature was raised to 300°C over about 3 h and kept at this level for 40 h. Then the pressure vessel was cooled to room temperature over a period of 3 to 4 h. The product was filtered and dried at 120°C for 16 h. The dried material was transferred to a solution of 233 mg Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub> in 440 ml water, stirred for 16 h, washed with 300 ml water and filtered (three times), dried at 120°C for 16 h, and calcined at 540 °C for 6 h.

The calcined clay was found by X-ray diffraction to possess the structure of calcined NiSMM. Elemental analysis yielded: Ni 22.4 ± 0.6 wt%, F 0.51 ± 0.03 wt%, Pd 0.98 ± 0.09 wt%. The BET surface area was 290 m<sup>2</sup> g<sup>-1</sup>.

*NiSMM 503.* The second portion of the slurry obtained in the preparation described above was transferred to the pressure vessel. The hydrothermal treatment was the same as that given above. The product was filtered, washed with 300 ml water, and filtered (three times), dried at 120°C for 16 h, and calcined at 540°C for 6 h. The resulting clay was found by X-ray diffraction to have the structure of calcined NiSMM. Elemental analysis revealed the nickel content to be 20.8 ± 0.5 wt%.

*Other SMM catalysts.* These were synthesized in the same way, but with different amounts of starting materials.

### B. Temperature-Programmed Reduction Experiments

About 0.2 g catalyst was dried in a stream of 5% O<sub>2</sub>/95% He at 180°C for 1 h and then cooled to -50°C. The O<sub>2</sub>/He stream was first replaced by a stream of N<sub>2</sub> and then by a stream of 5% H<sub>2</sub>/95% N<sub>2</sub> (5 ml h<sup>-1</sup>). The

temperature was increased at a rate of 5°C/min and the hydrogen uptake was measured with a thermal conductivity detector (TPR run 1). At about 350°C or higher the temperature was kept constant for 3 to 16 h. Next a reoxidation in 5% O<sub>2</sub>/95% He at 180°C was performed and the hydrogen uptake as a function of the temperature was measured as before (TPR run 2). The TPR profiles invariably contained a peak at ca -40°C due to physically adsorbed nitrogen desorbing from the sample. This peak has been omitted in our TPR results.

### C. CO Experiments

Metallic nickel present in reduced catalysts was removed as gaseous Ni(CO)<sub>4</sub> in a CO stream at 120°C. The CO effluent was passed through concentrated nitric acid to decompose the Ni(CO)<sub>4</sub>.

### D. X-Ray Diffraction

X-Ray powder diffraction patterns were recorded with a Philips diffractometer PW 1050 and a Nonius high-temperature Guinier camera Y909. For quantitative measurements of the formation of nickel particles (> ~2.0 nm) a mixture of 20 wt% nickel powder/SMM was used as a standard.

### E. Infrared Experiments

Infrared spectra of ammonia (ex Matheson, purity better than 99.999%) adsorbed onto self-sustaining calcined NiSMM 503 pellets were recorded with a Digilab FTS 15C Fourier transform infrared spectrometer, which was operated at a spectral resolution of 4 cm<sup>-1</sup>. Addition of 500 scans, using double precision word length, ensured the required signal:noise ratio of better than 100:1.

The NiSMM pellet was first evacuated at 540°C for 1 h, in a Pyrex ir cell, which closely resembled one described recently (20). Then ammonia was chemisorbed according to the procedure of Wright *et al.* (6), which consisted in contacting the cata-

lyst with 100 Torr ammonia at 170°C for 30 min, followed by evacuation at 150°C for 30 min to remove physisorbed ammonia. After cooling to room temperature, the infrared spectrum was recorded. The influences of reduction by hydrogen and treatment with carbon monoxide were investigated by subsequent evacuations (to remove ammonia), *in situ* hydrogen/carbon monoxide treatments and ammonia chemisorptions, followed by recording of the spectra.

### F. Hydroisomerization of Pentane

Pentane hydroisomerization experiments were carried out in a microflow tube reactor containing 1.5–2.0 g 30–80 mesh catalyst particles. The catalysts were first reduced in flowing hydrogen (1 bar) at temperatures in the range of 340–450°C for 16 h. Then the temperature was lowered to 250°C and the catalysts were run with a predried pentane feed under hydroisomerization conditions: WHSV: 2.0–2.7 g g<sup>-1</sup> h<sup>-1</sup>; total pressure: 30 bar; H<sub>2</sub>/pentane molar ratio: 1.25. The reactor effluent was analyzed on line by means of a gas-liquid chromatograph (flame ionization detector;  $\frac{1}{8}$ -in. diameter; 12 ft long; 10 wt% squalane on Chromosorb PAW 80–100 mesh; 50°C). In the experiments where reduced nickel was removed by CO a gold-coated reactor was used. First-order reaction rate constants were calculated according to

$$k = \text{WHSV}(iC_5)_{\text{eq}} \ln \left\{ \frac{(iC_5)_{\text{eq}} - (iC_5)_{\text{in}}}{(iC_5)_{\text{eq}} - (iC_5)_{\text{out}}} \right\},$$

where (iC<sub>5</sub>) is the mole fraction of isopentane in the C<sub>5</sub> paraffins and (iC<sub>5</sub>)<sub>eq</sub> = 0.709 at 250°C.

## RESULTS AND DISCUSSION

TPR run 1 of NiSMM 503 showed no hydrogen uptake at temperatures up to 345°C. At that temperature the reduction treatment was prolonged for 3 h. TPR run 2, after reoxidation at 180°C, did not show any hydrogen uptake either. A similar procedure but this time with a final reduction

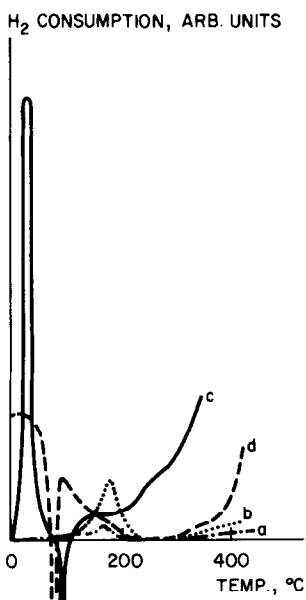


FIG. 1.  $H_2$  consumption as a function of temperature. (a) NiSMM 503, TPR run 2, after 3 h reduction at  $450^\circ\text{C}$ . (b) NiSMM 503, TPR run 2, after 16 h reduction at  $450^\circ\text{C}$ . (c) PdNiSMM 503, TPR run 1. (d) PdNiSMM 503, TPR run 2, after 3 h reduction at  $345^\circ\text{C}$ .

temperature of  $450^\circ\text{C}$  instead of  $345^\circ\text{C}$  gave a small nickel peak at about  $180^\circ\text{C}$  on TPR run 2 (Fig. 1, curve a), which became more pronounced upon a longer reduction time (curve b). TPR run 1 of PdNiSMM 503 (curve c) showed a palladium peak at about  $30^\circ\text{C}$ , followed by a hydrogen desorption peak. The reduction temperature was kept at  $345^\circ\text{C}$  for 3 h. TPR run 2, after reoxidation at  $180^\circ\text{C}$ , (curve d) gave a broad peak at about  $20^\circ\text{C}$ , indicating a palladium-nickel alloy, a desorption peak, due to the alloy or unalloyed palladium, and a shoulder at  $180^\circ\text{C}$ , which may be ascribed to free nickel. These results show that at  $450^\circ\text{C}$  nickel in NiSMM is reduced and they indicate that palladium promotes the nickel reduction.

X-Ray diffraction measurements of PdNiSMM 503 in flowing hydrogen and at increasing temperature ( $0.25^\circ\text{C}/\text{min}$ ) reveal that at  $380^\circ\text{C}$  nickel crystallites are formed (diameter ca. 10 nm) and that the SMM structure is partly destroyed, while for

NiSMM 503 the nickel crystallite formation starts at  $420^\circ\text{C}$  (diameter ca. 40 nm). These results are in agreement with those of the TPR measurements and prove that palladium promotes the reduction of nickel.

Figure 2 shows that at  $440^\circ\text{C}$  the amount of reduced nickel in NiSMM 503 strongly increases during the first hours and then levels off. Such a strong initial increase is also found with higher reduction temperatures ( $480^\circ\text{C}$  see Fig. 2). From Fig. 2 it also follows that a small increase in reduction temperature results in a large increase of metallic nickel: after reduction at  $440^\circ\text{C}$  for 16 h 3.2% of the nickel is present in the form of metal crystallites  $>2$  nm, while at  $450^\circ\text{C}$  this percentage is 7.9.

Exactly as reported by Swift and Black (12) we found that SMM exchanged with nickel (the finished catalyst contained 6 wt% nickel) and SMM impregnated with 16 wt% nickel gave catalysts that were nearly inactive for the hydroisomerization of pentane (on both catalysts about 1 wt% palladium had been introduced by impregnation; conversions to isopentane were 1–2%). It was also established that a reduction step (at  $343^\circ\text{C}$ ) was essential for the activation of PdNiSMM since a treatment in nitrogen instead of hydrogen gave an almost inactive catalyst (conversion to isopentane was about 1%). A good activity was obtained with PdNiSMM 503 after 16 h reduction in

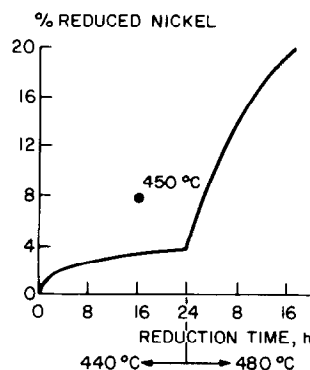


FIG. 2. Reduction of NiSMM 503 in flowing hydrogen measured by the intensity of the nickel (111) reflection.

flowing hydrogen at 343°C: an activity decline from 63 to 53% conversion to isopentane during the first 2 h was followed by stable operation for at least 19 h, the formation of cracking products amounting to less than 1%. NiSMM 503 reduced at 450°C for 16 h was much less active. In general, it was found that such palladium-free NiSMM catalysts gave initial conversions to isopentane of about 40%, which dropped to a stable conversion of about 15% after 2–5 h. The amount of cracking products, initially about 7%, decreased to about 1% during stable operation.

To clarify the role of zero-valent nickel formed during reduction, NiSMM 499 containing 25 wt% nickel was reduced at 450°C for 16 h and then treated with carbon monoxide for about 1½ weeks to remove the reduced nickel. X-Ray diffraction experiments had revealed that such a treatment led to the removal of the nickel crystallites without damaging the SMM structure. It appeared that this CO-treated catalyst was nearly inactive (2% conversion to isopentane and less than 0.2% cracking). Partial removal of reduced nickel (CO treatment for 48 h) gave a catalyst with a low activity, while a renewed 16 h reduction at 450°C nearly completely restored the original activity. A direct relation was found between the first-order reaction rate constant and the amount of metallic nickel present on the used catalysts as determined by X-ray diffraction (see Fig. 3, curve a).

NiSMM 499 containing 25 wt% nickel had a lower isomerization activity than NiSMM 503 containing 21 wt% nickel, while a higher amount of reduced nickel and therefore a higher activity was expected. However, in a separate reduction experiment, in which both clays were reduced together, it was found that NiSMM 503 contained more metallic nickel than NiSMM 499, again giving a direct relation between the rate constant and the amount of metallic nickel as determined by X-ray diffraction in the separate reduction experiment (see Fig. 3, curve b). We also checked

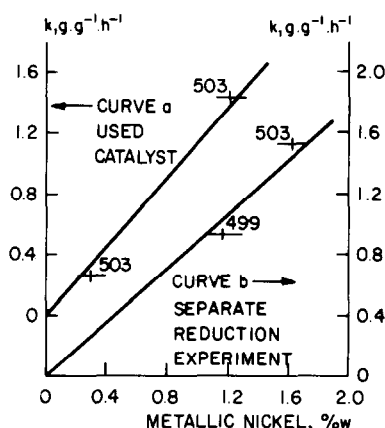


FIG. 3. First-order reaction constant of the initial conversion of pentane into isopentane.

whether CO adsorption could poison the activity. Before the pentane hydroisomerization test with a fresh NiSMM 499 sample a CO pulse (ca. 400 ml) was dosed. No change in activity was found. These results clearly demonstrate the activity of NiSMM to be related to the amount of metallic nickel present on the catalyst.

The acid sites of NiSMM were investigated by infrared analysis, using ammonia as a probe. Subtracting the spectrum of unreduced NiSMM (trace A in Fig. 4) from the spectrum of unreduced NiSMM plus chemisorbed ammonia (trace B in Fig. 4) gives the difference spectrum represented by trace C in Fig. 4 ("NH<sub>3</sub> ads" spectrum; 8× intensified). This spectrum shows a decrease in the 3750 cm<sup>-1</sup> band and an increase in the 3600 cm<sup>-1</sup> region, which leads to the supposition that some of the silanol groups (3750 cm<sup>-1</sup>) interact with NH<sub>3</sub> through hydrogen bridges, resulting in associated OH groups absorbing at lower frequencies (3600–3400 cm<sup>-1</sup>). Apparently, this interaction is strong enough for the NH<sub>3</sub> to withstand evacuation at 150°C (see Experimental).

In the region 3400–3000 cm<sup>-1</sup> a number of absorption bands due to N–H stretching modes can be observed. The larger of these (3350 and 3270 cm<sup>-1</sup>) are generally assigned to NH<sub>3</sub> coordinated to Lewis acid sites (6,

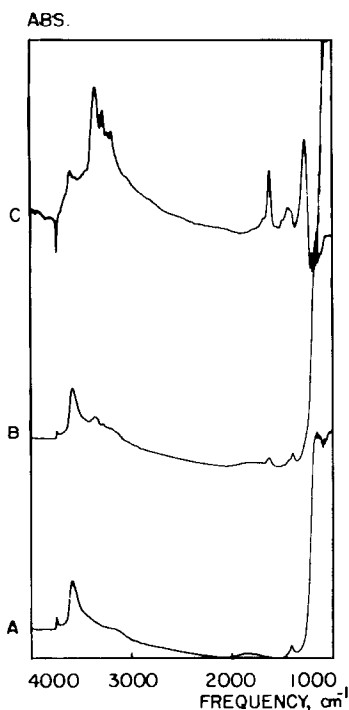


FIG. 4. Infrared spectra of unreduced NiSMM. (A) Before  $\text{NH}_3$  chemisorption. (B) After  $\text{NH}_3$  chemisorption. (C) Difference spectrum ("NH<sub>3</sub> ads") B-A, 8× intensified.

21), while the smaller ones (3035 and 3120  $\text{cm}^{-1}$ ) are due to N-H stretching frequencies of  $\text{NH}_3$  protonated by Brønsted acid sites. Bands due to N-H bending vibrations are observed in the region 1700–1200  $\text{cm}^{-1}$  (see Fig. 5). The strong band at 1620  $\text{cm}^{-1}$  is due to the asymmetric bending vibration of ammonia adsorbed onto Lewis acid sites, the band at 1445  $\text{cm}^{-1}$  is due to the  $\text{NH}_4^+$  bending vibration, while the weak 1680  $\text{cm}^{-1}$  band accompanies both types of  $\text{NH}_3$  adsorption. The strong band at 1280  $\text{cm}^{-1}$  is not always observed after ammonia adsorption, possibly due to its position being close to that of very strong lattice vibrations in oxide catalyst materials. However, in experiments with  $\text{Al}_2\text{O}_3$  Pliskin and Eischens (22) did observe the 1280  $\text{cm}^{-1}$  band and they assigned this strong band to the symmetric bending vibration of ammonia chemisorbed to alumina.

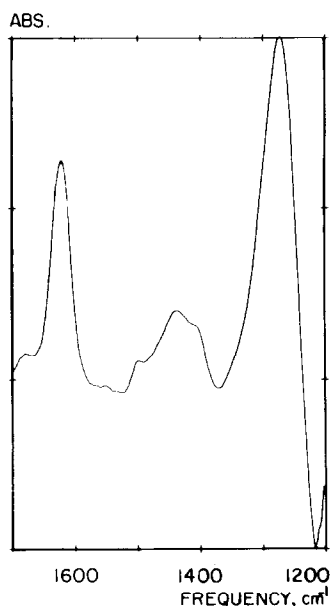


FIG. 5. Expanded plot of N-H bending region of trace C in Fig. 4.

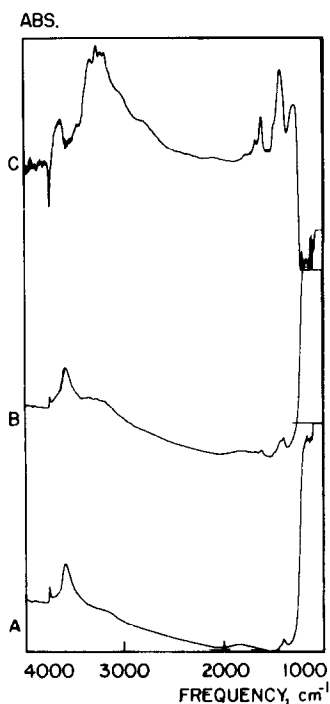


FIG. 6. Infrared spectra of reduced NiSMM. (A) Before  $\text{NH}_3$  chemisorption. (B) After  $\text{NH}_3$  chemisorption. (C) Difference spectrum ("NH<sub>3</sub> ads") B-A, 8× intensified.

The spectrum of the  $\text{NH}_3$  adsorbate with the reduced clay (Fig. 6) shows several phenomena which were also observed with the unreduced catalyst (cf. Fig. 4). The number of free silanol groups is reduced, resulting in an increased number of associated OH groups, while the presence of chemisorbed  $\text{NH}_3$  is demonstrated by the N–H stretching ( $3400\text{--}3000\text{ cm}^{-1}$ ) and N–H bending vibrations ( $1700\text{--}1200\text{ cm}^{-1}$ ).

Comparison of the intensities of the bands in the difference (“ $\text{NH}_3$  ads”) spectra obtained with reduced and unreduced NiSMM (traces C in Figs. 6 and 4; spectra are on the same scale) reveals that the number of Brønsted sites ( $1445\text{ cm}^{-1}$ ) increases by a factor of approximately 4 as a result of the reduction treatment, while the number of Lewis sites ( $1620\text{ cm}^{-1}$ ) decreases by some 25%. However, the relative amounts of Brønsted and Lewis acid sites depend strongly on the amount of water present in

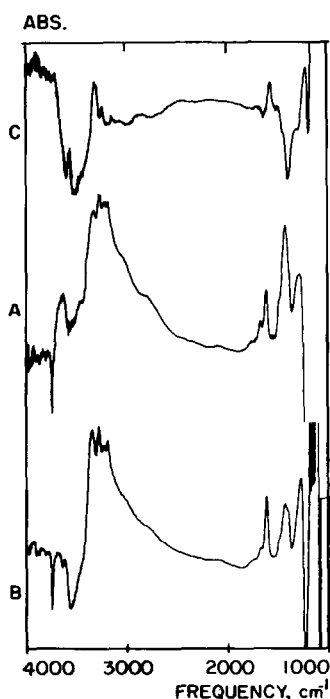


FIG. 7. “ $\text{NH}_3$  ads” on reduced NiSMM after successive dehydrations. (A) After 20 min evacuation at  $540^\circ\text{C}$ . (B) After 1.3 h evacuation at  $540^\circ\text{C}$ . (C) Change in “ $\text{NH}_3$  ads” on the same scale ( $B - A$ ).

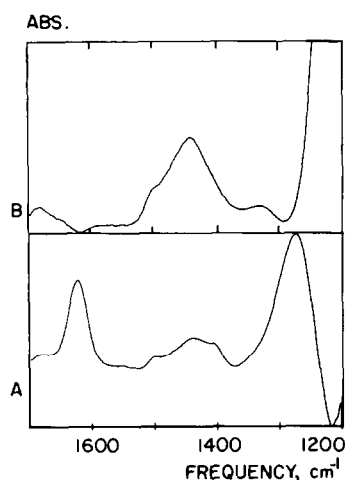


FIG. 8. Infrared spectra of reduced versus unreduced NiSMM. (A) “ $\text{NH}_3$  ads” on unreduced NiSMM. (B) Extra “ $\text{NH}_3$  ads” due to sites created by reduction.

the system, due to the reversible reaction  $\text{Lewis site} + \text{H}_2\text{O} \rightleftharpoons \text{Brønsted site}$  (see Fig. 7). Nevertheless, from a number of spectra of NiSMM in different hydration states it is concluded that reduction for 16 h at  $430^\circ\text{C}$  causes a marked increase in the total number of acid sites. This is especially clear from the example in Fig. 8, which shows a strong increase in Brønsted sites, while the number of Lewis sites remains constant.

Moreover, in these spectra the observed relative extinction coefficients of the N–H bands at  $1620$  and  $1445\text{ cm}^{-1}$  generally do not differ by more than a factor of 2, which enables us to estimate that the total number of acid sites (Lewis + Brønsted) approximately doubles by the reduction treatment. This increased number of acid sites may explain the enhanced activity of NiSMM-based catalysts in hydrocarbon conversion reactions.

An additional reduction treatment for 20 h at  $440^\circ\text{C}$  did not have a significant influence on the number of acid sites, which suggests that the number of acid sites cannot be increased beyond that obtained during 16 h reduction at  $430^\circ\text{C}$ .

The  $440^\circ\text{C}$  reduced NiSMM was subsequently treated with CO until formation of

$\text{Ni}(\text{CO})_4$  (gas phase) had ceased, indicating complete removal of metallic nickel. The "NH<sub>3</sub> ads" spectrum obtained after this treatment (Fig. 9, trace B) is virtually the same as the "NH<sub>3</sub> ads" spectrum before nickel leaching (Fig. 9, trace A), from which it is concluded that the acid sites are not poisoned by the CO treatment.

From the experiments with CO-treated NiSMM it now follows that the acid sites alone are not able to isomerize pentane. Furthermore, the pentane isomerization experiments demonstrate the activity to be proportional to the amount of metallic nickel. Therefore, there are two possibilities for the description of the isomerization of pentane. Firstly, a bond-shift mechanism could be operative, where only nickel sites are responsible for the isomerization activity; it would then be expected that metallic nickel is in a highly dispersed state (23, 24), the higher cracking activity of NiSMM as compared with PdNiSMM being due to nickel crystallites. Secondly, the isomerization may be described by a dual function mechanism, in which metal sites (nickel and/or palladium) are responsible for the

(de)hydrogenation and acid sites isomerize pentane into isopentene via a carbocation mechanism, the (de)hydrogenation being rate limiting. In a forthcoming paper, by Röbischläger *et al.* (25), conclusive experiments to discriminate between these two mechanisms will be described.

## CONCLUSIONS

(1) Palladium promotes the formation of zero-valent nickel during the reduction of NiSMM by hydrogen.

(2) The formation of zero-valent nickel is accompanied by the formation of acid sites, which may explain the enhanced activity of NiSMM-based catalysts in hydrocarbon conversion reactions.

(3) While reduced NiSMM is an active hydroisomerization catalyst, its acid sites alone, i.e., in the absence of a hydrogenation function such as zero-valent nickel, are not able to isomerize pentane into isopentane.

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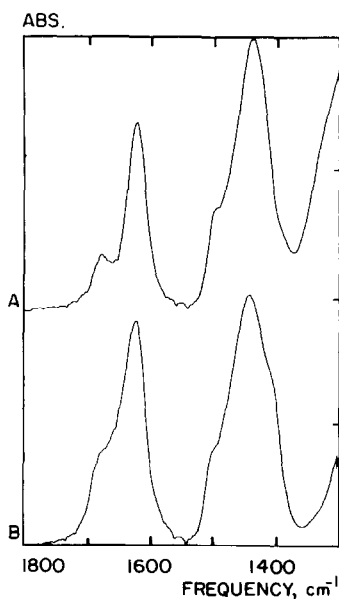


FIG. 9. "NH<sub>3</sub> ads" on reduced NiSMM before (trace A) and after (trace B) leaching of nickel.



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