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On the Hydroisomerization Activity of Nickel-Substituted Mica Montmorillonite

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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 hydroisomerizations 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.

INTRODUCTION

Less than a decade ago Swift and Black (*1*) reported that replacement of octahedrally coordinated aluminum ions by nickel or cobalt in synthetic smectite clays results in a new type of catalyst, called nickel (or cobalt) substituted mica montmorillonite (Ni(Co)SMM), which is very active for 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 forms an interesting alternative to zeolites in cases where effects due to pore diffusion limitations have to be avoided.

So far no explanation of its high catalytic activity has been given. From our Laboratory one pertinent paper (*2*) has appeared, dealing with the catalytic properties and containing an infrared spectroscopic study of the adsorption of ammonia on this type of catalyst. It shows that lattice Ni^{2+} has to be reduced to zero-valent nickel if the catalyst is to become active for the isomerization of pentane and that the activity of the catalyst decreases when metallic nickel is removed by treatment with CO. From elemental analysis and XRD it appears that Ni^{2+} substitutes for Al^{3+} ions in the octahedral layers such that charge neutrality is maintained. An experiment with Ni^{2+} exchanged on beidellite resulted in very poor hydroisomerization catalysts. Heinerman *et al.* (*2*) also demonstrated that much more ammonia in the form of NH_4^+ is adsorbed on the catalyst after nickel reduction than before.

Work by Burch (*3*) and Sohn and Ozaki (*4, 5*) indicates that highly disperse nickel may enter into a special kind of interaction with silica, leading to a high activity. The ammonia adsorption experiments (*2*), on the other hand, demonstrate an enhanced acidity after reduction. So a dual function mechanism, in which metal sites are responsible for the (de)hydrogenation and acid sites isomerize pentene into methylbutene via a carbocation mechanism, may also be an explanation.

Using 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 is investigated in detail by

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Fourier transform/infrared spectroscopy (FT/IR) and hydrogen chemisorption. The relative activities of the acidic and the metallic function of the catalyst are studied using the selectivity in consecutive reactions as a yardstick.

EXPERIMENTAL

Catalysts. The NiSMM catalysts used were of the following global composition

$$(Al_{1.1}Ni_{4.4})\text{octa}\ (Si_{6.6}Al_{1.4})\text{tetra}\ O_{20}(OH)_{3.2}F_{0.8}(NH_4)_{1.4}$$

We used the same synthesis procedure as detailed by Heinerman *et al.* (*2*).

A typical reaction mixture used for the preparation of beidellite consisted of 88 g SiO_2/Al_2O_3 (25% Al_2O_3), 67.2 g Al(isoprop)$_3$, 9.1 g NH_4F, and some water. About 120 g of white product was obtained after hydrothermal treatment (16 hr 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

$$(Al_4)\text{octa}(Si_{7.3}Al_{0.7})\text{tetra}\ O_{20}(OH)_{3.2}F_{0.9}(NH_4)_{0.7}$$

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 were exchanged onto the catalysts using the tetraammine chloride complexes.

The samples were dried at 120°C and calcined for 0.5 hr at 540°C, prior to reduction in flowing hydrogen at temperatures from 350 to 450°C.

The XRD pattern displayed in Fig. 1 clearly demonstrates the layered structure of the material obtained. This is confirmed by transmission electron microscopic studies (*6*).

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 transform infrared spectrometer.

Hydrogen chemisorption. The chemisorption of hydrogen was studied in a volumetric apparatus at room temperature and

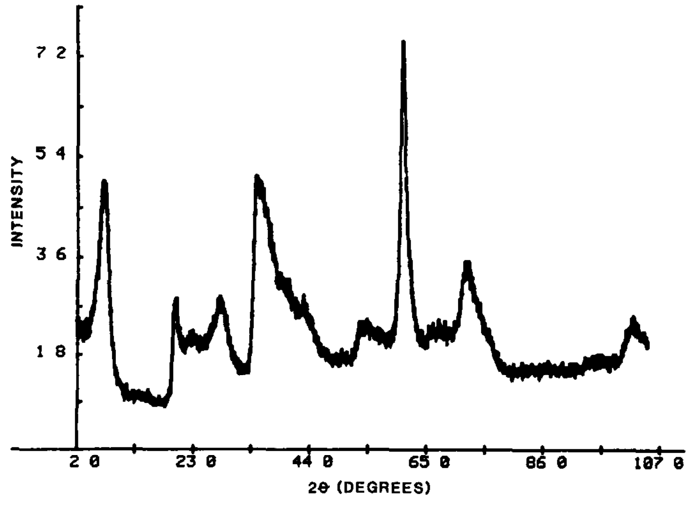

FIG. 1. XRD of nickel-substituted mica montmorillonite (NiSMM) prepared according to the procedure detailed in Ref. *2*.

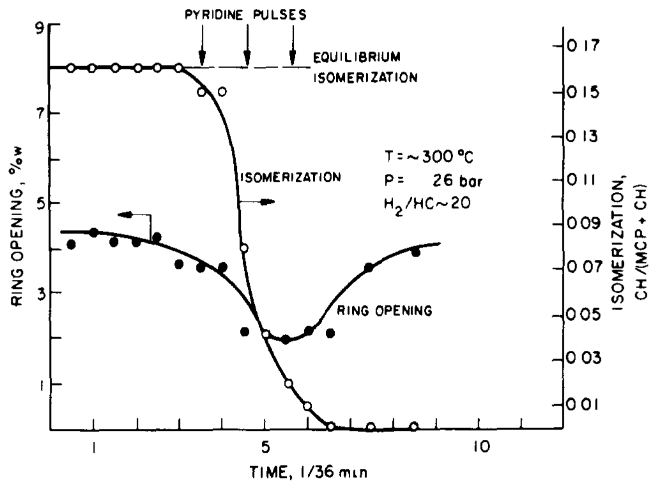

FIG 2 Effect of pyridine on the conversion of MCP

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 additional 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 H_2/hydrocarbon (HC) molar ratio of 22 4, and a WHSV of 3 3 g/g hr over fresh Pd–NiSMM led to a conversion of 56%, nearly without cracking This isomerization activity was totally and irreversibly destroyed after injection of about 10^{21} molecules pyridine per g Pd–NiSMM Benzene hydrogenation over the poisoned catalyst (260°C, 26 bar, H_2/HC = 25) showed that the hydrogenation function of the catalyst was still active enough to hydrogenate benzene totally to cyclohexane, indicating 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 in order to have a better check on 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 it 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 (*7*), 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 (*8*)

The reactions of MCP at ca 300°C are displayed in Fig 2 The initial CH/(CH + MCP) ratio shown indicates that equilibrium isomerization conversion is obtained The second class of products found are about 4% of hexanes resulting from ring opening The found *n*-hexane/iso-hexanes ratio is 0 4 Since this agrees neither with

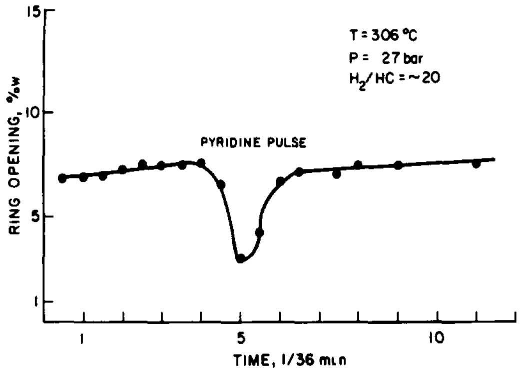

FIG 3 Effect of pyridine on the conversion of MCP, second pyridine pulse

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 (*9, 10*) Therefore, it is concluded that MCP ring opening over NiSMM is catalyzed by the metal sites, which are only reversibly poisoned by pyridine, while isomerization is catalyzed by the acidic sites, which are irreversibly poisoned by pyridine Figure 3 shows neatly the reproducibility of the reversible poisoning of the metal-catalyzed MCP ring opening over NiSMM Since we have shown the importance of the acidic sites of NiSMM for isomerization and since it has been found previously that metal sites are also required for alkane isomerization over NiSMM (*2*), it is concluded that this reaction follows a bifunctional mechanism

The Acidic Sites

FT/IR measurements of adsorbed NH_3 on NiSMM catalysts have shown that the number of acidic sites, most probably Brønsted sites, increases due to Ni reduction (*2*) This suggests that the newly formed acidic sites are responsible for the increased activity of NiSMM compared with, e g , beidellite in which no Ni^{2+} is substituted for Al^{3+} 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 Fig 4) The relative amounts of pyridine desorbed by pumping at 150, 250, and 400°C are given in Fig 5 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 hr 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 Fig 4), which shows five times (case B) as many Brønsted sites as before reduction (case A) The number of

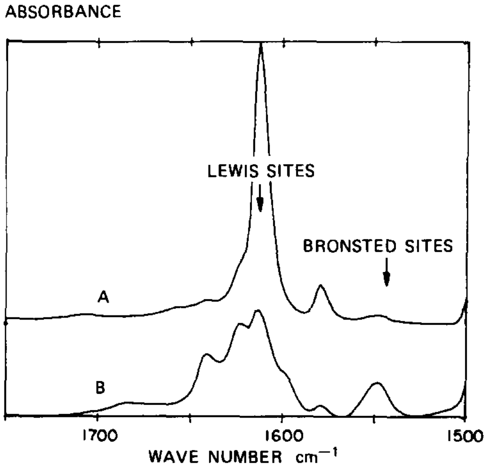

FIG 4 Fourier transform infrared spectra of pyridine adsorbed before (B) and after (A) reduction of Pd–NiSMM

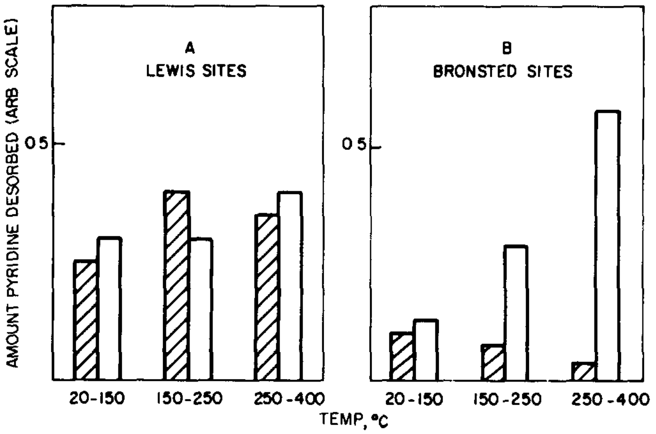

FIG 5 Amount of pyridine desorbed as a function of temperature for reduced (shaded bars) and unreduced Pd–NiSMM (nonshaded bars)

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 Fig 5)

The Lewis and Brønsted acidities of Pd–beidellite do not change at all during the reduction treatment This means that (a) the water, which is 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 (Fig 6) 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 (H_2/HC = 1 25, WHSV = 2 g/l hr) we obtained a *n*-pentane conversion of 1 8%, 0 9% was converted to iso-pentane This corresponds to a k_{isom} of about 1 g g^{-1} hr^{-1} Thus the measured isomerization activities are in qualitative 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

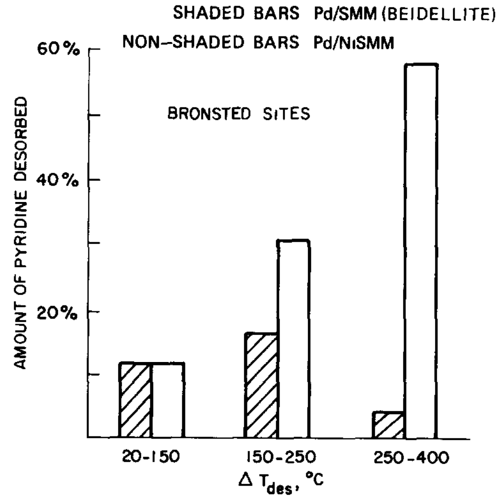

FIG 6 Amount of pyridine desorbed from reduced Pd–NiSMM catalysts relative to Pd–SMM

TABLE 1

H_2 Chemisorption

Catalyst	Pd–NiSMM (B)[a]	Pd–NiSMM (A)[b]	Pd–SMM (B)[a]	Pd–SMM (A)[b]	Pt–NiSMM (B)[a]	Pt–NiSMM (B)[b]
%w Pd/Pt	0 7	0 7	0 7	0 7	0 73	0 73
Reduction treatment	H_2 chemisorption (μmol/g cat)					
1 hr 120°C	4 8		1 5			
1 hr 350°C		4 4	17 1[c]	5 3	8 9	11 0
16 hr 350°C	24 2	10 2			15 6	22 9
+2 hr 450°C		15 9				
H/Me ratio[d]		0 13	0 5	0 16	0 5	0 6

[a] Exchange onto dried catalyst

[b] Exchange onto calcined catalyst

[c] 0 5 hr 16 9 μmol/g cat

[d] See text

impregnated on the catalyst prior to calcination and reduction Pt and Pd are known to catalyze the reduction of Ni (*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 (*2*) For metal- and bifunctionally catalyzed reactions it is essential to know the dispersion and surface area of the metal

TEM shows that after 16 hr reduction at 440°C Ni crystallites of sizes from 5 to 15 nm are formed Hydrogen chemisorption reveals that 0 14%w Ni° 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 (*2*) 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, in addition, 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 possible presence of alloys cannot be ruled out

We have also tried to discriminate between reduced Ni and Pd or Pt by hydrogen chemisorption Since Ni reduction is slow compared with the reduction of Pd or Pt, we related the amount of H_2 chemisorbed after 1 hr 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 1) After prolonged reduction the H_2 chemisorption capacity of the catalysts increases due to Ni reduction After 16 hr 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

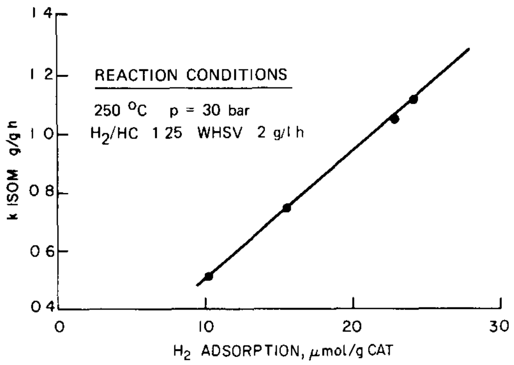

FIG. 7. k_{isom} as a function of H_2 adsorption.

Balance Between Metallic and Acidic Functions

In the section on hydroisomerization we have shown that paraffin isomerization over Pd–NiSMM is a bifunctionally catalyzed reaction. The metallic and acidic 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 metallic function (*2*). Pt–NiSMM and Pd–NiSMM catalysts are only about 2–5 times more active than pure reduced NiSMM (*2*), 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 1 we found a correlation between the H_2 adsorption capacity after 16 hr reduction at 350°C and the activity for *n*-pentane isomerization after the same reduction procedure (Fig. 7). So far it cannot be decided whether this increase in activity is due to the increased number of metal sites available or to an increased number of strong acidic sites formed after prolonged Ni reduction or both. Therefore it is necessary to have an independent measure of the balance between the metallic and the acidic 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 acidic function, the selectivity for intermediate products 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 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 Fig. 8 the yield of iso-decane is plotted against the conversion of *n*-decane over NiSMM reduced at 450°C (Ni_s^0 = 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.

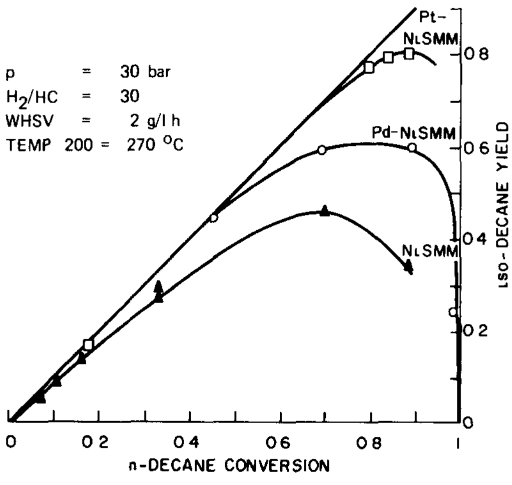

FIG. 8. Yield of iso-decanes versus *n*-decane conversion for various NiSMM catalysts.

These 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 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

DISCUSSION AND CONCLUSIONS

The isomerization of *n*-alkanes over Ni–SMM is a bifunctional reaction, i e , both the metal and the acidic 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%w 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 Ni–SMM prepared by the conventional procedure, one may suspect it to be responsible for the enhanced acidity However, Ni–SMM prepared without fluorine gave the same enhancements after nickel reduction, so that fluorine cannot be responsible for the increased acidity

Elsewhere a model for the highly acidic sites is discussed supported by electrostatic potential calculations (*11*) According to that model the activity is due to generation of protons coordinated to oxygen ions that connect the silicon-containing tetrahedra with aluminum-containing octahedra Such sites can only contribute to catalysis at the lateral planes or at lattice dislocations The latter have been observed by TEM and are generated because of nickel reduction However, rearrangement of silica tetrahedra and initial alumina octahedra into zeolite type tetrahedra[1] cannot be excluded

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