σ-alkyl–π-alkene complexes with two or three carbon atoms between the σ-alkyl and the π-alkene bond have been described (*9*).

Like methyl oleate, other internal alkenes such as cyclohexene and methyl-3-hexenoate are only slightly reactive. On the other hand, alkenes having a terminal double bond are hydrogenated quite easily. Terminal alkenes have the possibility to form a linear alkyl in the half-hydrogenated state whereas oleate must form a secondary alkyl. Steric requirements are probably less stringent for linear alkyl than for secondary alkyl formation. The low isomerization tendency of 1-hexene could also point in the direction of highly favored linear alkyl formation. Although for linoleate the same steric restrictions hold as for oleate, hydrogenation is here promoted by the formation of a 1,4-alkadiene or a σ-alkyl–π-alkene complex. Indeed, isolinoleate (with more than two carbon atoms between the double bonds) is not hydrogenated.

It seems to us that the most interesting property of this catalytic system is the ability to combine a good selectivity with a low positional isomerization tendency. The *trans* double bond in hydrogenated linoleate and isomerized oleate is still mainly located at the original Δ-9 or Δ-12 and the Δ-9 position respectively.

The catalyst is not indefinitely stable, slower rates being observed upon reintroduction of alkene after a complete hydrogenation run. In some cases, a slight deposition of a black material is formed, causing destruction of the catalytic properties. The nature of the active complex remains to be established. By analogy with its rhodium counterpart, one would be tempted to formulate the active catalyst as $(\text{dmf})_3\text{NiCl}(\text{BH}_4)$. On the other hand, the color of the catalytic mixture resembles that of soluble Ziegler-type catalysts. It is generally accepted that these contain metal in a reduced form, solubilized and stabilized by solvent and reducing agent.

We have made a few attempts to isolate a complex from the solution, but these have proved unsuccessful so far.

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On the Existence of Hydroxyl Nests in Acid-Extracted Mordenites

The nature of catalytic action in zeolites is a matter of debate, although there seems to be consensus that activity derives from the existence of tetrahedrally or trigonally coordinated aluminum ions in the lattice. A useful approach to this problem is the possibility of varying the silica:alumina ratio in a zeolite of a given type, along with detailed characterization of the physical, chemical, and catalytic properties in relation to the aluminum content.

Barrer and Makki first showed that the aluminum in a high-silica zeolite, clinoptilolite, could be extracted with acid to give a "silica pseudomorph," and they suggested that a nest of four hydroxyl groups replaced each Al ion extracted (*1*). Acid extraction of aluminum from mordenite, another high-silica zeolite, has since received considerable study (*2–6*), but the existence of hydroxyl nests in extracted samples is still moot. A very recent report by Eberly, Kimberlin, and Voorhies is of particular interest in that ir studies showed no new OH groups formed by acid extraction (*6*).

This note reports studies of several acid-extracted mordenite samples by thermogravimetric analysis (tga), NH_3 chemisorption for acid sites, and N_2 adsorption for pore volume. The results show no evidence for thermally stable hydroxyl nests in the extracted samples, while the NH_3 chemisorption values bear a close relation to the residual Al in the samples.

EXPERIMENTAL

A synthetic hydrogen mordenite (Norton Co. "H-Zeolon," Lot No. TA-4) was ground and sieved to 45–60 mesh size. Thirty grams of ground sample were extracted in a flask with 800 ml of aqueous HCl at 100°. Four extractions were conducted on separate 30 g samples: two for different times of extraction (8 vs 24 hr), and two for different HCl concentrations (6 vs 8 *N*). After the extractions, the catalyst samples were filtered and washed until the filtrate was acid-free. The samples were dried overnight in an air oven at 110°C.

The original H-mordenite pellets were said to be self-bonded. We confirmed that heating the pellets in a stream of O_2 for 3½ hr at 500°C did not produce any detectable amount of CO_2.

The tga measurements were made with a modified Ainsworth BCT balance. A 0.7–0.8 g sample, contained in a porcelain crucible, was suspended by a thin quartz rod from the left arm of balance. Heating was by a Marshall furnace controlled by a Hewlett–Packard 240 M temperature programmer. Preliminary studies of isothermal weight loss indicated that the following stepped temperature program resulted in reasonably "steady-state" weights at each temperature: 30 min each at 100, 200, 300, 400 and 500°; 60 min at 600, 700 and 800°; and 30 min at 900 and 950° (the highest temperature studied). A slow, metered stream of pure O_2 was maintained past the sample during the tga, and buoyancy and drag corrections were made for each temperature. At least duplicate analyses were made on each sample.

Total pore volume was determined from the N_2 adsorption at —195° at a relative pressure ($p/p°$) of 0.25. Adsorption was measured by a flow system, with the use of an Engelhard Isorpta analyzer (model 3A-2), after the sample had been predried (*in situ*) in flowing O_2 and then flowing He for a total of 5 hr at 500°.

Ammonia chemisorption was also determined with the Isorpta analyzer. Sample predrying was the same as that used in the pore volume measurement. Partly on the basis of literature reports, the "ammonia chemisorption" was arbitrarily taken as the amount adsorbed at 250° and an ammonia partial pressure of 11.2 Torr during an adsorption cycle.

Chemical analyses on the original and extracted samples were kindly determined by the Norton Company.

RESULTS AND DISCUSSION

Table 1 summarizes the chemical and physical data for three samples: the original H-mordenite (No. 1), an intermediate sample (No. 2) extracted at 100° for 8 hr with 6 *N* HCl, and the most severely treated sample (No. 5) extracted at 100° for 24 hr with 8 *N* HCl. The tga curves for these materials, based on sample weights at room temperature, are shown in Fig. 1.

As expected, HCl extraction markedly decreases the content of aluminum (Table 1); presumably greater removal could have been achieved if smaller catalyst particles and more severe extraction conditions had been employed. Of particular interest, in

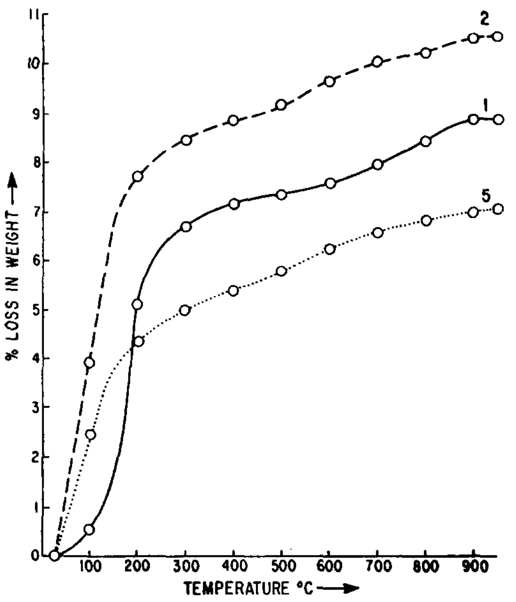

FIG. 1. Thermogravimetric analysis (tga) curves for Samples 1, 2, and 5.

connection with the hydroxyl nest hypothesis, is the progressively smaller loss on ignition (L.O.I.), for samples initially dried at 110°, as the aluminum is progressively extracted.

The tga curves, for samples exposed to air during weighing into the crucible, indicate the greatest % weight loss at 950° for Sample No. 2. It is clear from Fig. 1, however, that the samples contain large amounts of adventitious, physically bound water that is easily removed at relatively low temperatures. One may attempt to calculate the structural hydroxyl content by correcting the total weight loss (to 950°) for the amount of physically bound water. For zeolites, however, it is not clear at what lower temperature this physically bound water is removed in 1 hr; an arbitrary choice must be made. If the tga results are recomputed on the arbitrary basis of the sample weight at 100°, the total weight loss between 100 and 950° decreases monotonically as the aluminum content decreases (see Table 1). For Samples 1, 2, and 5, the % weight losses between 100 and 950° are 8.4, 6.9, and 4.7, respectively. Similar results are obtained if the calculation is arbitrarily based on the weight at 200°: the % weight losses between 200 and 950° are 4.0, 3.0, and 2.8, respectively, for Samples 1, 2, and 5. We also note that the incremental weight change from 900 to 950° is very small for all samples.

The pore volume, as measured by the

TABLE 1
PHYSICAL AND CHEMICAL CHARACTERIZATION

Sample No. description	1 Original H-mordenite	2 6 *N* HCl, 8 hr	3 8 *N* HCl, 24 hr
Analysis, wt % SiO_2	78.55	85.39	88.43
Al_2O_3	9.08	3.64	2.31
Fe_2O_3	0.27	0.09	0.09
TiO_2	0.40	0.36	0.35
Na_2O	0.77	0.11	0.16
L.O.I.	10.65	9.66	8.56
wt ratio, $SiO_2:Al_2O_3$	8.65	23.5	38.3
% wt loss, 100°–950°[a]	8.4	6.9	4.7
% wt loss, 200°–950°[b]	4.0	3.0	2.8
Pore vol, ml/g[c]	0.163	0.172	0.166
NH_3 chemisorbed, 10^3 (moles/g)[c]	1.69	0.955	0.373
Al content, 10^3 (g atoms/g)[c]	1.98	0.79	0.495
NH_3/Al, moles/g-atom	0.85	1.21	0.75

[a] From tga: $\frac{\text{wt at } 100° - \text{wt at } 950°}{\text{wt at } 100} \times 100.$

[b] From tga: $\frac{\text{wt at } 200° - \text{wt at } 950°}{\text{wt at } 200°} \times 100.$

[c] Dry catalyst basis.

N_2 taken up at −195° at $p/p^\circ = 0.25$, is essentially unchanged by the acid extraction.

The ammonia chemisorption also decreases monotonically as the aluminum content decreases (Table 1). Of particular interest is the fact that the molar ratio (NH_3:Al) of ammonia chemisorbed relative to total aluminum in the sample is 1 ± 0.25 for all samples.

The following conclusions may be drawn from these data:

(1) If hydroxyl nests are formed in acid-extracted mordenites, they are not stable above 100°.

(2) Such hydroxyl nests, if initially formed during extraction, would play no role in catalytic reactions carried out at temperatures above 100°.

(3) Such hydroxyl nests, if initially formed during extraction, do not chemisorb ammonia at 250° and a partial pressure of 11.2 Torr.

(4) The amount of ammonia chemisorbed at these arbitrary conditions is roughly stoichiometric (1:1) with the total amount of aluminum present in the mordenite lattice.

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Rate Coefficients from Pulsed Microcatalytic Reactors—Nonlinear Kinetics with Linear Isotherms*

While the use of pulsed microcatalytic reactors has been widely used in many laboratories since its introduction (*1*) the extraction of quantitative rate coefficients from data obtained by this technique for systems with nonlinear kinetics and/or adsorption isotherms has been difficult. Previous consideration of this problem (*2*) has shown that by introducing (1) a dispersion column upstream of the catalyst bed and (2) concentration sensors immediately before and immediately after the catalyst bed, the problem of pulse dispersion could be circumvented and the resulting first-order differential equation could be solved numerically for nonlinear kinetics. In order to use the results of the calculation to extract rate coefficients, however, it is necessary to obtain the net linear velocity of the reactants (judged by the motion of the reactant pulse maximum through the catalyst bed), whereas it is the carrier gas velocity which is more commonly measured. In this note, we show that for the special case of a linear isotherm it is possible to use the numerical results (*2*) with only data on the carrier gas velocity

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