

Effect of $\text{SiO}_2/\text{Al}_2\text{O}_3$ Ratio on Physicochemical Properties of Mordenite and Activity for *n*-Pentane Isomerization*

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A series of acid mordenites having $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios from 12 to 97 was prepared for a study of their physical and catalytic properties. The removal of alumina by acid extraction results in a shrinkage in the unit cell. This is indicated by an increase in the frequency of the infrared lattice vibrations and a shift in the position of the X-ray diffraction lines. Infrared spectra show OH groups absorbing at 3740 and 3590 cm^{-1} . The latter are no longer present on severely acid extracted mordenites. NH_3 adsorption isobars at 8 mm show that the surface acidity decreases in a regular manner with an increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. At the same time, acid treatment opens up more of the channels to permit the adsorption of Decalin. The mordenite becomes less resistant to the adsorptive diffusion of these large molecules. Catalysts containing 0.5% Pd were tested for the hydroisomerization of *n*-pentane. In this reaction, surface acidity appears to be the dominant factor and the catalyst activity decreases with an increase in $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of the mordenite.

I. INTRODUCTION

Mordenite is a crystalline aluminosilicate with a pore structure consisting of parallel tubes having an approximately elliptical cross section with a major and minor diameter of 6.95 and 5.81 Å, respectively (1). Its synthetic forms have surface areas up to about 600 m^2/g and hence, are useful both as catalysts and adsorbents (2-4). For catalytic purposes, synthetic mordenite, particularly in its hydrogen or decationized form, has exceptionally high activity for isomerization and cracking reactions (5-11). However, activity maintenance appears to be poorer than that of other catalysts having a more accessible pore structure.

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Mordenite differs from other zeolites in the extent to which alumina can be removed from the structure without altering significantly the crystallinity of the material as measured by its X-ray diffraction pattern (12, 13). Mordenite normally has a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of about 10. However, this can be progressively increased to the point where nearly all the alumina is removed (11). The removal of alumina is generally accomplished by treatment with strong mineral acids. Previous reports have shown that the cracking of cumene and hydrocracking of *n*-decane and Decalin are much greater with a mordenite having a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of 64 than one with a ratio of 12 (8, 12). Weller and Bauer (10), over a much more limited range, found that the cracking of *n*-hexane increases with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. A maximum, however, was ob-

served at a $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio near 17.5. Kranich *et al.* (11), reported that at high $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios, the removal of alumina resulted in a loss of cracking activity for cumene. Beecher and Voorhies (9) studied the hydroisomerization of *n*-paraffins on synthetic mordenite. Although, for hydrocracking, a metal such as Pd, Pt, or Ni is incorporated on the mordenite, this is not absolutely essential for hydroisomerization (9). However in this case, the activity decreases as molecular weight is increased, particularly in going from *n*-C₆ to *n*-C₇. Presumably this is because the intrinsic hydrogenation activity of pure H-mordenite with no added metal is inadequate to maintain a clean catalyst surface with *n*-C₇.

To extend our knowledge in this area, a series of alumina-deficient mordenites was prepared having $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios from 12 to 97. The acidity of the catalysts was characterized by the adsorption of NH_3 at 8 mm over a wide temperature range. Since the adsorption behavior, particularly toward large molecules, was altered significantly by acid treatment, results on the adsorption of Decalin are included. To measure the catalyst activity, 0.5% Pd was incorporated on each of the catalysts and the hydroisomerization of *n*-pentane determined.

II. METHODS

Catalysts. The catalytic materials consisted of a 0.5% Pd incorporated on a hydrogen mordenite base. A list is given in Table 1. H-M(12), H-M(14), and H-M(97) were obtained directly from the Norton Chemical Company. The remaining

materials were prepared by extracting alumina from H-M(12) with 6 *N* HCl solution for various times up to 8 hr at refluxing temperature ($\sim 100^\circ\text{C}$). The Pd was incorporated from a $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ aqueous solution. Prior to charging to the reactor, the catalysts were calcined in air at 538°C for 3 hr after stepwise temperature increases.

Infrared studies. Two techniques were used to measure the infrared spectra of the solids. The first involved the separation of an ultrafine particle size material by sedimentation from water. This was then compressed into a 1.25-in. disk containing about 120 mg of solid. The use of ultrafine particle size material prevented excessive loss of incident radiation by scattering and permitted good spectra to be obtained in the OH stretch region. Spectra were recorded at elevated temperatures after physically adsorbed material had been removed by vacuum. The second technique involved the preparation of similarly sized disks containing 1% of the catalyst in a KBr matrix. This permitted the observation of lattice vibrations in the lower frequency region below 1200 cm^{-1} . Spectra were recorded with a Cary-White Model 90 infrared spectrophotometer. Details of the unit were published previously (14).

Adsorption measurements. For Decalin adsorption, about 20 mg of catalyst was supported on one arm of a Cahn microbalance. Adsorbed impurities were removed by evacuation at elevated temperature. The sample was then cooled to 93°C and small volumes of Decalin pipetted into the system through a Hg-covered glass frit.

TABLE I
PROPERTIES OF MORDENITE CATALYSTS

Catalyst ^a designation	Wt % Na_2O	Surface area, m^2/g	NH_3 adsorption at 371°C and 8 mm (mmoles/g)	Decalin adsorption at 93°C and 0.12 mm (mmoles/g)
Pd-H-M (12)	Nil	540	1.55	0.20
Pd-H-M (14)	0.90	512	0.45	0.27
Pd-H-M (25)	0.03	550	0.76	0.29
Pd-H-M (66)	Nil	602	0.25	0.33
Pd-H-M (93)	0.03	602	0.20	0.49
Pd-H-M (97)	Nil	594	0.10	0.42

^a The numbers in parentheses represent $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratios.

Weight changes were continuously recorded. Pressures were read with a Model 145, precision pressure gage (Texas Instruments).

The microbalance was also used to measure the ammonia adsorption isobar. In this case, after removal of adsorbed impurities, the sample was exposed to 8 mm NH_3 pressure at 427°C. The temperature was then gradually lowered to 93°C and the weight increase continuously recorded.

Hydroisomerization of $n\text{-C}_5$. The hydroisomerization reactions were carried out in a fixed-bed reactor which was immersed in fluidized sand bath to maintain isothermal conditions in the reactor. A schematic diagram of the equipment is shown in Fig. 1. Liquid n -pentane (99+ mole % pure), fed by a Ruska pump, was mixed with dry electrolytic hydrogen from a cylinder through a d/p cell flowmeter before entering the reactor system. Pressure in the reactor was controlled by a back-pressure regulator. The product gas was measured with a wet test meter, and the product liquid (if any) was collected and weighed. The product gas and liquid were analyzed by a gas chromatograph.

Before feeding n -pentane at the start of a run, the catalyst was reduced in an atmosphere of hydrogen for 3 hr at the temperatures and pressures specified for the hydroisomerization run. Typical hydroiso-

merization conditions were as follows: 288°C, 32 atm, eight volumes of pentane per hour per volume of catalyst and 3.4 moles of hydrogen per mole of hydrocarbon.

III. RESULTS

Infrared examination. The removal of alumina by acid treatment results in changes in the lattice vibrations of the crystal. Spectra are shown in Fig. 2. The lattice vibrations of H-M(66) all occur at significantly higher frequencies than those of H-M(12). This is an indication of a smaller unit cell. This would not be unexpected if the alumina tetrahedra were replaced by silica tetrahedra since the Si-O bond is shorter than the Al-O. The unit cell shrinkage was also indicated by X-ray diffraction experiments (12, 13).

Hydrogen mordenite with a standard ratio of 12 has two types of hydroxyl groups as shown in the upper portion of Fig. 3. On the basis of studies on other solids, the groups at 3740 cm^{-1} are most likely associated with the silica tetrahedra. The lower frequency groups at 3590 cm^{-1} are seen on H-M(12) but not on H-M(66). This suggests that these groups might be associated with a structural feature of the mordenite induced by the alumina tetrahedra.

NH_3 adsorption. The adsorption isobars of NH_3 on a series of 0.5% Pd on hydrogen mordenite catalysts are shown in Fig. 4. Temperature can be used to distinguish the strengths of acid sites. Sites of higher acidity will retain NH_3 to a greater degree as the temperature is raised. Thus, the curves in Fig. 4 reflect the acidity distribution. As the alumina is removed, the level of acidity decreases. This is generally true at all temperature levels. However, there is an exception in that isobars of Pd-H-M(14) and Pd-H-M(25) intersect near 260°C. The former has less than the expected number of high-strength acid sites. This may be attributed to its comparatively high soda content of 0.90% (Table 1). The amount of NH_3 adsorbed at 371°C was selected as a measure of the strong acid sites and this information is listed in Table 1.

Decalin adsorption. In early studies, we

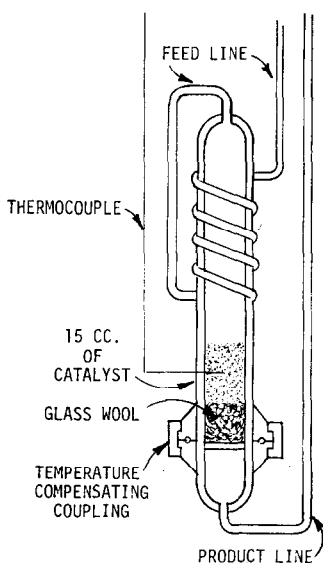


FIG. 1. Details of reactor system.

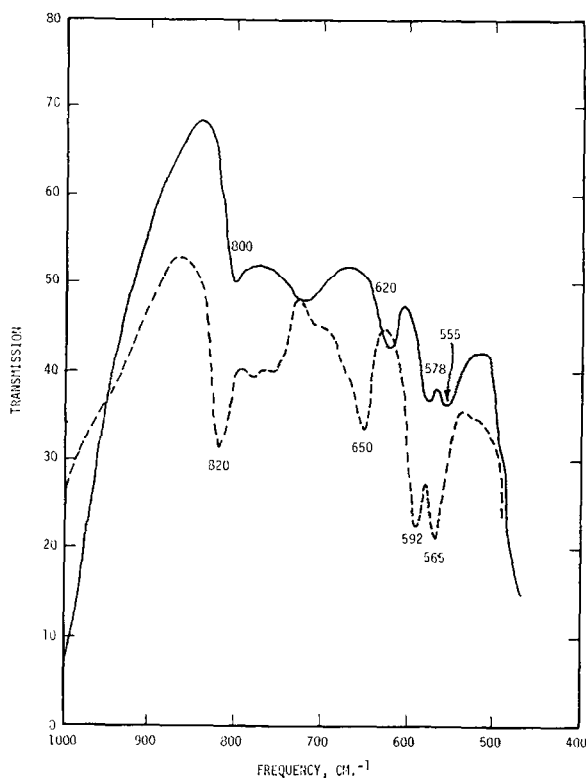


FIG. 2. Infrared spectra of H-M (12) and H-M (66). Spectra were recorded at room temperature on KBr disks containing 1% of the mordenite. The solid and dashed lines represent spectra obtained with H-M (12) and H-M (66), respectively.

found that mordenites which were otherwise similar often showed great differences in their ability to adsorb Decalin. This was exhibited both in the rates of adsorption as well as in the equilibrium adsorption capacities. Adsorption rate data at 93°C are shown in Fig. 5. The greater the degree of alumina removal the faster the rate of Decalin adsorption. Apparently, the acid treatment removes obstructions from the adsorption channels thereby lowering the diffusion resistance. It also makes more of them available for Decalin adsorption. Equilibrium capacities are listed in Table 1.

***n*-C₅ Isomerization.** The integral reactor, previously described, was employed to obtain the kinetic data for the reversible reaction, $n\text{-C}_5 \rightleftharpoons i\text{-C}_5$, and the rate constant, k , was calculated upon integration of the kinetic model as described by Voorhies and Bryant (15).

The procedure followed to calculate rela-

tive isomerization activities was to select an appropriate reference catalyst (in this case, Pd H-mordenite with a SiO₂/Al₂O₃ ratio of 12) and to react *n*-pentane over this catalyst at 8 v/v/hr, 32 atm, and 3.4 moles H₂/mole *n*-C₅ at different temperatures so as to obtain the Arrhenius equation relating the rate constant, k , to the inverse of the absolute temperature:

$$k_{\text{ref}} = (k_0)_{\text{ref}} e^{-\Delta H/RT}, \quad (1)$$

where k_{ref} = isomerization rate constant for reference catalyst, $\frac{\text{cm}^3}{\text{g-sec}}$;

$(k_0)_{\text{ref}}$ = frequency factor for reference catalyst, $\frac{\text{cm}^3}{\text{g-sec}}$;

ΔH = activation energy, kcal/mole; and

T = temperature, °K.

An identical procedure was followed to

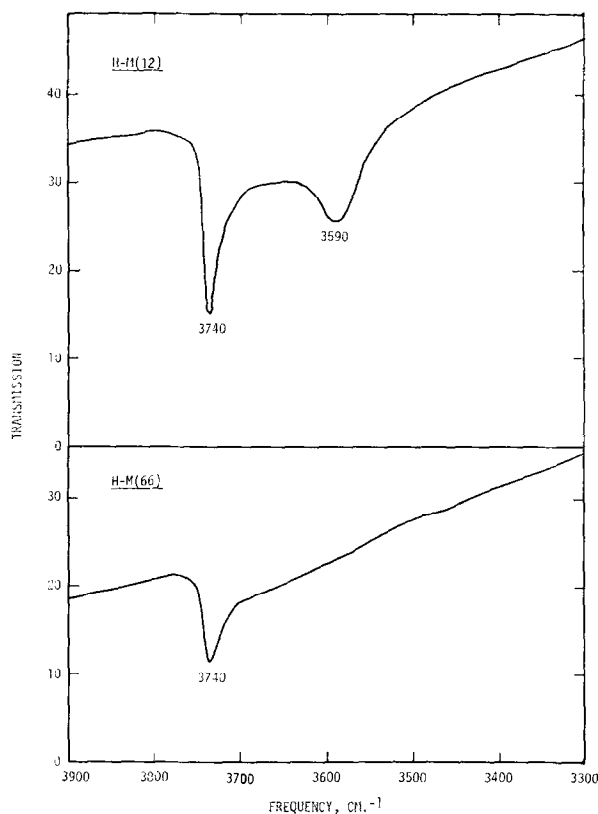


Fig. 3. Infrared spectra of mordenites at 427°C under vacuum.

evaluate the rate constants for the "unknown" catalyst as a function of temperature according to the equation

$$k_u = (k_o)_u e^{-\Delta H/RT}, \quad (2)$$

where k_u = isomerization rate constant for unknown catalyst, $\frac{\text{cm}^3}{\text{g-sec}}$;

$(k_o)_u$ = frequency factor for unknown catalyst, $\frac{\text{cm}^3}{\text{g-sec}}$.

The activation energies for a wide variety of mordenite catalysts tested at the L.S.U. Petroleum Laboratories for *n*-pentane isomerization closely approximate 30 kcal/mole. Relative activity numbers are reported by dividing the rate constant of the unknown catalyst, k_u , by the rate constant of the reference catalyst, k_{ref} , at 288°C, and multiplying by 100.

A summary of the experimental condi-

tions and the results obtained are presented in Table 2.

IV. DISCUSSION

Acid extraction produces profound changes in the chemical and physical properties of mordenite. The concept of silica tetrahedra replacing the alumina tetrahedra is not inconsistent with the experimental data. The decrease in unit cell as reflected by the infrared lattice vibrations and X-ray diffraction patterns is expected in view of the shorter length of the Si-O bond. Other investigators have proposed that the alumina tetrahedra are replaced by hydroxyl groups (16, 17). Our infrared spectra, however, show no new OH groups formed by acid extraction. In fact, they indicate a substantial reduction in the low frequency groups at 3590 cm^{-1} . The spectrum of H-M(66) is essentially identical to that of pure silica gel. Hence, this pro-

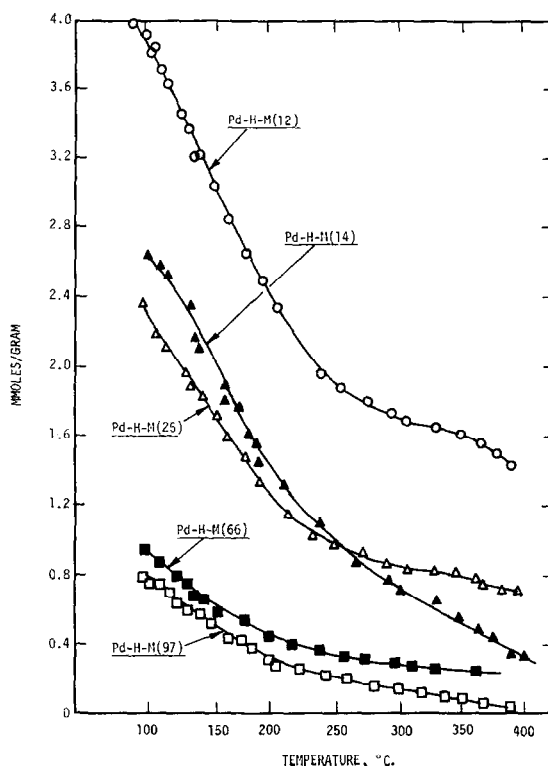


FIG. 4. Adsorption isobars of NH_3 at 8 mm.

posal does not appear to explain the spectral results unless the changes envisioned are beyond the scope of detection by our infrared techniques. It could also be that alumina tetrahedra are merely removed from the crystal leaving appropriate vacancies. Our experimental results are not sufficient to prove or disprove this concept. If this were the case, however, it is surprising that so little change occurs in the X-ray diffraction pattern. Careful density measurements might be useful in answering this question.

The removal of alumina results in the formation of a less acidic catalyst surface as seen from the ammonia adsorption isobars. Part of this loss is due to the lower concentration of acidic OH groups in the intracrystalline channels. However, it is not impossible that some Lewis acid centers might also be lost due to the removal of alumina. Concomitantly, acid treatment serves to open up more of the pores to permit the adsorption of Decalin. The mordenite becomes less resistant to the adsorptive

TABLE 2
HYDROISOMERIZATION OF *n*-PENTANE AT 288°C AND 32 ATM

Catalyst designation	Feed rate w/hr/w	Mole H_2 / mole <i>n</i> - C_5	Mole % C_1 - C_4	% <i>i</i> - C_5 in total C_5	k , $\text{cm}^3/\text{g}\cdot\text{sec}$	Relative activity
Pd-H-M (12)	7.51	3.57	2.90	37.7	0.104	100
Pd-H-M (14)	6.95	3.07	0.00	26.3	0.052	50
Pd-H-M (25)	7.48	3.22	1.14	33.5	0.081	78
Pd-H-M (66)	8.28	3.30	0.10	20.8	0.049	47
Pd-H-M (93)	7.88	3.60	0.00	6.8	0.024	23
Pd-H-M (97)	1.68	9.56	0.00	13.6	0.015	14

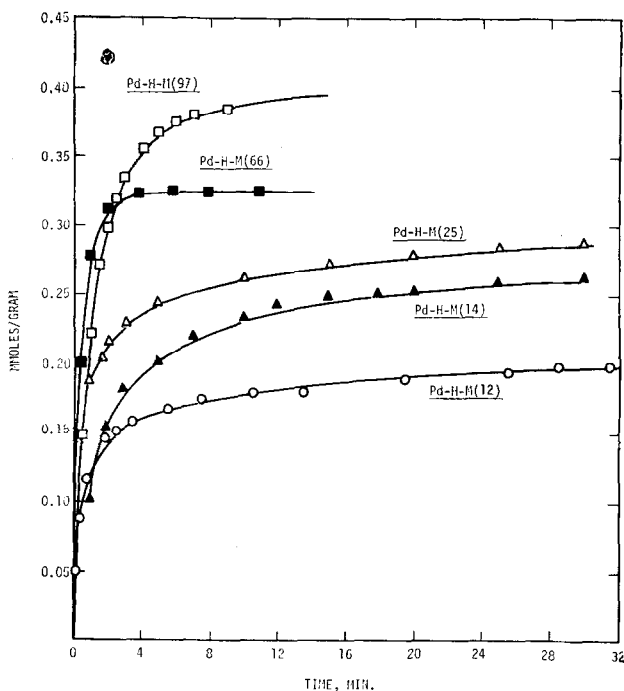


FIG. 5. Adsorption of Decalin at 93°C and 0.12 mm.

diffusion of these large molecules. In relating these properties to catalysis, we find that acidity appears to be the dominant factor for the hydroisomerization of *n*-pentane. This is shown in Fig. 6. Here, the amount of NH_3 adsorbed at elevated temperatures is plotted against the relative activity for *n*- C_5 isomerization. For both mea-

surements, the catalysts were calcined at elevated temperatures; however, of necessity, vacuum was employed for the ammonia isobar determination. This difference has minor effect on the absolute values and no effect on the relative order.

With one exception, Pd-H-M(14), the increase in acidity coincides with increasing

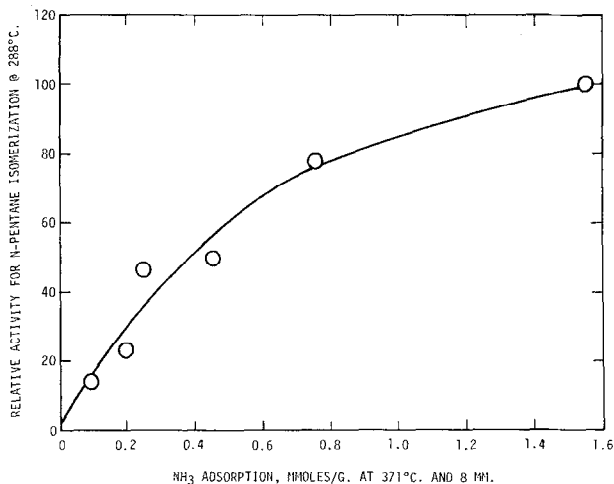


FIG. 6. Correlation of pentane isomerization activity with acidity.

alumina content (Table 1). As previously mentioned, Pd-H-M(14) has a higher than normal soda content which accounts for its lower activity. Changes in the accessibility of the pore structure do not appear to play a part. This latter factor might assume a greater importance as the molecular size of the reactant is increased. Thus, in the previously published results on hydrocracking of decane and Decalin (8), the higher activity of alumina-deficient mordenite results from decreased diffusion resistance. The interaction of surface acidity and pore accessibility might well account for the apparently conflicting reports on the effect of alumina deficiency on catalytic activity.

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