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Sorption and Diffusivity Characteristics of Acid-Leached Mordenites

The apparent diffusivity for the binary liquid systems benzene-cumene and cyclohexane-cumene in H-mordenite crystals at 25°C to 44°C was increased by an order of magnitude or more after the zeolite was acid-leached to increase the silica-alumina mole ratio from the range of 14 to 18 to the range of 70 to 89. The calculated diffusivities, which range from 10^{-12} to 10^{-16} cm^2/s, decrease with approach to sorption equilibrium and may be markedly reduced under some circumstances by adsorption of molecules from the bulk liquid, causing blockage of pores.

Comparison of sorption capacities as a function of silica-alumina ratio as reported by various investigators indicates that considerable differences exist in the properties of acid-leached mordenites of the same silica-alumina ratio but of different origins.

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SCOPE

H-mordenite and acid-leached mordenites have remarkable catalytic activities for acid-catalyzed reactions, but the rate and selectivity of these reactions can be profoundly affected by the rate of counterdiffusion of product and reactant molecules inside the fine pore structure of these zeolites. Acid leaching removes alumina from the silica-alumina matrix and opens up the pores of mordenites, thereby increasing the rate of diffusion. However, leaching also reduces the concentration of acid sites, thereby presumably decreasing the intrinsic reactivity of the catalyst. The two effects act in opposite directions on the apparent reactivity of the mordenite under diffusion-limiting conditions.

A principle objective of this work was to determine quantitatively the effect of acid leaching on diffusivity in mordenites. Diffusion measurements were made by observing the rate of disappearance of a hydrocarbon species A by adsorption from a dilute solution of A in B into mordenite crystals previously saturated with B—termed here *adsorption measurements*; or by observing the rate of appearance of B from saturated mordenite into bulk liquid consisting initially of pure A—termed here *desorption measurements*.

Sorption capacities for benzene or cumene vapors were also determined as a function of silica-alumina ratio and compared to previous reports on sorption of these and other hydrocarbons. Sorption capacities are of interest in themselves in connection with adsorption processes, and they also provide some insight into the nature of the fine pore structure.

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CONCLUSIONS AND SIGNIFICANCE

Our comparison of the change in sorption capacity with silica-alumina ratio in acid-leached mordenites as reported by various investigators shows that these vary greatly and leads us to conclude that considerable differences exist in the pore size distribution and possibly other properties of various samples of acid-leached mordenites of the same silica-alumina ratio. This ratio as such is therefore an inadequate measure of the physiochemical properties of these materials. We suggest that variations in the leaching procedure used to arrive at a specified silica-alumina ratio, for example, a short and severe leach vs. a long and mild treatment may have a marked effect on sorption capacity and presumably also on diffusivity. The distribution of number and kind of acid sites would presumably also be affected, leading to variations in chemical reactivity.

The diffusivity increased by about an order of magnitude when the silica-alumina mole ratio was increased by leaching from the range of 14 to 18 to the range of 70 to 89. The apparent diffusivity may be markedly reduced (for example, by two or more orders of magnitude under some circumstances) by pore blockage by a strongly adsorbed species in the bulk liquid. Leaching opens up the pores of mordenite particles and can increase the access of exterior fluids to the interior of the solid. Further studies are needed to relate methods of leaching to sorption, diffusion, and reactivity characteristics of mordenites.

Hydrogen mordenite and alumina-deficient mordenites prepared by acid leaching exhibit remarkably high catalytic activities for a variety of acid-catalyzed reactions, and a large body of literature has developed in recent years concerned with reaction studies and physiochemical properties of these materials. Since most of the catalytic area lies within pores that are approximately 6 × 7 Å in the ideal crystal, it is evident that the rates of diffusion of reactant and product molecules within these tiny passageways may under many circumstances be a rate-limiting process and therefore have a profound effect upon the apparent activity and selectivity of these catalysts.

Recent papers on H-mordenite-catalyzed reactions, which also give guidance to earlier literature, include studies of hydrocracking of *n*-hexane and cyclohexane (Voorhies and Hatcher, 1969), of hexane isomerization (Beecher and Voorhies, 1969), and of methanol dehydration (Swabb and Gates, 1972). Acid-leached mordenites of various silica-alumina ratios were studied by Eberly and Kimberlin (1970) for cracking of cumene, by Beecher et al. (1968) for hydrocracking of *n*-decane and Decalin, by Hopper and Voorhies (1972) for hydroisomerization of cyclohexane and *n*-pentane, and by Thakur and Weller (1973) for cracking of hexane.

Diffusion limitations were believed to have occurred in several cases, but it is difficult to prove this unequivocally. Methods commonly used with conventional catalyst pellets and powders to determine whether pore diffusion is a significant resistance are unfortunately difficult to apply when diffusion through micropores of a zeolite crystal is of concern. The effect of varying pellet or particle size is a powerful diagnostic test if the substance is truly isotropic in its properties but to change the inherent crystal size of a zeolite involves modifying the conditions of synthesis which may alter the diffusivity characteristics. Likewise crushing or grinding the crystals can markedly affect their diffusivity. In a study on Na-mordenite (Satterfield and Frabetti, 1967) 2.5μ crystals were found to have an effective diffusion coefficient about 50 times greater than that in another sample of crystals about 21 × 21 × 33μ in size. Dry grinding to reduce the larger crystals to about 7.5μ size reduced the diffusivity by a factor of about 35.

Another diagnostic test proceeds from the fact that the apparent activation energy for certain simple intrinsic kinetics under highly diffusion-limiting conditions is the arithmetic mean of the true activation energy for the reaction itself and that for diffusion. In some conventional catalytic systems the second is usually small relative to the first, and hence the apparent activation energy is about one-half of the intrinsic value. In zeolites, however, activation energies for diffusion are much higher than those normally encountered and may be comparable to those for the reaction itself, hence a marked drop in activation energy may not occur under diffusion-limiting circumstances.

With these precautions in mind there is still good evidence that diffusion of hydrocarbons is a rate-limiting step in some observed reactions on acid-leached mordenites, for example, hydrocracking of *n*-decane and Decalin (Beecher et al., 1968) and cracking of cumene (Eberly and Kimberlin, 1970). Particularly striking are observations that the catalytic activity passed through a maximum as the silica-alumina ratio was varied. This, for example, was reported by Kranich et al. (1970) for isomerization of 1-butene with mordenites varying from 12 wt. % to < 0.1 wt. % Al_2O_3 and by Weller and Brauer (1969) for *n*-hexane hydrocracking over the SiO_2/Al_2O_3 mole ratio range of 15.5 to 17.7. The removal of alumina by acid-leaching reduces the number of acid sites while simultaneously opening up passageways for diffusion. The two factors operate in opposite directions in their effect on observed reactivity, and conceivably a maximum in the rate under some circumstances might represent an optimum between severe diffusion limitations at low silica-alumina ratios and low acid site concentrations at high ratios.

Several previous studies have indicated that acid-leaching opens up the mordenite pores, as indicated by an increase in sorption capacity, and this can plausibly be taken as indicating that the diffusivity would presumably also be increased. However, only brief information seems to be available on the effect of acid-leaching on diffusivity as such. Beecher et al. (1968) give some fragmentary data which show a 1.5- to 3-fold increase in the diffusivity of toluene, *n*-octane, or Decalin at 200°F. in an aluminum-deficient mordenite catalyst compared to an equivalent conventional H-mordenite catalyst and Eberly and Kimberlin (1970) showed qualitatively that adsorptive diffusion rates were greater in a 64/1 ratio mordenite than in a conventional 12/1 ratio material. Eberly et al. (1971) also showed qualitatively that alumina removal increased the rate of Decalin adsorption.

A principal objective of the present studies was to make a careful examination of the effect of acid-leaching of mordenites on their diffusion characteristics; chosen for this purpose was the liquid counterdiffusion of two binary systems, cyclohexane-cumene, and benzene-cumene. The effect of leaching on sorption capacity was also examined, and present results were compared and contrasted to previously reported studies.

The ideal unit cell formula for Na-mordenite is

$$Na_8\,(AlO_2)_8\,(SiO_2)_{40}\cdot 24H_2O$$

TABLE 1. CHARACTERISTICS OF H-MORDENITE SAMPLES(1)

Sample name	Surface area, m^2/g	Cl, wt. %	Na, wt. %	SiO_2, wt. %	Al_2O_3, wt. %	Al atoms / cell	SiO_2 / Al_2O_3	X-ray crystallinity(2)
Zeolon 100H	—	—	0.30	71.8	9.9	6.7	12.32	89.7
M14	475	0.01	0.18	73.21	8.71	5.9	14.3	100.0
M18	464	0.02	<0.1	76.47	7.07	4.8	18.4	98.7
M70	560	0.02	Nil	83.06	2.01	1.4	70.2	87.7
M89	495	0.05	Nil	84.87	1.61	1.1	89.7	76.0

[1] The chemical composition of the Zeolon 100H was determined at the Central Analytical Facility of M.I.T. Those of the samples M14, M18, M70, and M89 were supplied by the Sun Oil Company.

[2] Measured at M.I.T. by relative line intensity, arbitrarily assigning 100% to M14.

although different preparations of Na-mordenite may have silica-alumina ratios varying by 10% or more. H-mordenite can be prepared from the sodium form by ion exchange with an ammonium compound followed by calcination or by mild acid treatment; the latter may, however, remove a small amount of alumina as well. More severe acid treatment can remove increasing amounts of alumina, and SiO_2/Al_2O_3 ratios exceeding 600 can be prepared without significant variation of the basic crystal lattice (Kranich et al., 1971).

Barrer and Makki (1964) and Barrer and Coughlan (1968) postulated that each aluminum atom removed was replaced by four hydroxylic hydrogens, while others proposed that it was replaced by a silicon atom forming a silica tetrahedron. The former hypothesis would produce more hydroxyl groups and the latter would result in a shrinkage of the unit cell dimension because the Si-O bond (1.61 Å) is shorter than the Al-O bond (1.75 Å). However, Eberly et al. (1971) reported that no new hydroxyl groups were formed by acid extraction as indicated by infrared spectra. Dubinin et al. (1968) found a decrease of 1% in certain interplane distances, revealed from X-ray diffraction patterns, as the silica-alumina mole ratio was increased from 10 to 69. This decrease in interplane distance might confirm the postulate of replacing Al by Si. However, it is not impossible that the alumina tetrahedra are merely removed from the crystal lattice leaving appropriate vacancies. Evidence available does not clearly support one hypothesis over the other.

MATERIALS

The mordenites were all provided from the Norton Company, but came to us through two different routes. First, conventional Na- and H-mordenites designated as Zeolon 100Na and Zeolon 100H, respectively, were supplied directly to us by the Norton Company. Secondly, the Sun Oil Company supplied to us a series of four H-mordenites of different silica-alumina ratios. The first member of this series, designated by us as M14, was a commercial sample of Zeolon 100H obtained by the Sun Oil Company from the Norton Company, from which three alumina-deficient H-mordenites with silica-alumina mole ratios ranging from 18.4 to 89.7 (designated as M18, M70, and M89) were prepared by leaching with aqueous HCl at temperatures of 50° to 90°C. The product was washed repeatedly with distilled water until no residual chloride ion could be detected by test with silver nitrate. Shown in Table 1 are the chemical compositions and surface areas of the mordenite samples together with their relative X-ray crystallinity. There was little effect of acid-leaching on the X-ray pattern, in agreement with previous reports.

Although the M14 and Zeolon 100H are samples of the same product, comparison of the two in Table 1 indicates some differences, perhaps reflecting possible changes in the production process at different times. Zeolon 100H is believed to be made by mild acid treatment of Zeolon 100Na. A small amount of alumina is apparently leached out at the same time as the sodium is exchanged because the silica-alumina ratios of Zeolon 100H and M14 are slightly higher than for the Zeolon 100 Na. (This latter was 10.1 mole ratio as reported by the Norton Company and 9.8 as determined at the Central Analytical Facility at M.I.T.) The Zeolon 100H had an average particle size of 1.7 microns and a standard deviation of 1.0 microns. Based on measurements at M.I.T., the mean particle diameter of the M series was taken to be 2 microns with a standard deviation of 1.2 microns. Particle shapes were approximately spherical. The number of aluminum atoms per unit cell for each sample was calculated by assuming that Zeolon 100 Na had the ideal unit cell containing 8 aluminum atoms.

Hydrocarbons used were of the highest purity available commercially and were pre-purified with a mixture of 5A and 13X molecular sieves before use. Purities as determined by gas chromatography by us were as follows: Benzene (99.962%), cumene (99.943%), cyclohexane (99.918%). The supplier was Aldrich Chemical Company except for the benzene which was supplied by Allied Chemical.

APPARATUS AND PROCEDURE

Before use the mordenite was activated to remove water of saturation or any adsorbed gaseous impurities by slowly heating the material in a temperature-programmed oven from 50 to 500°C at a rate of 1°C/min. under vacuum. After reaching 500°C, the activated zeolite was kept at this temperature for an additional three hours and then was allowed to cool slowly in the oven to near room temperature.

The experimental apparatus was the same as that used and described previously (Satterfield and Cheng, 1972a, 1972b). It essentially consisted of a 3-neck 500-ml. flask connected with a Cole-Parmer closed system stirrer driven by a variable speed motor and immersed in an isothermal bath.

Two types of experiments were carried out, termed here *adsorption measurements* or *desorption measurements*. In adsorption measurements, about 10 to 12 grams of freshly activated zeolite were introduced into the 3-neck flask containing about 80 to 100 grams of hydrocarbon B. The flask was sealed tightly and immersed in the isothermal bath at a pre-set temperature, and the zeolite-hydrocarbon mixture was kept constantly stirred for one night. At the beginning of a run, about 2 to 3 grams of hydrocarbon A were added to the flask, thus forming a dilute solution of A in B. The rate of disappearance of A from this solution into the mordenite was followed by withdrawing samples of the slurry of about 1 ml each from the flask at predetermined time periods. These were filtered as they were withdrawn, and the concentration of A in the liquid portion of the sample was analyzed by gas chromatography.

In the case of desorption measurements, hydrocarbon B was first adsorbed into the mordenite from the vapor phase at a relative pressure, $P/P_0 \leq 0.3$. After saturation, the mordenite was transferred to a 3-neck 500-ml flask, as used for adsorption measurements. At zero time about 80 to 100 grams of pure hydrocarbon A were added to the flask. Samples of hydrocarbon-mordenite slurry were withdrawn from the flask and analyzed for the appearance of hydrocarbon B into the bulk liquid.

Taking the cyclohexane-cumene system as an example, in both types of measurements the mordenite was initially saturated with cyclohexane. In adsorption measurements the rate of removal of cumene by adsorption from a dilute solution in cyclohexane was followed. In desorption measurements the rate of appearance of cyclohexane into initially pure cumene was followed. In an ideal system in which counterdiffusion occurred freely, both measurements would be expected to yield the same value of a counterdiffusion coefficient. In fact, the rate processes observed here under some circumstances seemed to reflect primarily a rate of adsorption rather than a rate of diffusion as such, as will be shown. In desorption measurements the cumene concentration in the bulk liquid was much higher than in adsorption measurements which under some circumstances apparently led to pore blockage by adsorbed cumene molecules. The apparent counterdiffusion coefficients under these conditions were thus much less than those calculated from adsorption measurements.

Normally the diffusion run was in progress for 8 hours, and about 15 to 17 samples were taken. Then two more samples of about 5 ml each were withdrawn from the flask and transferred to a tube which was, in turn, sealed tightly. These two samples were kept at the run temperature for a month or two in order to determine the equilibrium composition.

DATA REDUCTION

Data were analyzed in terms of Fick's Law, applying three different models:

1. Diffusion in spheres of uniform size
2. Diffusion in spheres with the known particle size distribution (which was nearly a normal distribution) and
3. Diffusion in flat plate geometry.

In the ideal mordenite crystal the main pores comprise an array of parallel tubes open at both ends and flat plate geometry would be the appropriate model. Here, however, the particles are polycrystalline and leached to varying degrees and results are presented in terms of diffusion in a sphere of uniform radius, taken to be 2 microns. Results in terms of the other two models are given by Chiu (1973) and discussed briefly below.

The solution to the unsteady state diffusion equation applied to a sphere with proper initial boundary conditions is

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{6\alpha(\alpha + 1)\, e^{-Dq_n^2 t/a^2}}{9 + 9\alpha + q_n^2\alpha^2} \tag{1}$$

where M_t = amount of material having diffused out or in at time t, for desorption or adsorption, respectively

M_∞ = amount of material having diffused out or in after infinite time, for desorption or adsorption, respectively

D = effective diffusion coefficient, cm^2/s

t = time, s

a = radius of the sphere, cm

The q_n's are the nonzero, positive roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \tag{2}$$

and the parameter α for adsorptive runs is defined by

$$\alpha = \frac{1 - F_a}{F_a}$$

where F_a is the fraction of the material being adsorbed, added to the flask, which actually did adsorb at equilibrium.

From the experimental data, an uptake curve, M_t/M_∞ vs. t, can be calculated. This was fitted sectionally to the theoretical uptake curve, Equation (1), to obtain a value of D which can simultaneously satisfy both curves. In other words, a few data points in the immediate vicinity of the point at which the diffusivity was to be evaluated were fitted to the theoretical uptake curve by a least square curve fitting technique. This mode of analysis was used to evaluate effective diffusivities at $M_t/M_\infty = 0.3$, 0.5 and 0.7.

Over the early portion of the diffusion process, the following simplified equation becomes a good approximation to Equation (1):

$$\frac{M_t}{M_\infty} = \frac{6}{\sqrt{\pi}} \left(\frac{Dt}{a^2} \right)^{1/2} \tag{3}$$

Therefore, the initial diffusivity was evaluated from the slope of a plot of M_t/M_∞ vs. $t^{1/2}$, for $M_t/M_\infty \leqq 0.3$. For evaluation of the effect of leaching on diffusivity, we believe that the data obtained in the neighborhood of M_t/M_∞ of 0.3 are probably the most meaningful. Initial rate data were influenced by the details of the particle size distribution. Above M_t/M_∞ of 0.5 or so, data scattered increasingly.

Although Fick's Law with a constant coefficient is commonly used for analysis of diffusion studies in zeolites, results here deviated substantially from it with any of the three models used for analysis. Such deviations may be caused by one or more of the following:

1. The effect of particle size distribution may not be properly allowed for.
2. The assumption that sorption equilibrium is established at all times may not be valid, for example, the rate of adsorption or desorption may be rate-controlling rather than diffusion as such.
3. Fick's law may be followed, but the diffusivity may not in fact be independent of concentration.
4. The zeolite particles may be anisotropic in structure.
5. A linear adsorption isotherm is usually assumed, but this will almost surely not be valid over a wide concentration range.

The data are presented here all in terms of a uniform particle size, but the observations were also carefully analyzed by Chiu (1973) allowing for the known particle size distribution. Although this may alter the numerical value of the diffusivity reported, especially for the initial diffusivity, deviations from Fick's law were not primarily caused by this factor nor did adjustment for the particle size distribution affect the trends found of effect of silica-alumina ratio on the results or the overall conclusions.

The deviations observed here were apparently caused primarily for the second and fourth reasons.

For diffusion in a sphere, analysis in terms of the known particle size distribution decreased the absolute value of the diffusivity calculated for a sphere of 2-micron radius by a factor of 5 at M_t/M_∞ of zero and a factor of about 2.3 at M_t/M_∞ of 0.3. If flat plate geometry were assumed instead of uniform spheres, the diffusivity is increased by a factor of 9 at M_t/M_∞ of zero and about 8.5 at M_t/M_∞ of 0.3. For both geometries the value of the factor is affected slightly at all finite values of M_t/M_∞ by the value of F_a.

RESULTS AND DISCUSSION—SORPTION CAPACITIES

Prior to making desorption diffusion measurements, the mordenite was first presaturated with either benzene or cyclohexane from the vapor phase at room temperature at a relative pressure P/P_0 of 0.28 to 0.30. In doing so one can obtain the total sorption capacity of the zeolite, which includes sorption of the hydrocarbon onto the surface of the particles and into various structural defects as well as within zeolite pores. One can also obtain an internal sorption capacity by subtracting from the total, the amount

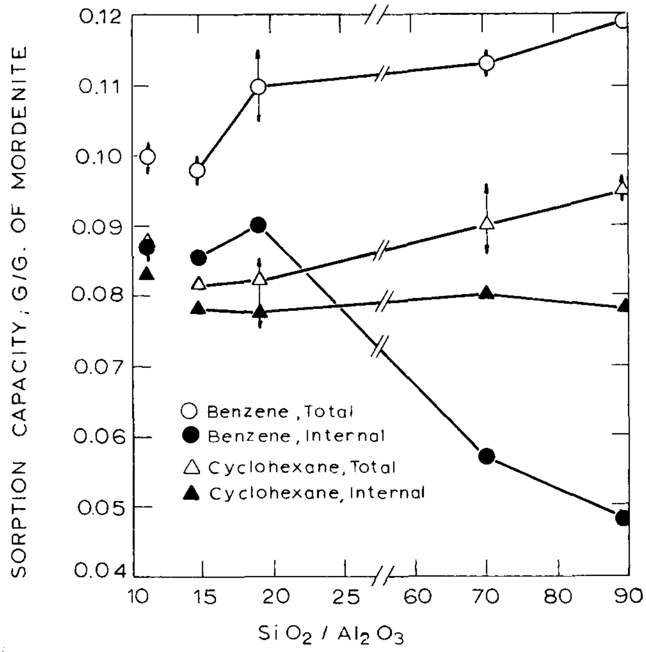

Fig. 1. Effect of silica-alumina mole ratio on total and internal sorption capacities of benzene and cyclohexane in H-Mordenites. Present study.

of preadsorbed hydrocarbon appearing in the bulk liquid upon first contact with the zeolite, evaluated by extrapolating to zero time a plot of concentration versus square root of time. The internal sorption capacity represents hydrocarbon in the internal pores or otherwise held tenaciously to the mordenite.

Figure 1 gives total and internal sorption capacities, as defined above, for the mordenites used in this study and Figure 2 presents total sorption capacities for this and various other studies on leached mordenites as reported in the literature. In both figures the isolated points are for Zeolon 100 and can be compared to the connected points using the same symbol which represents the M series of mordenites. In Figure 1 each point is an average value from three or more runs and the vertical arrows for the total sorption capacity indicate the spread in values. A similar range of values was found for the internal sorption capacities.

Figure 1 shows a marked difference at high silica-alumina ratios between the internal sorption capacity for benzene and cyclohexane. The leaching process not only increases the average effective pore size, but also may well produce an anisotropic structure (see later) with pores on the outside of the particles larger than those towards the center. Hence benzene, which is a slightly smaller molecule (6.3 × 3.0 Å) than cyclohexane (6.6 × 4.8 Å) may have diffused out of the outer portions of the mordenite particles very rapidly.

Figure 2 compares the total sorption capacities found in our work with the previous literature, including two other studies with benzene. Dobruskin et al. (1969) give data over a narrow range of composition, but the capacity they report for the lowest silica-alumina ratio is far below that for Zeolon 100. Nakano et al. (1971) reported data on benzene adsorption on two series of acid-leached mordenites, one of which was ground in a ball mill before leaching. There is little difference between the sorption behavior of the two series, but both show considerably lower capacity than our samples and a maximum sorption at a silica-alumina ratio of about 20 to 22. The sorption capacities for cumene reported by Piguzova et al. (1969) likewise reached a maximum at an intermediate composition, a sample having a silica-alumina mole ratio of 19. In direct contrast, Eberly and Kimberlin (1971) reported an increase for cumene adsorption in a comparable range of silica-alumina ratio material although measurements were at a much lower relative pressure. As has been previously noted, mordenites with considerably different adsorptive properties can be prepared by varying the synthesis conditions (Sand, 1968), but the change in structure which leads to this difference is still obscure.

Figure 2 shows that the change in sorption capacity with degree of acid-leaching also varies markedly with different samples. In all cases aqueous HCl was the leaching agent but different investigators used different combinations of time, temperature, and concentration to achieve the various desired silica-alumina ratios. Leaching of any material frequently produces an anisotropic pore structure, those pores near the outside being larger on average than those further into the interior. Starting with a particular mordenite, a specified silica-alumina ratio reached by, for example, leaching with a short contact time at high temperature and concentration vs. long contact time and less severe conditions might be expected to result in different degrees of structural inhomogeneity. Whether variation in the leaching method or in the original starting material is the dominating factor in the different sorption properties reported by different investigators is not clear at present. In any event the fact that some samples show a marked peak in sorption capacity with increase in silica-alumina ratio whereas others do not strongly suggest that considerable differences exist in the pore-size distribution of various samples of acid-leached mordenites

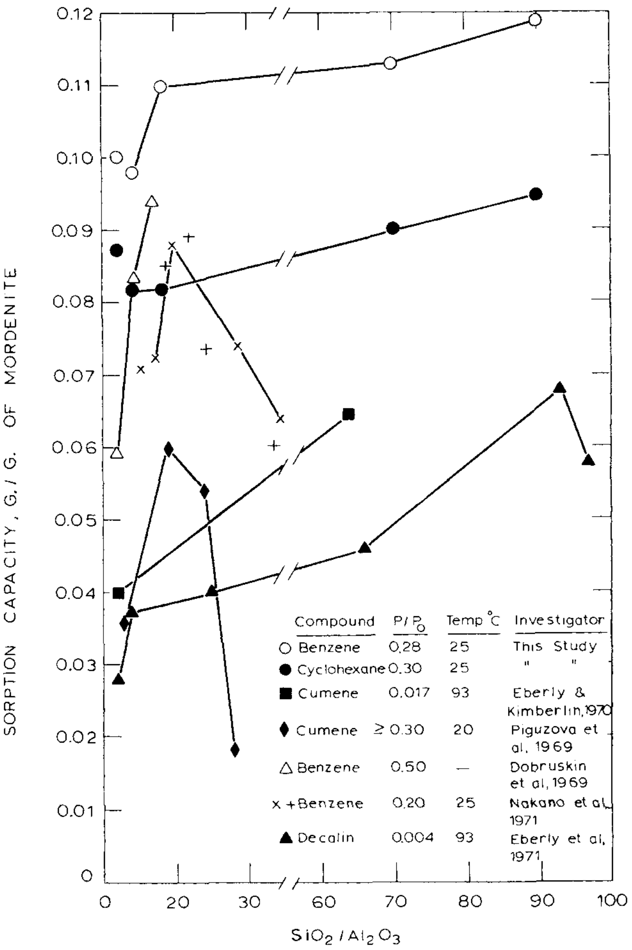

Fig. 2. Effect of silica-alumina mole ratio on total sorption capacity in H-mordenites. Summary of studies in the literature.

of the same silica-alumina ratio. We may speculate correspondingly that different samples of mordenites having the same silica-alumina ratio may have a different distribution of number and kind of acid sites internally, which could have a significant effect on catalytic reactivity. The drop in total sorption capacity with increase in silica-alumina ratio reported by some investigators probably represents the development in their particular mordenite of pores of sufficiently large size such that complete capillary condensation no longer occurred in them.

RESULTS AND DISCUSSION—DIFFUSION STUDIES

The diffusion studies were made with the binary systems cyclohexane-cumene or benzene-cumene. The size of these molecules is nearly that of mordenite pores yet they diffuse in mordenite at readily-measurable rates. Data were obtained at 25, 35, and 44°C on all mordenite samples by both adsorption and desorption measurements. Values of the apparent diffusivity were calculated for M_t/M_∞ values of 0, 0.3, 0.5, and 0.7 and for the three different geometries described. Only a representative selection of the more significant results is presented here. All diffusivities reported are those calculated for the model consisting of uniform spheres of 2 microns radius.

Desorption Measurements

Figure 3 shows the effect of silica-alumina ratio on the desorption diffusivity of cyclohexane into cumene as the bulk liquid at three temperatures, 25, 35, and 44°C, at $M_t/M_\infty = 0.3$. The isolated points are for Zeolon 100H; the other four are for M14, M18, M70, and M89. Two observations are noteworthy (1) different samples of H-mordenite of nearly identical silica-alumina ratio (Zeolon 100H and M14) can have substantially different apparent diffusivities, and (2) the apparent diffusivity increased by three to four orders of magnitude as the silica-alumina mole ratio was increased from 14 to 89; the initial diffusivity (at $M_t/M_\infty \rightarrow 0$) also increased by two to three orders of magnitude over the same silica-alumina ratio (data not shown). Figure 4 is a similar plot for the desorption diffusivity at $M_t/M_\infty = 0.3$ of benzene into cumene as the bulk liquid. The effects of silica-alumina ratio are less pronounced, but again a large increase in diffusivity occurred upon leaching. About one order of magnitude overall increase occurred for the diffusivity as measured at initial conditions and two and a half orders at $M_t/M_\infty = 0.5$ (Chiu, 1973).

Comparison of Figures 3 and 4 shows relatively little difference between the desorption diffusivity of cyclohexane or benzene in the high ratio mordenites, but the benzene diffuses out much faster than cyclohexane from the low ratio material. As the silica-alumina ratio is increased the effective pore size for diffusion increases, but the degree of acidity drops, which presumably affects the interaction energy between diffusing species and the zeolite. The dominating factor here seems to be the fact that benzene (6.3 × 3.0 Å) is slightly smaller than cyclohexane (6.6 × 4.8 Å). The effect of critical molecular diameter of the liquid on diffusivity is most pronounced when molecular diameter and pore size are nearly the same, as would be most closely approached with the low silica-alumina ratio material. Although the results are presented in terms of an effective diffusivity we believe, as discussed subsequently, that the rate of diffusion under desorptive-type measurements in the low silica-alumina ratio material is markedly limited by pore blockage from adsorbed cumene molecules so the true diffusivity for M14 and M18 is substantially greater than the values shown.

The presaturated component, benzene or cyclohexane,

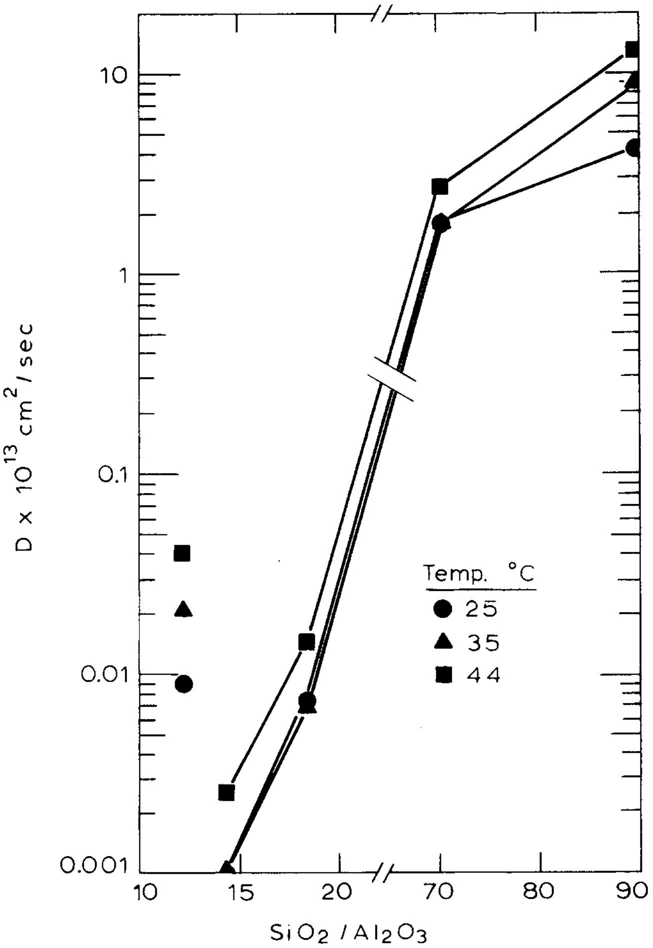

Fig. 3. Effect of silica-alumina mole ratio on desorption diffusivity of cyclohexane into cumene at $M_t/M_\infty = 0.3$.

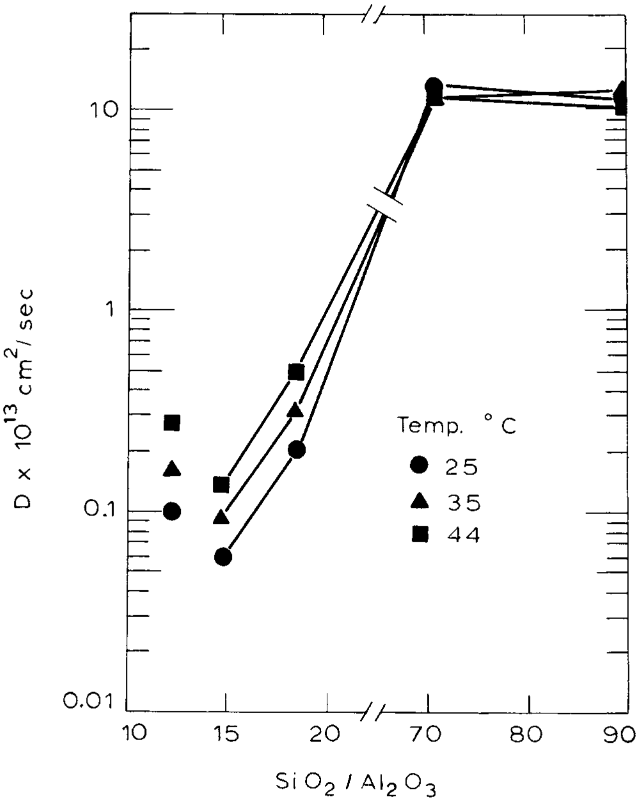

Fig. 4. Effect of silica-alumina mole ratio on desorption diffusivity of benzene into cumene at $M_t/M_\infty = 0.3$.

did not totally desorb in any desorption measurements on mordenites. However, the amount that finally desorbed from the mordenite increased as the silica-alumina ratio was increased, as shown on Figures 5 and 6. These results probably represent steady state values rather than a true equilibrium. It was not attempted to approach the equilibrium from the other side.

Both the diffusion and steady state sorption equilibrium observations show that the pore structure is indeed opened up by the leaching process. Katzer (1969) (see also Satterfield et al., 1971) reported that an average of 10% of the internally adsorbed benzene diffused out at 25°C at steady state from the H-mordenite he studied, having a silica-alumina mole ratio of 12. This is less than half the values obtained in this study on Zeolon 100H and M14 at

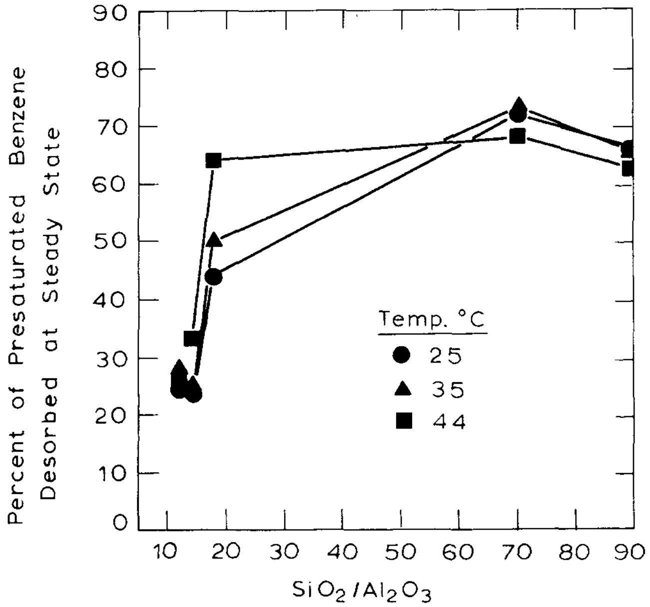

Fig. 5. Effect of silica-alumina mole ratio on percent of presaturated benzene desorbed into cumene at steady state.

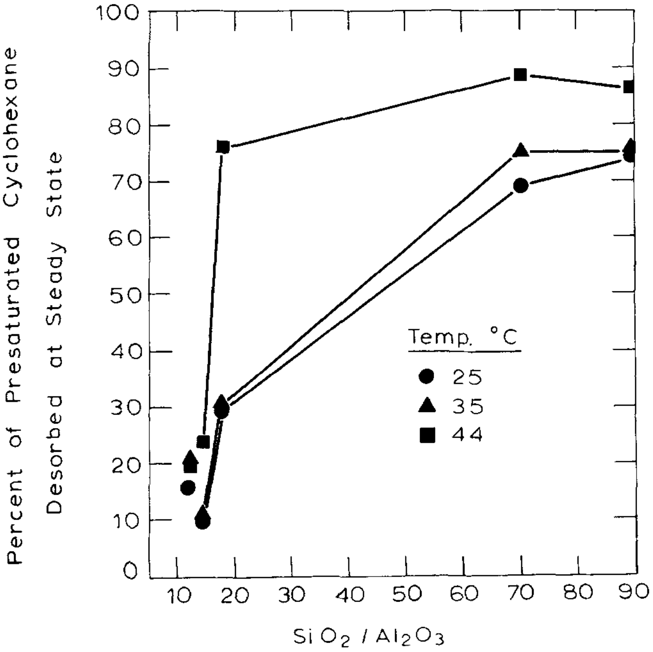

Fig. 6. Effect of silica-alumina mole ratio on percent of presaturated cyclohexane desorbed into cumene at steady state.

the same temperature. The initial diffusivities for benzene desorbing into cumene that he obtained averaged 0.18×10^{-13} cm^2/s, after converting his data to a spherical model. This is about one order of magnitude smaller than that obtained in this work, 1.3×10^{-13} cm^2/s, for the similar materials, Zeolon 100H and M14. Both observations indicate that Zeolon 100H and M14 both had a somewhat more open pore structure than the mordenite he studied.

In general, if the initial diffusivity were of the order of about 10^{-12} cm^2/s or greater, Fick's law with a constant diffusion coefficient was followed closely from M_t/M_∞ of 0 to 0.3 or 0.5 but above $M_t/M_\infty = 0.5$, the diffusivity dropped off substantially with percent uptake regardless of the initial diffusivity. Leaching would be expected to produce an anisotropic pore structure with the average pore size being larger on the outside of particles than in the center. The marked drop in diffusivity with percent uptake is consistent with this picture but does not prove it since even unleached mordenites show the same effect. A revealing experiment might be to compare the diffusivity characteristics of two samples having the same silica-alumina ratio but prepared by different leaching techniques. A severe, short leach, for example, would be expected to produce a more anisotropic structure and more variation in diffusivity with percent uptake than that produced by a slow mild procedure. Different acids, use of chelating agents to prevent re-precipitation of alumina and other techniques may also have a pronounced effect.

Comparison of Adsorption and Desorption Measurements

Figure 7 presents the adsorption diffusivity at $M_t/M_\infty = 0.3$ of cumene into cyclohexane-saturated H-mordenites vs. silica-alumina mole ratio. An increase in the silica-alumina mole ratio from 14 to 89 by leaching increased the diffusivity by an order of magnitude or more when evaluated at either M_t/M_∞ of 0.3, 0.5 or 0.7 (latter results not shown). Similar measurements could not be made for adsorption of cumene into benzene-saturated mordenites.

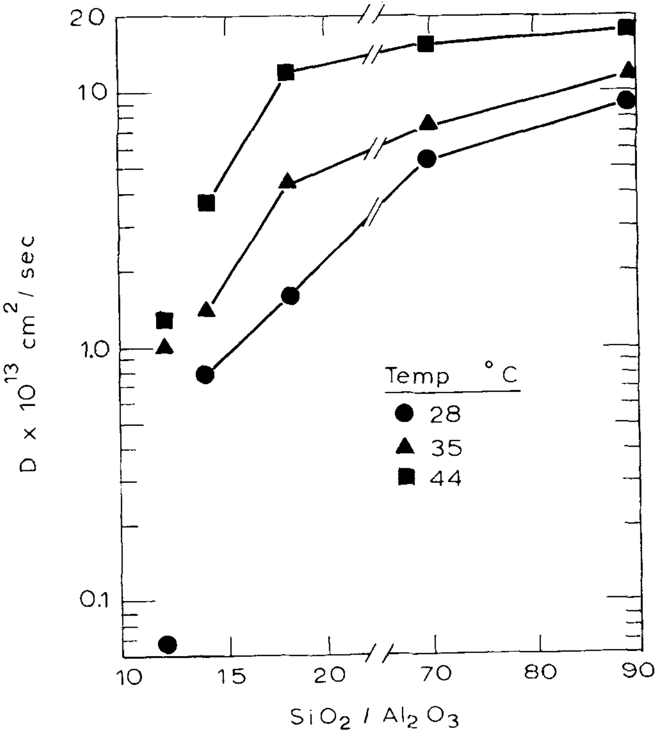

Fig. 7. Effect of silica-alumina mole ratio on adsorption diffusivity of cumene into cyclohexane-saturated H-mordenites at $M_t/M_\infty = 0.3$.

When mordenite was presaturated with benzene and placed in a dilute solution of cumene in benzene in the usual adsorption-type measurement, no significant amount of cumene was removed from the bulk liquid.

Comparison of the adsorption and desorption diffusivities for cumene-cyclohexane in the M series of mordenites on Figures 3 and 7 shows that the calculated diffusivities for adsorption-type measurements are higher by two or more orders of magnitude than those for desorption-type measurements at the low silica-alumina ratios, but they approach one another at high values of the ratio. This can be explained by the reduction in acidity of the high ratio material and the interaction of this effect with the different experimental boundary conditions for the two types of measurement. For desorption type measurements the concentration of cumene in the bulk liquid is nearly 100% whereas for adsorption-type measurements it is quite dilute. We can hypothesize that when the highly acidic and relatively unleached mordenites, M14, M18 and Zeolon 100H, are contacted with cumene, the cumene molecules are strongly adsorbed on the zeolite surface, blocking pore mouths, and thus forming a barrier to the preadsorbed cyclohexane molecules diffusing out. For the adsorption studies on the contrary, the concentration of the cumene in the bulk is less than 2% by weight, so the concentration of adsorbed cumene at the interface is presumably less than with the desorption studies. The preadsorbed cyclohexane molecules can thus diffuse out more readily. With M70 and M89 the acidity is lower, so the strength of cumene adsorption is presumably less and also the pores are presumably larger so that a physical blocking of pore mouths becomes less effective. The desorption diffusivities are therefore believed to be dominated by adsorption processes and pore blocking, at least at relatively low silica-alumina ratios, while the adsorption measurements are a better reflection of diffusion as such.

Further evidence for this view is the observation in the studies of cyclohexane desorbing into cumene that the apparent diffusivity under initial conditions decreased with an increase in temperature, suggesting that the pores were quickly blocked by adsorbing cumene molecules, the rate of adsorption increasing at higher temperatures. Furthermore, at elevated temperatures the rate of desorption decreased unusually rapidly with degree of uptake and became so slow that it could not be accurately calculated at values of M_t/M_∞ much above 0.3. Pore blocking by cumene also presumably occurs when benzene desorbs into cumene, although benzene, being a smaller molecule than cyclohexane, diffuses out faster and the blocking effect is less pronounced. In an earlier study (Satterfield et al., 1971), it was shown that cumene slowly undergoes disproportionation to benzene and diisopropyl benzene while adsorbed on H-mordenite at room temperature. The blocking effect postulated above may have been, at least in part, caused by adsorbed diisopropyl benzene.

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