Diffusion in Sodium Mordenite

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The rates of diffusion of CH_4, n-C_4H_{10}, iso-C_4H_{10}, and C_4F_{10} into well-characterized single crystals of sodium mordenite were studied at 25° to 100°C., using a rapidly responding constant-volume system. The diffusion coefficients are of the order of 10^{-8} to 10^{-9} sq. cm/sec. and exhibit a maximum value with time, probably due to an initial temperature increase caused by the heat of sorption. The implications to catalysis of these and other studies of diffusion in zeolites are discussed.

The widespread recent application of zeolites (molecular sieves) in selective adsorption processes and in catalysis has focused attention on the diffusion characteristics of molecules inside the tiny pores of these materials, for this can have a profound effect on dispersion in adsorption rocesses and on reaction activity and selectivity in catalyis. The molecular sieve crystals may be bonded together o form pellets or, as in cracking catalysts, they may be ncorporated into a gel matrix. However, diffusion studies eported on these forms of molecular sieves may be diffiult to interpret because of the complex pore structure resent and uncertainties concerning the effect of the elleting process, use of binders, etc., on the ease of access f diffusing molecules into the pores of the zeolite. By tudying single crystals of uniform size, the above diffiulties can be avoided but the experimental limitations set y apparatus constraints and the heterogeneous nature of ven single crystals must be clearly recognized in interpreting results. The present study used a rapidly responding, constant-volume sorption system but the results emphasize that initial temperature transients that can occur in such an experimental apparatus may substantially affect the results reported. The zeolite was a well-characterized sample of sodium mordenite. The two-dimensional pore structure characteristic of mordenites enhances the effect of structural heterogeneities on diffusion. Markedly different sorption and diffusion characteristics may be found for different samples of synthetic mordenite, which can greatly affect their behavior in adsorption and catalytic processes.

In an earlier study (*11*) the diffusion characteristics of the C_1 to C_4 paraffin hydrocarbon vapors into single crystals of sodium mordenite were investigated using a constant-pressure apparatus. The present study used a sample of the identical material previously used but in a different type of sorption apparatus that permitted accurate measurement of faster sorption processes. The sodium-mordenite comprised single crystals of average dimensions $21 \times 21 \times 33\ \mu$, described previously in detail (*11*). Some additional information concerning the possible presence of extrazeolitic pores in the single crystals of this material was obtained by sorption of krypton at the temperature of liquid nitrogen, −196°C. At a P/P_0 of 0.62 the sorption capacity was about 67 cu.cm. (measured at STP) per gram of anhydrous sample. The extent to which larger extrazeolitic pores are present can be roughly estimated by applying the Kelvin equation to the krypton isotherm. Taking the surface tension as 15 dynes/cm. and the molar volume as 31 ml. (*2*) and neglecting the thickness of the adsorbed layer on walls of the pores, adsorption of krypton at P/P_0 above 0.016 would represent sorption into pores above 7 Å. diameter. By this procedure 17% of the pore volume would be in pores above 7 Å. diameter and 11% in pores above 13Å. diameter; 6% of the total represents pores in the range 13 to 24 Å. Rees and Khalid (*8*) reported the saturation capacity of a sodium-mordenite they studied to be 104.7 cu.cm. (at STP) per gram from measurements at −150°C. Application of the Kelvin equation to their isotherm for −150°C. yields a pore-size distribution fairly similar to ours. This procedure is of course subject to various criticisms which render the numbers somewhat unreliable, such as the questionable applicability of the Kelvin equation to such small pores, but it appears that an appreciable volume fraction of extrazeolitic pores was present in both samples of mordenite.

APPARATUS AND PROCEDURE

A sample of mordenite (up to 0.5 g.) was held in a thin layer in a 25 cu. cm. sorption bulb connected by a valve to a 250 cu. cm. storage bulb. The internal volume of the glass tubing on the sorption side of the apparatus was about 150 cu. cm. Volumes were determined accurately by measurements with helium at known temperatures. The vacuum system—a liquid nitrogen trap, oil diffusion pump, and mechanical pump—was capable of maintaining a pressure of 1μ or less. The pressure in the sorption bulb was monitored by a differential pressure transducer (MKS Baratron) that was capable of measuring a change of pressure of 1μ and a maximum differential pressure of 30 mm. Hg. By pressurizing the vacuum side of the transducer, it was possible to measure pressures in the sorption bulb above 30 mm. Hg absolute. The transducer signal was recorded by a Heath Servo Recorder with a chart speed of 12 in./min. Factory calibration indicated the average error in the differential pressure reading was 0.1% for a ΔP over 10 mm. Hg and 0.8% for a ΔP below 0.8 mm. Hg. This apparatus made it possible to record pressure changes within 1 sec. after admission of the vapor.

The sample of mordenite in the sorption bulb was activated by heating at 350°C. for 4 hr. or more at a pressure of 1μ or less. The sample and bulb were then cooled to the experimental temperature, sorption gas was allowed to enter at time zero, and the pressure was then measured as a function of time until equilibrium was reached. The sample of mordenite was changed only a few times, when design modifications were made to the apparatus. No evidence was found for a decrease in sorption capacity throughout a series of runs. The system is similar to that used by Brandt and Rudloff (*1*), and more details are given by Margetts (*6*). All data are reported on the basis of weight of mordenite in the anhydrous form.

MATHEMATICAL ANALYSIS

The solution to the equation for transient diffusion into a sphere from a constant-volume system is given by Crank (3) and Brandt and Rudloff (1):

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

where the q_n are the nonzero roots of

$$\tan q_n = \frac{3q_n}{3 + \alpha q_n^2} \qquad (2)$$

The parameter α in Equations (1) and (2) is defined by

$$\frac{P_f}{P_i} = \frac{1}{1 + \alpha} \qquad (3)$$

Numerical solutions are given by Rudloff (10) as a function of the fractional uptake of sorbate from the gas phase F defined as

$$F = \frac{P_i - P_f}{P_i} = \frac{\alpha}{1 + \alpha} \qquad (4)$$

F is therefore dependent on the final equilibrium between the sorbate gas and the sodium-mordenite sorbent. The general behavior of the solutions to Equation (1) is that for any given value of M_t/M_∞, the higher the value of F the lower the value of the calculated diffusion coefficient. At values of M_t/M_∞ approaching zero, M_t/M_∞ becomes proportional to $\sqrt{t}$, as in a constant-pressure system.

This treatment assumes a constant value of the diffusivity, that is, that Fick's law is obeyed, that the concentration of the adsorbed vapor at the outside crystal surface is in equilibrium with the gas phase, and that it is proportional to the gas-phase pressure over the pressure range studied in a particular run. For nonspherical particles, data are commonly expressed in terms of a reduced diffusion coefficient $D^* = D/a^2$ which sidesteps the necessity to assign a value for the equivalent radius. A rectangular parallelepiped of dimensions 21 × 21 × 33 μ has the same volume as a sphere of radius 15 μ, so D may be estimated as $D = 2.25 \times 10^{-6} D^*$ sq.cm./sec. This is the same definition of D as used previously (11).

RESULTS AND DISCUSSION

Sorption Rates

A typical set of results for *n*-butane at 25°C. is shown in Figure 1, and the principal results are summarized in Table 1. Each range of pressures and of D^* represents the extreme values for three to five runs. An essentially linear relationship between M_t/M_∞ and $\sqrt{t}$ during the initial portion of the sorption is obtained even when the diffusion process deviates substantially from Fick's law. A more sensitive method of determining the variation of the effective diffusion coefficient with experimental conditions is to graph D^* as a function of M_t/M_∞. Figures 2 and 3 for methane and *n*-butane, respectively, at 25°C. are typical in that a maximum value of D^* was usually observed at a value of M_t/M_∞ in the range of about 0.2 to 0.5. This was not an artifact associated with variation in the fractional uptake F.

The only similar report to our knowledge is that of Brandt and Rudloff (1), who studied rates of sorption of several vapors on naturally occurring samples of chabazite in a similar type of apparatus. Chabazite has somewhat smaller pores than sodium-mordenite. With methane at 97.7° and 22.7°C. and with argon at 22.8°C., they observed a relatively fast initial sorption, although the opposite effect was observed with carbon dioxide. Theoreti-

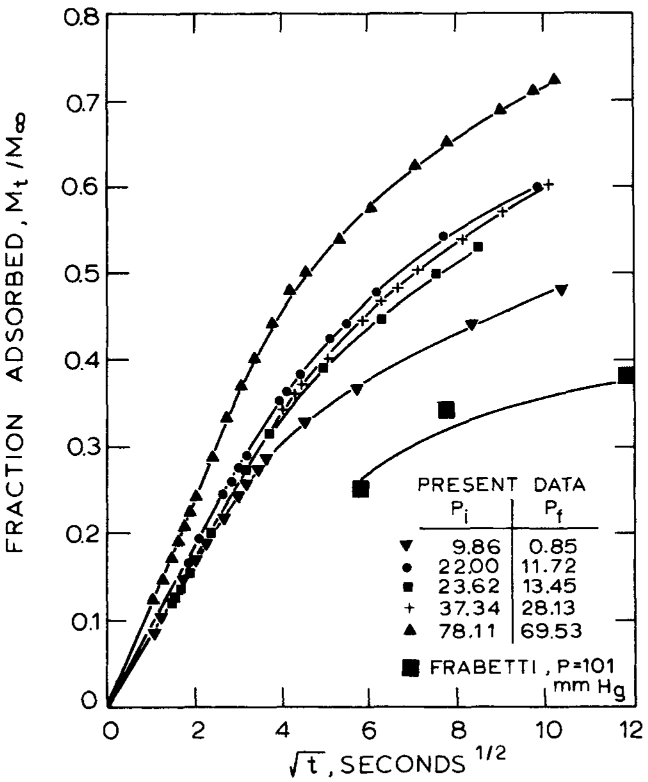

Fig. 1. Fraction absorbed as a function of time; *n*-butane, 25°C.

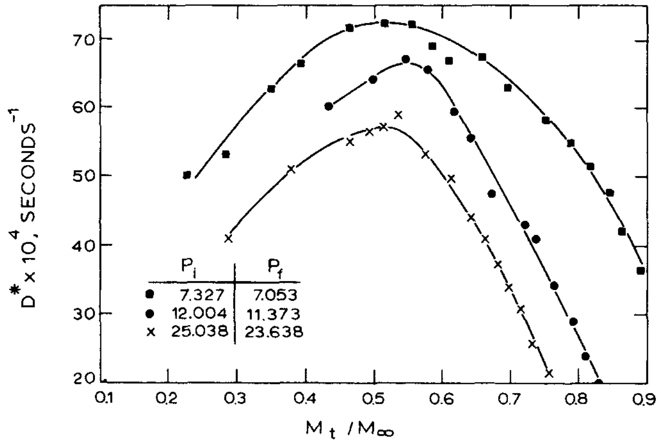

Fig. 2. Reduced diffusivity D^* as a function of the fraction of methane adsorbed, 25°C.

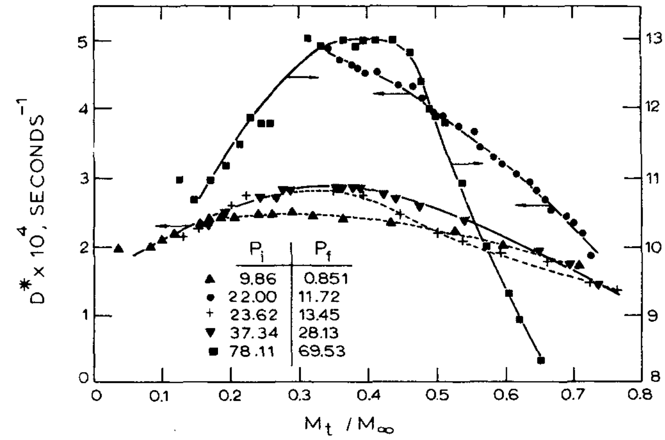

Fig. 3. Reduced diffusivity D^* as a function of the fraction of *n*-butane adsorbed; 25°C.

cal considerations that apply both to their sample and ours indicate that this degree of variation cannot be ascribed to shape, size, or surface irregularities if internal diffusion indeed obeyed Fick's law. Brandt and Rudloff discuss several models of a heterogeneous structure that might be used to interpret their data. Except for their studies with argon, however, our rates of sorption are much faster than those they report and a more likely, although not exclusive, explanation for our results is that a momentary initial temperature increase occurred, caused by the heat of sorption.

Consider the data for CH_4 sorption at 25°C. as an illustration. Taking the heat of sorption as 8 kcal./g.-mole, and the sorption equilibrium as 10^{-4} mole/g., the adiabatic temperature rise in sorption at 25°C. and 30 mm. Hg is about 29°C. An increase in temperature increases the mobility of sorbed species but decreases the driving force since the quantity sorbed at equilibrium decreases. A maximum in D^* can occur for various combinations of true activation energy for diffusion, effect of temperature on sorption equilibria, and cooling rate. As an example, neglecting the effect of temperature on mobility, the experimentally observed results are consistent with the zeolite existing at a temperature 6°C. above ambient at the end of 2 sec. and then cooling down to 25°C. during the next few seconds. With the butanes, the diffusion coefficient is smaller but the equilibrium sorption is greater. There is also a heat effect associated with expansion of a gas into a vacuum but an unsteady state analysis of the transfer of heat in our system indicates that the gas temperature would reach essentially the wall temperature in a small fraction of a second. Furthermore, measurements in which the zeolite was omitted from the system showed no variation of pressure with time after the initial input of gas.

The data summarized in Table 1 show values of D^* calculated at $M_t/M_\infty = 0.5$ and the equivalent values of D. At high values of the fractional uptake F, data become increasingly unreliable and erroneously low values of D^* were obtained. The range of values of F shown in Table 1 represents the conditions studied in which there was no significant effect of F on D^*.

With methane at 25°C. D^* decreases moderately with increased pressure but the opposite effect is observed with n-butane. The diffusion coefficient for isobutane is about one-half that of the normal isomer. Fluorinated hydrocarbons have higher heats of sorption on zeolites than the corresponding hydrocarbons (*10*), indicating a higher degree of interaction, and the critical diameter of C_4F_{10} is about 6.3 Å. as compared to about 4.9 Å. for C_4H_{10}, both of which effects would be expected to reduce the diffusion coefficient. However, the diffusion coefficient of C_4F_{10} (*isomeric composition unknown*) is about the same as that of iso-C_4H_{10} and about one-half that of n-C_4H_{10}.

Activation energies were calculated by the Clausius-Clapeyron equation as a function of initial pressure and the diffusivity, the latter calculated from specified values of M_t/M_∞ in the range of 0.2 to 0.5. Since Fick's law is not closely obeyed, the calculated value of the activation energy E varies considerably with the conditions chosen and should be regarded only as approximate. For methane at 10 mm. Hg initial pressure, E was 1.5 and 5.5 kcal./mole for M_t/M_∞ of 0.3 and 0.5, respectively; for isobutane at 10 mm. Hg, $E = 3.0$ and 1.6 for M_t/M_∞ of 0.2 and 0.5; for perfluorobutane at 10 mm. Hg, $E = 4.5$ and 2.4 for M_t/M_∞ of 0.2 and 0.5.

Comparison of the present data with those of Frabetti for CH_4 at 25°C. showed the same values of M_t/M_∞ as a function of $\sqrt{t}$, within the accuracy of the results (*6*). However, the present values of D are about two to four times higher than his, because the first data points Frabetti could record came at about 30 sec., which in several cases did not correspond to the linear portion of the curve, as developed more accurately here, so his values are unquestionably low. However, the present values may be slightly too high because of an initial temperature effect.

The present results with n-butane at 25°C. are compared with those of Frabetti in Figure 1. The curves of M_t/M_∞ versus $\sqrt{t}$ obtained here are clearly higher than those found by Frabetti, and the values of the effective diffusivity (compared at the same value of P_i) are greater than his, again by a factor of from 2 to 4. In both cases the effective diffusivity increased with increasing pressure. Frabetti's coefficients for n-butane are based on an observed linear relationship between M_t/M_∞ and $\sqrt{t}$, so the reason for the difference in this case is not the slower response of Frabetti's apparatus.

Sorption Equilibria

Studies in the present constant-volume apparatus were made at 25°, 65°, and 110°C. and initial pressures of 2 to 109 mm. Hg with methane and at 25°C. and initial pressures of 10 to 78 mm. Hg with n-butane, which permitted comparison with the earlier studies by Frabetti in a constant-pressure apparatus. Within experimental accuracy, the quantities of methane sorbed at equilibrium were identical in the two studies. The results with n-butane, shown in Figure 4, indicate higher equilibrium values than those obtained by Frabetti, especially at pressures below 20 mm. Hg. His studies at 25°C. extended to pressures of 200 mm. Hg and showed that the value of about

TABLE 1. SUMMARY OF DIFFUSION STUDIES IN SODIUM MORDENITE*

Compound	Temp., °C.	Initial pressure, mm. Hg	F	$D^* \times 10^4$ at $M_t/M_\infty = 0.5$	$D \times 10^{10}$, sq. cm./sec.
CH_4	25	25 to 1.7	0.03 to 0.24	82 to 55	184 to 123
	100	22 to 12	0.01 to 0.02	131 to 136	294 to 304
n-C_4H_{10}	25	78 to 10	0.1 to 0.9	11.9 to 2.3	26.8 to 5.2
iso-C_4H_{10}	25	45 to 10	0.15 to 0.63	5.6 to 1.1	12.6 to 2.5
	100	52 to 19	0.12 to 0.24	8.2 to 5.0	18.4 to 11.2
	200	24 to 6	0.12 to 0.26	8.9 to 5.4	20 to 12.1
C_4F_{10}	25	176 to 9	0.01 to 0.14	4.9 to 1.2	11 to 2.7
	100	46 to 7	0.02 to 0.08	4.8 to 3.2	11 to 7.2
	200	38 to 10	0.01 to 0.02	5.1 to 6.4	11.5 to 14.4

* More complete tables are given by Margetts (*6*).

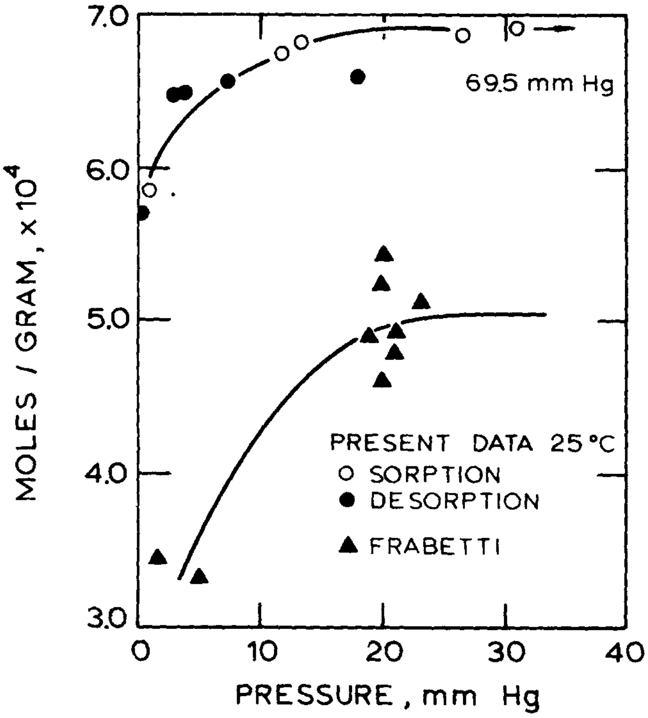

Fig. 4. Equilibrium sorption of *n*-butane.

5×10^{-4} g.-moles/g. represented saturation of the zeolitic portion of the crystals.

The heats of sorption, from equilibrium data, were approximately 7.9, 8.5, and 10.0 kcal./mole for methane, isobutane, and perfluorobutane, respectively, at sorption levels of 0.1 to 0.2×10^{-4} moles/g. The value obtained for methane is approximately twice that estimated by Frabetti, but his value was calculated at a sorption level of 1.0 to 2.2×10^{-4} moles/g. The present data represent the results of both sorption and desorption runs. The fractional uptake was greater at lower initial pressures and the higher degree of sorption found here, especially at low final pressures, may well represent a hysteresis effect, that is, some *n*-butane could have been irreversibly absorbed at the higher initial pressure. However, it is not clear why the saturation sorption value here (about 6.9×10^{-4} g.-moles/g.) is significantly greater than the value of about 5×10^{-4}, reported by Frabetti on the same material ($P/P_0 = 0.11$ for butane at 25°C. and 200 mm. Hg). If the system were truly isothermal and isobaric, this could not be ascribed to a hysteresis effect, since the highest initial pressures here are still less than those studied by Frabetti. However, this effect may be associated in some way with the sudden pressure and temperature surge that occurs initially in this type of apparatus.

IMPLICATIONS IN CATALYSIS

Variability in Properties of Mordenite

One of the significant observations from this and our previous study of sodium mordenite is the great variability in the sorption equilibrium and diffusion characteristics between different samples of synthesized material and the substantial degree of departure from Fick's law. Recent studies by Katzer (*4*, *12*, *13*) of liquid-phase diffusion in Y zeolites and in hydrogen-mordenite and those of Riekert (*9*) for C_2-C_5 hydrocarbons in similar materials show that for a specified sorbate Fick's law is followed much more closely in the Y zeolites than in mordenite. This observation is plausible since with the two-dimensional pore structure in mordenite, only a slight degree of blocking of pores or variation in structure would be needed to cause a major effect on diffusion properties, in contrast to the effect on the three-dimensional and larger pore structure of the X and Y type zeolites.

It was shown previously that this sample of sodium-mordenite exhibited much higher diffusion coefficients than that exhibited in sodium-mordenite synthesized by Barrer, or in sodium-mordenite synthesized in the Norton Company pilot plant. Another good measure of the accessibility of pores in the sodium-mordenite structure is given by the amount of benzene sorbed at saturation, because the benzene molecule is only slightly smaller than the pores in the ideal mordenite crystal. For the sample of mordenite used here, saturation was about 3.2×10^{-4} g.-moles benzene/g. (*11*). A sample of commercial mordenite provided by the Norton Company (Lot BG-11) showed about one-half this value from measurements with a Cahn Electrobalance.

Diffusion Limitations in Reactions on Mordenite

Catalysts based on mordenite have been reported to have a high activity for various acid-catalyzed reactions but different laboratories have found greatly differing kinetic behavior. Although this may represent variations in intrinsic reactivity stemming from different activation procedures, different samples of material, or other treatments, it is also possible that they may instead reflect, at least in some cases, a diffusion-limited reaction in which the effective diffusivities of product and reactant molecules vary substantially with different preparations of the catalyst.

At the present time these possibilities are speculative, since it is difficult to make even order of magnitude estimates of diffusion coefficients in molecular sieves under reaction conditions, for at least three other reasons:

1. In reaction, counterdiffusion of reactant and product molecules must occur, and the binary diffusion coefficient will be much smaller than that for sorption into an initially empty sorbent, but little is known about counterdiffusion in zeolites. In brief studies with C_2H_6 and CO_2 in zeolite Ht at −80°C., Riekert (*9*) reported the binary diffusion coefficient to be an order of magnitude less than the unidimensional coefficient, and preliminary work at M.I.T. with liquid-phase sorption in Y zeolite indicates the difference may be as great as three orders of magnitude.

2. In catalysis the sodium is usually replaced by other cations, by hydrogen, or the zeolite is decationized. Recent studies showed that the diffusion coefficients for 1-methyl naphthalene desorbing from type Y zeolite into cumene varied by two orders of magnitude with different ion exchanged forms (*4*, *12*). Sorption capacity studies with molecules of various sizes in hydrogen-mordenite show that its pores are somewhat larger than those of sodium-mordenite. However, brief diffusion studies with the present mordenite showed little difference between the diffusion coefficients for benzene or propane in the sodium versus the hydrogen form (*11*). With benzene and cumene in hydrogen-mordenite at 25°C. counterdiffusion was so slow that it could not be observed (*4*, *13*). The effect on the diffusion coefficient of a larger pore size in hydrogen-mordenite may be counterbalanced by increasing interaction with or chemisorption of diffusing molecules onto the pore wall. Katzer (*4*, *13*) has shown that cumene in hydrogen-mordenite will disproportionate to benzene and diisopropyl benzene at a measurable rate even at room temperature and the internal formation of a larger molecule can have a restricting effect on diffusion.

3. Reactions are usually at considerably higher temperatures than those at which diffusion has been studied,

TABLE 2. SOME CRITICAL HALF-LIVES FOR REACTIONS ON MOLECULAR SIEVES

V_f/V_c	D, sq. cm./sec.	Critical half-life
1.0	10^{-8}	0.17 sec.
(packed bed)	10^{-10}	17.2 sec.
	10^{-12}	28.6 min.
10.0	10^{-8}	1.7 sec.
(slurry reactor)	10^{-10}	2.86 min.
	10^{-12}	4.77 hr.

Radius of crystal: 1 μ.

but little is known of the effective activation energies for diffusion in zeolites.

Although there are many uncertainties about the values of diffusivities under reaction conditions, a simple effectiveness factor calculation indicates the region of values of the effective diffusivity at which effects caused by diffusion will become appreciable. Taking a value of the Thiele modulus $\phi_s = 2$ as representing the onset of diffusion limitations and assuming first-order reaction, one can estimate a critical half-life as

$$\theta_{1/2} = \frac{\ln 2}{4} \frac{R^2}{D} \times \frac{V_f}{V_c} \qquad (5)$$

where V_f/V_c is the ratio of fluid volume in the reactor to zeolite volume. If the observed half-life is much less than that calculated by Equation (5), the reaction is probably affected by diffusion. Table 2 shows the results of calculations for two typical examples: (1) a reactor in which the zeolite volume is equal to fluid volume, as one might have in a packed bed; and (2) a ratio of liquid volume to zeolite volume of 10:1, as one might have with liquid reactants in a stirred vessel. It is assumed that diffusion in the macropores of the pellets is a negligible resistance and that the zeolite crystals are 1 μ in radius.

Table 2 shows that for half-lives typically encountered for industrial reactions, diffusion in the zeolite crystals will not be a limiting process unless the diffusion coefficient under reaction conditions is less than about 10^{-8} to 10^{-10} sq.cm./sec.

The only reaction study on mordenite to our knowledge in which diffusion was clearly shown not to be a limiting factor is that reported by Miale, Chen, and Weisz (7) on *n*-hexane cracking on synthetic hydrogen-mordenite. The fact that the observed activation energy, 30 kcal./mole, was the same as that observed on much less active amorphous silica-alumina and other molecular sieve catalysts indicates that diffusion effects were negligible. They report data at about 270° and 310°C. At their highest temperature, about 310°C., the first-order rate constant was about 0.1 sec.$^{-1}$. Their particles were in the range of 12 to 28 mesh but the ultimate crystal sizes for commercial hydrogen-mordenite are about 1 μ radius. With a value of the Thiele modulus $\phi_s = 2$ as representing the onset of diffusion limitations, the value of D in the study of Miale, Chen, and Weisz must have exceeded the value calculated from Equation (6) below:

$$\phi_s = 2 = R\sqrt{\frac{k_v}{D}} \qquad (6)$$

$$D_{310} \geq \frac{(10^{-8})(0.1)}{2^2} = 2.5 \times 10^{-10} \text{ sq.cm./sec.}$$

Order of magnitude calculations show that this is consistent with diffusion measurements in mordenite. Frabetti reported data on D_{eff} in sodium-mordenite at 25°C. for the C_1 to C_4 paraffins, dropping from 3.3×10^{-9} sq.cm./sec. for CH_4 to 1.2×10^{-9} for C_4H_{10}. The value for C_6H_{14} at 25°C. is probably of the order of 10^{-9}. With an effective activation energy of 5 kcal., an increase in temperature from 25° to 310°C. increases the diffusivity by a factor of 60, indicating a value for D_{310} of the order of 10^{-7} to 10^{-8}. Neglecting the difference between the sodium and hydrogen forms of mordenite, which may, in fact, be appreciable, the hexane diffusivity could be reduced by two to three orders of magnitude by counter-diffusion and still not be a limiting factor in these hexane cracking studies.

ACKNOWLEDGMENT

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NOTATION

a = spherical particle radius, cm.
D = diffusion coefficient, sq.cm./sec.
D^* = reduced diffusion coefficient, sec.$^{-1}$, $D^* = D/a^2$
E = activation energy for diffusion, kcal./mole
F = fractional uptake of sorbate from gas phase, $F = (P_i - P_f)/P_i$
k_v = reaction rate constant, cu.cm. fluid/(cu.cm. cat.) (sec.) = sec.$^{-1}$
M_t = amount of sorbate adsorbed at time t, moles/g.
M_∞ = amount of sorbate adsorbed at infinite time, moles/g.
n = parameter in diffusion equation [Equation (1)]
P = pressure, mm. Hg
P_i = initial pressure, mm. Hg
P_f = final pressure at infinite time, mm. Hg
P_0 = vapor pressure
q_n = parameter in diffusion equation [Equation (1)]
R = gas constant
T = temperature
t = time, sec.

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