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Effective Diffusivities in Zeolites

3. Effects of Polarity, Cation Density, and Site Occupancy in ZSM-5

SIGFRIDO F. GARCIA[1] AND PAUL B. WEISZ[2]

Department of Chemical Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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The effective diffusivity that determines the catalytic reaction inhibition (utilization factor) in the steady-state process of catalysis, D_{ss}, differs from that derived from nonsteady-state sorption kinetics, D_{ns} (e.g., "uptake diffusivity"). D_{ss} is obtainable from D_{ns} by a transformation based on the equilibrium ratio c_T/c_o of the total sorbed concentration to the applied vapor phase concentration c_o. D_{ss} is several orders of magnitude larger than D_{ns}. For *o*-xylene in siliceous ZSM-5, D_{ss} was found to be virtually invariant with temperature. Introducing a polar NH_2 substituent in place of CH_3 does not alter the temperature independence, i.e., it does not introduce or alter "activation energy." In fact, a larger diffusivity results, presumably from the slightly smaller effective molecular size. Introducing a high sodium cation density in the zeolite structure creates a temperature dpendence of D_{ss}. However, it is shown to be a result of the high percentage of occupancy of transition (jump) sites by sorbed molecules which diminishes with increasing temperature. These several observations allow important conclusions to be drawn concerning the real or apparent nature of "activated" diffusion in the zeolite.

INTRODUCTION

As is the case for other porous particles, catalytic performance of zeolite crystals depends on the effective internal diffusivities D_{ss} for the reacting molecular species applied at concentration c_o at the external boundary of the crystal of size R. The reaction rate dn/dt will be reduced when the criterion Φ for the onset of diffusion inhibition in terms of observable parameters (*1*) exceeds unity, i.e., when

$$\Phi = (1/3)\,(1/c_0)\,(dn/dt)\,(r^2/D_{ss}) > 1. \quad (1)$$

In general, one object of catalyst design is to avoid diffusion inhibition. However, in zeolites one can create deliberate selectivity advantages, i.e., shape selectivity, among different molecular components when their effective diffusivities differ widely within the zeolite crystal structure (*2*). In fact, for sufficiently strong diffusion inhibition, the selectivity for the reaction rates r_a and r_b of two components a and b of otherwise similar reactivity will approach the value $r_a/r_b = [D_{ss,a}/D_{ss,b}]^{1/2}$; see (*2c*). Therefore, the catalytically effective diffusivities in zeolites of molecules of different structure become important parameters in the design and understanding of shape-selective catalytic conversion processes.

Diffusivity determinations have resulted in reports of widely varying magnitudes. Many are based on routine Fick analysis of uptake or desorption time measurements. In a previous paper (*3*) we discussed how the diffusivities D_{ns} routinely derived from the time response behavior of such nonsteady-state methods of measurement must be translated to the effective diffusivity D_{ss} operative in a steady state process such as catalysis: with a knowledge of the total internally sorbed concentration c_T in equilibrium with c_o,

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[1] Current address: UOP Co., Tarrytown Technical Center, Tarrytown, NY 10591.

[2] To whom correspondence should be addressed.

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$$D_{ss} = \beta\,(c_T/c_o)\,D_{ns}. \qquad (2)$$

β is a correction factor that depends on the curvature of the adsorption isotherm $c_T = f(c_o)$. For most purposes it can be ignored as it will be near 1.0 in gas-phase operations at catalytic temperature. In no case will it be greater than 1.5 (see (*3*, *15*)).

We embarked (*3*, *4*) on a study of the diffusivities in ZSM-5 zeolite, applicable to steady-state catalysis under conditions most likely prevailing in high-temperature vapor-phase catalytic process operation: small fractional occupancy of sorption sites. This allows applicability of considerations of relatively simple classical stochastic motion between sorption sites. It may avoid appreciable lowering of successful jump frequency by occupation of sites, as well as undue molecule/molecule interaction. To further restrict the mechanistic inquiry, we have chosen aromatic molecules as the diffusing species; they are rigid structures not subject to possible transitions in structure (effective molecular size) due to bond rotations, folding, etc. This eliminates additional parameters involving dynamics of molecular shape, which could influence shape-dependent diffusivity.

We briefly review the findings and mechanistic conclusions concerning the effective steady-state diffusivities of *ortho*-xylene in siliceous ZSM-5 of negligible cationic site density (Si/Al). We then report on the effect of introducing polarity into the diffusing molecule, by substituting an NH_2 group in place of one methyl group in *o*-xylene, and we report on the effective diffusivities resulting from the introduction of polarity in the zeolite due to Na cations in the ZSM-5 (Si/Al = 40) crystal structure. These observations lead to important mechanistic conclusions.

BACKGROUND: OBSERVATIONS, MECHANISM, AND THEORY

Figure 1 summarizes the previous findings (*3*, *4*) for *ortho*-xylene diffusion in highly siliceous ZSM-5 (Si/Al = 2600): The uptake derived diffusivities D_{ns} (below in Fig. 1) are concentration and temperature dependent, with an apparent activation energy of 9 kcal/mole. When the steady-state diffusivities D_{ss} are obtained, all data—taken over the entire temperature range and a 300 : 1 variation in concentration—reduce to a single value (above in Fig. 1) of about 2×10^{-10} cm^2/sec, some two to four orders of magnitude greater than the various values of D_{ns}.

The findings were consistent with a simple model of diffusion illustrated by Fig. 1B. Molecules exist externally at c_o. In any volume element, a much larger concentration is sorbed within the zeolite. At low enough coverage, nearly all molecules occupy adsorption sites (channel intersections) at energy level $-Q_A$ as demonstrated by Reischman *et al.* (*5*).[3]

Diffusional progress along the crystallite is slow compared to the local ad/desorption kinetics; therefore, there prevails an equilibrium condition between c_T and the mobile concentration c_m bidding for stochastic transitions from one to the next sorptive site. c_m at the boundary is equal to c_o. The relationship $c_T = f(c_o)$ is the observed adsorption isotherm which defines the equilbrium.

In the steady state, the rate of diffusional transport $(dn/dt)_{ss}$ is

$$(dn/dt)_{ss} = c_m \cdot D \cdot f, \qquad (3)$$

where D is the classical intrinsic diffusivity, $D = v \cdot x$ (v = velocity and x = distance of the successful "jump"), and f is a statistical factor, namely, the probability of the host molecule to successfully passage to the next jump site. f involves the chances of positional, geometric, and directional fit for passage, and the fractional concentration of nonoccupied jump sites.

The appearance of an "activation en-

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[3] We assumed that channel intersections are the sites of strong adsorption as demonstrated for *p*-xylene by Reischman *et al.* (*5*). More recently, Talu (*6*) proposed that the major sorption location is the midpoint between channel intersections, without reference to the work of (*5*). Our considerations are the same, depending on the existence of the "jump sites," regardless of their properly assigned location.

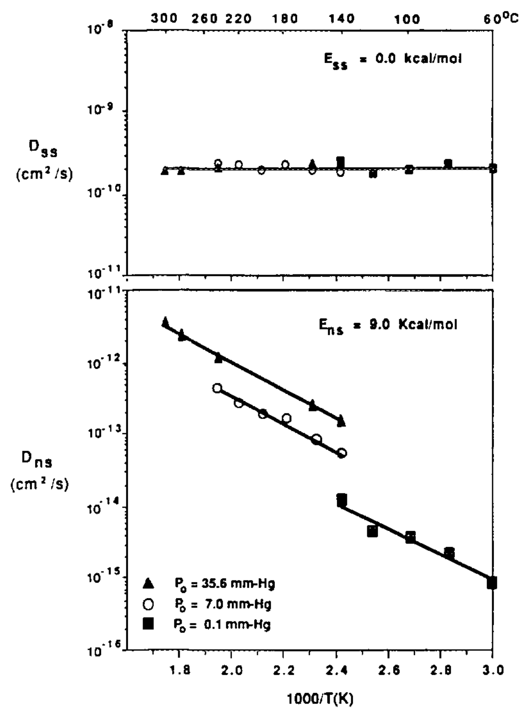

FIG. 1. Below: Measured "uptake diffusivities" for *o*-xylene in siliceous ZSM-5, at different concentrations and temperatures; above: Steady-state diffusivities D_{ss} for all corresponding cases of D_{ns} below.

ergy" in the nonequilibrium methods of diffusivity determinations can, in fact, be considered to be an artifact: in the routine methodology applied to the Fick solution, an apparently higher diffusivity value at higher temperature results from the shorter observed time to reach *fractional* saturation; however, this is a consequence of the decreasing *total* amount of sorbed (immobilized) molecules c_T with higher temperature rather than the result of a faster rate of diffusion. The factor (c_T/c_o) in formula (2) can therefore be considered to be an "accumulation factor" that corrects for the size of the "reservoir." This phenomenon is inoperative in the steady-state process, where the "reservoir" of sorbed molecules has already been supplied to a state of equilibrium.

The lack of a temperature dependence of D_{ss} indicated that no repulsive forces are encountered by the concentration of mobile molecules c_m for *o*-xylene in siliceous ZSM-5 (*3*, *4*), i.e., the molecules of c_m are not at a different energy level than those of c_o, i.e., $c_m = c_o$.

If repulsive forces were active upon transiting molecules, D_{ss} would show a temperature dependence corresponding to an activation energy (energy barrier) Q_B between adsorption sites, as shown in Fig. 2A.

We have now examined the effects of (a) adding polarity to the host molecule and (b) introducing a high density of cationic sites into the zeolite structure: we report comparative observations of the diffusivities of *ortho*-toluidine vs *ortho*-xylene, and the changes in behavior upon employing Na-ZSM-5 (Si/Al = 40) in place of the nonpolar siliceous ZSM-5 (Si/Al = 2600).

These measures must alter the thermodynamic, i.e., equilibrium sorptive properties. Thus, they provide a test for separating mass transport effects from equilibrium phenomena. They provide an important test for

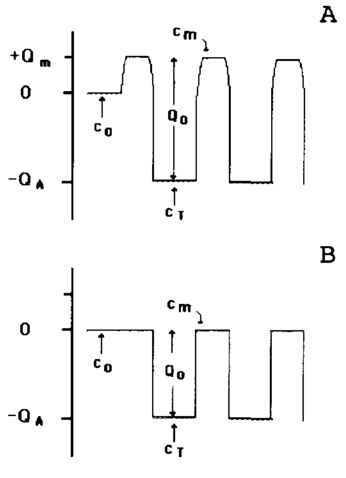

FIG. 2. Energy diagram of molecular states within ZSM-5 zeolite. $-Q_A$ = adsorption (immobilization) energy on channel intersections; $+Q_m$ is additional repulsive energy for passage of channel; c_o is externally applied sorbate (reactant) concentration; and c_m is concentration of mobile molecules energetically capable of channel transition. (A) General case; (B) in absence of repulsive forces in channel.

the question: is the parallelism observed for *o*-xylene between the temperature dependence of the uptake diffusivity D_{ns} ("activation energy") and of the equilibrium amount sorbed (heat of sorption) merely a fortuitous accident?

EXPERIMENTAL

The experimental procedures and materials employed are those described in our previous report (*3*). In addition, the Na-form of an Al-rich ZSM-5 zeolite (Si/Al = 40) was obtained as follows: template-free samples of the ZSM-5 sample were ion exchanged in 1 *N* NaCl solution controlled to pH 8–9 by addition of NaOH. This cation form had no measurable catalytic activity for *o*-xylene transformation at the conditions of the diffusion measurements. The average crystallite size was 0.7 μm, comparable to that of the siliceous ZSM-5 (0.5 μm) used in the previous report. Absence of catalytic activity for xylene isomerization at the temperatures employed in this study was ascertained by chromatographic analysis after contact.

RESULTS

Equilibrium Sorption Properties

The equilibrium sorption capacity was measured at the conditions of the diffusion measurements for the temperature range from 140 to 240°C and at a vapor pressure of p = 7.0 mm Hg for *o*-xylene and 0.1 mm Hg for *o*-toluidine. All data for *o*-toluidine are obtained at p = 0.1 mm Hg. Because of its lower boiling point and greater adsorption strength, this low pressure was chosen for all measurements to avoid high coverage or even capillary condensation phenomena at the low temperatures.

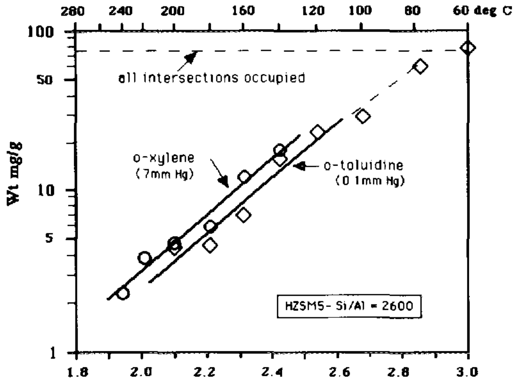

FIG. 3. Measured adsorption isobars for *o*-xylene and *o*-toluidine in the siliceous ZSM-5 structure (Si/Al = 2600).

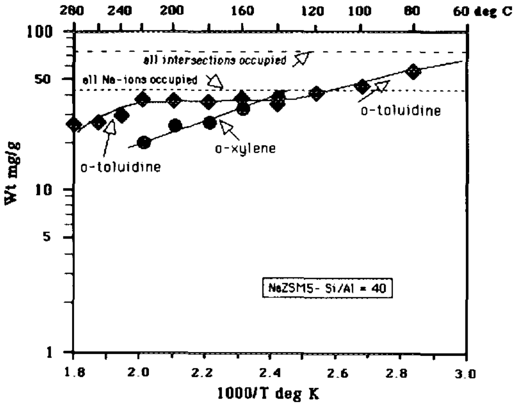

FIG. 4. Measured adsorption isobars for *o*-xylene and *o*-toluidine in the Na–ZSM-5 structure (Si/Al = 40).

The results are shown in Fig. 3 for the siliceous ZSM-5 (Si/Al = 2600), and in Fig. 4 for the Na-ZSM-5 (Si/Al = 40). Sorption data at temperatures below 140°C are included for general information.

Diffusivities D_{ns} and D_{ss}

All uptake diffusivities, D_{ns}, were determined as previously described in Ref. (*3*), from standard translation of the uptake kinetics by Fick's second law and the crystal size. We note good agreement of the "uptake diffusivities" D_{ns} of *o*-xylene on H-ZSM-5 reported[4] by Mirth *et al.* (*7*).

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[4] Mirth *et al.* (*7*) report a D_{ns} value of 5×10^{-13} cm²/sec at 200°C. A previous report for *o*-xylene by Wu *et al.* (*8*) of 2×10^{-12} cm²/sec was reported for a temperature of 20°C, with no pressure specified. Such low temperature measurements, unless carried out at purposefully very low p/p_o, are subject to greatly altered transport mechanisms.

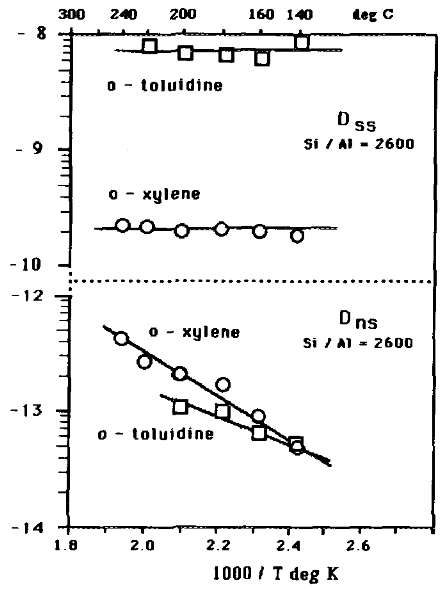

FIG. 5. "Uptake diffusivities" D_{ns} and steady-state (catalytic) diffusivities D_{ss} for *o*-toluidine, compared to *o*-xylene, for siliceous ZSM-5. The ordinate is the log of the diffusivity in cm²/s.

The steady-state diffusivities, D_{ss}, are obtained (*3*) from the respective D_{ns} values by multiplication with the accumulation factor c_T/c_o using the appropriate equilibrium data summarized in Figs. 3 and 4 and the applied gaseous vapor pressure *p*. The catalytically active diffusivity D_{ss} of *o*-xylene was experimentally shown (*4*) to be equal or greater than 10^{-10} cm²/sec.

For comparing diffusion behavior of *o*-xylene, $C_6H_4(CH_3)_2$, and that of *o*-toluidine, $C_6H_4(CH_3,NH_2)$, in the siliceous zeolite of Si/Al = 2600, the observed diffusivities D_{ns} and resulting D_{ss} are shown in Fig. 5.

In order to demonstrate the effect of introducing the Na-cation into the zeolite, Fig. 6 shows the results for the diffusivities of *o*-xylene in the Na-zeolite (Si/Al =40) in comparison with those on siliceous zeolite (Si/Al = 2600).

For *o*-toluidine in the Na-zeolite, the observed data are shown in Fig. 7. For overview and comparison, they are reproduced with those for *o*-toluidine in the siliceous zeolite.

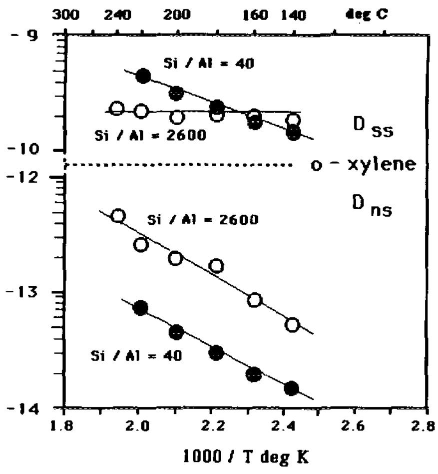

FIG. 6. "Uptake diffusivities" D_{ns} and steady-state (catalytic) diffusivities D_{ss} for *o*-xylene in Na–ZSM-5 (Si/Al = 40), compared to *o*-xylene in siliceous ZSM-5 (Si/Al = 2600). The ordinate is the log of the diffusivity in cm²/s.

DISCUSSION

Structural Reference Data

For evaluating the results it is important to note the following quantitative reference points:

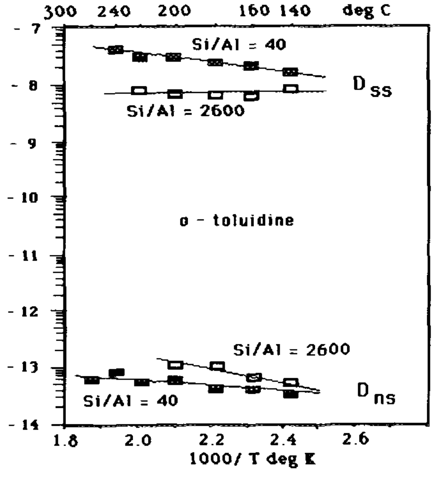

FIG. 7. The steady-state (catalytic) diffusivities D_{ss} for *o*-xylene in Na–ZSM-5 (Si/Al = 40) as measured, and after correction based on changing density of free "jump sites" (occupancy correction). The ordinate is the log of the diffusivity in cm²/s.

(a) the concentration of channel intersections in the ZSM-5 zeolite crystal is 0.7 mmol/g;

(b) if all intersections were occupied by sorbate molecules, their weight density would be 74 mg/g zeolite (with the molecular weights being 106 and 107 for *o*-xylene and *o*-toluidine, respectively);

(c) the high-silica ZSM-5 sample contains a negligible concentration of cationic sites, while the Na–ZSM-5 sample of Si/Al = 40 contains 0.4 mmole/gram of Na-cations. When these constitute adsorption sites they would yield a weight of sorbate of 42.4 mg/g of zeolite at full cation occupancy.

Equilibrium Properties

For the siliceous zeolite, the equilibrium occupancy of *o*-xylene (at the operating pressure of 7 mm Hg) is seen (Fig. 3) to range from 3 mg/g at 240°C to 10 mg/g at 140°C. The data for *o*-toluidine (at a pressure of 0.1 mm Hg) span nearly the same values. The two pressures were chosen to be similarly removed from the respective normal vapor pressures, namely, $p/p_o \approx 0.008$; it is interesting to note therefore that the observed adsorption affinities on siliceous ZSM-5 behave similarly as those on nonpolar chromatographic substrates (i.e., "boiling point columns" such as Carbowax).

It follows that our diffusion determinations for the siliceous ZSM-5 are made at conditions of a sorbate concentration c_T corresponding to 4 to 14% of the concentration of total intersections, i.e., a range of relatively "low occupancy." This allows us to assume close applicability of a simple stochastic process of diffusion with near constant number of "jump sites."

For the Na–ZSM-5, see Fig. 4, the equilibrium sorption quantities are seen to rise towards occupancy equivalent to the concentration of cation sites (42.2 mg/g adsorbate) for *o*-xylene. The stronger adsorption and the preference of Na-sites for adsorption confirms previous observations by Lechert and Schweitzer (*9*).

For *o*-toluidine, the approach is more rapid, but indicates "spill over" to adsorption on intersections, beyond (below) 140°C. The stronger adsorption of *o*-toluidine compared to *o*-xylene on the polar Na-zeolite is again analogous to the behavior of relatively stronger chromatographic adsorption (retention time) resulting from the addition of a polarizable substituent to a molecule.

Diffusivities D_{ns} and D_{ss}

o-Toluidine vs o-xylene on siliceous zeolite. (See Fig. 5). The diffusivities D_{ns} determined from uptake rate measurements on the siliceous zeolite would suggest a smaller diffusivity as well as a smaller "activation energy" for *o*-toluidine than for *o*-xylene. This would be an unexpected combination for a truly "activated" process. However, the transformation which previously led (Fig. 1 and Ref. (*3*)) to a temperature independent steady-state diffusivity D_{ss} four *o*-xylene, leads to a temperature-independent diffusivity also for *o*-toluidine.

The diffusivity of *o*-toluidine is, in fact, greater than that for *o*-xylene. An examination of the relative molecular volume MV and of the minimum dimension for passage r_m using Allinger's MM2 force field on MacroModel by Clark Spill gives MV = 117.5 Å^3 and $r_m = 5.16 + h$ Å for *o*-xylene, and MV = 111.6 Å^3 and $r_m = 5.02 + h$ Å for *o*-toluidine (h = diameter of hydrogen atom). The *o*-toluidine molecule is smaller, with an effective minimum dimension 0.14 Å smaller than for *o*-xylene.

o-Xylene in Na- vs siliceous ZSM-5. In contrast to the siliceous ZSM5 crystal, the D_{ss} diffusivity of *o*-xylene on the Na-zeolite (Fig. 6) shows a small temperature dependence, or apparent activation energy corresponding to about 4.5 kcal/mole. If this temperature dependence were due to an activation energy to overcome an additional energy barrier (e.g., due to space constriction by the size of sodium ions or due to unfavorable electrostatic forces), one would expect the magnitude of the D_{ss} for the Na-zeolite to be lower.

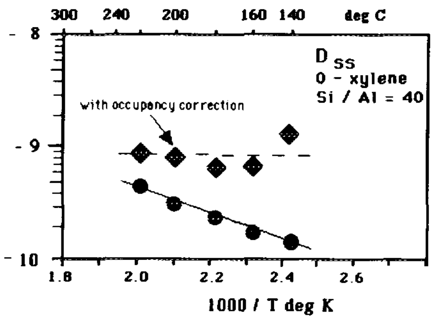

FIG. 8. Comparison of D_{ns} and D_{ss} diffusivities of *o*-toluidine for Na-zeolite (Si/Al = 40) and siliceous zeolite (Si/Al = 2600). The ordinate is the log of the diffusivity in cm²/s.

An inspection of the adsorption data on the sodium zeolite, Fig. 4, indicates, however, that the jump sites, now the Na-sites, are no longer as sparsely occupied as they were for the siliceous zeolite, and a considerable change in jump site availability takes place over the temperature range of observation. In other words, jump sites are rapidly freed with increasing temperature. If we correct the D_{ss} data of *o*-xylene in the Na-zeolite (Si/Al = 40) of Fig. 6, by the relative number of free Na-sites according to Fig. 4, we obtain corrected D_{ss} diffusivity figures based on equal availability of jump sites at the various temperatures. These "corrected" data are shown and compared with the measured data in Fig. 8. It is seen that the rising steady-state diffusivity with temperature, measured in the 140 to 240°C range, is consistent with the change in statistical occupancy and is, again, not due to an activation energy.

The magnitude of D_{ss} of *o*-xylene in Na-zeolite (Fig. 6) is not smaller than that in the siliceous form. This stands in contrast to the behavior of the nonsteady-state derived diffusivity D_{ns}. As discussed, this is caused by the much larger accumulation factor representing the greater adsorption capacity of the Na-zeolite; it causes the longer delay in fractional sorption in the uptake methodology.

Our data actually suggest a higher steady-state diffusivity in Na–ZSM-5 zeolite than in siliceous (nonpolar) zeolite. However, it is good to remember that comparisons of absolute diffusivities between zeolite samples from different synthesis procedures (such as to obtain very different Si/Al ratios) can introduce differences due to various parameters: diffusivities depend on the square of the effective particle size, whose distribution is difficult to determine accurately; on crystallite shape (morphology); and on variations in Al-gradient which would effect the nonsteady-state diffusion time, especially in the case of the strongly sorbing Na-form.

o-Toluidene in Na- vs siliceous ZSM-5. Figure 7 shows a temperature dependence of D_{ss} for toluidine when moving in the Na-zeolite, analogous to the case of *o*-xylene. An examination of the sorption data, Fig. 4, shows that the correction for site occupancy discussed for the case of *o*-xylene is clearly even more applicable for *o*-toluidine. Occupancy of Na-sites is close to saturation, and the involvement of "spill over" to intersections is indicated. Inasmuch as we do not know the siting of Na-atoms vis-à-vis intersections (including at intersections ?), it is not appropriate to attempt any quantitative corrections. It is reasonable to conclude, however, that, as in the case of *o*-xylene, the observed temperature dependence is again caused by the statistical factor (probability of successful jump) related to the varying degree of occupation of sites with temperature.

The magnitude of the D_{ss} diffusivity of *o*-toluidine is greater than that of *o*-xylene on Na-zeolite, as it was on siliceous zeolite, in accordance with its smaller effective molecular size (see above).

CONCLUSIONS

In the siliceous ZSM-5 zeolite, introducing a polarizable group in place of CH_3 in *o*-xylene does not alter the fact that the steady-state diffusivity D_{ss} shows no variation with temperature, indicating no change in energy barrier for the diffusive motion.

In view of the *larger* magnitude of the D_{ss} diffusivities of *o*-toluidine compared to *o*-xylene, the polarizibility of the amino- vs the methyl-substituent clearly does not add any energy barrier Q_m for channel passage, nor is there evidence for additional physical obstruction by Na-ions. At best, it would be masked by the favorable effect of the smaller effective molecular size of the toluidine.

In the case of the Na-zeolite, the temperature dependencies observed for both sorbates are seen to be caused by a decrease in the number of available unoccupied jump sites (sorption sites). The temperature dependence is not related to an activation energy for diffusive motion. This temperature dependence will occur at conditions of high coverage, i.e., at low temperature and for strongly sorbing actions such as sodium, at high concentrations.

The equality of the temperature dependence ("activation energy") of the "uptake" derived diffusivity and that of the amount of equilibrium sorption observed for *o*-xylene was not a fortuitous accident.

The steady-state diffusivity D_{ss} applicable for evaluation of the catalytic utilization factor as per formula (1) is properly obtained from the diffusion coefficient D_{ns} derived from the time dependence of fractional uptake (or other nonsteady-state method) by multiplication with the accumulation factor c_T/c_o according to formula (2).

It is interesting to note that, conversely, for a given D_{ss} diffusivity, the "uptake diffusivity" D_{ns} that would be derived by the standard Fick methodology must decrease for any conditions that increase equilibrium sorption. This explains the general observation of a parallelism between slower "uptake diffusivities" accompanying larger sorption capacity (see, e.g., Forni *et al.* (*10*), Roethe *et al.* (*11*), Vavlitis *et al.* (*12*), and Choudhary and Srinivasan (*13*)). Such variation can be the result of the nature of the cation employed or simply an increase in cation density. Qureshi and Wei (*14*) have noted "that aluminum decreases diffusivity and increases sorption." The quantity of aluminum represents the density of cations, of course, thus increasing the sorption reservoir.

This trend is an artifact of the routine Fickian interpretation of sorption experiments leading to D_{ns}. It is not a phenomenon involving a variation of a true diffusion coefficient.

For all cases studied we have no evidence for a true "activation energy" of the relevant diffusivity D_{ss}, i.e., there is no temperature dependency of the concentration of the mobile (i.e., the stochastically active) host population, c_m.

The apparent "activation energies" observed in "uptake" diffusivities (or other non-equilibrium method based values of) D_{ns} result from the temperature dependence of the reservoir (concentration) of adsorbed molecules, rather than any variation of the concentration of the transiting mobile species (c_m); it is the latter which would characterize the basic physical chemistry of an "activated diffusion."

It follows that Fig. 2B adequately represents the mechanisms at hand for the ZSM-5 zeolite and the molecules studied. We may note that constancy of D_{ss} with temperature was observed by us (*3*) for two additional molecular species, namely, 2-methyl naphthalene and *para*-xylene.

These findings indicate that catalytic diffusivities D_{ss} derived from "uptake" measurements corrected by the (large!) thermodynamically related adsorption factor c_T/c_o according to formula (2) may be reasonably well used even at higher temperatures than were available in the uptake measurements. It is good to remember, however, that uptake conditions should be under conditions of sparse coverage. This will also avoid involvement of different transport mechanisms (see Ref. (*3*)).

An example for a successful extrapolation to higher catalytic temperature is found in the work of Post *et al.* (see Ref. (*15*)). They also found the near equality in temperature dependence of the uptake diffusivity and the diminishing degree of sorption for 2,2-dimethylbutane, so as to effect a virtual cancellation of the temperature dependence of the catalytically applicable diffusivity D_{ss}. This further supports the generality of our thesis beyond the observations reported by us (here and in Refs. (*3*, *4*)) on *o*-xylene, *o*-toluidine, *p*-xylene, and 2-methylnaphthalene on ZSM-5 zeolite.

It seems timely to abandon unquestioned translation of historically and rigidly accepted formalisms (the Fickian derivation of "diffusivity" from fractional uptake) into mechanistic conclusions; instead, persuasive observational evidence must be considered to properly modify such formalisms to accommodate additional mechanistic elements encountered in a newly studied medium.

Such necessary modifications are needed for many analogous circumstances of diffusion accompanied by molecular sorption (immobilization) (*15*, *16*). The formalisms modifying the classical Fick diffusion equation including numerical solutions for isotherms ranging from weak sorption (Henry's law), Langmuir isotherms of any degree of sorption strength, to strong or virtually irreversible sorption, are available (*15*, *17*). They have applicability to diffusion transport in a variety of media, such as in the penetration of dyes into natural or synthetic fibers (*16*, *18*), ion exchange (*16*), and others.

In most catalytic vapor phase operations, we are likely to be operating at the low coverage conditions used in this study. However, we must concede that there are some current and potential low temperature, high pressure, or liquid-phase catalytic processes, where the above observations and mechanistic considerations will be altered. The mechanism of diffusion will be greatly different. However, a clear distinction will still have to be made there also, between transport observations by nonsteady-state methods and steady-state diffusion in catalytic application.

ACKNOWLEDGMENTS

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