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Effective Diffusivities in Zeolites

2. Experimental Appraisal of Effective Shape-Selective Diffusivity in ZSM-5 Catalysis

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A method is described for experimentally probing the molecular shape-sensitive diffusivity of a molecular species effective during the steady-state process of catalysis in a zeolite. It does not require the use of catalyst samples of differing and known particle (i.e., crystallite) sizes but with otherwise identical properties. It can be carried out on a single catalyst sample. The method makes use of hydrogen–deuterium transfer as the catalytic reaction. Instead of comparing reaction rates on different crystallite sizes, it makes use of altering the magnitude of a pseudo-first-order reaction rate constant to probe for the effect of diffusion inhibition. The method is used here to examine the magnitude of the catalytically effective diffusivity of *ortho*-xylene is ZSM-5, in comparison to the "uptake diffusivity" derived from sorption measurements.

INTRODUCTION

In shape-selective zeolite catalysis, reaction selectivity advantages can be achieved for specific reactants or potential products with effective diffusivities favored by a smaller effective molecular shape or size for passage in the zeolite crystal structure (*1*). Therefore, the catalytically effective diffusivities D_{ss} of variously constructed molecules are basic parameters in the design and understanding of shape selective catalytic processes. In separate investigations (*2, 3*), we have discussed how diffusivities D_{ns} derived from the time response behavior in nonsteady-state procedures, such as the "uptake"determinations, must be translated to the effective diffusivity for catalysis D_{ss} which involves a steady-state process, and which are generally some two to four orders of magnitude larger. For example, while the uptake diffusivity of *o*-xylene in siliceous ZSM-5 varies from 5 to 50 × 10^{-14} cm^2/sec for the temperature change from 140 to 240°C, at 7 mmHg vapor pressure, the catalytically relevant diffusivity was indicated to be about 2 × 10^{-10} cm^2/sec, invariant over the entire temperature range and over a 300-fold variation in vapor pressure.

In spite of the importance of knowledge of steady-state diffusivity magnitudes, only a few studies have attempted to determine these on zeolite catalysts under actual catalytic operating conditions (*4, 5*). Such measurements have customarily required comparitive measurements of reaction rate dn/dt at reactant concentration c, on catalyst samples of differing particle sizes R, in order to vary the Thiele modulus by known ratios. The diffusivity is then derived by graphic or computer analysis (*6, 7*); or from the reaction and size parameters at which the quantity below exceeds unity, i.e.,

$$(1/3)\ (1/c)\ (dn/dt)\ (R^2/D) > 1. \quad (1)$$

This traditional method can be quite acceptable for probing catalyst particles of

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millimeter and screenable size fractions. In probing intrazeolite diffusivities, however, we deal with crystallites of diameters in the micron or submicrometer range, where it is difficult to obtain samples of quantitative well characterized and uniform particle size as well as morphology. It is still more difficult to generate or reliably separate two or more samples of quite different particle sizes with otherwise equal morphology and catalytic properties.

Furthermore, if we wish to ascertain the catalytic diffusion coefficients of a particular reactant molecule in the zeolite, with relevancy to shape-selectivity, any change in shape or size accompanying catalysis of the reactant increases the complexity of analysis.

A NEW APPROACH

In principle, the Thiele modulus $\varphi = R \times (k/D)^{1/2}$, can be varied by controlling the intrinsic first-order reaction rate constant k, rather than by changing the particle dimension R. However, it is generally not possible to alter k controllably, reliably, and by known magnitudes. In principle, we will accomplish this task by choosing a second-order, bimolecular reaction involving the species c_0 whose diffusivity is to be probed reacting with a second species c_x, and providing c_x in sufficient excess so that the reaction $dn_0/dt = k' \times c_x \times c_0$ will become a pseudo-first-order reaction:

$$dn_0/dt = k \times c_0 \times \eta; \quad (k = k' \times c_x). \quad (2)$$

η is the effectiveness factor, which is unity in the absence of diffusion inhibition. Thus the "new" reaction rate constant k, and thereby the Thiele modulus, can be changed controllably by changing the concentration of c_x.

The catalyzed rate to be observed is the deuterium donation $C_8H_{10} \rightarrow C_8H_9D$ in *o*-xylene, via H–D exchange. It preserves shape and size of the reactant. The deuterium donor is the concentration of deuterated protonic catalyst sites s_D, which is varied by feeding varying concentrations of per-deuterobenzene, C_6D_6. The H–D exchanges of sites with aromatics take place easily on acid zeolites (*8*); they involve the aromatic ring hydrogen positions, but not the methyl hydrogens. We have found this catalysis rapid enough on even very sparse Brønsted sites to proceed with useful conversion, and in the absence of appreciable shape-altering side reactions such as isomerization, or methyl transfer between xylene molecules.

We observe, simultaneously, the rate of catalytic deuteration of *o*-xylene dn_o/dt, $C_8H_{10} \rightarrow C_8H_9D$, and the rate of catalytic deuteration of benzene dn_B/dt, $C_6H_6 \rightarrow C_6H_5D$. This is done while the catalyst is exposured, in a steady state, to a mixture of benzene C_6H_6 and an excess of deuterobenzene C_6D_6 as the deuterium donor. The variation in the concentration of deuterium donor sites s_D is achieved by variation of the concentration of C_6D_6. We have for the two reactions:

$$r_0 = dn_o/dt = k_o \times c_o \times S_D \times \eta \quad (3a)$$

$$r_B = dn_B/dt = k_B \times c_B \times S_D. \quad (3b)$$

During the continuous flow catalytic operation, the catalyst protonic sites are presented with a proportion of ring-aromatic D- atoms to total (D + H) atoms in the gas phase, i.e.,

$$f_D = 6\,P_{C6D6}/[6\,P_{C6D6} + 6\,P_{C6H6} + 4\,P_{C8H10}] \quad (4)$$

with P being the relative vapor pressures (or concentrations) employed in the external vapor phase of deutero-benzene, benzene, and *o*-xylene. It is of interest that in the presence of any isotope effect with regard to the exchange reaction of D ↔ H from aromatic ring to catalyst site, with an equilibrium constant K, the *site* density of D, F_D, is actually

$$S_D/S = F_D = 6\,K\,P_{C6D6}/[6\,K\,P_{C6D6} + 6\,P_{C6H6} + 4\,P_{C8H10}]. \quad (5)$$

However, it is not necessary to have *ad hoc* knowledge of K and of the exchange

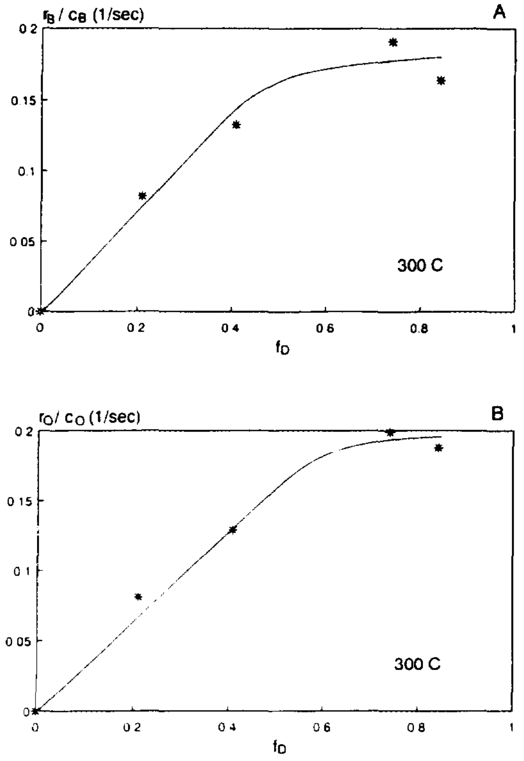

FIG. 1. The observed rates of deuteration of *o*-xylene (r_o/c_o) and of benzene (r_B/c_B) at 300°C achieved by increasing the fraction f_D of deuterium donor atoms in the gas phase.

equilibrium, since both observed reactions depend on the same functional change of s_D, so that a comparison of the rates of conversion of the *o*-xylene and of benzene, from (3a) and (3b),

$$(dn_o/dt) \times (1/c_o)/ (dn_B/dt) \times (1/c_B) = (k_o/k_B) \times \eta. \quad (6)$$

As we increase the concentration of the deuterium donor C_6D_6, the conversion ratio (6) remains constant as long as $\eta = 1$; if and when it drops below the constant value, this defines onset of diffusion inhibition. When this occurs the diffusivity is determinable from the then prevailing rate of *o*-xylene deuteration dn_o/dt, *o*-xylene concentration c_o and the particle size R, by the traditional analysis.

Aside from this, the isotope effect K actually is determinable from the observed curvature of either the *o*-xylene or the benzene conversion alone (3a) or (3b) with increasing pressure P_{C6D6}, over the range of operation where the ratio itself (6) remains constant. Thus, the analysis differentiates between diffusion inhibition of *o*-xylene and D–H isotope effect.

EXPERIMENTAL

The catalyst sample was H-ZSM-5 with Si/Al ratio of 2600. This highly siliceous zeolite was chosen for two reasons: One was our objective to verify the steady-state diffusivity determined by our previous work (*2*). The other was to minimize *o*-xylene conversion to structural isomers, inasmuch as this would complicate the analysis and interpretation of the diffusivity of the shape-selectivity inhibited diffusivity of *o*-xylene. One gram of catalyst mixed with 6.7 g of 30/50 Vycor chips were held in a glass reactor of 6.1 cm^3 volume. The catalyst particle size distribution averaged at about $R = 0.25$ μm. The prepared mixtures of the liquid aromatics fractions were fed from a syringe pump into a preheater section at 160°C, where the vaporized product was mixed with helium. While the relative vapor pressures of benzene and deutero-benzene were changed, the concentration of the primary reactant, *o*-xylene, was held constant at 7 mmHg, and

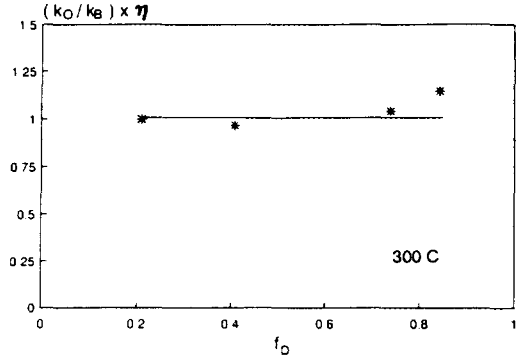

FIG. 2. The ratio of rates of deuteration of *o*-xylene and of benzene remains constant with increasing rate at 300°C.

the total gaseous flow-rate (and thereby the contact time) was held constant at 138 cm^3/min by suitable choice of the helium flow-rate.

The product stream was collected in a dry ice/acetone trap. Samples of the product were analyzed for unreacted and deuterated *o*-xylene and benzene, for calculating the rate of moles of deuterium transferred to undeuterated *o*-xylene and benzene reactants. A Varian gas chromatograph (Model 3700) with a 5% Bentone-34 column (7.58 m × 0.492 mm) was used to determine the concentrations of total *o*-xylene and benzene in both feed and product streams. A Finnigan MAT (700 Ion Trap Detector) mass spectrograph/gas chromatograph, with a fused silica column (film thickness = 1 μm, column dimension of 60 m × 0.257 mm), was used to determine the relative concentrations of the various deuterated species. Sample amounts injected were kept constant in volume to avoid effects in the ionization chamber on the measured fragmentation patterns.

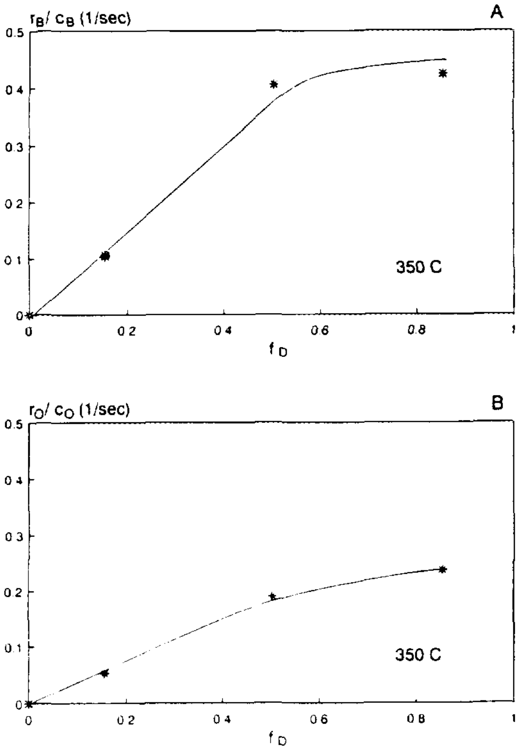

FIG. 3. Observed rates of deuteration of *o*-xylene (r_o/c_o) and of benzene (r_B/c_B) at 350°C achieved by increasing the fraction f_D of deuterium donor atoms in the gas phase.

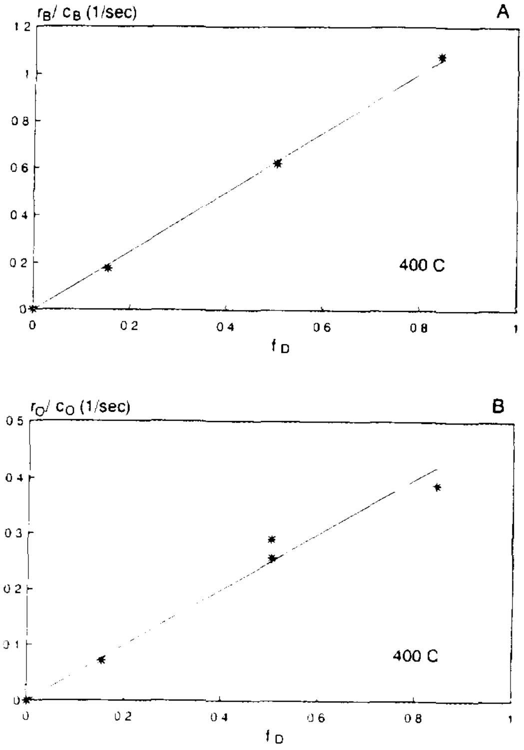

FIG. 4. Observed rates of deuteration of *o*-xylene (r_o/c_o) and of benzene (r_B/c_B) at 400°C achieved by increasing the fraction f_D of deuterium donor atoms in the gas phase.

The lack of isomerization activity was confirmed by chromatographic product analysis. Such conversion never exceeded 1% at the highest temperature investigated.

RESULTS

At T = 300°C, the deuteration of the undeuterated *o*-xylene and benzene was studied for P_{C8H10} = 7 mmHg, P_{C6H6} = 70 mmHg, and with the deuterium source P_{C6D6} changing from 20 to 400 mmHg. The observed course of the respective rates r_o/c_o and r_B/c_B is presented in Fig. 1. The rate behavior

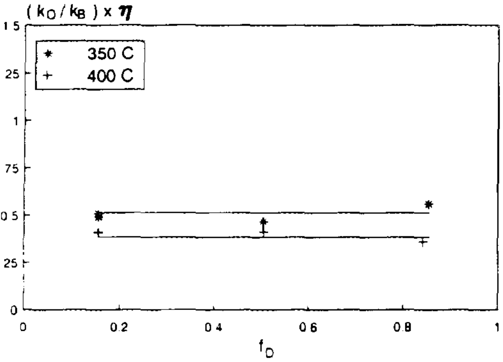

FIG. 5. The ratio of rates of deuteration of *o*-xylene and of benzene remains constant with increasing reaction rates, from 300 to 400°C.

is obviously identical within experimental accuracy, i.e., deviation of linearity occurs for both components. This is best demonstrated by the ratio of the relative rates (according to formula (6)), shown in Fig. 2.

In order to accelerate the reaction rates, to further approach conditions of eventual diffusion inhibition of *o*-xylene, measurements were undertaken at 350 and 400°C. The *o*-xylene concentration was the same and constant. The total undeuterated plus deuterated benzene concentration was held constant at 470 mmHg, but the relative concentrations of C_6H_6 and C_6D_6 were changed between the limits of 70 and 400 mmHg. Keeping the total aromatic ring concentration constant was to assure elimination of any possible kinetic complexity introduced by non-linearity of aromatics/site occupation. Figures 3 and 4 show the results. Figure 5 shows the appropriate ratios of the rates for a direct comparison of behavior with increasing reaction rate.

DISCUSSION

1. The Diffusivity of o-Xylene

The constancy of the conversion ratios of *o*-xylene to benzene conversion being constant for all variations of reaction rate (induced by changing the deuterium donor concentration), at each of the three, and especially at the highest temperature of 400°C, see Figs. 2 and 5, indicates that over the entire range of reaction rates, no diffusion inhibition of *o*-xylene is obtained.

From the highest rate observed for *o*-xylene at 400°C, which is $(1/c_o)(dn_o/dt) = 0.4$ $\sec^{-1}$ (see Fig. 4B), and $R = 2.5 \times 10^{-5}$ cm, we obtain from the criterion (*1*)

$$D_{ss} > (1/3) \times 0.4 \times (2.5 \times 10^{-5})^2 = 0.8 \times 10^{-10}\ \text{cm}^2/\text{sec}.$$

This is an agreement with the steady-state diffusivity of *o*-xylene $D_{ss} = 2 \times 10^{-10}$ cm^2/sec previously derived by us (*2, 3*) from the uptake measurements which, in themselves, represented values of $D_{ns} = 5$ to 50×10^{-14} cm^2/sec. Clearly the catalytic observations are inconsistent with the latter.

2. The D–H Isotope Effect

The curvature of the D-to-H transfer reactions with increased catalyst site loadings with D sites, f_D indicates the existence of an appreciable preference of deuteration over protonation of the catalyst sites, i.e., of $K > 1$ in formula (5) for $S_D/(S_D + S_H)$. We can determine K by examining for which K in (5) the curvature of the observed data (Figs. 1 and 3) disappears, i.e., when the abscissa represents F_D rather than the gas-phase characteristic f_D. Figure 6 shows that

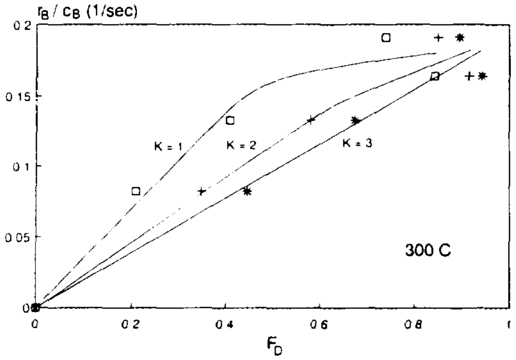

FIG. 6. Deuteration rates plotted against the fraction of deuterium donor atoms presented by the catalyst sites as a result of isotope effects characterized by the equilibrium constant K of donation of D vs H to the catalyst hydroxyl sites.

the isotope effect is strongest at 300°C, with $K = 3$. It declines to $K = 1$, i.e., no isotope effect, at 400°C as seen from the linearity of observed primary data in Fig. 4.

CONCLUSION

We have demonstrated a method for appraisal of diffusional effects in a zeolite that can be used on a single catalyst sample, i.e., it does not require samples of known and differing crystallite size. We have used such a method to appraise the magnitude of catalytically effective diffusivity D_{ss} of *ortho*-xylene in ZSM-5 zeolite. We have found D_{ss} to be of the order of 10^{-10} cm^2/sec or better, in contrast to the diffusivity measured by the nonsteady-state method of adsorption ("uptake"), which is some three orders of magnitude smaller.

The general method, using variation of a pseudo-first-order reaction rate constant, is extendable to a variety of reactants.

Incidentally, we have demonstrated the existence and magnitude of a D–H isotope effect for the exchange of the atoms between aromatic rings in the gas phase and the protonic sites of zeolite catalyst.

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