Sorption and Diffusion of Benzene in HZSM-5 and Silicalite Crystals

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Introduction

The discovery of intermediate-pore zeolites such as ZSM-5 and ZSM-11 based on the ten-membered oxygen rings prompted considerable increase in the use of zeolites in many novel separative, adsorptive and shape-selective catalytic processes. ZSM-5 has the same pore size as many of the commercially important aromatics and substituted paraffinic molecules. A wide range of adsorptive and catalytic applications of ZSM-5 has been proposed based on the size and configuration of diffusing molecules. Few studies, however, have been reported on intrinsic sorption and diffusion of aromatics and substituted paraffins in this zeolite.

The adsorption equilibria of aromatic hydrocarbons on ZSM-5 and its aluminum-deficient structural analog silicalite have been measured by Jacobs et al. (1981), Stach et al. (1986), and Pope (1984, 1986). Adsorption of benzene on ZSM-5 has been investigated by Doelle et al. (1981) and by Choudhary and Srinivasan (1987a). Adsorption and diffusion of C_6–C_8 aromatics in silicalite from the gas phase have been reported by Wu et al. (1983) and for ZSM-5 in liquid phase by Choudhary and Singh (1986). Choudhary and Srinivasan (1987b,c) have measured diffusion of benzene in HZSM-5 under catalytic conditions using a dynamic sorption/desorption technique.

When the sorption and diffusion data from above sources are analyzed, the data on sorption capacity are found to be consistent. For example, the limiting sorption capacity of ZSM-5 for benzene is found to be 0.1 to 0.12 kg/kg. For diffusion, however, the reported data do not show the same consistency. For example, the values of corrected diffusivities, D_o, for a cyclic hydrocarbon such as benzene have been found to vary over two to three orders of magnitude [5×10^{-15} m^2/s as reported by Wu et al. (1983) at 373 K vs. 5×10^{-13} reported by Zikanova et al. (1987) at 393 K]. Olson et al. (1981) reported a value of 10^{-11} at 588 K, whereas Choudhary and Srinivasan (1987b) report values of 10^{-15} in the same temperature range. In addition, Zikanova et al. (1987) report that the corrected diffusivities decrease with sorbate concentration, whereas Choudhary and Srinivasan (1987b) report the corrected diffusivities to increase with the concentration.

The primary objective of this work is to measure the kinetics of benzene adsorption on ZSM-5 as a function of crystal size, temperature, and concentration to ascertain the variation of diffusivities and adsorption isotherms with temperature and sorbate concentration. The results will serve to increase the database on the adsorptive and diffusive properties of ZSM-5 for aromatic hydrocarbons.

Experimental

Preparation and characterization

Crystals of four different sizes were synthesized. ZSM-5 crystals were synthesized using the standard hydrothermal technique, while the synthesis of the large silicalite crystals was based on the preparative protocol of Hayhurst and Lee (1986). Morphology of the crystals was orthorhombic with penetration twinning along the major axis. The characteristic crystal sizes, as measured by the length of the major axis were 15 μm, 45 μm for the ZSM-5 crystals, and 105 and 270 μm for the silicalite crystals. The Si/Al ratio of the ZSM-5 crystals was estimated to be 90 based on the initial synthesis composition, but the large crystals were prepared without aluminum addition. The zeolite samples were calcined at 823 K in air for three hours to remove the occluded template. For the HZSM-5 crystals, calcination was followed by three exchanges with ammonium chloride to remove residual sodium. The NH_4-ZSM-5 was again calcined to produce the hydrogen form of the zeolite.

The crystals were characterized by X-ray diffraction, scanning electron microscopy and oxygen pore volume (as determined by oxygen adsorption at 90 K). The X-ray diffraction analysis indicated that all test materials were well crystallized ZSM-5. The scanning electron micrographs, Figure 1, showed

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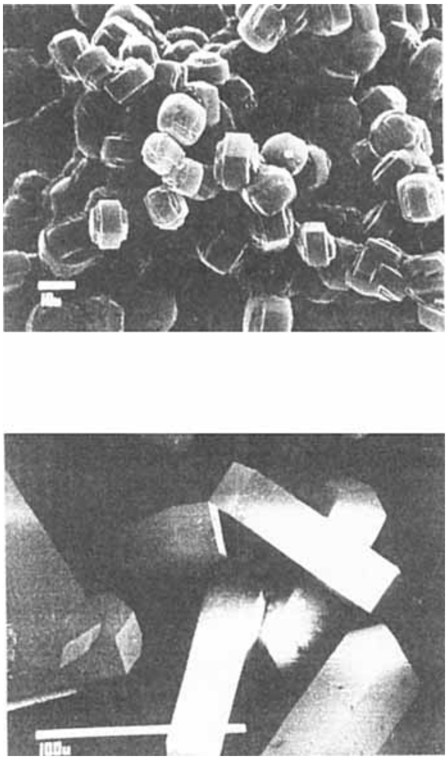

Figure 1. Scanning electron micrographs of the zeolite samples used in this study.

that the crystals were rectangular with each having a single penetration twin along the c-axis. This morphology was the same for all zeolites tested. The micrographs further confirmed that the samples were well crystallized and free of unreacted gel. The crystal size for all samples was uniform. The pore volumes for several of the test zeolites were determined by oxygen adsorption at 90 K in a McBain-Bakr adsorption balance. The calculated volumes ranged from 0.15 to 0.16 L/kg and they compared well with the value reported by Flanigan et al. (1978).

From the crystal morphology, it was clear that a spherical geometry could be used to model diffusion in HZSM-5 crystals of 15- and 45-μm size. Since the large 105- and 270-μm silicalite crystals approximated a rectangular parallelopiped in shape, equivalent radii ($r = 3/a$) were used in the evaluation of the diffusivities.

Sorption apparatus and experimental procedure

Equilibrium sorption capacity and rate measurements were carried out gravimetrically using a Cahn 1000 vacuum microbalance system. A turbomolecular pump coupled with a dual-stage rotary-vane vacuum pump was used to evacuate the system to 10^{-3} Pa. The temperature of the sample chamber was controlled to within ±0.5 K. The samples were dehydrated, recalcined, and activated *in situ* at 723 K.

To initiate a run, a predetermined amount of diffusant gas was injected into the sample chamber and sample weight was monitored as a function of time. After equilibrium was achieved, gas pressure was increased in increments of 50 to 100 Pa to obtain uptake curves over a wide range of diffusant gas pressures. A detailed description of the apparatus and the experimental protocol are given by Evanina (1985).

Experiments were carried out with different sample depths for each crystal size. Several runs also were carried out for both sorption and desorption to check for consistency in the values of diffusivities and sorption capacities.

Results and Discussion

Benzene sorption

Sorption isotherms were measured at 298, 303, 323 and 343 K for each crystal size, Figure 2. The benzene isotherms were found to be rectangular in shape with majority of the uptake

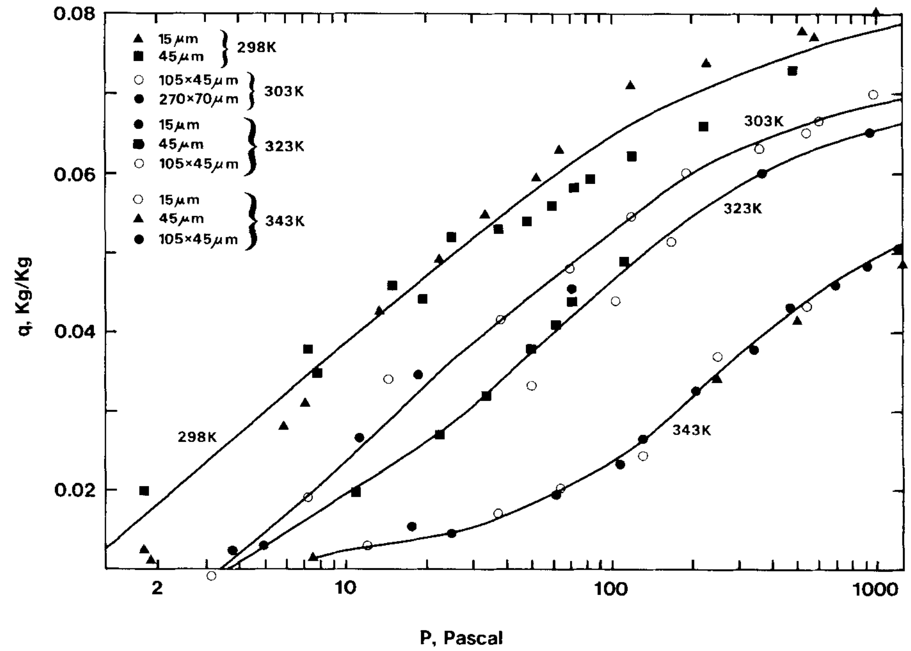

Figure 2. Sorption isotherms of benzene on the HZSM-5 crystal samples at different temperatures.

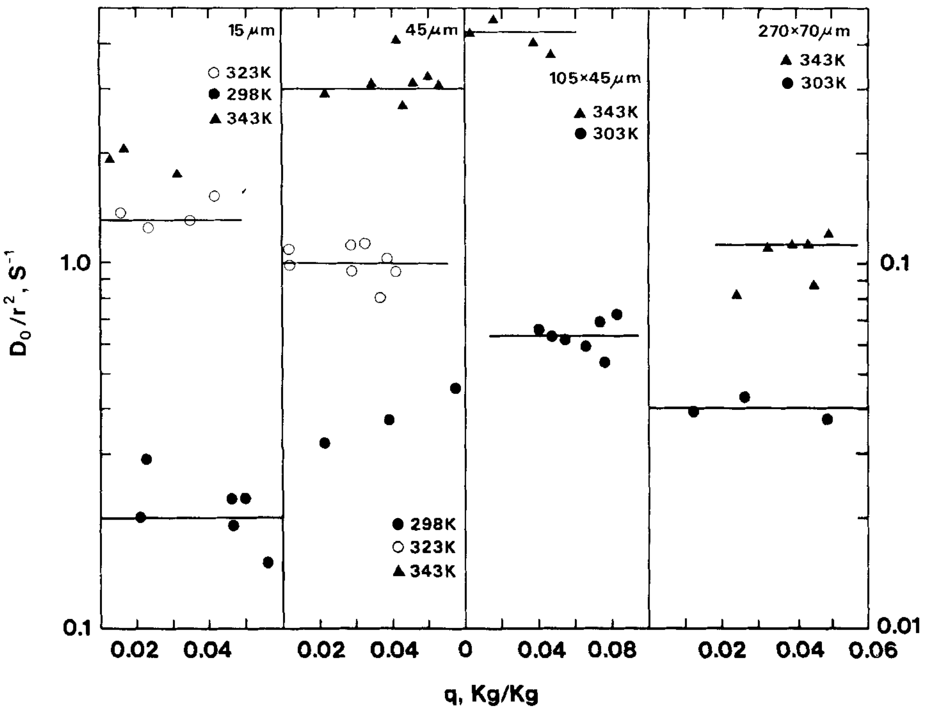

Figure 3. Variation of diffusional time constants with sorbate concentration for different crystal sizes.

occurring at relatively low pressures. The isotherms at 323 and 343 K show that the sorption capacity of both HZSM-5 and silicalite crystals for benzene are nearly equal. Benzene adsorption on two different sizes of large silicalite crystals is nearly identical as shown by the isotherm at 303 K. The 15-μm crystals show considerably greater sorption capacity in the range of 40 to 650 Pa at 298 K than that exhibited by 45-μm crystals. Both crystals, however, show the same sorption capacity at higher pressures. Reasons for the difference in sorption capacity at lower pressures are not clear. In general, the sorption data measured for all samples are in good agreement with one another. The sorption capacity of ZSM-5 obtained in the present study of about 0.12 kg/kg is in good agreement with the value of 0.11 reported by Wu et al. (1983) and 0.105 reported by Choudhary and Singh (1986).

Diffusion of benzene

Uptake rates were analyzed to determine the diffusivity of benzene in ZSM-5. The absence of significant thermal or bed diffusion resistance was confirmed by identical experiments with different sample configurations.

It has been shown by Ruthven et al. (1980) and Yucel and Ruthven (1980a,b) that in small crystals, sorption rates may be

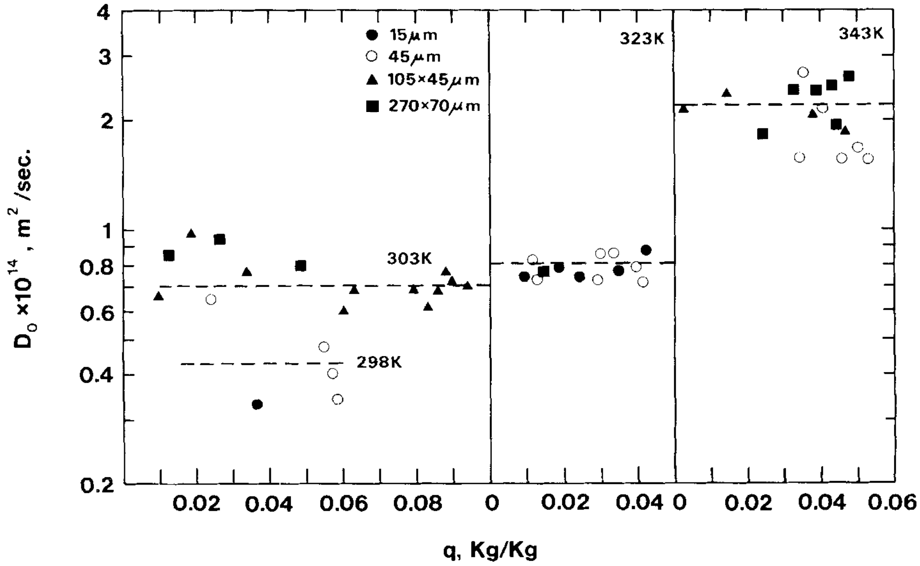

Figure 4. Variation of corrected diffusivity with sorbate concentration at different temperatures.

controlled by the combined effects of external heat transfer and intracrystalline diffusion. The uptake curve, under nonisothermal conditions, is determined by two dimensionless parameters $\alpha = (ha/\rho C_s)/(D/r^2)$ and $\beta = (\Delta H/C_s)(\delta q/\delta T)_p$. Under the conditions of either rapid heat transfer ($\alpha \rightarrow \infty$), negligible heat of adsorption or large thermal capacity ($\beta \rightarrow 0$), the expression for nonisothermal uptake reduces to that for isothermal sorption. The value of diffusion time constants for benzene from uptake data on large crystals is about 10^{-4} s^{-1} whereas Ruthven and his coworkers (1980, 1980a, 1980b) have carried out uptake experiments under the conditions of heat transfer control and have determined the value of $ha/\rho C_s$ in the range of 0.02 to 0.1 s^{-1}. This gives the value of α in the range of 200–1000 which is large enough for the process to be considered isothermal.

Based on the above arguments, all the uptake curves were analyzed assuming isothermal conditions. Wherever possible, the intracrystalline diffusivity was determined based on the analysis of initial and final portions of the uptake curves as well as data fitting over the entire curve (Ruthven, 1984). The transport diffusivity so obtained was corrected for the effect of adsorbate concentration by dividing by the Darken's correction factor $d(\ln p)/d(\ln q)$. The correction factors were obtained from the experimentally determined sorption isotherms. The results are summarized in Figures 3 and 4.

The transport diffusivity, D, increased by an order of magnitude with the adsorbed concentration of benzene. The corrected diffusivities, on the other hand, were found to be essentially independent of the sorbate concentration as shown in Figures 3 and 4. Figure 3 shows the variation of the diffusional time constants with benzene loading for each of the four crystal sizes. Although some scatter in the data is observed, the data show diffusional time constants for each crystal size to increase with temperature as expected. Moreover, for a given temperature, the time constants remain invariant and are independent of the amount of benzene adsorbed, Table 1.

If the intrinsic diffusivities are independent of crystal size as would be expected, the diffusional time constants, D_o/r^2, should vary inversely as the square of the crystal radius. The ratio of diffusional time constants for 15 and 45 μm crystals is between 7 and 10 and in reasonable agreement with 9, predicted by the inverse of the square of the ratio of the crystal radii. Similarly, the ratio of the equivalent radius of 270 × 70 μm to 105 × 45 μm crystals is 1.75 (46.5 μm/26.5 μm), hence the ratio of time constants of small crystals to large crystals should be about 3. For 343 K, the ratio is found to be 4 whereas for 323 K, the ratio is lower than expected, i.e., about 1.6. In general, the diffusional time constants do vary inversely as the square of the crystal radius; therefore, it is reasonable to conclude that the measured diffusivities are independent of the crystal size.

Table 1. Values of Diffusional Time Constants at Different Temperatures For Each Size Fraction

Temp. K	Diffusional Time Constants, 10^4 s^{-1} 15 μm	45 μm	105 × 45 μm	270 × 70 μm
298	0.2	0.036	—	—
303	—	—	0.063	0.04
323	1.03	0.1	—	—
343	2.0	0.3	0.43	0.103

The diffusion data for all size fractions for each of the temperature are combined and plotted in Figure 4. As shown in Figure 3, the corrected diffusivities are found to be independent of the amount of adsorbed benzene. The calculated diffusivity of benzene varies from 4×10^{-15} to 2×10^{-14} m^2/s in the temperature range of 298 to 343 K. These values are higher by two orders of magnitude than those reported by Wu et al. (1983). Zikanova et al. (1987) report benzene diffusivities that are one order of magnitude higher; however, they measured diffusivities at a higher range of temperatures (303–423 K). The values reported by Choudhary and Srinivasan (1987b) are much lower (10^{-15} to 10^{-16}) in spite of carrying out the measurements at much higher temperatures (523 to 673 K). They used a dynamic sorption/desorption technique with a continuous flow of gases through the zeolite sample. But in the analysis of their data, they used an equation that was derived for a static system. This may be the reason for such a large discrepancy between our results and those of Choudhary and Srinivasan.

The variation of the corrected diffusivity with temperature was used to calculate the activation energy for diffusion, E, assuming an Arrhenius-type relationship, Figure 5. The activation energy for the intracrystalline diffusion of benzene is calculated to be 28.8 kJ/mol. It compares well with the value of 27 kJ/mol for the same system reported by Zikanova and coworkers (1987). Choudhary and Srinivasan (1987b) again report a considerably higher value of 67 kJ/mol than that determined here.

Conclusions

Data reported here represent a comprehensive study of adsorption and diffusion of benzene into HZSM-5 and silicalite crystals of varying sizes. Based on the equilibrium capacity, it is concluded that benzene is adsorbed quite strongly on the protonated form of ZSM-5 crystals as well as on silicalite. Sorption capacities obtained in the present study are in reasonable agreement with the values reported in literature.

Analysis of the rate of benzene uptake curves for both HZSM-5 and silicalite crystals shows that the kinetics of ben-

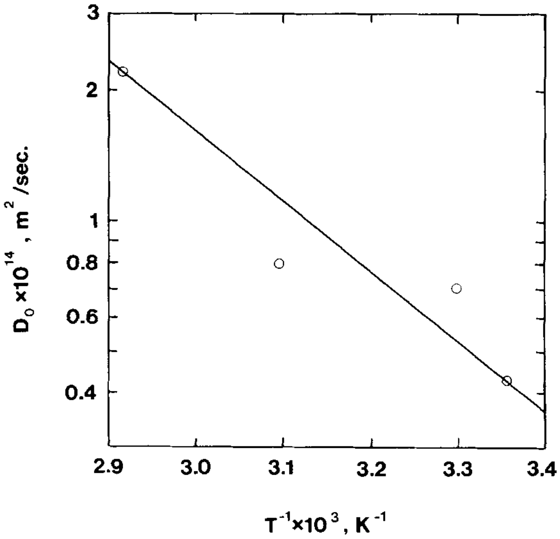

Figure 5. Arrhenius plot for the diffusion of benzene in ZSM-5.

zene sorption are controlled by intracrystalline diffusion. This is not surprising because the kinetic diameter of benzene molecule is larger than the pore opening of ZSM-5 resulting in slow uptake of benzene. Benzene diffusivities in HZSM-5 and silicalite crystals were found nearly equal. This is not surprising as the crystal structure of both zeolites are similar. The diffusional time constants show the expected variation with the square of the crystal radius and the diffusivities obtained from different size fractions are similar.

Acknowledgment

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Notation

a = external surface area per unit volume of adsorbent
C_s = effective heat capacity of adsorbent sample
D = intracrystalline diffusivity
D_o = corrected intracrystalline diffusivity
E = activation energy for intracrystalline diffusion
h = external heat transfer coefficient
p = partial pressure of adsorbate
q = equilibrium adsorbed phase concentration
r = equivalent radius of zeolite crystal
T = sorption temperature

Greek letters

α = dimensionless parameter in nonisothermal sorption
β = dimensionless parameter in nonisothermal sorption
ρ = density of adsorbent sample
$-\Delta H$ = heat of sorption

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