1995

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1143

Intracrystalline Diffusion of Benzene in Silicalite: Effect of Structural Heterogeneity

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The sorption kinetics of benzene in silicalite have been measured gravimetrically using large silicalite crystals of sizes 350 μm × 105 μm × 105 μm and 270 μm × 70 μm × 70 μm in the temperature range 283–343 K. Experiments were performed under conditions that ensured isothermal operation with intracrystalline diffusion control. An analytical expression for the Darken's correction factor ($\delta \ln P / \delta \ln a$) was derived based on the Hill–de-Boer equation and was used to determine the variation of corrected diffusivity with concentration. The transport diffusivity varied significantly with the adsorbed-phase concentration but the corrected diffusivity was found to be essentially independent of the concentration. However, at temperatures below the surface transition temperature, a maximum in corrected diffusivity was observed at an adsorbed-phase concentration of four molecules per unit cell (uc). This maximum is the direct result of the type IV isotherm exhibited by the silicalite–benzene system below the surface transition temperature. It is proposed that the increase in corrected diffusivity at the critical adsorbed-phase concentration of 4 molecules uc^{-1} arises from reorientation of benzene molecules resulting in a much more efficient packing in the pore channel system.

The adsorptive and diffusive properties of ZSM-5 and its aluminium-free structural analogue, silicalite, with benzene, toluene and xylenes have been investigated by a number of researchers. A comprehensive review of intracrystalline diffusivity of benzene in ZSM-5 and silicalite has been presented by Karger and Ruthven[1,2] which reports the use of a variety of macroscopic methods: gravimetric,[3–10] zero-length column,[11] circulating system,[12] piezometric,[10,13,14] frequency-response techniques[15] and tracer exchange.[16] In general, diffusivities determined with ZSM-5 are lower than those determined with silicalite. Most of the work cited above has been conducted with small crystals[3,4,6,8,9,12,13,15] and, even in cases where large crystals were used,[5,7,10,11,14] the intracrystalline diffusivity was determined over a rather narrow loading range. There is also a considerable scatter in the values of the reported diffusivities (10^{-12} to 10–16 m^2 s^{-1}). In addition, opposing trends have been observed for the variation of transport and corrected diffusivity with the adsorbed-phase concentration. Zikanova *et al.*[10] report transport diffusivities to be nearly constant and the corrected diffusivities to decrease with increasing adsorbed-phase concentration. On the other hand, the corrected diffusivity has been found to increase with the adsorbed-phase concentration.[17,18] No significant increase in the values of transport diffusivities has been observed[12] with adsorbate loadings up to *ca.* 3 molecules uc^{-1}. Over a narrow adsorbate loading range, the transport diffusivities have been reported[5] to increase with concentration but the corrected diffusivities were essentially independent of concentration. These discrepancies appear too significant to be attributed solely to differences in zeolite composition, methods of zeolite synthesis, type of zeolites (Na or H form of ZSM-5, silicalite) used in experiments and the experimental procedures used in different studies.

In this paper, the results of a comprehensive study on sorption kinetics of benzene in large crystals of silicalite are presented. Sorption uptake rates have been measured over a wide range of adsorbed-phase loadings to determine the variation of transport and corrected diffusivities with concentration. Two different crystal sizes have been used to verify the presence of the intracrystalline diffusion control. Results

from this study, along with the information available in the literature for the benzene–pentasil zeolite system, have been used to understand the microdynamics of benzene molecules in the silicalite pore system. Silicalite was chosen over ZSM-5 as the adsorbent because it does not contain any cation and, therefore, heterogeneity that may arise in ZSM-5 owing to the presence of the electrostatic field is significantly reduced.

Experimental

Silicalite crystals were synthesized without aluminium in accordance with the preparative protocol described by Hayhurst and Lee.[19] Two different samples of crystal, of 270 μm × 70 μm × 70 μm and 350 μm × 105 μm × 105 μm in size, were used. Scanning electron micrographs of the samples showed that the crystals were rectangular with each having a single penetration twin along the *c* axis. The micrographs further confirmed that the samples were well crystallized and uniform in size. Since the crystals approximated a rectangular parallelpiped in shape, equivalent radii ($r_e = 3V/A$) were used in the evaluation of diffusivities.

A standard Cahn 1000 vacuum microbalance was employed to measure the uptake curves. About 15 mg of silicalite crystals were spread over a stainless-steel-wire-mesh sample pan of 3 cm diameter so that the thickness of the adsorbent bed was about one to two crystals high. This ensured that the diffusional resistance of the macropore bed was eliminated. The volume of the sorption system was large enough and the concentration-step-change small enough to assume that the adsorbate concentration on the surface of the crystals remained constant during the course of the sorption–desorption runs. The samples were activated at 823 K and degassed *in situ* at 723 K under a vacuum of 10^{-5} Torr for 12 h. A predetermined amount of sample gas was then injected into the sample chamber and the sample weight was monitored as a function of time. After equilibrium was achieved, the gas pressure was increased in small increments to obtain uptake curves over a wide range of diffusant-gas pressures. Several runs were performed for both sorption and desorption to check for consistency in the values of sorption capacities and diffusivities. A detailed description of the experimental apparatus and procedure can be found elsewhere.[20] The uptake curve was analysed in the initial and long time regions to determine the transport diffusivity (*D*) at

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a given adsorbed-phase concentration.[21] Corrected diffusivities (D_0) were calculated from the transport diffusivities by the application of the Darken's correction factor

$$D = D_0 \left| \frac{\partial(\ln P)}{\partial(\ln a)} \right|_T \qquad (1)$$

Equilibrium Sorption Model

In a series of papers from this laboratory,[22,23] it has been shown that the sorption isotherms of benzene on these samples exhibited a stepwise nature at low temperatures. The nature of the isotherm changes from type I to type IV as the temperature is lowered. For the benzene–silicalite system, the transition from type I to type IV was experimentally shown to occur at the adsorbed-phase concentration of 4 molecules uc^{-1}. The temperature at which this transition occurs has been termed the phase-transition temperature. To explain this behaviour, it was proposed that silicalite contains two distinct but homogeneous adsorption patches represented by the straight (l-patch) and zigzag channels (s-patch). They also assumed that the Hill–de-Boer equation can be used to model adsorption on each of the patches

$$P = K_i \frac{\theta_i}{1 - \theta_i} \exp\left[\frac{\theta_i}{1 - \theta_i} - \left(\frac{2\alpha}{k\beta}\right)_i \frac{\theta_i}{T} \right]; \quad i = 1, s \qquad (2)$$

This equation is capable of exhibiting either a type I or type IV isotherm depending on the value of the parameter $2\alpha/k\beta$. At low temperatures, the equation exhibits an inflection (type V isotherm). As the temperature is increased, the inflection disappears and the isotherm becomes type I. The overall adsorption isotherm (either type IV or type I) was described by the summation of the individual isotherms in each of the homogeneous pore systems. The expression for the overall adsorption isotherm was then fitted to the experimentally measured adsorption isotherm and the parameters appearing in the Hill–de-Boer equation for each of the patches were determined. The values of the parameters so determined were consistent with the physical picture of straight channels being occupied before the sinusoidal channel. This equation for the overall sorption isotherm was differentiated and an analytical expression for the Darken's correction factor, F, was derived as follows:

$$F = \left| \frac{\partial(\ln P)}{\partial(\ln a)} \right|_T = a_t (a_s^\infty f_s + a_1^\infty f_1)^{-1} \qquad (3)$$

where

$$f_i = \left[\frac{1}{\theta_i(1 - \theta_i)^2} - \left(\frac{2\alpha}{k\beta}\right)_i \frac{1}{T} \right]^{-1}; \quad i = 1, s \qquad (4)$$

The above equations show that the correction factor is dependent on the total amount adsorbed (a_t), the degree of occupancy of both l- and s-patches $(\theta_1$ and $\theta_s)$ and the interaction between adsorbed molecules $(2\alpha/k\beta)_i$. The parameter values determined earlier were used to calculate the variation of F as a function of adsorbate loading. The nature of the variation of F with the adsorbed-phase concentration for benzene is shown in Fig. 1 for a temperature where the sorption isotherm is of type IV. This curve is different from the correction-factor curve for type I isotherms in that it shows a local maximum at an intermediate concentration corresponding to the adsorbed-phase concentration at which the isotherm shows a step. The values of the parameters[22] were found to be consistent with the geometric and physico-chemical aspects of the adsorbent–adsorbate system being investigated.
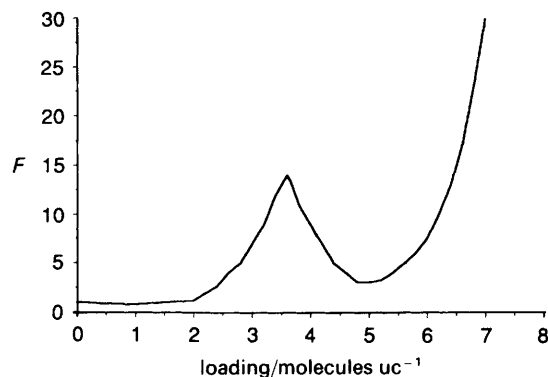

Fig 1 Variation in F with benzene loading for a type IV isotherm

Results and Discussion

The variation of D, F and D_0 with the adsorbed-phase concentration at 343 K (where the isotherm is of type I) is shown in Fig. 2. These data show that at 343 K, the transport diffusivities increase monotonically with the adsorbed-phase concentration but so does the correction factor. The net effect is that the corrected diffusivities do not change significantly with the adsorbed-phase concentration. The increase in transport diffusivities can be attributed entirely to the shape of the sorption isotherm. The differential transport diffusivities of benzene determined from the uptake curves as a function of the adsorbed phase concentration at 283, 293, 303, 323 and 343 K are shown in Fig. 3. The corresponding corrected diffusivities at the same temperatures are shown in Fig. 4. Isotherms at the lower three temperatures are of type IV whereas those at 323 and 343 K are of type I. The data show that the transport and the corrected diffusivities are relatively
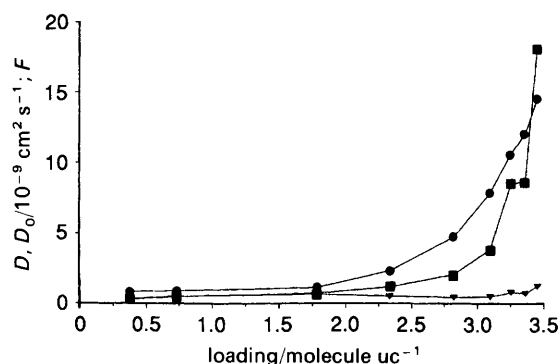

Fig. 2 D (■), F (●) and D_0 (▼) as a function of loading at 343 K $(r_e = 46.68\ \mu m)$
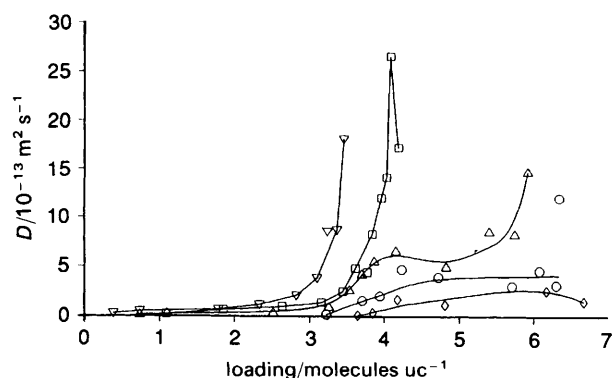

Fig. 3 Transport diffusivities of benzene in silicalite as a function of loading at 283 (◇), 293 (○), 303 (△), 323 (□) and 343 K (▽) $(r_e = 46.48\ \mu m)$
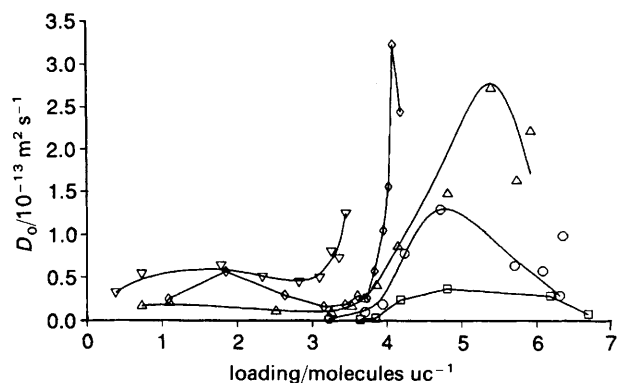
Fig. 4 Corrected diffusivities of benzene in silicalite as a function of loading at different 283 ($\square$), 293 ($\bigcirc$), 303 ($\triangle$), 323 ($\diamond$) and 343 K (∇) ($r_c = 46.68$ µm)

Fig. 6 Corrected diffusivity as a function of loading at 343 K for two crystals with $r_c = 46.48$ ($\blacksquare$) and 64.34 µm ($\bullet$)

constant at 10^{-14} m^2 s^{-1} up to ca. 3 molecules uc^{-1}. As the loading is increased beyond 3 molecules uc^{-1}, both the transport and the corrected diffusivities increase sharply. For temperatures below the phase-transition temperature (isotherm is of type IV), the corrected diffusivities appear to show local maxima at 4.5–5.5 molecules uc^{-1}.

These figures demonstrate that the behaviour of corrected diffusivities as a function of the adsorbed-phase concentration depends on the temperature. At temperatures above the phase-transition temperature, the corrected diffusivities are nearly independent of the adsorbed-phase concentration (Fig. 2) whereas at temperatures below the phase-transition temperature, the values of D_0 are nearly constant until the adsorbed-phase concentration reaches ca. 4 molecules uc^{-1}. At or near this concentration, D_0 increases sharply, reaches a maximum value and then starts decreasing. The maximum diffusivity is about an order of magnitude higher than the diffusivity at a lower concentration. It is significant to note that these maxima occur at or near a concentration at which the isotherms show the stepwise behaviour. Such maxima, to our knowledge, have not been reported previously in the literature. The apparent and corrected diffusivities exhibit vastly different behaviour depending on the temperature and the range of adsorbed-phase concentrations being investigated. It is, therefore, possible to observe different types of behaviour such as constant diffusivity, increasing diffusivity or decreasing diffusivity with increasing sorbate loading depending on the range of adsorbate loading being investigated.

The variation of intracrystalline diffusivities as a function of adsorbed-phase concentration for two different sized crystal is shown in Fig. 5 and 6 at 303 and 343 K. At 303 K (type IV isotherm) both crystal sizes show maximum values of corrected diffusivities at about 5 molecules uc^{-1}. At 343 K,
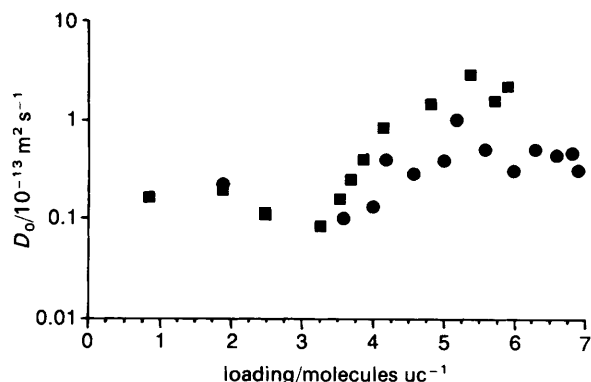

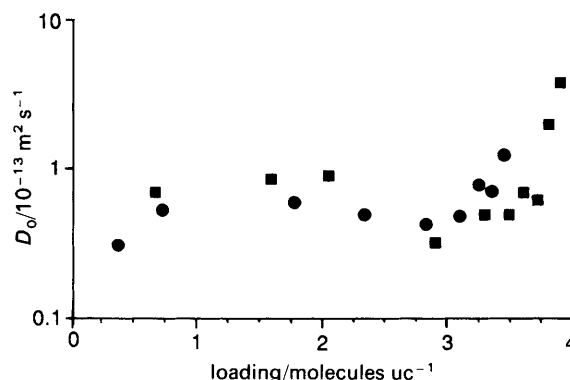**Fig. 5** Corrected diffusivity as a function of loading at 303 K for two crystals with $r_c = 46.48$ ($\bullet$) and 64.34 µm ($\blacksquare$)

(type I isotherm) the corrected diffusivity is nearly constant with some tendency to rise as the critical adsorbed-phase concentration of 4 molecules uc^{-1} is reached. Measurements on the two crystal sizes give about the same values of corrected diffusivities and they also exhibit the same trends. These results prove that the sorption kinetics are controlled by intracrystalline diffusion.

The data on benzene sorption isotherms[22,23] together with the results on sorption kinetics reported here, provide a conceptual picture of the mobility of benzene in the silicalite pore structure. It has been postulated[22,23] that the stepwise nature of the isotherms results from 'structural heterogeneity'. The structural heterogeneity arises from the presence of two nearly identical pore channels, circular zigzag channels and the elliptical straight channels, and diffusion of a tightly fitting molecule such as benzene through these pores. The nature of the benzene sorption isotherms changes from type I to type IV with decreasing temperature. These results suggest that the initial benzene adsorption in silicalite takes place preferentially in straight large channels and/or intersections until the adsorbed-phase concentration reaches the critical concentration of ca. 4 molecules uc^{-1}. This critical absorbed-phase concentration corresponds to a molecule occupying each available intersection. Once the concentration increases beyond 4 molecules uc^{-1}, the adsorbate–adsorbate interactions increase to a point where the adsorbate molecules are pushed from the channel intersections into the smaller elliptical zigzag pores. This is also the concentration where the corrected diffusivity increases rather sharply. The sudden jump in the corrected diffusivity may be attributed to the availability of the relatively less densely occupied sinusoidal pore channels and sites within for sorption. As the adsorbate concentration increases further, the elliptical pore channels are occupied more densely, thereby decreasing the mobility of the molecules and, hence, leading to the decrease in the corrected diffusivity that is experimentally observed.

Based on these results, it is proposed that the initial benzene adsorption occurs in the middle of straight channels. As the adsorbate–adsorbate interactions increase, the benzene molecules get pushed out at the channel intersections. Further increase in the adsorbed phase concentration increases the adsorbate–adsorbate interactions to such an extent that the benzene molecules are then forced into the smaller zigzag channels.

Conclusions

The sorption kinetics of benzene in large crystals of silicalite have been studied gravimetrically at different temperatures. The corrected diffusivities were found to be nearly indepen-

dent of the adsorbed-phase concentration. However, for temperatures at which benzene isotherms exhibited stepwise nature, the corrected diffusivities showed maxima at concentrations of about 4–5 molecules uc^{-1}. It was postulated that initial adsorption of benzene in silicalite occurs in the large circular zigzag channels and at channel intersections, until the concentration reaches 4 molecules uc^{-1}. At this point, adsorbate–adsorbate interactions become pronounced and further adsorption takes place in smaller elliptical channels. As the adsorbed molecules are pushed out from channel intersections into relatively less densely occupied smaller channels, the rate of mass transfer increases, resulting in increased corrected diffusivity.

Glossary

a	amount adsorbed/mmol g^{-1} (or molecules uc^{-1})
a_∞	absolute saturation capacity/mmol g^{-1}
A	external surface area of particle/cm^2
D	transport diffusivity/$cm^2\ s^{-1}$
D_0	corrected diffusivity/$cm^2\ s^{-1}$
f	factor defined by eqn. (4)
F	Darken's correction factor
k	parameter characterizing sorbate–sorbent interaction
P	pressure/Torr
r_e	radius of an equivalent spherical particle/cm
T	temperature/K
V	volume/cm^3
θ	fractional coverage, a_s/a_s^∞, a_l/a_l^∞
w	$2\alpha/k\beta$, parameter characterizing sorbate–sorbate interaction

Subscripts

l	l-patch
s	s-patch
t	total

Superscript

∞	maximum amount adsorbed

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