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Diffusion of n-Decane in 5A Zeolite Crystals

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In a recent paper Caro, Kärger and Bülow (1980) showed that the rate of adsorption of n-decane from the liquid phase into 5A zeolite crystals is controlled by a surface blocking effect rather than by intracrystalline diffusion. We have measured the sorption of n-decane from the vapour phase into Linde 5A zeolite crystals at much higher temperatures (250–323°C). A typical set of experimental uptake curves is shown in Figure 1. The uptake rate was found to be essentially independent of the quantity and configuration of the zeolite crystal sample indicating the absence of any significant bed diffusion or heat transfer limitations.

For a diffusional process, in the long time region, the fractional uptake (m_t/m_∞) is given by:

$$1 - m_t/m_\infty \approx (6/\pi^2)\exp(-\pi^2 Dt/r^2) \qquad (1)$$

while for a surface barrier limited process:

$$1 - m_t/m_\infty \approx \exp(-3\alpha t/r) \qquad (2)$$

where D is the intracrystalline diffusivity; r, the equivalent radius of the crystal; α, the barrier coefficient; and t, time. It is evident that the form of the uptake curves shown in figure 1 is consistent with the diffusion model (Eq. 1) rather than the surface barrier model (Eq. 2) since the zero time intercepts of the extrapolation of the long time region of the semilog arithmic plot of $(1 - m_t/m_\infty)$ vs. t are all close to $6/\pi^2$.

The diffusivity shows the usual strong positive concentration dependence (Figure 2). Corrected diffusivities (D_o) calculated according to the expression:

$$D = D_o(dlnp/dlnc) \qquad (3)$$

where *dlnp/dlnc* is the non-linearity correction factor derived from the equilibrium isotherm are essentially independent of concentration, as observed previously for n-heptane and other light hydrocarbons in 5A zeolite. (See, for example, Doetsch, Ruthven and

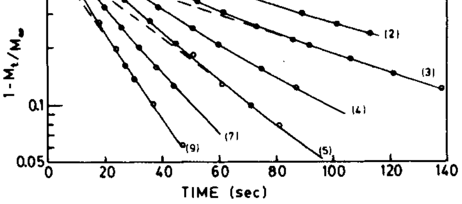

Figure 1. Experimental uptake curves for n-decane in Linde 5A zeolite crystal (mean diameter 3.6 μm). The curves are for the following pressure steps (in Pa): (2): 1.86–10.6; (3): 10.6–19.0; (4): 19.0–33; (5): 33–44; (7): 56–71; (9): 82–97.

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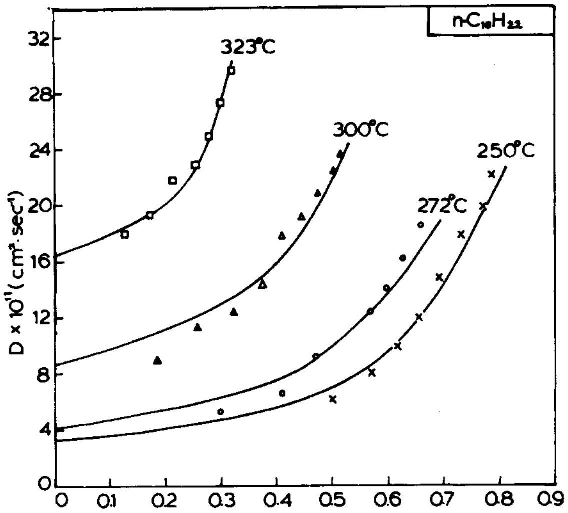

Figure 2. Concentration dependence of differential diffusivities for n-decane in 5A zeolite, calculated from the experimental uptake curves.

Loughlin, 1974). It therefore seems that the surface barrier resistance observed in the liquid phase at lower temperatures is indeed due to the blocking effect of the solvent, rather than to an intracrystalline barrier.

Extrapolation of the present limiting differential diffusivity data suggests that at 295 K $D_o \approx 2 - 6 \times 10^{-15}$ $cm^2 \cdot s^{-1}$. This is considerably lower than the apparent integral diffusivities observed by Caro et al. However, in view of the strong positive concentration dependence of the differential diffusivity these results are not necessarily inconsistent.

A more detailed report of our studies will be published shortly.

NOTATION

c = sorbate concentration
D = intracrystalline diffusivity
D_o = corrected diffusivity (Eq. 3)
m_t/m_∞ = fractional approach to equilibrium in an uptake experiment
P = equilibrium sorbate pressure
r = equivalent radius of zeolite crystals
t = time
α = constant of proportionality for surface resistance model (Caro et al., 1980)

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Extrapolating Conversions to Zero External Gradients in Vapor Phase Catalytic Recirculation Reactors

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In vapor phase catalytic studies, recirculation reactors are often used in obtaining kinetic data. These reactors provide the high mass flows in the catalyst bed typical of industrial conditions and minimize the temperature and concentration gradients external to the catalyst. An example for these type of reactors which has recently become popular is the Berty reactor (Berty et al., 1969) with the blower and return line enclosed in an autoclave. In our recent study of cyclohexane dehydrogenation kinetics at atmospheric pressure with the Berty reactor (Schneider et al., 1978), we have found external temperature gradients to be significant. In this communication a method for extrapolating conversions to zero external gradients is outlined and shown to be significantly superior to the method traditionally used.

Extrapolation to zero external gradients is commonly done by plotting conversion (X) vs. the reciprocal mass velocity (ϕ) over the catalyst bed. As the mass velocity approaches infinity ($\phi \rightarrow 0$), external gradients are essentially eliminated. Therefore, a polynomial fit for a plot of X vs. ϕ would yield conversion at zero external gradients (X^∞) upon intersection with the ordinate. Our analysis here was carried out with the objective of developing a functional relationship based on theoretical considerations to see if the corresponding extrapolation is superior to the one outlined above.

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