Evidence of Single-File Diffusion by tracer ZLC Method

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Introduction

With growing interest for the use of one-dimensional (1-D) zeolites in separation and reaction processes, the need to understand diffusion and transport properties of molecules within the channels of these materials is becoming more eminent. The mechanism used to describe passage of molecules inside narrow 1-D micropores is called single-file diffusion. Typically, this behavior is observed within 1-D pore structures with channel diameters comparable to size of diffusing molecules. Under this circumstance, molecules cannot pass over one another resulting into high degree of mutual correlation between the movements of different molecules. In this paper, we report an experimental confirmation of single-file mechanism in toluene/ZSM-12 system using tracer Zero Length Column **(**TZLC) technique.

Experimental Details

The detailed synthesis procedure for ZSM-12 sample used in this study is described elsewhere (1). The sample was characterized by standard methods to obtain textural and morphological properties, such as BET area, XRD and SEM. The values of 330 m^2/g and 0.111 *ml/g* were obtained for BET and micropore volume, respectively. β-zeolite that was used as a comparative material in this study has BET area of 725 m^2/g, SiO_2/Al_2O_3 of 50 and Na_2O wt of 0.05. Traditional ZLC experiments were carried out following the method described by Eic and Ruthven (2), while tracer ZLC was performed with deuterated toluene as suggested in Ref (3).

Single-File theory

Under conditions of single-file diffusion the mean square displacement, in the z direction considering the long time region, is given by (4):

$$< z^2(t) > = l^2 \left(\frac{1-\theta}{\theta} \right) \sqrt{\frac{2t}{\pi \tau}}$$

The self-diffusivity ($\mathscr{D}$) can be defined, in accordance with the Einstein equation, as $\mathscr{D} = <z^2(t)>/2t)$ (4).

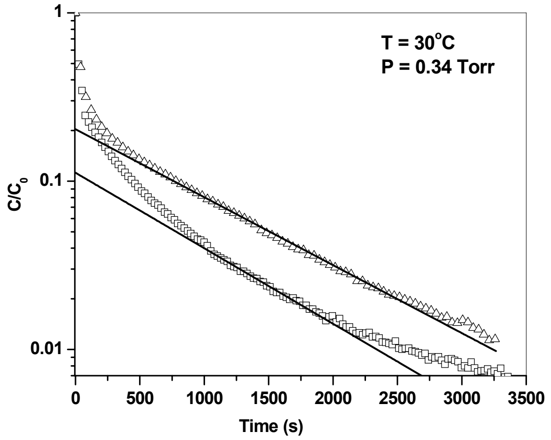
Combining both equations gives a time varying self-diffusivity:

$$\mathscr{D} = l^2\left(\frac{1-\theta}{\theta}\right)\frac{1}{\sqrt{2\pi\tau t}}$$

which clearly shows that $\mathscr{D}$ is not constant for single-file systems but decreases with time, i.e., response becomes curved in the long time region.

Results and Discussion

Figures 1 and 2 show the effect of sorbate loading on the tracer exchange profiles for toluene in the 1-D ZSM-12 and 3-D β-zeolite under similar experimental conditions.



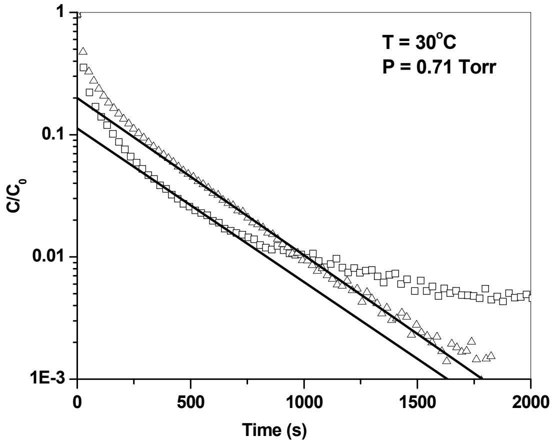


Fig.1 TZLC exchange profile at P=0.34 torr Fig.2 TZLC exchange profile at P =0.71 torr (□) ZSM-12 and (Δ) β-zeolite. Solid lines represent theoretical predictions based on Fick's models

It could be seen from above figures that the longtime tracer exchange asymptote of toluene/ZSM-12 system is non-linear, e.g., deviates from the straight line particularly at higher loading, while that of the reference 3-D β-zeolite is clearly linear. Furthermore, theoretical prediction based on normal Fickian 1-D diffusion model poorly predicts the longtime limit of toluene/ZSM-12 system, while the 3-D Fick's model compares favorably with the obtained experimental data for toluene/β-zeolite under all conditions studied. This provides significant evidence that unlike for the 3-D zeolites, e.g., β-zeolite, the normal Fickian diffusion model cannot be used to interpret the longtime limit for the 1-D toluene/ZSM-12 system. This study also proved that the relatively simple TZLC technique can be conveniently used to validate single-file diffusion.

References

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