Diffusion Measurements through Embedded Zeolite Crystals

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For the first time, a macroscopic method was used to measure directly diffusivity of fast diffusing species such as methane in silicalite. A form of Wicke–Kallenbach technique was applied to measure intracrystalline diffusivity. The technique uses a single embedded zeolite crystal as a membrane and a mass-selective detector to determine the transient mass response and hence the diffusion flux passing through the membrane. A concentration-difference driving force is used rather than a pressure-difference driving force. The diffusivities calculated from both adsorption and desorption transients were in excellent agreement, thus providing a check for the self-consistency of the data. The diffusivities of carbon dioxide, methane, ethane, propane and butane in silicalite between 30 and 70°C have been compared with those from the literature. The diffusivities reported here are between those measured with microscopic methods and those measured with other macroscopic methods.

Introduction

Significant effort has been devoted to developing applications of zeolites as novel adsorbents and catalysts by the academic and the industrial community. Different types of zeolites have been developed for numerous applications that exploit their high surface area and well-defined pore structure where the adsorption sites or the active centers are accessible only through a molecular-sized window. Adsorption processes are generally classified as equilibrium and kinetic separation. Although most zeolite-based separation processes are equilibrium separations, the rate of transport through the internal pore structure still plays a significant role. Thus, extensive theoretical and experimental work has been devoted to predicting and measuring intracrystalline diffusivities in zeolites (Ruthven, 1984; Karger and Ruthven, 1992).

Diffusivity measurements can be grouped in two basic categories: macroscopic and microscopic. The former is based on the measurement of a macroscopic property that is related to the rate of internal transport and thus to the diffusivity. A classic example is the gravimetric uptake rate measurement. Macroscopic techniques, in general, are rather easily influenced by other transport processes. Especially important is the interference by heat transfer that always exists since adsorption is exothermic (Bulow et al., 1984). When macroscopic techniques are used to measure intracrystalline diffusivity, a major emphasis is placed on reducing the impact of all extraneous mass and heat-transfer resistances so that the micropore diffusional resistance is the rate-controlling step. More recently developed macroscopic methods such as zero-length column (ZLC) (Eic and Ruthven, 1989; Ruthven et al., 1992) and frequency response (FR) (Bulow et al., 1989; Shen and Rees, 1991a,b, 1994) are aimed at further reducing the impact of other transport processes. Even these state-of-the-art techniques are only partially satisfactory in measuring fast diffusion processes such as that of methane in silicalite.

In microscopic methods, the diffusion coefficients are inferred from molecular mobility in the micropores. These methods include pulsed field gradient nuclear magnetic resonance (PFG–NMR) (Heink et al., 1992; Hong et al., 1991) and neutron scattering (Jobic et al., 1989). While macroscopic methods measure slow diffusion processes accurately, microscopic techniques are more reliable for the measurement of fast diffusion processes. When both macroscopic and microscopic techniques are used to measure intracrystalline diffusivities for the same system, the results often widely differ, sometimes exceeding several orders of magnitude. A variety of explanations have been offered for these differences (Karger and Ruthven, 1989, 1992). A major factor is believed to be that the two methods are most accurate at two different extremes of slow and rapid diffusion. Therefore, there are very few systems in zeolite diffusion in which the results from the two techniques show agreement.

As nonexperimental tools, molecular-dynamic (MD) and Monte Carlo (MC) simulations have been successfully used to study adsorption and diffusion of molecules in zeolite. The MC simulation provides information on equilibrium properties, whereas the MD simulation also provides information on dynamic properties such as diffusivities. Numerous MD simulations have been performed on the transport of hydrocarbons in zeolites (Nicholas et al., 1993; Nowak et al., 1991; June et al., 1992; Goodbody et al., 1991). The diffusivities by MD simulations agree well with the microscopic data obtained by PFG–NMR measurement.

The technique of measuring diffusivity with a single zeolite crystal membrane was first developed by Paravar and Hayhurst (1984) and Wernick and Osterhuber (1984, 1985). Later, the technique was applied to measure the intracrystalline diffusivities of C_4 hydrocarbons (Shah et al., 1993) and aromatics (Shah and Liou, 1994) in silicalite. In the preceding studies, a membrane was fabricated from a large zeolite crystal. A differential pressure was applied across the membrane and the rise in pressure was measured on the low-pressure side. The pressure rise was quite small (of the order of 5×10^{-3} torr for a 10-h period) since the amount of substance passing through a single crystal was extremely small (10^{-10} mol/min). The analysis of data required a linear extrapolation of the pressure transient to absolute zero in order to determine the time-lag that is related to the diffusivity. The sensitivity and linearity of pressure transducers in this low range were critical for the accuracy of the results. Although the final diffusivities were in agreement with other data, the linear extrapolation in the vicinity of zero pressure did not provide unequivocal diffusivity results.

A few of the several intrinsic advantages of the membrane technique are: (1) the heat effect of adsorption on diffusion is minimized, if not eliminated; (2) the diffusion process can be studied under steady-state conditions; and (3) diffusivity along different directions can be measured by appropriately orienting the crystal due to the well-defined geometry of the system. However, there were several disadvantages with the earlier membrane experimental apparatus. The driving force applied was the pressure difference and not the concentration difference. The difficulty in accurately measuring the small pressure rise near zero pressure has already been alluded to. In addition, measurement of multicomponent diffusion (co- and counter-) was not possible.

In this article, we describe the improvements in the experimental technique that address and overcome the shortcomings just cited and the associated new data-analysis method. The single-zeolite-crystal technique has been modified by incorporating a high-sensitivity mass selective detector (MSD) to measure the concentration of the diffusing species. Although the amount of substance diffusing through the crystal is extremely small, it can still be accurately measured by the MSD. To further improve the sensitivity, more than one crystal was used to fabricate the membrane. The method has been improved to such an extent that it now becomes possible to measure micropore diffusivity of fast-diffusing species such as C_1 to C_4 alkanes in silicalite.

The experimental system and data analysis are described in detail in this article. We also report a set of diffusivity measurements for carbon dioxide and C_1–C_4 alkanes in silicalite at several tem peratures. These values are compared with those measured experimentally with FR, ZLC, and PFG–NMR methods and those predicted from MD simulations.

Experimental Studies

Fabrication of membrane

The heart of this technique is the single-zeolite-crystal membrane. Large silicalite crystals (initial size $100 \times 100 \times 300$ μm) were mounted in a hole (1 mm dia.) at the center of an aluminum disk to form the membrane. Fabrication of the membrane was performed in a manner similar to the previous attempts; an epoxy was used to bind the crystal to the disk. Several epoxy formulations were screened for acceptable performance. The epoxy was cured in an oven at 100°C overnight. Both sides of the disk were then carefully hand-polished to expose the two sides of the crystal. The membrane was examined under an optical and a scanning electron microscope (SEM), and an acceptable membrane was placed in the permeability cell. A SEM picture of the fabricated membrane with the exposed crystal surface is shown in Figure 1. The crystal was oriented in the *c* direction. The figure shows the cross-sectional area perpendicular to the direction of diffusion.

Experimental apparatus

The details of the experimental apparatus are shown in Figure 2. The permeability cell is designed to minimize the dead volume and is enlarged here to show its details. An adsorbate gas flows on the source side of the membrane and the helium gas flows on the receiving side of the membrane. The volume on each side of the cell has been reduced to about 1.2 cc. At a typical "carrier" helium flow rate, this translates to a 0.3-s time lag within the instrument. Thus, the highest diffusivity that can be measured without significant

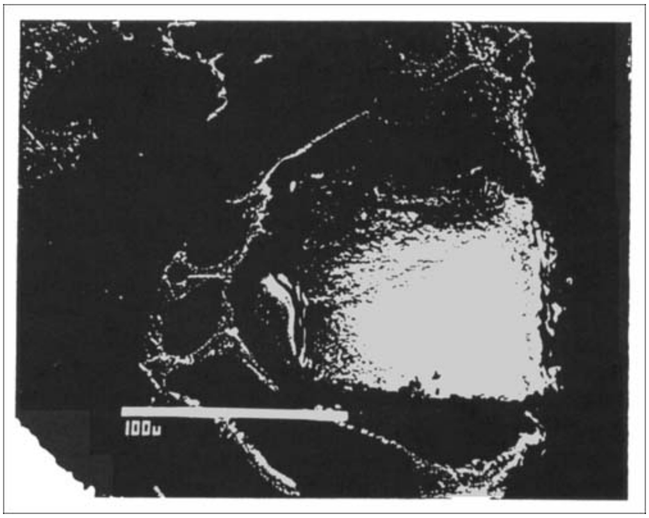

Figure 1. Scanning electron micrograph of a zeolite membrane with the exposed surface of zeolite crystal.

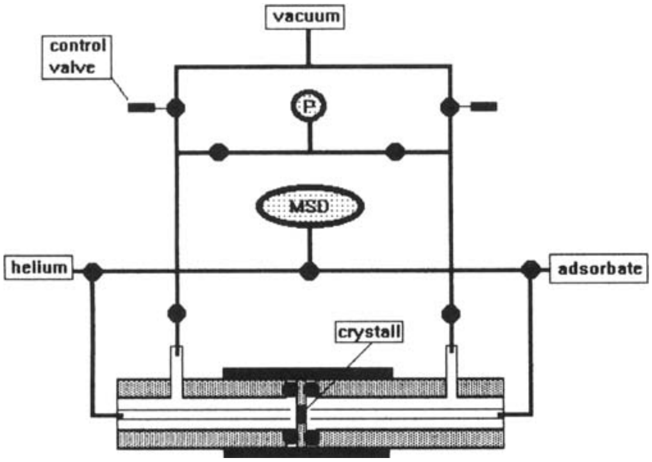

Figure 2. Experimental apparatus.

error is 3×10^{-5} cm^2/s. The permeability cell and the associated valves are fitted in a gas chromatograph oven. The entire permeability cell assembly can thus be maintained at any desired temperature within ±0.5°C.

The flowing helium in the receiving side brings the adsorbate from the membrane directly to the MSD. The MSD transfer line is custom-built for our purpose. The MSD has its own vacuum system that maintains a high vacuum (10^{-5} to 10^{-7} torr). An external vacuum pump is attached to the experimental assembly, and it is capable of producing a vacuum of 10^{-2} torr in the system. Flow controllers are placed in the two lines to regulate the flow of the helium and adsorbate gases in the system. A specially designed holder is also attached to the gas lines so that liquid adsorbates can be vaporized and introduced to the source side of the membrane.

Experimental procedure

The membrane is first tested for structural integrity by exposing the source side to a pressure of 18 torr of triethylamine (TEA). TEA molecules have a diameter of 7.4 Å, which is larger than the silicalite channel opening of about 5.6 Å. The membrane is considered to be free of defects if TEA is not detected by the MSD over an extended time (10 hours or more).

Before each experiment the membrane is activated by flowing helium on both sides at a temperature of 75°C under full vacuum for at least 3 hours. The pure adsorbate is then introduced to the source side at the desired pressure, which matches the receiving-side helium pressure. A constant flow of an adsorbate is maintained on the source side in order to prevent the pressure from decaying with time. The MSD is used to continuously detect the diffusing specie in the helium carrier gas. The concentration change is monitored as a function of time with the help of a Hewlett-Packard chemstation. For every sample, diffusivity measurements were performed at 30, 50 and 70°C. The diffusion activation energies were determined from these measurements.

Existence of helium on the receiving side and adsorbate on the source side would normally correspond to counterdiffusion if the system was not selective, that is, polymer membranes and capillary. Zeolite crystal is highly selective for the diffusing species. Helium is used as a "nonadsorbing" reference gas in all adsorption work. Nonadsorbing, in the Gibbs definition of adsorption, means the concentration of helium in the micropores equals that in the gas phase (7.94×10^{-4} mmol/cm^3, in these experiments). The adsorbed phase concentration of methane (the least strongly adsorbed specie in this work) is 2.54×10^{-2} mmol/cm^3 or about 32 times higher than that of helium. The concentration ratio of butane (the most strongly adsorbed species) to helium is about 5,300 in the micropores. These high selectivity ratios justify the assumption that the effect of the presence of helium on the micropore diffusion of other species is negligible. Similar conclusions about the impact of lighter species on the diffusion of heavy species were also drawn by Qureshi and Wei (1990) and Sircar (1992).

Linearity of the MSD response

The accuracy of the calculated diffusivity depends on the linearity of the MSD response. The linearity of the MSD response was checked with carbon dioxide at different inlet pressures. Assuming constant diffusivity in the crystal, the material balance of the diffusing specie at steady state on the receiving side gives

$$VC_f = NA = \frac{ADK}{l}(C_0 - C_f). \tag{1}$$

Rearranging the preceding equation gives the steady-state concentration of the adsorbate in the helium stream

$$C_f = \frac{ADK/l}{(V + ADK/l)}C_0. \tag{2}$$

This equation shows that the steady-state concentration on the receiving side increases linearly with the source side pressure if the experiments are carried out in Henry's Law region (Rees, 1991). If, in addition, the MSD response is linear with concentration, Eq. 2 indicates that the MSD response varies linearly with the pressure of the source side.

Figure 3 shows the steady-state MSD abundance of CO_2 on the receiving side and the CO_2-calculated diffusivities as a function of source-side pressure. The diffusivities derived from transient responses are constant and independent of pressure, indicating Henry's Law behavior. The steady-state abundance also increases linearly with the pressure on the source side, and the line goes through the origin. These two experimental observations clearly establish the linearity of the MSD response.

Data Analysis

The zeolitic diffusivity from the Wicke–Kallenbach technique can be calculated from either unsteady-state or steady-state responses. The unsteady-state calculations require only the transient response, but not the absolute concentrations. The use of steady-state calculations requires absolute concentrations that can only be determined by extensive calibration. In this part of our work, we have used only unsteady-state transients to calculate the diffusivity.

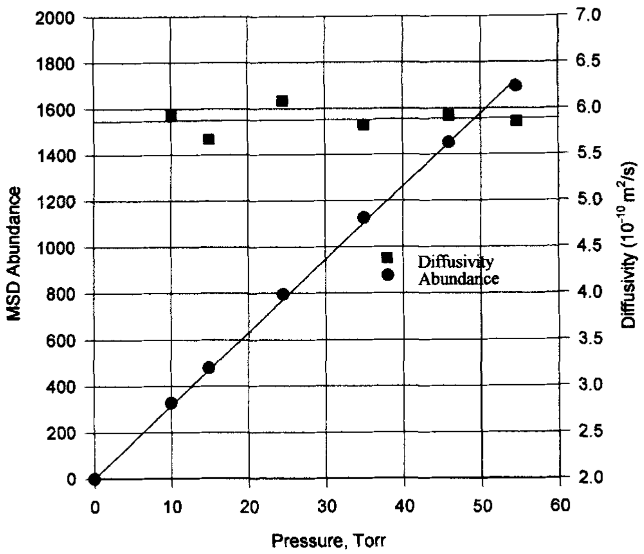

Figure 3. Effect of source pressure on CO_2 diffusivity and abundance change.

Adsorption transient

An unsteady-state material balance describing the diffusion of an adsorbate in the adsorbed phase leads to the following partial differential equation.

$$\frac{\partial q}{\partial t} = D\frac{\partial^2 q}{\partial x^2}. \tag{3}$$

Equation 3 assumes that the diffusivity is constant. The boundary and initial conditions for this partial differential equation are

$$\begin{array}{lll} q = 0 & 0 < x < L & t = 0 \\ q = 0 & x = 0 & t > 0 \\ q = q_0 & x = L & t > 0. \end{array} \tag{4}$$

The solution for the adsorbate concentration can be found as

$$q = \sum_{n=1}^{\infty} \frac{2q_0(-1)^n}{n\pi}\exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right)\sin\frac{n\pi x}{L} + \frac{q_0 x}{L}. \tag{5}$$

The concentration of the adsorbate in the helium flow is

$$VC_f = -AD\left.\frac{\partial q}{\partial x}\right|_{x=0}. \tag{6}$$

The derivative can be calculated from Eq. 5 as

$$\left.\frac{\partial q}{\partial x}\right|_{x=0} = \frac{2q_0}{L}\sum_{n=0}^{\infty}(-1)^{n+1}\exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right) + \frac{q_0}{L}. \tag{7}$$

Substituting Eq. 7 in Eq. 6 gives

$$C_f = \frac{ADq_0}{LV}\left[2\sum_{n=1}^{\infty}(-1)^{n+1}\exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right) + 1\right]. \tag{8}$$

Since the MSD response is linear with concentration in the helium flow, Eq. 8 is written in terms of two parameters, a and b

$$\text{Abundance} = a\left[2 * \sum_{n=1}^{\infty}(-1)^{n+1}\exp(-bn^2 t) + 1\right]. \tag{9}$$

During data analysis, the entire experimental response curve is used to determine the parameters a and b by nonlinear regression. The diffusivity values are then calculated from the parameter b.

Desorption transient

The desorption transient equation can be obtained in a similar way. The concentration in the helium flow, for this case, is given by

$$C_f = \frac{2DAq_0}{VL}\sum_{n=1}^{\infty}(-1)^{n+1}\exp\left(-\frac{Dn^2\pi^2 t}{L^2}\right). \tag{10}$$

In terms of a and b, the preceding equation becomes:

$$\text{Abundance} = 2 * a\sum_{n=1}^{\infty}(-1)^{n+1}\exp(-bn^2 t). \tag{11}$$

During data analysis, the diffusivities were also calculated by fitting desorption transients to abundance expression given by Eq. 11. The results of diffusivity values from the desorption transient and adsorption transient are in excellent agreement for all species in this work. Typical adsorption and desorption transients along with the curve fits and the corresponding values of a and b are shown in Figure 4. The adsorption parameters are also used to fit the data from the desorption part, the curve calculated by using the adsorption parameters and the curve fitted from its own data are on top of each other. The consistency of results is apparent by the prediction of desorption transient from the parameters obtained from adsorption as shown in the figure.

In addition to comparing diffusivity values from adsorption and desorption transient, a series of experiments was performed with CO_2 at 30°C under identical experimental conditions at different times to check the repeatability and the reproducibility of the results. It was found that the reproducibility of the measurements was excellent with 0.4×10^{-10} m^2/s standard deviation or about 5% coefficient of variation.

Results and Discussions

Diffusivities

The transport diffusivities of methane, ethane, propane, and butane in silicalite determined at 5-torr pressure and 30°, 50°, and 70°C are shown in Figure 5. The diffusivities of normal alkanes are relatively high and of the order of 10^{-10} m^2/s, and decrease as expected with the carbon number. The trans-

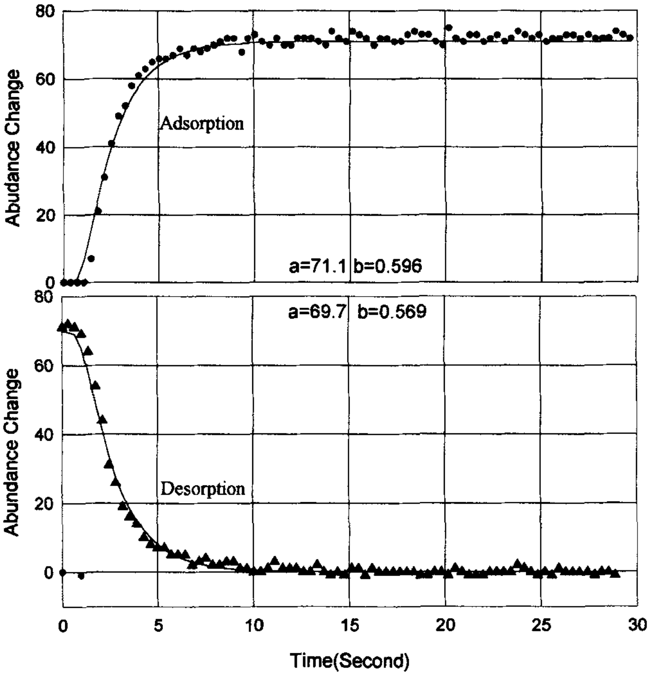

Figure 4. Typical MSD response for adsorption and desorption transients and curve fits to determine the best values of *a* and *b*.

port diffusivity result is a function of both the nature of the molecular movements and the influence of concentration. The corrected diffusivities are calculated from the transport diffusivities by applying Darken's correction factors (Karger and Ruthven, 1992). The measurements for methane and ethane are in Henry's law region (Rees, 1991). The correcting factors for propane and butane are small enough to justify the use of transport diffusivity in the transient analysis; see Eq. 3. The equilibrium data of Abdul-Rehman et al. (1990) was then used to convert the transport diffusivity to corrected diffusivity.

The corrected diffusivities of alkanes are also shown in Figure 5. Note that the corrected diffusivities show almost a linear relationship with carbon number, whereas transport diffusivities do not. The critical diameter of these alkanes is almost identical (4.2 Å), which is smaller than the channel diameter of silicalite (5.6 Å). The length of the molecules plays an important role since the diffusion path is not straight; the molecules must rotate while diffusing through the straight and zigzag channels in sequence.

Activation energy

The effect of temperature on the corrected diffusivities of alkanes and CO_2, hence the Arrhenius relationship, is depicted in Figure 6. The activation energy increases from methane to butane and is in the range of 5.1 to 10 kJ/mol, as shown in Figure 7. Also shown in the figure are literature results obtained from the compilation of Karger and Ruthven (1992). Caro et al. (1985) measured diffusivity of C_1 to C_3 alkanes in H-ZSM-5 by PFG-NMR and determined the energy of activation for methane, ethane, and propane as 4, 5 and 7.5 kJ/mol. These values compare quite well with the values determined in this work, as shown in the figure. Other values determined by Eic and Ruthven (1989) using ZLC and Van den Begin et al. (1989) using square wave for propane are 13 and 6.7 kJ/mol and are also shown in the figure. While the square-wave result is close to ours, the ZLC data for propane is almost twice as much as that obtained by any other techniques.

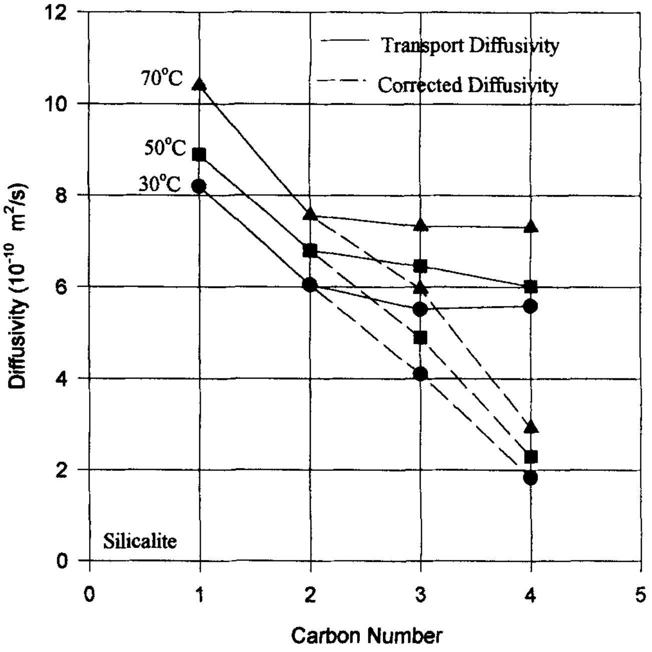

Figure 5. Transport diffusivity and corrected diffusivity of normal alkanes in silicalite.

Comparison with literature data

The main purpose of this study was to test the Wicke–Kallenbach version of the single-crystal diffusivity measurement

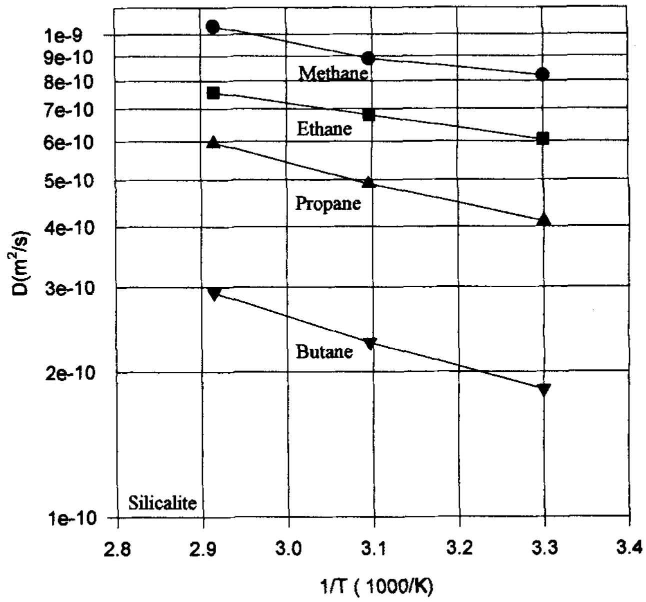

Figure 6. Temperature dependence of hydrocarbon diffusivity in silicalite.

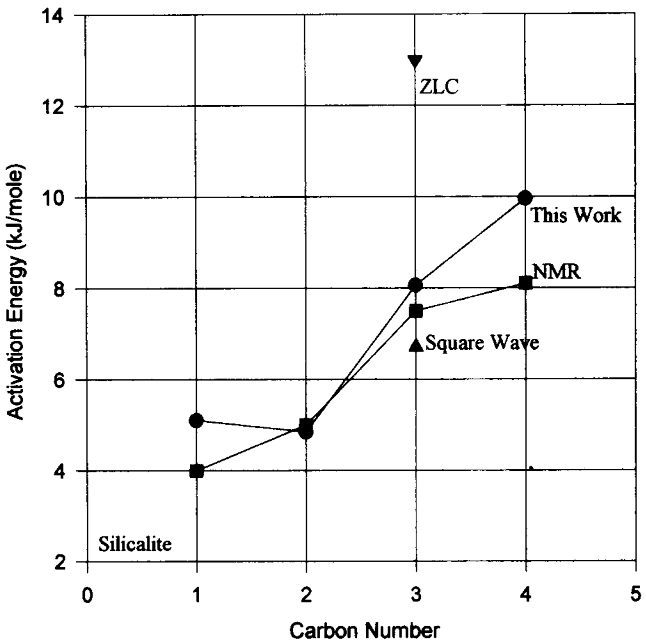

Figure 7. Activation energy of diffusion for normal alkanes in silicalite.

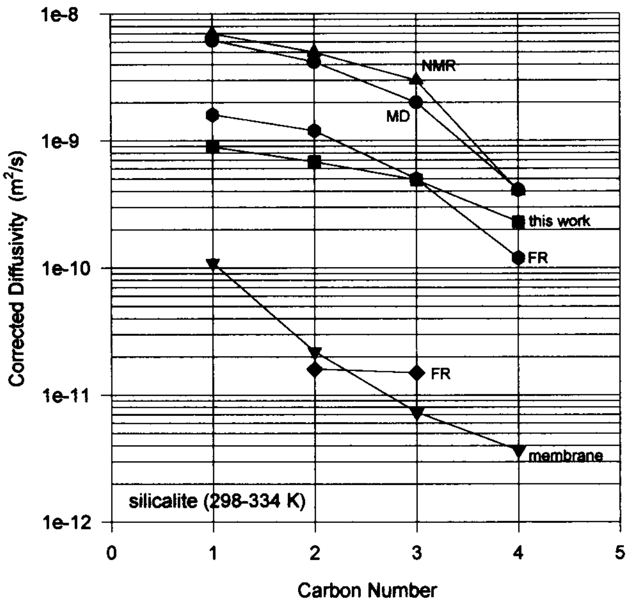

Figure 8. Comparison of diffusivities from different sources for normal alkanes in silicalite.

technique and determine its range of applicability. To test the validity of the technique, a rigorous comparison of our results and literature data was carried out. Diffusion of hydrocarbons in zeolites was studied by several research groups using different methods. Although the differences between diffusivities measured by microscopic and macroscopic methods have been explained for some systems, there are still significant differences that cannot be explained for other systems (Karger and Ruthven, 1989). The microscopic methods measure self-diffusivity and the macroscopic methods measure transport diffusivity. Usually the measurements with macroscopic method are either performed at low concentrations or the results are corrected by the Darken equation. This, therefore, cannot be considered as the cause of the discrepancy. Karger and Ruthven (1989) provided an excellent discussion on the comparison of the macroscopic and microscopic methods and why the discrepancies arise between these two types of measurements.

Figure 8 shows the diffusivity data for the systems under consideration from different sources. The results of the present work are shown along with the results from the FR measurements (Shen et al., 1991b; van den Begin et al., 1989; Bulow et al., 1989), NMR measurements (Karger et al., 1982; Caro et al., 1985; Heink et al., 1992), MD simulation results (Nowak et al., 1991; Nicholas et al., 1993; Goodbody et al., 1991), and previous membrane measurements (Hayhurst and Paravar, 1988). As usual, the agreement between the NMR measurements and MD simulations is very good. Our data show excellent agreement with the results from FR measurements. In most cases, our results and FR results are about one order of magnitude smaller than those from NMR measurements. The trends displayed by all different measurements in Figure 8 are quite similar except for the FR results by Bulow et al. (1989).

The previous membrane measurements are one order of magnitude smaller than our results. We believe that the results obtained in the present work are more accurate due to improved experimental apparatus, procedure, and the method of data analysis. The incorporation of a sensitive MSD allows us to monitor small rises in adsorbate concentrations with high accuracy. The present system imposes a concentration-gradient driving force as opposed to the pressure-difference driving force in previous measurements. The present system is dynamic rather than static. Both sides of the membrane are subjected to flowing gases. This reduces time delay, minimizes film resistances, and reduces the impact of contamination if present.

One explanation for the difference of one order of magnitude between our results and NMR measurements might be the existence of concentration gradients in our measurements and in the FR technique. A concentration gradient generally exists in the applications of adsorption. The NMR technique measures the mobility of molecules in the pores under equilibrium conditions without any gradients. Most MD calculations except a few recent efforts (Ford and Glandt, 1995a,b) are also performed for equilibrium systems. We believe that the good agreement between the NMR and MD results because both are applied under equilibrium conditions, whereas a gradient exists for all macroscopic techniques including ours.

Data by other macroscopic techniques such as uptake measurement for alkanes in silicalite are not available because the diffusion is too fast to be measured accurately. Most of the macroscopic methods are accurate for relatively slow diffusion processes. As newer methods are developed, these limits are being expanded. For example, ZLC has been used to measure diffusion of propane in silicalite (Eic and Ruthven, 1989). The FR method has been used to measure the diffusivity of ethane in silicalite (Bulow et al., 1989; van den Begin et al., 1989). With the present experimental technique, we have been able to measure successfully the diffusion of such small molecules as methane and carbon dioxide in silicalite.

A major advantage of this technique is the ability to measure diffusivity under steady-state conditions. That requires the calibration of the MSD response with concentration. In addition, the technique can be used to measure co- and counterdiffusivities in a binary system and directional diffusivity in anisotropic pore systems. The next phase of the work is directed toward meeting these goals.

Conclusions

The Wicke–Kallenbach technique, which uses a single zeolite crystal as membrane, has been applied for the first time to measure intracrystalline diffusivities of fast-diffusing species. The systematic study of diffusion of lower alkanes and carbon dioxide in silicalite proved that the technique provides highly reproducible and accurate measurements. An upper limit of diffusivity that can be measured with this technique was established as 3.0×10^{-9} m^2/s. The method also overcomes many of the limitations of the previously used static measurements.

Acknowledgment

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Notation

A = cross-sectional area of crystal, cm^2
C_0 = concentration of species in the gas phase at source and receiving side
q_0, q = concentration of adsorbates in adsorbed phase at source and receiving side
D, D_0 = transport and corrected diffusivity, cm^2/s
K = Henry constant, dimensionless
L = diffusion path length, cm
N = flux of the diffusing specie, mol/(cm$^2\cdot$s)
t = time
V = volumetric flow rates of helium, cm^3/s
x = length of diffusion paths

Literature Cited

Abdul-Rehman, H. B., M. A. Hasanain, and K. F. Loughlin, "Quaternary, Ternary, Binary and Pure Component Sorption on Zeolites: 1. Light Alkanes on Linde S-115 Silicalite at Moderate to High Pressures," *Ind. Eng. Chem. Res.*, **29**, 1525 (1990).

Bulow, M., H. Schlodder, L. V. C. Rees, and R. E. Richards, "Molecular Mobility of Hydrocarbon ZSM/Silicalite System Studied by Sorption Uptake and FR Methods," *Proc. Int. Zeolites Conf.*, Elsevier Science, New York, 579 (1989).

Bulow, M., P. Struve, and W. Mietk, "Experimental Evidence of the Influence of Sorption-Heat Release Process on the Sorption Kinetics of Benzene in NaX Zeolite Crystals," *J. Chem. Soc., Farad. Trans.*, **80**(1), 813 (1984).

Caro, J., M. Bulow, W. Schirmer, J. Karger, W. Heink, and H. Pfeifer, "Microdynamics of Methane, Ethane and Propane in ZSM-5 Type Zeolites," *J. Chem. Soc., Farad. Trans.*, **81**, 2541 (1985).

Eic, M., and D. M. Ruthven, "Intracrystalline Diffusion of Linear Paraffins and Benzene in Silicalite Studied by the ZLC Method," *Proc. Int. Conf. on Zeolites*, Elsevier, Amsterdam, p. 897 (1989).

Ford, D., and E. Glandt, "Pore Mouth Selectivity in the Separation of Mixtures on Microporous Adsorbents," AIChE Meeting, Miami Beach, FL (1995a).

Ford, D., and E. Glandt, "A Molecular Simulation Study of Barriers to Mass Transfer at the Mouths of Very Small Pores," Int. Conf. on Fundamental Adsorption (1995b).

Goodbody, S. J., K. Watanabe, D. M. Gowan, J. P. R. B. Walton, and N. Quirke, "Molecular Simulation of Methane and Butane in Silicalite," *J. Chem. Soc., Farad. Trans.*, **87**(13), 1951 (1991).

Hayhurst, D. T., and A. R. Paravar, "Diffusion of C_1 to C_5 Normal Paraffins in Silicalite," *Zeolites*, **8**, 27 (1988).

Heink, W., J. Karger, and H. Pfeifer, "High-Temperature Pulsed Field Gradient Nuclear Magnetic Resonance Self-diffusion Measurement of n-alkanes in MFI-type Zeolites," *J. Chem. Soc., Farad. Trans.*, **88**(23), 3505 (1992).

Hong, U., J. Karger, R. Kramer, H. Pfeifer, and G. Seiffert, "PFG NMR Study of Diffusion Anisotropy in Oriented ZSM-5 Type Zeolite Crystallites," *Zeolites*, **11**, 816 (1991).

Jobic, H., M. Bee, J. Caro, M. Bulow, and J. Karger, "Molecular Self-diffusion of Methane in Zeolite ZSM-5 by Quasi-elastic Neutron Scattering and Nuclear Magnetic Resonance Pulsed Field Gradient Technique," *J. Chem. Soc., Farad. Trans.*, **85**(1), 4201 (1989).

June, R. L., A. T. Bell, and D. N. Theodorou, "Molecular Dynamics Studies of Butane and Hexane in Silicalite," *J. Phys. Chem.*, **96**, 1051 (1992).

Karger, J., and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids*, Wiley, New York (1992).

Karger, J., and D. M. Ruthven, "On the Comparison Between Macroscopic and NMR Measurements of Intracrystalline Diffusion in Zeolites," *Zeolites*, **9**, 267 (1989).

Karger, J., W. Krause, and H. Pfeifer, "Intracrystalline Diffusion in ZSM-5 Zeolites," *Z. Phys. Chem.*, **264**, 838 (1982).

Nicholas, J. B., F. R. Trouw, J. E. Mertz, L. E. Iton, and A. J. Hopfinger, "Molecular Dynamics Simulation of Propane and Methane in Silicalite," *J. Phys. Chem.*, **97**, 4149 (1993).

Nowak, A. K., C. J. J. den Ouden, S. D. Pickett, B. Smit, A. K. Cheetham, M. F. M. Post, and J. M. Thomas, "Mobility of Adsorbed Species in Zeolites: Methane, Ethane and Propane Diffusivities," *J. Phys. Chem.*, **95**, 848 (1991).

Paravar, A. R., and D. T. Hayhurst, "Direct Measurement of Diffusivity for Butane across a Single Large Silicalite Crystal," *Proc. 6th Int. Zeolites Conf.*, D. Olson and A. Bisio, eds., Butterworths, Guildford, England, p. 217 (1984).

Qureshi, W. R., and James Wei, "One- and Two-Component Diffusion in Zeolite ZSM-5," *J. Catal.*, **126**, 126 (1990).

Rees, L. V. C., "Sorption and Separation of Binary Mixtures of CH_4, N_2, and CO_2 in Zeolites," *Catalysis and Adsorption by Zeolite*, G. Ohlmann, ed., Elsevier Science, New York, p. 61 (1991).

Ruthven, D. M., P. Stapleton, and K. Dahlke, "Application of the ZLC Method t the Measurement of Intracrystalline Counter-Diffusion in Liquid-Zeolite Systems," *Proc. Int. Conf. on Zeolites*, Montreal, p. 97 (1992).

Ruthven, D. M., *Principles of Adsorption and Adsorption Processes*, Wiley, New York (1984).

Shah, D. B., S. Chokchai-acha, and D. T. Hayhurst, "Measurement of Transport Rates of C_4 Hydrocarbons across a Single-crystal Zeolite Membrane," *J. Chem. Soc., Farad. Trans.*, **89**(16), 3161 (1993).

Shah, D. B., and H. Y. Liou, "Time-lag Measurements for Diffusion of Aromatics Through a Silicalite Membrane," *Zeolites*, **14**, 541 (1994).

Shen, D., and L. V. C. Rees, "Diffusivities of Benzene in HZSM-5, Silicalite-1 and NaX Determined by Frequency-Response Techniques," *Zeolites*, **11**, 666 (1991a).

Shen, D., and L. V. C. Rees, "Adsorption and Diffusion of n-Butane and 2-Butyne in Silicalite-1," *Zeolites*, **11**, 684 (1991b).

Shen, D., and L. V. C. Rees, "Study of Fast Diffusion in Zeolites using a Higher Harmonic Frequency Response Method," *J. Chem. Soc., Farad. Trans.*, **90**(19), 3011 (1994).

Sircar Shivaji, "Novel Application of Adsorption Technology," *Fundamentals of Adsorption*, M. Suzuki, ed., Kodansha, Tokyo, p. 1 (1992).

Van den Begin, N. G., L. V. C. Rees, J. Caro, and M. Bulow, "Fast Adsorption-Desorption Kinetics of Hydrocarbons in Silicalite-1 by the Single-Step Frequency Response Method," *Zeolites*, **9**, 287 (1989).

Wernick, D. L., and E. J. Osterhuber, "Permeation Through a Single Crystal of Zeolite NaX," *J. Membrane Sci.*, **22**, 137 (1985).

Wernick, D. L., and E. J. Osterhuber, *Proc. Int. Conf. on Zeolites*, D. Olson and A. Bisio, eds., Butterworths, Guildford, England, p. 122 (1984).

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