

Diffusion of Volatile Organic Chemicals in Porous Media. 2. Alcohol/Templated Porous Carbon Systems

Billur Sakintuna, Onur Çuhadar, and Yuda Yürüm*

Faculty of Engineering and Natural Sciences, Sabanci University, Tuzla, Istanbul 34956, Turkey

Received October 21, 2005. Revised Manuscript Received February 27, 2006

The aim of the present report was to measure the diffusion coefficients, modes of transport, and activation energies of some alcohols into templated porous carbons. Diffusion coefficients and activation energies of methanol, ethanol, *n*-propanol, and *n*-butanol into the templated porous carbons were measured, and the modes of transport of alcohols was determined at 24–28 °C. As the molecular weight of the alcohols increased, diffusion coefficients decreased and activation energy for diffusion increased. The diffusion constants increased linearly with an increase in the temperature. The diffusion of alcohols in the porous carbons obeyed the anomalous transport mechanism. With increasing molecular weight of the volatile alcohols, the activation energies also increased.

Introduction

Seferinoglu and Yürüm,¹ and recently Sakintuna et al.,² proposed a calculation method for the measurement of coefficients of diffusion of volatile chemicals into porous media. The calculations of diffusion coefficients, modes of transport, and activation energies of some alcohols into the mesoporous carbons in the present study are based on these reports.^{1,2}

Ordered mesoporous carbons (OMCs) make up a class of nanomaterials which were greatly developed in the last decade. Many recipes have been suggested to synthesize new OMCs of complex assemblies by using different carbon precursors and optimizing synthesis conditions (see the review article and references therein).³ In recent years, there has been growing interest in the new applications of OMCs because of their ability to interact with molecules not only with their surfaces but also in the bulk of the material.^{4–16} The size distribution and topology

of pores in materials of similar compositions can be very different, depending on the method of synthesis.

Since they have hydrophobic surfaces, high surface area, large pore volumes, chemical inertness, good mechanical stability, and good thermal stability, porous carbons are widely used as industrial adsorbents.³ Application areas are wide including gas separation, water purification, catalyst support, chromatography columns, storage of natural gas, and use as electrodes of an electric double-layer capacitor.

Diffusion plays an essential role in most phenomena occurring to molecules in porous media, e.g., it favors adsorption, makes separation of similar molecules effective, and drives chemical reactions both on the reagent side to lead the reactants into the active sites and on the product side to select and extract the species resulting from the reaction. Various techniques for the measurement of intracrystalline diffusion have been developed^{17–23} which widely vary in scope, degree of experimental and theoretical sophistication, and range of applicability. For a large number of the indirect methods, the diffusing species, or its concentration profile in the microporous material, is not directly observed; the diffusivity is rather calculated from the external measurement of pressure, concentration, or sample weight. Such computations require suitable models which describe all transport phenomena and possible sorption processes that can occur in the experimental setup.

The determination of diffusion coefficients is based on uptake measurement of the volatile component by sorbents. Analysis of the sorption data can be accomplished by various means. A

* To whom correspondence should be addressed. Phone: 90-216-483 9512. Fax: 90-216-483 9550. E-mail: yyurum@sabanciuniv.edu.

- (1) Seferinoglu, M.; Yürüm, Y. *Energy Fuels* **2001**, *15*, 135–140.
- (2) Sakintuna, B.; Fakioglu, E.; Yürüm, Y. *Energy Fuels* **2005**, *19*, 2219–2224.
- (3) Sakintuna, B.; Yürüm, Y. *Ind. Eng. Chem. Res.* **2005**, *44*, 2893–2902.
- (4) Sevilla, M.; Fuertes, A. B. *Carbon* **2006**, *44*, 468–474.
- (5) Lo, A. Y.; Huang, S. J.; Chen, W. H.; Peng, Y. R.; Kuo, C. T.; Liu, S. B. *Thin Solid Films* **2006**, *498*, 193–197.
- (6) Ania, C. O.; Bandosz, T. J. *Microporous Mesoporous Mater.* **2006**, *89*, 315–324.
- (7) Joo, J. B.; Kim, P.; Kim, W.; Kim, J.; Yi, J. *Catal. Today* **2006**, *111*, 171–175.
- (8) Weidenthaler, C.; Lu, A.-H.; Schmidt, W.; Schüth, F. *Microporous Mesoporous Mater.* **2006**, *88*, 238–243.
- (9) Wang, L.; Lin, K.; Di, Y.; Zhang, D.; Li, C.; Yang, Q.; Yin, C.; Sun, Z.; Jiang, D.; Xiao, F.-S. *Microporous Mesoporous Mater.* **2005**, *86*, 81–88.
- (10) Hampsey, J. E.; Hu, Q.; Wu, Z.; Rice, L.; Pang, J.; Lu, Y. *Carbon* **2005**, *43*, 2977–2982.
- (11) Zhou, L.; Liu, X.; Li, J.; Wang, N.; Wang, Z.; Zhou, Y. *Chem. Phys. Lett.* **2005**, *413*, 6–9.
- (12) Lu, A.-H.; Li, W.-C.; Schmidt, W.; Schüth, F. *Microporous Mesoporous Mater.* **2005**, *80*, 117–128.
- (13) Sevilla, M.; Alvarez, S.; Fuertes, A. B. *Microporous Mesoporous Mater.* **2005**, *74*, 49–58.
- (14) Fuertes, A. B. *Microporous Mesoporous Mater.* **2004**, *67*, 273–281.

- (15) Alvarez, S.; Fuertes, A. B. *Carbon* **2004**, *42*, 433–436.
- (16) Fuertes, A. B.; Nevskaja, D. M. *Microporous Mesoporous Mater.* **2003**, *62*, 177–190.
- (17) Kainourgiakis, M. E.; Stubos, A. K.; Konstantinou, N. D.; Kanellopoulos, N. K.; Milisic, V. *J. Membr. Sci.* **1996**, *114*, 215, 225.
- (18) Domontis, P.; Suffritti, G. B. *Chem. Rev.* **1997**, *97*, 2845–2878.
- (19) Haberlandt, R. *Thin Solid Films* **1998**, *330*, 34–45.
- (20) Lood, W. P.; Verheijen, P. J. T.; Moulijn, J. A. *Chem. Eng. Sci.* **2000**, *55*, 51–65.
- (21) Rallabandi, P. S.; Ford, D. M. *J. Membr. Sci.* **2000**, *171*, 239–252.
- (22) Quintard, M.; Bletzacker, L.; Chenu, D.; Whitaker, S. *Chem. Eng. Sci.* **2006**, *61*, 2643–2669.
- (23) Valdés-Parada, F. J.; Goyeau, B.; Ochoa-Tapia, J. A. *Chem. Eng. Sci.* **2006**, *61*, 1692–1704.

convenient method of analysis involves fitting the sorption data to empirical eq 1.²⁴ It is possible to express the initial rate of diffusional solvent penetration in terms of the equation:

$$\frac{M_t}{M_\infty} = kt^n \quad (1)$$

where M_t is the amount of solvent diffused in the macromolecular structure at time t , M_∞ is the amount of solvent diffused at steady state, t is the release time, k is the rate constant which depends on structural characteristics of the system, and n is an exponent characteristic of the mode of transport of the solvent in the porous structure which varies with diffusion mechanism and particle geometry.

Sorption mechanisms in macromolecular systems such as solid coals may be defined in terms of two limiting cases of Fickian diffusion and case II transport.²⁴ When $n = 0.5$, the solute diffuses through and is released from the adsorbent with a quasi-Fickian diffusion mechanism. For values of $n > 0.5$, non-Fickian solute diffusion is observed. When $n = 0.85$, case II transport occurs, and values of n between 0.5 and 1.0 indicate anomalous transport. Values above $n = 0.85$ are possible and are termed "super-case II". It is important that cited work showed that the expected values of n are sensitive to the assumed particle shape. For an infinite plain sheet, the values would be 0.5 and 1.0 for Fickian and pure case II, respectively, and in the case of an infinite cylinder, 0.45 and 0.89, respectively.²⁴ There may be differences in the diffusion behavior of different sections of the zeolite. Thus, the values of n can be used only as a rough guide as to the nature of the process. Different n and k values can be found in the literature.²⁵ Equation 1 is useful for preliminary analysis of sorption data, although it may be used up to 60% of the final weight of penetrant imbibed and it has no provisions for analysis of details, such as inflections or penetrant loss with time.^{26,27} In the graph of $\ln(M_t/M_\infty)$ versus $\ln t$, $\ln k$ is the intercept and n is the slope.^{1,28}

When a porous adsorbent system is placed in contact with a solvent (penetrant) gas, diffusion of the penetrant in the porous material may be followed by measuring the uptake of the solvent. Diffusion in the silicalite crystals can be described by Fickian diffusion with concentration-independent diffusivity, D . In Fick formulation, the driving force for diffusive transport is the gradient of chemical potential of concentration, rather than the gradient of concentration.²⁹ The kinetics of the diffusion into the sphere in Fick formulation is expressed by eq 3.³⁰

The diffusion coefficient is supposed to be constant. The basic equation, in spherical coordinates, to be solved is

$$\frac{\partial C_A}{\partial t} = D \left(\frac{\partial^2 C_A}{\partial r^2} + \frac{2}{r} \frac{\partial C_A}{\partial r} \right) \quad (2)$$

with the initial conditions

$$\begin{aligned} C_A &= C_\infty & \text{for } r = r_0 & \text{at } t > 0 \\ C_A(r) &= C = \text{const} & \text{for } 0 < r < r_0 & \text{at } t = 0 \end{aligned}$$

where C_A is the solid phase concentration (mol cm^{-3}), D is the

diffusion coefficient, constant throughout the process ($\text{m}^2 \text{s}^{-1}$), t is the time (s), r is the distance from the particle center (m), C is the initial solid phase concentration (mol cm^{-3}), and r_0 is the particle radius (m). The exact solution of eq 2 is eq 3 for gas phase diffusion to the solid solute.²⁸

Assuming the zeolite particles are of spherical shape, the solution of Fick's second law of diffusion in spherical systems gives^{1,31}

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-Dn^2\pi^2 \frac{t}{a^2}\right) \quad (3)$$

where M_t and M_∞ represent the amount of solvent diffused entering the spheres with radius a at times t and steady state, respectively, and n is an integer coming from the solution of Fick's second law. D is the coefficient of diffusion of the solvent. This equation is based on the assumption that the particle radius does not change, which is true for zeolite particles. The solution to eq 3 is given by eq 4.³²

$$\frac{M_t}{M_\infty} = 6 \left(\frac{Dt}{a^2} \right)^{1/2} \left[\pi^{-1/2} + 2 \sum_{n=1}^{\infty} i \operatorname{erfc} \frac{na}{\sqrt{Dt}} \right] - \frac{3Dt}{a^2} \quad (4)$$

For small times, eq 4 approximates to

$$\frac{M_t}{M_\infty} = 6 \left[\frac{Dt}{\pi a^2} \right]^{1/2} - \frac{3Dt}{a^2} \quad (5)$$

Neglecting the contribution of the term $3Dt/a^2$, the value of D is found from the slope of a plot of M_t/M_∞ versus $t^{1/2}$.

Diffusion is an activated process, i.e., to occur it requires overcoming an energy barrier. Other activated processes are found in zeolites, the most common examples being the adsorption of a molecule which from a gas or a liquid enters into the micropores and, especially, chemical reactions occurring in the channel and cavities. If the activation energy is smaller than, equal to, or slightly larger than the available thermal energy $k_B T$, the probability of overcoming the energy barrier is sufficiently high to allow the activated process to occur for a statistically meaningful number of times during a reasonably long simulation. Activation energies of diffusion are calculated using the equation below:

$$D = D_0 e^{-E_A/RT} \quad (6)$$

$$\ln D = \ln D_0 - \frac{E_A}{RT} \quad (7)$$

where D_0 is a temperature-independent preexponential ($\text{m}^2 \text{s}^{-1}$) and E_A is the activation energy for diffusion.³³

In this study, the diffusion coefficients, modes of transport, and activation energies of some alcohols into the porous carbons were studied. A templated carbonization method was proposed for the synthesis of porous carbons. Natural zeolite has been used as an inorganic template used to synthesize porous carbon materials. Templating, the process of filling the external and/or internal pores of an inorganic material with a carbon precursor

(24) Otake, Y.; Suuberg, E. M. *Energy Fuels* **1997**, *11*, 1155–1164.

(25) Gao, H.; Nollura, M.; Murata, S.; Artok, L. *Energy Fuels* **1999**, *13*, 518–528.

(26) Peppas, N. A.; Franson, N. M. *Polym. Phys. Ed.* **1983**, *21*, 983–997.

(27) Peppas, N. A.; Lucht, L. M. *Chem. Eng. Commun.* **1985**, *37*, 333.

(28) Inglezakis, V. J.; Grigoropoulou, H. P. *J. Colloid Interface Sci.* **2001**, *234*, 434–441.

(29) Ruthven, D. M. *Chem. Eng. Sci.* **2004**, *59*, 4531–4545.

(30) Hall, P. J.; Thomas, K. M.; Marsh, H. *Fuel* **1992**, *71*, 1271–1275.

(31) Crank, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford, London, 1976.

(32) Ndaji, F. E.; Thomas, K. M. *Fuel* **1993**, *72*, 1525–1530.

(33) Callister, W. D. *Material Science and Engineering*, 2nd ed.; New York, 1991.

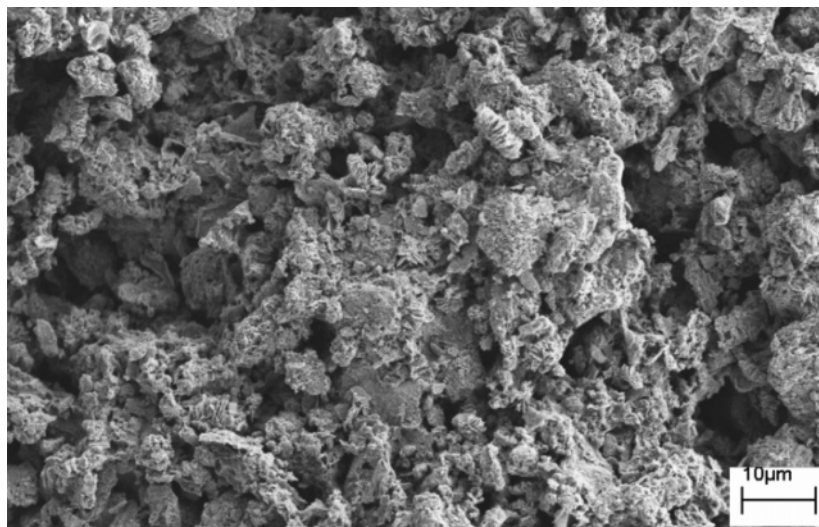


Figure 1. SEM image of natural zeolite templated carbon, carbonized at 700 °C.

and chemically separating the resulting material from the template, was used in this survey.

The template carbonization method allows one to control carbon structure in terms of various aspects such as pore structure and microscopic morphology, which makes this method very attractive. The synthesis conditions and type of template introduce controllable features to the resulting carbon product. To control the pore diameter of the porous carbons is very essential in industrial applications. The presence of micropores is essential for the adsorption of small gas molecules on activated carbons. However, when the adsorbates are polymers, dyes, or vitamins, only mesopores allow the adsorption of such giant molecules. Also, nanostructured carbon materials are potentially of great technological interest for the development of new catalysts, electronic components, fuel cell components, and hydrogen storage equipment. The aim of the present report was to measure the diffusion coefficients, modes of transport, and activation energies of some alcohols into the porous structure of the templated porous carbons.

Experimental Section

Materials. Turkish Manisa Gördes zeolite clinoptilolite, obtained from Enli Mining Corp., Izmir, Turkey (95% clinoptilolite), was used as the templating agent in the present study. Clinoptilolite was the predominant zeolite mineral produced in Turkey, especially in the Gördes area, about 130 km northeast of Manisa.

The solvents, methanol, ethanol, *n*-propanol, and *n*-butanol, were purchased from Aldrich, and they were used as received.

Procedure of the Synthesis of Natural Zeolite Templated Porous Carbons Obtained from Furfuryl Alcohol (FA). An excess of FA was mixed with zeolite in a ratio of 10 mL FA per gram zeolite, at room temperature for 5 days. The zeolite and FA mixture was then centrifuged at 2500 rpm for 30 min. The FA impregnated zeolite was polymerized at 80 °C for 24 h under argon flow at 110 mL min⁻¹, after which the temperature was raised to 150 °C for 8 h. To carbonize, the polymerized FA/zeolite composite was heated to 700–1000 °C at a 5 °C min⁻¹ rate and dwelled there for 3 h. The carbonized FA/zeolite composite was mixed with HF for 24 h. The resulting carbon was filtered and washed three times with water (200 mL each) and dried in an oven at 100 °C.

Characterization of Templated Porous Carbons. The surface area (BET)^{34,35} of the templated carbons was determined using a Micromeritics ASAP 2000 instrument. The measurement was performed at the liquid nitrogen boiling point of 77 K. The BET surface area of the templated carbons was determined from the adsorption isotherms for the degassed sample. The pore volume

distribution was calculated using a procedure developed by Barrett et al.³⁶ A Leo Supra 35VP field emission scanning electron microscope (SEM), Leo 32, was used for imaging. Imaging was generally done at an accelerating voltage of 2–5 keV, using the secondary electron imaging technique.

General Procedure of Measuring Coefficients of Diffusion.

An adiabatic isothermal setup^{1,2} designed and built in our laboratories was used in the diffusion experiments. A Sartorius CP 124S analytical balance with a 0.0001 g accuracy was placed in a Memmert Model 300 laboratory oven. At the start of the experiment, approximately 1.0000 g of 100% degassed with heating carbon sample was evenly distributed in a Petri dish and its initial weight was recorded. Four wide beakers filled with a total of 200 mL alcohol were used in each experiment, and they were placed in the closest vicinity of the balance pan. The temperature of the experiment was set, and the system was closed. After the temperature reached a constant set value 24.0–28.0 °C, the weight increase of the carbon due to alcohol vapor uptake was recorded every 5 s with the aid of Sarto Connect software installed on the PC. The experiment was continued until the software collected 2000 data points, and a constant weight was attained. All experiments were repeated at least five times.

Calculation of coefficients of diffusion, modes of transport, and activation energies of simple alcohols into porous carbons was based on a previous reports.^{1,2} For the calculation of coefficients of diffusion, the following assumptions are made: the diffusion mechanism obeys Fick's law, the crystallites possess spherical shape, the concentration profile of the sorbed gas in these spheres shows radial symmetry, the diffusion is assumed to be isotropic, it can be described by a single diffusion coefficient rather than a diffusion tensor, and the diffusion coefficient does not depend on sorbate concentration.

Results and Discussion

Diffusion coefficients, modes of transport, and activation energies of simple alcohols into the porous structure of a Turkish natural zeolite, which was used in the present study, were studied previously by Sakintuna et al.² In the present report, the diffusion of alcohols into zeolite templated porous carbons was investigated.

(34) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

(35) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723–1732.

(36) Barrett, E. P.; Jayner, L. G.; Halenda, P. H. *J. Am. Chem. Soc.* **1951**, *73*, 373.

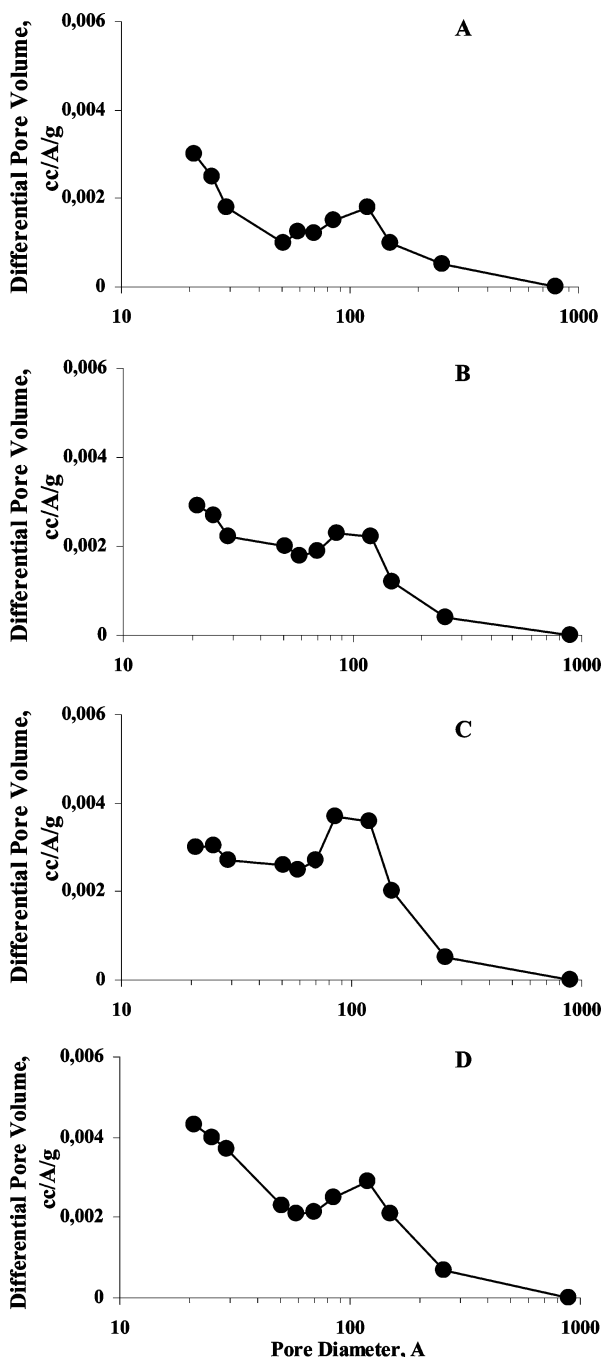


Figure 2. Pore size distribution of natural zeolite templated carbons, carbonized at (A) 700, (B) 800, (C) 900, and (D) 1000 °C.

Poly(furfuryl alcohol) (PFA) was carbonized inside the natural zeolite clinoptilolite channels at different temperatures. Porous carbons were obtained after HF washing of the template. BET surface areas of natural zeolite templated carbons were 397, 350, 405, and 367 $\text{m}^2 \text{g}^{-1}$ at 700, 800, 900, and 1000 °C, respectively. BET surface areas seemed to show almost no change with increasing temperature. SEM images of natural zeolite templated carbon, carbonized at 700 °C shown in Figure 1, indicated that the zeolite framework is reflected in the templated porous carbon. The pore size distribution of natural zeolite templated carbons were shown in Figure 2. The average pore diameter of porous carbons, carbonized at 700, 800, 900, and 1000 °C, was measured as 11 nm and indicated the presence of pores of mainly mesoporous nature.

Alcohol Uptake and Coefficients of Diffusion. The coefficients of diffusion of methanol, ethanol, *n*-propanol, and

Table 1. Coefficients of Diffusion of Volatile Alcohols in Natural Zeolite Templated Porous Carbon, Carbonized at 700 °C

alcohol type	T (°C)	D (m^2/s)
methanol	24.0	2.05×10^{-14}
	26.0	2.95×10^{-14}
	28.0	3.37×10^{-14}
ethanol	24.0	9.98×10^{-15}
	26.0	1.54×10^{-14}
	28.0	2.49×10^{-14}
<i>n</i> -propanol	24.0	8.57×10^{-15}
	26.0	1.96×10^{-14}
	28.0	2.11×10^{-14}
<i>n</i> -butanol	24.0	1.59×10^{-15}
	26.0	2.97×10^{-15}
	28.0	5.21×10^{-15}

Table 2. Coefficients of Diffusion of Volatile Alcohols in Natural Zeolite Templated Porous Carbon, Carbonized at 800 °C

alcohol type	T (°C)	D ($\text{m}^2 \text{s}^{-1}$)
methanol	24.0	1.31×10^{-14}
	26.0	1.87×10^{-14}
	28.0	2.37×10^{-14}
ethanol	24.0	1.18×10^{-14}
	26.0	1.25×10^{-14}
	28.0	2.52×10^{-14}
<i>n</i> -propanol	24.0	3.85×10^{-15}
	26.0	1.12×10^{-14}
	28.0	1.81×10^{-14}
<i>n</i> -butanol	24.0	1.45×10^{-15}
	26.0	3.00×10^{-15}
	28.0	4.10×10^{-15}

Table 3. Coefficients of Diffusion of Volatile Alcohols in Natural Zeolite Templated Porous Carbon, Carbonized at 900 °C

alcohol type	T (°C)	D (m^2/s)
methanol	24.0	1.92×10^{-14}
	26.0	2.41×10^{-14}
	28.0	2.86×10^{-14}
ethanol	24.0	1.21×10^{-14}
	26.0	1.41×10^{-14}
	28.0	2.13×10^{-14}
<i>n</i> -propanol	24.0	7.85×10^{-15}
	26.0	1.57×10^{-14}
	28.0	1.66×10^{-14}
<i>n</i> -butanol	24.0	3.21×10^{-15}
	26.0	5.00×10^{-15}
	28.0	7.99×10^{-15}

Table 4. Coefficients of Diffusion of Volatile Alcohols in Natural Zeolite Templated Porous Carbon, Carbonized at 1000 °C

alcohol type	T (°C)	D ($\text{m}^2 \text{s}^{-1}$)
methanol	24.0	1.49×10^{-14}
	26.0	1.86×10^{-14}
	28.0	2.18×10^{-14}
ethanol	24.0	1.57×10^{-14}
	26.0	2.08×10^{-14}
	28.0	2.35×10^{-14}
<i>n</i> -propanol	24.0	7.23×10^{-15}
	26.0	1.33×10^{-14}
	28.0	1.42×10^{-14}
<i>n</i> -butanol	24.0	2.41×10^{-15}
	26.0	2.51×10^{-15}
	28.0	7.46×10^{-15}

n-butanol at 24.0, 26.0, and 28.0 °C into porous carbons which were carbonized at 700, 800, 900, and 1000 °C are presented in Tables 1–4, respectively.

In all of the carbons, the coefficients of diffusion of alcohols increased with an increase in the diffusion temperature due to the higher mobility of volatile molecules. The coefficient of diffusion of methanol in the porous carbon, carbonized at 700 °C, increased from 2.05×10^{-14} to $3.37 \times 10^{-14} \text{ m}^2 \text{g}^{-1}$ when the diffusion temperature was elevated from 24.0 to 28.0 °C, respectively.

Seferinoglu and Yürüm¹ also observed that the diffusion of pyridine in coal increased with increasing temperature. Prasetyo et al.³⁷ studied the surface diffusion of hydrocarbon vapors on activated carbon by using a constant molar flow method. They concluded that the surface diffusivity increases with temperature according to the Arrhenius law and decreases with the molecular weight of the adsorbate. Sakintuna et al.² investigated the diffusion of simple alcohols into the porous structure of natural zeolite. The diffusion constants increased linearly with an increase in the temperature.²

The higher the molecular weight of the alcohol, the lower the coefficient of diffusion observed in all porous carbons, carbonized at different temperatures, owing to steric hindrances. The diffusion of methanol in the porous carbons seemed to be less, compared to those of the other alcohols. The coefficients of diffusion of methanol, ethanol, *n*-propanol, and *n*-butanol in the porous carbon, carbonized at 700 °C, were 2.05×10^{-14} , 9.98×10^{-15} , 8.57×10^{-15} , and $1.59 \times 10^{-15} \text{ m}^2 \text{ g}^{-1}$ at 24.0 °C, respectively. Prasetyo et al.³⁷ studied the surface diffusion of ethanol under constant flow over the porous carbons. Coefficients of diffusion measured by these workers are much higher ($7.09 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$) than those measured in the present work.

Do and co-workers^{38–40} proposed a model for diffusion of adsorbed species in activated carbon. In that model, it was assumed that the carbon is composed of units of graphitic layers. Molecules enter one end of the unit, diffuse within the graphitic units, and then evaporate from the other end of the unit. The process of entering the pore and leaving the pore would have energy equivalent to that of adsorption. Therefore, the “observed” activation energy for surface diffusion will fall between the activation energy for diffusion within the graphitic unit and the heat of adsorption. This seems reasonable as, for larger molecules, one would expect that the penetration into the graphitic network is more difficult than that of smaller molecules. This is the case that one would observe for a carbon molecular sieve.

The coefficients of diffusion of methanol into natural zeolite which was used a template in the present study, at 24.0, 26.0, and 28 °C were measured as 4.53×10^{-14} , 4.76×10^{-14} , and $5.00 \times 10^{-14} \text{ m}^2 \text{ s}^{-1}$, respectively.² The calculated coefficients of diffusion of volatile molecules in the porous carbons were lower than those observed in the natural zeolite that was used as a template for the carbons.² The large number and array of different functional groups on the carbon surface (e.g., carboxylic, carbonyl, hydroxyl, ether, quinone, lactone, anhydride, etc.) imply that there are many types of solute–adsorbent interactions.⁴¹ The electrostatic interaction between the hydroxyl group of alcohols and the functional groups such as carboxylic acid on the carbon surface can explain such results.

Diffusional Rate Constants and Modes of Transport of the Solvent. The diffusion rate constants, diffusion exponents, and transport mechanisms of different alcohols in the porous carbons, carbonized at 700, 800, 900, and 1000 °C, are presented in Tables 5–8, respectively. In all samples, acceptable regression coefficients (R^2) were observed. It seemed that diffusion of alcohols in porous carbons could also be approximated with a first-order rate law for all of the alcohols studied.

Table 5. Diffusion Rate Constants, Diffusion Exponents, and Transport Mechanisms of Volatile Alcohols in Natural Zeolite Templated Porous Carbon, Carbonized at 700 °C

alcohol type	T (°C)	k (s ⁻¹)	n	R^2	activation energy of diffusion (kJ/mol)
methanol	24.0	3.13×10^{-4}	0.96	0.984	92.3
	26.0	1.33×10^{-3}	0.73	0.983	
	28.0	5.15×10^{-3}	0.62	0.966	
ethanol	24.0	3.94×10^{-4}	1.00	0.963	169.7
	26.0	7.38×10^{-4}	0.99	0.969	
	28.0	4.30×10^{-3}	0.71	0.953	
<i>n</i> -propanol	24.0	2.55×10^{-4}	1.00	0.995	167.8
	26.0	2.90×10^{-4}	1.00	0.991	
	28.0	2.00×10^{-3}	0.69	0.988	
<i>n</i> -butanol	24.0	1.15×10^{-4}	1.00	0.994	220.7
	26.0	3.31×10^{-4}	1.00	0.985	
	28.0	1.18×10^{-3}	0.95	0.970	

Table 6. Diffusion Rate Constants, Diffusion Exponents, and Transport Mechanisms of Volatile Alcohols in Natural Zeolite Templated Porous Carbon, Carbonized at 800 °C

alcohol type	T (°C)	k (s ⁻¹)	n	R^2	activation energy of diffusion (kJ mol ⁻¹)
methanol	24.0	5.33×10^{-4}	0.98	0.935	111.1
	26.0	3.82×10^{-3}	0.67	0.945	
	28.0	4.14×10^{-3}	0.67	0.948	
ethanol	24.0	4.19×10^{-4}	0.98	0.998	140.7
	26.0	3.19×10^{-3}	0.62	0.996	
	28.0	4.28×10^{-3}	0.54	0.998	
<i>n</i> -propanol	24.0	3.61×10^{-5}	1.00	0.990	191.2
	26.0	5.87×10^{-4}	0.99	0.977	
	28.0	2.82×10^{-3}	0.74	0.976	
<i>n</i> -butanol	24.0	3.11×10^{-4}	1.00	0.958	193.0
	26.0	4.59×10^{-4}	1.00	0.990	
	28.0	8.61×10^{-4}	0.96	0.967	

Table 7. Diffusion Rate Constants, Diffusion Exponents, and Transport Mechanisms of Volatile Alcohols in Natural Zeolite Templated Porous Carbon, Carbonized at 900 °C

alcohol type	T (°C)	k (s ⁻¹)	n	R^2	activation energy of diffusion (kJ mol ⁻¹)
methanol	24.0	1.90×10^{-3}	0.85	0.992	74.2
	26.0	3.45×10^{-3}	0.81	0.981	
	28.0	4.66×10^{-3}	0.75	0.978	
ethanol	24.0	4.83×10^{-4}	1.00	0.983	104.4
	26.0	9.03×10^{-4}	0.49	0.987	
	28.0	4.00×10^{-3}	1.00	0.989	
<i>n</i> -propanol	24.0	2.29×10^{-4}	1.00	0.992	139.6
	26.0	3.20×10^{-4}	1.00	0.993	
	28.0	8.89×10^{-4}	1.00	0.978	
<i>n</i> -butanol	24.0	3.00×10^{-4}	0.98	0.998	169.3
	26.0	3.40×10^{-4}	0.99	0.996	
	28.0	1.00×10^{-3}	0.99	0.998	

As the temperature of diffusion was increased, the diffusion rate constants increased for all the samples. The diffusion rate constant of methanol over porous carbon, carbonized at 700 °C, was increased from 3.13×10^{-4} to $5.15 \times 10^{-3} \text{ s}^{-1}$ when the diffusion temperature increased from 24.0 to 28.0 °C.

The diffusion exponents, n , were calculated to be between 0.58 and 1.00 in all of the experiments done at all temperatures, indicating an anomalous diffusion mechanism. The anomalous coefficients of diffusion in the literature usually are in the range of 0.6–1.0.^{1,42–44} Although the literature is similar to our results, it is clear that those different techniques, models, and assumptions (crystal shape and size) may strongly affect the results.

Activation Energies of Diffusion for the Alcohols. The activation energies of diffusion measured for methanol, ethanol,

(37) Prasetyo, I.; Do, H. D.; Do, D. D. *Chem. Eng. Sci.* **2002**, *57*, 133–141.

(38) Do, D. D. *Chem. Eng. Sci.* **1996**, *51*, 4145–4158.

(39) Do, D. D.; Wang, K. *AIChE J.* **1998**, *44*, 68.

(40) Do, D. D.; Wang, K. *Carbon* **1998**, *36*, 1539.

(41) Figueiredo, J. L.; Pereira, M. F. R.; Freitas, M. M. A.; Orfao, J. J. M. *Carbon* **1999**, *37*, 1379.

(42) Peppas, N. A. *Polymer* **1997**, *38*, 3425.

(43) Peppas, N. A.; Lucht, L. M. *Chem. Eng. Commun.* **1985**, *37*, 333.

(44) Neogi, P. Transport Phenomena in Polymer Membranes. In *Diffusion in Polymers*; Neogi, P., Ed.; Marcel Dekker Inc.: New York, 1996; pp 173–209.

Table 8. Diffusion Rate Constants, Diffusion Exponents, and Transport Mechanisms of Volatile Alcohols in Natural Zeolite Templated Porous Carbon, Carbonized at 1000 °C

alcohol type	<i>T</i> (°C)	<i>k</i> (s ⁻¹)	<i>n</i>	<i>R</i> ²	activation energy of diffusion (kJ mol ⁻¹)
methanol	24.0	5.65 × 10 ⁻⁴	1.00	0.972	70.6
	26.0	4.39 × 10 ⁻³	0.95	0.960	
	28.0	5.35 × 10 ⁻³	0.87	0.962	
ethanol	24.0	2.31 × 10 ⁻⁴	0.97	0.997	76.2
	26.0	9.60 × 10 ⁻⁴	0.96	0.991	
	28.0	5.00 × 10 ⁻³	0.98	0.989	
<i>n</i> -propanol	24.0	3.22 × 10 ⁻⁴	1.00	0.979	125.5
	26.0	1.07 × 10 ⁻³	0.89	0.963	
	28.0	1.36 × 10 ⁻³	0.84	0.981	
<i>n</i> -butanol	24.0	4.00 × 10 ⁻⁴	1.00	0.979	208.9
	26.0	5.00 × 10 ⁻⁴	0.59	0.956	
	28.0	4.00 × 10 ⁻⁴	0.58	0.971	

n-propanol, and *n*-butanol over porous carbons carbonized at 700–1000 °C were presented in Tables 5–8. With increasing molecular weight of the volatile alcohols, the activation energies also increased. The activation energy of methanol in the porous carbons was measured to be the smallest among those of the alcohols, and in terms of diffusion coefficients, methanol at all temperatures was the greatest. Similar results were observed in the diffusion of alcohols in natural zeolites.

It is interesting to compare the activation energies measured in natural zeolite² and natural zeolite templated porous carbons. Calculated activation energies in natural zeolite were 18.3, 46.4, 79.7, 57.3, and 90.1 kJ mol⁻¹ for methanol, ethanol, *n*-propanol, *i*-propanol, and *n*-butanol, respectively. The activation energy for diffusion of methanol was 220.7 kJ mol⁻¹ over porous carbon, carbonized at 700 °C. Although the operating conditions are the same, the diffused methanol molecule over porous carbon has to overcome an energy barrier twice as much as that of natural zeolite. This is most likely due to the polarity of alcohols. Compounds containing the –OH group are generally highly polar and have an appreciable electrostatic field due to the resultant dipoles.⁴⁵ Being polar molecules, alcohols have stronger interaction with the carbon surface which is dispersed with functional groups.

Since the morphology of porous carbon is very complex, obtaining reliable data is one of the major problems in our quest for determining the coefficients of diffusion of volatile molecules

in this material. The irregularity of the pore structure, resulting in energetic heterogeneity of the solid surface, makes the nature of the diffusion on porous carbon materials very complicated. A detailed pore structure for this material cannot be fully determined due to the complexity of the morphology of templated porous carbons. Nevertheless, informative description can be obtained by measuring the physical properties (e.g., porosity, pore size distribution, and BET surface area) and the diffusion characteristics of organic volatile molecules on this material.

Conclusions

Diffusion coefficients, modes of transport, and activation energies of simple alcohols into the templated porous carbons were studied.

As the molecular weight of the solvent increases, coefficients of diffusion decrease, activation energies for diffusion increase, and the time necessary to come to equilibrium increases. The diffusion of *n*-butanol seemed to be less, compared to those of the smaller alcohols. In all of the samples, the coefficients of diffusion increased linearly with an increase in the temperature. The diffusion of alcohols in the porous carbons obeyed an anomalous transport mechanism. Diffusion rate constants slightly increased as the temperature was increased.

The calculated coefficients of diffusion of volatile molecules in the porous carbons were lower than those observed in the natural zeolite.² The large number and array of different functional groups on the carbon surface imply that there are many types of solute–adsorbent interactions. The electrostatic interaction between the hydroxyl group of alcohols and the functional groups such as carboxylic acid on the carbon surface can explain such results.

It is interesting to compare the activation energies measured in natural zeolite and natural zeolite templated porous carbons. The activation energies for diffusion of methanol were 90.1 and 220.7 kJ mol⁻¹ for natural zeolite and porous carbon, carbonized at 700 °C, respectively. This is most likely due to the polarity of alcohols. Compounds containing the –OH group are generally highly polar and have an appreciable electrostatic field due to the resultant dipoles. Being polar molecules, alcohols have stronger interaction with the carbon surface which is dispersed with functional groups.⁴⁶

EF0503461

(45) Glasstone, S.; Lewis, D. *Element of physical chemistry*; Macmillan: London, 1946.

(46) Warren, B. E. *Phys. Rev.* **1934**, *2*, 551.