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Diffusion of alcohols and aromatics in a mesoporous MCM-41 material

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ABSTRACT

The aim of the present paper was to measure the apparent diffusivities, Knudsen diffusivities, pore diffusivities and activation energies of diffusion at 26–32 °C and to determine the modes of transport of some alcohols (methanol, ethanol, propanol, *n*-butanol) and aromatics (benzene, ethylbenzene, propylbenzene, toluene, *o*-xylene, *m*-xylene, *p*-xylene) into the mesoporous structure of MCM-41 synthesized. As the molecular weight of the alcohols and aromatics increased, apparent diffusivities decreased and the activation energy for diffusion increased. Lower molecular weight alcohols and aromatics had higher diffusivities compared to those with higher molecular weight alcohols at the same temperatures. The diffusion of isomeric molecules within the mesoporous channels were affected by the position of branching. The deterministic behavior depended on the molecular weight, length of side chain and ortho, meta and para isomerism of the molecule. Increasing the temperature raised the kinetic energy of the molecules, which resulted in an increase in the diffusivities of the alcohols and aromatics in MCM-41. Diffusion rate constants of alcohols and aromatics increased with increasing temperature within the range of 26–32 °C, and the rate decreased as the molecular weight of the diffusing chemical increased. The diffusion of alcohols and aromatics in MCM-41 obeyed the anomalous transport mechanism. Diffusion exponents, *n*, being in the range of 0.99–1.07, indicated an anomalous diffusion (non-Fickian/super-Case II) mechanism for alcohol diffusion. However, for the case of aromatics, diffusion exponents, from 0.7 to 1.00, indicated that the diffusion mechanisms were either non-Fickian or non-Fickian/super-Case II depending on the substitution to the benzene ring. Activation energies of alcohols and aromatics were also in good agreement with the values of diffusivities of alcohols and aromatics such that larger activation energies resulted in smaller diffusivities. Alcohols and aromatics with greater solubility parameters were found to have greater diffusivities.

1. Introduction

Diffusion is the random transfer of molecules or small particles, occurring due to thermal energy. A better understanding of this phenomenon will aid in optimizing separation, kinetics, and catalytic processes industrial applications. For example, in separation processes, the necessity to comprehend the diffusion phenomena is obvious. In addition, membrane-based separations also rely on the diffusion properties of the utilized membrane. Therefore, to advance in practical applications, diffusion must be precisely understood.

Zeolites and related materials are microporous crystalline solids of special interest in the chemical and the petroleum industries, which are used as catalysts and sorbents [1]. For these applications, migration or diffusion of sorbed molecules through the pores and cages within the crystals plays a dominant role. Various techniques for the measurement of intracrystalline diffusion have been developed [2–7], which widely vary in scope, degree of experimental and theoretical sophistication, and range of applicability. For a large number of indirect methods, the diffusivity is calculated from the external measurement of pressure, concentration, or sample weight. Seferinoglu and Yürüm [8] measured the diffusivities of pyridine in raw and acid-washed low-rank coals. The method they used was simple and precise for the measurement of diffusivities of solvents in coals. Ritger and Peppas [9] and Howell and Peppas [10] studied diffusion processes to describe the transport kinetics for pyridine in coal. Bludau et al. [11] studied the uptake of pyridine into mordenite and H-ZSM-5. Their data evaluation was based on the solution of Fick's second law, using diffusivities for the whole process. Dyer and White [12] studied cation diffusion in a natural zeolite called clinoptilolite and compared three different approaches to determine diffusivities, including Fick's second law of diffusion, which was found to produce similar results with other approaches. The applicability of various models for the determination of ion exchange diffusivities in clinoptilolite was examined in another study [13]. Marecka and

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Mianowski [14] used Fick's second law to determine sorption of carbon dioxide and methane in a highly metamorphosed coal, and the results of the model were compared with the experimental kinetics of nitrogen sorption on type A zeolite.

It is proposed that there are at least five limiting types of diffusion for the molecules flowing through a zeolitic material [15]:

Case a. Unrestricted intracrystalline diffusion: the molecule moves in the channels and cavities of a crystallite without crossing the surface of the solid or extended crystal defects.

Case b. Modified intracrystalline diffusion: the particle crosses extended (e.g., dislocations and mosaic boundaries) or localized (e.g., vacancies and cations in noncrystallographic positions) crystal defects hindering or, sometimes, enhancing its motion.

Case c. Restricted intracrystalline diffusion: the molecule is reflected at the crystal boundary because of a very low probability of desorption.

Case d. Intercrystalline diffusion: the molecule migrates between different crystals, so it is sorbed most of the time but not confined to the same crystal. Sometimes this type of diffusion involves surface film formation and diffusion on the zeolite surface.

Case e. Diffusion in the fluid phase: the particle remains in the gas or liquid phase, confined only by the walls of the vessel containing the sample.

Volatile organic chemicals are one of the main side products of industry and deserve a detailed study for the applications where diffusion is important. Moreover, diffusion of volatile vapors inside zeolites is complicated because molecules not only diffuse through pores but also interact with the solid surface. Pore structure and interaction between the fluid and solid phases influence the overall diffusion rate, and therefore intraparticle diffusivity is usually system-dependent and has to be estimated experimentally. MCM-41 has high potential as an adsorbent for small and bulky adsorbate molecules due to its mesoporous structure and high surface area. Adsorption of N_2 [16–22] and water [18,23–25] on MCM-41 has been thoroughly investigated. There are also some studies based on heavier hydrocarbons, such as benzene [26,27], toluene [28], cyclopentane [29,30], cyclohexane [29–32], propane, and methane [33] on MCM-41.

For the calculation of the diffusivities, the following assumptions were made:

i. the diffusion mechanism obeyed Fick's law,
ii. the crystallites possessed a spherical shape,
iii. the concentration profile of the sorbed vapor in these spheres showed radial symmetry,
iv. the diffusion was assumed to be isotropic and it could be described by a single diffusivity rather than a diffusion tensor, and
v. the diffusivity did not depend on sorbate concentration.

The determination of diffusivities is based on the uptake measurement of the volatile component by MCM-41. A convenient method of analysis involves fitting the sorption data to empirical Eq. (1). It is possible to express the initial rate of diffusional solvent penetration in terms of this equation:

$$\frac{M_t}{M_\infty} = kt^n \tag{1}$$

where M_t is the amount of solvent diffused in to the macromolecular structure at time t,M_∞ is the amount of solvent diffused after a steady state condition is reached, 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 and varies with the diffusion mechanism and particle geometry.

When a porous adsorbent material is placed in contact with a solvent (penetrant) vapor, 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 [34]. The kinetics of the diffusion into the sphere in Fick formulation is expressed by Eq. (2) [8].

$$\frac{M_t}{M_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp(-\mathrm{D}n^2\pi^2\frac{\mathrm{t}}{\alpha^2}) \tag{2}$$

where M_t and M_∞ represent the amount of solvent vapor 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 diffusivity of the solvent vapor. This equation is based on the assumption that the particle radius does not change, which is true for zeolite particles. The solution to Eq. (2) is given in Eq. (3) [35].

$$\frac{M_t}{M_\infty} = 6\left(\frac{\mathrm{Dt}}{\mathrm{a}^2}\right)^{\frac{1}{2}}\left[\pi\frac{-1}{2} + 2\sum_{n=1}^{\infty}\mathrm{ierfc}\frac{\mathrm{na}}{\sqrt{\mathrm{Dt}}}\right] - 3\frac{\mathrm{Dt}}{\mathrm{a}^2} \tag{3}$$

For short periods of diffusion, Eq. (3) approximates to

$$\frac{M_t}{M_\infty} = 6\left[\frac{\mathrm{Dt}}{\pi\alpha^2}\right] - \frac{3\mathrm{Dt}}{\mathrm{a}^2} \tag{4}$$

Neglecting the contribution of the term $3\mathrm{Dt}/\mathrm{a}^2$, the value of D can be found from the slope of a plot of M_t/M_∞ versus $t^{1/2}$. In this study, the apparent diffusivities were calculated from the first 60% of the ramp of the uptake versus time graph. Here, the diffusion was assumed to show a linear behavior [36,37]. This linear range also includes the surface barrier resistance including resistances of reflecting boundaries and absorbing boundaries [38].

Graphs of M_t/M_∞ versus $t^{1/2}$ for the solvent vapor diffusion in mesopores were plotted in order to calculate the apparent diffusivities. The slope of this graph was used to calculate the apparent diffusivities. The type of transport mechanisms of volatile solvents in the mesopores of MCM-41 materials were predicted from the values of diffusion rate constants, k, and diffusion exponents, n, which were calculated from the graphs of $\ln(M_t/M_\infty)$ versus $\ln t$.

Pore diffusion that is the movement of fluids (gas or liquid) into the interstices of porous solids or membranes occurs in membrane separation, zeolite adsorption and reverse osmosis. Diffusion inside particles is complicated because molecules not only diffuse through pores but also interact with the solid surface. Pore structure and interaction between the fluid and solid phases influence the overall diffusion rate, and therefore intraparticle

Table 1
Physical and structural properties of MCM-41 type material synthesized by microwave assisted direct synthesis method.

Sample ID(Power/Time) (W/Min.)	BET surface area, (m^2/g)	BJH des. pore volume, (cm^3/g)	BJH des. pore Diameter,r_p, (nm)	Interplanar spacing, d_{100}, (nm)	Lattice parameter,a, (nm)	Pore qall thickness,δ, (nm)	Particle porosity, ε_m
MCM-41 (120/30)	1438	0.53	4.00	3.64	4.20	0.38	0.54