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Diffusion Characterization of a Novel Mesoporous Zeolitic Material

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Abstract. The last several years have seen a dramatic increase in the synthesis of new nanoporous materials. The promising ones include mesoporous molecular sieves (MMS) which are being developed as inorganic systems with 20–300 Å in pore dimensions, and having a narrow pore-size distribution. More recently significant efforts have been made to obtain MMS materials with enhanced hydrothermal stability and acidity. UL-zeolites belong to this class of materials in which zeolites are in the form of nano-particles, and are inter-grown in one-dimensional mesoporous structure being used as a matrix, e.g., SBA-15. UL-silicalite is one of the typical representatives of the UL-zeolites. These composite zeolitic materials possess a unique bi-porous structure consisting of micro- and mesopores. The main objective of this study is to characterize UL-silicalite with respect to its transport (diffusive) property and correlate this property with its structure using the zero length column (ZLC) method. *n*-Heptane, toluene and o-xylene were chosen as probe molecules with different kinetic diameters. Results reveal that the transport process of these probe molecules in UL-silicalite seems to be governed by combined surface/mesopore diffusion in which interconnecting micropores can also make a contribution to the overall transport process. The one-dimensional mesopore structure has strong influence on the overall transport rate. The obtained effective diffusivities of the probe molecules in UL-silicalite were found to be over one order of magnitude higher than in pure silicalite crystals, which were used as reference samples.

Keywords: diffusion, adsorption, micro-mesoporous materials, UL-silicalite, silicalite, ZLC method

Introduction

Since the discovery of hexagonally ordered MMS material named MCM-41 by Mobil scientists (Beck et al., 1992; Kresge et al., 1992), a considerable number of other ordered mesoporous materials such as HMS (Tanev et al., 1994; Tanev and Pinnavaia, 1995), MSU (Bagshaw et al., 1995), FSM-16 (Inagaki et al., 1993), PCH (Galarneau et al., 1995), KIT-1 (Ryoo et al., 1996), SBA-15 (Zhao et al., 1998) and MCF (Schmidt-Winkel et al., 1999), have been synthesized. Although these materials have relatively large pores (20–300 Å), they were limited in their industrial application due to their weak or medium acidity, which comes from amorphous nature of their walls, as well as low hydrothermal stability. More recently significant efforts have been made to obtain MMS materials with enhanced hydrothermal stability and acidity. Preparations of various

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composite materials, i.e. zeolite faujasite/MCM-41 (Kloetetra et al., 1996), MFI/MCM-41 (Karlsson et al., 1999), ZSM-5/MCM-41 (Huang et al., 2000), UL-zeolites (Trong-On and Kaliaguine, 2003) and ZCMesoAS (Trong-On and Kaliaguine, 2002) have been reported. UL-zeolites are known to have bi-porous structure consisting of micro- and mesopores in which zeolites are in the form of nano-particles, and are intergrown in one-dimensional mesoporous structure being used as a matrix. This novel class of composite materials is able to overcome the limitation of both zeolites and MMS materials and is expected to have more potential for applications in industry (Trong-On et al., 2001).

In order to evaluate the potential use of bi-porous MMS materials in industry, diffusion characterization is considered an important step in their overall characterization. In contrast to numerous diffusion studies on microporous materials like zeolites (Kärger and Ruthven, 1992), similar studies on MMS materials have been rather limited (Hansen et al., 1998; Stallmach et al., 2000; Gjerdaker et al., 2001; Seebacher et al., 2002). The microscopic methods, i.e. PFG NMR and confocal microscopy were only limited to highly mobile molecules that were used in these studies on mesoporous materials. The ZLC is a macroscopic method which has been successfully employed in a number of previous studies (Jiang et al., 2001; Jiang and Eić, 2003). This study systematically investigates the diffusion of *n*-heptane, toluene and o-xylene in UL-silicalite material at different temperatures using the standard ZLC technique. Similar measurements were also carried out for the same species in pure silicalite crystals being used as a reference material.

Experimental

Materials

UL-silicalite was obtained using an amorphous mesoporous material as a precursor, which has wormhole-like mesoporous silica structures and thick silica wall (Yang et al., 1998), followed by a secondary templated crystallization at 120°C and 6 days of aging. Tetrapropylammonium hydroxide (TPAOH) was used as template. The detailed account of synthesis procedure was provided elsewhere (Trong-On and Kaliaguine, 2003). Single silicalite crystals as a reference material were also synthesized according to the reported method (Trong-On et al., 1998). The physical properties of silicalite and UL-silicalite that are listed in Table 1 were obtained from nitrogen isotherms at 77 K using an Omnisorp-100 sorptometer. Crystallinities in % were obtained from XRD diagrams using the pure silicalite sample as a reference. The average radii estimated from the scanning electron microscope (SEM) micrographs are of 0.56 and 0.16 μm for well-shaped UL-silicalite single particles, and pure silicalite crystals, respectively which are both approximated as spheres. Some of the UL-silicalite particles are loosely bound into larger agglomerates, which can be easily disintegrated in a sonic vibrator.

Adsorption Isotherm Measurements

Adsorption isotherms of the probe sorbates on UL-silicalite sample were measured by a CAHN digital microbalance. Before carrying out isotherm measurements, about 8–10 milligrams of sample was regenerated by heating at 100°C, and then at 250°C for 3 and 6 hours, respectively. Isotherm datum points were obtained from the stable reading of microbalance after incrementing the sorbate pressure stepwise.

Diffusion Runs

The single component diffusion measurements were carried out using ZLC method. About 1–2 mg of sample was placed between two sinter discs in the ZLC column. Prior to measurement, the sample was activated overnight at 270°C purging with a small flow rate of helium (~10 cm^3/min). The sample was then

Table 1. Physicochemical properties of silicalite and UL-silicalite.

Sample	Treatment time (day)	T (°C)	S_{BET} (m^2/g)	S_{BJH} (m^2/g)	$S_{\mathrm{micropore}}$ (m^2/g)	Micropore volume (cm^3/g)	Mesopore volume (cm^3/g)	Mesopore diameter (Å)	Crystallinity (%)
Silicalite	5	175	380	55	325	0.145	0.258	–	100
UL-silicalite	6	120	480	215	265	0.103	1.043	220	47

equilibrated with sorbate diluted in a helium flow. The sorbate concentration was maintained low enough (0–0.01 torr pressure range or 0–0.0002 on the relative pressure scale) to be in the linear range of equilibrium isotherm as required by the ZLC theory. Desorption was performed by purging with pure helium at a flow rate high enough to maintain a very low sorbate concentration at the external surface of the particles, thus minimizing external mass and heat transfer resistances as required by the ZLC theory (Eić and Ruthven, 1988). A purge flow rate of 120 cm^3/min helium was used in this study. The change of effluent sorbate concentration from the ZLC column was measured by a flame ionization detector (FID), which was connected to a computer for the data acquisition and analysis. Blank curves (without a sample) were also obtained to estimate a cut-off point for the ZLC analysis (Jiang et al., 2001).

Theory

Detailed analysis of the ZLC desorption curve was presented by EiĆ and Ruthven (1988). For a linear equilibrium system with uniform spherical particles and negligible gas hold-up in the ZLC bed, the normalized effluent gas concentration (c/c_o) versus time (t) for spherical model with radius R is given by:

$$\frac{c}{c_o} = 2\mathrm{L}\sum_{n=1}^{\infty}\frac{\exp\left(-\beta_{\mathrm{n}}^2 D_{\mathrm{eff}}\, t/R^2\right)}{\left[\beta_n^2 + L(L-1)\right]} \tag{1}$$

where D_{eff} is effective diffusivity and β_n are eigenvalues given by the roots of the auxiliary equation:

$$\beta_n \cot\beta_n + L - 1 = 0 \tag{2}$$

$$\text{and}\mathrm{L} = \left(\frac{1}{3}\right)\left(\frac{\text{Purge Flow Rate}}{\text{Crystal Volume}}\right)\left(\frac{R^2}{KD_{\mathrm{eff}}}\right) = \frac{FR^2}{3KV_{\mathrm{s}}D_{\mathrm{eff}}} \tag{3}$$

where F is purge flow rate, V_s is adsorbent volume, R is individual particle radius and K is dimensionless Henry Law constant.

Effective diffusion time constant (D_{eff}/R^2) can be extracted by fitting Eqs. (1)–(3) to the experimental ZLC data using SigmaPlot 2001 software tool. This procedure has been referred as the full solution method.

Table 2. Diffusivity data of different sorbates on UL-silicalite and silicalite samples at $P <$ 0.01 torr.

Samples	Sorbate	T (°C)	L	D_{eff}/R^2 (s^{-1})	D_{eff} (m^{2}s^{-1})	E (kJ/mol)
UL-silicalite	n-Heptane	70	6	3.07×10^{-4}	0.96×10^{-16}	46.6
		80	5.5	4.61×10^{-4}	1.44×10^{-16}	
		90	5.5	7.56×10^{-4}	2.37×10^{-16}	
	Toluene	40	12	1.58×10^{-4}	0.49×10^{-16}	43.7
		50	10	2.68×10^{-4}	0.84×10^{-16}	
		60	9	4.33×10^{-4}	1.36×10^{-16}	
	o-Xylene	80	13	1.74×10^{-4}	0.55×10^{-16}	55.1
		90	13	2.89×10^{-4}	0.91×10^{-16}	
		100	14	4.76×10^{-4}	1.49×10^{-16}	
Silicalite	n-Heptane	80	12.5	1.43×10^{-4}	0.37×10^{-17}	61.2
		90	10	2.47×10^{-4}	0.63×10^{-17}	
		100	9	4.37×10^{-4}	1.12×10^{-17}	
	Toluene	70	33	0.80×10^{-4}	0.20×10^{-17}	63.4
		80	30	1.45×10^{-4}	0.37×10^{-17}	
		90	26	2.74×10^{-4}	0.70×10^{-17}	
	o-Xylene	80	19	0.67×10^{-4}	0.17×10^{-17}	79.8
		100	14	2.97×10^{-4}	0.76×10^{-17}	
		120	13	10.6×10^{-4}	2.71×10^{-17}	

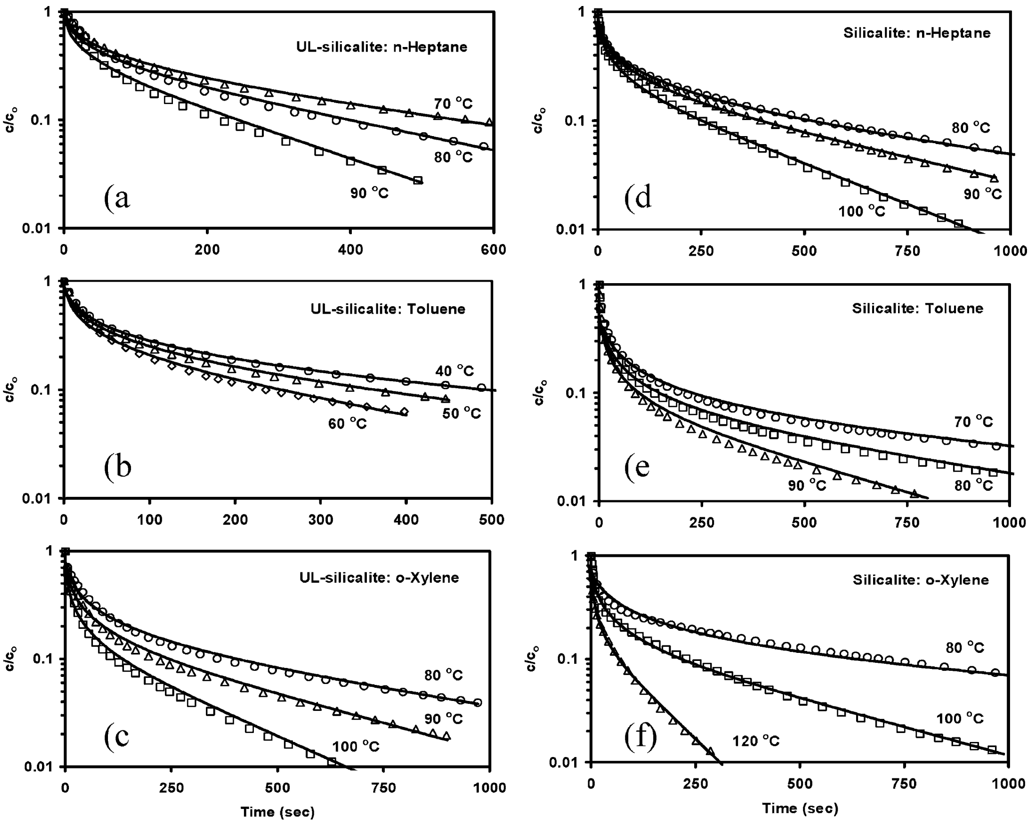

Figure 1. Experimental (symbols) and theoretical (solid lines) ZLC curves for *n*-heptane, toluene and o-xylene in UL-silicalite and silicalite samples.

Results and Discussion

The experimental ZLC desorption curves of *n*-heptane, toluene and o-xylene in UL-silicalite and silicalite samples at different temperatures were fitted by the ZLC model as shown in Fig. 1. The extracted effective diffusion time constants and corresponding L values are listed in Table 2. All L values were found to be greater than 5, which has been used as a criterion for diffusion controlled processes (Jiang and Eić, 2003). Good agreements between experimental data and the model fits are clearly observed. The mass transport through UL-silicalite structure can be approximated by a parallel process in which the effective diffusivity is represented as a sum of contributions from both phases:

$$D_{\text{eff}} = D'_{\text{surf}} + p_{\text{ch}} D_{\text{ch}} \tag{4}$$

where D'_{surf} is given by $1/D'_{\text{surf}} = 1/D_{\text{surf}} + 1/D_{\text{intra}}$ (D_{surf} and D_{intra} are considered to be combined surface diffusion and micropore diffusion through the thin walls). The second term of Eq. (4) refers to contribution in the gas phase, where p_{ch} and D_{ch} denote relative amount of sorbate and its diffusivity in the main channel space respectively. p_{ch} is much less than 1, and is inversely proportional to adsorption affinity, i.e., Henry's Law constant. Since the crystallinity of UL-silicalite is only about 50% (Table 1), the surface of the walls may be considered to consist of both crystalline nano-particles as well as an amorphous phase. The sorbate molecule may effectively slide along the surface rather than execute long trajectories with significant radial displacement in the mesoporous channel.

Furthermore sorbate molecules can penetrate the walls via microporous interconnecting channels remaining from the original mesoporous structure. All of these contributions combine in a complex bimodal structure of the UL-silicalite (Trong-On and Kaliaguine, 2001). Limited isotherm data for the sorbates at low pressures, i.e., $P < 0.85$ torr are presented

Table 3. Equilibrium parameters of different sorbates on UL-silicalite sample.

Sample	Sorbate	T (°C)	Henry's constant × 10^{-5}	Monolayer capacity (mmol/g)
UL-silicalite	n-Heptane	30	19.96	1.29
		80	1.68	0.87
	Toluene	50	1.18	1.07
		80	0.37	0.87
	o-Xylene	80	0.44	0.70
		100	0.18	0.53

in Table 3. Generally all three sorbates are strongly adsorbed, in particular n-heptane. It is somewhat surprising that n-heptane is more strongly adsorbed than the aromatic sorbates (toluene and o-xylene), i.e., much higher Henry's constant reflecting adsorption affinity in the linear region of isotherms.

The effective diffusivities of all three species in pure silicalite as a reference sample are also included in Table 2. The sequence of diffusivities in this sample is somewhat different with respect to n-heptane, which shows slower diffusivity than aromatic sorbate toluene. One of the plausible explanations could be related to relatively very high surface area of small crystals, thus rendering surface diffusion a major contributing factor in the overall transport process. In addition, small crystals are more prone to imperfections and faults in crystal structure that could significantly reduce micropore diffusion. The effective diffusivities of probe molecules in UL-silicalite are in the same order as for silicalite, i.e., toluene > n-heptane > o-xylene, while activation energies are in the reverse order. Relatively slow diffusion of the probe molecule with smallest kinetic diameter (n-heptane) is at least partially due to the very strong adsorption of these species in UL-silicalite. As shown in Fig. 1(a) n-heptane desorption curve exhibits a smaller initial concentration drop when compared to other ZLC curves (b–f) indicating equilibrium control limit in the initial part of the process (relatively low L value). n-heptane and toluene have close activation energies, which indicate a significant contribution of surface diffusion (independent of molecular size) on the mass transfer through very small silicalite crystals, i.e., 0.32 μm, which were chosen as a reference sample. Activation energies in the silicalite sample are generally much higher than in UL-silicalite indicating a more pronounced surface/micropore diffusion mechanism that occurs in small silicalite crystals. By comparing two adsorbents it is apparent from Table 2 that the effective diffusivities of probe molecules in UL-silicalite are about one and a half order of magnitude higher than in pure silicalite crystals. This trend demonstrates the strong influence of the mesoporous structure in facilitating mass transport through the complex micro-/mesopore structure of the novel materials.

Conclusions

The transport properties of n-heptane, toluene and o-xylene in UL-silicalite have been investigated at low concentration levels and several temperatures using ZLC technique. Similar measurements were also carried out involving the same species in pure silicalite crystals for the comparisons. Transport of probe molecules through the bi-porous UL-silicalite sample seems to be controlled by a complex mechanism combining surface/micropore/mesopore resistances. The one-dimensional mesopore structure has strong influence on facilitating the overall transport rate. Effective diffusivities of probe molecules in UL-silicalite sample are generally much higher in comparison with the reference silicalite crystals indicating a mass transfer process being enhanced by mesoporous structure of the UL-silicalite sample.

Extension of diffusion and structural characterizations of UL-silicalite are currently being carried out. This should contribute to better correlation between the complex bi-modal structure of the UL-silicalite and diffusive behaviour of different probe molecules.

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