DETERMINATION OF PORE ACCESSIBILITY OF NANOPOROUS CARBONS USING TRANSITION STATE THEORY

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Abstract

We present results of the crossing time of carbon dioxide and methane between two neighboring pores based on an atomistic structural model of a saccharose char (Nguyen et al., 2006), calculated over a wide range of temperatures using transition state theory (TST). The striking feature of the results is that while very fast diffusion of carbon dioxide at temperatures of 273 K or higher, with crossing time lying within the molecular dynamics scale (10^{-4} to 10^{-6} s), leads to instantaneous equilibrium at experimental time scales, extremely slow diffusion of methane below 200 K with large crossing time (> 500 days) well beyond experimental time scale (> several days) creates accessibility problems. However, the crossing time of methane above 263 K (>several minutes) significantly reduces with increasing temperature, indicating improvement of its accessibility with increasing temperature. Comparison with our recently calculated results of the crossing time of nitrogen at 77 K (Nguyen and Bhatia, 2007), suggests that for microporous materials having small window sizes, through which diffusion is strongly temperature-controlled, the use of pore size distribution extracted from nitrogen adsorption at 77 K may severely underestimate supercritical adsorption isotherms of nitrogen itself as well as argon, nitrogen, carbon dioxide, and methane at low pressure range. These effects are experimentally confirmed here.

Introduction

Porous carbons are attractive adsorbents with extremely high adsorption capacity and provide a strong adsorption field by virtue of their high density. However, in practice they contain a wide range of pore sizes, which reduces their selectivity. High adsorption selectivity is essential for capturing, storing, and separating a specific species from its mixtures, and is obtained when pore sizes are reduced to molecular dimension. Such ultrafine pores are found in carbon molecular sieves (CMS), dehydrated zeolites, and polymer derived CMS, with pore entrances through which transport of adsorbates to neighboring pores or pore cavities occurs via an activated diffusion process. Although such activated diffusion or pore accessibility is experimentally shown to be strongly temperature dependent, its molecular level basis has been scarcely investigated in the existing literature. Such understanding has significance for enhancement of adsorption selectivity of CMS by temperature adjustment, especially for separation of important mixtures of small molecules such as CO_2/CH_4, CO_2/H_2 or H_2/D_2, as well as accurate prediction of adsorption equilibrium and dynamics properties, and explanation of hysteresis in such materials.

In recent work (Nguyen and Bhatia, 2007), we have proposed a novel algorithm, which enables one to determine pore accessibility in an atomistic structural model of a disordered nanoporous material. This algorithm has been successfully utilized to determine pore accessibility of nitrogen and argon in the atomistic structural model of a saccharose char, obtained using the hybrid reverse Monte Carlo technique (HRMC) (Nguyen et al., 2006), and further validated using transition state theory (TST). From the above work, several striking features including temperature-dependent pore connectivity of nitrogen and argon in the structural model of saccharose char, and pore connectivity problem of nitrogen at 77 K but not argon at 87 K have been found. In this work, we investigate pore accessibility of carbon dioxide and methane in the saccharose char for a wide temperature range using transition state theory. In order to validate the above findings we theoretically investigate adsorption equilibrium of methane at 263 K and carbon dioxide at 323 K in the glassy carbon of Pérez-Mendoza et al. (2006), using structural parameters obtained from interpretation of experimental measurements of nitrogen at 77 K by our finite wall thickness (FWT) model, and compare the results with experimental data.

Methodology

Experimental procedure

A glassy carbon (P3M), synthesized by Pérez-Mendoza et al. (2006), and provided to us, was degassed at 300°C overnight prior to nitrogen adsorption at 77 K. A Micromeritics ASAP 2010 volumetric adsorption analyzer was used to obtain nitrogen adsorption data at 77 K in the carbon. Further, a Rubotherm GmbH gravimetric instrument was utilized to obtain the high pressure adsorption isotherm of CO_2 at 323 K in this carbon.

Mathematical modelling

Figure 1 illustrates our atomistic molecular model for the saccharose char (Nguyen et al., 2006) chosen here to study pore accessibility.
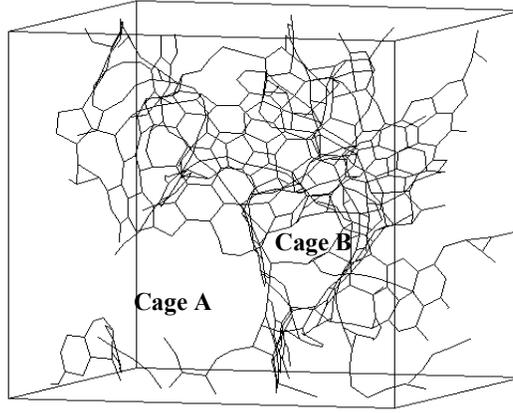

Figure 1. Snapshot of converged configuration of activated saccharose char (Nguyen et al., 2006). Cages A, B depict the detected open and closed pores respectively (Nguyen and Bhatia, 2007).

Here we apply transition state theory, as described in our recent work (Nguyen and Bhatia, 2007), to determine the crossing time of a single carbon dioxide or methane molecule from cage A to cage B, i.e. adsorption time, $\tau_{A\text{->}B}$, and the desorption time, $\tau_{B\text{->}A}$, in the atomistic structural model of saccharose char at low loading limit (Nguyen and Bhatia, 2007). Cages A and B were identified in our recent work (Nguyen and Bhatia, 2007) and are reproduced in Figure 1. According to TST, the crossing time is given as

$$\tau_{A\rightarrow B} = \frac{1}{k_{A\rightarrow B}} \qquad (1)$$

where $k_{A\rightarrow B}$ is a diffusion rate constant, given by TST as

$$k_{A\rightarrow B} = \kappa \sqrt{\frac{k_B T}{2\pi m}} \frac{\int\limits_{DS} e^{-\beta\phi_{sf}(\mathbf{r})} d^2\mathbf{r}}{\int\limits_{V_{cageA}} e^{-\beta\phi_{sf}(\mathbf{r})} d^3\mathbf{r}} \qquad (2)$$

Here κ is a transmission coefficient that represents the fraction of particles starting on top of the barrier with velocity towards cage B that successfully reach cage B, k_B is the Boltzmann constant, T is temperature and m is the mass of the particle. As previously shown (Nguyen and Bhatia, 2007), κ is approximately about unity for N_2 and Ar. In this work, κ is adapted to be unity for carbon dioxide and methane. ϕ_{sf} is the interaction potential between the adsorbate particle i at position $\mathbf{r}$ and all solid atoms of the adsorbent phase, given as

$$\phi_{sf}(\mathbf{r}) = \sum_{j=1} u(|\mathbf{r}_j - \mathbf{r}|) \tag{3}$$

where u is the LJ (12-6) solid-fluid pair potential, given as

$$u(r) = 4\varepsilon_{sf}\left[\left(\frac{\sigma_{sf}}{r}\right)^{12} - \left(\frac{\sigma_{sf}}{r}\right)^{6}\right] \tag{4}$$

To evaluate the integral in the numerator of Eq. (1) we choose the width (b) of a small cubic box, which contains the dividing surface, to be sufficiently small such that the energy landscape adjacent to the saddle point is similar for surfaces parallel to the diving surface. Here we assign b to be 0.1Å. The integral term on the right hand side (R.H.S.) of eq.(2) can be rewritten as

$$\frac{\int_{DS} e^{-\beta\phi_{sf}(\mathbf{r})} d^2\mathbf{r}}{\int_{cageA} e^{-\beta\phi_{sf}(\mathbf{r})} d^3\mathbf{r}} = \frac{1}{b}\cdot\frac{\int_{V_{box}} e^{-\beta\phi_{sf}(\mathbf{r})} d^3\mathbf{r}}{\int_{cageA} e^{-\beta\phi_{sf}(\mathbf{r})} d^3\mathbf{r}} \tag{5}$$

The two integrals in R.H.S. of eq.(5) can be directly evaluated using Monte Carlo integration. Accordingly, eq.(5) is rewritten for the case of one particle in cage A as

$$\frac{\int_{DS} e^{-\beta\phi_{sf}(\mathbf{r}')} d^2\mathbf{r}'}{\int_{cageA} e^{-\beta\phi_{sf}(\mathbf{r})} d^3\mathbf{r}} = \frac{1}{b}\cdot\frac{\frac{V_{box}}{\tau'_{max}}\sum_{n'=1}^{\tau'_{max}} e^{-\beta\phi_{sf}(\mathbf{r}'_n)}}{\frac{V_{cageA}}{\tau_{max}}\sum_{n=1}^{\tau_{max}} e^{-\beta\phi_{sf}(\mathbf{r}_n)}} \tag{6}$$

Where τ_{max} and τ'_{max} are the number of Monte Carlo (MC) trials. When the particle in the cage A falls in the dividing surface it is expected to vibrate around the saddle point of this surface due to extremely high energy around this saddle point. Accordingly, for sufficiently large number of MC trials, eq.(6) can be equivalently expressed as

$$\frac{\int_{DS} e^{-\beta\phi_{sf}(\mathbf{r}')} d^2\mathbf{r}'}{\int_{cageA} e^{-\beta\phi_{sf}(\mathbf{r})} d^3\mathbf{r}} = \frac{1}{b}\cdot\frac{e^{-\beta\langle\phi_{sf}\rangle_{N,V_{box},T}}}{\sum_{n=1}^{\tau_{max}} e^{-\beta\phi_{sf}(\mathbf{r}_n)}} \tag{7}$$

where τ_{max} is the number of grid points in cage A, which is now approximately equal to the ratio of V_{cageA} to V_{box}. $\mathbf{r}_n$ is the coordinate of grid points in cage A. Thus, for a single particle the crossing time, $\tau_{A\to B}$, from cage A to cage B is finally obtained as

$$\tau_{A\to B} = \frac{b}{\kappa}\sqrt{\frac{2\pi m}{k_B T}}e^{\beta E_a} \tag{8}$$

where $\beta = \dfrac{1}{k_B T}$ and E_a is the effective activation energy, given as

$$E_a = \left\langle \phi_{sf} \right\rangle_{N,V_{box},T} + k_B T \ln(\sum_{n=1}^{\tau_{max}} e^{-\beta \phi_{sf}(\mathbf{r}_n)}) \qquad (9)$$

We have evaluated the crossing time in Eq. (8) considering Lennard-Jones (LJ) interactions. All LJ parameters for carbon dioxide and methane as well as cross LJ parameters for solid-fluid interaction between carbon atom and these compounds used in the current work are presented in Table 1.

Table 1. LJ parameters for carbon dioxide and methane used in this work

Interaction	σ_f (Å)	ε_f/k (K)	Interaction	σ_{cf} (Å)	ε_{cf}/k (K)
CO_2-CO_2	3.6481	246.15	CO_2-C	3.429	81.49
CH_4-CH_4	3.81	148.1	CH_4-C	3.605	64.4

Results and discussion

Adsorption and desorption times of carbon dioxide and methane

Table 2 depicts calculated results of the adsorption and desorption times of carbon dioxide and methane in the atomistic structural model of saccharose char over a wide temperature range using transition state theory, as briefly described in the above section. From this table, it can be seen that adsorption and desorption times of carbon dioxide at 273 K and higher temperatures, in the range 10^{-6}-10^{-4} s, lie within the molecular dynamics time scale, indicating instantaneous adsorption equilibrium of this compound at experimental time scales.

Table 2. Results of the crossing times of carbon dioxide and methane

Carbon dioxide			Methane		
Temperature (^{o}K)	$\tau_{A->B}$ (s)	$\tau_{B->A}$ (s)	Temperature (K)	$\tau_{A->B}$ (s)	$\tau_{B->A}$ (s)
273	5.9209×10^{-5}	1.7996×10^{-4}	200	4.4559×10^{7}	5.3373×10^{7}
283	3.7958×10^{-5}	9.5426×10^{-5}	253	8.2091×10^{3}	3.8807×10^{3}
293	2.529×10^{-5}	5.2853×10^{-5}	263	2.4836×10^{3}	9.9048×10^{2}
303	1.7468×10^{-5}	3.0498×10^{-5}	273	8.2799×10^{2}	2.7938×10^{2}
313	1.2408×10^{-5}	1.8187×10^{-5}	283	3.0135×10^{2}	8.6321×10^{1}
323	9.0849×10^{-6}	1.1234×10^{-5}	323	1.0488×10^{1}	1.6270×10^{0}

Although hysteresis at experimental time scales is not observed in this work due to its short desorption time, it can be expected if the window size reduces. On the other hand, extremely long adsorption time of a single methane molecule below 200 K (> 500 days) falls beyond the experimental adsorption time scale, indicating pore accessibility problem of methane at 200 K and lower temperatures. However, the adsorption time of a single methane molecule (< a few minutes) significantly reduces above 263 K. The desorption time of methane at 200 K is significantly greater than the corresponding adsorption time by more than 100 days, suggesting

hysteresis of methane in the temperature range of 200-263 K. Indeed, hysteresis of methane at supercritical condition at low pressure was experimentally observed in carbon molecular sieves by Koresh J. E. et. al. (1990). This suggests that the use of the pore size distribution (PSD) extracted from carbon dioxide at 273 K can provide correct prediction of supercritical methane adsorption above 263 K. However, it is noted that the molecular size of methane (3.81Å) is larger than that of carbon dioxide (3.6481Å). Accordingly, it is inferred that the activation energy of methane can exceed its kinetic energy if the window size becomes slightly smaller, due to the fact that solid-fluid interaction of methane with the carbon atom then falls into the steeply repulsive region. This leads to overprediction of supercritical methane adsorption data if the PSD extracted from carbon dioxide adsorption measurements is used (Heuchel et al., 1999).

Slow diffusion of nitrogen at 77 K at experimental time scales in glassy carbon

In recent work (Nguyen and Bhatia, 2007), it was predicted that nitrogen has extremely slow diffusion rate at 77 K, with its the crossing time from cage A to B in the saccharose char ranging from several hours to several years, while the crossing time of argon at 87 K is only several minutes. In the current work, we have experimentally confirmed this finding by interpretation of adsorption measurements of nitrogen at 77 K and carbon dioxide at 323 K in a glassy carbon (P3M), reported by Pérez-Mendoza et al. (2006), using the FWT model (Nguyen and Bhatia, 2004). In order to confirm slow nitrogen diffusion at 77 K, we set a long equilibrium time (3 hours) for measurement of the nitrogen adsorption isotherm at 77 K. In Figure 2 we compare the adsorption isotherm of nitrogen at 77 K in the glassy carbon, reported by Pérez-Mendoza et al. (2006) and that obtained in our laboratory. From this figure, it can be seen that both isotherms are essentially identical in the high pressure range ($p/p_o > 10^{-4}$), but our result shows significantly higher amount adsorbed at low pressure. In Figure 3 it is interesting to see that the use of PSD extracted from our nitrogen adsorption data using the FWT model provides significant improvement of prediction of experimental methane adsorption data, reported by Pérez-Mendoza et al. (2006), especially at low pressure, despite significant underestimation of the data at high pressure range. On the other hand, it is noted that the use of PSD extracted from our nitrogen adsorption data at 77 K predicts correctly supercritical carbon dioxide adsorption measurement at 323 K using LJ parameters taken from our previous work (Nguyen et al., 2005) but which very slightly underpredicts at high pressure, as depicted in Figure 4.
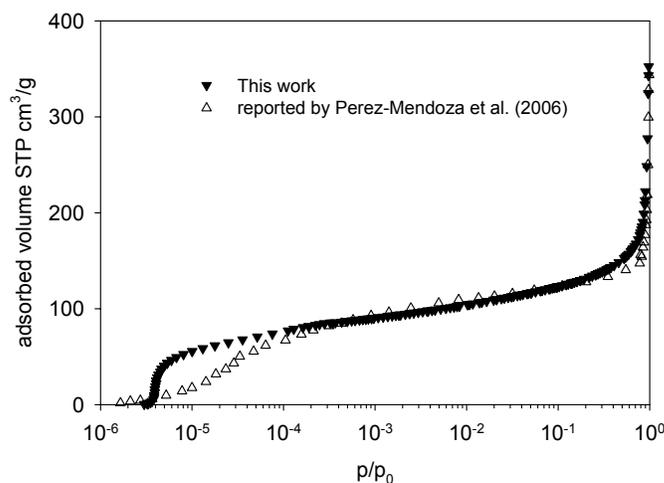

Figure 2. Experimental nitrogen adsorption in a glassy carbon (P3M) at 77 K

Accordingly, such significant underprediction of methane adsorption data, reported by Pérez-Mendoza et al. (2006), using the PSD extracted from our nitrogen adsorption data at 77 K may be assigned to a slight variation of micropore structure of the glassy carbon, reported by Pérez-Mendoza et al. (2006), from that received by us. However, further investigation on this issue is needed. Consequently, the underestimation of experimental adsorption data of carbon dioxide at 323 K and methane at 263 K using the PSD extracted from nitrogen adsorption data at 77 K confirm higher accessibility of these compounds at supercritical conditions than that of nitrogen at 77 K. This is consistent with the above calculated results of crossing time of carbon dioxide and methane.
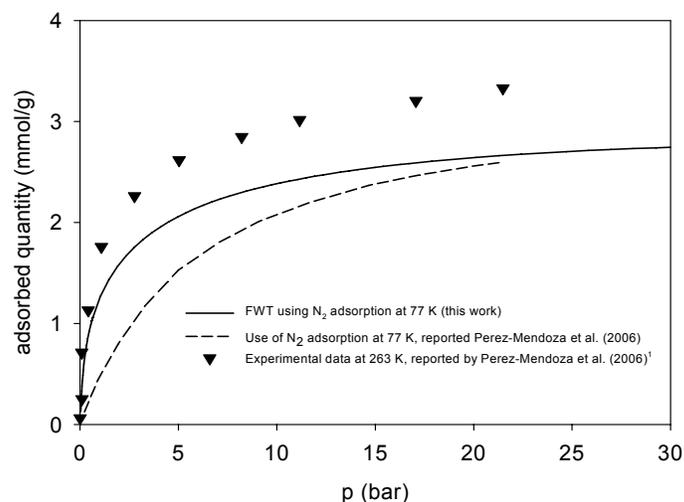
Figure 3. Prediction of adsorption equilibrium of methane in the glassy carbon at 263 K.
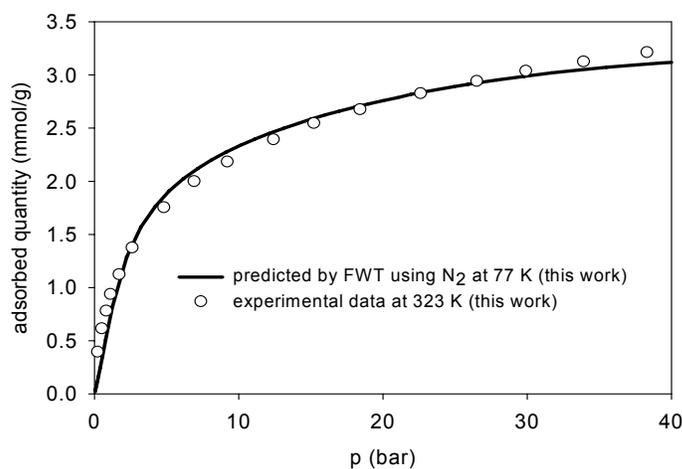

Figure 4. Prediction of adsorption equilibrium of carbon dioxide in the glassy carbon at 323 K.

Conclusions

The main goal of this work is to theoretically investigate pore accessibility of various gases (N_2, CO_2, CH_4) in the atomistic structural model of saccharose char, and to provide explanation of the long standing problem of pore accessibility of these gases in nanoporous carbon, especially in carbon molecular sieves. Accordingly, crossing times (adsorption and desorption times) of a single molecule (carbon dioxide, methane in this work and argon and nitrogen in recent work (Nguyen and Bhatia, 2007)) through cages A and B in the atomistic structural model of saccharose char over a wide temperature range is determined using transition state theory. The crossing times or diffusion rates of all the investigated gases are strongly temperature dependent, implying the importance of appropriately choosing temperature to improve selectivity. No hysteresis and pore accessibility problem has been found for carbon dioxide at 273 K and higher temperatures. However, for mrthane there existe hysteresis in the temperature range of 200-263 K, and a pore accessibility problem at 200 K and lower temperatures. Nitrogen adsorption at 77 K in glassy carbons is experimentally shown to be slow. Further, underestimation of methane and carbon dioxide adsorption at 263 K and 323 K is consistent with the

calculated results of the crossing times of these compounds presented in this work. Finally, it is clear from this work that the use of subcritical nitrogen adsorption at 77 K for characterization of microporous carbons may lead to serious errors in the determination of micropore volume while the use of carbon dioxide isotherm at 273 K and methane above 313 K are appropriate choices for this task.

Acknowledgement

References

Heuchel M.; Davies, G. M.; Buss, E.; and Seaton, N. A. 1999. Adsorption of carbon dioxide and methane and their mixtures on an activated carbon: Simulation and experiment. Langmuir 15(25):8695-8705.

Koresh, J. E.; Kim, T-H; Walker D. R. B.; and Koros W. J. 1990. Study of ultramicroporous carbons by high-pressure sorption part5.-CH4 isotherm and diffusion kinetics. J. Chem. Soc. Faraday Trans. 86(12):2267-70.

Nguyen, T. X.; Bhatia, S. K.; Jain, S. K. and Gubbins, K. E. 2006. Structure of saccharose-based carbon and transport of confined fluids: hybrid reverse Monte Carlo reconstruction and simulation studies. *Mol. Sim.* 32(7):567-77.

Nguyen, T. X. and Bhatia, S. K. 2007. Determination of pore accessibility in disordered nanoporous materials. J. Phys. Chem. C. 111(5):2212-22.

Nguyen, T. X. and Bhatia, S. K. 2004. Probing the pore wall structure of nanoporous carbons using adsorption. Langmuir 20(9):3532-35.

Nguyen, T. X.; Bhatia, S. K.; and Nicholson, D. 2005. Prediction of high-pressure adsorption equilibrium of supercritical gases using density functional theory. Langmuir 21(7):3187-97.

Perez-Mendoza M.; Schumacher , C.; Suárez-García; Almazán- Almazán, Domingo-García; López-Garzón; Seaton, N.A. Analysis of the microprous texture of a glassy carbon by adsorption measurements and Montecarlo simulation. Evolution with chemical and physical activation. Carbon 44 (4):638-645.