Supporting Information

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Characterization of Micro-Mesoporous Materials from Nitrogen and Toluene Adsorption: Experiment and Modeling

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SI1. Solid-fluid interactions and molecular simulations details.

Interactions between each of the carbon atoms of toluene molecule and a structureless cylindrical layer of solid atoms were described using the potential of Tjatjopoulos et al [1].

$$U_{\mathrm{sf}}(r,R)=\pi^2\rho_s\varepsilon_{sf}\sigma_{sf}^2\left[\frac{63}{32}\left[\frac{R-r}{\sigma_{sf}}\left(1+\frac{r}{R}\right)\right]^{-10}F\left[-\frac{9}{2},-\frac{9}{2};1;\left(\frac{r}{R}\right)^2\right]-\right.$$

$$\left.3\left[\frac{R-r}{\sigma_{sf}}\left(1+\frac{r}{R}\right)\right]^{-4}F\left[-\frac{3}{2},-\frac{3}{2};1;\left(\frac{r}{R}\right)^2\right]\right] \qquad \text{(S1)}$$

where, r is the radial coordinate of the fluid atom reckoned from the pore center, R is the radial coordinate of the adsorption centers (pore radius), ρ_s is the surface number density of adsorption centers, $F[\alpha,\beta,\gamma,\delta]$ is the hypergeometric series. This solid-fluid potential was used for all seven carbon sites of the toluene molecule: $\rho_s\varepsilon_{sf}/k$ = 1584.5 K/nm^2, σ_{sf}=0.32nm

Surface heterogeneity was modeled by randomly placed attractive and repulsive sites in addition to the uniform potential given by Eq. S1. These additional sites were located at a distance of 0.32 nm from the surface (just slightly less than the minima of the solid-fluid potential, Eq. S1). Each site created a spherical potential well of 0.38nm in radius. If the center of mass of a toluene molecule was found within the well, a perturbation energy ε_{ww} was added to the total solid-fluid energy of the molecule. Three types of sites were introduced: attractive sites with ε_{ww}/k = -980 K and ε_{ww}/k = -780 K, and repulsive sites with ε_{ww}/k = 780 K. Attractive sites were introduced in order to increase adsorption at low pressures. Repulsive sites were introduced in order to prevent the formation of a dense monolayer of toluene molecules oriented parallel to the wall. The surface number densities of the sites were 0.14, 0.83 and 0.66 nm^{-2}, respectively. The sites were randomly distributed over the surface, and were allowed to overlap. It was found that random generation of sites with a given density did not affect appreciably the adsorption isotherms. An example of the distribution of attractive and repulsive sites on the surface of a 4.5 nm diameter pore is shown in Figure S2.

Adsorption/desorption isotherms were simulated using the standard grand canonical MC (GCMC) method [2]. The pressure of the vapor-liquid equilibrium transition in mesopores was determined using the gauge cell simulation method [3]. At each given pressure, ca. 450000 trial insertions, removals and displacements per toluene molecule were performed. Equilibration was performed over the last 300000 steps. Periodic boundary conditions with a period of not less than 3.9 nm (for the smallest pore) were applied in the longitudinal direction. The maximum number of toluene molecules in the largest 7.3 nm diameter pore considered was about 1040.

Table S1. LJ parameters of fluid-fluid and solid-fluid interactions.

ε_{CH}/k, K	50.5	ε_{CH3}/k, K	98.0
σ_{CH}, nm	0.3695	σ_{CH3}, nm	0.375
ε_{C}/k, K	21.0	$\rho_s\varepsilon_{sf}/k$, K/nm^2	1584.5
σ_{C}, nm	0.388	σ_{sf}, nm	0.32

σ is the effective atom diameter and ε is the well depth of the LJ potential. The molecular model for toluene is based on a model of Wick et al [4]. The LJ potential for fluid-fluid interactions was truncated at 0.97nm. Parameters for interactions between unlike carbons are obtained via Lorentz-Berthelot rules: $\sigma_{ij} = (\sigma_i + \sigma_j)/2$, $\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2}$

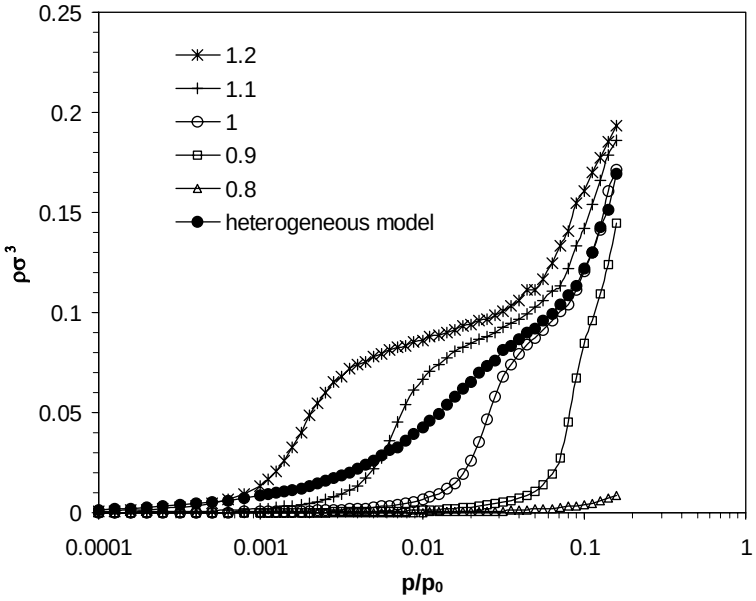

Figure S1. Simulated toluene adsorption isotherms on MCM-41 silica at 298 K. Heterogeneous potential model is compared with the uniform potential model (Eq. S1). The numbers on the legend correspond to the ratio of the effective solid-fluid LJ energy constant to the value actually used (see Table S1).

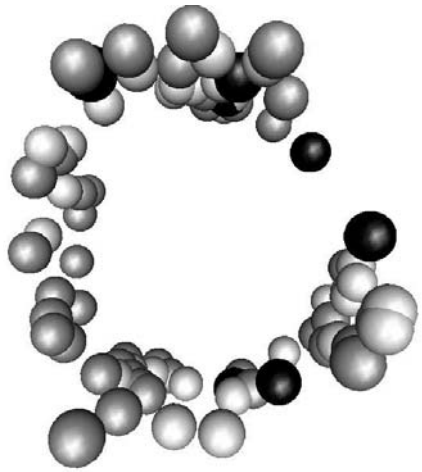

Figure S2. Distribution of attractive and repulsive sites on the surface of 4.5 nm diameter cylindrical pore. The three types of sites are shown as black, gray and light gray, respectively (see text).

SI2. Derjaguin-Broekhoff-de Boer Equations

In a cylindrical pore of radius R_P, the thickness of the adsorbed film h is determined by the balance of the capillary and disjoining pressures , and is given by the following equation [5]:

$$\Pi(h)V_L + \frac{\gamma V_L}{R_P - h} = RT\ln(P_0/P) \tag{S2}$$

Here γ =28.5 mN/m and V_L =0.1 cm^3/mmol are the surface tension and the molar volume of toluene at 298 K, respectively; $\Pi(h)$ is the disjoining pressure. For the adsorption of toluene on MCM-41-type silica substrates, we used an exponential form [6] of the disjoining pressure isotherm:

$$\ln(P_0/P) = \frac{V_L\Pi(h)}{RT} = \frac{F(h)}{RT} = Ke^{-h/L} \tag{S3}$$

with the parameters K =8.13 and L =0.27 nm we had chosen to reproduce the mono-multilayer part of the isotherm on reference MCM-41.

Capillary condensation occurs at the limit of stability of the adsorption film. The limit of stability corresponds to the critical film thickness $h = h_{cr}$, given by:

$$-\left(\frac{d\Pi(h)}{dh}\right)_{h=h_{cr}} = \frac{\gamma}{\left(R_P - h_{cr}\right)^2} \tag{S4}$$

Desorption from a cylindrical capillary is determined by the condition of formation of an equilibrium meniscus given by the Derjaguin equation [7,8]:

$$RT\ln(P_0/P) = \frac{2\gamma V_L + \frac{2V_L}{(R_P - h_e)}\int_{h_e}^{R_P}(R_P - h)\Pi(h)dh}{R_P - h_e} \tag{S5}$$

Here, h_e is the thickness of the adsorbed film in equilibrium with the meniscus, given by Eq. (S2).

SI3. Hybrid MC-DBdB Method for Pore Size Distribution Calculations.

The pore size distribution is determined from the generalized adsorption equation, which represents the experimental isotherm $N_{\exp}(P/P_0)$ as a combination of the theoretical isotherms in pores of different diameters *D*. MC simulated isotherms were used in pores smaller than D^*= 4.5 nm in diameter and DBdB calculated isotherms were used in larger pores:

$$N_{\exp}(P/P_0) = \int_{D_{MIN}}^{D^*} N_{MC}(D, P/P_0)\varphi(D)dD + \int_{D^*}^{D_{MAX}} N_{DBdB}(D, P/P_0)\varphi(D)dD \qquad \text{(S6)}$$

Here $N_{theor}(D, P/P_0)$ is the kernel of MC simulated isotherms; $N_{DBdB}(D, P/P_0)$ is the kernel of DBdB isotherms, and $\varphi(D)$ is the pore size distribution function. Solution of the integral equation (S6) was obtained by regularization methods [9,10].

References

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