42d A Simulation Study of Capillary Condensation and Freezing of Krypton within Realistic Models of MCM-41 Materials

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Templated mesoporous silica material MCM-41 consists of hexagonal arrays of cylindrical pores with diameters between 1.5 and 20 nm, narrow pore size distributions and negligible pore networking. These and other properties make MCM-41 materials suitable for a number of applications in catalysis, adsorption, optics and electronics, low-k materials, and as host materials for polymers, nanoparticles and enzymes [1]. In addition, these materials are ideal for fundamental studies aimed at determining the effect of surface forces, confinement and reduced dimensionality on the phase behavior of host molecules. Recently, Coasne et al. [2,3] developed a fully atomistic model of MCM-41 materials, based on the morphological features of a mesoscale model obtained from lattice Monte Carlo simulations mimicking the synthesis of MCM-41 materials [4]. In doing this "downscaling" process, we were able to include atomic details in their pore model, as well as use accurate potentials to represent the adsorbate-wall interactions [2,3]. Pores with an important degree of surface roughness and structural defects were obtained from this simulation protocol [2,3], so that the effect of those variables on the phase behavior of confined molecules can be assessed. In that sense, we report molecular simulations of capillary condensation and freezing of krypton within silica mesopores with an average pore diameter of 6.4 nm. Three atomistic pore models were used: (1) the MCM-41 model developed in Refs. [2,3]; (2) a smooth, regular cylindrical pore; and (3) a cylindrical pore with constrictions. Results for gas adsorption [2,3,5] indicate that these phenomena are significantly affected by surface roughness and structural defects: marked differences were observed in the adsorption isotherms, isosteric heat curves and pore filling mechanisms for the three pore models. An investigation of the freezing behavior of Kr confined in these pore models is currently in progress, to determine the effect of pore surface roughness and structural defects on the freezing temperature and on the global and local structure of the solid phases. Preliminary results for freezing [5] show that the dense phase of Kr inside these three pore models exhibit a liquid-like global structure, even at T=87 K (29 K below the bulk triple point); however, crystal-like clusters are observed in the central regions of the three pores at T=72 K, surrounded by amorphous clusters of particles close to the pore walls.

[1] For recent reviews, see P. Selvam, S. K. Bhatia and C. G. Sonwane, Ind. Eng. Chem. Res., 40 (2001) 3237; G. J. de A. A. Soler-Illia, C. Sanchez, B. Lebeau and J. Patarin, Chem. Rev., 102 (2002) 4093; F. Schüth and W. Schmidt, Adv. Mater., 14 (2002) 629. [2] B. Coasne, F. R. Hung, F. R. Siperstein and K. E. Gubbins, Ann. Chim-Sci. Mat., in press (2005). [3] B. Coasne, F. R. Hung, R. J.-M. Pellenq, F. R. Siperstein and K. E. Gubbins, Langmuir, submitted (2005). [4] F. R. Siperstein and K. E. Gubbins, Mol. Sim., 27 (2001) 339; Langmuir, 19 (2003) 2049. [5] F. R. Hung, B. Coasne, K. E. Gubbins, F. R. Siperstein and M. Sliwinska-Bartkowiak, Stud. Surf. Sci. Catal., submitted (2005).