Simulation of argon, krypton and nitrogen adsorption in silicalite

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Nitrogen adsorption isotherm in silicalite at 77 K has a well-defined hysteresis loop in the region of $p/p^o = 0.12 - 0.15$ that is not associated with capillary condensation[1]. It has been suggested that this hysteresis loop is related a solid-liquid transition considering that the ratio of densities before and after the hysteresis loop is similar to the ratio of densities between liquid and solid nitrogen.

Microcalorimetric and high-resolution adsorption measurements have revealed the presence of an additional small sub-step in the nitrogen adsorption isotherm, and the presence of small steps in both argon and krypton adsorption isotherms[2−3].

In the case of argon, the step is associated to an exothermic change and has been related to a transition from a disordered phase to a solid like structure. Krypton, on the other hand, shows a very simmilar behavior to argon at low pressures, but the step observed is associated to an endothermic change[3]. While there is not a satisfactory experimental explanation to this phenomena, it is believed that is related to stronger confinement effects for krypton than for argon in silicalite.

Nitrogen undergoes a similar overall change, but it takes place in two stages. The first transition involves a change from disoreder mobile phase to a localized state called *lattice fluid-like phase*. The second transition led to the formation of a solid-like commensurate structure.

In this work, we calculate the adsorption isotherms for argon, krypton and nitrogen in silicalite using grand canonical Monte Carlo simulations. The main transitions for argon and nitrogen in silicalite have been observed previously[4] although the small sub-step in the nitrogen adsorption isotherm was not found. Argon and krypton are modeled as single Lennard-Jones spheres and nitrogen is modeled as a two cen-tre Lennard-Jones spheres with point quadrupole. Silicalite is modeled as a rigid framework, assigning effective potentials to the oxygen atoms that account for dispersion interaction of both oxygen and silicon atoms. The solid-fluid interactions are pretabulated in a grid over the assymetric unit cell, with spacing between points of approximately 0.001 nm.The solid-fluid potential at any point is obtained from linear interpolation between the eight nearest grid points.

Calculated adsorption isotherms at 77 K, enthalpies of adsorption and radial distribution functions for the three fluids are compared with experimental evidence. Comparison in the adsorption behavior of nonpolar fluids of different sizes (argon and krypton) are presented.

It is traditionally accepted that for microporous adsorbents, fluid-fluid interactions are not as important as fluid-solid interactions. Here is shown that at high loadings fluid-fluid interactions, and in particular quadrupole-quadrupole interactions, can be responsible for differences in the behavior of adsorbed spherical nonpolar molecules. and linear molecules containing a quadrupole moment.

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