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Molecular simulation of water adsorption in silicalite: Effect of silanol groups and different cations

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ABSTRACT

Using GCMC and MD simulations we investigated the effect of silanol groups and extraframework cations on water adsorption, diffusion and the structure of water in silicalite. The adsorption of water was enhanced with the introduction of defects. In the case of cations this enhancement was much more significant. Below the saturation pressure of water no filling of pores by water molecules was observed. Introduction of silanol nests did not result in significant changes in water structure and self diffusion. On the other hand, the presence of cations decreased self diffusivity of water and changed the water structure observed in the defect-free silicalite. Silanol nests were found to be weak defects and have a limited effect on water adsorption. The model we used in this study satisfactorily predicted adsorption isotherms and heats of adsorption, however, self diffusion coefficients of water were underestimated which is attributed to the rigid treatment of the silicalite lattice.

1. Introduction

Zeolites are microporous aluminosilicate materials traditionally used in catalysis, ion exchange, and separation applications [1]. Silicalite is an all-silica MFI type zeolite [2]. Silicalite generally is accepted as a hydrophobic material, [3] and in several experimental studies it was shown to preferentially adsorb organics from water [4–8]. The hydrophobicity of silicalite is attributed to the $\equiv$Si–O–Si$\equiv$ bonds, however, defects in the structure of silicalite allow certain amounts of water to be adsorbed [9]. There are two common types of defects. The first are the extraframework cations, which account for non-neutrality of the silicalite framework due to presence of aluminum sites which substitute the missing silicon atoms [10]. The second type of defect is Si–OH groups. During the synthesis of a zeolite, broken Si–O bonds are attacked by water molecules and Si–OH groups are formed instead of continuous Si–O–Si network. This may occur either on the external surface of a zeolite, where Si–O–Si network is terminated and oxygen atoms cannot be bonded to a Silicon atom, or within the zeolite lattice where a silicon atom is missing. In the latter case four Si–OH groups are formed per each missing silicon atom and this structure is called a silanol nest [11,12].

Although the behavior of water in silicalite is interesting, experimental and simulation studies of water adsorption in silicalite are not abundant in the literature. While most of the experimental data regarding water adsorption in silicalite were obtained below saturation pressure, [6,13–17] there are a few studies which focused on the capillary filling effect observed at very high pressures [18,19].

Perhaps the most thorough work on water adsorption in ZSM-5 crystals was the study reported by Olson et al. [15]. In that experimental work, they evaluated ZSM-5 samples provided by Mobil Research & Development Corporation having SiO_2/Al_2O_3 ratios of 72 up to 8660. The Al-sites were ion exchanged with NH_4^+, and subsequently calcined to transform the sites to the proton form. They noted that the water adsorption capacity was proportional to the framework Al-content; however, they reported that the water adsorption, reported as H_2O/Al was remarkably uniform at a level of four over a wide range of Al-contents. They suggested that this supported the prior conclusion that water molecules hydrate the Al-proton site. In samples in which the proton form was converted to the Cs form as the compensating cations, it was demonstrated that the Cs form adsorbed much less water, as expected, based on the lower energy of hydration and the isosteric heat of adsorption. Finally, they noted that water adsorbed on the silanol groups on the external crystal surface were weakly attracted compared to adsorption associated with Al-proton sites.

Molecular dynamics studies showed a low density structure for water molecules in silicalite with self diffusivity coefficients somewhat higher than its bulk value [20–25]. Grand Canonical Monte

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Carlo (GCMC) simulations were also performed to obtain water adsorption isotherms over a broad range of pressure. These studies included simulations of siliceous silicalite [26–28] as well as the ones with defects including Na^+cations and silanol groups [27,29–31].

In this paper, we report the effect of silanol nests, and Li^+, Na^+, K^+, $Rb^+$and Cs^+cations on the adsorption and diffusion of water in silicalite and using GCMC and MD simulations. The results are presented in comparison with available experimental data and results from other simulations found in the literature.

2. Simulation methods

2.1. Interaction potentials

In this study we performed atomistic simulations. Atoms interacted with each other through a pairwise-additive potential which included a 12–6 Lennard–Jones (LJ) term accounting for short range van der Waals interactions and a coulomb term accounting for the long range electrostatic interactions:

$$V_{ij} = 4\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right] + \frac{q_i q_j}{4\varepsilon_0 r_{ij}} \quad (1)$$

where i and j are atoms of water and silicalite, q is the partial charge on the atomic sites, ε_0 is the dielectric constant which is 1.0 for vacuum, r is the distance between two atoms, and ε and σ are LJ well depth and diameter, respectively. Lorentz–Berthelot mixing rules were used to calculate the ε and σ between different atomic species.

2.2. GCMC and MD simulations

Grand canonical Monte Carlo simulations are widely used to study adsorption in porous materials, such as zeolites and metal-organic frameworks, in the molecular level. A simulation in the grand canonical ensemble takes advantage of the fact that in equilibrium conditions chemical potential of a gas in the bulk phase is equal to the chemical potential of its adsorbed phase. In a GCMC simulation the chemical potential, volume and temperature of the system is kept fixed, whereas the number of molecules fluctuates. For a successful simulation, the simulation is run well beyond the point at which the equilibrium condition is satisfied at the imposed chemical potential, e.g. energy profile of the system converges to a certain value. To obtain an isotherm, GCMC simulations are run at different points over a range of pressures. Then, at each isotherm point the number of molecules is averaged in the equilibrated regime to find the loading at the pressure of interest. All simulated isotherms reported in this study were obtained at 298 K. We used the MUSIC simulation code to do the GCMC simulations [32,33]. Each simulation consisted of a 25 million step equilibration run followed by another 25 million step production run. Insertion, deletion, translation and rotation of water molecules were performed with equal probability. Insertions and deletions were biased using the energy biasing scheme [34]. The isosteric heats of adsorption at low loading, Qst, were calculated from [34]

$$Q_{st} = RT - \left(\frac{\partial\langle V\rangle}{\partial\langle N\rangle}\right)_T \quad (2)$$

where R is the gas constant,<V> is the average potential energy of the adsorbed phase, and <N> is the average number of molecules adsorbed. The average potential energy includes contributions from water–silicalite and water–water interactions.

Molecular dynamics simulations were performed with the DL_POLY simulation package [35,36]. All MD simulations were run in the NVT ensemble where the number of molecules, the volume, and the temperature were kept fixed. A Nosé – Hoover thermostat was used to maintain the desired simulation temperature [37]. Each MD simulation was run for 2 million steps with a time step of 1 fs. The initial half million of these steps were for equilibrating the system. Self diffusivity coefficients were calculated from the mean square displacements using the Einstein relation [38]

$$D_s = \frac{1}{6N}\lim_{t\to\infty}\frac{d}{dt}\left\langle\sum_{i=1}^{N}(r_i(t) - r_0(0))^2\right\rangle \quad (3)$$

where N is the number of water molecules, t is the time and r is the position of the center of mass of the molecule.

In all GCMC and MD simulations the simulation box consisted of 12 unit cells of silicalite. Periodic boundary conditions in all directions and a cut-off distance of 14 Å were applied. The Ewald sum method was used to compute the coulombic interactions.

2.3. Silicalite model

The structure of silicalite was taken from the work of Artioli et al. which is orthorhombic (*Pnma*) [39]. The location of the defect sites has been a matter of many experimental and theoretical studies. Several favorable defect sites were reported for silicalite in the literature, [40–45] and there is not a consensus on the most favorable one. However, T12 was reported as a favorable site by most of them. Therefore, T12 sites were chosen to place the defects. To create a silanol nest a silicon atom from one of the T12 sites were deleted and unsaturated oxygens were saturated by adding hydrogens. Up to four silanol nests per unit cell were considered. Similarly, for a cation site, a T12 silicon atom was replaced by an aluminum atom and a cation was placed near the aluminum site. Two cations per unit cell were considered. Then, the structure of the silanol nests and the position of the cations were optimized with Density Functional Theory (DFT) calculations using the GGA PW91 functional [46]. The same functional was used by Sokol et al. [47] in the DFT study of the common hydrogen containing defects, including silanol groups, in microporous silica and aluminosilicate materials. We performed our DFT calculations with DMol^3 [48,49] software using a full unit cell of silicalite. During the optimization of the silanol nests all atoms were held fixed at their crystallographic positions except the silicon, oxygen, and hydrogen atoms which formed the silanol nest. On the other hand, in the case of optimizing the cation positions, only the cations were allowed to move and other atoms were kept fixed.

Partial charges of the silicalite atoms were determined by the charge equilibration method developed by Rappe and Goddard [50]. In this method charges depend on the environment, that is, an atom type can possess different values (although the values are usually close to each other) depending on its location in the framework. This is different than the usual convention of assigning the same charge value to the same type of atom in molecular mechanics simulations. However, the charge equilibration method has the advantage of representing charge differences for the same atom type in different locations. For instance, in defect-free silicalite the average charge for the silicon atoms were found to be 1.25 with an average deviation of less than 4%. This average value compares well with silicon charges obtained by some other theoretical methods which vary between 1.1 and 1.49 [51–56]. Moreover, with this method charges are calculated within seconds which makes it a very convenient method to calculate charges upon structural changes. LJ parameters for oxygen atoms were taken from the work of Gupta and coworkers [33]. Silicon and hydrogen atoms interacted with other atoms through the Coulombic potential only, and therefore, did not require any LJ parameters. LJ parameters for cation atoms were taken from the work of Aqvist