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Adsorption of Water and Aromatics in Faujasite Zeolites: A Molecular Simulation Study

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Abstract. We report a molecular simulation study of the equilibrium adsorption of water and aromatics in zeolite faujasite NaY. The Monte Carlo simulation methodology used in this work allows the nonframework cations to redistribute upon adsorption of fluids. We indeed observe a cation redistribution in model NaY upon water adsorption. The same phenomenon is observed in presence of adsorbed xylene molecules in the framework. A very small amount of water (some 5% weight) leads to the observed cation redistribution. The consequence of this is a change by a factor of 4 in the adsorption selectivity of NaY in favor of *p*-xylene, when a mixture of *m* and *p*-xylene are exposed to the zeolite sample.

Keywords: adsorption, separation, zeolites, molecular simulation, water

1. Introduction

The interest in the properties of water confined in the nanometer-scale channels and pores of zeolites and other inorganic open framework materials dates back to the pioneer work of Barrer (Barrer and Bratt, 1959). From a practical point of view, water plays a key role in many applications such as ion-exchange and separation. It has been observed for some time that the presence of pre-adsorbed water in the porous solid affects the adsorption selectivity with respect to the hydrocarbon mixture that one wants to separate (Malka-Edery et al., 2001). Most often, traces of water tend to “kill” the adsorption selectivity observed in the dry solid, and can thus severely handicap an intended process. From time to time though, selectivity enhancement was observed. It was found for instance that 3%-weight of water enhances selectivity of barium-X faujasite in favour of *p*-xylene (in a binary mixture of $m-$xylene and *p*-xylene) with respect to the dry solid situation.

The issue addressed in the present work is the effect of small amount of water on the separation processes involving hydrocarbon mixtures, as in the case of the above-mentioned separation of xylene isomers. The mechanism producing these effects is poorly understood. Being able to understand and predict the effect of water on fluid (such as hydrocarbons) adsorption is considered as a key challenge in the adsorption community today (see the Keynote Lecture of F. Meunier at FOA7 in Nagasaki (Meunier, 2001)). From the fundamental point of view, water in zeolites represents a model system for a wide range of experimental as well as theoretical investigations, aimed at understanding the effect of confinement on the structure (Ohba et al., 2004), dynamics (Devautour et al., 2001; Demontis and Suffritti, 1997) and thermodynamics (Boddenberg et al., 2002; Moose et al., 2001) of molecular fluids.

Adsorption properties in zeolites are closely related to the location of nonframework cations and to their accessibility to adsorbed molecules. The partition of these cations among the different sites does not usually change during the course of the (non polar) hydrocarbon adsorption process. On the other hand, cation redistribution is suspected to occur upon adsorption of polar molecules. Recently, a change in the cation location upon water adsorption has also been predicted in zeolite sodium-mordenite by molecular dynamics simulation (Maurin et al., 2004).

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We report here a molecular simulation study of water and aromatics adsorption in zeolite sodium faujasite NaY and NaX. We use a recently developed Monte Carlo simulation method that enables the nonframework cation distribution to change upon water adsorption (Beauvais et al., 2004). Until now, most of the theoretical adsorption studies were using fixed cation distributions (Fuchs and Cheetham, 2001).

2. Models and Methods

We performed molecular simulations using the recently developed "canonical replica-exchange Monte Carlo" method (Beauvais et al., 2004). In this method, several independent realizations of the system are simulated simultaneously, each differing in temperature. As the simulation proceeds, systems at adjacent temperatures are allowed to interchange configurations from time to time, subject to a specific acceptance criteria. These swap moves considerably improve the sampling of configuration space. The higher temperatures are chosen in such a way that the system can easily overcome energy barriers and thus can provide the low-temperature systems with configurations that cover a broad range of configuration space. This method was used here to compute the stable cation distribution of $Na_{48}Y$ at room temperature for different water content ranging from 0 to 370 molecules per unit cell.

Faujasite is known to be a very stable zeolite (even in its dehydrated form), and hydration has very little impact on its overall structure (Lewis et al., 2002). We thus used a rigid framework system, as in our previous studies (Lachet et al., 2001). As no hydrolysis takes place upon water adsorption, due to the weak bonding of water with the faujasite framework, we used the simple TIP4P effective potential model for water (Jorgensen et al., 1983).

The cation force field has been adapted from the work of Jaramillo and Auerbach (Jaramillo et al., 2001). The cation-framework potential consists of an exp-6 repulsion-dispersion term that acts between the cation and the oxygen atoms of the faujasite and a Coulombic term that acts between the cation and both the oxygen and T atoms of the framework. Sodium cations interact with each other through a single Coulombic term. The water-framework interaction is calculated using Lennard-Jones type potential with faujasite oxygen atoms ($\sigma_{\text{water-O}} = 3.31$ Å and $\sigma_{\text{water-O}} = 70.05$ K) and sodium cations ($\sigma_{\text{water-Na}} = 2.87$ Å and $\sigma_{\text{water-Na}} = 78.32$ K). Ewald sums were used to calculate the long-range Coulombic terms. We performed replica exchange canonical Monte Carlo simulations of the sodium cations and TIP4P water molecules subjected to the external field imposed by the rigid faujasite framework host. For each water content, eight independent realizations of the system were simulated simultaneously. The chosen temperatures ranged between 300 and 2325 K.

3. Results

The computed stable sodium cation distributions at 300 K are shown in Fig. 1. For low water content, we observed a solvation of the site II cations in the supercages (solvation enthalpy is larger for site II cations than for other type of cations). Above ~60 molecules per unit cell (i.e. roughly 2 water molecules per site II cation), a redistribution of site I and I′ cations takes place. Sodium cations progressively move from site I to neighbouring sites I′ in the sodalite cage. This is accompanied by a progressive occupancy of the sodalite cages by water molecules (Fig. 2).

Although these data were obtained using equilibrium Monte Carlo simulations (i.e. we have no direct information on the cation and water dynamics), it seems clear that we are faced with a concerted cation-water motion. To begin with, water molecules are preferentially adsorbed in sites II. By the time each site II cation is solvated by roughly 2 water molecules, it becomes energetically interesting for water molecules to solvate site I cations. As the hexagonal prism connecting two sodalite cages is too small to accommodate a water molecule, cations in site I will progressively move to

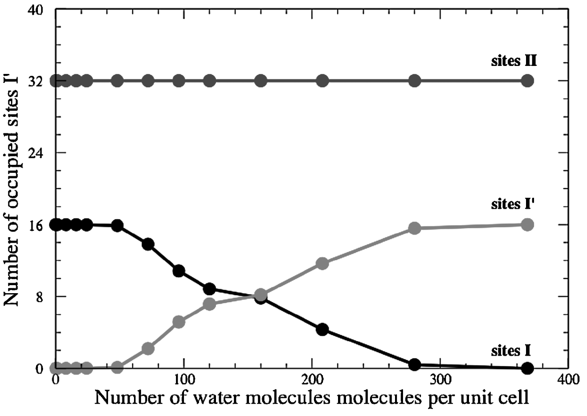

Figure 1. Sodium cation distributions for different water content.

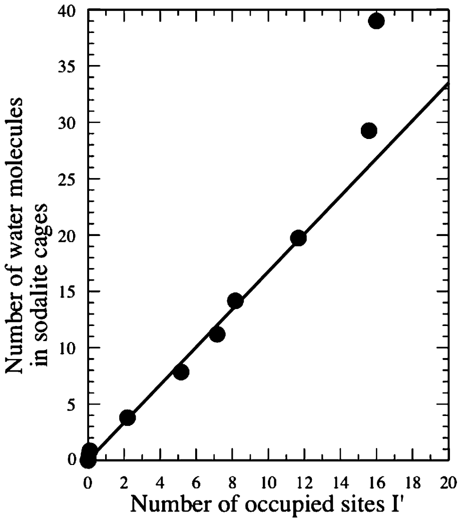

Figure 2. Number of water molecules in the sodalite cages as a function of the site I′ occupancy. The slope of the solid line is close to 2 molecules per site I′ cation.

sites I′, enabling water molecules to adsorb in sodalite cages. This is, to our best knowledge, the first numerical evidence of nonframework cation *redistribution* upon water adsorption in a zeolitic material.

We have carried out the same Monte Carlo simulations of cation distributions in $Na_{48}Y$ with different water content, in the presence of pre-adsorbed *m*-xylene molecules (4 molecules per supercage, which corresponds to the maximum equilibrium loading). The results are shown in Fig. 3. At low water content, both xylene and water molecules are preferentially attracted by site II cations. Since sodalite cages are too small to accommodate a xylene molecule, there is a steric (entropic) effect that favours xylene adsorption at sites II and water adsorption in the sodalite cages. For this reason the I-I′ cation redistribution is taking place for a lower water content than in the previous case (dotted line in Fig. 3). This demonstrates that a very small amount of water in a hydrocarbon-zeolite host-guest system can lead to a redistribution of the nonframework cations.

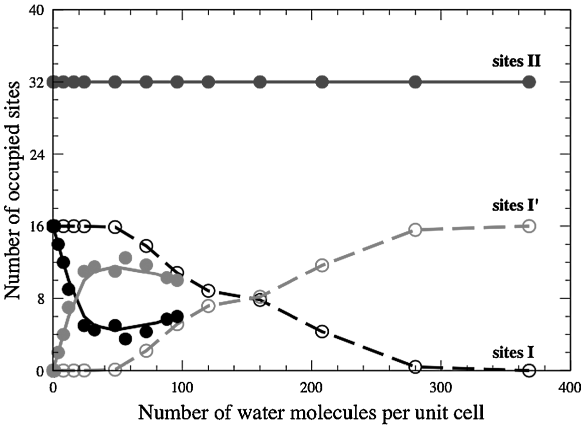

Figure 3. Sodium cation distributions for different water content, in presence of 4 m-xylene molecules per supercage. The dotted line corresponds to the data shown in Fig. 1.

Finally, an adsorption selectivity analysis has been undertaken for an equimolar mixture of *m*- and *p*-xylene, using the methods developed earlier in the case of dry faujasites (Lachet et al., 2001). We found that the cation redistribution, observed in this system for a very low water content (roughly 5%-weight, see Fig. 3) leads to a decrease by a factor of 4 in the adsorption selectivity of NaY in favour of *m*-xylene. A study of the molecular mechanism which links the cation redistribution to the change in adsorption selectivity is under way.

4. Conclusion

We have reported, in this work, a clear-cut numerical evidence of a nonframework cation redistribution upon water adsorption in sodium Y faujasite zeolite. We suggest a mechanism producing this effect, based on a concerted motion of water molecules (from supercages to sodalite cages) and sodium cations (from site I in the hexagonal prisms to site I′ in the sodalite cages). When the faujasite supercages are filled with xylene molecules, the cation redistribution takes place for a very low water content and the adsorption selectivity is modified by a factor of four. This is in keeping with the experimental findings of a dramatic effect of water traces on some separation processes. One should be aware that the described redistribution mechanism is not a general one. It will obviously depend on the Si:Al ratio and the nature of the zeolite framework.

The molecular simulation tools used in this work can, in principle, be extended to any type of guest-host systems. These methods enable to disclose the molecular mechanisms of cation redistribution and adsorption selectivity in a given multicomponent system. This should help, in the near future, in the rational design of nano-porous materials for separation purposes.

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