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Effect of Water Adsorption on the Thermodynamics and Dynamics of the Extra-Framework Cations in Zeolite Systems

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1. Introduction

This work consisted of exploring the effect of water on both the distribution of the extra-framework cations and on their interactions with the framework in zeolite systems. From a practical point of view, this study was performed because water plays a key role in many applications involving adsorption and, more particularly, in ion-exchange which is carried out in aqueous solution. It is thus well known that water improves the efficiency of this process by co-ordinating the cations and hence increasing their mobility [1]. Dielectric Relaxation Spectroscopy (DRS) experiments performed on different types of aluminosilicate zeolites characterised by various Si/Al ratios, recently showed that the cations are progressively de-trapped from their initially occupied sites in the dehydrated state, as the number of water molecules per unit cell increases [2,3]. Furthermore, it was also pointed out a weakening of the interactions between the extra-framework cations and the zeolite framework with increasing water content.

2. Results and discussion

Our aim was then to model the hydration process in these zeolites and to provide a microscopic description of the effect of water on the exchangeable cations behaviour by means of atomistic simulation based on interatomic potential and modelling methods including both Monte Carlo and Molecular Dynamics. For this purpose, various types of interatomic potentials for both the zeolite framework and water were selected to describe the potential energy surface of this complex system and their influence on the simulated results was pointed out. The polarisabilities of both water molecules and the zeolite framework were thus taken into account by the core - shell model in the oxygen atoms [4,5]. The Monte Carlo method allowed us to isolate the lowest energy structures corresponding to various hydration rate. It was thus pointed out that for a typical zeolite, Na^+-Mordenite, the extra-framework of the main channels are progressively extracted from their initial sites as the number of water molecules increases. By contrast, the cations in the small channels are only slightly perturbed by water occupying neighbouring side pockets and remain trapped in the same initial positions whatever the hydration rate.

Once well equilibrated configurations were obtained using the Monte Carlo technique, Molecular Dynamics simulations in the NVT ensemble using Isokinetic Evans thermostat were performed in order to study the diffusion of cations / water molecules within the aluminosilicate zeolites. It is noteworthy that the framework was treated as being flexible in these simulations. The Mean Square Displacements (MSD) of the extra-framework cations were then evaluted in both the dehydrated and totally hydrated zeolites. In the case of Na-Mordenites, these simulations show that the cations located in the small channels are not displaced, presenting only small vibrational amplitudes around their mean positions. By contrast, the cations in the main channels are characterised by motions on a large scale corresponding to displacements towards the whole cavity. The originality of this work was then to compare at each step of the modelling approach the simulated results with experimental data obtained by DRS. This successful confrontation allowed us to obtain a good qualitative agreement experiment-theory.

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