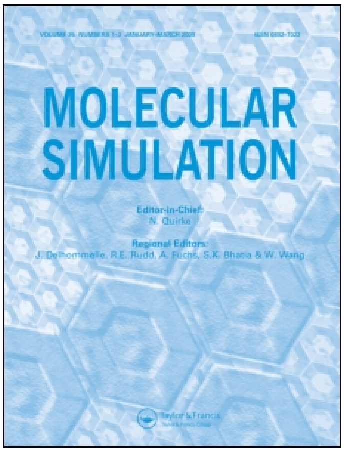

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Static and Dynamic Properties of the Nonframework Cations in Na-Mordenites Zeolite

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This work consists of exploring the effect of Si/Al ratio and water content on both the static and dynamic properties of the extra-framework cations in a typical zeolite system Na^+-Mordenites. Atomistic simulations based on interatomic potentials and minimisation techniques have been used to determine the location of the cations as a function of the Si/Al ratio and the hydration level. Our calculations showed two different cation behaviours depending on the type of channels that they occupy, the positions of the cations in the main channels being substantially perturbed upon the sorption of water molecules whereas those of the cations located in the small side channels being only slightly shifted. By contrast, the populations of the cation sites have almost the same trend when the Si/Al ratio varies. We have then developed a Monte Carlo technique specialised for the simulation of rare events to study the activated cations motions in this zeolite. Mean activation barriers are obtained from minimum energy paths (MEP) calculated for lattices with various Si/Al ratio, by using a Metropolis algorithm. Finally, Molecular Dynamics (MD) simulations allowed us to compare the mobility of the cations in hydrated and dehydrated states and confirmed the results expected from the previous static calculations. This modelling has been successfully compared with experimental data obtained by dielectric relaxation spectroscopy (DRS) and provided a microscopic description of the static and dynamic properties of the extra-framework cations.

Keywords: Na-Mordenites; Si/Al ratio; Monte Carlo technique; Metropolis algorithm

INTRODUCTION

Zeolites have major applications in catalysis [1] and ion-exchange [2] as well as in selective adsorption and separation [3]. The range of applications is growing rapidly and covers a variety of industries [4,5]: separation of components in refinery or chemical plant process streams (e.g. separation of normal and isoalkanes); the purification of feed streams (e.g. CO_2 removal from natural gas) and of streams to be released to the atmosphere or contaminated groundwater (e.g. removal of volatile organic compounds); the control of evaporative hydrocarbon emissions, adsorptive storage of natural gas as an automotive fuel; oxygen production from air at both an industrial scale and in miniaturised units, for medical purposes. The range of applications of this technology thus spans industrial production, environmental protection and medical applications. The processes involved in the applications described above have been widely studied over many years, but it is only within the last decade that the increasing power of computer modelling methods has started to have a major impact on this area of science [6–8].

Another field of interest which has only recently begun to be developed is that of base catalysis, where alkali metal-exchanged zeolites, in particular, have been shown to be effective in catalysing reactions such as alkylation of aromatics [9]. The basicity of such zeolites arises from the enhanced electron-rich character of the framework oxygen atoms, and is dependent on the identity and level of exchange of the extra-framework cations. There is an increasing realisation that the partition of the extra-framework cations may be perturbed substantially upon

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sorption of different molecules, leading to changes in the framework electron density and in the mode of physical binding of the guest species [10]. The dynamic and static properties of the extra-framework cations are thus crucial in terms of understanding the fundamental chemistry of these materials, and more particularly where experimental techniques have not yet provided unambiguous answers.

As we know that zeolites are model materials, we can easily investigate the evolution of the extra-framework cation properties as a function of many parameters such as the nature of both the cations and adsorbed molecules, the water content and the Si/Al ratio. In this way, we have focused our attention on a typical Na^+-Mordenite characterised by the ideal composition $Na_xSi_{48-x}Al_xO_{96}{\cdot}n\,H_2O$ where we modified the Si/Al ratio from 5 to 11 with x ranging from 4 to 8 and the degree of hydration with n ranging from 0 (dehydrated state) to 24 (totally hydrated state) [11]. We then explored the static and dynamic properties of the extra-framework cations depending on these two parameters. From a practical point of view, this study was performed because firstly, the Si/Al ratio strongly influences the acidity of the framework which can have considerable consequences on the catalytic properties of these materials [12] and secondly, water plays a key role in many applications involving adsorption and, more particularly, in ion-exchange which is carried out in aqueous solution [13].

In this way the first step of this work was to simulate the equilibrium positions of the extra-framework cations by combining pair potential model and energy minimisation techniques [14]. The distributions of these cations were then directly compared with experimental data obtained by X-ray diffraction (XRD) [15] and dielectric relaxation spectroscopy (DRS) [16,17]. This approach was the first attempt which proposed both to define the evolution of the distribution of the extra-framework cations among their different crystallographic sites as a function of the Si/Al ratio [14,18], and to provide a detailed microscopic description of the effect of water on the exchangeable cations behaviour [19] in accordance with experimental data extracted from DRS [16,17,20]. The second step of this investigation was to explore the microscopic mechanism of the activated cation motions involving either collective or single cation jumps, by means of an original constrained optimisation approach based on Monte Carlo method [21,22]. These simulated results were then compared with the activation barriers measured experimentally by DRS [16,17,20]. This work was the first approach that reproduced well the experimental data related to cations motions in zeolites. The next step was to study the mobility of the extra-framework cations as a function of the water content by means of Molecular Dynamics (MD) simulations.

The originality of this investigation was then to compare at each step of the simulation the calculated results with experimental data obtained by DRS.

COMPUTATIONAL METHODOLOGY

Microscopic Description of the Mordenite Lattice

From a microscopic point of view, the crystals of Mordenites are chemically disordered because of the large possible number of co-existing aluminum distributions for a given Si/Al ratio. The first step was thus to define the Mordenite lattice by combining experimental data obtained by ^{29}Si NMR spectroscopy and Monte Carlo simulations for each Si/Al ratio [14,18]. This consists of generating aluminum configurations taking into account the Lowenstein rule and selecting the only ones which accurately reproduce the average co-ordination of Si to Al in the first co-ordination shell, i.e. the populations of Si-nAl ($n = 0, 1, 2$) obtained experimentally. This step allowed us to provide a realistic structural model of Al distribution in chemically disordered zeolite system. We neglect the periodicity effect introduced by considering only one unit cell during the simulation.

Location of the Extra-framework Cations

Once the host structure was well established, the next step consisted of simulating the equilibrium location of the counter-ions Na^+ by means of energy minimisation techniques combining Monte Carlo simulated annealing procedure which we have implemented in a parallel code [14] and various minimisers available in *General Utility Lattice Program* (GULP) program [23]. The potential energy surface of the system was evaluated by appropriate pair potential models including flexibility and polarizability of the aluminosilicate framework and polarizable water molecules via shell model on oxygen atoms. The calculations were then performed using periodic boundary conditions and crystallographic unit cell of Mordenite $Si_{40}Al_8O_{96}Na_8$ with space group P1 to avoid any symmetry constraint.

In this way, we evaluated a mean population of the cation sites from the average of 100 selected representative aluminum configurations for each considered Si/Al ratio [14]. Moreover, as a statistical treatment of the effect of hydration on a sample of Mordenite lattices corresponding to various distributions of the Al atoms would be very highly computationally demanding and thus unfeasible, we used a judicious Aluminium configuration in order to develop a microscopic description of the effect of hydration on Na^+-Mordenite. We then built the structure of the fully hydrated Na^+-Mordenite by adding the water molecules at every step. The details of both the interatomic potentials and the minimisation procedures used in this study are fully described in our previous publications [14,18,19].

Exploration of the Cation Motions and Evaluation of the Activation Barriers

This step consisted of selecting two degenerated distributions of cations A and B for a given (Si,Al) configuration. Transitions between these different distributions were then envisaged as possible localised relaxation mechanisms involving the hopping of one or several cations. The confirmation of this hypothesis needed the evaluation of the corresponding activation barrier. In this way, we developed an approach consisting of following the minimum energy path (MEP) from the initial sites through the transition states to the final sites. This technique is well known to provide a picture of the most probable path for a considered hopping process and a good evaluation of the activation barrier. The MEP was thus obtained by using a constrained optimisation approach which drags the cations from their starting sites in a first configuration, namely A, to their final sites in a second one, namely B. The various steps of this procedure are detailed in our previous articles [21,22]. This methodology allowed us to follow the evolution of both the energy and the dipole moment as function of a reaction co-ordinate defined as the relative length covered along the reaction path leading cations from A to B. We then extracted the activation barriers involved in single and collective cation hopping processes.

Mobility of the Extra-framework Cations

The interatomic potentials previously used to model the interactions within the whole system were implemented in *DLPOLY* program [24]. We selected the optimised structures obtained by the minimisation procedure as starting configurations and the minimised cell dimensions were kept fixed during the MD runs. We extended the c-parameter by a factor 2 in order to explore a larger domain in this direction. The MD simulations were run in a NVT ensemble using Isokinetic Evans thermostat [25] for 200 ps including 50 ps equilibration period where the Na^+ cations were maintained fixed in their initial positions. It is noteworthy that the framework was treated as being flexible in these simulations. Furthermore, the shell model which is included both in oxygen of the framework and of the water molecules was treated by the adiabatic shell model approach [26] which consists of assigning a small mass to the shell (0.2 um). Due to this later point and in order to maintain a stable system, we have used a very small time step of 0.2 fs. Positions were then stored every 0.1 ps which allowed us to evaluate the Mean Square Displacements (MSD) of the extra-framework cations in both the dehydrated and totally hydrated Mordenites by means of the following classical equation:

$$\mathrm{MSD}(t) = \left\langle \Delta r_j^2(t) \right\rangle = \frac{1}{N}\sum_{j=1}^{N} \Delta r_j^2(t) = \frac{1}{N}\sum_{j=1}^{N} (r_j(t) - r_j(0))^2$$

where N corresponds to the number of extra-frameworks considered in the estimation of the MSD and we used a multiple time step in order to improve the statistic of the calculation.

RESULTS AND DISCUSSION

Location of the Extra-framework Cations

The theoretical mean populations of the cation sites calculated from the average of 100 selected representative Al configurations for each Si/Al ratio reveals that the cations are mainly located on crystallographic sites I (small channels) and sites IV and VI (main channels) as defined in Fig. 1, in agreement with XRD data available for Na^+-Mordenite with Si/Al around 5 [11]. Other sites named II and III according to the classification established by Mortier [15] are also occupied by a slighter fraction of the cations. However, we

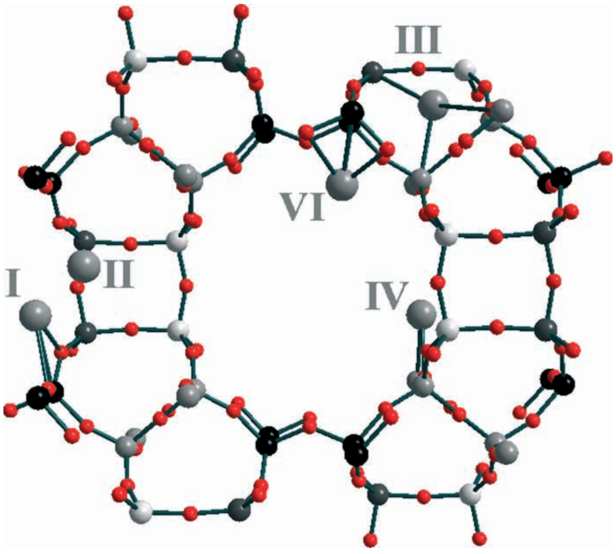

FIGURE 1 Representation of the unit cell of Mordenite. Description of the different cation sites names I, II, III, IV and VI. (Colour version available online.)

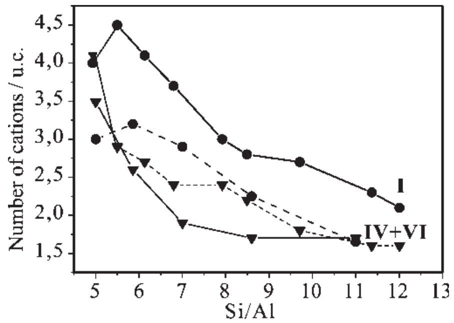

FIGURE 2 Evolution of the population of the cation sites (site I in circle, sites IV and VI in triangle) determined both experimentally (solid lines) and theoretically (dashed lines) as a function of the Si/Al ratio.

observed a nice agreement between the evolutions of the populations of the cations determined both by our simulation and by DRS experiments performed on Na^+-Mordenites characterised by Si/Al ratios ranging from 5.5 to 12 (Fig. 2) [17].

Furthermore, we have shown that the extra-framework cations are located half in the main channels (sites IV and VI) and half in the small channels (site I), for the (Si,Al) configuration selected for treating the hydration process (Fig. 3a). We then obtained the lowest energy structures corresponding to hydration levels ranging from 1 to 24 water molecules per unit cell. From this procedure, we observed that the two first water molecules do not interact strongly with the extra-framework cations. Next, the cations of the main channels are progressively extracted from their initial sites at 3, 6, 7 and 11 H_2O/u.c. 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 level. The structure of the fully hydrated Na^+-Mordenite is given in Fig. 3b. These results are in good qualitative agreement with DRS data [20] which predicts that the population of site I remains constant whatever the H_2O content, and that the occupations of sites IV and VI dramatically decrease in the range 3.2–8.7 H_2O per unit cell.

Exploration of the Cation Motions and Evaluation of the Activation Barriers

A typical result of the MEP calculated at room temperature between two degenerated configurations A and B (Fig. 4a) for Na^+ Mordenite characterised by Si/Al = 11 is represented in Fig. 4b. We can observe that the transition shown involves mainly the hopping of two of the four cations (Fig. 4a) between different crystallographic sites. The activation barrier is about 0.7 eV. This calculated activation barrier is within the same order of magnitude than those measured experimentally by DRS [16,17]. On the other hand, we can observe in Fig. 4c that the stable states A and B correspond to configurations with different dipole moments and that the MEP from A to B involves a variation of this dipole moment. Therefore, these transitions represent the possible microscopic mechanisms for dielectric relaxation. However, the MEP calculated by using a Monte Carlo approach does not provide information on the sequential or collective nature of the cation motions in the unit cell during a transition since the time does not enter in the simulation. A simple way to get an estimation of activation energy of random sequential jumps from these theoretical data may be obtained by frozen part of the cations during a transition from A to B allowing only one cation to move. The resulting activation barrier is still within the same order of magnitude than those observed experimentally. We have thus shown that both collective or sequential hops may be considered in the dielectric relaxation mechanism.

Finally, from a representative sample of such 10 transitions for each Si/Al ratio, we evaluated a mean activation energy of 0.55 and 0.65 eV for Si/Al = 5 and 11, respectively. These calculated values are in good agreement with the mean de-trapping energy

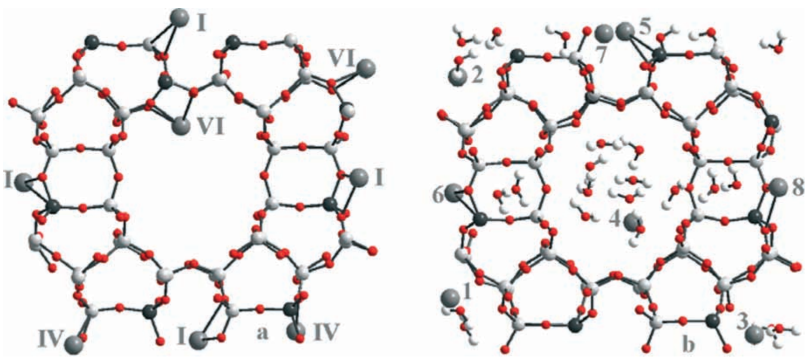

FIGURE 3 Representation of the structures of the dehydrated (a) and fully hydrated (b) Na^+-Mordenites. The cations in the main channels (1, 2, 3 and 4) are de-trapped from their initial sites where as the cations in the small channels (5, 6, 7 and 8) remain trapped in the same cavity. (Colour version available online.)

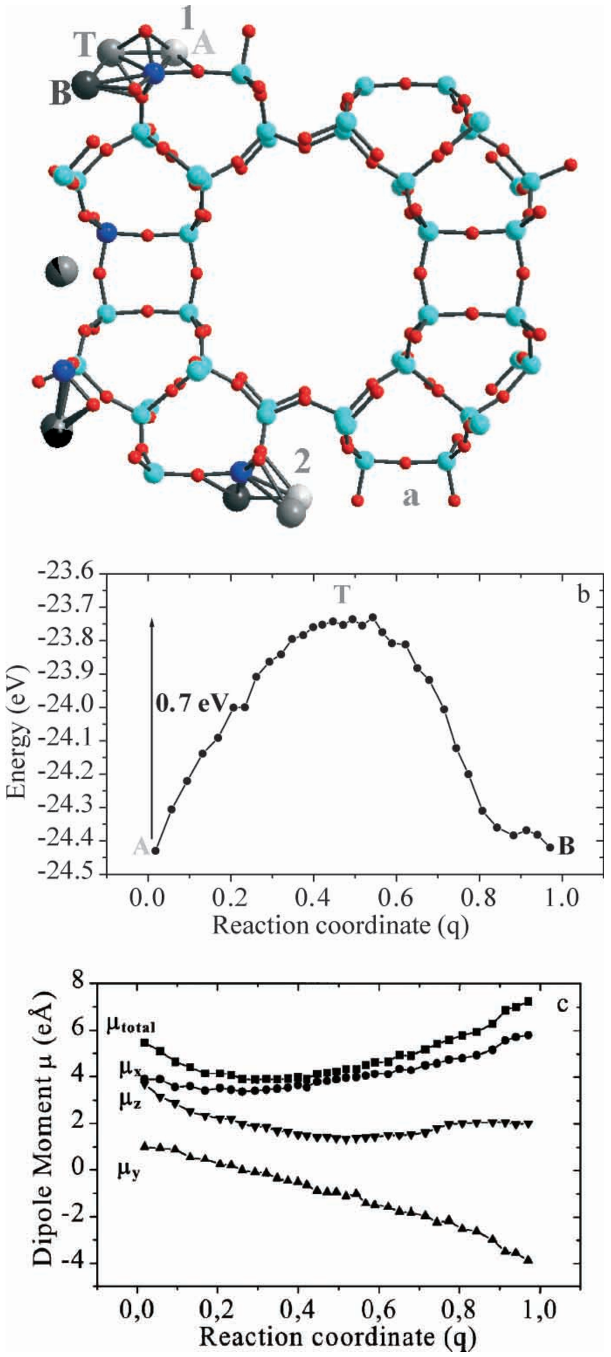

FIGURE 4 (a) Representation of two stable configurations A and B of the Na^+ in the unit cell of Mordenite with $Si/Al = 11$. (b) Energy of the cations as a function of the reaction coordinate q (see text) for the minimum energy path between A and B calculated at 300 K. This transition corresponds to a jump of cation 1 from site I to side pocket combined with a jump of cation 2 from side pocket to main channels, the other cations remaining in the same cavity around their initial crystallographic sites. T represents the transition state. (c) Variation of the dipole moment as a function of the reaction coordinate q. (Colour version available online.)

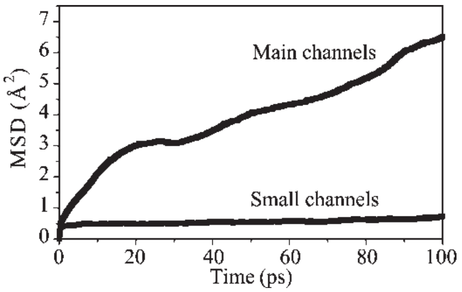

FIGURE 5 Mean square displacement plots for sodium cations located both in the main and small channels at 300 K in the fully hydrated Na^+-Mordenite.

observed experimentally by dielectric relaxation which are 0.78 and 0.83 eV for $Si/Al = 5$ and 11, respectively. The calculated values are rigidly shifted by about -0.2 eV compared to the experimental ones, mainly because the periodic boundary conditions used overestimates the correlations between the hops and because of the necessarily limited accuracy of our electrostatic potential energy surface.

Mobility of the Extra-framework Cations

Analysis of the MSD plots calculated from the MD run at 300 K shows that both cations in small and main channels in dehydrated Mordenite are essentially immobile at this temperature. Then we investigated the MSD for the two types of cations in the hydrated state. We can observe that the cations located in the small channels are not displaced presenting only small vibrational amplitudes around their mean positions (Fig. 5). By contrast, the cations in the main channels are characterised by motions on a large scale (Fig. 5) corresponding to displacements towards the whole cavity. Then, we have tried to correlate these results with the detrapping energy of the cations from their initial sites which have been measured experimentally by DRS [20]. In the case of the cations located in the main channels, we observed a well-pronounced decrease of this energy when the number of water molecules increases. This decrease comes from 0.75 eV in the dehydrated state to 0.40 eV in the hydrated sample for the cations in the main channels and from 0.80 to 0.6 eV for the cations in the small channels. This result can be interpreted microscopically by an increase of mobility of these extra-framework cations, the water interacting directly, pushing them away from the framework and thus leading to weaker cations–framework interactions. On the other hand, we have also observed a decrease of the detrapping energy for the cations in the small channels but less pronounced than in the later case. This decrease cannot be explained by an enhancement of the mobility of the cations induced by direct interactions with water molecules but rather by cations–water interactions over longer distances, induced by water located in neighbouring side pockets, which are much weaker than those found for the cations in the main channels, leading to a smaller decrease of the detrapping energy.

CONCLUSION

This work consisted of investigating the cation behaviours in zeolites as a function of two parameters i.e. Si/Al ratio and H_2O content. We have thus shown that the populations of the cations sites in the small and main channels follow almost the same trend when Si/Al ratio increases, and that their de-trapping energy increases with Si/Al. On the other hand, we pointed out two different cation behaviours as a function of hydration rate in terms of location and mobility, depending on their initial positions in main or small channels. We have thus observed that the cations in the small channels remain trapped in the same sites whatever the water content and that they do not exhibit any significant changes in their mobility. By contrast, the cations in the main channels are progressively extracted from their initial sites upon hydration and they are characterised by motions on a large scale. The originality of this study was to compare, at each step, these simulated results with experimental data extracted from DRS. This successful confrontation allowed us to provide a microscopic description of both the static and dynamic properties of the extra-framework cations in a typical zeolite Na^+-Mordenite.

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