Simulating non-framework cation location in aluminosilicate zeolites

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The non-framework cation positions for Li$^+$ in dehydrated zeolite Li-A(BW) and for Na$^+$ in zeolite 4A are simulated by a straightforward combination of Monte Carlo and structure optimization techniques, using only a framework structure model and appropriate interatomic potentials.

The positions of non-framework cations in aluminosilicate zeolites can control or fine-tune their sorptive and catalytic properties. Measurement, however, requires careful and usually protracted analyses of accurate single-crystal or powder diffraction data. In cases for which extensive experimental data are available, simple site-filling models[1] or statistical mechanics analyses[2,3] can yield insight into relative site energies; earlier analyses have also attempted to quantify the relative importance of short- and long-range interactions in controlling site occupancy patterns.[4] There have been prior atomistic simulations in this area,[5–10] however, as far as we are aware, there has been no attempt to simulate non-framework cation positions based solely on a knowledge of the framework structure, in a zeolite system for which validatory experimental data are available.

We describe here illustrative results from new modelling approaches in two systems chosen, firstly, because reasonable structural data are available and, secondly, because the Si/Al distributions are known precisely; they both have Si/Al ratios of unity and hence strict Si/Al alternation.

The procedure applied was originally developed for probing the preferred binding sites of molecular sorbates[11] and takes as input a suitable framework model. For zeolite Li-A(BW), this is the unit cell and framework Si, Al and O coordinates taken from a crystallographic refinement.[12,13] For zeolite A, we again use accurate crystal structure data[14] but reduce the published a = 24.61 Å supercell to an a = 12.305 Å triclinic, $P1$, subcell by trimming the full supercell contents to the $0 \leqslant x < 0.5$, $0 \leqslant y < 0.5$, $0 \leqslant z < 0.5$ volume. Loewenstein's rule and the T-site connectivity in the LTA framework require the supercell model for zeolite A with Si/Al = 1.0. The subcell model has anti-Loewenstein linkages across each of the unit- cell cube faces, but it nevertheless proves suitable for probing approximate non-framework cation arrangements.

A charge-balancing complement of 4 Li$^+$ or 12 Na$^+$ respectively is then introduced *via* the Monte Carlo packing procedure[11] that successively introduces cations into the model at non-clashing positions. Although this procedure can apply a number of constraints, boundary conditions and parameterizations, the simplest usage scenario was pursued here, in which only short-range non-bonded terms were used to gauge the viability of each new cation position introduced. For both zeolites Li-A(BW) and 4A, thirty distinct initial non-framework cation configurations were created, each of which was then subjected to a full or partial structure optimization[10] using the new aluminosilicate zeolite forcefield, cvff_aug,[15] and the Discover3.2 simulations environment.[15] As the results demonstrate, the arbitrary choice of 30 starting points represents a reasonable yet computationally tractable selection of trial calculations.[16] The Ewald summation technique was used to evaluate the Coulomb terms.

For zeolite Li-A(BW), the coordinates of all atoms in the unit cell were allowed to vary independently in constant volume optimizations of each of the thirty distinct starting configurations. Analyses of the optimized structures entailed automatic determination of their space group symmetries, using an individual atom catchment radius of 0.2 Å,[15] and comparison against structural data for the hydrated material.[12,13] Fully half of the thirty distinct initial structures converged to an identical minimum, of space group $Pna2_1$ (no. 33) that overlays closely on the known crystal structure.[12,13] In detail, the optimized energies were, in reverse order in energy, −7946.5 kcal mol^{-1} (cal = 4.184 J) (space group number 33–15 identical occurrences), −7936.3 (14–1), −7925.9 (7–2); −7920.6 (7–1), −7919.1 (1–1), −7918.7 (1–1), −7899.4 (1–1), −7893.0 (33–1) kcal mol^{-1} and then 7 different structures of symmetry $P1$ (no. 1), with energies from −7891.6 to −7881.1 kcal mol^{-1}.

For zeolite 4A, given the substantially greater complexity of the structure, the framework atom coordinates were fixed in the structure optimizations and only the coordinates of the 12 independent sodium cations were allowed to vary. The final model symmetry was $P1$ in each case. The zeolite 4A results were analysed, by inspection, in terms of the site populations of each of the different types of non-framework cation site. Out of the 30 cases, the 11 lowest energy configurations had the 'correct' configuration[14] of 8 Na$^+$ cations on 6-rings, 3 Na$^+$ cations on 8-rings, and 1 Na$^+$ cation adjacent to a 4-ring; these ranged in energy from −10737.9 to −10729.4 kcal mol^{-1}. (One of these configurations is illustrated in Fig. 1.) As in the Li-A(BW) case, there was then a significant jump to the energy of the next configuration, −10688.2 kcal mol^{-1}; the remaining structures ranged in energy up to −10325.7 kcal mol^{-1}. The loose acceptance criteria chosen for the Monte Carlo docking

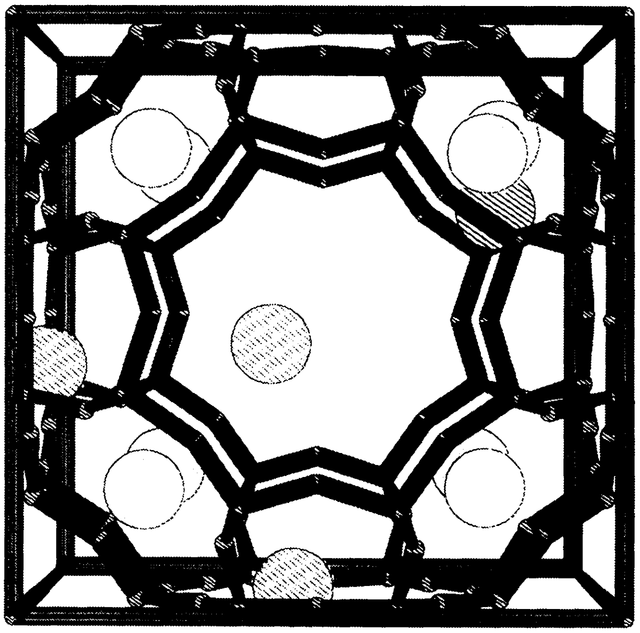

Fig. 1 A representative simulated configuration of Na$^+$ ions (shown as spheres) in zeolite A. Ions in 6-rings are shown as lightly shaded, 8- rings more darkly shaded, and '4-ring' shaded with solid lines.

procedure allowed, on occasion, Na^+ cations to be located within the double 4-rings, from which they could not then escape during the subsequent structure optimization.

In both zeolite Li-A(BW) and zeolite 4A, the correct non-framework cation configuration is predicted, in an unambiguous fashion, based solely on a model for the aluminosilicate framework. An important aspect of this study is that it has applied modelling and simulation techniques that are now routinely available. Although zeolite structural chemistry does include several more complicated systems (ongoing studies of cation placement in zeolite X with Si/Al 1.26, for example, entail placement of 86 cations in a unit cell of volume *ca.* 15 600 Å with 576 independent framework constituent atoms), zeolite 4A is a definitively practical example case. The potentials employed were developed to be simple and readily transferable,[15] rather than reproducing the full structure to a high degree of accuracy; the present results validate their efficacy in this capacity. The structures obtained in these two zeolite cases are quite sufficient to allow further model refinement against measured powder diffraction data or based on substantially more computationally expensive or more locally accurate interatomic potentials.

This study clearly demonstrates the practical value that simulation now offers. The 30 successive packing calculations consumed, respectively, for zeolite Li-A(BW) and zeolite 4A, some 3 and 12 s on a workstation, with each structure optimization then requiring an additional 2 or 8 min. respectively. In the latter case, in which the local structure provided by the simulations and the sample-averaged structure yielded by diffraction differ, the modelling results even provide the opportunity of exploring the local effects of the site disorder. These encouraging results establish a basis for extensions to still more complex systems that possess larger unit cells, such as zeolite X and Y, and mixed cation systems, and to structures for which less direct experimental data are available.

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