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A hydration-controlled nano-valve in a zeolite?†

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Ion-exchange and dehydration in clinoptilolite are simulated revealing a novel feature, a hydration-controlled nano-valve, which explains hitherto anomalous behaviour of this important zeolite system.

Clinoptilolite is a naturally occurring and abundant zeolite with ideal formula $Na_6Al_6Si_{30}O_{72}{\cdot}nH_2O$ in the sodium form. It is known for its high cation exchange and water capacity and has been used[1,2] for water purification, animal feed additives, and in the treatment of nuclear waste by adsorption of heavy ions. It also has potential for gas purification, and this was the original interest behind this study: cations in clinoptilolite are known to be mobile in the hydrated state, and therefore the choice of cation and extent of hydration together offer some potential for design in the zeolite's function. One would like to fine-tune the openings within its channels so that one gas molecule is preferentially admitted over another, and be able to exploit this in gas purification through technological processes such as selective temperature/pressure swing adsorption.[3] However it is difficult to predict the ionic behaviour of a given zeolite system: for example, if two different cations are exchanged into a zeolite the resultant behaviour is not necessarily a simple mixture of those of the single cation forms—in other words, the behaviour is non-additive. This is the case with clinoptilolite: its nitrogen uptake, relative to methane, increases significantly[4] away from either the pure Ca- or pure K-form. This anomalous result typifies such non-additivity and requires an explanation that is currently lacking in the literature.

The simulation of a complete ion-exchange process is an ambitious venture requiring an adequate combination of atom potentials and simulation schedule. The exchange route from pure Ca- to a 50 : 50 Ca/K-clinoptilolite was chosen as an ideal prototype for study. The potentials used were obtained from the well characterized universal force-fields of Rappe *et al.*[5] with modifications by Burchardt *et al.*[6] for atom types which occur in zeolite frameworks, together with formal charges for the cations and partial charges for water (Jorgensen[7]), methane (Righini *et al.*[8]) and nitrogen (Murthy *et al.*[9]); cross term parameters for heterogeneous pairs (*e.g.* cation–water) were taken as the geometric mean of the corresponding homonuclear parameters given in these publications.[5,6] The simulation schedule devised (Table 1) was a combination of various Monte-Carlo and molecular dynamics stages with key features: first, the cations are allowed to be mobile, with or without their variable hydration spheres, and frequent total relaxations permit the zeolite framework to respond to this mobility; the repeated simulated annealing ensures that sufficient configurations are explored away from local minima; and the approach used in the ion-exchange (step no. 5) is pragmatic, not attempting to simulate either the thermodynamics or kinetics of the ion-exchange, but purely to obtain reasonable starting configurations for the exchanged state.

As the water content of the Ca-clinoptilolite is increased (stages 2 to 4) the Ca^{2+} cations in the main (10c) channel are progressively hydrated away from the framework oxygens towards the centre of the main channel [Fig. 1(a)]. This (50%) fraction of Ca^{2+} cations then becomes accessible and can be easily exchanged by twice the number of K^+ cations (to preserve charge neutrality) resulting in a hydrated 50 : 50 Ca : K-clinoptilolite [Fig. 1(b)]. After ion-exchange the water continues to play a key role during dehydration, firstly by allowing the newly arrived K^+ cations to gradually approach their eventual destination [Fig. 1(b), (c)]: this gradual exploration is crucial since the simulation fails if this stage is omitted or if the dehydration is performed too rapidly, and this itself reflects a well known feature that zeolite stability is generally very sensitive to mode of dehydration.[11] The water plays a second, more subtle, role during dehydration by mediating the displacement of the K^+ cations to their final (dehydrated) positions [Fig. 1(c), (d)]: the mechanism by which this occurs is that during dehydration the loss of water reduces the effective dielectric medium so that pairs of neighbouring Ca^{2+} cations experience an increasing electrostatic repulsion which is transmitted to the neighbouring K^+ cations. Thus two Ca^{2+} cations, each just inside the minor (8c) side channels, push both K^+ cations by approximately 1.7 Å so that they protrude into the main (10c)

Table 1 Summary of the 7 stages employed in the simulation schedule for modelling hydration, ion-exchange and dehydration of clinoptilolite. The starting framework structure (stage 1) is based on the published structure[10] using an ideal Si : Al ratio of 5 : 1 so that 1 in 6 tetrahedral atoms is an Al; these Al sites are chosen randomly except being subject to Loewenstein's rule.[13] Whereas various initial cation sites can be used for stages 1–4, the crucial insertion in stage 5 has so far only been attempted using positions close to those in the published structure,[10] and as illustrated in Fig. 1(b). Cations and waters can move freely during all simulated annealing (stages 2c, 6a) *and* molecular dynamics (stages 2b, 6b) cycles, whereas the framework atoms move during just the molecular dynamics (stages 2b, 6b) cycles. All stages are taken to the equilibration: Monte-Carlo (stages 2a, 6b) cycles exceed a minimum of 10^6 configurations; molecular dynamics cycles are typically 10^4 steps of 10^{-15} s; simulated annealing cycles are typically 2×10^4 steps of 10^{-15} s, generating an effective annealing temperature range of 300–600 K

Stage	Brief description
1	Start with a suitable clinoptilolite framework structure
2a	A sequence of grand canonical Monte-Carlo (GCMC) simulations at $T = 300$ K for increasing pressure, in which water molecules are inserted/destroyed within each fixed framework
2b	Molecular dynamics under constant N,P,T for the *whole* system (framework atoms plus waters and cations) for each pressure step
2c	Simulated annealing for mobile water molecules and cations within the fixed framework
3	Loop around steps 2a, 2b, 2c until the final water loading, N, and pressure, P, are achieved
4	Molecular dynamics under constant N,P,T for the whole system (framework atoms plus waters and cations)
5	Removal of least energetically bound Ca^{2+} cations and semi-random insertion of exchange-cations (K^+) up to electrical neutrality
6a	Simulated annealing for the mobile water molecules and cations within the fixed framework
6b	Molecular dynamics under constant N,P,T for the *whole* system: framework atoms plus waters and cations
6b	GCMC (or equivalent) simulations with decreasing pressure
7	Cycle around steps 6b + 6a to complete dehydration ($N = 0$)

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† The term 'valve' is used here to denote adjustable flow in either channel direction.

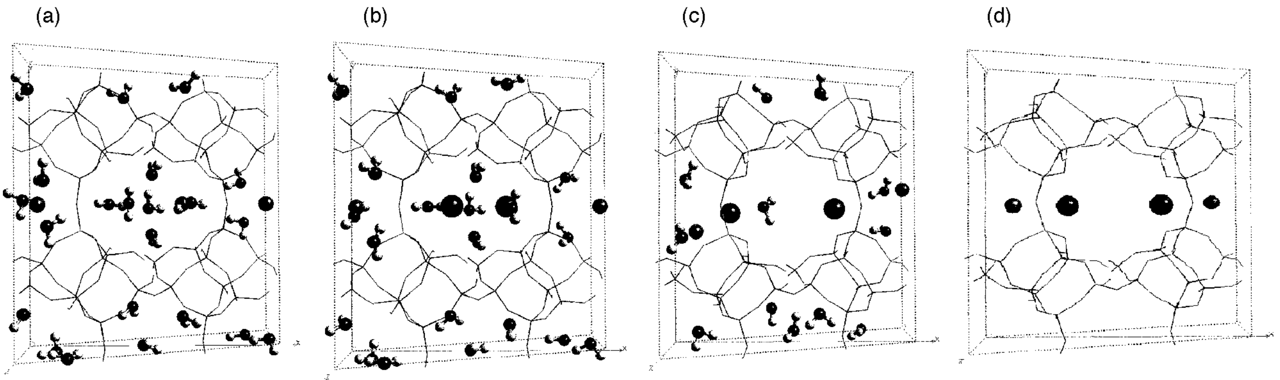

Fig. 1 Computer graphic snapshots obtained during the nano-valve simulation of clinoptilolite: (a) full hydration with the Ca^{2+} cation hydrated away from the framework; (b) a starting configuration after exchange of one Ca^{2+} by two K^+ cations; (c) during dehydration the two K^+ cations approach their framework sites; (d) on complete dehydration the Ca^{2+}–Ca^{2+} repulsion is transmitted to the K^+ cations so that they project into the main (central) 10c channel.

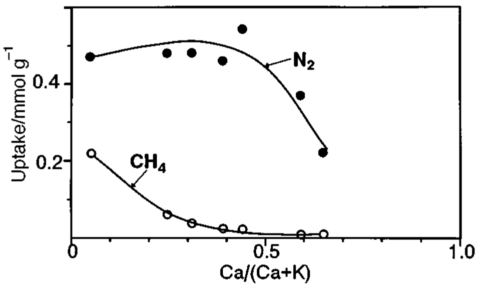

Fig. 2 Dynamic uptake, after 24 seconds exposure of activated clinoptilolite to nitrogen and methane at approximately 1 atmosphere pressure, as a function of the Ca/(Ca + K) ratio. The relative uptake increases significantly away from either the pure potassium (Ca/(Ca + K) = 0) or pure calcium (Ca/Ca + K) = 1) forms. (Data from Robinson *et al.*[4]).

channel reducing its effective diameter from *ca.* 7.2 to 3.8 Å (the actual final Ca–K separations are ~ 4.3 Å). This lever effect produces a constriction in the main channel which can be described as a 'nano-valve' in the sense that the degree of constriction varies with the degree of dehydration and that the ensuing flow restriction will be down the main channel in the direction of the pressure gradient driving the gas flow; the essential action is illustrated in the graphical abstract.

A difficulty with clinoptilolite is that it is extremely difficult to synthesise, yet the natural form suffers from poor crystallinity. This has prevented[11] a definitive location of cation positions by Rietveld refinement of powder diffraction data as was possible in other studies.[12] However EXAFS spectroscopy is capable of yielding one-dimensional (angle-averaged) information on the local cation environment regardless of specimen crystallinity. Calcium and potassium K-edge EXAFS measurements (Daresbury SRS) on dehydrated Ca : K-clinoptilolite yield average nearest neighbour peaks[11] which are indeed consistent with the nano-valve model described here (the operative Ca^{2+} cation coordinated to 3 framework oxygens (~ 2.35 Å distance) and K^+ to 4 framework oxygens (~ 3.0 Å); details and typical plots are available as electronic supplementary information; see http://www.rsc.org/suppdata/cc/1998/2527). However one could conceivably invoke alternative configurations which satisfy these EXAFS-deduced ion coordinations, and therefore some additional confirmation of the nano-valve action is desirable. This has been provided by gas adsorption data (Robinson *et al.*[4]) which show (Fig. 2) that the differential uptake between nitrogen and methane is maximised with the binary cation forms of clinoptilolite. We see from simulations[11] that the diffusion of methane and nitrogen (Table 2) is entirely *via* the main channel of the zeolite, and that methane diffusion is severely restricted relative to nitrogen since the constricted opening of the nano-valve falls in between the kinetic diameters of methane (3.8 Å) and nitrogen (3.0 Å, when axially aligned). Experimental measurements of gas uptake reflect a combination of such kinetic effects with thermodynamic aspects (loading capacity), though kinetic effects would dominate with pressure swing adsorption.

Table 2 Diffusion constants for methane and nitrogen down the main (10c) channel of the single (K^+) and double (50 : 50 Ca^{2+}/K^+) cation forms of clinoptilolite, obtained by *impulse molecular dynamics*. In this method, individual methane or nitrogen molecules are released within the main channel and equilibrated using a 20 ps period of molecular dynamics (individual steps of 10^{-15} s) followed by a further ≥ 100 ps of molecular dynamics during which the displacement down the channel is traced; the mean diffusion constant is then obtained from the straight line slope of the displacement-squared (*versus* time) plots, of which typical versions have been deposited as electronic supplementary information (see text). One notes that while the absolute values with the Ca/K form are decreased, the relative ratio of nitrogen over methane increases markedly. Diffusion constants are given in units of 10^{-9} m^2 s^{-1}.

Gas	K-clinoptilolite	K/Ca-clinoptilolite
CH_4	0.81	$< 10^{-5}$
N_2	6.48	2.88

In conclusion, this nano-valve, revealed by simulation, explains the anomalous $CH_4 : N_2$ gas adsorption by the binary (Ca/K) cation form of clinoptilolite. It also suggests that the nano-valve might even be continuously controlled by varying the degree of dehydration during calcination of the zeolite. We expect that many other properties (*e.g.* immobilisation in zeolites) might now be similarly predicted provided the effects of water are taken into account.

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