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Simultaneous occupation of SI and SI′ cation sites in dehydrated zeolite LSX†

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Simultaneous occupation of adjacent SI (or SIa) and SI′ sites is calculated to be favourable in dehydrated zeolite K-LSX (supporting the experimental work of Paillaud *et al.*[1]), although such a configuration is unlikely in other dehydrated LSX zeolites.

The Si/Al ratio of the framework has a profound effect on the physical properties of zeolites, directly impacting their utility. The number of extra-framework cations is governed by the Si/Al, whilst their location is also affected by the distribution of Al in the framework. At Si/Al > 1 the Al is (generally) disordered, resulting in many possible, often partially occupied, cation sites; making precise characterisation difficult. In zeolites with the FAU framework, five possible cation sites have been identified (some are illustrated in Fig. 1). A common feature of many structural investigations of FAU zeolites is the assertion that simultaneous occupation of adjacent SI and SI′ sites is not possible; and occupation of these sites are very often constrained during structure refinement.

Low Silica Zeolite X (LSX) has Si/Al = 1[2] and we may expect the cations to be more ordered than in other FAU materials, due to the ordered framework. Neither pure K-LSX nor pure Na-LSX have been synthesised directly; both Na^+ and K^+ are required, which are subsequently exchanged. Plévert *et al.*,[3] in a study of dehydrated Li-LSX, report that SI′ sites are preferentially occupied over SI and that simultaneous occupation of adjacent SI and SI′ sites was unlikely. Lee *et al.*,[4] in a study of hydrated (Na,K)-LSX of varying compositions, state (as do many studies of zeolites X and Y) that finding cations of the same type at both SI and SI′ simultaneously is unlikely due to short intercationic distances. As K^+ levels increase, they suggest that Na^+ migrates from SI′ to SI to make room for K^+ at SI′. Paillaud *et al.*[1] challenged the above arguments in a combined X-ray diffraction and K-NMR study of dehydrated K-LSX. They propose that two K^+ cations *can* occupy simultaneously an SI′ site and a new site, SIa–see Fig. 1. The latter is a displacement of the SI site away from the occupied SI′ site, towards the opposite side of the double-6-ring (D6R), giving a K^+–K^+ distance of 3.58 Å.

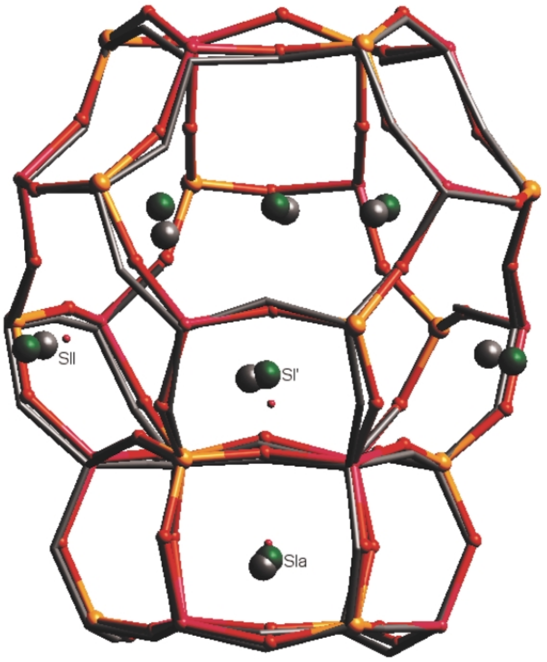

Fig. 1 Calculated most stable K^+ positions (green) in K-LSX and the experimental results of Paillaud *et al.*[1] (grey, including the framework). The labelled SII site is the one modified in our calculations, together with the cation at SI′ above the D6R and the symmetry equivalent SI′ below the D6R (not shown). Experimental cation sites for NaX are also shown in pink. *Maximum* deviation from experiment is ~0.25Å.

Computational studies of cation sites in FAU materials, have focused on NaX and NaY compositions, most taking experimental populations of SI and SI′. Here we consider the details of SI and SI′ occupation, specifically in LSX with a range of cations.

We applied standard lattice energy minimisation and Mott–Littleton defect methodologies[5] to determine the equilibrium geometries (effectively at 0 K) of the bulk and of cations in specific geometries; the GULP code[6] was used throughout. A formally charged parameter set described by Jackson and Catlow[7] was used.

The experimental structure of K-LSX from Paillaud *et al.*[1] was energy minimised with no symmetry constraints. Two initial calculations were performed with: (i) occupied SI′ sites with SI vacant and (ii) alternating SI and SI′ occupied. Both were found to be equal in energy, perhaps suggesting that there is little preference for siting K^+ in either combination. The calculated cell parameters are within ≈ 0.7% of experiment: 25.41, 25.33 and 25.01 Å compared to 25.32, 25.17 and 25.18 Å,[1] retaining the Fddd symmetry. Calculations, with local modifications made to the cation distribution—in the pure K-LSX composition—were then performed using the Mott–Littleton method,[5] on the structure with vacant S1 sites. Relative energies of stable combinations of cations at the SI, adjacent SI′, and SII sites are given in Table 1.

We discuss first the most significant result, that of simultaneous occupation of adjacent SI (or SIa) and SI′ sites. It is clear, that in a pure K-LSX composition, occupation of adjacent SIa and SI′ sites can occur. Furthermore, it is the most energetically favoured distribution; although only marginally, as suggested by our initial unit cell calculations (above). The only other cation compositions resulting in energy minima with both SIa and SI′ occupied have K^+ at SIa with either Na^+ or Li^+ at SI′. However, these are not the most stable for these particular compositions (see below). Other cation distributions lead to migration of the cations to other sites (usually SI′): for example two Na^+ preferentially occupy two SI′ sites. Lee *et al.*[4] state that the short K^+–K^+ distance of ~3.3 Å would preclude simultaneous occupancy and imposed a constraint in their refinements to avoid such a possibility. In our calculations the SI cation moves 0.347 Å to SIa: a K^+–K^+ distance of 3.512 Å. Paillaud *et al.*[1] report a distance of 3.58 Å (see Fig. 1).

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† Electronic supplementary information (ESI) available: further illustrations for K-LSX. See http://www.rsc.org/suppdata/cc/b2/b207505a/

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When both Na$^+$ and K$^+$ are present, Na$^+$ at SI is unstable and both Na$^+$ and K$^+$ are located at SI′ upon energy minimisation. However, if K$^+$ is in the D6R, we obtain an energy minimum, with K$^+$ displaced again to SIa on the opposite site of the D6R from the Na$^+$ at the SI′ site. This result contrasts with that of Lee *et al.*[4] who refined (Na, K)-LSX materials so that simultaneous occupation of SI and SI′ could only occur with Na$^+$ at SI. They report a Na$^+$–K$^+$ distance of 3.19 Å, which compares well with our value of 3.09 Å, but with the cations swapped. However, for this mixed Na$^+$/K$^+$ system, the most stable configuration is calculated to have Na$^+$ at one SI′ and the K$^+$ at the other SI′ site (by ~0.3 eV). Similarly for a mixed K$^+$/Li$^+$ system, the configuration with SIa and SI′ occupied is less stable than where both cations are at SI′ sites (by ~0.5 eV) and considerably less stable than when the K$^+$ is at SII with the two Li$^+$ at the SI′ sites (by ~1 eV). Thus, we would only expect significant simultaneous occupation of SI (SIa) and SI′ to occur in K-LSX and at high levels of K$^+$ in mixed systems.

For (Na,K)-LSX, Lee *et al.*[4] determined that Na$^+$ cations at SI′ were initially replaced by K$^+$ and that Na$^+$ cations subsequently migrate from SI′ to SI to accommodate further K$^+$ at SI′. Our calculations suggest that K$^+$ would replace Na$^+$ at SII before those at SI′ (a system with 2 Na$^+$ and 1 K$^+$ is least stable when the Na$^+$ is at SII–Table 1). Further exchange would result in K$^+$ occupying SI′, with any remaining Na$^+$ still at SI′. However, we find no evidence of Na$^+$ occupying SI in a LSX framework. When K$^+$ replaces the Na$^+$ remaining at SI′, we would also expect migration of K$^+$ into the SIa site (from SI′). The latter is consistent (although with the identities of the cations reversed) with the observation of Lee *et al.*,[4] given the constraints used in their refinement and the difficultly in distinguishing between the different cations. However, we do note that these experiments[4] are on hydrated samples and we are currently determining the effect of water on cation positions and possible ion-exchange migration pathways.

The stability of K$^+$ at SIa can be correlated to the observation that LSX does not form when K$^+$ is absent. We suggest that the presence of K$^+$ facilitates the formation of the D6R with Si/Al = 1. K$^+$ can coordinate strongly within the D6R, whilst the smaller Li$^+$ and Na$^+$ can only satisfy coordination by being at SI′, although at a different position above the 6R. Since two cations are required to charge balance a D6R with Si/Al = 1, it appears clear that K$^+$, with a lower charge density, is essential.

For the case of Na-LSX (and (Na,K)-LSX, where only Na$^+$ are near the D6R) and Li-LSX, we find no minima with SI and SI′ simultaneously occupied. In each case, the cations occupy both SI′ sites, with variations in SI′ distance above the D6R, in agreement with experimental studies[3,4] (see ESI†).

Table 1 Stable cation sites in LSX in the vicinity of a D6R. Note that relative energies can only be satisfactorily compared for the same compositions, as a complete thermodynamic cycle is not considered here (but will be considered in a further paper). *i.e.* These energies do not predict that the presence of Na$^+$ stabilises the LSX structure over K$^+$

	Cation site[a]				
SIa	SI′ (u)	SI′ (d)	SII	E_{rel}/eV[b]	A$^+$–A$^+$/Å[c]
K	K	—	K	0.00	3.512
—	K	K	K	0.13	5.807
—	K	Na	K	−1.97	4.702
K	Na	—	K	−1.62	3.090
K	K	—	Na	−1.59	3.512
—	Na	Na	K	−3.96	4.028
—	K	Na	Na	−3.59	4.731
K	Na	—	Na	−3.23	3.090
—	Li	Li	K	−7.28	3.583
	K	Li	Li	−6.83	4.698
K	Li	—	Li	−6.27	2.911
—	Na	Na	Na	−5.73	4.034
—	Li	Li	Li	−10.54	3.599

[a] u and d denote above and below the same D6R. The SIa site is below the centre of the D6R (see Fig. 1). [b] Energy relative to the most stable K-LSX distribution. [c] Closest cation-cation distance.

Table 2 Stable cation sites when one Al in the D6R is replaced by Si

Cation	Site[a]	E_{rel}[b]/eV
K$^+$	SI	0.0
	SI′ (same)	0.8
	SI′ (other)	0.6
Na$^+$	SI (other)	0.0
	SI (same)	0.1
Li$^+$	SI′ (other)	0.0
	SI′ (same)	<0.1

[a] Positions of the cations are referred to relative to the Si site–either the *same* side of the D6R cavity as the Si or the *other* side. [b] Relative energy are given for the same cation only *e.g.* K$^+$ at SI′ is only 0.8 eV less stable than K$^+$ at SI, and not of Na$^+$.

We may also find insights into cation distributions in zeolite X. By replacing one Al in the D6R with Si, we increase the local Si/Al, so that only one cation is now needed to maintain electroneutrality (Table 2). For K$^+$ we find that the SI site is the most favoured, with very small displacements from the centre of the D6R (~0.1 Å) dependant on the exact position of the extra Si. K$^+$ at SI′ is also stable, but is less favourable. For Na$^+$, cations placed at SI′ migrate to the SI site; the only stable configuration. The SI site is again split, as found previously in similar calculations[8] and by Na-NMR.[9] For Li$^+$, only SI′ (but in the plane of the 6-ring) is stable. It is clear, therefore, that for Si/Al > 1, the relative populations of SI and SI′ sites are wholly dependant on the *local* Si/Al. Thus, for NaX, if a D6R has Si/Al = 1, then Na$^+$ will be at SI′. However, with one excess Si in the D6R the Na$^+$ prefers SI. For a Si/Al = 1.26 (typical for zeolite X) and assuming a random distribution of the excess Si, 5/8 of the D6R may be expected to have an excess Si, favouring SI′ occupation which would significantly reduce SI occupation; as observed. We are currently evaluating a number of models to correlate these results with the average occupations obtained from diffraction studies.

To conclude, we have found that simultaneous occupation of adjacent SI (or SIa) and SI′ sites is possible in the case of dehydrated K-LSX. Such a distribution may also occur at high K$^+$ concentration of (K,Na)-LSX, but require the K$^+$ to be at the SIa site. Furthermore, Na$^+$ will not occupy SI (or SIa), which is preferred by K$^+$. A similar distribution (whilst an energy minimum) is less likely in (K,Li)-LSX. No other cation combinations considered lead to such simultaneous occupation of SI and SI′. Furthermore, we have shown how the local Si/Al has a profound effect on the cations location; increasing the Si/Al of the D6R results in significant cation migration. All our calculated geometries are consistent with the experimental literature. However, they reveal detail (speciation for example) that may become lost, due to averaging of the structure, due to the complexity of fitting a refinement, or by the imposition of unsuitable constraints upon the model during refinement.

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