

Short cation–cation distances in zeolites – the case of K–LSX

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Zeolites with the faujasite structure (FAU) are extensively used as catalysts and in gas separation. A detailed knowledge of their structure, particularly the positions of extra–framework cations in the case of gas adsorption, is therefore central to understanding their performance. Typically zeolites X (Si/Al ~.1.1–1.5) and Y (Si/Al ~5–11) are used. A common assertion of structural determinations is that the two partially occupied cation sites labelled S1 and S1' (Figure 1) are not occupied simultaneously.

Low Sodium Zeolite X (LSX) [1] on the other hand has Si/Al=1 and consequently a larger number of extra–framework cations. However, the same constraint on cation site occupation is used. For example, Lee *et al* [2] state that in K–LSX, simultaneous occupation of the S1 and S1' sites could not occur due to the short K⁺–K⁺ distance of ~3.3Å and they therefore constrained their crystallographic refinements to prevent such an occurrence. However, this assumption has recently been challenged by Paillaud *et al* [3] who provided NMR and neutron diffraction evidence that adjacent S1 and S1' sites are simultaneously occupied; although with the S1 cation being displaced to a new site, referred to as S1a. Nevertheless, this remains a controversial result.

We report here the result of a computational study of the structure of LSX, with a variety of extra–framework cations, aimed at determining if such configurations are likely. Our calculations reveal that simultaneous occupation of S1 and S1' is the most stable combination of cations near the double 6–ring in K–LSX and (K,Na)–LSX (Si/Al=1). Furthermore, we found that the K⁺ is displaced from the S1 site, to the S1a site described by Paillaud *et al* [3]. Remarkable agreement is found between experiment and calculation, with K⁺–K⁺ distances of 3.52 Å and 3.512Å respectively.

We will also present results which demonstrate how these occupations are strongly dependant on the local Si/Al. For example, Na⁺ prefers the S1 site over S1' once the local Si/Al in the double six ring increases from 1 to 1.17. Such results have important ramifications for the experimental and computational models of other FAU structured materials with Si/Al>1.

References

- [1] G. H. Köhl, *Zeolites*, 1987, **7**, 451.
- [2] Y. J. Lee, S. W. Carr, and J. B. Parise, *Chem. Mater.*, 1998, **10**, 2561.
- [3] J.–L. Paillaud, P. Caullet, L. Delmotte, J.–C. Mougénol, S. Kayiran and B. Lledos, *Stud. Surf. Sci. Catal.*, 2001, **135**, 09–O–01