Ionic and Metallic Clusters in Zeolites

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$Na_4{}^{3+}$ ionic clusters, probably located inside sodalite cages, are formed when zeolite Na^+-Y is exposed to Na or K vapour and $K_4{}^{3+}$ clusters when K^+-Y is exposed to the vapour of Na or K, but $Rb_4{}^{3+}$ cannot be observed (by e.s.r. spectroscopy) using Rb^+-Y under comparable conditions; at higher concentrations of metal vapour intracrystalline metallic particles are formed.

Rabo and Kasai[1—3] have shown that, when dehydrated Na^+-exchanged zeolite Y is exposed to sodium vapour, the white aluminosilicate powder becomes pink. E.s.r. studies indicate the formation of $Na_4{}^{3+}$ clusters, but the precise location of these has been in doubt.[1—3] We have confirmed and extended these studies to K^+- and Rb^+-exchanged zeolite Y, and conclude, first, that two distinct species are present in the zeolite depending on the concentration of the assimilated metal and, second, that $Na_4{}^{3+}$ and $K_4{}^{3+}$ clusters are almost certainly accommodated (see below) within the sodalite cages (β-cages) in the structure, as shown in Figure 1.

Samples were prepared by treating dehydrated zeolite with

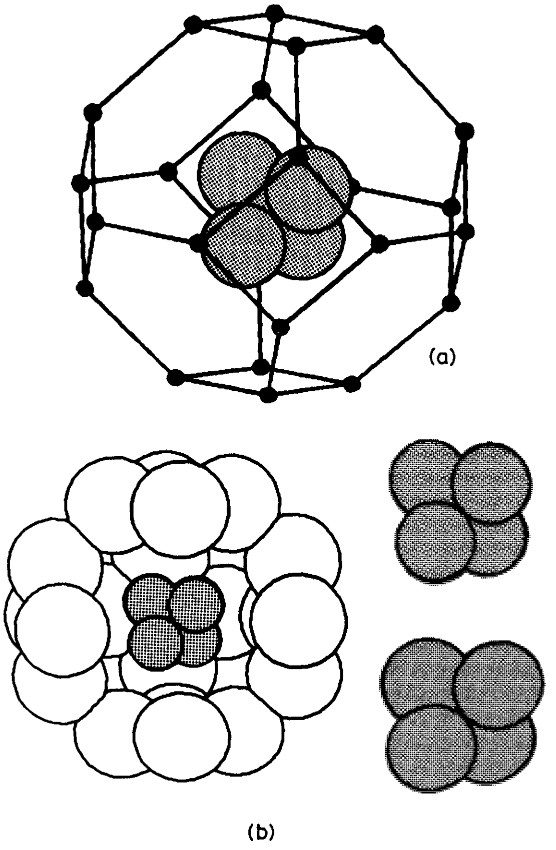

Figure 1. (a) Illustration of a sodalite cage containing a Na_4^{3+} cluster of (presumed) tetrahedral geometry, and percentage metallic character/radii as gauged from our e.s.r. data (Table 1). Radii are drawn around the centre of each Na^+ ion; for clarity the tetrahedral Si, Al constituents of the zeolitic framework (located at the corners of the cage) are not drawn to scale. Oxygen atoms, half-way along the edge are omitted. (b) (At left) A scale view (allowing for percentage metallic character, Table 1) of a Na_4^{3+} cluster within a sodalite cage. Van der Waals boundaries (thin lines) by the framework atoms (Si, Al) plus the 'real' size of the cluster are given. (Top right) A K_4^{3+} cluster, again drawn using the metallic character shown in Table 1, shown at the same scale as the view on the left. (Bottom right) A hypothetical Rb_4^{3+} cluster with (assumed) 30% metallic character at each Rb^+ ion shown on the same scale as the view on the left. This 30% value is derived from an extrapolation of the corresponding values in the Na_4^{3+} and K_4^{3+} clusters (Table 1).

alkali metal vapour in sealed quartz reaction vessels. The complete experimental procedure will be published elsewhere.[4] First and second derivative e.s.r. spectra were recorded on a Varian E-109 spectrometer operating at X-band frequencies, and using 100 kHz modulation frequency.

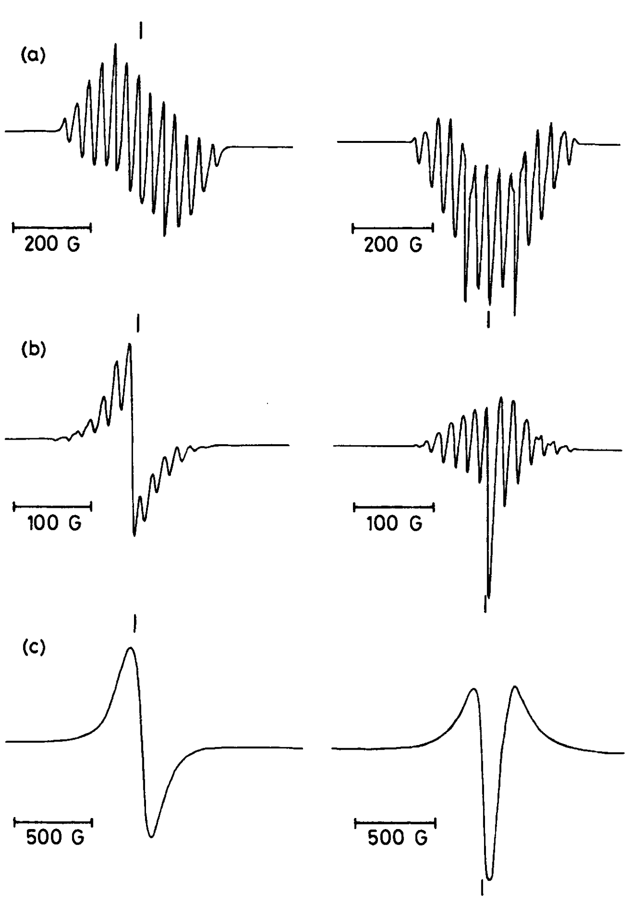

Figure 2. E.s.r. spectra of alkali doped-zeolite Y samples. In all cases, first derivative spectra are shown on the left; second derivative spectra on the right. The marker corresponds to a diphenylpicrylhydrazyl signal at g 2.0036 (1 G = 10^{-4} T). (a) The Na_4^{3+} cluster in zeolite Na^+-Y at 120 K. (b) The K_4^{3+} cluster in zeolite K^+-Y at 120 K. (c) The rubidium metallic cluster (120 K) observed in Rb^+-Y zeolite after exposure to Rb vapour.

Table 1. E.s.r. parameters for ionic and metallic clusters in zeolite Y, and the corresponding bulk metals.

		g-Value		
Metal	% Atomic character in M_4^{3+} cluster[a]	Ionic cluster (M_4^{3+})	Metallic cluster	Bulk metal
Sodium	41	1.999	1.9997	2.0015[b]
Potassium	80	1.995	1.9978	1.9997[b]
Rubidium	—	—	1.989	1.9984[c]

[a] Total electron (spin) density summed over 4 equivalent alkali nuclei.
[b] Ref. 7. [c] Ref. 8.

The e.s.r. results are summarized in Figure 2 and Table 1. Modest uptake of the alkali metal vapour (of the order of one alkali atom per sodalite cage) leads to the formation of Na_4^{3+} clusters in zeolite Na^+-Y, and K_4^{3+} clusters in zeolite K^+-Y. It is remarkable that the kind of cluster obtained depends *entirely* on the cationic form of the parent zeolite, and not on which particular alkali metal is sorbed. Thus, Na_4^{3+} clusters are formed when sodium, potassium, or rubidium vapour enters zeolite Na^+-Y, and K_4^{3+} clusters result when sodium or potassium vapour enters zeolite K^+-Y. No e.s.r. signals indicative of the formation of Rb_4^{3+} clusters were ever found in corresponding experiments with Rb^+-exchanged zeolite Y. The reactions of Na^+- and K^+-exchanged zeolite with alkali metal vapour can therefore be written (in a manner formally akin to the formation of an F-centre) as shown in equations (1) and (2), where M° represents sodium, potassium, or rubidium metal.

$$4Na^+ + M^\circ \rightarrow Na_4^{3+} + M^+ \quad (1)$$

$$4K^+ + M^\circ \rightarrow K_4^{3+} + M^+ \quad (2)$$

The evidence that the Na_4^{3+} and K_4^{3+} clusters initially formed are located within the sodalite cages as shown in

Figure 1 comes from two sources. Firstly, spectra similar to those shown in Figure 2(a) were also obtained when Na vapour entered zeolite Na$^+$-A[4] and Na$^+$-sodalite,[5] the structure of the latter material being composed *entirely* of sodalite cages. Secondly, the fact that Na_4^{3+} is formed even when K or Rb vapour enters zeolite Na$^+$-Y (and K_4^{3+} when K$^+$-Y is exposed to Na vapour) shows that the alkali ions of which the cluster is composed reside originally in the sodalite cages.

The percentage atomic character (or *n*s-orbital occupation) of the M_4^{3+} clusters can be obtained from a comparison of the hyperfine splittings with those of an isolated alkali atom; the relevant values are 41% for the Na_4^{3+} cluster, and 80% for the K_4^{3+} cluster. The appropriate values *per alkali ion* (nucleus) are then one quarter of these values. Thus the unpaired electron (spin) density *at each* sodium or potassium nucleus in the M_4^{3+} cluster is lower than the corresponding isolated free-atom value.

Exposure to higher concentrations of metal vapour resulted in dark-coloured samples with e.s.r. signals characteristic of small metallic particles.[6] These may also be initially located within the sodalite cages, but at high (metal) doping levels the large metallic clusters clearly cannot, for reasons of space, be accommodated in these β-cages. The *g*-values of these metallic clusters show a marked dependence on the metal spin-orbit coupling constant, reminiscent of the situation in bulk metals.[6—8]

Presumably, the reason why Rb_4^{3+} clusters have not been observed is (i) such clusters are intrinsically unstable, or (ii) they are too large to be accommodated within the sodalite cages. Work is now in hand to characterize the postulated tetrahedral geometry of these alkali clusters, but computer simulations shown in Figure 1 already suggest that spatial considerations are important.

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References

1. P. H. Kasai, *J. Chem. Phys.*, 1965, **43**, 3322.
2. J. A. Rabo, C. L. Angell, P. H. Kasai, and V. Schomaker, *Discuss. Faraday Soc.*, 1966, **41**, 328.
3. J. A. Rabo and P. H. Kasai, *Prog. Solid State Chem.*, 1975, **9**, 1; see also R. M. Barrer, 'Zeolites and Clay Minerals as Sorbents and Molecular Sieves,' Academic Press, London & New York, 1978.
4. M. R. Harrison, P. P. Edwards, J. Klinowski, J. M. Thomas, D. C. Johnson, and C. J. Page, *J. Solid State Chem.*, to be submitted.
5. R. M. Barrer and J. F. Cole, *J. Phys. Chem.*, 1968, **29**, 1755; see also J. M. Thomas in 'Physics and Chemistry of Electrons and Ions in Condensed Matter,' Proceedings of NATO Davy A.S.I., Cambridge, September, 1983, eds. J. A. Acrivos, N. F. Mott, and A. D. Yoffe, D. Reidel, 1984, in the press.
6. R. N. Edwards, P. P. Edwards, S. C. Guy, and D. C. Johnson, *J. Phys. Chem.*, in the press.
7. F. Beuneu and P. Monod, *Phys. Rev. B*, 1978, **19**, 2422.
8. W. M. Walsh, L. W. Rupp, and P. H. Schmidt, *Phys. Rev. Lett.*, 1972, **16**, 181.