Fe^{3+} Ions in Crystalline Aluminosilicate Frameworks: Electron Spin Resonance, Phosphorescence, and Thermal Studies

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Summary E.s.r., phosphorescence, and thermal studies of the synthetic zeolites mordenite and faujasite indicate that the Fe^{3+} impurity ions occupy tetrahedral Si^{4+} or Al^{3+} positions in the framework.

In recent years a number of papers and patents in the literature have claimed that it is possible to synthesise zeolites containing ions other than Al^{3+} or Si^{4+} in the framework.[1–3] That this is possible has been proved so far only for Ga^{3+} and Ge^{4+}: gallogermanates have been synthesised analogous to known zeolites.[3] In previous publications evidence for framework substitution has relied on the non-exchangeability of the ion.[1,2] In view of recent work on salt occlusion in zeolites[4] the non-exchangeability criterion is no longer sufficient evidence.

A technique which can give information about the co-ordination of the impurity ion is required. Therefore we have studied the synthetic zeolites mordenite and faujasite, both of which contained trace amounts (*ca.* 0·1% by weight) of non-exchangeable Fe^{3+}, using e.s.r. and phosphorescence spectroscopy. We have obtained results which establish that the Fe^{3+} ions in these zeolites have tetrahedral co-ordination.

In *X*-band e.s.r. studies of powders of Linde Y and Norton Zeolon (mordenite) in the fully hydrated state we have observed a signal with $g_{\text{eff}} = 4{\cdot}3$.

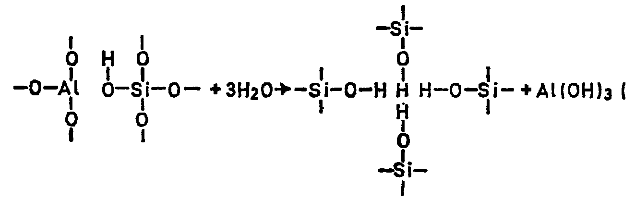
This result can be interpreted with the Spin Hamiltonian:

$$\boldsymbol{H} = g\beta HS_z + DS_z^2 + E(S_x^2 - S_y^2) \text{ with } D = 0, E \neq 0.$$

This means that the co-ordination around the Fe^{3+} is rhombically distorted. Griffith[5] has pointed out that such a condition can be achieved both through distorted octahedral and tetrahedral co-ordination. That the symmetry of the Fe^{3+} species in hydrated Zeolon and Linde Y is tetrahedral has been confirmed using phosphorescence spectroscopy. We have observed an emission band around 5000 Å in both zeolites and this emission is due to the transition $^4T_1\ (d_\gamma^3 d_\varepsilon^2) \rightarrow {}^6A_1\ (d_\gamma^2 d_\varepsilon^3)$. Octahedral Fe^{3+} would give a peak around 7000 Å corresponding to the transition $^4T_{1g}(d_\varepsilon^4 d_\gamma^1) \rightarrow {}^6A_{1g}(d_\varepsilon^3 d_\gamma^2)$.[6]

For the thermal studies the NH_4^+ forms of both Linde Y and Norton Zeolon were prepared conventionally by batch exchange and the effect of heating *in vacuo* at temperatures between 300 and 700° was studied using e.s.r. Above 400° a broad ferromagnetic resonance was observed in both the NH_4Y and ammonium Zeolon samples. No such phenomenon was observed in sodium Zeolon and only a weak ferromagnetic signal was observed in NaY above 500°. Guinier photographs showed no substantial loss of crystallinity though in both NH_4Y and ammonium Zeolon there was a decrease in lattice spacing in samples treated above 500° This will be discussed in a later publication.

The significant factor in the heat treatment of the NH_4 forms of both Y and Zeolon was the decrease in intensity of the $g_{\text{eff}} = 4{\cdot}3$ signal concomitant with the increase in intensity of the ferromagnetic resonance. This suggests that the Fe^{3+} ions are in the framework and precipitate out during the process of deammoniation and dehydroxylation to form small particles of a ferromagnetic iron–oxygen species. Support for this suggestion is given in a recent paper by Kerr[7] in which he pointed out that during heating of the hydrogen form of zeolite Y reaction (1) can occur, *i.e.* a reaction occurs between framework trico-ordinated Al^{3+} ions and water present in the environs to produce an Al^{3+} deficient product and $Al(OH)_3$. Kerr has pointed out that such an effect can occur even under vacuum heating.[8] The reaction represented by equation (1) provides a mechanism whereby Fe^{3+} can come out of the framework along with Al^{3+} to give $Fe(OH)_3$ and $Al(OH)_3$, which one could readily envisage as forming a ferromagnetic species. This would also account for the absence of a ferromagnetic resonance in our samples of sodium Zeolon since there would be very few trico-ordinated Fe^{3+} ions in the Na^+ form of the zeolite. The appearance of the weaker ferromagnetic signal above 500° in NaY can be attributed to a slight Na^+ deficiency in this zeolite *i.e.* some of the cations balancing the framework charge are H^+ ions. Above 500° dehydration occurs in Y zeolite which could lead to the formation of some reactive trico-ordinated Fe^{3+} species.


(1)

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