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## The Incorporation of Heteroatoms into Faujastic Framework by Secondary Synthesis Using Aqueous Fluoride Complexes

**J. Dwyer* and K. Karim**
*Chemistry Department, UMIST, PO Box 88, Manchester M60 1QD, UK*

Gallium atoms can be introduced into the framework of the faujasitic zeolite by treatment of zeolites with an aqueous solution of the metal fluoride.

Zeolite Y, which has the faujastic framework structure, is the active component in catalysts for the processing of gas-oil by fluid catalytic cracking.[1] The activity and selectivity patterns in the transformation of hydrocarbons over acidic zeolite Y depend strongly upon the concentration and distribution of aluminium atoms within the framework and are also influenced by non-framework species such as counterions or occluded non-zeolite phases.[2] Secondary syntheses involving either gas phase or solution phase[4] sources of silica have been reported. For example, careful treatment of zeolite Y in the ammonium form with ammonium hexafluorosilicate can result in crystalline faujasitic zeolites with the framework Si/Al $< 7$.[4]

Since the catalytic properties of zeolites are also influenced by the presence of heteroatoms within the framework, there is interest in developing secondary synthesis involving the controlled replacement of framework tetrahedral atoms by heteroatoms.[5] The present Communication describes the successful substitution of a portion of the framework aluminium atoms by gallium.

Zeolite-Y (Si/Al = 2.5, ex-Crosfield Catalysts), in the ammonium form was slurried with ammonium acetate solution (3.4 mol dm$^{-3}$). The slurry (10 g zeolite to 100 cm$^3$ solution) was heated to reaction temperature (70–80 °C) and the solution of gallium nitrate and ammonium fluoride was added over a period of 3–4 h.[6]

The products were filtered and washed by heating at 80–85 °C for 2 h in ammonium sulphate solution (1.5 mol dm$^{-3}$) using a ratio of solid to solution of 1 : 10. Washing was repeated to remove the fluoride. The degree of framework substitution of Ga for Al was controlled by varying the amount of the Ga fluoride complexes used. The modified materials were characterised by X-ray powder diffraction, FTIR and solid-state NMR.

Fig. 1(*a*) shows changes in the unit cell parameter of the (cubic) faujasite as a function of replacement of aluminium by gallium. For comparison, results for substitution of Si for Al are also shown in Fig. 1. The increase in cell parameters when Ga atoms replace Al reflects changes in the M–O bond lengths (1.72 and 1.69 Å). Fig. 1(*b*), which confirms the trend in Fig. 1(*a*), shows the changes in the IR frequency for the framework bands (symmetric stretch) in the region 770–820 cm$^{-1}$. The decrease in frequency on replacement of Al by Ga, again reflects the order of T–O bond lengths. Increased T–O bond lengths results in a reduced frequency of vibration. The increase in the unit cell size when Ga replaces Al is documented for the faujastic structure[7] but in some structures there may be a reduction in cell size (sodalite)[8] or no observable change.[9] Consequently, although substitution may not lead to a change in the unit cell size, a clear trend in cell

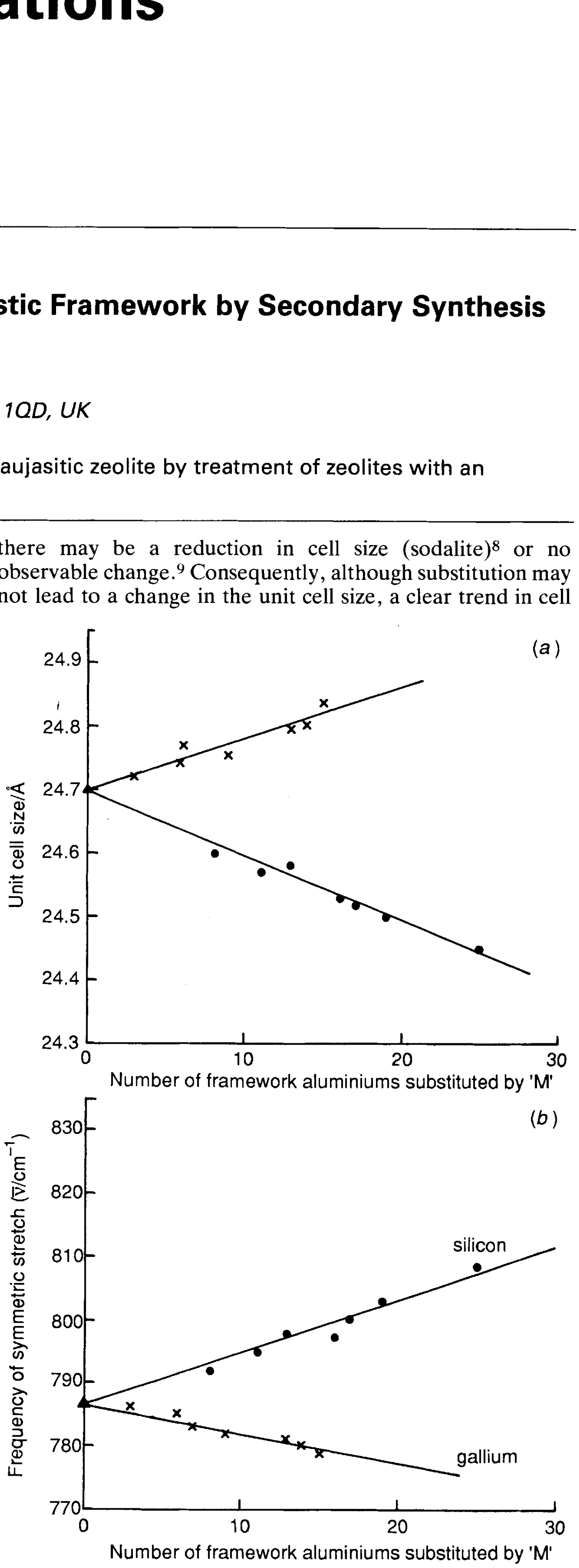

**Fig. 1** Substitution of aluminium in the faujasite framework by M (M = Ga or Si) using aqueous metal fluorides. (*a*) Unit cell parameter; (*b*) frequency of symmetric stretch.

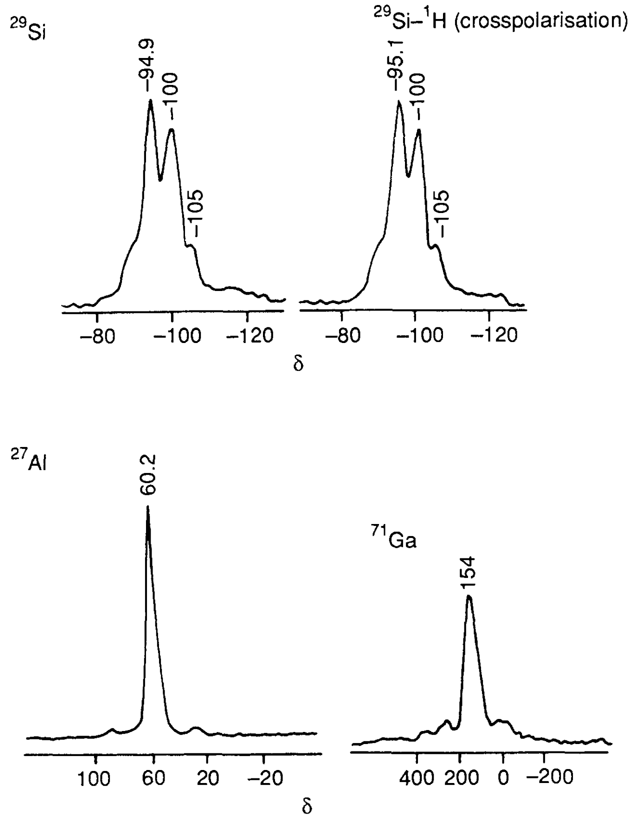

**Fig. 2** Solid-state MAS-NMR spectra for [Ga]AlY zeolite

parameter is good evidence for incorporation of heteroatoms into the framework. In the present study further evidence is also provided by solid-state NMR (Fig. 2). The $^{27}$Al and $^{71}$Ga spectra show single peaks with resonances assigned to tetrahedral environments. There is no evidence for the occlusion of dislodged aluminium, which would be expected to appear as a peak at δ *ca.* 0 nor is there evidence for extra-framework octahedral occluded gallium. Comparison of the $^{29}$Si NMR with and without $^{1}$H–$^{29}$Si cross polarisation clearly shows (Fig. 2) that there is little evidence for the existence of silanol groups or nests, which would result in an enhanced intensity of the peak at δ *ca.* 100.[10] Moreover, FTIR and nitrogen sorption studies[11] provide no evidence for a significant increase in defect sites or in silanol groups associated with amorphous material.

A comparison of [Ga]AlY prepared by secondary synthesis with ion-exchange and impregnation of Ga shows that neither method results in substitution of Ga into the framework.[11]

In conclusion, the present work clearly shows that Ga can be substituted into the faujasitic framework by secondary synthesis using aqueous metal fluoride complexes. The present results contrast with those for $BF_4^-$ where there is no substitution of B into the zeolite framework[12] and are in accord with results for Fe, Ti,[13] Sn and Cr substitution.[14]

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