# Ga, Ti Avoidance in the Microporous Titanogallosilicate ETGS-10

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Gallium is incorporated into the microporous titanosilicate ETS-10 to give ETGS-10; the isomorphous substitution occurs exclusively at silicon sites such that gallium avoids neighbouring titanium.

Recently, we have solved the structure of the microporous titanosilicate ETS-10,[1,2] previously synthesized by others.[3] The structure of ETS-10 may be described in terms of an intergrowth of two end member polymorphs, terms A and B, both of which consist of a three-dimensional 12-membered ring structure. Polymorph A belongs to a chiral space group and, like zeolite β, has a spiral channel. Unlike other zeolite-type materials, ETS-10 contains framework atoms in sixfold coordination: the titanium(IV) atoms are corner-sharing octahedra and the silicon atoms are corner-sharing tetrahedra. Hence, for every framework titanium there is an associated 2− charge. The anhydrous formula of ETS-10 is $M^{m+}_{2/m}TiSi_5O_{13}$, where M is a cation with charge *m* ($Na^+$ and $K^+$ in the as-prepared material). In order to improve the acid characteristics of ETS-10 we have systematically studied the isomorphous substitution of silicon and titanium by certain heteroatoms. Recently, we have shown that aluminium is incorporated exclusively at tetrahedral silicon sites (yielding ETAS-10) such that aluminium avoids neighbouring titanium.[4] Now we report that gallium may also be incorporated in the framework of ETS-10 (yielding ETGS-10) at the same silicon sites.

ETGS-10 with Si:Ga = 13 (as measured by $^{29}Si$ NMR, see below) was prepared using a modification of the ETAS-10 synthesis.† The samples were characterized by solid-state NMR, powder X-ray diffraction, scanning electron microscopy and chemical analysis.

Fig. 1 shows the $^{29}Si$ magic-angle spinning (MAS) NMR spectra of ETS-10, ETAS-10 and ETGS-10. For the ensuing arguments, the choice of polymorph is irrelevant as the local T-site environment remains unaffected. In ETS-10 there are two types of silicon chemical environments, Si(3Si, 1Ti) and Si(4Si, 0Ti), which give the two groups of resonances at δ −94 to −97 and δ *ca.* −103.7, respectively. The ratio of these environments is 4:1. The spectrum reveals a further crystallographic splitting of the Si(3Si, 1Ti) site.[1,2] The spectrum of ETAS-10 contains all the ETS-10 resonances plus two other peaks *ca.* 4 ppm downfield from the Si(3Si, 1Ti) signals. These have been ascribed to the framework incorporation of aluminium to produce Si(2Si, 1Al, 1Ti) environments.[4] It is important to note that there is no signal *ca.* 4 ppm downfield from the Si(4Si, 0Ti) resonance, showing no aluminium substitution neighbouring this silicon site and, hence, providing a direct proof of Al, Ti avoidance. The $^{27}Al$ MAS NMR (Fig. 2) spectrum is also indicative of this effect since it contains a single resonance at δ *ca.* 60 assigned to Al(4Si). A small contribution from six-coordinated aluminium (*ca.* 2%) is evidenced by resonances between δ 0 and −10. The $^{29}Si$ MAS NMR spectrum of gallium-substituted ETS-10 resembles the spectrum of ETAS-10: a broad peak is seen downfield from the Si(3Si, 1Ti) signals. This peak can be deconvoluted into two component signals, each one *ca.* 1.5 ppm downfield from the Si(2Si, 1Al, 1Ti) resonances, and which we assign to Si(2Si, 1Ga, 1Ti) as similar downfield shifts of the $^{29}Si$ resonances have been reported for gallium-substituted zeolites.[5] No signals are observed in the

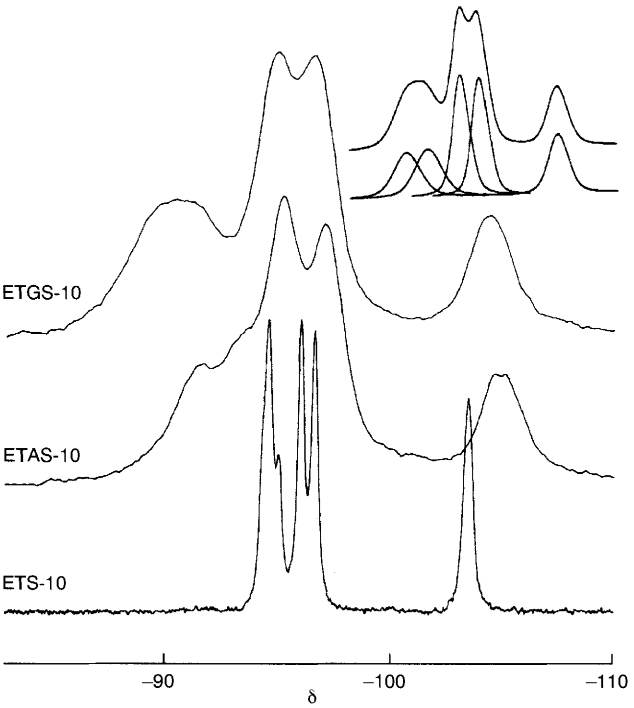

**Fig. 1** $^{29}Si$ MAS NMR spectra of ETS-10, ETAS-10 (Si:Al = 14) and ETGS-10 (Si:Ga = 13; inset shows deconvolution) recorded at 79.5 MHz on a Bruker MSL 400P spectrometer, using 40° radiofrequency pulses, 40 s recycle delays and a spinning rate of 5.5 kHz. Chemical shifts are quoted relative to $SiMe_4$.

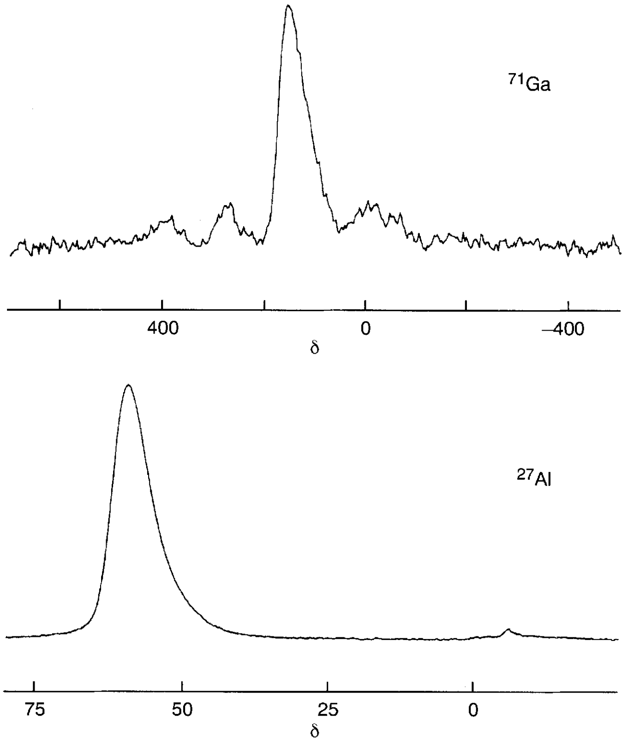

**Fig. 2** $^{27}Al$ and $^{71}Ga$ MAS NMR spectra of ETAS-10 (Si:Al = 14) and ETGS-10 (Si:Ga = 13) recorded at 104.26 and 121.98 MHz, respectively, on a Bruker MSL 400P spectrometer, using very short, 0.6 μs (equivalent to 10° and 15°), and powerful radiofrequency pulses, respectively. The recycle delay was 0.5 s and the spinning rate was 15 kHz. Chemical shifts are quoted relative to $[Al(H_2O)_6]^{3+}$ and $[Ga(H_2O)_6]^{3+}$, respectively.

range $\delta$ −99 to −103 of ETGS-10. Detailed analysis of spectral intensities, following the arguments presented elsewhere for ETAS-10,[4] allow framework Si : Ga and Si : Ti ratios (13 and 4.8, respectively) to be calculated from eqns. (1) and (2).

$$\mathrm{Si/Ga} = \frac{\sum_{n=0}^{4-m} \sum_{m=0}^{4-n} I_{\mathrm{Si}(n\mathrm{Ga},m\mathrm{Ti})}}{0.25 \sum_{n=0}^{4-m} \sum_{m=0}^{4-n} nI_{\mathrm{Si}(n\mathrm{Ga},m\mathrm{Ti})}} \tag{1}$$

$$\mathrm{Si/Ti} = \frac{\sum_{n=0}^{4-m} \sum_{m=0}^{4-n} I_{\mathrm{Si}(n\mathrm{Ga},m\mathrm{Ti})}}{0.25 \sum_{n=0}^{4-m} \sum_{m=0}^{4-n} mI_{\mathrm{Si}(n\mathrm{Ga},m\mathrm{Ti})}} \tag{2}$$

On the other hand, the $^{71}$Ga MAS NMR spectrum of fully hydrated ETGS-10 (see Fig. 2) displays a broad peak at $\delta$ *ca.* 160 which is characteristic of four-coordinated gallium. Bradley *et al.* have recently found a correlation between the $^{27}$Al and $^{71}$Ga chemical shifts (shift of the peak maximum and/or isotropic shift) of several different oxides [$\delta(^{71}\mathrm{Ga})$ 2.83, $\delta(^{27}\mathrm{Al})$ − 4.50].[6] using the chemical shift of the peak maximum of the ETAS-10 $^{27}$Al resonance ($\delta$ 60) we have estimated for the gallium analogue (ETGS-10) a $^{71}$Ga shift of $\delta$ 165, in good agreement with the experimental result. This further supports the assignment of the $^{29}$Si spectrum and confirms that gallium avoids neighbouring titanium in ETGS-10. Previous work on ETAS-10 has revealed that at relatively high aluminium concentrations, slight deviations from the Al, Ti avoidance rule are observed.[4] Hence, it is possible that Ga, Ti avoidance also breaks down for ETGS-10 at high gallium concentrations. Work is now in progress to assess this possibility.

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## Footnote

† An alkaline solution was made by mixing 11.43 g sodium silicate ($Na_2O$ 8% *m*/*m*, $SiO_2$ 27% *m*/*m*), 7.56 g $H_2O$, 1.68 g NaOH and 0.94 g KF. A mixed Ti : Ga solution was made by adding 5.70 g $TiCl_3$ (1.9 mol dm$^{-3}$ solution of $TiCl_3$ in 2.0 mol dm$^{-3}$ HCl) to 0.78 g $CaCl_3$. The alkaline silicate solution and the mixed Ti–Ga solution were combined with thorough stirring. 0.12 g Seed ETS-10 was added to the resulting gel. This gel, with a composition 4.58 $Na_2O$ : 0.93 $K_2O$ : 5.91 $SiO_2$ : $TiO_2$ : 0.25 $Ga_2O_3$ : 126 $H_2O$, was autoclaved under autogeneous pressure for 5 d at 200 °C. The resulting product was cooled to room temp., filtered and washed with distilled water and dried overnight at 120 °C. The dried powder (5.3 g) was then treated with 10.0 g NaOH (5% *m*/*m* solution) for 24 h at 200 °C, after which it was cooled, filtered, washed and dried as previously. The final product was calcined in air for 2 h at 350 °C ($^{71}$Ga NMR shows that this treatment does not extract gallium from the framework).

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