^{17}O 3QMAS-NMR OF SYNTHETIC ALKALI ALUMINOSILICATE GEL

P. Duxson, F. Separovic, G.C. Lukey, J.S.J. van Deventer (University of Melbourne); Z.H. Gan (NHMFL)

Introduction

^{17}O 3QMAS NMR can be used to detect T-O-T sites (where T is tetrahedrally coordinated Si or Al) in alkali aluminosilicates. The quadrupolar coupling constants for the three different T-O-T linkages (Al-O-Al, Si-O-Al and Si-O-Si) increase with the radius of alkali cations (Li < Na < K). By contrast, thermodynamic predictions suggest that Al,Si order is decreased by use of large radius alkali cations (Na and K). Use of high magnetic fields improves spectral resolution because the chemical shift difference is increased in frequency terms, while the quadrupolar interaction is independent of the field. Coupled with improved sensitivity at high field, differences in Al,Si ordering may be determined in Na- and K-aluminosilicates with different Si/Al ratios.

Experimental

Aluminosilicate gels were prepared by reaction of a synthetic powder ($2{\cdot}SiO_2.Al_2O_3$) in alkali solution (H_2O/M_2O = 11, M = Na or K), containing 20% $H_2{}^{17}O$. The nominal chemical composition of the specimens was $MAlSiO_4$. Samples were cured at 40°C for 24 hours, crushed and dried to eliminate isotropic NMR signals from water. ^{17}O 3QMAS NMR experiments were carried out on the 830 MHz instrument at NHMFL, operating at a Larmor frequency of 112.452 MHz, using an NHMFL single resonance broadband 4 mm MAS probe and a spinning speed of 10 kHz.

Results and Discussion

^{17}O 3QMAS NMR spectra of alkali aluminosilicate gels with Si/Al ratio of unity prepared with different alkali cations, sodium and potassium are shown in Fig. 1. The Na-specimen (Fig. 1a) exhibits two peaks indicative of Al-O-Si and Si-O-Si linkages, with the larger intensity associated with Al-O-Si. From a mass balance perspective, contributions from Al-O-Al must be present in the shoulder of the main Al-O-Si peak. The K-specimen (Fig. 1b) exhibits a greater degree of disorder, as indicated by the larger Si-O-Si peak. A third peak is clearly seen at approximately 80 ppm, possibly due to octahedral Al-O-Al linkages.

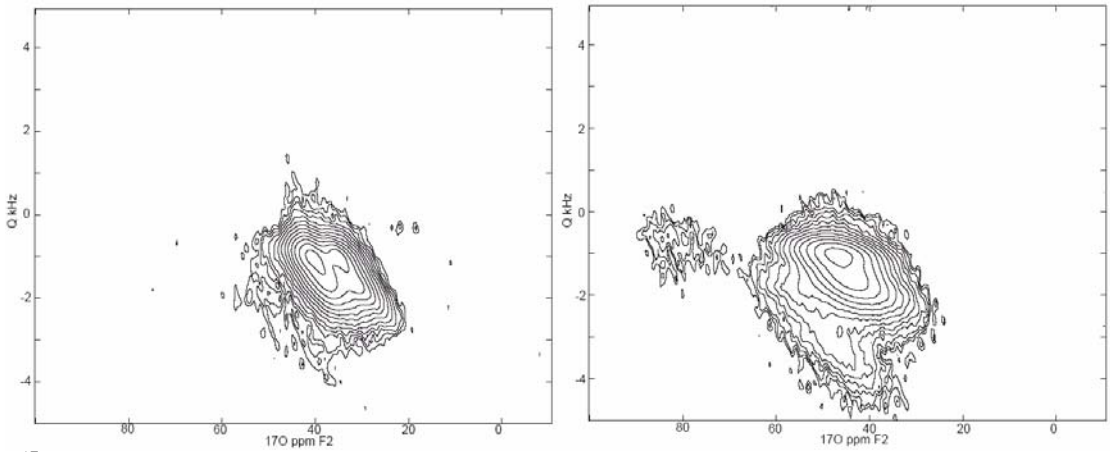

Figure 1. ^{17}O 3QMAS NMR spectra of alkali aluminosilicate gels with Si/Al ratio of 1, synthesised by reaction with (a) NaOH, and (b) KOH.

Conclusions

The variation in the degree of Al,Si ordering observed in Fig. 1 correlates well with thermodynamic predictions [1], and directly demonstrates the effect of alkali on the degree of ordering in the short-range structure of aluminosilicates.

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References

[1] Provis, J.L., Chemistry of Materials, **17**, 2976-2986 (2005).