An NMR Study of the Reaction of Water with $AlPO_4$-5

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$AlPO_4$-5 undergoes a readily reversible structural transformation, by reaction with water; both chemisorption and physisorption of water occur on this molecular sieve; up to *ca.* 40% of the original 4-co-ordinate Al is converted into 6-co-ordinate Al.

$AlPO_4$-5 comprises alternating AlO_4 and PO_4 tetrahedra linked together to form a microporous structure with a unidimensional pore system of diameter approximately 8 Å.[1] NMR studies of this material and the analogous SAPO-5 have been performed by a number of workers.[2—6] In some cases[3,6] the ^{27}Al spectrum consists of a single, symmetric line, while in others[2,4,5] the major peak is skewed and a minor additional high field peak is apparent. The presence of the high field signal has been attributed[4] to counter-cation, extra-lattice Al which acts as a Lewis acid site for methanol conversion to hydrocarbons. We have discovered a relationship between the appearance of the ^{27}Al and the ^{31}P NMR spectra, and the water content in $AlPO_4$-5. Variations in reported spectra are found to be due to differences in sample preparation and water contents. These materials undergo a readily reversible structural transformation, by reaction with water, to form 6-co-ordinate Al which is responsible for the high field ^{27}Al peak. This unusual structural transformation has implications for the catalytic, ion exchange, and sorptive properties of $AlPO_4$-5 and explains the unexpectedly high water adsorption capacity.

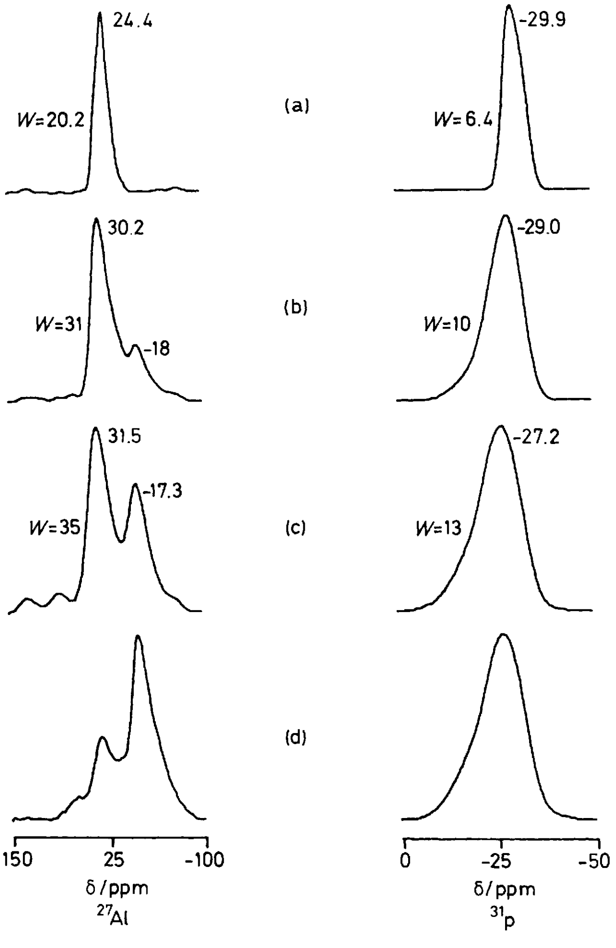

Figure 1. ^{27}Al (left) and ^{31}P (right) spectra of $AlPO_4$-5 after addition of (a), 0, (b) 0.2, and (c) 0.28 cm^3 H_2O/g $AlPO_4$-5. Peak positions and widths (*W*), in p.p.m., of Bloch decay spectra are shown. The cross polarisation spectra after saturation with water are given in (d). Shifts are referenced to 85% H_3PO_4 for ^{31}P, and 1 M $Al(NO_3)_3$ solution for ^{27}Al.

An $AlPO_4$-5 sample was synthesised following a literature procedure, using triethylamine as the structure-directing species. The calcined sample was separated into seven portions, dried at 200 °C for 10 h, then cooled and stored in sealed vials. Various amounts of water (0—0.28 cm^3 H_2O/g dry $AlPO_4$-5) were injected into each portion and then left to equilibrate at 25 °C, after which they were packed under dry nitrogen into sealed rotors for magic angle spinning NMR at 5 kHz in a Doty probe on a Varian XL200 spectrometer.

The ^{27}Al and ^{31}P spectra of $AlPO_4$-5 with water contents of 0, 0.20, and a maximum uptake of 0.28 cm^3 g^{-1} are shown in Figure 1(a—c), respectively. The peak positions and widths (*W*) are given on the spectra. The dehydrated starting material showed a single symmetric ^{31}P peak, similar to a previous study[3] at 6.4 T. As water was added, the peak shifted downfield and broadened due to an increasing intensity in the vicinity of δ -15 p.p.m.

The single ^{27}Al peak in dehydrated $AlPO_4$-5 is consistent with the shifts and electric field gradient (efg) parameters reported by Müller *et al.*[3] for 4-co-ordinate Al (*ca.* δ 24 p.p.m.). On addition of water the peak due to 4-co-ordinate Al shifted downfield, broadened, and reduced in intensity, while there was a concomitant increase in the intensity of a broad peak near -18 p.p.m. This high field peak is typical of 6-co-ordinate Al in aluminium phosphates[8] and has been observed in $AlPO_4$-17,[2] variscite,[9] and metavariscite.[10] The total intensity remained constant and comparison with standards indicated that all of the Al was NMR visible. Up to 40% of the Al could be made 6-co-ordinate and the reaction was readily reversible by storing over P_2O_5. It is remarkable that such a large proportion of the framework can be affected without causing structural collapse.

Since both the ^{27}Al and the ^{31}P NMR spectra are affected by hydration and since a reduction in the efg at Al would normally produce a downfield shift accompanied by a reduction in the width, it seems likely that the peak broadening is due to shifts from a variety of environments, while the downfield shift is due to a reduction in the Al–O–P bond angles.[11] Lattice distortions are also apparent through changes to the unit cell parameters. Powder *X*-ray diffraction studies showed that hydration caused a reduction in the *a*-parameter (13.71 *cf.* 13.78 Å) and an increase in the *c*-parameter (8.44 *cf.* 8.38 Å).

The ^{27}Al and ^{31}P cross-polarisation spectra of fully hydrated $AlPO_4$-5 are shown in Figure 1(d). In the ^{27}Al spectrum the high field peak is enhanced relative to the low field peak, consistent with chemisorption of water to form the 6-co-ordinate Al. The ^{31}P spectrum is identical to the non-cross-polarised spectrum [Figure 1(c)], showing that all P atoms are equally accessible to protons.

In conclusion, the intensity of the peak from 6-co-ordinate Al has been shown to depend on the water content and is not a measure of the ion-exchange capacity of $AlPO_4$-5.

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