CHEMISTRY LETTERS, pp. 1747-1750, 1985.

ALUMINIUM-27, PHOSPHORUS-31, AND SILICON-29 MAS NMR STUDIES OF THE SILICOALUMINOPHOSPHATE MOLECULAR SIEVE SAPO-5

Ian P. APPLEYARD, Robin K. HARRIS,* and Frank R. FITCH†
Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England
† Laporte Industries Limited, PO Box 2, Moorfield Road, Widnes, Cheshire WA8 OJU, England

Multinuclear MAS NMR has been used to study, for the first time, a member of a new family of molecular sieves, the silicoaluminophosphates, SAPO-5. The silicon-29 NMR spectra are consistent with tetrahedral (framework) silicon and provide information concerning the method of substitution of the silicon atoms into the aluminophosphate lattice.

SAPO-5[1] is a member of a recently-synthesised family of silicoaluminophosphate materials.[2] It is topologically related to the novel structure type found for $AlPO_4$-5,[3] an aluminophosphate molecular sieve.[4] The SAPO molecular sieves are synthesised hydrothermally using organic amines or quaternary ammonium salts as templates. The materials crystallize at 100-200 °C from reactive mixtures containing the template, reactive alumina (boehmite), phosphoric acid and silica sol. Amorphous or dense crystalline materials form in the absence of the template species. The amount of silicon can be varied in the SAPO materials according to synthesis conditions. Both the precursor (Pr_3N-SAPO-5) and the calcined form (in air at 600 °C) of SAPO-5 have been studied in the present work; their X-ray powder diffraction data correspond to those reported in the literature.[5]

Our NMR measurements were carried out at a magnetic field strength of 4.7 Tesla in combination with the magic-angle spinning (MAS) technique and, for some spectra, cross-polarization (CP) and/or high-power decoupling (HPD) from protons present in water molecules or hydroxyl groups. Spinning rates of ca. 3 kHz were used. Between 80 and 110 transients were acquired each for the ^{31}P and ^{27}Al MAS NMR spectra, using recycle delays of 6 s for ^{31}P (CP/HPD) and 2 s for ^{27}Al (single pulse excitation (SPE)-no HPD). The low silicon loading in this particular SAPO-5 sample (ca. 5%), means that for the ^{29}Si spectra (SPE-no HPD), a large number of transients (between 12000 and 18000, with a recycle delay of 10 s) were required for a reasonable S/N ratio.

Figure 1 shows ^{27}Al and ^{31}P MAS NMR spectra of the silicoaluminophosphate molecular sieve (both the precursor and calcined forms). Experimental chemical shifts and linewidths are collated in Table 1. The data are consistent with those reported in previous studies[6,7] on $AlPO_4$-5, confirming that the basic structure

of SAPO-5 consists of alternating AlO_4 and PO_4 tetrahedra. Surprisingly, substitution of silicon into the aluminophosphate lattice does not appear to have affected the ^{31}P or ^{27}Al MAS NMR spectra noticeably. The small peak to the high-frequency side of the main ^{27}Al resonance appears to be a spinning sideband; it occurs for $AlPO_4$-5 samples also. The ^{31}P MAS NMR spectrum of the 'as-synthesised' precursor (Pr_3N-SAPO-5), however, has a shoulder to high frequency not observed for $AlPO_4$-5. This shoulder is no longer visible after calcination, suggesting that it arises from framework phosphorus nuclei adjacent to occluded organic template molecules. Carbon-13 CP/MAS NMR is at present being used to evaluate this hypothesis. The chemical shift difference between the precursor and calcined SAPO-5 may be attributed to the dehydrated nature of SAPO-5 relative to Pr_3N-SAPO-5. Such a shift has not been mentioned previously in the literature but we have noted that it occurs for $AlPO_4$-5 also. It is still possible to cross-polarise to give a ^{31}P NMR signal following calcination, probably because water molecules in the pores are strongly coordinated with phosphorus atoms in the framework. It is relevant to note that SAPO-5 can be synthesised with a variable silicon content and consequently will exhibit moderate to high hydrophilic surface properties.

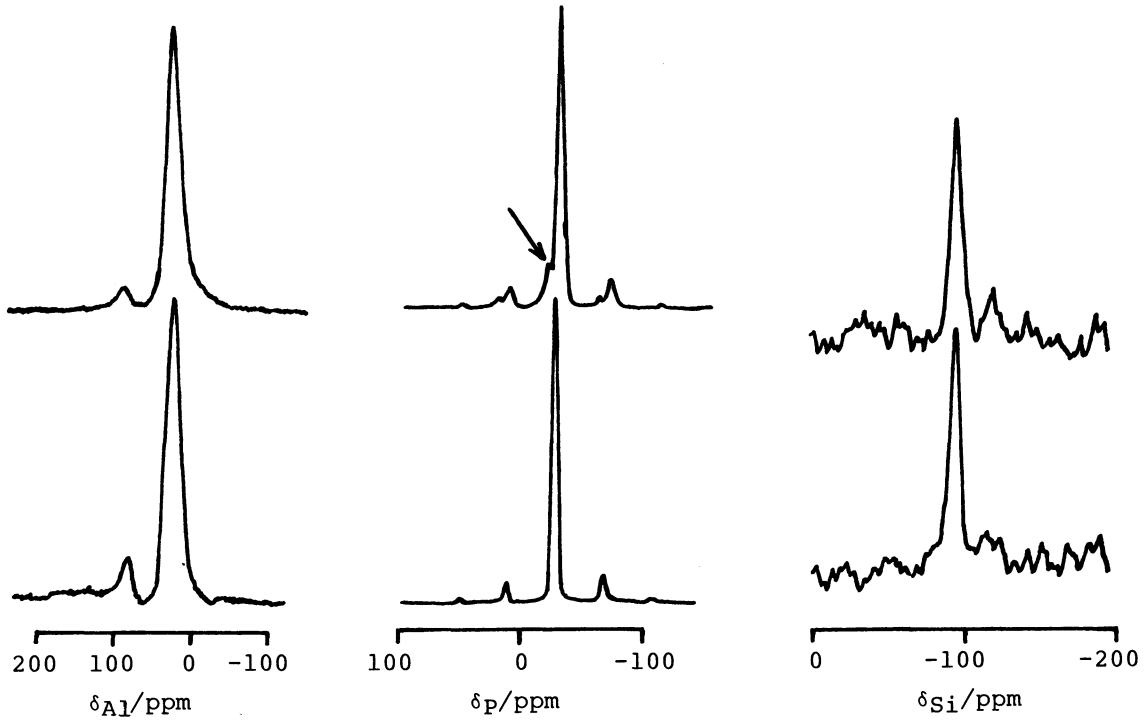

Fig. 1. Aluminium-27 (left), phosphorus-31 (centre) and silicon-29 (right) MAS NMR spectra (obtained at 50.1, 80.0, and 39.7 MHz respectively) for the precursor (upper spectra) and calcined (lower spectra) forms of SAPO-5. The shoulder on the ^{31}P spectrum of the precursor, mentioned in the text, is indicated by an arrow. Other minor peaks are attributed to spinning sidebands. A line-broadening of 100 Hz has been applied to the ^{29}Si spectra. The chemical shift scales are given relative to signals for aqueous $[Al(H_2O)_6]^{3+}$, 85% H_3PO_4, and Me_4Si for ^{27}Al, ^{31}P, and ^{29}Si respectively.

Table 1. ^{27}Al and ^{31}P NMR data for Pr_3N-SAPO-5 and SAPO-5

	Aluminium-27		Phosphorus-31	
	Chemical shift/ppm	Linewidth/Hz	Chemical shift/ppm	Linewidth/Hz
Pr_3N-SAPO-5	33.5	1200	-28.4	540
SAPO-5	24.1	1100	-29.6	400

Figure 1 also shows ^{29}Si MAS NMR spectra of the precursor and calcined forms of SAPO-5. Only a single resonance line, with a chemical shift of ca. -92 ppm, is observed in both spectra (within the limits of resolution). The linewidths (before line broadening is applied) are substantial, being 200 Hz for the precursor and 260 Hz for the calcined sample. The silicon atoms can substitute into the aluminophosphate framework via (1) silicon substitution for aluminium, (2) silicon substitution for phosphorus, or (3) simultaneous substitution of two silicons for one aluminium and one phosphorus. Lok et al.[2] consider that the second and third possibilities are more likely than the first. There are, indeed, chemical grounds (e.g. that there may be a small excess Al over P, and that SAPO undergoes cation exchange) for excluding route (1) as more important than route (2). Our own sample analyses as $Si_{0.05}Al_{0.48}P_{0.47}$, though the proportions of aluminium and phosphorus are equal within experimental error. If route (3) were important, at least two ^{29}Si signals should be observed, corresponding to Q°(4Al) and Q°(4P), if substitution is at isolated AlO_4 and PO_4 tetrahedra, provided resolution is adequate -- unfortunately, there is little or no information in the literature on the effect of a Si-O-P linkage on the ^{29}Si resonance. The absence of a signal at ca. -112 ppm shows there are no large clusters of SiO_2 or extra-framework silica. One reasonable conclusion is that route (2) is the dominant contributor. However, the ^{29}Si chemical shift (ca. -92 ppm) is an unusual one for silicon atoms in a Q°(4Al) environment. There is, it is true, precedence for such a shift in the case of zeolite A, the ^{29}Si NMR spectrum of which was at first controversial. Presumably, the unusual shift for SAPO-5 may be caused by strained angles at silicon and/or by the influence of the second-sphere phosphorus atoms. It is, alternatively, possible that route (3) is dominant, with substitution at contiguous AlO_4 and PO_4 tetrahedra and with inadequate resolution to distinguish Q^1(3Al) and Q^1(3P). It is hoped to produce further evidence regarding the environment of silicon atoms in SAPO-5 by using ^{29}Si enrichment and improving spectral resolution.

One of us (I.P.A.) would like to thank the S.E.R.C. and Laporte Industries Ltd. for a Research Studentship under the CASE Award Scheme. We are grateful to Mr. P.J. Croskerry (Laporte Industries Ltd.) for preparation of the SAPO-5 sample.

References

1) The acronym SAPO is derived from $(Si_xAl_yP_z)O_2$ where x, y, and z represent the mole fractions of silicon, aluminium and phosphorus, ranging from 0.01 to 0.98, 0.01 to 0.60 and 0.01 to 0.52, respectively, with x + y + z = 1. The number following the hyphen in SAPO-5 etc. denotes a specific type of structure.

2) B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan, and E.M. Flanigen, J. Am. Chem. Soc., 106, 6093 (1984).

3) J.M. Bennet, J.P. Cohen, E.M. Flanigen, J.J. Pluth, and J.V. Smith, "Intrazeolite Chemistry," The American Chemical Society, Washington DC (1983), pp. 110-118.

4) S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, and E.M. Flanigen, J. Am. Chem. Soc., 104, 1146 (1982); S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannan, and E.M. Flanigen, "Intrazeolite Chemistry," The American Chemical Society, Washington DC (1983), pp. 79-106.

5) B.M. Lok, C.A. Messina, R.L. Patton, R.T. Gajek, T.R. Cannan, and E.M. Flanigen, U.S. Patent 4 440 871, (1984).

6) C.S. Blackwell and R.L. Patton, J. Phys. Chem., 88, 6135 (1984).

7) D. Muller, E. Jahn, B. Fahlke, G. Ladwig, and U. Haubenreisser, Zeolites, 5, 53 (1985).

(Received August 17, 1985)