SAPO-46 Molecular Sieve: Incorporation of Silicon at Crystallographically Independent Sites

A. M. Prakash,[a] **C. V. V. Satyanarayana,**[b] **S. Ashtekar**[a] **and D. K. Chakrabarty***[a]

[a] *Solid State Laboratory, Department of Chemistry, Indian Institute of Technology, Bombay 400 076, India*
[b] *Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Bombay 400 076, India*

Silicon substitution for phosphorus at crystallographically distinct sites resulting in the creation of two silicon environments has been observed in SAPO-46 molecular sieves.

In continuation of our work on the environment of framework atoms in silicoaluminophosphate (SAPO) molecular sieves such as SAPO-5 and SAPO-11,[1] SAPO-34[2] and SAPO-44,[3] we report here the incorporation of silicon in SAPO-46, a novel large pore silicoaluminophosphate of AFS topology. The structure type 46, first synthesized in MeAPO/MeAPSO family,[4] has a unique three-dimensional pore structure with hexagonal symmetry and lattice parameters a = 13.3 Å and c = 26.9 Å.[5] The structure is based on capped six-membered rings with a unidimensional 12-ring channel system having a free aperture of about 8 Å cross-linked through 8-rings. Detailed synthesis procedures for the compositional variants such as MAPO-46,[6] MAPSO-46[4] and CoAPSO-46[7] have been reported. However, no information is available on the synthesis of SAPO-46.

SAPO-46 was crystallized hydrothermally from a gel of composition 4.0 $Pr^n{}_2NH$: 0.4 SiO_2 : 1.0 Al_2O_2 : 1.2 P_2O_5 : 55 H_2O, using di-(*n*-propylamine as the organic template. In a typical synthesis, 23 g of phosphoric acid (85%, Merck) was diluted with 20 g of water. Pseudoboehmite (Catapal-B, Vista) was slowly added to it with vigorous stirring and 2.41 g of fumed silica (Aerosil-200, Sigma) in 40 g of water was then added dropwise followed by dropwise addition of di-*n*-propylamine. After adding 25 g of water, the mixture was stirred and the pH was adjusted to 7.7 by using phosphoric acid. This was then heated in an autoclave at 150 °C for an initial period of 96 hours and at 180 °C for a further period of 120 hours. After crystallization the product was thoroughly washed with water and dried at 100 °C for 12 hours.

Fig. 1 shows the X-ray powder diffraction pattern of as-synthesised SAPO-46. The observed d-values are in confirmity with those values reported[4,6,7] in literature for other compositional variants. The incorporation of silicon in SAPO molecular sieves can be visualised in terms of silicon substitution in a hypothetical aluminophosphate ($AlPO_4$) framework. Silicon can substitute aluminium (mechanism 1), phosphorus (mechanism 2) or an aluminium–phosphorus pair (mechanism 3). Lok *et al.*[8] reported that mechanisms 2 and 3 are more likely than mechanism 1 in the formation of SAPO materials since they exhibit cation exchange and they show an excess of aluminium over phosphorus in their composition. Moreover, mechanism 1 leads to Si–O–P bonds in the molecular sieve framework for which no positive evidence so far exists.[10] The framework chemical composition of the product was determined by ICP-AES analysis as $(Si_{0.13}Al_{0.50}P_{0.37})O_2$. This is a typical SAPO composition in which silicon substitution appears to be taking place *via* mechanism **2**.[8]

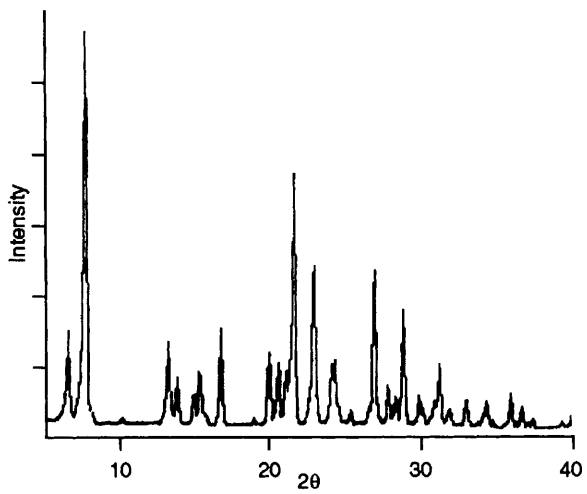

Fig. 1 X-ray powder diffraction pattern of as-synthesized SAPO-46 molecular sieve

Fig. 2 shows the ^{31}P, ^{29}Si and ^{27}Al solid-state MAS NMR spectra of SAPO-46 in the as-synthesized form. The ^{29}Si NMR spectrum shows two intense peaks at δ −89.3 and −92.7 and a weak, broad peak at *ca.* δ −110 (ref. $SiMe_4$). Significantly, no resonances were observed in the chemical shift range δ −95 to −105, normally assigned to Si (2 Al, 2 Si) and Si (1 Al, 3 Si) environments in silicon-rich SAPO materials where aluminosilicate domains exist next to SAPO domains.[9] The observed chemical shifts in the range δ −89 to −110 excludes the presence of Si–O–P linkages[10] and hence isolated substitution of silicon *via* mechanism 1 and 3 are highly unlikely to occur. Although the formation of silica islands of the first kind, where one Si atom is surrounded by four silicon atoms, is consistent with the observed ^{29}Si NMR spectrum in which the δ −93 resonance corresponds to Si (3 Al, 1 Si) coordination in the framework, we rule out this possibility as it can not account for the observed intensity ratio of the two peaks in the ^{29}Si NMR spectrum and chemical analysis results. It is reasonable to believe that the resonances at δ −89 and −93 are due to Si (4 Al) species at two crystallographically different sites in the framework resulted by the replacement of P by Si from the respective sites. Fig. 3 illustrates a part of the 12-membered ring channel of SAPO-46, where four doubly capped six-membered ring units are connected to form an 8-ring channel. The tetrahedral site at the apex of the capped 6-ring (T_1 sites) is in a different environment than those sites located in the six-membered rings (T_2 sites). For random substitution of Si in a hypothetical $AlPO_4$-46 framework, one would expect an intensity ratio of 1 : 6 between the two peaks in the ^{29}Si NMR spectrum. The spectrum simulation by deconvolution, however, gives an intensity ratio of 1.2 : 1. The result of chemical analysis shows seven silicon atoms per unit cell. If it is assumed that the Si atoms have a preference for the T_1 sites, an occupancy ratio of 4 : 3 for the two types of sites that will give an NMR intensity ratio 1.3 : 1 is expected. This is very close to the observed intensity ratio. Similar observations may be expected in other silicon substituted $AlPO_4$ materials where crystallographically differing sites exist. Unfortunately, the ^{29}Si NMR spectrum observed for the material with VPI-5 structure in which such different sites are actually present, is broad. Besides, the material has a low concentration of silicon that hinders the recording of a well resolved spectrum.[11]

The ^{31}P NMR spectrum shows a sharp resonance at δ −26 and a shoulder at δ −31 (ref. H_3PO_4). Resonances in the range δ −25 to −35 are normally assigned to tetrahedral phosphorus environments in $AlPO_4$ based molecular sieves.[12] Based on our interpretation of the ^{29}Si NMR spectrum, the occupation of T_1 sites by P atoms is not possible. The second peak appears as a shoulder and it was not amenable to deconvolution. After removing the template by calcination,

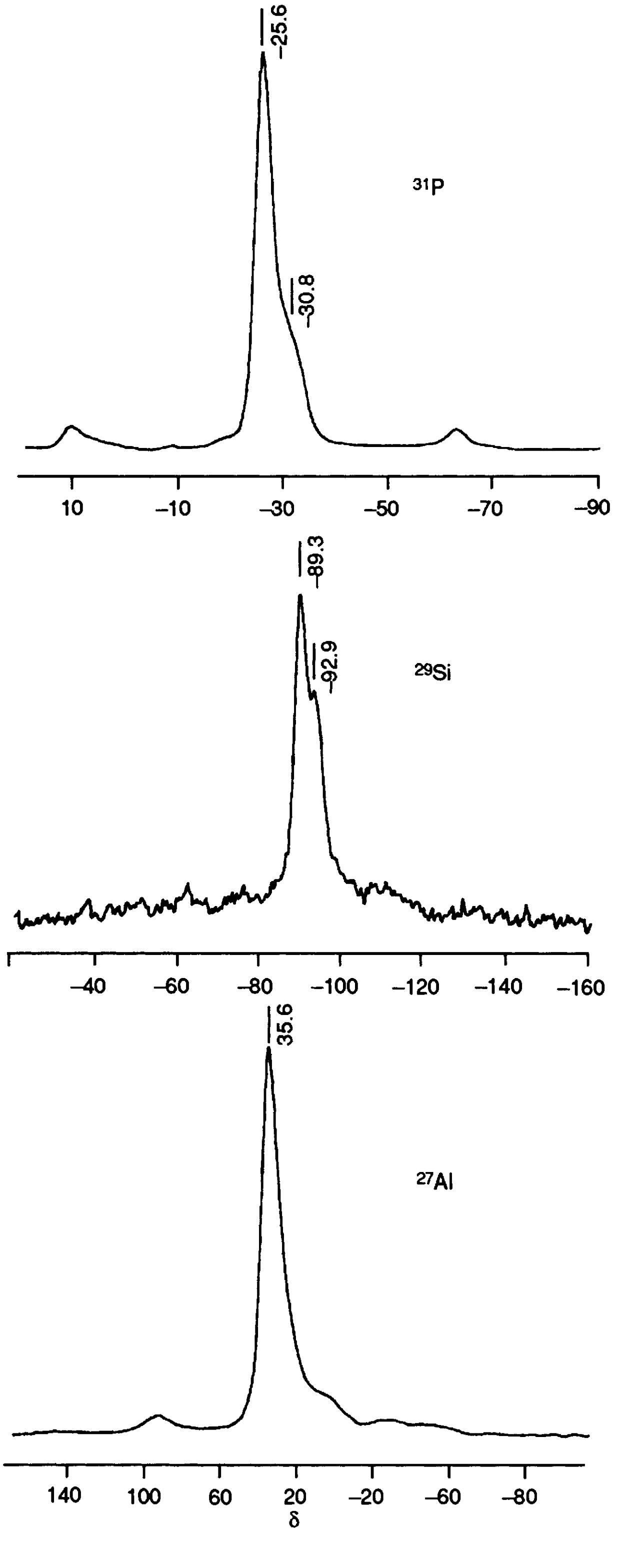

Fig. 2 ^{31}P, ^{29}Si and ^{27}Al MAS NMR spectra of as-synthesized SAPO-46

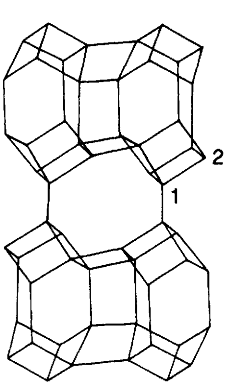

Fig. 3 Doubly capped six-membered ring units of SAPO-46 showing two crystallographic inequivalent sites (positions 1 and 2) in the framework

the two peaks became separated, with enhancement in intensity of the peak at δ −31. We suggest that absorption of water by the detemplated sample may lead to some interaction with the phosphorus atoms leading to this enhancement. In fact, the calcined sample could take up 23% m/m of moisture. This aspect of the ^{31}P spectrum needs further investigation.

The ^{27}Al NMR spectrum shows a single, slightly unsymmetrical peak at δ 36 [ref. $Al(NO_3)_3$ (aq.)] characteristic of tetrahedrally coordinated aluminium in the framework. This may be either due to Al(4P) or Al(3P, 1Si) or both.[10] As in the case of ^{29}Si NMR, one may expect two resonances corresponding to two independent sites which aluminium can occupy. The anisotropic second-order quadrupolar interactions in ^{27}Al NMR, however, greatly reduce the chance of observing such a spectrum. We believe that by using the technique of double rotation NMR, such splitting can be resolved in the case of aluminium also.

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