Synthesis and characterization of mesoporous SAPO

Basab Chakraborty,[a] Alex C. Pulikottil,[a] Siddhartha Das[b] and Balasubramaniam Viswanathan*[a]

[a] *Department of Chemistry, Indian Institute of Technology, Madras 600 036, India*
[b] *Department of Metallurgical Engineering, Indian Institute of Technology, Madras 600 036, India*

Self-assembled ordered cetyltrimethylammonium bromide (CTAB) is used as a template for the synthesis of mesoporous silicoaluminophosphates with varying Si/Al ratio.

Aluminophosphate-based molecular sieves are known to exist in a wide range of structural and compositional diversity. Substitution of Si in the framework of aluminophosphate molecular sieves imparts acidity to the material and makes it active for a variety of acid catalysed reactions. These materials exhibit characteristics of zeolites and of aluminophosphates and also unusual properties ascribable to its composition. The extent of Si substitution in the aluminophosphate is however limited and is determined by the topology of the structure. The synthesis of phosphate-based molecular sieves has resulted in the formation of large pore materials with ring systems greater than the conventional 12T atom rings present in large-pore zeolites.[1,2] In all these systems, in spite of their large pores, their pore openings do not exceed 10–12 Å.

Self-assembled ordered organic molecules can be used to direct the synthesis of molecular sieves by a cooperative assembly of inorganic matrix over organic arrays. This approach was first used by Kresge *et al.*[3] to synthesize a family of silica-based mesoporous molecular sieves designated as M41S. Sayari *et al.*[4] have adopted this approach to synthesize a lamellar aluminophosphate using long-chain alkyl- or dimethylalkyl-amine as structure directing agents. Here, we have extended the use of cetyltrimethylammonium bromide (CTAB) as a structure directing agent for the first time, for the synthesis of silicoaluminophosphates with the aim of obtaining large-pore mesoporous materials.

In a typical synthesis, 8 g of aluminium isopropoxide (Loba Chemie) was mixed with dilute phosphoric acid (6.2 ml H_3PO_4 in 60 ml H_2O) and stirred vigorously for 1 h at 333 K. This was followed by the addition of CTAB (8 g in 20 ml H_2O) with subsequent addition of the appropriate amount of tetraethylorthosilicate (Merck) dissolved in 4 ml of tetramethylammonium hydroxide and the gel was stirred for another hour. The pH of the resulting gel was around 2.5. The molar composition of the resulting gel thus obtained was 71.2 P_2O_5 : 26.8 Al_2O_3 : 1.0 SiO_2 : 31.5 CTAB : 6082 H_2O.

The gel was autoclaved for 48 h at 383 K without stirring. After crystallization the pH of the mother liquor increased to 7. The crystalline materials were washed several times with hot water and dried in an air oven at 383 K for 12 h. Samples were calcined initially in nitrogen atmosphere for 1 h at 873 K followed by heating in air for 12 h.

All samples were characterized using XRD, TEM, sorption studies and solid-state MAS NMR measurements. X-Ray diffractograms were recorded on a Rich Seifert XRD 3000P instrument using Cu-Kα radiation (35 kV, 30 mA, 2° min^{-1}). TEM studies were carried out on a Philips CM12 scanning transmission electron microscope operating at 100 kV. Adsorption isotherms were determined at 77 K using a Carlo Erba sorptomatic series 1800 instrument using nitrogen as the adsorbent. MAS NMR spectra were recorded using a JEOL GSX400 instrument. The Larmor frequencies were 104.1, 161.8, 79.4 MHz for ^{27}Al, ^{31}P and ^{29}Si respectively. Data were acquired at a MAS speed of 5.5 KHz.

X-Ray diffractograms of all the calcined samples of silicoaluminophosphates (SAPO) shown in Fig. 1 indicate the crystalline nature of all the samples. All the samples exhibit characteristic low-angle peaks typical of mesoporous materials. The low-angle peaks are indexed on the basis of hexagonal symmetry. The d_{100} values for all the samples are given in Table 1. There are two peaks at 2θ 20.39 and 20.74° for sample S-III and in the same 2θ range for the other two samples in the X-ray diffractograms studied. The indexing of these planes from which these reflections arise could not be done immediately as the precise value of both the lattice parameters could not be obtained from indexing the low-angle reflections, namely 100, 110 and 200. Hence these peaks have been left unindexed. However a single-crystal X-ray study will be able to resolve this aspect. The crystal of the calcined SAPO materials as revealed from TEM studies have a faceted nature. From the two dimensional projected image, as obtained from TEM, it appears that the synthesised materials have hexagonal external morphology. The crystals are found to grow along the densely packed plane. The average size of the crystals is found to be 50–75 nm. It can be seen from the chemical analysis results of the synthesised materials given in Table 1 that not all of the silica in the original gel is incorporated in the synthesised materials. No change in phases is also observed in the XRD pattern with increase in silica content of the synthesised SAPO materials.

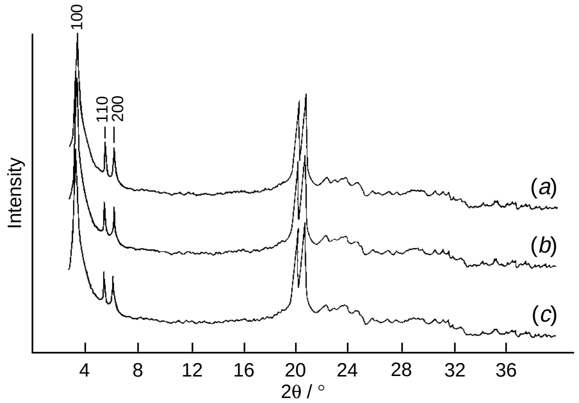

Fig. 1 XRD patterns of the calcined mesoporous SAPO materials; (*a*) S-I, (*b*) S-II, (*c*) S-III

Table 1 The molar ratios of the synthesis gel and that of the samples as obtained from elemental analysis along with the surface areas, pore diameters and d_{100} line spacings of the samples

	Al/P molar ratio		Al/Si molar ratio				
Sample	Gel	As synth.	Gel	As synth.	d_{100}/ Å	Surface area/ $m^2\ g^{-1}$	Pore diameter/ Å
S-I	0.38	0.81	87.1	90.02	28.14	920	29
S-II	0.38	1.01	53.7	61.04	28.28	940	30
S-III	0.38	1.13	29.3	34.80	28.44	980	30

Nitrogen adsorption isotherms of all the samples show type IV isotherm behaviour with hysteresis in the mesopore filling region. The pore size distributions computed on the basis of BJH analysis indicate a narrow distribution with the maximum centred around 30 Å reflecting a uniform pore texture of the samples. All the samples exhibit surface areas around 900 m^2 g^{-1}. The average pore diameters and the BET surface areas of all the samples are given in Table 1.

Solid-state MAS NMR was carried out in order to understand the local structure and environments in these samples. The solid-state MAS NMR spectra of ^{29}Si, ^{27}Al and ^{31}P nucleii of the calcined S-III are shown in Fig. 2. The ^{27}Al MAS NMR spectrum of the calcined S-III sample gives a single sharp resonance at δ 37.2 which is typical of Al in tetrahedral coordination.[5] The absence of other resonance lines implies the absence of amorphous or other phases in which aluminium has higher coordination in the synthesised samples. The ^{31}P MAS NMR spectrum of the calcined S-III samples [Fig. 2(*b*)] consists of a sharp peak centred at δ −30.9 indicating a uniform environment of the phosphorus atom. This is characteristic of tetrahedrally coordinated phosphorus in silicoaluminophosphates.[5] The single symmetric peak at δ −30.9 can be assigned to a single P(4Al) environment.[6] This resonance is observed for all the three SAPO samples irrespective of the amount of Si present. This is in agreement with the fact that P–O–Si linkages are absent in silicoaluminophosphates. The presence of such a sharp single signal for ^{31}P and ^{27}Al further confirms the phase homogeneity of the prepared samples. Although much information on the local environment of P and Al could not be directly deduced from the ^{31}P and ^{27}Al MAS NMR, ^{29}Si MAS NMR [Fig. 2(*a*)] provides a better insight into the local ordering of silicon in these mesoporous silicoaluminophosphates. Peaks centred around δ −90.1, −94.3, −98, −104 and −108.2 are observed indicating a multiple environment for Si in these samples. The resonances thus obtained were assigned as follows: δ −90.1 to Si(4Al), δ −94.3 to Si(3Al), δ −98 to Si(2Al), δ −104 to Si(1Al) and δ −108.2 to Si(0Al). Similar assignments are reported in literature for the various environments of Si in SAPOs.[7–9] The absence of any other peak in the range δ −86 to −111 excludes the possibility of P–O–Si linkages.[7] A detailed NMR studies on these materials will be reported soon.

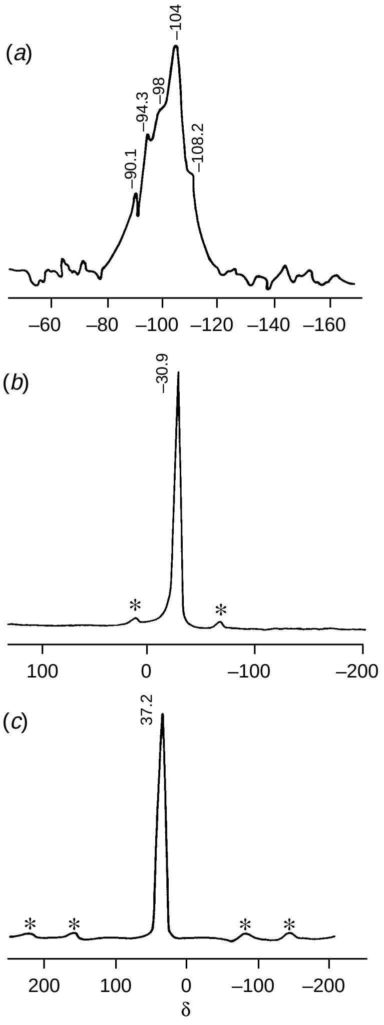

Fig. 2 Solid-state MAS NMR of the calcined S-III sample, (*a*) ^{29}Si, (*b*) ^{31}P and (*c*) ^{27}Al; * indicates spinning side bands

Mesoporous silicoaluminophosphates with pore size of *ca.* 30 Å with varying amounts of Si content have been synthesised. The local environment around Si, Al and P is found to be similar in comparison to other SAPO materials.

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