# Synthesis of $AlPO_4$-17 from Non-aqueous Systems

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An aluminophosphate molecule sieve ($AlPO_4$-17) has been synthesised from a non-aqueous system in the presence of methylamine as a templating agent and has been characterized by means of X-ray powder diffraction (XRD), scanning electron microscopy (SEM), (IR), differential thermal analysis (DTA) and thermogravimetric analysis (TG).

Recently, workers at this laboratory,[1,2] reported several aluminphosphate molecular sieves synthesized from non-aqueous system, including JDF-20 from ethylene glycol, whose channel is constructed by 20 T-atoms, the largest ring among synthetic zeolite and zeolite-like materials so far found. However, until now, only few kinds of molecular sieves have been synthesized from non-aqueous systems. Here we report the synthesis of $AlPO_4$-17 from a non-aqueous system (methanol–ethylene glycol) in the presence of methylamine as templating agent.

Aluminium triisopropoxide and phosphoric acid (85 wt% $H_3PO_4$) were used exclusively as the aluminium and phosphate starting materials respectively. Aluminium triisopropoxide was added to ethylene glycol, and methylamine was added dropwise to the stirred mixture; methanol and then phosphorous acid were then added dropwise. The whole mixture was stirred until it became homogeneous. Crystallisation of the reaction mixture was carried out in a stainless steel autoclave at 180 °C for 5 d. The crystallisation products were filtered off, washed with water, and dried at ambient temperature. The typical reactants composition was 1.0 $Al_2O_3$ : 1.8 $P_2O_3$ : 13.4 $MeNH_2$ : 13.4 MeOH : 88.0 ethylene glycol. The X-ray powder diffraction (XRD) pattern of the $AlPO_4$-17 so synthesised is shown in Fig. 1; the peak positions are similar to the XRD pattern of $AlPO_4$-17 prepared in aqueous media, although peak intensities differ. Scanning electron microscopy (SEM) shows that the $AlPO_4$-17 exists as platelets (Fig. 2), and also indicates that the product is pure. The IR spectrum shows three bands at 1272–955, 801–625 and 575 $cm^{-1}$, which are characteristic of aluminophosphate molecular sieves. The asymmetric stretching vibrations of the P–O–Al unit occur at 1271.9, 1145.3 and 955.47 $cm^{-1}$ and symmetric stretching vibration of P–O–Al is at 625.00 $cm^{-1}$. The band at 575.78 $cm^{-1}$ arises from the vibration of the characteristic aluminophosphate framework. The $AlPO_4$-17 sample was subjected to thermal analysis on a Perkin-Elmer differential thermal analysis (DTA) instrument under a flow of $N_2$ at a rate of 10 °C $min^{-1}$ (Fig. 3). Thermogravimetric analysis indicated losses of 20.0% m/m from 69 to 591 °C. This mass loss corresponds to the amount of organic molecules and water adsorbed by $AlPO_4$-17. The exothermic peak at 626 °C is caused by a phase change.

$AlPO_4$-17 was calcined at 270 °C at $10^{-3}$ Torr for 1 h and Brunauer–Emmett–Teller (BET) adsorption experiments on the calcined sample showed that it was a type I adsorption isotherm, and indicated that the amount of adsorbed water was 8.6% m/m.

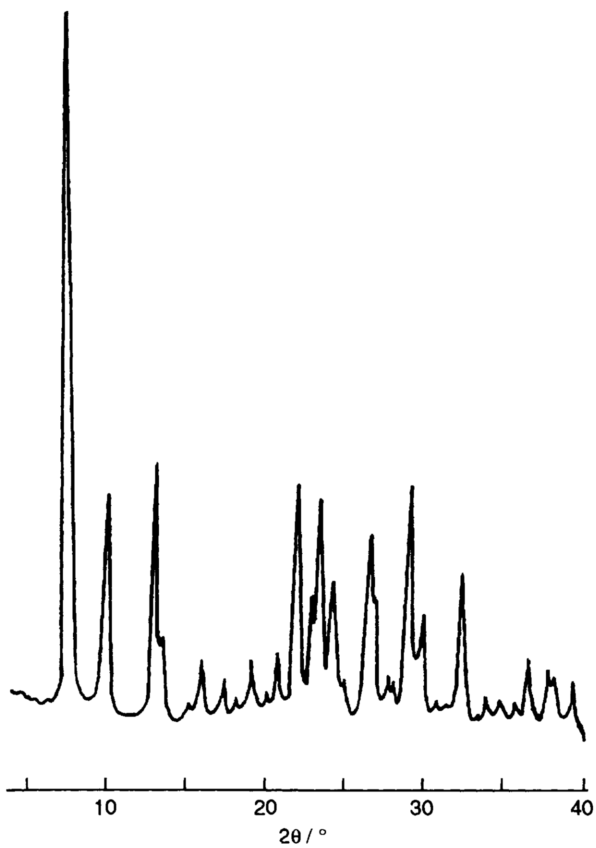


**Fig. 1** XRD pattern of $AlPO_4$-17 as synthesized from the system 1.0 $Al_2O_3$ : 1.8 $P_2O_3$ : 13.4 $MeNH_2$ : 13.4 MeOH : 88.0 ethylene glycol

**Fig. 2** Scanning electron micrographs of $AlPO_4$-17

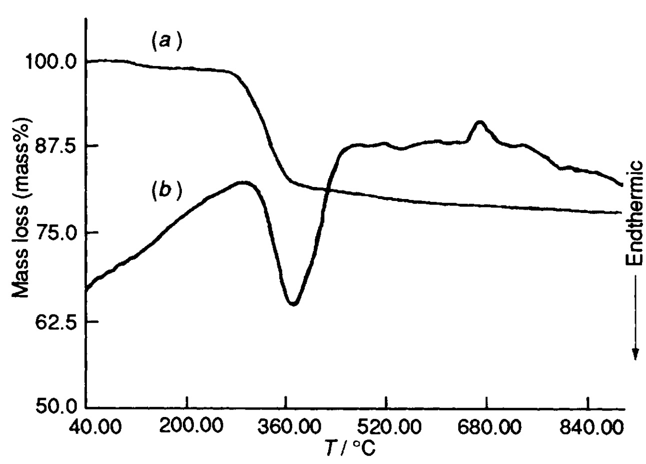


**Fig. 3** Thermal gravimetry (*a*) and DTA (*b*) for $AlPO_4$-17

The solvent employed in the synthesis of $AlPO_4$-17 is essentially non-aqueous. Water is present in $H_3PO_4$, $MeNH_2$ and other reagents, but it does not play a significant role. An important aspect of the synthesis of $AlPO_4$-17 is the use of methylamine as the templating agent, in marked contrast to syntheses in aqueous systems. The latter[3] usually employs large molecules, such as quinuclidine, piperidine or cyclohexylamine *etc.*, as the templating agent. Methylamine, owing to its small size, has little chance to act as a template during the synthesis of $AlPO_4$-*n* in aqueous systems. In our system we believe that $MeNH_2$ and the solvent interact during the reaction leading to the formation of $AlPO_4$-17, and its successful synthesis suggests that other suitable templating agents for differing $AlPO_4$-*n* structures in non-aqueous media may be found. It should be noted, however, that the use of a *mixed* solvent was required. If ethylene glycol or methanol are used above the reaction is unsuccessful. Using other alcohols, *e.g.* $C_2$–$C_8$ alcohols, led to the same result.

In summary, the synthesis of $AlPO_4$-17 will contribute substantially to our understanding of the nature and chemistry of $AlPO_4$-*n* and other related materials. Owing to the greater diversity of non-aqueous systems there is a considerable potential for the synthesis of a variety of novel molecular sieves by the use of this technique.

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