Synthesis and characterization of AlPO-36, the missing end-member of ATS structure

M. Hassan Zahedi-Niaki, Praphulla N. Joshi and Serge Kaliaguine*

Department of Chemical Engineering, Laval University, Ste-Foy, Quebec, Canada G1K 7P4

A new large-pore aluminophosphate with the ATS structure (AlPO-36) is synthesized hydrothermally; XRD, SEM, FTIR, XPS, ^{27}Al and ^{31}P MAS NMR provide evidence for its physicochemical characterization.

Examples of aluminophosphate (AlPO) and silicoaluminophosphate (SAPO) molecular sieves syntheses were first reported by Wilson *et al.*[1] and Lok *et al.*[2] respectively. The addition of other elements further expanded the number and diversity of the aluminophosphate family. These new materials comprise MeAPOs, MeAPSOs, ElAPOs and ElAPSOs.[3] Some structure types first reported as silicoaluminophosphates (SAPOs) and/or metal aluminophosphates (MeAPOs), were later synthesized as pure aluminophosphates containing no silicon or other metals. Examples of these types are AlPO-34,[4] AlPO-39[4] and AlPO-41.[5] The difficulty of their synthesis comes from the fact that the organic template used in the gel preparation can direct different structure types, depending on gel composition. For example, faujasite type silicoaluminophosphate (SAPO-37) may be prepared using a mixture of TPAOH and TMAOH as template. Removing silicon from the same gel results in the crystallization of AlPO-5 and/or AlPO-20 with no AlPO-37.[6]

Tripropylamine (NPr_3) is found to direct MFI and ATS structure types in aluminophosphate molecular sieves. To date the ATS structure was only reported for metal aluminophosphates[7] (Zn, Fe, Co, Mg, Mn), silicoaluminophosphates[8] and more recently TAPO-36.[9] Structure type 36 (ATS) has triclinic symmetry and consists of columns of four- and six-ring nets parallel to the *c*-axis generating an elliptical twelve-ring channel with side pockets and a pore opening of 7.4 × 6.5 Å.

The present communication is the first report of a procedure for the synthesis of AlPO-36, a new member and the parent of structure type 36 with ATS topology.

The hydrothermal synthesis of AlPO-36 was established based on a series of preparations using different gel compositions and heating protocols. Phosphoric acid (85% by mass, Fisher Scientific Co.) and pseudoboehmite (catapal B Vista Chemical Co.) were used as P and Al sources respectively. The most crystalline AlPO-36 samples were synthesized with the gel composition 1.70 $Pr_3N : Al_2O_3 : P_2O_5 : 80\ H_2O$. Heating of this gel in an autoclave under autogenous pressure has a critical effect on the nature of the final product. If heated directly at 423 K as reported for MAPO-36 and CoAPO-36,[7] AlPO-5 will be crystallized. However, we found that ageing the gel at 393 K for 120 h followed by heating at 413 K for 72 h produces pure AlPO-36 with no contribution due to AlPO-5 or any other amorphous or crystalline material. Based on a series of systematic syntheses, we claim that the ageing step at 393 K has a definite effect on the nature of the final product.

In a typical gel preparation phosphoric acid was first diluted with water, and to it pseudoboehmite was added in portions. The slurry was stirred continuously until a homogeneous mixture was obtained. Then NPr_3 was added dropwise. Finally the entire gel was further stirred for 1 h and transferred into a Teflon-coated stainless-steel autoclave for hydrothermal crystallization. At the end of the heating period the autoclave was quenched in cold water and the solid product was separated by centrifugation and repeatedly washed with distilled water followed by drying at 353 K for 5 h. Calcination was performed at 823 K overnight. As-synthesized and calcined AlPO-36 samples were characterized by XRD, bulk chemical analysis, SEM, FTIR, XPS, and solid-state ^{27}Al and ^{31}P MAS NMR.

The XRD *d*-spacing values of calcined AlPO-36 compared with those of MAPO-36[7] are presented in Table 1. The X-ray diffraction data are in agreement with those published[8] for other compositional variants with ATS topology. XRD also revealed that AlPO-36 is free from other crystalline phases.

The bulk chemical composition of AlPO-36 as determined by ICP is $Al_{0.51}P_{0.49}O_2$. Fig. 1 shows a scanning electron micrograph of the needle-like crystal aggregate of AlPO-36 and

Table 1 XRD powder data of MAPO-36[a] and calcined AlPO-36

MAPO-36		AlPO-36	
d/Å	$(I/I_0) \times 100$	d/Å	$(I/I_0) \times 100$
11.2	100	11.14	100
10.8	31	10.73	24
6.54	4	6.57	6
5.59	11	5.62	2
5.39	31	5.38	18
4.64	13	4.65	28
4.24	34	4.29	12
4.10	15	4.08	9
4.03	13	3.99	26
3.95	14	3.92	4
3.72	5	3.79	3
3.27	12	3.24	13
3.15	7	3.14	8
3.08	6	3.07	6
2.80	7	2.80	4
2.58	5	2.58	9

[a] Data from ref. 7.

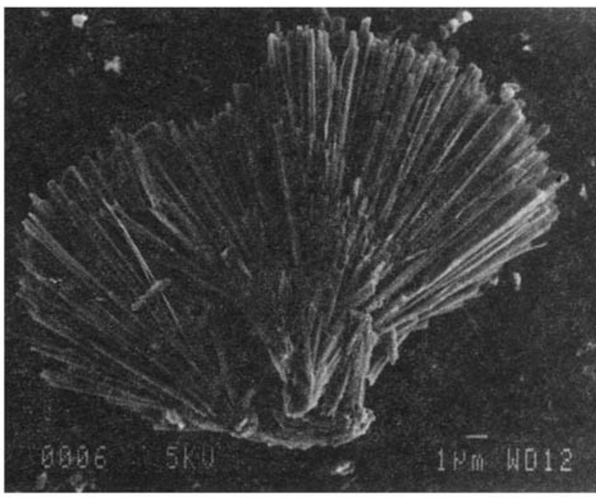

Fig. 1 Scanning electron micrograph of Pr_3N–AlPO-36

is the first SEM picture of an AlPO-36 crystal to be published.

Fig. 2 shows the mid-FTIR spectra of the structure region for the as-synthesized and calcined forms of AlPO-36. Both spectra exhibited a strongest vibration in the region 1250–1000 cm^{-1}. The broad band in the region 1100–1000 cm^{-1} is characteristic of zeolitic materials and has been assigned[10] to the asymmetric stretching of tetrahedra. In both as-synthesized and calcined forms of AlPO-36 this region was found to be shifted to higher wavenumbers compared to aluminosilicate molecular sieves. The presence of a larger amount of phosphorus is responsible for this shift as the P–O bond distance is shorter than that of Si–O and/or Al–O bonds. The as-synthesized AlPO-36 sample exhibited a framework IR pattern similar to that reported for MAPO-36[11] with some additional weak bands and shifts in characteristic bands reflecting the variation in the framework composition. The prominent bands associated with symmetrical stretching modes (at *ca.* 726 cm^{-1}), vibrations in the double ring region (at *ca.* 669, 635 and 567 cm^{-1}) and T–O bending modes (at *ca.* 485, 474 cm^{-1}) were observed. The disappearance of the weak bands at 824, 698, 610 and 543 cm^{-1} after calcination suggests the influence of template and/or heat treatment yielding structural changes. *In situ* IR spectra obtained after adsorption followed by desorption of pyridine at 338 K of calcined AlPO-36 samples (pretreated at 798 K) did not show a band at 1543 cm^{-1} ascribed to Bronsted-acid sites.[12] The absence of Bronsted-acid sites indicates that the framework of crystalline AlPO-36 is neutral with no extraframework cations and no ion-exchange capacity.

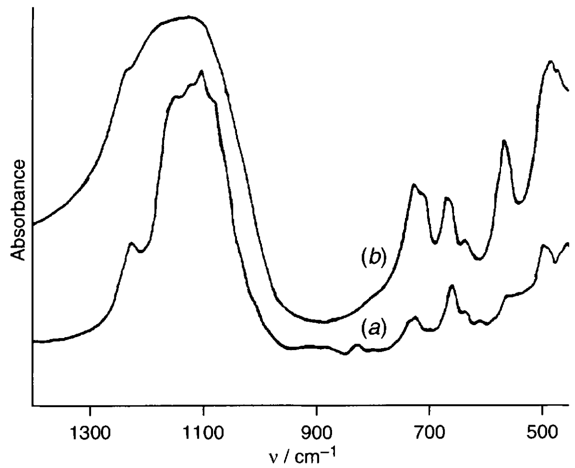

Fig. 2 Mid-IR spectra of as-synthesized (*a*) and calcined (*b*) AlPO-36

XPS binding energies of Al 2p, P 2p and O 1s in the AlPO-36 lattice are 74.4, 134.4 and 532.0 eV respectively; the C 1s binding energy (284.6 eV) being used as a reference. The surface chemical composition is $Al_{0.54}P_{0.45}O_2$; similar minor surface enrichments in Al were also reported for AlPO-5 and AlPO-11.[13]

The ^{27}Al MAS NMR of the as-synthesized AlPO-36 sample exhibited a single peak at δ 38.9 [relative to $Al(NO_3)_3$ (aq), pH $\approx$ 1] indicative[14] of a tetrahedral environment. The spectrum of a calcined, non-rehydrated AlPO-36 sample displayed multiple resonance maxima at δ 38.4 and 33.4 showing tetrahedral Al in the AlPO-36 framework. Upon calcination, the asymmetry to lower field of the ^{27}Al signal might be associated with residual quadrupolar lineshape and/or another similar Al species with a chemical shift of δ −25.2. A similarly simple spectrum is observed for the ^{31}P MAS NMR of air-exposed calcined AlPO-36 showing only one peak at δ −27.3 (relative to 85% H_3PO_4) which is consistent with PO_4 tetrahedra.

In conclusion, XRD, SEM, FTIR, XPS and ^{27}Al and ^{31}P MAS NMR characterization techniques confirm that a new kind of aluminophosphate molecular sieve with the ATS structure has been synthesized.

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