Synthesis, Characterization and Structure of Mu-7, a New Layered Aluminophosphate with a 4 x 8 Network

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(Received October 19, 1998; CL-980799)

A new layered aluminophosphate (Mu-7) was prepared in a quasi non aqueous system, using methylformamide (MF) as solvent in addition to restricted amounts of water. MF is decomposed during the synthesis and the resulting methylamine is found occluded in the interlayer spacing of this new material. Mu-7 is built from zigzag ladder chains leading to layers containing only 4- and 8-membered rings. It is the first layered aluminophosphate having a 4x8 network.

Since the discovery of porous aluminophosphates by Wilson et al.,[1] the mechanisms of formation of these compounds have been widely debated in the literature. Their crystallization was recently claimed to proceed through the initial formation of mono- and bidimensional inorganic anionic species.[2,3] Upon hydrolysis and condensation reactions processes, these intermediates could eventually lead to three dimensional frameworks. Numerous layered aluminophosphates have been obtained using an organic solvent in addition to restricted amounts of water in the reaction mixture.[4-12] Under such conditions, hydrolysis and condensation reactions kinetics are lowered in comparison to hydrothermal systems. Until now, the only established compositions for such layered structures are $[Al_3P_4O_{16}]^{3-}$, $[(Al_2P_3O_{12}H_x]^{(3-x)-}$ (x=1-2),[3] $[AlP_2O_8]^{3-}$,[13,14] $[Al(HPO_4)_2(H_2O)_2]^-$ [15] and $[Al_4P_5O_{20}H]^{2-}$.[12] These compounds involve layers consisting of 4x6, 4x6x8 and 4x6x12 networks.

In the present work, we report the synthesis, characterization and the structure determination of a new layered aluminophosphate characterized by a 4x8 network and named Mu-7 (Mu for Mulhouse). This compound was obtained in a quasi-non aqueous system using methylformamide (MF) as the main solvent. This family of solvents was recently successfully used to obtain a monoclinic variant of the sodalite-type aluminophosphate[12] and a new layered aluminophosphate (Mu-4)[16] using dimethyl- and diethylformamide respectively.

Mu-7 was synthesized from a quasi non-aqueous mixture using methylformamide as solvent. Typically, the molar composition of the starting gel was 0.75 Al_2O_3 : 1.0 P_2O_5 : 3.3 H_2O : 10.0 MF. The restricted amounts of water stemmed from the aluminum and phosphorus sources. The gel was prepared by first adding 1.40 g of pseudo-boehmite (Condéa, hydrated alumina, water loss at 600 °C : 24.4 wt%) to 8.0 g of methylformamide (Fluka, analytical grade). The resulting suspension was stirred until homogeneity. 3.21 g of orthophosphoric acid (Fluka, 85 wt% in water) were further added. The final mixture was stirred at room temperature for 30 min and then heated in a Teflon-lined stainless-steel autoclave at 170 °C under autogenous pressure for 7 days in static conditions. The crystalline product consisting of pure Mu-7 with no other crystalline phase was filtered, washed thoroughly with water and dried at 80 °C overnight.

The powder X-ray diffractogram of the as-synthesized Mu-7 fits well the symmetry and cell parameters determined from the single crystal structure analysis (see below).

Mu-7 consists of sharp plate-like crystals with variable dimensions (often less than 1 μm). The largest platelets proved to be appropriate for a single crystal structure determination.

The ^{13}C CPMAS-NMR spectroscopy clearly shows that methylamine (MA) is occluded into the structure of Mu-7. The spectrum consists of only one peak located at 26.2 ppm that was attributed to methyl groups.[17] This value of chemical shift better agrees with the one recorded for protonated methylamine (26.3 ppm) in comparison to the non protonated amine (27.8 ppm). No line corresponding to a carbonyl group is observed around 160 ppm,[17] which means that MF is decomposed into MA and carbon monoxide under our experimental conditions, following the well addressed scheme :

$$CH_3NCHO \xrightarrow{[H_3O^+]} CH_3NH_3^+ + CO \quad (1)^{18}$$

Such a phenomenon was previously observed with dimethyl-[19] and diethylformamide[12] used as solvents to prepare aluminophosphate type materials at temperatures that favors their respective decomposition according to equation (1). The nature of the amide (MF) basically as precursor to the corresponding amine (MA) is the main synthesis variable yielding selectively pure aluminophosphate crystalline phase (Mu-7).

The amounts of Al, P, C and N in the as-synthesized product were determined by bulk chemical analysis using inductively coupled plasma emission spectroscopy (Al, P) and coulometry and catharometry (C, N). The Al/P, P/C and C/N ratios obtained were 0.8, 1.3 and 1.1 respectively. These ratios are in good agreement with the chemical formula of the new layered aluminophosphate determined from the structure analysis (see below) which is $[CH_3NH_3]_3[Al_3P_4O_{16}]$. The TG and DSC curves were recorded on a Setaram TG/DSC111 thermoanalyser by heating the as synthesized material from ambient temperature to 750 °C at a rate of 5 °C.min^{-1} under air flow. A first weight loss recorded between 20 and 200 °C (3.0 wt%) is attributed to the release of physisorbed water. On the basis of the structure analysis, no water was found in the material. Its presence might be attributed to the particular crystal morphology : the residual water could indeed be located between the aggregated platelets. The second weight loss (18.1 wt%), occurring between 230 and 400 °C, corresponds to the thermal decomposition of the methylamonium cations. This loss is relatively close to the one excepted (17.2 wt%) from the formula derived from the structure analysis. The removal of the organics is accompanied by an endotherm immediately followed by an exothermic peak (360 °C) that reflects the oxidation of the organic residues as soon as they are released from the layered aluminophosphate. As confirmed by XRD, after heating at 750 °C a dense phase is obtained.

The ^{31}P MAS-NMR spectrum of Mu-7 is composed of two

resonance lines located at -19.5 and -16.2 ppm, with an intensity ratio close to 3/1. The two components are assigned to the four distinct crystallographic phosphorus sites. Three of these sites characterized by the NMR line at -19.5 ppm have a similar environment. ^{27}Al MAS-NMR shows three main lines corresponding to tetrahedrally coordinated Al sitting in three distinct crystallographic sites. They are located at 45.0, 39.4 and 36.6 ppm and their intensity ratio is close to 1/1/1.

The structure analysis performed on single crystal reveals that Mu-7 involves a novel layer topology. ^{31}P and ^{27}Al MAS-NMR data suggest that there are four and three distinct crystallographic sites accommodating respectively phosphorus and aluminum atoms, leading to a Al/P molar ratio equal to 0.75. This is confirmed by the structure determination. The structure consists in anionic $[Al_3P_4O_{16}]^{3-}$ sheets perpendicular to the [011] axis (Figure 1) and built from single Al_2P_2 4-rings interconnected to form zigzag ladder chains with a strict alternation of AlO_4 and PO_4 tetrahedra.

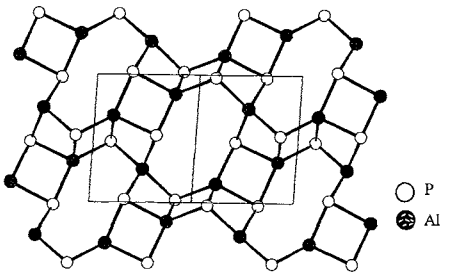

Figure 1. Projection of the structure of Mu-7 along [011]. For clarity, the oxygen and hydrogen atoms are omitted. Al and P are located alternatively at the corners of the single 4-rings units.

The connectivity between the chains leads to a layer with only 4- and 8-membered rings (MR). Such a 4x8 network is novel for layered aluminophosphates. So far, only 4x6, 4x6x8 and 4x6x12 nets were known and the 4x8 one was hypothetical.[20] Each AlO_4 tetrahedron with a mean Al-O bond length equal to 0.1730 nm shares its oxygen atoms with tetrahedral phosphorus atoms which are only 3-connected into the layers and display a terminal oxygen atom (P=O, mean bond length = 0.1488 nm). The protonated methylamine is located in the interlayer spacing and neutralizes one negative charge of the aluminophosphate inorganic sheet. Strong hydrogen bonds are evidenced between the organic species and the inorganic layers (N---O $\approx$ 0.27-0.29 nm). The structure logically collapses unpon the thermal decomposition of the amine.

In conclusion, a new layered aluminophosphate has been obtained in a quasi-non aqueous system involving methylformamide as the main solvent, in addition to restricted amounts of water. During the synthesis, the solvent is decomposed into methylamine which is occluded in its protonated form between the inorganic sheets. The layers involve 4- and 8-membered rings, thus leading to a new kind of net for lamellar aluminophosphates. The slow *in situ* liberation of amine in the reaction mixture was found to be the key step for the crystallization of the new phase. Indeed, the synthesis performed in the presence of methylamine does not lead to Mu-7 but to a mixture of poorly crystallized unidentified aluminophosphates.

For the structure determination, 2114 intensities from a single crystal (100x100x20μm) were collected on a four-circle Picker STOE DIF4 diffractometer (CuKα radiation) in omega scan mode with a 2θ range of 8.1-100.00°. The structure was solved by direct method using the SHELXS-86[21] program and refined using the SHELXL-93[22] program.1541 independent reflections fulfilled the condition I>2σI. The hydrogen atoms of the amine were placed with geometrical constraints which finally led to R_1=0.0372 and wR_2=0.0873 for 1541 reflections and R_1=0.0698 and wR_2=0.0988 for all data.

Crystal data for $[CH_3NH_3]_3[Al_3P_4O_{16}]$: formula weight M=557, triclinic, P-1, a=0.8368(7), b=1.1274(10), c=1.1462(12) nm, α=72.40(7), β=89.45(8), γ=85.37(7)°, V=1027.2(17)Å^3 and Z=2. A detailed description of the structure including the atomic coordinates, displacement parameters, bond lengths and angles of Mu-7 will be published elsewhere.[23]

References and Notes

1 S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.*, **101**, 1146 (1982).
2 S. Oliver, A. Kuperman, A. Lough, and G. A. Ozin, *Chem. Mater.*, **8**, 2391 (1996).
3 S. Oliver, A. Kuperman, and G. A. Ozin, *Angew. Chem. Int. Ed.*, **37**, 46 (1998).
4 A. M. Chippindale, A. V. Powell, L. M. Bull, R. H. Jones, A. K. Cheetham, J. M. Thomas, and R. Xu, *J. Solid State Chem.*, **96**, 199 (1992).
5 A. M. Chippindale, S. Natarajan, J. M. Thomas, and R. H. Jones, *J. Solid State Chem.*, **111**, 18 (1994).
6 A. M. Chippindale, Q. Huo, R. H. Jones, J. M. Thomas, R. Walton, and R. Xu, *Stud. Surf. Sci. Catal.*, **98**, 26 (1995).
7 S. Oliver, A. Kuperman, A. Lough, and G. A. Ozin, *Inorg. Chem.*, **35**, 6373 (1996).
8 S. Oliver, A. Kuperman, A. Lough, and G. A. Ozin, *J. Mater. Chem.*, **7**, 807 (1997).
9 A. M. Chippindale, A. R. Cowley, Q. Huo, R. H. Jones, A. D. Law, J. M. Thomas, and R. Xu, *J. Chem. Soc., Dalton Trans.*, **1997**, 2639.
10 Q. Gao, J. Chen., R. Xu, and Y. Yue, *Chem. Mater.*, **9**, 457 (1997).
11 Q. Gao, B. Li, J. Chen, I. Williams, J. Zheng, and D. Barber, *J. Solid State Chem.*, **129**, 37 (1997).
12 L. Vidal, V. Gramlich, J. Patarin, and Z. Gabelica, *Eur. J. Solid State Inorg. Chem.*, in press.
13 W. Tielli, Y. Long, and W. Pang, *J. Solid State Chem.*, **89**, 392 (1990).
14 K. R. Morgan, G. J. Gainsford, and N. B. Milestone, *J. Chem. Soc., Chem. Commun.*, **1997**, 61.
15 M. A. Leech, A. R. Cowley, K. Prout, and A. M. Chippindale, *Chem. Mater.*, **10**, 451 (1998).
16 L. Vidal, J. L. Paillaud, and Z. Gabelica, *J. Microporous and Mesoporous Mater.*, in press.
17 H. O. Kalinowski, S. Berger, and S. Braun, "^{13}C NMR Spektroscopie", ed by G. T. Verlag, Stuttgart-New York, (1984).
18 A. B. Thomas, and E. G. Rochow, *J. Amer. Chem. Soc.*, **79**, 1843 (1957).
19 J. L. Paillaud, B. Marler, and H. Kessler, *J. Chem. Soc., Chem. Commun.*, **1996**, 1293.
20 I. D. Williams, Q. Gao, J. Chen, L. Y. Ngai, Z. Li, and R. Xu, *J. Chem. Soc., Chem. Commun.*, **1996**, 1781.
21 G. M. Sheldrick, "Program for the Resolution of Crystal Structures", University of Göttingen, Germany (1986).
22 G. M. Sheldrick, "Program for the Resolution of Crystal Structures", University of Göttingen, Germany (1993).
23 L. Vidal, V. Gramlich, J. Patarin, and Z. Gabelica, in preparation.