A STRUCTURE DIRECTING ROLE OF 3-(METHYLAMINO)PROPYLAMINE IN THE CRYSTALLIZATION OF OPEN-FRAMEWORK METALLOPHOSPHATES

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ABSTRACT

A structure directing role of 3-(methylamino)propylamine (MPA) was examined in the hydrothermal crystallization of several metallophosphates [metal (M) – Zn, Al and Al/Mn(II), Al/Cr(III) and Al/Co(II)]. The influence of temperature, molar ratio of reactants, reaction time and presence of fluoride ions in the reaction mixtures were also investigated. Crystal structure of the obtained products was examined by powder and single crystal X-ray diffraction method. Interactions of the MPA with metallophosphate lattice were studied by thermogravimetric analysis (TG/DTG) and ^{27}Al, ^{31}P and ^{19}F solid state NMR. Elemental analysis was determined by Energy-dispersive X-ray spectroscopy (EDS).

Keywords: aluminophosphates, zincophosphates, MPA, template, open-framework.

INTRODUCTION

Quaternary ammonium ions and organic amines play an important, structure-directing, role in open-framework aluminophosphate (AlPO) synthesis. These chemicals (structure-directing agents, SDA) are essential for the organization of the building units into an aluminophosphate network [1]. An SDA does not lead only to crystallization of AlPOs, but is also responsible for some properties of AlPOs, such as catalytic activity or thermal stability [2]. In the synthesis of AlPOs, an SDA can direct a variety of open-frameworks under different conditions, and an open-framework can be directed by many SDAs [3]. Although the detailed functional mechanism of SDAs is still not clear, it has been known that SDA remains encapsulated into as-synthesized AlPOs and stabilizes the framework *via* hydrogen bonds, van der Walls and/or electrostatic interactions [4]. Thus, investigation of the influence of SDAs on the crystallization process is important for understanding the mechanism of structure-directing action in the crystallization of AlPOs.

The data about structure directing ability of the MPA molecule has been very scarce [5]. In this work hydrothermal crystallization of several metallophosphates was investigated in the presence of MPA as well as MPA and fluoride ions.

EXPERIMENTAL

Two reaction mixtures were prepared: with fluoride and fluoride-free. The sources of aluminum, cobalt(II), manganese(II), chromium(III) and zinc were $Al(OH)_3$, $Co(CH_3COO)_2 \cdot 4H_2O$, $Mn(CH_3COO)_2 \cdot 4H_2O$, $CrCl_3 \cdot 6H_2O$ and $Zn(CH_3COO)_2 \cdot 2H_2O$, respectively. Orthophosphoric acid (85 wt.%) was used as the phosphorous source, while hydrofluoric acid (40 wt.%) was used as the source of fluoride ions in the fluoride-containing reactive mixtures. 98 wt.% MPA (as a template) was used. The composition of the reaction mixtures were given in the Table 1. The reaction mixtures were obtained by a successive addition of H_3PO_4, HF (only in the fluoride-containing mixtures) and MPA to the water suspension of metal salts and/or $Al(OH)_3$ under vigorous stirring. The resulting gel was transferred into a Teflon-lined stainless steel autoclave and left to crystallize during 4-7 days. The obtained products were filtered off, washed with demineralized water and dried at 60 °C.

Table 1. Composition of the reaction mixtures and the crystallization conditions.

Product	Composition of the reaction mixture	Crystallization time, days	Crystallization temperature, °C	Crystalline phase
Composition of the fluoride-free reaction mixture				
AlPO	$0.5Al_2O_3:0.5P_2O_5:0.5MPA:100H_2O$	7-10	160	AlPO-21
CoAPO	$0.4Al_2O_3:0.2CoO:0.5P_2O_5:0.5MPA:100H_2O$	6-10	160	CoAPO-21
CrAPO	$0.4Al_2O_3:0.1Cr_2O_3:0.5P_2O_5:0.5MPA:100H_2O$	7-10	190	CrAPO-21
MnAPO	$0.4Al_2O_3:0.2MnO:0.5P_2O_5:0.5MPA:100H_2O$	4-7	190	MnAPO-21
ZnPO	$ZnO:1.5P_2O_5:2MPA:100H_2O$	2-6	120-160	Novel phase
Composition of the fluoride-containing reaction mixture				
APOF	$0.5Al_2O_3:0.5P_2O_5:0.5MPA:1HF:100H_2O$	4-7	160	ULM-3
CoAPOF	$0.4Al_2O_3:0.2CoO:0.5P_2O_5:0.5MPA:1HF:100H_2O$	4-7	160	ULM-3
CrAPOF	$0.4Al_2O_3:0.1Cr_2O_3:0.5P_2O_5:0.5MPA:1HF:100H_2O$	4-7	160	ULM-3
MnAPOF	$0.4Al_2O_3:0.2MnO:0.5P_2O_5:0.5MPA:1HF:100H_2O$	4-7	130-160	*

Mixture of different crystalline phases.

RESULTS AND DISCUSSION

Powder X-ray diffraction analysis (PXRD) analysis showed that MPA exerts different structure-directing role depending mainly on the composition of reaction mixtures and crystallization conditions. Crystallization of the reaction mixtures containing only Al- and P-reactants, or containing P-component, Al/Co^{2+}, Al/Cr^{3+} or Al/Mn^{2+} ions, yielded crystalline products with the aluminophosphate topology denoted as the structure type 21 [6]. A representative PXRD pattern is given in Figure 1a.
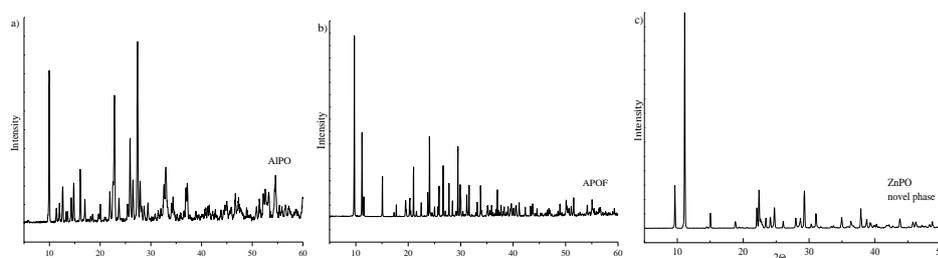

Figure 1. PXRD patterns of: a) AlPO (AlPO-21); b) APOF (ULM-3); c) ZnPO-novel phase.

Single crystal X-ray analysis showed that the MPA is located inside the 8-membered ring channels of the AlPO framework (Fig. 2). It is held within the channels through hydrogen bonds with the framework oxygen atoms. Each MPA forms two such bonds, with the N···O distances being 2.914 and 2.985 Å [7].
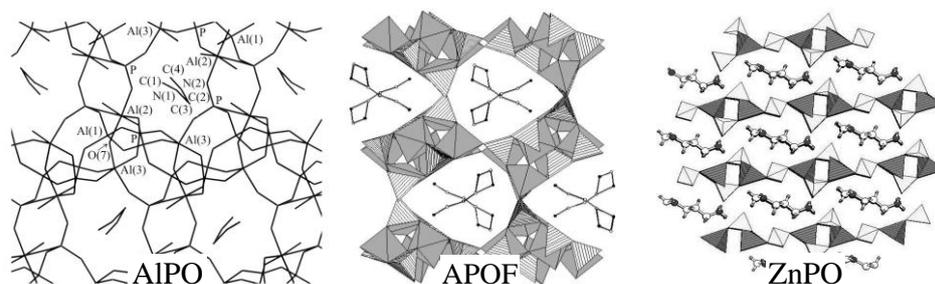

Figure 2. Position of MPA species in the structure of the AlPO, APOF and ZnPO.

Table 2. Results of EDS analysis (in at.%).

Sample	Zn	Al	P	Co	Cr	Mn
AlPO		16.8	19.3			
CoAPO		15.8	20.6	3.1		
CrAPO		22.1	26.4		1.0	
MnAPO		18.1	24.2			6.8
ZnPO	25.9		16.6			

The results of EDS presented in Table 2 indicate that the products obtained from reaction mixtures with two metal ions (Al/Co, Al/Cr and Al/Mn) contain Co(II), Cr(III) and Mn(II) in the aluminophosphate lattice occupying the aluminium crystallographic sites. The fluoride ions have a co-structure directing role in the crystallization of the metallophosphates obtained with MPA. From fluoride-containing reaction mixture a fluoroaluminophosphate (APOF) was crystallized displaying

PXRD pattern (Fig. 1b) which entirely corresponds to that of the open-framework gallophosphate, ULM-3 [8]. The structure of the ULM-3 exhibits a three-dimensional network consisting of specific structural units, $Al_3(PO_4)F_2$, in which aluminum adopts two coordination environments: two trigonal bipyramidal geometries, AlO_4F, and one octahedral geometry, AlO_4F_2. The connection of the Al-containing building blocks and PO_4 units leads to the formation of two pore systems: 10- and 8-ring channels in which MPA is located (Fig. 2) [9]. One-dimensional ^{27}Al, ^{31}P, and ^{19}F MAS NMR spectra (Fig. 3) confirm the presence of three distinct aluminum, three distinct phosphorus, and two distinct fluorine sites in the asymmetric unit of APOF. PXRD patterns of CoAPOF and CrAPOF correspond also to ULM-3 while the MnAPOF product seems to be a mixture of different crystalline phases.
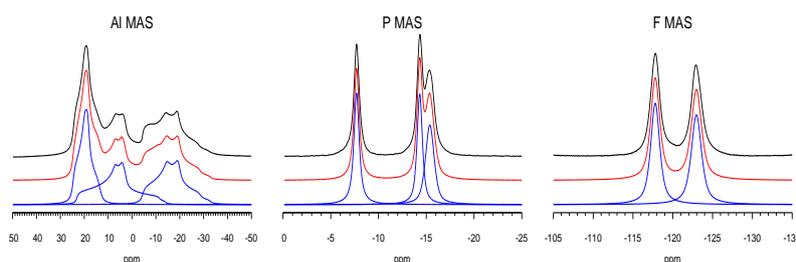

Figure 3. ^{27}Al, ^{31}P and ^{19}F MAS NMR spectra of APOF. Experimental spectrum (top line) is compared to model (middle line) obtained as a sum of individual signals (bottom lines).

Crystallization of the reaction mixture with Zn- and P-component gave the novel crystalline phase (ZnPO - Fig. 1c). Single crystal structure analysis shows that the ZnPO is built of macroanionic $[Zn_2(PO_4)(HPO_4)(H_2PO_4)]^{2-}$ layers and intercalated by doubly protonated MPA cations (Fig. 2). The layers are built tetrahedral units ZnO_4 and $PO_4/HPO_4/H_2PO_4$. The inorganic framework and MPA interact *via* a network of hydrogen bonds being important for stabilization of the structure [10, 11].

Fig. 4 shows the morphology of the crystalline products. Monocrystals or crystalline aggregates were formed depending mainly of the composition of reaction mixture. AlPO, CrAPO, CoAPO, CoAPOF and ZnPO are plate-like crystals of about 100-140 µm in length. APOF and MnAPOF crystallized as ball aggregates of about 50 µm in diameter. CrAPOF appears in a form of irregular aggregates of about 200 µm in length.
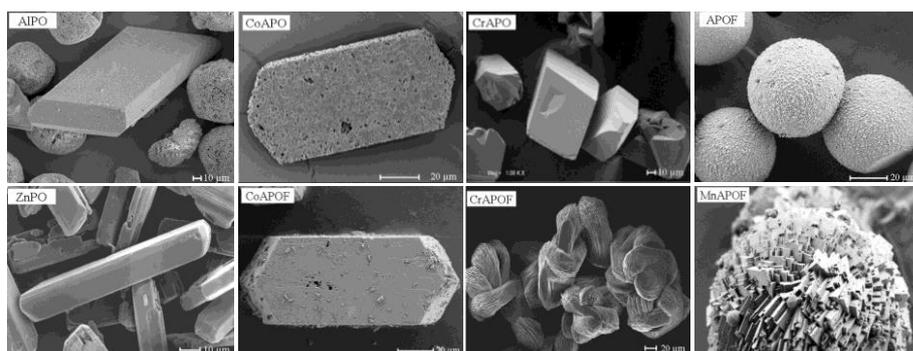

Figure 4. SEM photos of obtained metallo-phosphates.

Fig. 5 shows thermal behavior of the as-synthesized products. All the samples exhibit a strong DTG maximum at temperature higher than 300 °C corresponding to MPA decomposition. The position of the maximum differs with the crystal structures of the products indicating that the interactions of MPA with inorganic lattice depend on the framework type. This was further confirmed by the detailed kinetic analyses. The decomposition of MPA in AlPO proceeds in a single-step reaction with the E_a of 173 kJ mol^{-1} whereas the decomposition in APOF is a multi-step reaction with the average value of E_a of 209 kJ mol^{-1}. In APOF lattice doubly protonated MPA interacts with *via* hydrogen and electrostatic bonds with negatively charged lattice.

MPA present in the ZnPO decomposes in a three-step process for which the first step occurs with the highest E_a (343 kJ mol^{-1}). This is attributed both to strong hydrogen bonds as well as to electrostatic bonds which hold the protonated MPA and zincophosphate layers together. The

thermal decomposition of the MPA present in AlPO led to a transformation of AlPO$_4$-21 to AlPO$_4$-25 [12]. In other systems, interactions of the MPA with inorganic frameworks are so strong that their breakage leads to a loss of crystallinity.
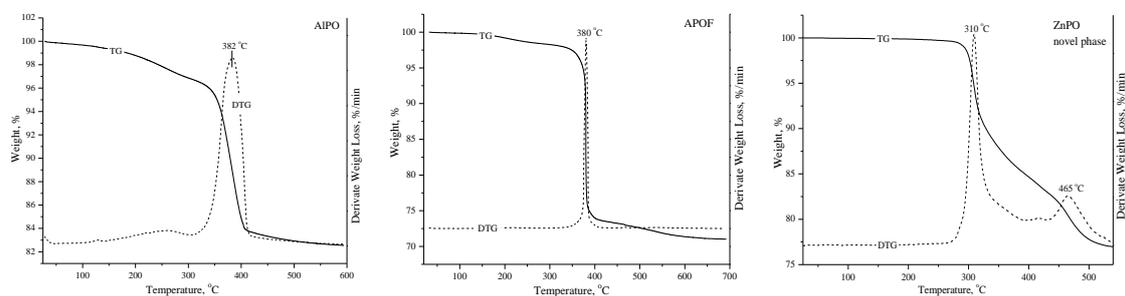

Figure 5. TG/DTG curves of the AlPO, APOF and ZnPO.

CONCLUSIONS

The study shows that MPA exerts a different structure-directing role in the crystalization of open-framework metallophosphates. The crystal structure of the obtained products depends mainly on the composition of reaction mixtures. MPA directs crystallization of reaction mixtures with Al-, P- and transition metal ions to crystalline products with the structure type 21. Fluoride ions have a co-structure directing role in the presence of MPA. Crystalline AlPO, CoAPO and CrAPO with the structure of ULM-3 crystallized in the presence of MPA and fluoride ions.

Layered ZnPO with a novel structure crystallizes in the presence of MPA. Interactions of MPA and macroanionic $[Zn_2(PO_4)(HPO_4)(H_2PO_4)]^{2-}$ layers are found to be crucial for the thermal stability of the ZnPO.

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