3-(Methylamino)propylamine as a templating agent in the synthesis of phosphate-based inorganic polymers

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Abstract: 3-(Methylamino)propylamine (MPA) was studied as a structure-directing agent (template) in the synthesis of open-framework phosphate-based materials. The influence of temperature, mole ratio of reactants, crystallization time and presence of fluoride ions on the crystallization of aluminophosphate, transition metal-substituted aluminophosphate (transition metal – Mn(II), Cr(III) and Co(II)) and zincophosphate was also investigated. MPA exhibited a templating role and in all the as-synthesized crystalline products, it is entrapped in an inorganic lattice interacting with the framework *via* hydrogen or/and electrostatic interactions. According to detailed thermal analysis, the type of interactions seems to be crucial for the thermal behavior of MPA and for the thermal stability of the organic–inorganic crystal system. Structural analysis suggested that the formed crystalline structures had no mutual structural analogy. This indicates that the precise role of the organic (guest) component in nucleation process for the open-framework phosphates (host) is very complex as is the nucleation process itself.

Keywords: microporous; aluminophosphates; MAPO; zinc phosphate; open framework.

INTRODUCTION

Phosphate-based inorganic materials are mainly crystalline solids with well-defined crystal structures. The crystal structure is built from tetrahedral phosphate building units that are connected in 1-, 2- or 3-dimensions *via* oxygen atoms to metal oxide units possessing different geometries (tetrahedral, pyramidal or octahedral). The typical metal cation in these materials is aluminum, although zinc and gallium also readily form porous metallophosphates. Metallophoshates typically crystallize from a reactive gel containing inorganic reactants and an organic reactant that plays the role of a structure-directing agent (temp-

late). Usually, different amines and/or quaternary ammonium cations exhibit template ability in the synthesis of metallophosphates.[1] It should be added that the relationship between the template and the crystal type of the formed metallophosphate has not yet been well established.[1] It is known that the organic template itself is not the sole factor involved in the structure-directing role. Namely, various other parameters also influence the crystallization process, such as the source of the inorganic components, pH, conditions of crystallization, *etc*. However, the presence of organic species in the crystallization process is crucial. Without the organics, a metallophosphate cannot be formed.

The template species remain after crystallization in the lattice pores and their removal from the channels and cages is necessary in order to achieve lattice porosity.[2] The removal of the template is performed by a thermal treatment (calcination), usually in an air atmosphere at about 500 °C. The calcined product usually possesses molecular sieving, catalytic and/or adsorptive properties.[3,4]

Moreover, in order to obtain novel materials with catalytic properties for specific reaction systems, as well as to obtain materials of desired selectivity, various investigations were directed towards transition metal substituted aluminophosphates.[5] Incorporation of transition metal cations in an aluminophosphate lattice at the aluminum or phosphorous crystallographic sites brings a charge into neutral aluminophosphate skeleton and greatly affects its catalytic and adsorptive properties. In addition, the use of fluoride ions in the synthesis of porous aluminophosphates led to the emergence of novel and zeolite-like aluminophosphate structures. As an example, an open-framework aluminophosphate with a chabazite structure can be obtained only if fluoride ions are present in the reactive gel.[6]

Different organic species were studied as templates in the synthesis of porous phosphates. For some of them (such as di-*n*-propylamine), a structural specifity is conspicuous: di-*n*-propylamine directs the crystallization of different framework structures by slightly changing the synthesis parameters. On the other hand, the formation of one structure type (AlPO$_4$–5) can be realized using more than twenty different amines and quaternary amine cations.[1]

In this work, the structure-directing role of one simple amine, 3-(methylamino)propylamine (MPA), which has not been studied so far in the synthesis of open-framework phosphates, was investigated. The influence of temperature, mole ratio of reactants, crystallization time and the presence of fluoride in the crystallization of several metallophosphate was examined using MPA as a template. Moreover, crystallization under two heating regimes, hydrothermal and microwave heating, was studied.

EXPERIMENTAL

Preparation of fluoride-free reaction mixtures

Aluminophosphates, zincophosphates and transition metal-substituted aluminophosphates were obtained under hydrothermal conditions using the mole ratio of the reactants

given in Table I. The sources of zinc, aluminum, cobalt(II) and chromium (III) were $Zn(CH_3COO)_2 \cdot 2H_2O$ (Fluka), $Al(OH)_3$ (Sigma-Aldrich), $Co(CH_3COO)_2 \cdot 4H_2O$ (Sigma-Aldrich), $Mn(CH_3COO)_2 \cdot 4H_2O$ (Sigma-Aldrich) and CrO_3 (Fluka), respectively. To enhance the chromium reactivity, chromium(III) was obtained *in situ* by reduction of CrO_3 using ethanol (Sigma-Aldrich).[7] Orthophosphoric acid, H_3PO_4 (85 wt. % Sigma-Aldrich), was used as the phosphorous source. MPA was used as a 98 wt. % solution (Sigma-Aldrich).

TABLE I. Composition of the reaction mixtures and the crystallization conditions

Product	Composition of the reaction mixture	Crystallization time, days	Crystallization temperature, °C	Crystalline phase
ZnPO-A	$ZnO:2.75P_2O_5:2MPA:100H_2O$	6–12	120	Hopeite
		6	160	Novel phase
ZnPO-B	$ZnO:1.5P_2O_5:2MPA:100H_2O$	6	120	Novel phase
		2–6	160	Novel phase
AlPO	$0.5Al_2O_3:0.5P_2O_5:0.5MPA:$:$100H_2O$	7–10	160	$AlPO_4$-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-12

Reaction gels were prepared by intensive stirring of the reactants using an ULTRA-TURRAX®, IKA® T18 stirrer. The synthesis proceeds in several steps. First, an aqueous suspension of metal salts or $Al(OH)_3$ and 85 wt. % H_3PO_4 was prepared by vigorous stirring. The obtained mixture was stirred until homogeneity (about 30 min) and finally, MPA was added dropwise. The resulting gel was intensively stirred for another 30 min and then transferred into a Teflon-lined stainless steel autoclave and left to crystallize at 160–190 °C in an oven or under microwave radiation (Milestone, Ethos TC).

Preparation of fluoride-containing reaction mixtures

Fluoride-containing reactive mixtures were prepared in a manner similar to that described above. Hydrofluoric acid (40 wt. %, Fluka) was used as the source of fluoride and it was added in the first step of the reactive mixture preparation. The employed mole ratios of the reactants are given in Table II.

Characterization

The crystallinty of the products was studied by XRD analysis using a PANalytical X'Pert PRO diffractometer and CuK_α radiation. The data obtained at room temperature were collected in the 2θ range from 5 to 75° in steps of 0.017° with a total measurement time of 4 h. The high temperature X-ray diffraction (HTXRD) patterns were recorded at four different temperatures, *i.e.*, room temperature and at 573, 623 and 673 K.

The size and morphology of the crystals as well as the elemental analyses were studied by a scanning electron microscope Zeiss Supra 35VP. Carbon, hydrogen and nitrogen were determined using a standard C–H–N analyzer. Fourier transformed infrared (FTIR) spectra were recorded in the 4000 to 400 cm⁻¹ range on a Digilab-FTS-80 spectrophotometer, using the KBr wafer technique. Thermal decomposition was performed using an SDT Q-600 simul-

taneous DSC–TGA instrument (TA Instruments). The samples (mass ≈10 mg) were heated in standard alumina 90-µl sample pans. All experiments were performed under synthetic air at a flow rate of 0.1 dm^3 min^{-1}.

TABLE II. Composition of the fluoride-containing reaction mixtures

Product	Composition of the reaction mixture	Crystallization time, days	Crystallization temperature, °C	Crystalline phase
APOF	$0.5Al_2O_3$:$0.5P_2O_5$:0.5MPA:1HF: :100H$_2$O	4–7	160	ULM-3
CoAPOF	$0.4Al_2O_3$:0.2CoO:$0.5P_2O_5$: :0.5MPA:1HF:100H$_2$O	4–7	160	ULM-3 and amorphous solids
CrAPOF	$0.4Al_2O_3$:$0.1Cr_2O_3$:$0.5P_2O_5$: :0.5MPA:1HF:100H$_2$O	4–7	160	ULM-3 and amorphous solids
MnAPOF	$0.4Al_2O_3$:0.2MnO:$0.5P_2O_5$: :0.5MPA:1HF:100H$_2$O	4–7	130	Mixture different crystalline phases
		4–7	160	Mixture different crystalline phases

RESULTS AND DISCUSSION

SEM analysis of the obtained products

The use of MPA yielded crystalline products with different morphologies depending on the crystallization conditions and composition of reactive mixtures. The SEM photographs of the products obtained by hydrothermal crystallization are shown in Fig. 1. The crystals appear as monocrystals or crystalline aggregates. Microwave-assisted heating yielded crystalline products mainly in the form of aggregates (not shown).

ZnPO, AlPO, CrAPO, CoAPO and CoAPOF were plate-like crystals of about 100–140 µm in length. APOF and MnAPOF crystallized as ball aggregates of about 50 µm in diameter. On closer inspection of the aggregates, it could be seen that they were in the form of plate conglomerates. CrAPOF appeared in the form of irregular aggregates of about 200 µm in length.

Structural analysis of the products obtained under hydrothermal conditions from fluoride-free reaction mixtures

Zincophosphates. For the preparation of the ZnPO products, two reaction mixtures (A and B) were found to be optimal in order to obtain crystalline products. Depending on the crystallization temperature, mixture A (with the Zn/P molar ratio of 1/5) yielded two crystalline phases: a dense ZnPO$_4$ phase – hopeite

(at 120 °C) and a novel crystalline product at 160 °C. From mixture B (with the Zn/P molar ratio of 1/3), the same novel phase was formed at both temperatures. Its XRD pattern is given in Fig. 2.
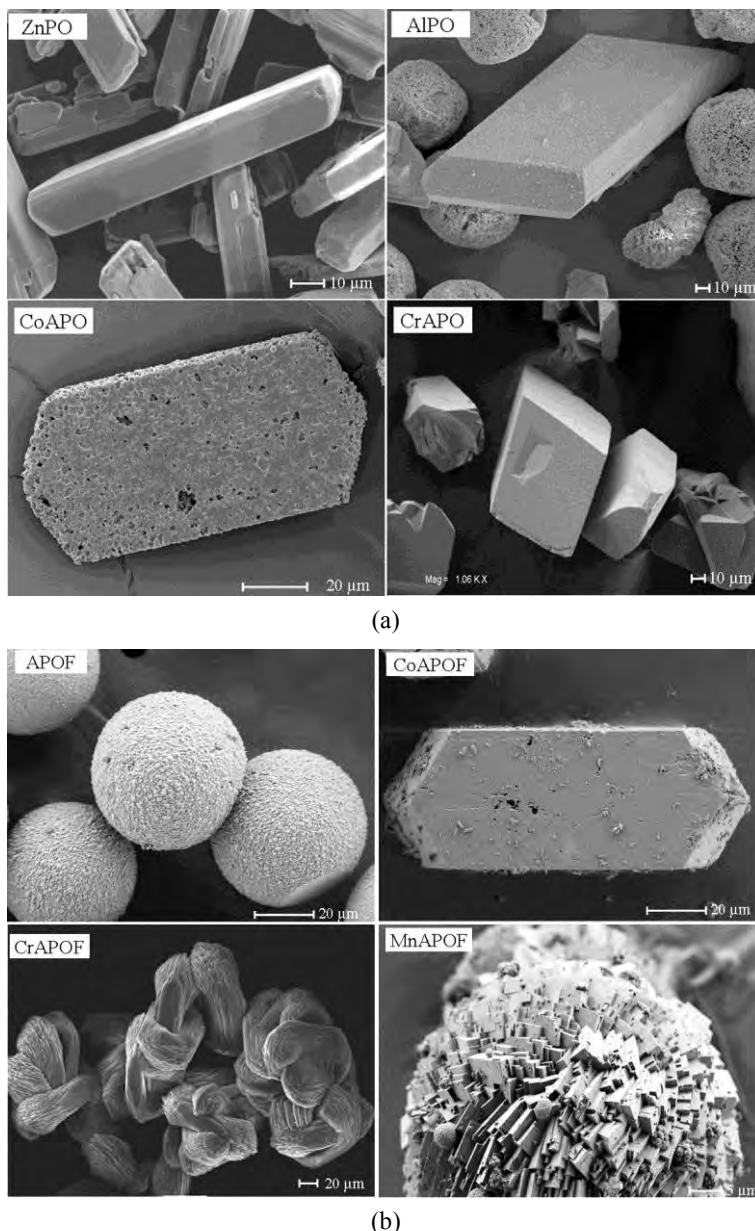

(a)

(b)

Fig. 1. SEM photograph of a) metallophosphates obtained under hydrothermal crystallization and b) the products obtained from fluoride-containing reactive mixtures.

Single crystal structure determination of the novel zincophosphate phase showed that the zincophosphate was built of macro-anionic $[Zn_2(PO_4)(HPO_4)(H_2PO_4)]^{2-}$ layers, which were intercalated by doubly protonated MPA cations (Fig. 3). The layers were built of ZnO_4 and $PO_4/HPO_4/H_2PO_4$ tetrahedra. Within the layers, small channels of an approximate diameter 3.7 Å were present. The inorganic framework and MPA interact *via* the template-to-framework N—H···O hydrogen bonds, which are important for stabilization of the structure.[8,9]
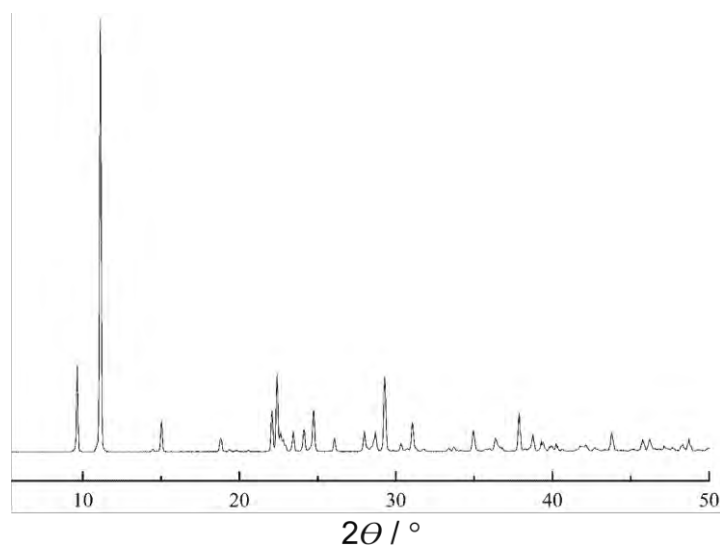

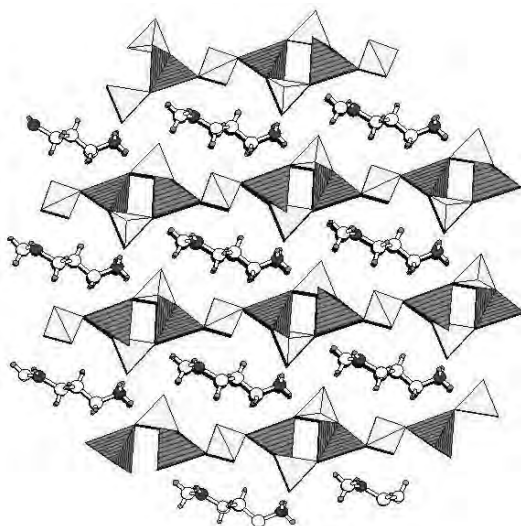Fig. 2. XRD pattern of the novel zincophosphate phase.

Fig. 3. A view of the novel zinco-phosphate, showing zincophosphate layers (dark gray tetrahedra – ZnO_4, light gray tetrahedra – phosphate building units) and intercalated doubly protonated MPA cations.

Aluminophosphates and metal-substituted aluminophosphates. Two types of reaction mixtures were studied: 1) the reaction mixture containing an alumino-phosphate and 2) the reaction mixture containing an aluminophosphate and some transition metal ions. Crystallization of both types of mixtures yielded crystalline products with the aluminophosphate topology denoted as the structure type 21.[10] Representative XRD patterns are given in Fig. 4. Hitherto, three different amines
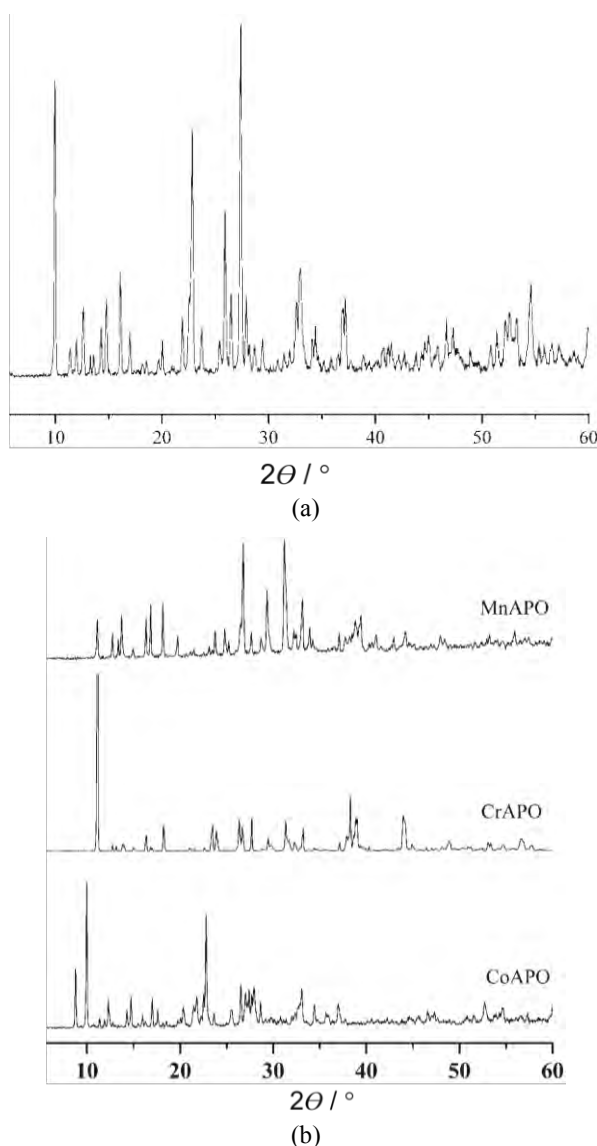

(a)

(b)

Fig. 4. XRD patterns of a) AlPO$_4$-21 and b) the metal-containing aluminophosphates [MAPO, M = Co(II), Cr(III), Mn(II)].

have been reported as templates for AlPO$_4$-21: 1,2-diaminopropane, pyrroli-dine[11] and *N,N,N′,N′*-tetramethyl-1,3-diaminopropane.[10] X-ray single crystal structure analysis of the aluminophosphate product showed that the AlPO$_4$-21 framework was built of corrugated aluminophosphates sheets, which were cross-linked by Al–O–P chains to form a network of straight eight-membered-ring channels extending along the *c* crystallographic axis. The MPA appeared to be disordered and positioned in the eight-membered-ring channels. It was held within the channels through strong hydrogen bonds: MPA forms two such bonds, the N···O distances being 2.914 and 2.985 Å.[12]

From the transition metal-containing aluminophosphate reaction mixtures, different crystalline products (MAPO) were obtained depending on the type of the transition metal cation (Table I). The XRD patterns (Fig. 4) revealed that from the Co(II)- and Cr(III)-containing mixtures, CoAPO and CrAPO products belonging to the structure type 21 crystallized, whereas the MnAPO obtained from the Mn(II)-containing reaction mixture belonged to the structural type 12.[13] The lattice of AlPO$_4$-12 is rather complex and is based on an interrupted net in which one of the P atoms is linked to only 3 Al atoms and one of the Al atoms is linked to only 3 P atoms.

The results of elemental analysis of the obtained products are given in Table III. It is evident that the metal content depended on the metal type, indicating that not only MPA but also transition metal cations influence the crystallization pro-cess. Moreover, the preparation of the transition metal-substituted aluminophos-phates (MAPOs) is important considering their catalytic application.[1] In a MAPO crystalline lattice, transition metal ions generally occupy aluminum crystallo-graphic sites, thereby generating different types of acid sites (Brønsted or Lewis) important for catalytic activity. Based on the results of the elemental analyses, it could be concluded that Co(II), Cr(III) and Mn(II) substitute aluminum in the parent aluminophosphate lattice. The (Al+M)/P molar ratio is approximately one in all the prepared samples.

TABLE III. Results of the energy-dispersive x-ray spectroscopy (EDS) analysis

Sample	Zn	Al	P	Co	Cr	Mn
ZnPO	25.9	–	16.6	–	–	–
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

Microwave-assisted heating. In order to study the influence of microwave radiation on the crystallization of the investigated reaction mixtures, microwave-assisted heating was also employed. Namely, it has been reported that the micro-

wave technique enables a more rapid crystallization than the conventional hydro-thermal method and leads to an improved crystal quality.[14]

Microwave radiation showed differing effects on the studied reaction systems. Crystallization of the novel ZnPO and AlPO$_4$-21 proceeded more rapidly under microwave-assisted heating: the crystalline products formed in the course of 2 h. However, for the MAPO products, the microwave radiation had a negative effect on the crystallization. For all the studied transition metal-containing reaction mixtures, no crystalline products were obtained.

Structural analysis of the products obtained under hydrothermal conditions from fluoride-containing reaction mixtures

Taking into account that the presence of fluoride ions in an aluminophosphate reaction mixture could lead to novel structures,[15] experiments with MPA in a fluoride-containing medium were performed. It is known that aluminum ions readily form complex species with fluoride ions, which increases the solubility of the aluminum source and accordingly influences the crystallization process. In the fluorinated aluminophosphate structures, the fluorine atoms usually bridge the aluminum-building units and typically occupy one or two vertices of the aluminum octahedral.[16]

The presence of fluoride in the aluminophosphate reaction mixture led to the formation of a crystalline product (APOF), the diffractogram (given in Fig. 5a) of which corresponded to that of the open-framework gallophosphate ULM-3.[17,18]

The single crystal X-ray structure analysis revealed an open-framework built up of hexa-nuclear units formed by three PO$_4$ tetrahedra, two AlO$_4$F trigonal bipyramids and one AlO$_4$F$_2$ octahedron. The three-dimensional framework was negatively charged and had two interconnected channel systems: 10-membered-ring channels running along the [101] direction and 8-membered-ring channels running along the [10-1] direction. The negative charge is compensated by doubly protonated MPA located in the 10-membered-ring channels (Fig. 6).[19]

The XRD patterns of CoAPOF and CrAPOF also showed the presence of the ULM-3 crystalline phase (Fig. 5b). However, a detailed EDS analysis did not confirm the presence of Co(II)- or Cr(III)-substituted products in the crystals found in the obtained products. It seems that the transition metal cations only contribute to nucleation of single crystals of the fluorinated aluminophosphate and do not become a part of the framework. Namely, the fluorinated aluminophosphate obtained from the Co(II)- and Cr(III)-free mixture appeared in the form of ball aggregates, in contrast to the single crystals formed in the presence of the metals (Fig. 1). The MnAPOF product seems to have consisted of different crystalline phases for which no structural analogs have been found.
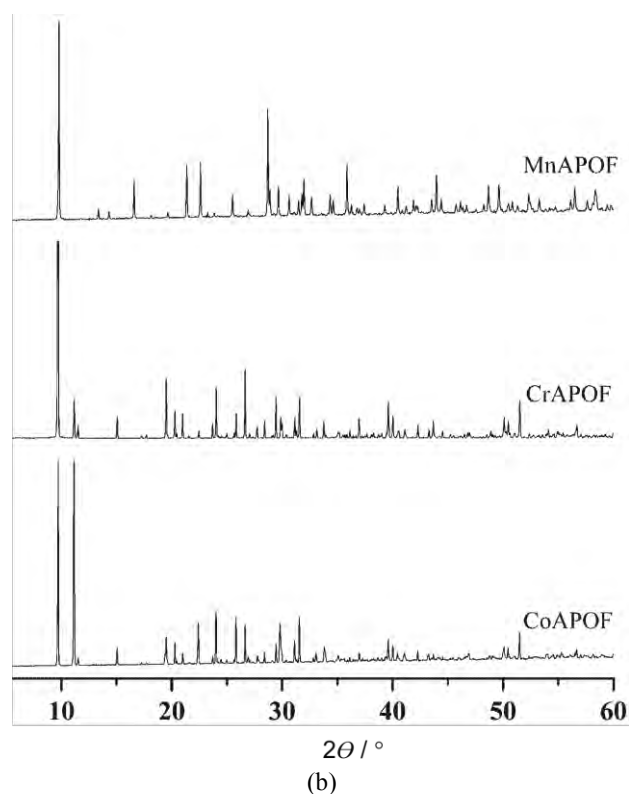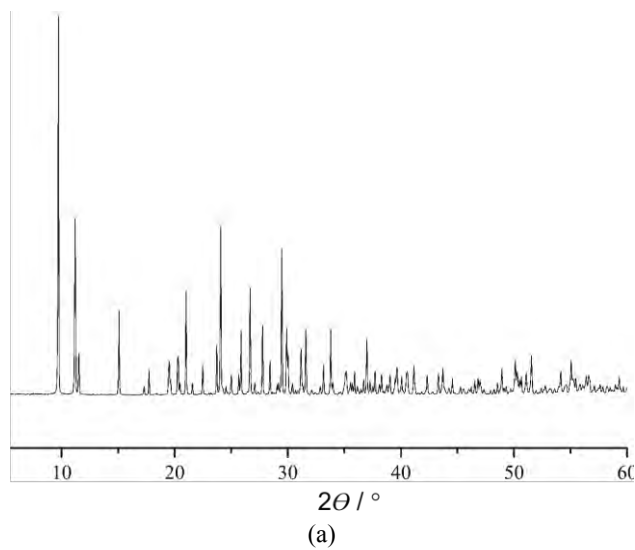
Fig. 5. XRD patterns of (a) the fluorinated aluminophosphate product (APOF) and (b) Co(II)-, Cr(III)- and Mn(II)-containing fluorinated aluminophosphates (CoAPOF, CrAPOF and MnAPOF, respectively).
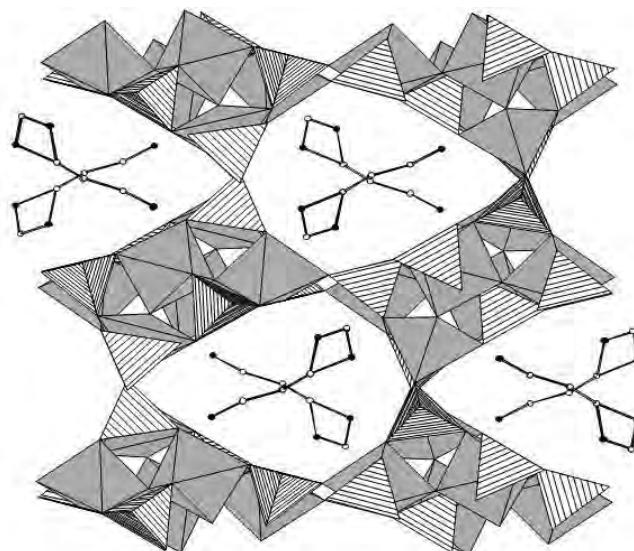
Fig. 6. Protonated MPA species in the 10-membered-ring channel of the fluorinated aluminophosphate framework.

Study of the organic/inorganic interactions

FTIR analysis. Figure 7 shows the FTIR spectra of the ZnPO, AlPO$_4$-21, CoAPO-21 and the fluorinated aluminophosphate (APOF). All the samples displayed vibrations that clearly show the vibrational features of the entrapped orga-
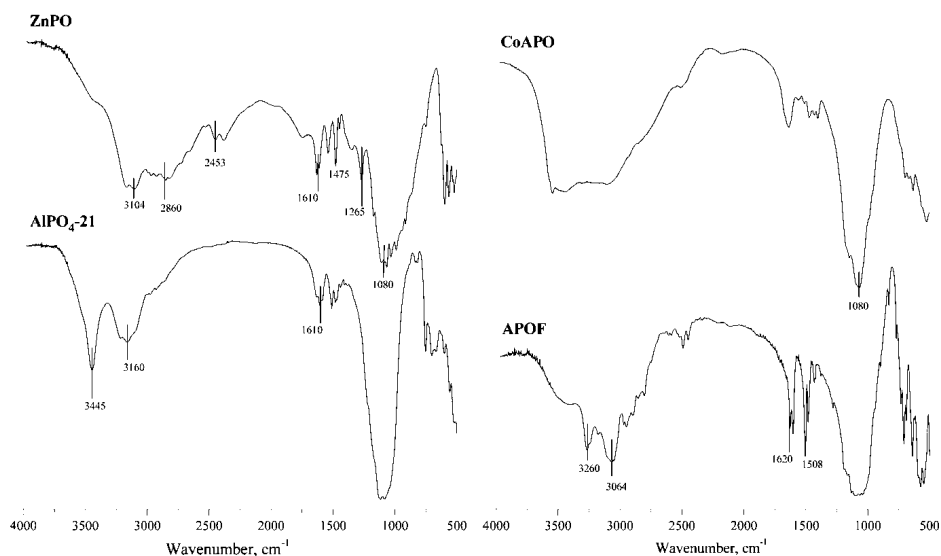

Fig. 7. FTIR spectra of the novel zincophosphate (ZnPO), AlPO$_4$-21, Co(II)-containing AlPO$_4$-21 (CoAPO-21) and the fluorinated aluminophosphate (APOF).

nic species. Vibrations displayed in the range 3200–2000 cm^{-1} correspond to amine groups,[20] and the bands appearing in the 1600–1350 cm^{-1} region are due to C–H bonds[21]. Strong bands at 3450 and 1620 cm^{-1} can be attributed to the water molecules present in the crystalline lattice.[22] All spectra except that of AlPO$_4$-21 display a strong band at about 1540 cm^{-1} which is attributed to NH$_3^+$, suggesting that the MPA species was protonated,[8] while the inorganic frameworks of ZnPO, CoAPO-21 and APOF were negatively charged.

TGA/DTG studies. To gain an insight into the strength of the organic/inorganic interactions, the thermal behavior of ZnPO, AlPO$_4$-21, MAPO-21 (M = Co(II), Cr(III), Mn(II)) and APOF were studied. The obtained results are shown in Fig. 8. All the samples exhibit a strong DTG maximum that could be attributed to the decomposition of MPA, according to the corresponding mass loss and the results of C–H–N analysis. The position of the maximum differs with the type of solid. This indicates that the entrapped MPA interacts in different ways with the inorganic frameworks. This was confirmed by detailed kinetics analyses.[8,12] Thus, MPA entrapped in ZnPO decomposes in a three-step process with the first step having the highest activation energy (343 kJ mol^{-1}). This is attributed to the strong hydrogen bonds and to electrostatic bonds, which hold the protonated MPA and zincophosphate layers together. The decomposition of MPA in AlPO$_4$-21 proceeded in a single-step reaction, with the activation energy lying in the range 173–151 kJ mol^{-1}.[12] In this solid, MPA interacts with the aluminophosphate framework only *via* hydrogen bonds. The MPA decomposition in APOF was a multi-step reaction with an average activation energy of 209 kJ mol^{-1}. In this solid, the anionic fluoro-aluminophosphate framework interacts with doubly protonated MPA *via* hydrogen and electrostatic bonds.[23]

The crystallinity of the calcined products was investigated by high temperature X-ray diffraction analysis. The patterns of AlPO$_4$-21 and APOF, being representative, are presented in Fig. 9. As can be seen, the decomposition of the MPA in AlPO$_4$-21 (as well as in MAPO-21) resulted in a crystal structure transformation. The XRD patterns of calcined AlPO$_4$-21 and MAPO-21 entirely corresponded to the aluminophosphate of structure type 25.[24] The decomposition of MPA in APOF resulted in a gradual loss of crystallinity and the formation of a dense trydimite aluminum phosphate. Similarly, ZnPO lost crystallinity during the decomposition of MPA and was converted into the dense hoppeite zinc phosphate (not shown).
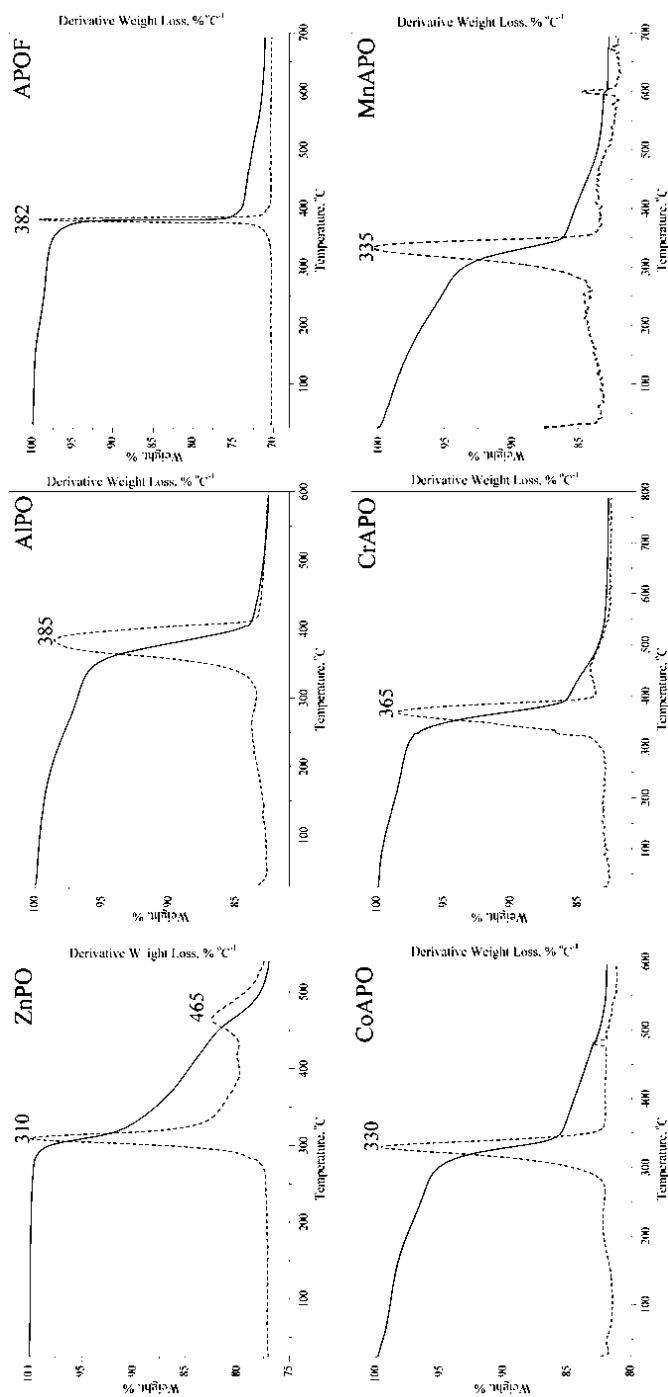
Fig. 8. TG and DTG curves of the novel zincophosphate (ZnPO), AlPO$_4$-21, the fluorinated aluminophosphate and Co(II)-, Cr(III)- and Mn(II)-containing aluminophosphates (CoAPO, CrAPO and MnAPO, respectively).
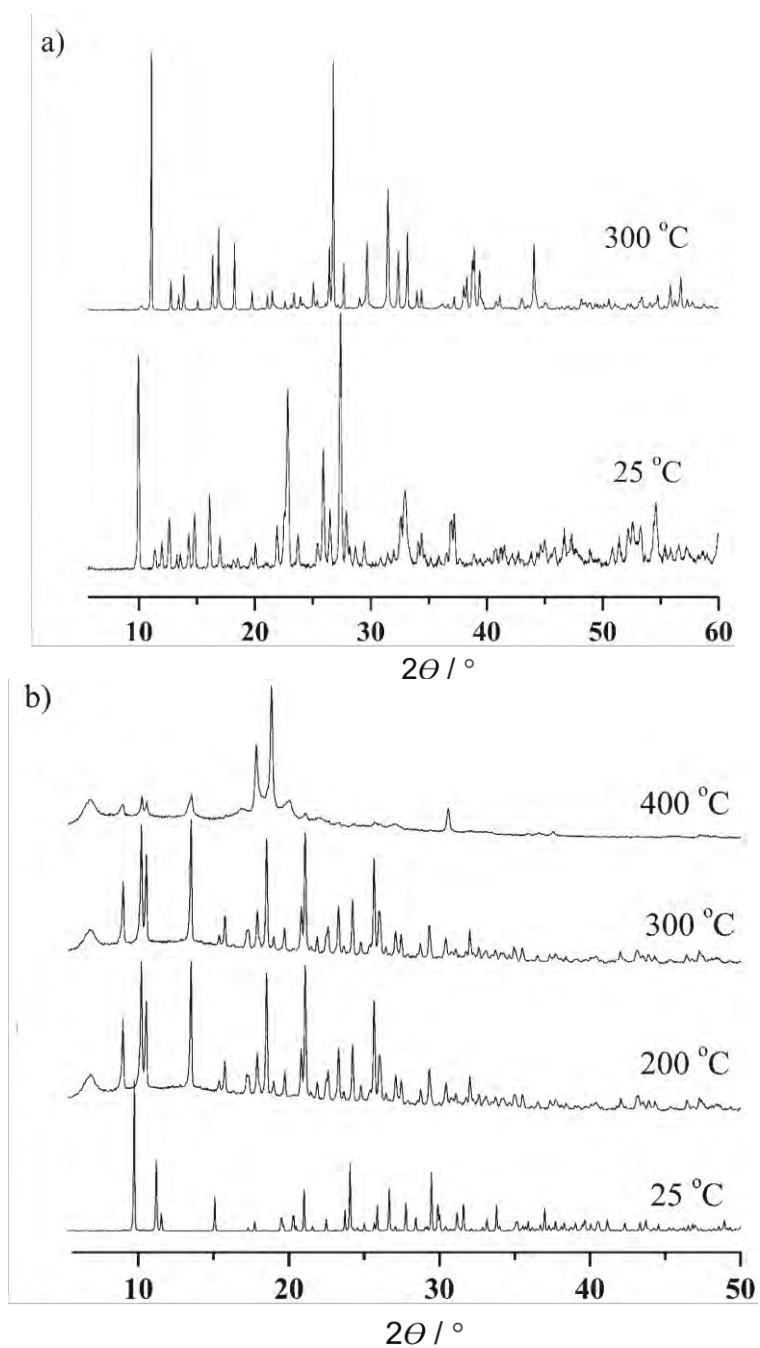
Fig. 9. The high temperature XRD patterns of a) AlPO$_4$-21 and b) the fluorinated aluminophosphate (APOF).

CONCLUSIONS

The results show that MPA, which has not been hitherto studied, as the structure-directing agent in the synthesis of open-framework phosphate-based materials played a structure-directing role. The presence of the diamine in a zinc phosphate reaction mixture led to crystallization of a layered zincophosphate with a novel structure. The layered zincophosphate crystallized not only under hydrothermal but also under microwave conditions. The microwave-assisted heating significantly decreases the crystallization time from 10 days to 2 h.

MPA has also the templating role in two types of reaction mixtures: 1) consisting of an aluminophosphate and 2) consisting of aluminophosphate and transition metal cations (Co(II), Cr(III) and Mn(II)). From mixture 1) and reaction mixture 2) containing Co and Cr, the same crystalline phase formed, corresponding to aluminophosphate of the structure type 21. From the Mn-containing mixture, a crystalline material of structure type 12 was obtained. This indicates that not only 3-(methylamino)propylamine, but also the type of the transition metal cation influenced the nucleation process. Microwave-assisted heating can also significantly decrease the crystallization time.

MPA exhibits the templating role in the fluoride-containing reaction mixtures. From an aluminophosphate reaction mixture, an open-framework aluminophosphate forms, having the structure of the gallophosphate ULM-3. The product from this reaction system is also a confirmation that not only the organic species but also the fluoride and transition metal ions affect the nucleation process. The presence of Co(II), Cr(III) and Mn(II) in fluoride-containing reaction mixtures resulted in either the formation of several unknown crystalline phases (Cr and Mn) or the fluorinated aluminophosphate with a ULM-3 structure.

In all obtained crystalline products, MPA was entrapped in the inorganic lattice interacting with the host framework *via* hydrogen and/or electrostatic interactions. The type of interactions affected not only its thermal stability but also the thermal stability of the organic–inorganic system. Finally, the formed structures have no mutual structural analogy, suggesting complexity of the nucleation process for the open-framework phosphates as well as complexity regarding the precise role of the organic (guest) component.

И З В О Д

3-(МЕТИЛАМИНО)ПРОПИЛАМИН КАО СТРУКТУРНИ АГЕНС У СИНТЕЗИ НЕОРГАНСКИХ ПОЛИМЕРА НА БАЗИ ФОСФАТА

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3-(Метламино)пропиламин (МПА) изучаван је као структурни агенс (темплат) у синтези порозних материјала на бази фосфата. Утицај температуре, молског односа реактаната, времена и присуства флуорид-јона на кристализацију алумофосфата, алумофосфата који у решетки садрже јоне прелазних елемената (прелазни елемент – Mn(II), Cr(III) и Co(II)) такође су изучавани. МПА испољава својства темплата и у свим синтетисаним кристалним производима заробљен је у неорганској решетки са којом остварује водоничне и/или електростатичке интеракције. Према детаљној термичкој анализи врста интеракција је од пресудног значаја за термичка својства МПА као и термичку стабилност читавог органско-неорганског кристалног система. Структурна анализа је указала да међу насталим кристалним структурама нема сличности. Ово указује да је улога органске („гостујуће") компоненте у процесу нуклеације порозних фосфата сложена као и сам процес нуклеације.

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