

# Hydrothermal synthesis and characterization of microporous crystals of trivalent metal-containing zirconium phosphates

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## Abstract

Two organically templated trivalent metal-containing crystalline zirconium phosphate materials FeZrPO-8 and AlZrPO-8 have been prepared hydrothermally by using fluoride as a mineralizer, and 1,6-diaminohexane (DAH) as templates. The powder XRD patterns indicate that the as-synthesized products are new materials. Substitutions of Al<sup>3+</sup> or Fe<sup>3+</sup> into Zr<sup>4+</sup> sites were confirmed by a combination of powder X-ray diffraction (XRD) and nuclear magnetic resonance (NMR) studies. The thermal behavior of the title compounds have been investigated using TG-DTA and X-ray thermodiffraction, which indicated that the inorganic framework of the compounds are thermally stable up to ~400 °C. © 2004 Elsevier B.V. All rights reserved.

**Keywords:** Hydrothermal synthesis; Zirconium phosphates; (<sup>31</sup>P, <sup>27</sup>Al) MAS NMR

## 1. Introduction

Metallophosphates have attracted a lot of interest in the past decades [1]. Among them, zirconium phosphates are very attractive materials for their applications in ion exchange, intercalation, ion conductivity, catalysis and molecular sorption [2,3]. Since the use of fluoride ions as mineralizers was introduced by Guth et al. [4] into hydrothermal preparation of zeolite, a good number of metal phosphate fluorides have been obtained. Recently, the fluoride route has led to the first zirconium phosphate (ZrPO-1) with three-dimensional open-framework structure [5]. More recently, Férey and co-workers [6] reported the synthesis and ab initio structure determination of a new three-dimensional mixed-valence oxyfluorinated titanium phosphate MIL-15, and two organically templated mixed-valent Ti<sup>III</sup>/Ti<sup>IV</sup> phosphates with open-framework structures were also synthesized [7,8]. This indicated that the synthesis of M<sup>III</sup>/M<sup>IV</sup> phosphate with a three-dimensional open-framework structure was possible.

To the best of our knowledge, organically templated metal-containing zirconium phosphate has not been obtained up to now. Recently, we have devoted effort toward

hydrothermal synthesis of the organically templated trivalent metal-containing zirconium phosphates to obtain possible new types of materials with valuable properties. Due to the substitution of trivalent metal ions for Zr<sup>4+</sup> in the framework of zirconium phosphate, a series of new materials (denoted here MeZrPO-*n*) have been hydrothermally synthesized. The goal of this work is to synthesize zirconium-based mixed-metal M<sup>III</sup>/M<sup>IV</sup> phosphates, which represent the first zirconium homologue to the well-known metal-containing aluminium phosphate molecular sieves (MeAlPO-*n*) [9]. In the paper, we report the organically templated trivalent metal-containing zirconium phosphates FeZrPO-8 and AlZrPO-8, which were synthesized hydrothermally by using 1,6-diaminohexane (DAH) as the structure-directing agent. The as-synthesized products are studied by X-ray powder diffraction, X-ray fluorescence analysis, scanning electron microscope, IR spectroscopy, <sup>31</sup>P and <sup>27</sup>Al MAS NMR spectra, X-ray thermodiffraction, and thermogravimetric and differential thermal analyses.

## 2. Experimental

### 2.1. Synthesis

The two compounds were hydrothermally prepared from a starting mixture containing 1,6-diaminohexane (DAH) as the structure-directing agent. The compounds were obtained

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as a pure single-phase material by adjusting the synthetic conditions. For compound FeZrPO-8,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , DAH, ammonium fluoride, phosphoric acid (85%), and distilled water were mixed in the mole ratio of 1:3:6:3:6:300. For compound AlZrPO-8,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , DAH, ammonium fluoride, phosphoric acid (85%), and distilled water were mixed in the mole ratio of 1:3:6:3:6:300. The mixture was sealed in a 100 mL Teflon-lined stainless steel autoclave with a filling capacity of  $\sim 70\%$  and heated at 463 K for 7 days under autogenous pressure. The resulting products were separated by centrifugation, washed thoroughly with distilled water, and dried in an oven at 100 °C for 24 h.

The X-ray fluorescence analysis gave ratios Me/F (Me = Fe or Al), Zr/F and P/F, respectively, of 1.99, 4.28 and 8.40 for FeZrPO-8 and 1.96, 4.54 and 8.62 for AlZrPO-8.

## 2.2. Characterization

X-ray powder diffraction (XRD) patterns of products were obtained on a D/max-rb diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5405 \text{ \AA}$ ); Fe, Al, Zr, P and F content of the as-synthesized samples were determined from Philips Magix 2424 X-ray fluorescence analyzer. For scanning electron microscope (SEM), the sample powder was dispersed in ethyl alcohol for a few seconds. A drop of this suspension was then placed as a thin film supported over specimen grid. The photograph was taken using KYKY-1000D microscope. Infrared spectra (IR) were recorded on a Bruker EQUINOX 55 FTIR spectrometer using KBr pellet technique.  $^{31}\text{P}$  and  $^{27}\text{Al}$  MAS NMR spectra were obtained at room temperature in a DRX-400 Bruker spectrometer. The frequencies used for  $^{31}\text{P}$  and  $^{27}\text{Al}$  were 161.9 and 104.3 MHz, respectively. Samples were spun at 6 and 8 kHz, and spectra were acquired using a BBO MAS probe (4 mm zirconia rotor). Typical radio frequency pulses of 2.0  $\mu\text{s}$  for  $^{31}\text{P}$  and 0.6  $\mu\text{s}$  for  $^{27}\text{Al}$  were used. The recycle time between successive scans was 2 s for phosphorus and aluminium. The  $^{31}\text{P}$  and  $^{27}\text{Al}$  chemical shift values are externally referenced to 85%  $\text{H}_3\text{PO}_4$  and 1%  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  aqueous solutions, respectively. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) results were obtained on a Perkin-Elmer Pyris 1 thermogravimetric analyzer and a Perkin-Elmer DTA 7 differential thermal analyzer, respectively, in air with a heating rate of 10 °C/min over a 50–800 °C temperature range. The X-ray thermodiffraction was performed in the furnace of a D/max-rb diffractometer in the  $\theta$ -2 $\theta$  mode, the heating rate was 10 °C/min from room temperature to 900 °C temperature range.

## 3. Results and discussion

### 3.1. Synthesis

It is found that the use of hydrothermal techniques and the involvement of fluoride ions are very essential in the

formation of the title compounds. If  $\text{NH}_4\text{F}$  is omitted from the reaction mixtures, only amorphous metal phosphate is obtained. Due to the use of fluoride, recently a series of fluorine-containing zirconium [10,11] or titanium [12] phosphates were obtained. In addition, the formation of the title compounds has been shown sensitive to the organic templates. When 1,6-diaminohexane (DAH) is used as the template, a series of organically templated trivalent metal-containing zirconium fluorophosphates can be obtained. Several trivalent metal-containing zirconium fluorophosphates with other types of structure were also prepared in the presence of diamines such as ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane, and 1,4-diaminobutane by our group. It seems that the presence of diamines is crucial for the formation of the organically templated trivalent metal-containing zirconium fluorophosphates.

### 3.2. Characterization

The XRD patterns of two as-synthesized samples are shown in Fig. 1. The products recovered are of high crystalline, and a single intense peak is observed at low angle, corresponding to  $d$ -spacing of 15.25 and 15.20  $\text{\AA}$  in FeZrPO-8 and AlZrPO-8 phases, respectively. Because of the structural similarity of the two compounds, both of them show almost the same diffracting positions of XRD. It can be seen from Fig. 1 that the XRD patterns of both compounds is very similar, we therefore assume that the structure of FeZrPO-8 is identical to that of AlZrPO-8 although the nature of trivalent metal ion incorporated is different. In contrast to the powder X-ray patterns of the known phases of zirconium fluorophosphate, the as-synthesized materials proved to be a new phase, which are different from the previously reported zirconium fluorophosphates [10].

SEM photograph of FeZrPO-8 is shown in Fig. 2. The crystals are homogeneous with ball-like morphology indicating that the solid is phase pure. The average particle size is about 1000 nm.

The  $^{31}\text{P}$  and  $^{27}\text{Al}$  MAS NMR spectra of AlZrPO-8 are shown in Figs. 3 and 4, respectively. Investigations

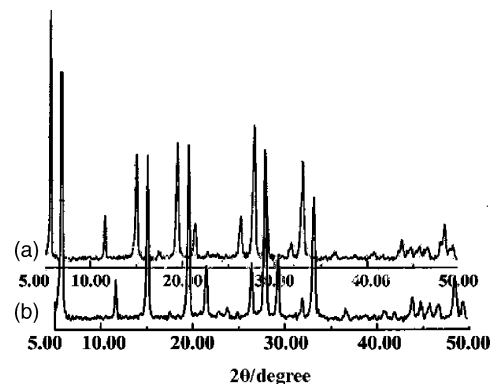


Fig. 1. XRD patterns of (a) FeZrPO-8 and (b) AlZrPO-8.

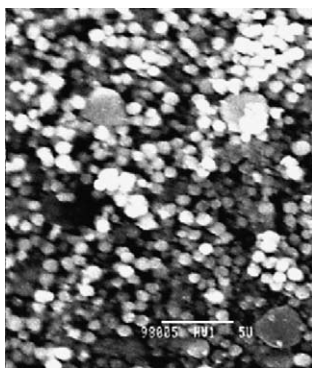
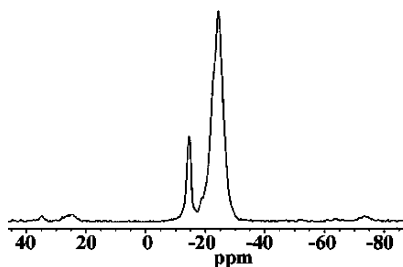


Fig. 2. The SEM of FeZrPO-8.

Fig. 3. The  $^{31}\text{P}$  MAS NMR spectra of AlZrPO-8.

of  $\gamma$ -zirconium phosphate ( $\gamma\text{-Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ;  $\gamma\text{-ZrP}$ ) and  $\alpha$ -zirconium phosphate ( $\alpha\text{-Zr}(\text{PO}_4)(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ ;  $\alpha\text{-ZrP}$ ) by  $^{31}\text{P}$  MAS NMR have been published by Clayden [13]. He showed that where  $\gamma\text{-ZrP}$  has only one  $^{31}\text{P}$  resonance ( $-18.7$  ppm)  $\alpha\text{-ZrP}$  has two  $^{31}\text{P}$  resonances ( $-9.4$  and  $-27.4$  ppm) of equal integrated intensity, and proposed that the resonances for the ( $\text{PO}_4$ ), ( $\text{HPO}_4$ ), and ( $\text{H}_2\text{PO}_4$ ) groups in  $\gamma\text{-ZrP}$  and  $\alpha\text{-ZrP}$  are at  $-27.4$ ,  $-18.7$ , and  $-9.4$  ppm. In studies of a series of layered Ti, Zr, and Al phosphates by MAS NMR spectroscopy, Nakayama et al. have also reported that the isotropic  $^{31}\text{P}$  chemical shifts of  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$  groups appear around  $-10$ ,  $-20$ , and  $-30$  ppm, respectively [14]. The  $^{31}\text{P}$  MAS NMR spectrum of AlZrPO-8 gives two peaks at  $-14.7$  and  $-24.6$  ppm with a relative intensity ratio of 1:3 (Fig. 3). On the basis of the previous studies in zirconium or titanium phosphates [13–15], we assigned the NMR peaks at  $-14.7$  ppm to the  $\text{HPO}_4$  group and  $-24.6$  ppm to the  $\text{PO}_4$  group. Considering these results it was concluded that AlZrPO-8 contains ( $\text{HPO}_4$ ) and ( $\text{PO}_4$ ) groups in the ratio of 1:3.

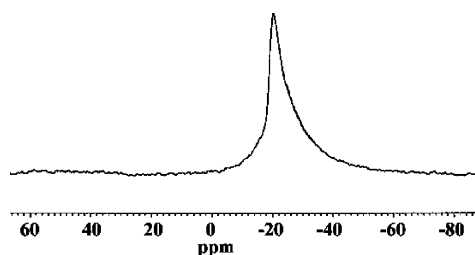
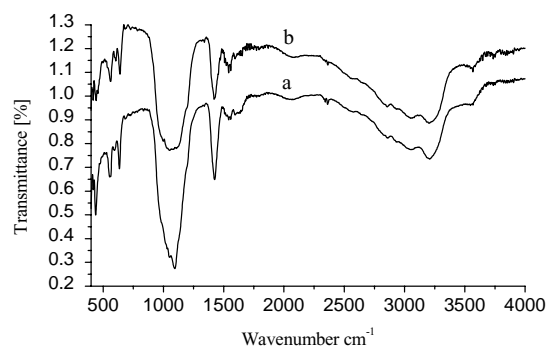
Fig. 4. The  $^{27}\text{Al}$  MAS NMR spectra of AlZrPO-8.

Fig. 5. The IR spectra of (a) FeZrPO-8 and (b) AlZrPO-8.

$^{27}\text{Al}$  magic angle spinning NMR spectroscopy is a powerful tool to probe the local Al environment and AlZrPO-8 has been studied by this technique. In a previous NMR study of LATP ( $\text{Li}_{1+y}\text{Al}_y\text{Ti}_{2-y}(\text{PO}_4)_3$ ) [16–18],  $^{27}\text{Al}$  resonances at  $\delta -15$  and  $40$  ppm were assigned to aluminium in octahedral ( $\text{Al}_\text{O}$ ) and tetrahedral ( $\text{Al}_\text{T}$ ) sites, respectively. The  $^{27}\text{Al}$  MAS NMR spectrum of AlZrPO-8 gives sharp peaks at  $-20.6$  ppm, which is assigned to Al in octahedral sites (Fig. 4). Since no Al-containing impurities were found in the X-ray diffractographs and  $^{27}\text{Al}$  MAS NMR spectroscopy, we assigned this signal to Al occupying the octahedral Zr sites in AlZrPO-8, and thus confirm the partly substitution of  $\text{Zr}^{4+}$  by  $\text{Al}^{3+}$  in the AlZrPO-8 framework.  $^{27}\text{Al}$  NMR results indicate that the metal ion  $\text{Fe}^{3+}$  or  $\text{Al}^{3+}$  is incorporated into the framework of the structure.

The infrared spectrum of FeZrPO-8 (Fig. 5) contains the broad characteristic bands for protonated amines at  $3200$ ,  $3050$  and  $2350$   $\text{cm}^{-1}$  corresponding to the combination and overlapping of the stretching vibrations of  $\text{NH}_3^+$  and  $\text{CH}_2$  groups, suggesting the 1,6-diaminohexane molecules are protonated. The band near  $1550$  and  $1620$   $\text{cm}^{-1}$  can be assigned to the  $\text{NH}_3^+$  bending vibration, this band is also indicative of the presence of the 1,6-diaminohexane molecules in its protonated form. The bending modes of the  $-\text{CH}_2-$  groups in the 1,6-diaminohexane appear around  $1400$   $\text{cm}^{-1}$ . The broad band is observed in the region  $1100$ – $900$   $\text{cm}^{-1}$ , and they correspond to the asymmetric stretching vibrations of  $\text{PO}_4$  units. An absorption at  $560$   $\text{cm}^{-1}$  appears as well, which is due to bending vibrations of phosphate groups [19–22]. The absorption bands of compound AlZrPO-8

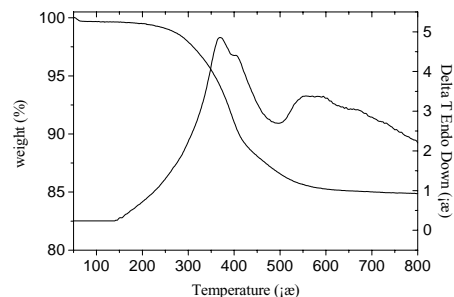


Fig. 6. The TG-DTA curve of FeZrPO-8.

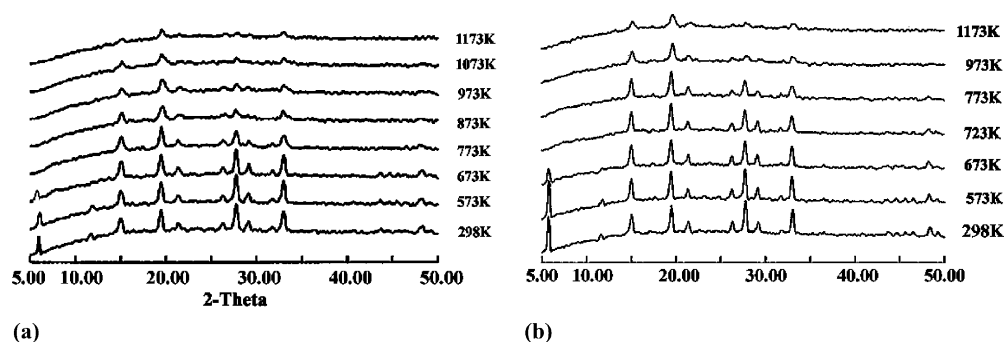


Fig. 7. X-ray thermodiffractogram of (a) FeZrPO-8 and (b) AlZrPO-8.

appear at 3570, 3200, 3050, 2854, 2360, 1600, 1544, 1422, 1050, 635, 559 and 444  $\text{cm}^{-1}$ . They include characteristic bands of amine molecules, phosphate groups, and OH groups. The assignment of these bands is similar to that for compound FeZrPO-8.

Thermogravimetric analysis of FeZrPO-8 (Fig. 6) shows that total weight loss of ca. 12.8% from 200 to 600 °C corresponds to the removal of amine, fluorine and the dehydration of  $\text{HPO}_4^{2-}$  groups. The DTA curve exhibits two exothermic peaks at approximately 370 and 590 °C, corresponding to the decomposition of the template, condensation due to the removal of  $\text{H}_2\text{O}$  and HF. For AlZrPO-8, the TG-DTA results indicate a total mass loss of 11.9% in the range 200–600 °C, which is attributed to the departure of the template molecule and the removal of  $\text{H}_2\text{O}$  and HF. In fact, the whole decomposition process is rather unspecific because several processes are overlaying each other in this temperature range.

The thermal evolution of FeZrPO-8 and AlZrPO-8 were performed using X-ray thermodiffractometry, which was applied to the two compounds to study their stability. When the compounds are heated, the thermal transformations are observed. For compound FeZrPO-8, X-ray thermodiffractogram (Fig. 7a) shows that no significant change of the diffraction peaks is observed when the calcination temperature is lower than 673 K, and the significant change of the basal structure take place between 673 and 773 K. Upon increasing the calcination temperature, the diffraction peaks is gradually weaken, and disappeared at about 973 K. For compound AlZrPO-8 (Fig. 7b), initially, between room temperature and 673 K, slight variations of the peak intensities are observed but the structure is, on the whole, retained up to 673 K. It indicated that AlZrPO-8 is stable up to 673 K. Above 673 K, a distinct change of the powder pattern is observed, and the intermediate phase (not identified) formed is very stable up to about 973 K.

#### 4. Conclusions

Two new organically templated trivalent metal-containing zirconium fluorophosphates FeZrPO-8 and AlZrPO-8 have been synthesized under hydrothermal condition. To the

best of our knowledge, this is the first report showing the hydrothermal synthesis of organo-directed trivalent metal-containing zirconium fluorophosphates. The presence of  $\text{F}^-$  in the reaction mixture is necessary for their formation. From the XRD powder diffraction measurement, the variations of trivalent metal ion incorporated do not lead to fundamental changes of the structure. Nuclear magnetic resonance (NMR) studies indicate that direct substitutions of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  into  $\text{Zr}^{4+}$  sites, and two compounds contain the ( $\text{HPO}_4$ ) and the ( $\text{PO}_4$ ) groups. The thermal behavior of the title compounds have been investigated by using X-ray thermodiffractometry, which indicated that the inorganic framework of the compounds are thermally stable up to ~673 K. Further investigation is in progress to solve the structure of the as-synthesized compounds, and to expand the field of microporous phase based on zirconium phosphate.

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