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Study on Synthesis and Intercalation Behavior of Layered Zirconium Proline-N-methylphosphonate-phosphate

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Abstract: Zirconium proline-N-methylphosphonate-phosphate (α-ZPMPP) was prepared in the presence of HF for the first time. The α-ZPMPP sample is highly crystallized with interlayer distance of 1.52 nm. The interlayer distance of complex of α-ZPMPP with *n*-butylamine (α-ZPMPP-BA) is in 0.45 nm larger than that of α-ZPMPP. The α-ZPMPP possesses different intercalation behavior of host-guest compound from α-ZP.

Keywords: Zirconium proline-N-methylphosphonate-phosphate, *n*-butylamine, intercalation complex, interlayer distance, host-guest compound.

Zirconium phosphate, phosphonate and phosphate-phosphonate are a kind of multifunctional materials which are highly interested by researchers for its high thermal and chemical stability, anti-acid and anti-basic properties. This kind of layered structure compounds are widely used as ion-exchangers, shape-selective absorbents, catalysts, catalyst supports and precursors for preparing intercalation complex[1-3]. Typical α-zirconium phosphate, $Zr(HPO_4)_2 \cdot H_2O$ (α-ZP), has interlayer distance of 0.76 nm and the zirconium atoms lie in the same plane with –POH groups pointing away from the layers[4]. The interlayer space can be modified through absorption, insertion, intercalation, pillaring or bonding connection with organic groups of certain size. Because of the regularity and designability of its structure, it is widely used as various solid functional materials.

During the past decades, much attention has been paid to the intercalation behavior of α-zirconium phosphate, many polar organic molecules and polynuclear complex ions were intercalated into α-zirconium phosphate[5]. Many intercalation compounds with organic molecules possessing strong basic character are obtained and they are stable to thermal treatment and washing. And the intercalation guest is restricted by their size and basicity. The state of inserted molecules, in tercalation steps and kinetic studies of the intercalation reactions are fully discussed[6-7]. Our group are interested in preparing zirconium phosphate-phosphonate, introducing different organic groups into zirconium phosphate-phosphonate to prepare different kinds of catalysts, catalyst supports and ion-exchangers[8].

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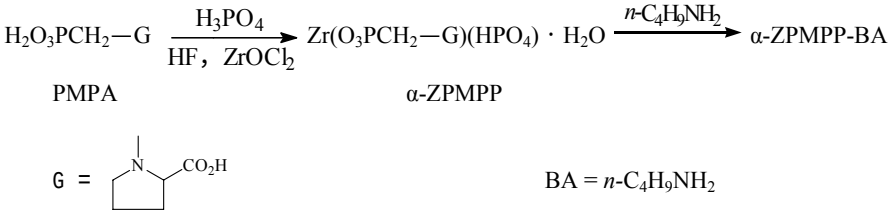
Although a lot of work have been done to α-zirconium phosphate intercalation, the intercalation of zirconium phosphate-phosphonate has been seldom dealt with[8]. In this paper we describe the synthesis of proline-N-methylphosphonate-phosphate (α-ZPMPP), a new zirconium phosphate- phosphonate ion-exchanger which was modified by L-proline, the intercalation complex of α-ZPMPP with *n*-butylamine for the first time. And the phase of *n*-butylamine within the interlayer space of the α-ZPMPP intercalation complex is also discussed. The synthesis route is as follows:



Experimental

C, H, N elemental analysis was performed by a PE-2400CHN instrument. IR, XRD, TG and DSC were recorded on Bio-Rad FTS-185 IR spectrophotometer, D/MAX-3C automatic X-ray diffraction instrument (Fe target) and NETZSCH STA 449C thermal-analysis instrument respectively.

Preparation of L-proline-methyl-phosphonic acid (PMPA)

A solution of (0.3 mol, 34.5 g) L-proline dissolved in 30 mL water, (0.3 mol, 24.6 g) crystalline phosphorous acid and 30 mL concentrated HCl were mixed, after the temperature reached to 95°C, 0.45 mol of aqueous 37% formaldehyde solution was added dropwise, the reaction mixture was kept at reflux temperature for 2 additional hrs. Then the reaction mixture was evaporated to a syrupy state and ethanol was added for crystallization.

Preparation of α-ZPMPP

$ZrOCl_2 \cdot 8H_2O$ (0.03 mol, 9.7 g) dissolved in 100 mL water was mixed with 40% hydrofluoric acid(0.24 mol) , (0.03 mol, 6.27 g) PMPA and (0.03 mol, 3.46 g) 85 % H_3PO_4 were dissolved in 100 mL water, the materials were mixed and stirred at 70°C for 72 hrs.

Intercalation n-butylamine into α-ZPMPP

40 mL *n*-butylamine was added to 1 g of α-ZPMPP and stirred at room temperature for 5 days, the crystal was washed with petroleum ether.

Results and Discussion

The IR spectrum of α-ZPMPP indicates that the sample contain both phosphate and proline-N-methyl- phosphonate groups. Characteristic bands 1050 cm^{-1} [ν (P-O (H))], 1247 cm^{-1} [ν (P-C)], 1314 cm^{-1} [ν (C-N), 3442 cm^{-1} [ν (O-H)], 1639 cm^{-1} [ν (-COOH)] are all present.

The XRD curves for α-ZPMPP and intercalation complex α-ZPMPP-BA are shown in **Figure 1** and **Figure 2**, respectively. The interlayer distance of α-ZPMPP is 1.52 nm, (2θ=7.3), which is much larger than α-ZP, and is attributed to the effect of proline group within the interlayer. The interlayer distance of intercalation complex α-ZPMPP-BA is 1.97 nm, (2θ=5.6), in 0.45 nm larger than that of α-ZPMPP，due to n-butylamine was uptaken by solid phase of α-ZPMPP and formation of α-ZPMPP-BA intercalation complex. It is shown from the sharp peaks of **Figure 1** and **2** that α-ZPMPP and intercalation complex α-ZPMPP-BA are both highly crystallized with pure crystal phase.

The TG-DSC curves for α-ZPMPP and α-ZPMPP-BA are shown in **Figure 3** and **4** respectively, and the stepwise mass losses are observed. For α-ZPMPP, the first step of mass– loss occurs from ambient temperature to 200°C ascribed to the loss of crystal water. The second step of mass–loss in the region of 200-350°C and ascribed to the loss of CO_2 from proline. The third step of mass–loss ranges from 350°C to 1000°C involves oxidation of the organic portion and dehydration of zirconium phosphate to yield zirconium pyropho-

Figure 1 The XRD of α-ZPMPP

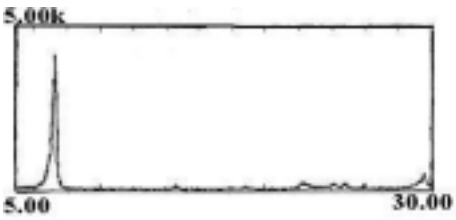


Figure 2 The XRD of α-ZPMPP-BA

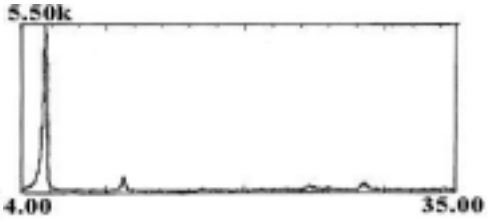


Figure 3 The TG-DSC of α-ZPMPP

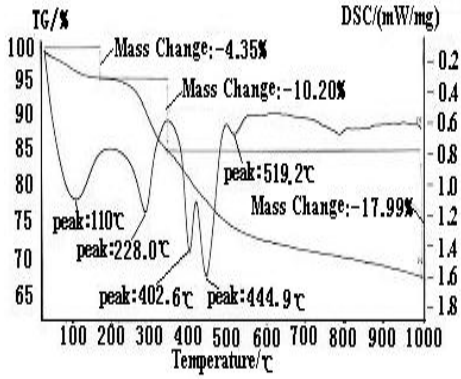
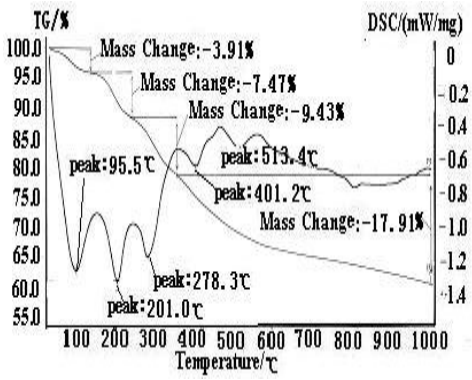


Figure 4 The TG-DSC of α-ZPMPP-BA



sphate. The intercalated complex α-ZPMPP-BA has an additional mass-loss at 150-250°C resulted from the loss of *n*-butylamine. With the intercalation of *n*-butylamine, the temperature of dehydration of crystal water in α-ZPMPP-BA reduced.

The structure of α-ZPMPP, $Zr(O_3PCH_2—G)(HPO_4)\cdot H_2O$, is half of the P–OH of α-zirconium phosphate replaced by N-methylproline group. Because of bulkiness of N-methylproline, the ideal structure of α-ZPMPP is that the P–OH and N-methylproline groups arrange as ABABAB alternatively. Although half of the P–OH replaced by amino-acidic group of α-ZPMPP compared with α-ZP, it is still readily to accept basic molecules to form intercalated compounds.

Usually，*n*-butylamine arranged as bimolecular layer formed within α-ZP-BA intercalation compound with formula as $Zr(HPO_4)_2\cdot H_2O\cdot 2\ n\text{-}C_4H_9NH_2$，and the interlayer distance increases from 0.76 nm of α-ZP to 1.86 nm of α-ZP-BA[2]. Calculation from the data of elemental analysis, XRD, TG and DSC for both α-ZPMPP and α-ZPMPP-BA intercalated complex, the *n*-butylamine form mono-molecule layer within the interlayer space of the α-ZPMPP-BA intercalation complex with formula as $Zr(O_3PCH_2–G)(HPO_4)\cdot H_2O\cdot 0.5\ n\text{-}C_4H_9NH_2$，in which two –COOH groups in different plane of α-ZPMPP point head to head in the interlayer space take up one *n*-butylamine molecule，formed ionic bond between *n*-butylamine and one of the –COOH group. Because of the bulky P-methylproline groups and the low acidity of –POH groups, the –POH within α-ZPMPP can not accept butylamine. The results indicate that，compared with α-ZP, it is a new class of organic-inorganic hybrid host compound of α-ZPMPP which possess different intercalation behavior of host-guest compound. The further investigation is on going.

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