Synthesis of crystalline zirconium phosphate by a minimalistic liquid assisted mechanochemistry-based approach

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Abstract: Zirconium phosphates have potential applications in areas of ion-exchange, catalysis, photochemistry, and biotechnology. However, synthesis methodologies to form crystalline α-zirconium phosphate ($Zr(HPO_4)_2\cdot H_2O$) typically involve the use of excess phosphoric acid, addition of HF or oxalic acid and long reflux times or hydrothermal conditions. Herein we report on a minimalistic sustainable route using to form highly crystalline α-zirconium phosphate within hours. The morphology can be changed from platelets to rod-shaped particles with fluoride addition. Key features of this minimal solvent synthesis are the excellent yields obtained with high atom economy under mild conditions and ease of scalability.

Keywords: Zirconium phosphate, crystallinity, liquid-assisted mechanochemistry.

1. Introduction

Zirconium phosphates find various applications such as cation exchangers in the treatment of nuclear wastes and radioactive wastewater, acid catalysts and catalyst supports, intercalation host for drugs or other molecules with desired performance, fast ion conductors and in chromatography.[1-3] Polymer nanocomposites with α-ZrP as filler show enhanced physico-chemical properties such as reduced gas permeability, better mechanical strength and thermostability.[4]

The most well-studied is $Zr(HPO_4)_2\cdot H_2O$ (α-ZrP) which has an ion exchange capacity up to 6.64 mequiv/g (2 mol H^+/mol). The material is stable in acidic conditions but under alkaline conditions, the amorphous form undergoes significant hydrolysis unlike crystalline α-ZrP.[1] Zirconium phosphate obtained by precipitation of zirconium salts with phosphates or phosphoric acid in aqueous solution is normally amorphous. o obtain the crystalline zirconium phosphate, a further step of refluxing in excess H_3PO_4 of 1–12 M for extended periods of 48 h or more is necessary.[5] Alternatively, crystalline α-ZrP can be obtained by direct precipitation in the presence of complexing agents such as hazardous hydrofluoric acid or oxalic acid.[6,7] However, the use of excess amounts of phosphoric acid and complexing agents is uneconomical and generates considerable amounts of wastes which require further treatment. Furthermore, in order to achieve high crystallinity, long synthesis times, ranging from days to weeks, are required.

We report herein a new approach to preparing crystalline α-ZrP. Instead of using the starting materials as aqueous solutions, we prepared α-ZrP from the as-obtained starting materials, i.e., solid zirconyl chloride and 85 % phosphoric acid. This will allow the highest possible concentration of reactants and dispense with the need to use excess phosphoric acid or complexing agents as in the current preparation methods. Furthermore, using a higher concentration should increase the rate of reaction which may reduce the long synthesis times of days to weeks required to achieve high crystallinity. We are pleased that this minimalistic approach with only the required reagents works excellently to give very high yields of α-ZrP in 1 to 24 h, depending on the desired crystallinity. We call this a “minimal solvent” synthesis as only water from the intrinsic reaction system can be involved. Interestingly, the morphology of the α-ZrP can be varied by addition of fluoride and some of the observed shapes have not been reported before.

2. Experimental

In a typical synthesis, a weighed amount of 85 wt.% H_3PO_4 was added dropwise to 1.07 g $ZrOCl_2\cdot 8H_2O$ placed in a 30 ml polypropylene container. A H_3PO_4/Zr mole ratio of either 2 or 3 was used. (Note: H_3PO_4/Zr = 2 is the stoichiometric ratio required to form α-ZrP). The effect of adding NH_4F or NaF was investigated using a F/Zr mole ratio from 0.2-1.The viscous solid mixture was stirred with a glass rod to ensure homogeneity and the container was capped and placed in an oven at 100 °C for 24 h. The solid product was washed by centrifugation with deionized water until no chloride ions were detected ($AgNO_3$ test) and dried overnight at 60 ˚C. The effect of temperature from room temperature to 150 °C was studied. The elemental composition of the samples was determined by ICP-OES. Powder X-ray diffraction, scanning electron microscopy, thermogravimetric analysis and solid state ^{31}P NMR measurements were performed.

3. Results and discussion

The powder X-ray diffractogram of the sample formed using $H_3PO_4/Zr = 2$ shows reflexes of only α–ZrP (Fig. 1). This is noteworthy as only the required stoichiometric amounts of reactants need to be added to successfully form α–ZrP. Using 1.5 times excess H_3PO_4 ($H_3PO_4/Zr = 3$) led to a highly crystalline sample with sharp well-resolved diffraction peaks. For comparison, α-ZrP prepared by the conventional reflux method, with total $H_3PO_4/Zr \sim 52.5$, was of lower crystallinity. Crystalline α-ZrP can be obtained even at room temperature with crystallinity increasing with synthesis temperature. The addition of fluoride (F/Zr 0. – 1) led to increased crystallinity as compared to α-ZrP synthesized without fluoride.

α-ZrP formed by the minimal solvent method revealed a platelet morphology (Fig. 2a). The addition of fluoride changed the morphology to long rods (~ 4 - 10 μm length) with triangular or prismatic cross section (Fig. 2b). Their large particle size makes them suitable as ion exchangers with advantages of reduced pressure drop in columns and ease of filtration.[12, 20] Furthermore, the different morphologies may affect their properties as intercalation hosts and polymer fillers. This opens up exciting possibilities for high performance materials for example, in coatings and corrosion resistance

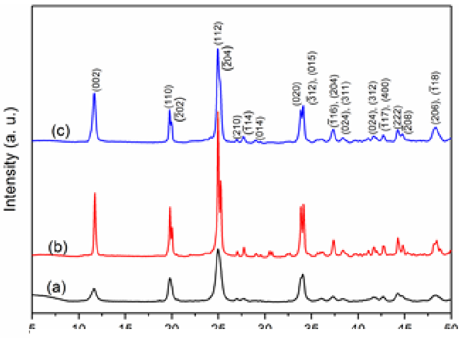

Figure 1. XRD of α-ZrP obtained by the minimum solvent method (100 °C, 24 h) using H_3PO_4/Zr molar ratios of (a) 2 (b) 3 and (c) reflux in 6 M H_3PO_4 for 48 h.

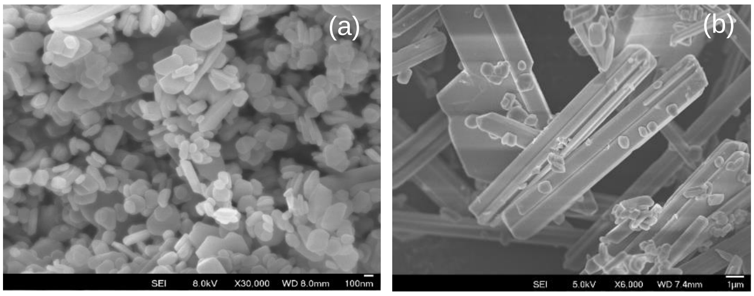

Figure 2. SEM images of α-ZrP synthesized by minimal solvent method at 100 °C (a) without fluoride and (b) with NaF at F/Zr 0.3.

4. Conclusions

A new green procedure is reported for the synthesis of α-ZrP with controllable crystallinity. Key features are the minimal use of reagents and the ease and simplicity of the procedure with short crystallization times, ease of scale up and excellent yield with high atom economy.

References

1. A. Clearfield, Solvent Extr. Ion Exch. 19 (2000) 655.
2. B. M. Mosby, A. Díaz, A. Clearfield, Dalton Trans. 43 (2014) 10328.
3. M. Pica, R. Vivani, A. Donnadio, E. Troni, S. Fop, M. Casciola, Inorg. Chem. 54 (2015) 9146.
4. L. Sun, W. J. Boo, D. Sun, A. Clearfield, H.-J. Sue, Chem. Mater. 19 (2007) 1749.
5. A. Clearfield, A. Oskarsson, C. Oskarsson, Ion Exch. Membr. 1 *(*1972) 91.
6. G. Alberti, E. Torracca, J. Inorg. Nucl. Chem. 30 (1968) 317.
7. S. E. Horsley, D. V. Nowell, J. Appl. Chem. Biotechn. 23 1(973) 215.
8. Y. Cheng, X. (T.) Wang, S. Jaenicke, G.-K. Chuah, ChemSusChem 10 (2017) 3235.