

## Comparison of the Preparation Methods of Mesoporous Phosphate Compounds Belonging to NZP Family

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**Key words:** mesoporous phosphate compounds with NZP structure; template PEO; sol-gel method; coprecipitation (CP); mechanochemical activity (MA)

**Abstract:** Using polyethylene oxide (PEO) as template, the new types of mesoporous phosphate compound which belongs to  $\text{NaZr}_2(\text{PO}_4)_3$  (NZP) family were synthesized by coprecipitate, sol-gel and mechanochemical activation (MA) route respectively. The physical phase and pore structure of the synthesized powder materials were characterized by X-ray diffraction (XRD) and  $\text{N}_2$  adsorption-desorption. The results showed that the crystalline NZP family compound with mesoporous structure is formed by sol-gel route followed with calcination as well as MA method followed with hydrothermal treatment when the mole ratio of PEO to Zr is 1:10, and the specific surface area, average pore diameter and pore volume of the synthesized powder is  $20\text{-}50\text{m}^2/\text{g}$ ,  $3\text{-}6\text{nm}$  and  $0.05\text{-}0.12\text{cm}^3/\text{g}$  respectively. The above research results indicate that it is promising to expand the application field of the powder of NZP family from low thermal expansion ceramics to catalytic materials.

### Introduction

NZP is an abbreviation of sodium zirconium phosphate, and the NZP family means a type of materials with the same crystal structure but different chemical components. Since its appearance in 1960s, NZP family has been widely studied based on the following representative potential applications such as fast ion conductor, immobilized radioactive waste and thermal shock resistance ceramics because of its fast ion conductivity, crystal structure with rich ion substitution and ultra-low thermal expansion. However, another important potential application of NZP family compounds in catalysis is seldom reported. In fact, NZP family compounds may become a new type of catalysis materials due to its special crystal structure and flexible chemical composition, but the physical properties such as pore structure of NZP compound used as advanced ceramic powder is very different from that properties of catalyst materials which must have developed pore structure rather than dense materials with perfect crystalline-type. Therefore, investigation of preparation methods to obtain the porous NZP family compounds is the first step to explore its application from ceramic to catalysis material.

In this paper, the influences of synthesis methods as well as preparation conditions on the phase and pore structure of NZP family compounds is investigated. The phosphorus compounds belong to NZP family with different composition were synthesized by coprecipitation (CP), mechanochemical (MA) and sol-gel (SG) methods respectively followed with hydrothermal treatment or calcinations to obtain crystalline NZP compounds. Our goal is to prepare NZP family compounds with uniform mesoporous structure, and for this purpose, PEO was taken as template with reference to the preparation of mesoporous molecular sieves<sup>[1]</sup>.

## Experimental

### Starting materials

All chemical reagents used in the experiment are CP grade: 98% $(\text{NH}_4)_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ , 99% $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , PEO(average  $M_v$ 100,000), 99.8% $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ (citric acid),99% $\text{CaCO}_3$ , 25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 40% $\text{HF}$ , 99% $(\text{NH}_4)_2\text{HPO}_4$ .

The solution of  $\text{ZrO}(\text{NO}_3)_2$  was prepared according to the reference[2].

### Preparation of samples

**Coprecipitate (CP) method.**  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3(\text{NHZP})$  was prepared by coprecipitation method followed with hydrothermal treatment. The stoichiometric amount of  $\text{ZrO}(\text{NO}_3)_2$  solution containing PEO was dropwise added to the  $(\text{NH}_4)_2\text{HPO}_4$  solution under continuous stirring, the amorphous precursor was formed immediately in the mixed solution as precipitate. Then the precipitate was moved into teflon-lined bombs and kept at  $160^\circ\text{C}$  for 24h During hydrothermal treatment,  $\text{HF}$  was added into the suspension at the mole ratio of  $\text{HF}/\text{Zr} = 1:2$ . After filtrated and dried at  $120^\circ\text{C}$  and calcined for removing the template, the sample noted as CP-1 was synthesized.

**Mechanochemical(MA) method.**  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3(\text{NHZP})$  was prepared by MA method followed with hydrothermal treatment. The process is as follows: the stoichiometric amount of  $\text{ZrOCl}_2$  and  $(\text{NH}_4)_3\text{PO}_4$  was activated in the high power ball mill for 8h, and activated mixture was moved into distilled water for dispersion, and a suspension was formed. The suspension was loaded into teflon-lined bombs and kept at  $160^\circ\text{C}$  for 24h for crystallization. At last, the template was removed by calcinations. For sample MA-1, PEO powder was mixed with the starting materials and added in the mill to active. For MA-2, PEO solution was added into the suspension before hydrothermal treatment.

**Sol-gel (SG) method.**  $\text{CaZr}_4(\text{PO}_4)_6(\text{CZP})$  was synthesized by sol-gel method with addition of organic reagents. In the sol-gel process, 0.5M of  $\text{ZrO}(\text{NO}_3)_2$  solution dissolved  $\text{CaCO}_3$  was dropwise added into the mixture of PEO and 1M of  $(\text{NH}_4)_2\text{HPO}_4$  including citric acid, glycol and EDTA(ethylene diamine tetraacetic acid) under continuous stirring. The sol turned into gel precursor gradually when it was heated at  $80^\circ\text{C}$ , and then the gel was dried at  $60^\circ\text{C}$  for 15h. After removing the template, the gel precursor was calcined at  $700^\circ\text{C}$  to obtain the crystalline sample The representative sample prepared in this way was marked as SG-1.

In above three methods, the template PEO was removed according to the program: heating at  $150^\circ\text{C}$  for 2h, and raise the temperature to  $350^\circ\text{C}$  for 2h, and then calcination at  $500^\circ\text{C}$  for 6h.

### Characterization of samples

**XRD.** X-ray diffraction (XRD) of samples was performed on a Rigaku D/max2200 X-ray diffractometer with nickel-filtered  $\text{CuK}\alpha$  radiation operated at 30kV and 300mA. XRD patterns are recorded in the  $2\theta$  range from  $10^\circ$  to  $90^\circ$  at a scanning speed of  $10^\circ/\text{min}$ .

**$\text{N}_2$  adsorption-desorption.**  $\text{N}_2$  adsorption-desorption were determined on a USA Quantachrome company NOVA Win2 instrument at liquid  $\text{N}_2$  temperature. Specific surface areas of the samples were calculated from the adsorption isotherms by BET method, and pore size distribution was obtained from adsorption branches of the isotherms by BJH method.

## Results and discussion

### XRD

Fig.1 showed the XRD patterns of the samples synthesized by CP and MA methods as well as the standard patterns of  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  with different crystalline- type.

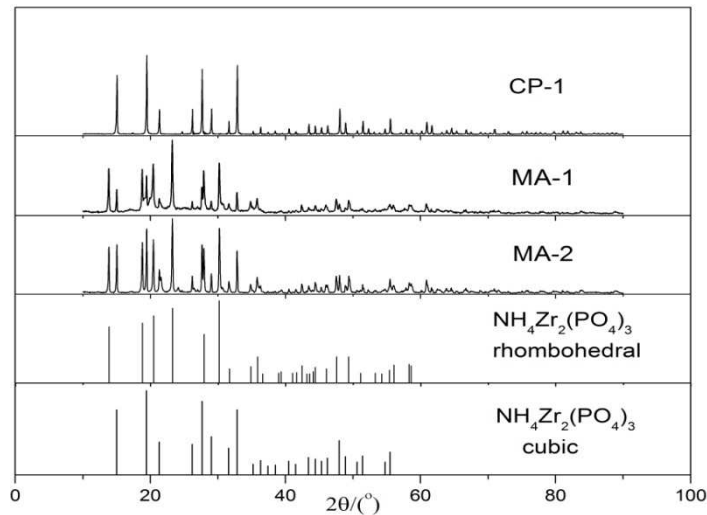


Fig.1. XRD patterns of samples synthesized by coprecipitate and MA methods and the standard pattern of the cubic and rhombohedral crystalline-type of  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$

It is well recognized that pure cubic crystal of  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  was formed in CP-1. Comparing with sample CP-1, two types of  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$  crystal---cubic and rhombohedral---were formed in MA samples. The result indicated that the addition of PEO as template did not affect the formation of  $\text{NH}_4\text{Zr}_2(\text{PO}_4)_3$ .

The XRD pattern of SG-1 is showed in Fig.2. It is easily recognized that the crystal compound of  $\text{CaZr}_4(\text{PO}_4)_6$  was formed in sol-gel route, and the organic reagents had no influence on the phase of CZP.

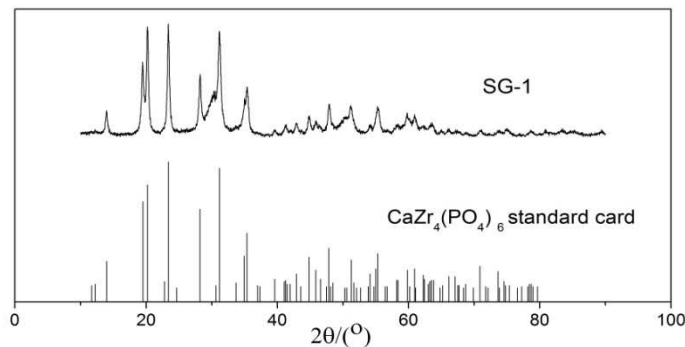


Fig.2. XRD pattern of SG-1 and the standard pattern of  $\text{CaZr}_4(\text{PO}_4)_6$

### $\text{N}_2$ adsorption and desorption isotherms

The  $\text{N}_2$  adsorption and desorption isotherms and pore size distributions of the NZP family phosphates powder prepared by the above three routes are shown in Fig3, and the pore structure data is summarized in Table1.

Table.1. Pore structure data of samples prepared by different methods

Sample	Specific surface area $/(\text{m}^2 \cdot \text{g}^{-1})$	Average pore size $/\text{nm}$	Pore volume $/(\text{cm}^3 \cdot \text{g}^{-1})$
CP-1	4.2	2.8	0.007
SG-1	51.2	6.2	0.118
MA-1	20.6	2.9	0.054
MA-2	5.4	3.2	0.013

As shows in Table.1, the specific surface area of CP-1 and MA-2 were only 4-5 $\text{m}^2/\text{g}$  which implied they are dense materials rather than porous materials, and the pore volume data proved the same thing. On the contrary, specific surface area of SG-1 and MA-1 reached 51.2 $\text{m}^2/\text{g}$  and

20.6m<sup>2</sup>/g respectively, and their pore volume was bigger than that of CP-1 and MA-2. The results indicated the porous materials with NZP structure can be prepared by sol-gel and mechanochemical method with PEO as template.

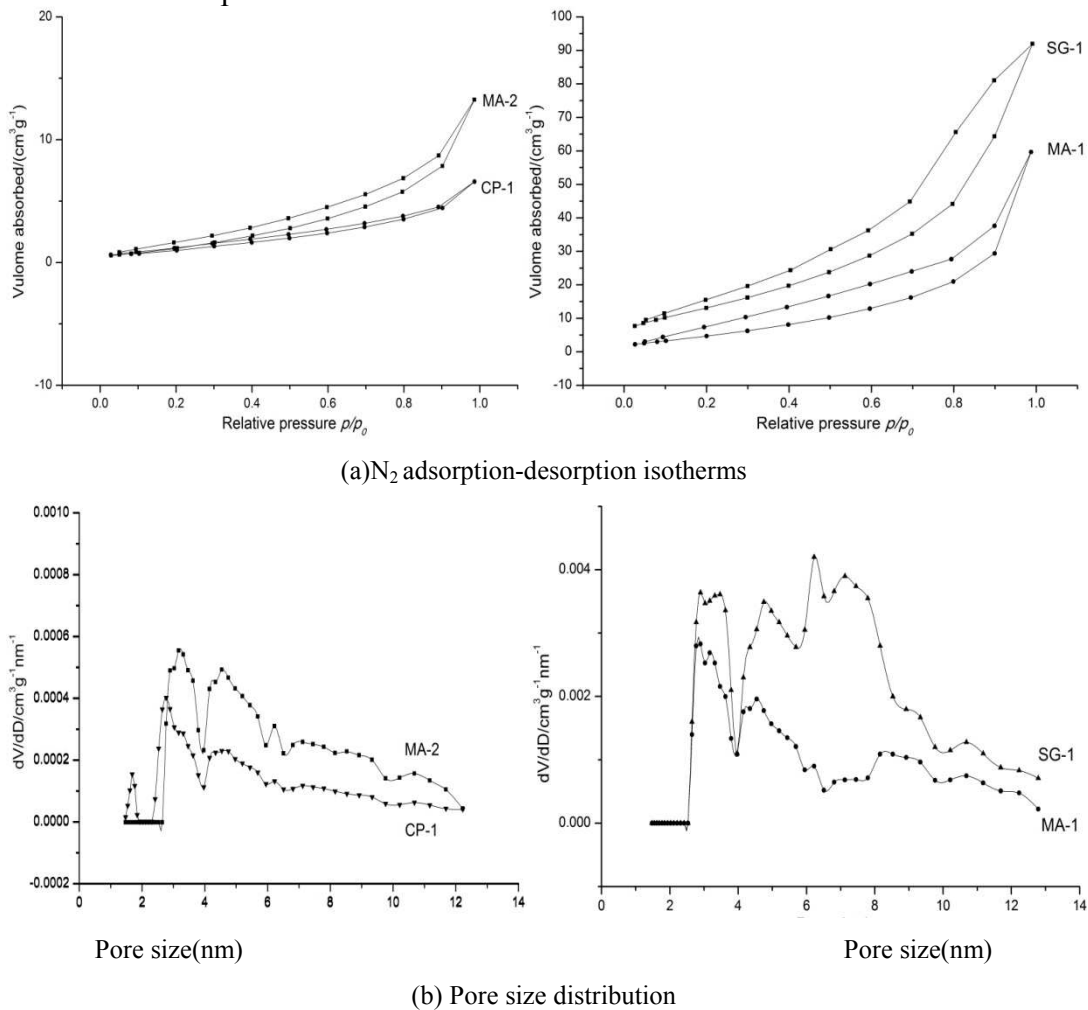


Fig.3. N<sub>2</sub> adsorption-desorption isotherms and pore size distribution of samples

The N<sub>2</sub> adsorption-desorption isotherm of SG-1 as shown in Fig.3a can be defined to Langmuir IV type<sup>[3]</sup>, which provides firm proofs for the existence of mesoporous structure in this sample. In the typical Langmuir IV isotherm, the abruption usually occurs at the relative pressure ratio  $P/P_0=0.2-0.4$ , and comparing with it, the abruption of the isotherm of SG-1 was at higher relative pressure ratio section ( $P/P_0>0.7$ ), which indicated the mesoporous size in this sample is bigger. Furthermore, this sample possesses the biggest specific surface area and pore volume. The reason that mesopore was formed in SG-1 is as follows: the interaction between the template and inorganic substance play an important role, therefore, to obtain a stable sol is a necessary condition for generation of the organic-inorganic mesoscopic phase, and mesopore was formed after removing the template .

International Union of Pure and Applied Chemistry (IUPAC) defined four different types of mesopore shape according to the adsorption-desorption hysteres loops in mesoporous materials<sup>[4]</sup>. The N<sub>2</sub> adsorption-desorption isotherm of SG-1 belongs to H3 type for bending at middle pressure ratio section ( $P/P_0=0.4\sim 0.6$ ) and rising steeply at high ratio section ( $P/P_0=0.7\sim 0.9$ ). The H3 type of hysteresis loop corresponds to heterogenetic pore shape, which means there are lots of pores of bigger size in SG-1. One of the reasons for existing different size pore in the sample is that the uniform mesoporous pore structure was destroyed under 700°C calcination and resulted in wide pore sizes distribution which was shown in Fig3b.

The N<sub>2</sub> absorption-desorption isotherm of sample MA-1 approach to Langmuir IV type which means MA-1 also belongs to mesoporous material. However, both the pore volume and pore size of MA-1 are smaller than that of SG-1. This attributes to the poor uniform in the solid reaction.

There is nearly no hysteresis loop in the N<sub>2</sub> absorption-desorption isotherm of sample CP-1 which implies CP-1 is dense material instead of porous material, and this is in consist with the smallest specific surface area and pore volume.

The differences between MA-1 and MA-2 were the timing when PEO was added in. For preparation of MA-1, PEO was added into the high power ball mill together with ZrOCl<sub>2</sub> and (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, in which PEO could mix with the precursor of NHZP more uniformly. In MA-2, PEO was added in after the precursor of NHZP was formed, its uniformity surely was not as good as MA-1.

## Conclusion

(1) The crystalline compounds belong to NZP family can be synthesized by coprecipitate, sol-gel and mechanochemical activation methods respectively.

(2) The mesoporous structure in NZP family phosphate NH<sub>4</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> obtained from MA and CaZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> prepared by SG can be formed by using PEO as template, and PEO is more efficient in sol-gel route according to the mole ratio of PEO:Zr = 1:10. The specific surface area, average pore diameter and pore volume of CaZr<sub>4</sub>(PO<sub>4</sub>)<sub>6</sub> and NH<sub>4</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> can reach 51.2m<sup>2</sup>/g and 20.6 m<sup>2</sup>/g, 6.2nm and 2.9nm as well as 0.118cm<sup>3</sup>/g and 0.054 cm<sup>3</sup>/g respectively.

(3) In MA method, the timing when PEO was added in is a key factor to form mesoporous structure. Mesoporous NH<sub>4</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> was formed when PEO was milled together with ZrOCl<sub>2</sub> and (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>, at the same time only dense NH<sub>4</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> could be obtained if PEO was added in hydrothermal treatment.

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## References

- [1] V.A.Sadykov, S.N.Pavlova et al. Scientific Based for the Synthesis of Highly Dispersed Framework Zirconium Phosphate Catalysts for Paraffin Isomerization and Selective Oxidation, *J. Kinetics and Catalysis*, 3(2001) 390-398
- [2] Li Yanping, Zhu Linhua. Hydrothermal synthesis of NH<sub>4</sub>Zr<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> belonging to NZP family, *J. Journal of Chinese Ceramic Society*, 10(2009) 1640-1644
- [3] Kruk M, Jaroniec M. Gas adsorption characterization of ordered organic-inorganic nanocomposite materials, *J. Chem Mater*, 13(2001) 3169–3183
- [4] Sing K S W, Everrtt D H, Haul R A W, et al. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity, *J. Pure Appl Chem*, 57(1985) 603–619