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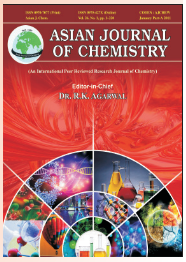

Preparation and Characterization of Silica Pillared α-Type Zirconium Phosphate†

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Silica pillared α-type zirconium phosphate (C-SiO_2-ZrP) was prepared *via* the sol-gel method. The results from X-ray diffraction, transmission electron microscopy and nitrogen adsorption-desorption suggested that the interlayer distance of C-SiO_2-ZrP was increased remarkably when compared to zirconium phosphate; C-SiO_2-ZrP had a mesoporous lamellar structure with high specific surface area and mesoporous volume.

Keywords: Silica, Pillared α-zirconium phosphate, Sol-gel.

INTRODUCTION

It is well known that the layered compounds such as montmorillonite clays pillared with inorganic oxides such as SiO_2, Al_2O_3 and TiO_2 have been studied intensively from both academic and industries fields due to their potential applications as sorbents, catalysts and catalyst supports[1,2]. Among those pillared clay materials, the silica pillared clay did not show the metal catalytic activity, but it provided the better conditions required by carriers including higher thermal stability and high specific surface area. The α-type zirconium phosphate (α-ZrP) is another kind of multi-functional layered powder materials, whose layers are formed by zirconium atoms which are connected by the oxygen atoms of phosphate groups, which gives rise to practical application since it possesses ion exchange properties, shape-selective adsorption and catalysis properties. Recently, pillared zirconium phosphates have been developed and shown application prospects in the field of photocatalysis and environmental protection[3,4]. It is therefore necessary to investigate the pillared zirconium phosphate with higher specific surface area and porous volume. In the paper, silica pillared α-ZrP was prepared *via* the sol-gel method. Characterization of the porous structure of the material was elucidated with X-ray diffraction, transmission electron microscopy and nitrogen adsorption-desorption.

EXPERIMENTAL

α-Type zirconium phosphate was synthesized by refluxing zirconyl chloride ($ZrOCl_2 \cdot 8H_2O$) in 10 mol/L H_3PO_4 for 24 h at 95 ºC. Silica pillared α-ZrP samples were synthesized by an acid-catalyzed sol-gel process. A α-ZrP exfoliated colloidal dispersion was firstly prepared by dripping ethylamine into a α-ZrP water suspension with ultrasonic agitation. A solution of tetraethoxysilane (TEOS) in ethanol was then added drop wise into the colloidal dispersion with stirring; the mixture was adjusted to pH = 3 using 1 mol/L HCl aqueous solution and stirred for 3 h at 50 ºC. A gel was obtained by increasing the pH by adding ammonia solution. The gel was kept for 24 h aging at room temperature then dried in an over at 80 ºC for 24 h, followed by heat treatment at 500 ºC for 6 h. The obtained powder is referred to as C-SiO_2-ZrP.

RESULTS AND DISCUSSION

Fig. 1 shows the XRD patterns of α-ZrP and C-SiO_2-ZrP powders. α-ZrP shows the 002 diffraction peak at $2\theta = 11.7$ degree with a basal interlayer spacing of 0.76 nm (Fig. 1A). As seen in Fig. 1(B), the d_{002} peak of C-SiO_2-ZrP shifts toward a lower angle with an increase of the spacing to 8.5 nm compared to α-ZrP, suggesting the pillaring of silica inside the gallery spaces of α-ZrP.

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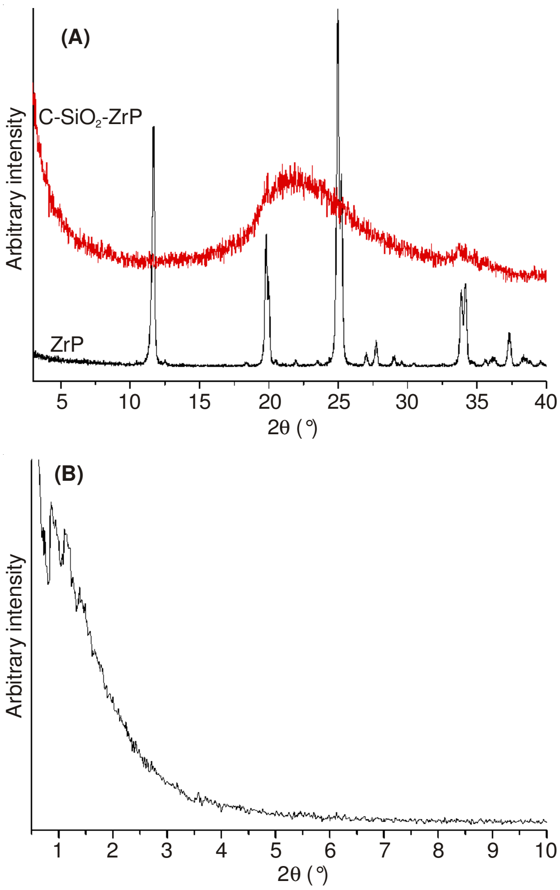

Fig. 1. XRD patterns of (A) a-ZrP and C-SiO_2-ZrP powders and (B) C-SiO_2-ZrP powder at low 2θ range

Fig. 2 gives the TEM images of C-SiO_2-ZrP powder. It can be seen that α-ZrP shows a typical lamellar microstructure by the stacking of phosphate nanolayers; the dark points denote the nanoscale silica particles, while the white layered areas signify the zirconium phosphate matrix. Clearly, silica particles are dispersed inside the interlayers of zirconium phosphate, which lead to the interlayer distance of C-SiO_2-ZrP is increased noticeably.

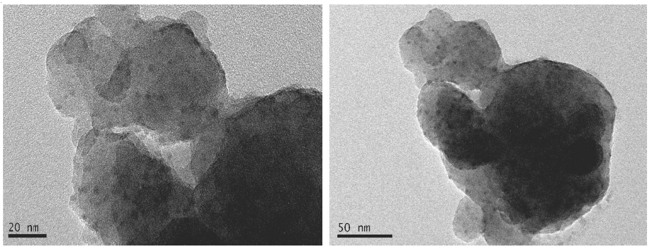

Fig. 2. TEM images of C-SiO_2-ZrP powder at different magnifications

Nitrogen adsorption-desorption measurements were performed at liquid nitrogen temperature (-196 ºC) on a surface area and porosity analyzer, Tristar II 3020M. Prior to measurements, the sample was degassed in vacuum at 300 ºC for 3 h. The nitrogen adsorption-desorption isotherm linear is shown in Fig. 3(A). The isotherm of the powder exhibits type IV hysteresis loops according to IUPAC classification. The branch of desorption shows an inflection knee at relative pressure P/P_0 = 0.4-0.5, which is characterized as mesoporous materials and suggests the existence of slit-shaped pores. After pillaring, specific surface area (S_{BET}) and mesoporous volume (V_{meso}) of C-SiO_2-ZrP sample are obviously increased to 423.6 m^2/g and 0.36 cm^3/g. Fig. 3(B) shows the pore size distribution of C-SiO_2-ZrP powder and its average pore diameter is 3.67 nm.

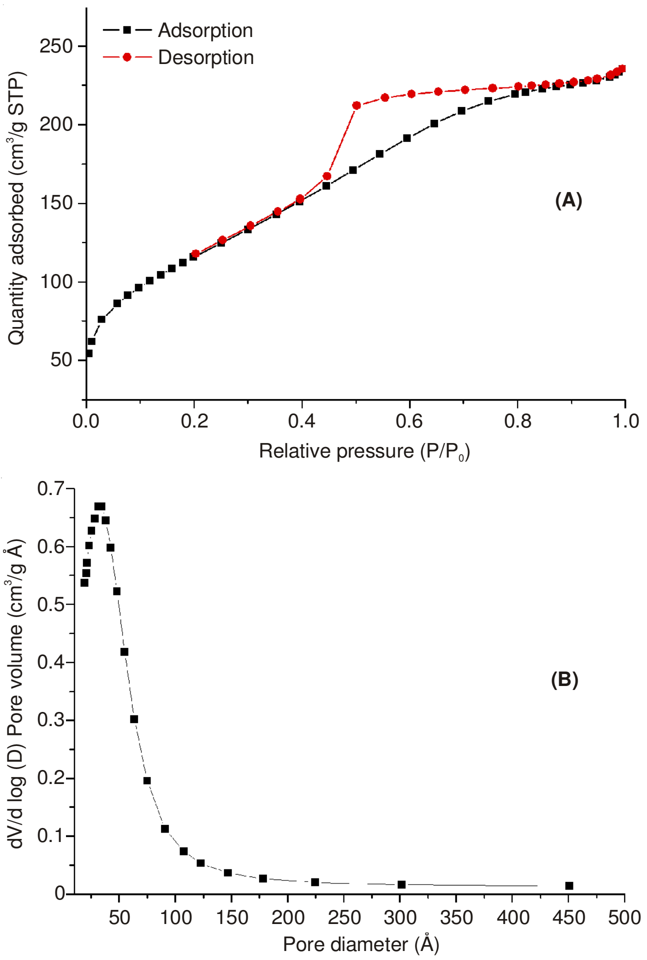

Fig. 3. Nitrogen adsorption-desorption isotherm linear plots (A) and pore size distribution (B) for C-SiO_2-ZrP powder

Conclusion

Silica pillared α-ZrP material with mesoporous lamellar structure was successfully obtained through sol-gel method. The pillaring of silica imparts the material with high specific surface area and mesoporous volume. The material holds high promising application prospects in the field of catalysis and adsorption.

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