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Microporous and Mesoporous Materials 84 (2005) 297–301
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

Controlled delamination and intercalation of layered microporous aluminophosphate by a novel two-step method

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Received 28 April 2005; received in revised form 4 May 2005; accepted 5 May 2005
Available online 12 July 2005

Abstract

Pure phase benzylamine and aniline intercalates of layered microporous aluminophosphate $[Al_3P_4O_{16}][CH_3(CH_2)_3NH_3]_3$ were obtained for the first time by a novel two-step method, including a delamination step in alkaline medium and an intercalation step in acidic medium. The pH value and the dielectric constant of the solution used in these two steps were decisive for the success of preparation of the new intercalates. XRD and various other techniques were employed for the characterization of the intercalate products and the elucidation of the working principle of the novel method.

Keywords: Layered microporous aluminophosphate; Two-step method; Delamination; Aromatic amine intercalation

1. Introduction

Numerous microporous aluminophosphates with non-unity Al/P ratios have been synthesized using solvothermal method [1,2]. The structures of these materials are diversified, including 1-D chain, 2-D layer and 3-D open framework structures. Their frameworks are negatively charged, and the charges are compensated by protonated organic ammonium cations located between the chains and sheets or in the channels. The stoichiometries of the framework anions are of $AlP_2O_8^{3-}$, $Al_2P_3O_{12}^{3-}$, $Al_3P_4O_{16}^{3-}$, $Al_3P_5O_{20}^{6-}$, $Al_4P_5O_{20}^{3-}$, $Al_5P_6O_{24}^{3-}$ and etc. Among them 2-D layered aluminophosphates are of particular interest because of their potential application in separation, catalysis or as functional materials [3].

Delamination and intercalation of these layered compounds are critical for the preparation of high surface area catalysts, thermally stable pillared materials and self-consistent films [3]. However, they are more difficult to bring about than those of ordinary layered metal phosphates due to the instability of the microporous sheets and their strong interaction with the protonated organic ammonium cations. Delamination and intercalation of layered aluminophosphates with $[Al_3P_4O_{16}]^{3-}$ and $[Al_2P_3O_{12}]^{3-}$ stoichiometries by C_2–C_{12} alkyl amines by a one-pot method were reported in our previous works [4–6]. Controlling the dielectric constant of the solution and the concentration of the alkylamine in the medium is decisive for gaining success. Saturated C_2–C_8 alkylamine intercalates of these aluminophosphates are obtained in solutions with dielectric constant of 50–70 and an amine concentration of 10 mmol/g.

Aromatic intercalates are more easily to be functionalized, e.g., various functional groups, such as sulfonic and nitro-group, can be readily substituted on the benzene ring. To extend the application of microporous

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1387-1811/$ - see front matter © 2005 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2005.05.008

aluminophosphates, the intercalation of the layered structures with aromatic amines has been attempted [7]. A saturated benzylamine (pK_a of 9.34) intercalate of aluminophosphate with $[Al_3P_4O_{16}]^{3-}$ stoichiometry has been obtained using the one-pot method under appropriate conditions. However, for aniline with lower basicity (pK_a of 4.60) the intercalation is unsuccessful under similar conditions, indicating that the basicity of amine may affect the delamination and intercalation processes besides the dielectric constant of the solution and the concentration of the amine.

In this paper, a novel two-step method for delamination and intercalation of layered aluminophosphate $[Al_3P_4O_{16}][CH_3(CH_2)_3NH_3]_3$ (abbreviated as AlP) is reported. In this method the delamination and intercalation processes proceed separately and sequentially under different controlled conditions, so that the dielectric constant and the pH value of the medium in these two steps can be varied to suit a wider variety of intercalating agents and to guarantee the success of exfoliation and reassembly of the aluminophosphate in the experiment.

2. Experimental

2.1. Sample preparation

AlP was prepared according to the procedures in the literature [8]. Al(iPrO$_3$)$_3$ (1.0 g) and phosphoric acid (0.63 ml) were added to butyl alcohol (7.86 ml). The mixture was stirred until homogeneous, and then butylamine (2.47 ml) was added under stirring. The gel was transferred to an autoclave and heated at 180 °C under autogenerous pressure for 10 d. The product was filtered, washed and dried in air.

For delamination, 200 mg of AlP and 20 ml of the buffer solution were placed in a closed bottle, stirred continuously for about 8 h, centrifuged and then dried in air. The delaminated aluminophosphate (~200 mg) and a calculated amount of benzylamine or aniline were added into 20 ml of ethanol/water mixture. Phosphoric acid or sulfuric acid was then added to adjust the pH value of the solution. The mixture was stirred for 1 d, and the final product was obtained by centrifugation.

2.2. Characterization

X-ray powder diffraction (XRD) patterns of the samples were recorded on a Rigaku D/MAX-IIA diffractometer with CuKα radiation at 30 kV and 20 mA and a Ni filter. Scanning electron microscopic (SEM) images were obtained on a Philips XL-30 scanning electron microscope. UV–vis spectra of the samples were recorded on a Shimadzu UV-2450 UV–visible spectrometer equipped with an integrating sphere attachment.

3. Results

3.1. Delamination of AlP

The XRD pattern of the as-synthesized AlP is shown in Fig. 1a. The (0 0 1) peak at 9.20° corresponds to an interlayer spacing of 0.96 nm, which is consistent with the single-crystal X-ray diffraction data in the literature [8]. The delamination of AlP was carried out in solutions with different ethanol/water ratios at pH of 10, and the observations of the systems by XRD were summarized in Fig. 1 and Table 1. AlP delaminates completely in pure water within 1 h, forming a clear colloidal solution. As the ethanol/water ratio is increased, the exfoliation of AlP becomes more difficult and the colloidization process is retarded. In the solution with ethanol/water ratio of 3:1, the layered structure of AlP remains intact after 10 h. This result is consistent with our previous

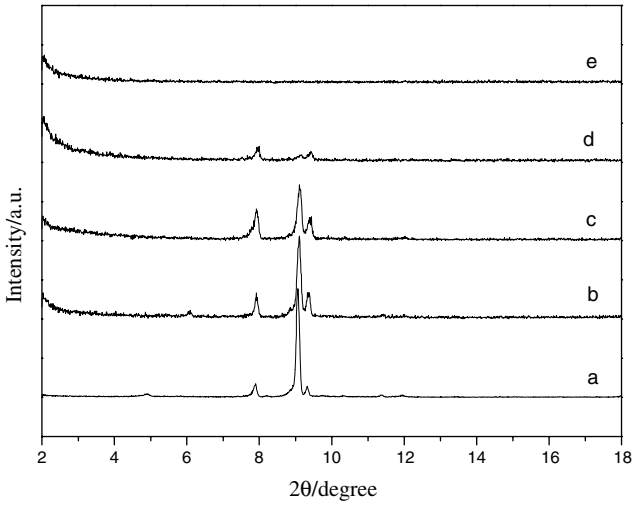

Fig. 1. XRD patterns of (a) original AlP and AlP delaminated in solutions with ethanol/water ratio of (b) 3:1; (c) 1:1; (d) 1:3; (e) 0 after an hour.

Table 1
Time for complete delamination of AlP in the different solutions

Ethanol/water ratio	3:1	1:1	1:3	0	0	0	0
Dielectric constant [9]	39.40	54.75	68.35	80.37	80.37	80.37	80.37
pH value	10	10	10	10	9	8	7
Time for complete delamination (h)	–	6	3	1	2	6	–