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Abstract

NaNKX-2 aluminophosphate crystals were synthesized for the first time in the Al2O3–P2O5–Na2O–H2O system without any organic additive. The NaNKX-2 crystals were obtained under autogeneous condition within 4 h, which was considerably fast and convenient. The study revealed that the use of basic synthesis condition and H3PO3 as the phosphorus source were the crucial factors in obtaining NaNKX-2 crystals. The NaNKX-2 crystals, which exhibited novel grain-like morphology, had a P:Al:Na ratio of 4:3:1.7. The potential of NaNKX-2 as a catalyst in basic-catalyzed cyanoethylation of methanol was also demonstrated.

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1. Introduction

Aluminophosphate (AlPO-n) material is a class of microporous materials which are widely used in adsorption, separation and catalysis [1–3]. Traditionally, they are synthesized under hydrothermal and solvothermal conditions [4,5]. Simple and safe method for obtaining aluminophosphate molecular sieves is also achieved by using ionic liquid-mediated synthesis [6]. In most cases, phosphoric acid (H3PO4) is used as the phosphorus source where organic templates are added to direct the formation of desired framework.

H3PO3 is a diprotic acid (pKa1 = 1.80, pKa2 = 6.15). Unlike H3PO4, it exists as a tautomer with P(OH)3 where the phosphorus ion exists as P(III) state [7]. As a result, it behaves differently from H3PO4 during the chemical reaction process. Recently, a new synthesis route of aluminophosphate materials based on phosphorous acid (H3PO3) as phosphorus source has been proposed [8]. In the synthesis process, NKX-2, an aluminophosphate, is formed. NKX-2 is an important intermediate for the synthesis of useful microporous aluminophosphates (SAPO-46, AIPO-47, AIPO-41, SAPO-31, AIPO-11, AIPO-5 and AIPO-CJ2) [8,9]. However, NKX-2 aluminophosphate so far could only be synthesized in the presence of amines or ionic liquids [8,10]. Furthermore, aluminophosphate and aluminophosphate materials with basicity are very rare considering their nearly neutral charge framework with no extra-framework cations [8,10].

In the present work, basic NaNKX-2 aluminophosphate was obtained for the first time using a facile organotemplate-free route where H3PO3 and NaOH were used as a phosphorous source and an inorganic base, respectively.

2. Experimental

2.1. Synthesis

The synthesis was carried out in a 50 mL Teflon-lined stainless steel autoclave. Typically, a clear solution was obtained by mixing H3PO3 (0.421 g, 85%, Sigma-Aldrich), aluminum isopropoxide (0.416 g, 98%, Sigma-Aldrich) and distilled water (0.0743 g). NaOH solution (0.416 g, 5 M, Merck) was then slowly added into the mixture to form a cloudy solution with a molar composition of 1Al2O3:3P2O5:4Na2O:100H2O. The mixture was autoclaved and heated at 180 °C for crystallization. The autoclave was cooled
down and the solid product was centrifuged (8000 rpm, 10 min) and washed before drying at 80 °C overnight.

2.2. Characterization

The XRD patterns of solids were obtained using a Bruker-AXS D8 diffractometer. The morphology of samples was studied by a FESEM (Leo Supra 50VP) microscope with an accelerating voltage of 20 kV. The chemical composition of sample was obtained by a Philips PW2404 XRF instrument. FTIR spectrum of NaNKX-2 was recorded using a Perkin Elmer spectrometer (System 2000).

2.3. Catalytic study

NaNKX-2 solid (0.20 g, 100 °C, 3 h), ethanol (76 mmol, 99%, Merck) and acrylonitrile (19 mmol, 99%, Merck) were mixed and reacted in a 15 mL Teflon lined autoclave at 150 °C under magnetically stirring (400 rpm). The reaction solution was withdrawn and analyzed using a GC (Hewlett-Packard 5880) and GC-MS (Perkin-Elmer GC-IR 2000 system).

3. Results and discussion

The XRD patterns of solid products after heating for 1, 2, 4 and 8 h are shown (Fig. 1). The data revealed that the solid was amorphous after 1 h of heating. As shown, the initial amorphous particles (ca. 80 nm) had irregular shapes (Fig. 2a). At 2 h, some XRD peaks started to appear at 2θ = 13.01°, 25.90°, 29.10°, 34.01° and 34.81° indicating the formation of NKX-2 crystalline phase (Fig. 1b) [10]. At this stage, the amorphous particles tended to agglomerate to form bulk solid in micrometer scale (Fig. 2b). Also, NKX-2 crystals (ca. 6.4 x 2.8 μm²) with a novel wheat grain-like morphology were detected. With increasing time to 4 h, the amorphous particles were fully transformed into discrete NKX-2 crystals with homogeneous crystallite size (Figs. 1c, 2c, Supplementary Information: S1). Further increasing crystallization time to 8 h, however, led to co-crystallization of aluminum metaphosphate, Al₂P₆O₁₈. (JCPDS 13-266) (Fig. 1d). This observation was supported by SEM data where the solids of spheric morphology were formed on the intergrown NKX-2 crystals (arrows shown in Fig. 2d).

NKX-2 aluminophosphate is usually hydrothermally synthesized in the presence of organic templates. The crystallization of NKX-2 usually takes 2–5 days at 180 °C [8]. The crystallization rate, however, can be enhanced by using ionothermal route (180 °C, 3 h) or by adding Fe³⁺ salt (180 °C, 20 min) [7,10]. The resulting crystals adapt cubic-, stick- or rounded rectangle-like shapes depending on the organic template used. Interestingly, in our work, NaNKX-2 crystals synthesized in sodium-containing system also experienced fast crystallization rate and different morphology of crystals was obtained (Figs. 1c, 2c). Such observation could be explained by the use of NaOH as a strong inorganic base and template instead of using amines. Furthermore, an attempt to use H₃PO₄ instead of H₃PO₃ for the synthesis of NaNKX-2 was also made for the same gel composition and crystallization conditions but without success. Thus, it indicated that the use of H₃PO₄ as phosphorus source was the key factor for the selective formation of NKX-2 phase under basic condition.

FTIR spectroscopy characterization of NaNKX-2 was performed to reveal their functional groups (Fig. 3). The bands at 3459 and 1654 cm⁻¹ were due to the O–H bonds from water [11]. The bands at 2480 and 1036 cm⁻¹ were attributed to the P–H stretching and deformation modes of HPO₄²⁻, respectively [10]. The signals at 1215 and 1141 cm⁻¹ corresponded to T–O (T=Al, P) asymmetric stretching mode. The band at 1187 cm⁻¹ is associated with the octahedrally coordinated aluminum [12]. Furthermore, four characteristic bands of NKX-2 framework (596, 558, 515, and 449 cm⁻¹), which were attributed to the T–O–T vibrations, were also shown [7]. Interestingly, the presence of external Na⁺O⁻ vibrations was also detected based on an additional weak shoulder band at 283 cm⁻¹ [13]. All the IR spectroscopy results further confirmed the synthesis of NaNKX-2 crystalline phase.

The NaNKX-2 crystals had a P:Al:Na ratio of 4:3:1.7 as revealed by XRF analysis. As computed, the P/Al ratio of NaNKX-2 (1.33) was slightly lower than that of NKX-2 (1.50) which was due to the high amount of Al needed for charge compensation of Na⁺ cations. Thus, the results indicated that NaNKX-2 crystals have negative charge framework compensated by Na⁺ basic cations. In order to verify this, their basic catalytic properties were evaluated in cyanooethylation reaction of methanol under autogeneous condition. As known, cyanooethylation is a mild-basic catalyzed reaction for the syntheses of drug intermediates and fine chemicals (alkoxypropionitriles, propanolamines and propionic acids). No conversion was achieved when NKX-2 (1Al₂O₃:1.6P₂O₅:3.5TEA:95H₂O, conversion of 58.1% with 3-ethoxy-propionitrile as the only product) was used as the catalyst under similar reaction condition.

In summary, NaNKX-2 aluminophosphite with unique morphology and moderate basicity has been successfully synthesized free of organotemplate. Fast crystallization rate is also achieved by using NaOH as inorganic base and template. From an environmental perspective, this synthesis is extremely beneficial as no harmful organotemplate is used and facile synthesis approach is adopted. The NaNKX-2 aluminophosphite can also be a potential mild base catalyst besides its potential intermediate in zeolite synthesis. Furthermore, this approach also makes synthesis of many useful aluminophosphate/aluminophosphite microporous materials free of organotemplate feasible.

![Fig. 1. XRD patterns of solid products after (a) 1 h, (b) 2 h, (c) 4 h and (d) 8 h. * indicates the presence of aluminum metaphosphate (JCPDS 13-266).](image-url)
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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2016.07.013.

References