Ionothermal synthesis of AlPO₄-34 molecular sieves using heterocyclic aromatic amine as the structure directing agent

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Abstract

AlPO₄-34 was synthesized ionothermally in 1-butyl-3-methyl imidazolium bromide using heterocyclic aromatic amine as the structure directing agent (SDA). The as-synthesized products were characterized through X-ray diffraction (XRD), scanning electron microscopy (SEM), nuclear magnetic resonance spectroscopy (NMR) and thermal gravimetric (TG) analysis. The factors affecting the crystallization were investigated. The results show that methyl-substituted heterocyclic aromatic amines can effectively direct to form AlPO₄-34 and reside in the channel solely. Meanwhile, the ionic liquid need not be consumed, it merely acts as a solvent. Hydrofluoric acid plays a crucial role in the synthesis process as a mineralizer. The morphology and crystallinity of the product can be controlled by the dosage of the SDA and the crystallization temperature. The synthesized product shows a good thermal stability, and maintains a very good crystalline structure after calcination at 550 °C in air.

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1. Introduction

AlPO₄-34 (IZA code CHA) is one of the most important molecular sieves of the aluminophosphate family.1 Its derivatives exhibit high activity and selectivity for ethylene and propylene in the methanol to olefins process due to the small pore size and moderate acid strength.2 Therefore the study on the synthesis of this topology is of great significance. In general, molecular sieves are synthesized by the hydrothermal method, often in sealed autoclaves under an autogenous pressure. By carefully optimizing the synthetic conditions the CHA topology could be made hydrothermally in the presence of several organic templates.3,4 As a novel method, ionothermal synthesis uses an ionic liquid as both the solvent and the template,5 which enables the synthesis of molecular sieves at an ambient pressure. This eliminates the safety concerns associated with the autogenous pressure of a traditional solvent.6 On the other hand, this synthetic method shows a good application prospect for both the material synthesis and mechanism studies.7–9 CHA topology has been synthesized in the imidazolium-based ionothermal system.5,10 In these cases, 1,3-dimethyl imidazolium was needed to act as the SDA.10 So not only a long crystallization time was necessary for the generation of the SDA through a transalkylation reaction, but also the solvent of the ionothermal system was consumed during the crystallization process.

In our former work, the organic amine was introduced into the ionothermal system to act as a cooperative SDA, which expands the application of this method for preparing molecular sieves by an additional synthetic variable.11–13 In the current work, AlPO₄-34 was synthesized ionothermally in 1-butyl-3-methyl imidazolium bromide using the introduced heterocyclic aromatic amines as the SDA directly. The reaction conditions affecting the crystallization were investigated.

2. Experimental

2.1. Ionothermal synthesis

1-Butyl-3-methyl imidazolium bromide ([BMIm]Br), was prepared by the neutralization of redistilled N-methyl imidazole (99.9%, Kaile Chemical Factory, Zhejiang China) and butyl bromide (AR, Sinopharm Chemical Reagent Co., Ltd.) according to the procedure reported in Ref.14. The reagents used for synthesizing molecular sieves were all commercially supplied. The synthesis experiments were carried out in an open beaker charged with 30 g [BMIm]Br ionic liquid. Then the following materials were added under vigorous stirring: H₃PO₄ (85 wt.% in water, AR), Al[OCH(CH₃)₂]₃ (AR), hydrofluoric acid (40 wt.% in water, AR) and various heterocyclic aromatic amines. Then the beaker was moved into an oil bath at a certain temperature for crystallization. The crystal product was washed thoroughly with distilled water and acetone, respectively, then dried at 110 °C for characterization. The organic template was removed by calcination at 550 °C under dynamic air. The following heterocyclic aromatic amines were used as additives: N-methyl imidazole, 2-methyl imidazole and 4-methyl pyridine.

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2.2. Characterizations

Powder X-ray diffraction analysis of the as-synthesized samples was performed on a PANalytical X′Pert PRO diffractometer fitted with Cu Kα radiation (λ = 1.5418 Å) operating at 40 mA and 40 kV. The thermal behavior was investigated with a Perkin Elmer Pyris 1 TGA instrument, using dynamic dry air, with a flow rate of 20 ml min⁻¹. The selected heating rate was 20 °C min⁻¹ and the temperature range was 30 to 850 °C. ¹³C CP/MAS NMR measurements were performed on a Varian Infinity plus-400 spectrometer. Scanning electron microscopy (SEM) was carried out on a Hitachi S4800 field-emission scanning electron microscope.

3. Results and discussion

3.1. Crystallization condition

The detailed crystallization conditions, heterocyclic aromatic amines and the reactant ratios for synthesizing CHA aluminophosphate molecular sieves in the [BMIm]Br system are listed in Table 1.

As can be seen from Table 1, by adding the above three aromatic amines, including N-methyl imidazole, 2-methyl imidazole and 4-methyl pyridine, the molecular sieve of the CHA topology can be obtained in the system. AlPO₄-11 (IZA code AEL) formed in the same conditions with no organic amines introduced. [12] This indicates that the introduction of heterocyclic aromatic amines changed the structure directing effect in the system, resulting in the pure product of the CHA topology. Moreover, the hydrofluoric acid plays a vital role as a mineralizer in promoting the framework crystallization. Fluorine-free or a small amount of fluorine (B-2 and B-3) can only lead to amorphous products.

In addition, the crystallinity of the CHA product is closely related to the dosage of the organic amine added. A larger dosage of organic amine will reduce the crystallinity. In fact, a larger dosage of organic amine makes an increase in nucleation and a decrease in the crystal growth because more phosphoric acid was neutralized in the system. For example, the crystallinity of product D-2 and D-1 is lower than that of product D-3 (see Fig. 1).

3.2. Structure directing effect

¹³C CP/MAS NMR spectroscopy of CHA sample was performed to investigate the organic guest in the channel, so as to study the structure directing effect of the ionic liquid and the added aromatic amine. As can be seen in Fig. 3, peaks at 135.3 ppm and 125.1 ppm are attributed to the carbon atoms on the imidazole rings, the carbon atom between the two nitrogen atoms and two adjacent carbon atoms (N-C-C-N, overlapped). As for the peak at 37.6 ppm, it is assigned to the substituted –CH₃ on the imidazole ring. These three peaks are related to four carbon atoms, whereas the cation of the ionic liquid, [BMIm]⁺ has a total of eight carbon atoms. Actually the intensity between 75 and 100 ppm could be attributed to the spinning sidebands due to magnetic field inhomogeneity. Therefore, it can be obviously confirmed that the organic compound in the CHA samples is N-methylimidazole from the number and the shift position of the peaks. Therefore, the introduced methyl-substituted heterocyclic aromatic amine act as the structure directing agent directly in the synthesis of the CHA topology. It is worth mentioning that the ionic liquid, the solvent of this system, is not consumed at all. After a simple distillation, it is feasible to recycle the ionic liquid for the synthesis of the next batch.
3.3. Thermal stability

Thermal gravimetric analysis performed on the molecular sieves can give thermal stability as well as the information of water and organic template in the pores. The TG results of the as-synthesized CHA solid (sample D-2) in a dynamic air atmosphere is shown in Fig. 4. There is a total weight loss of 23.61% till the sample was heated to 850 °C including two distinct stages. One is 2.54% before 200 °C with a regular peak in the DTG curve, attributing to the removal of physically adsorbed water in the molecular sieve. The other is 21.07% of the weight loss after 200 °C, the DTG curve in this stage shows two adjacent broad peaks, which can be attributed to the protonated N-methylimidazole balancing the negative charge of the framework as pore fillers.

The sample after calcinations at 550 °C was characterized by XRD (Fig. 4 inlet). The X-ray powder diffraction pattern of the calcined sample is quite different from that of the as-synthesized material due to the removal of moisture and the organic template, but its crystal
framework is still kept very well after calcination. Such change in the
diffraction peaks had also been reported. [15,16] This indicates that
water and organic matters in the small pores of the CHA interact
strongly with the frameworks.

4. Conclusions

A convenient and green method for the ionothermal synthesis
of AlPO$_4$-34 was proposed, using methyl-substituted heterocyclic
aromatic amines to act as the SDA solely. The solvent of this system,
1-butyl-3-methylimidazolium bromide ionic liquid, is not consumed at
all. The morphology and crystallinity of the product can be controlled by
the dosage of the SDA and the ionothermal crystallization temperature.

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