Microporous and Mesoporous Materials 183 (2014) 108–116

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

The dependence of the structure-directing effect of piperazine and the crystallization pathways of open-framework aluminophosphates on the local environment of the initial mixture

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ARTICLE INFO

Article history:
Received 10 July 2013
Received in revised form 27 August 2013
Accepted 2 September 2013
Available online 10 September 2013

Keywords:
Zeolite
Aluminophosphate
Templating effect
Structure-directing effect
Piperazine

ABSTRACT

In the synthetic system of Al_2O_3–x P_2O_5–6.4 piperazine–227 H_2O, three open-framework aluminophosphates (2D AlPO-CJ9, 3D AlPO-JU88, and 2D AP2pip) were obtained by varying the Al_2O_3/P_2O_5 ratio. The crystallization processes of AlPO-CJ9, AlPO-JU88, and AP2pip were investigated using solid state NMR in combination with XRD and other characterization techniques. The results showed that a small change in the Al_2O_3/P_2O_5 ratio can significantly affect the type and distribution of the small fragments formed during the crystallization process. The structure-directing effect of piperazine was influenced and modified by the Al_2O_3/P_2O_5 ratio. For compounds crystallized from the same synthetic system but separate synthetic batches, i.e., AlPO-CJ9, AlPO-JU88, and AP2pip, we found differences in the crystallization pathways of the small fragments, the types and distributions of the small fragments, the evolutions of the concentrations of Al and P and the pH values of the liquid phases. These differences were studied by comparing the crystallization processes of AlPO-CJ9, AlPO-JU88, and AP2pip from different synthetic batches and showed that the structural details of the same compounds obtained from different synthetic batches were different. Therefore, the topological structure-directing effect is more appropriate than the structure-directing effect in describing the role that the added agents played in the crystallization of open-framework materials. The structure-directing effect of the added agents and the crystallization pathways of the open-framework materials are dependent on the local environment, i.e., the types and distributions of the small fragments, the relative ratio of the species.

1. Introduction

Zeolites, a class of microporous crystalline aluminosilicate materials, have attracted considerable interest due to their wide applications in catalysis, ion exchange, separation, and adsorption [1–6]. In 1982, Wilson and co-workers reported a new class of microporous crystalline aluminophosphates, $AlPO_4$-n (n denotes a structure type), with neutral zeolite-like open-frameworks, a high degree of structural diversity, and a wide range of pore sizes and volumes [7,8]. Aluminophosphates have become a large family of crystalline open-framework materials, which display rich variety of structures, including neutral zeolite-like open-frameworks; a range of anionic open-frameworks with 0D cluster, 1D chain, 2D layer, and 3D framework structures; and a rich variety of stoichiometries [9–13]. Although numerous structures with open-frameworks have been successfully synthesized using methods based on empirical findings or by exploring synthetic parameters through trial and error [14,15], the rational design and synthesis of additional open-framework structures with desired architectures and properties is important. Rational design requires a clear understanding of the crystallization mechanism involved. Over the past decades, significant effort has been made in studies on the crystallization mechanism of aluminophosphates and other microporous materials using *ex situ* or *in situ* characterization techniques or new strategies [16–39]. However, the understanding of the crystallization mechanism of open-framework structures is still very limited due to the intrinsic complexity of the synthetic system and the limited resolution and sensitivity of current characterization techniques.

The synthesis of crystalline open-framework materials usually involves mixing inorganic ion sources, solvent, and an organic species, which is commonly called the “template” or “structure-directing agent”, and heating the resulting mixture in an autoclave at elevated temperature for a time ranging from a few hours to

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1387-1811/$ - see front matter © 2013 Elsevier Inc. All rights reserved.
http://dx.doi.org/10.1016/j.micromeso.2013.09.004

weeks. However, the successful formation of a crystalline open-framework structure is condition dependent (condition refers to synthetic parameters, including the nature and the relative ratios of the source materials in the initial mixture, the heating temperature, and the heating time). Among the synthetic parameters, the template or structure-directing agent is the most important factor. For any specific synthesis that can ordinarily crystallize an open-framework, the absence of the template or structure-directing agent will result in either an amorphous product or a dense phase. However, the method by which the structure-directing agent works during the synthetic process is still not clear. The knowledge of the nature of the structure-directing effect is still very limited. To investigate the nature of or to achieve a better understanding of the structure-directing effect, an effective strategy is to fix the type of the template or the structure-directing agent and change one single factor in the synthesis. By analyzing the resulting products and by monitoring the crystallization process of these products, we may generate an increased understanding of the structure-directing effect.

In this study, we selected the synthetic system of Al_2O_3–P_2O_5–piperazine–H_2O, and the ratios of Al_2O_3/piperazine and Al_2O_3/H_2O were fixed. The only variable was the Al_2O_3/P_2O_5 ratio. By varying the Al_2O_3/P_2O_5 ratio, we obtained three open-framework aluminophosphates, i.e., AlPO-CJ9 [40], AlPO-JU88 [41], and AP2pip [42]. The crystallization processes of these aluminophosphates were investigated. The results obtained in this study clearly show that the structure-directing effect of piperazine is condition dependent. The Al_2O_3/P_2O_5 ratio significantly affects the structure-directing effect of piperazine. The findings in this work suggest that the crystallization mechanism of open-framework materials consist of a “reaction mechanism” and a “crystallization pathway”, which are both condition dependent. To understand the crystallization mechanism of a specific open-framework material, we need to determine the reaction type between the source materials, the type and distribution of the species formed in the very early stage of synthesis, and the assembly pathway of these species to form the final structure.

2. Experimental sections

2.1. Synthesis

Boehmite (Catapal B, 72.7% Al_2O_3, Sasol) and phosphoric acid (85 wt% H_3PO_4) were used as aluminum and phosphorus sources, respectively. Piperazine hexahydrate ($C_4H_{10}N_2{\cdot}6H_2O$, denoted pip hereafter) was used as the structure-directing agent. A typical procedure for the preparation of a reaction mixture for AlPO-CJ9 (AlPO-JU88 and AP2pip) was conducted as follows: 11.04 g (12.42 g for AlPO-JU88 and 34.16 g for AP2pip) of 85% phosphoric acid was stirred with 120 g (90 g for AlPO-JU88 and 135 g for AP2pip) of water, and 3.36 g (2.52 g for AlPO-JU88 and 3.78 g for AP2pip) of boehmite was added. The mixture was thoroughly stirred for 1 h, and then, 29.18 g (21.88 g for AlPO-JU88 and 32.83 g for AP2pip) of piperazine hexahydrate was added with continuous stirring. The gel was further stirred for 1 h at ambient temperature to ensure homogeneity. While stirring, the same amount (15 mL) of the reaction mixture, with a molar ratio of Al_2O_3:2.0 P_2O_5 (3.0 for AlPO-JU88 and 5.5 for AP2pip):6.4 pip:227 H_2O, was loaded into each of several Teflon-lined autoclaves (volume: 45 mL). The autoclaves were then placed in a pre-heated oven at 180 °C. The heating records were started when all of the autoclaves were quickly loaded into the oven. The autoclaves were heated for different times and then were quenched in cold water. The pH of the liquid phase in each autoclave was measured. The resulting liquid and solid phases were separated by centrifugation (9500 rpm or 8475 g), and the solid phase was dried under vacuum at ambient temperature without any further washing in water. To obtain a pure and highly crystalline sample for NMR analysis, one sample, which crystallized over three days, was washed with water several times and is marked as “final” in the NMR spectra. The dried samples were sealed for later characterization.

2.2. Characterization

All NMR experiments were performed on a Varian Infinity-plus 400 spectrometer operating at a magnetic field strength of 9.4 T. The resonance frequencies in this field strength were 161.9 and 104.2 MHz for ^{31}P and ^{27}Al, respectively. A chemagnetics 5-mm triple-resonance MAS probe with a spinning rate of 8 kHz was employed to acquire ^{31}P and ^{27}Al NMR spectra. The ^{27}Al MAS spectra were acquired using a single pulse sequence with a short radio frequency (rf) pulse of 0.5 μs (corresponding to a $\pi/15$ flip angle) and a pulse delay of 1.0 s. The pulse length for ^{27}Al was measured using a 1 M $Al(NO_3)_3$ solution. Single-pulse ^{31}P MAS NMR experiments with ^1H decoupling were performed with a 90° pulse width of 4.6 μs, a 180 s recycle delay, and a ^1H decoupling strength of 42 kHz. The chemical shifts were referenced to a 85% H_3PO_4 solution for ^{31}P and a 1 M $Al(NO_3)_3$ solution for ^{27}Al. Powder XRD patterns were recorded on a Rigaku diffractometer equipped with a graphite monochromator using Cu Kα radiation ($\lambda = 1.5418$ Å). The pH values of the liquid phases were measured with a Sartorius PB-10 pH meter. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was performed on a Perkin-Elmer Optima 3300Dv spectrometer.

3. Results and discussion

During the preparation of the initial mixture, the ratios of Al_2O_3:pip and Al_2O_3:H_2O were fixed at 1:6.4 and 1: 227, respectively. The crystallization temperature was 180 °C. The only variable was the P_2O_5/Al_2O_3 ratio, which was varied from 1.0 to 8.0. The pH values of the initial mixtures with the various P_2O_5/Al_2O_3 ratios and the corresponding products, which crystallized for 3 days at 180 °C, are listed in Table 1. When the ratios of P_2O_5 to Al_2O_3 were 1.0 and 2.0, a layered aluminophosphate AlPO-CJ9 was obtained [40]. The pH values of the initial mixture were 10.2 and 7.98, respectively. Increasing this ratio to 3.0 and then further to 4.0 resulted in the formation of a pure 3D anionic aluminophosphate AlPO-JU88 [41]. The pH values of the initial mixtures reached 7.45 and 6.18, respectively. With a further increase of this ratio to 5.0, layered anionic aluminophosphate AP2pip appeared in addition to AlPO-JU88. The pH of the initial mixture was 4.78. When this ratio was increased to 5.5 and 6.0, the pH values of the initial mixture were decreased to 4.7 and 4.61, respectively, and pure AP2pip was obtained [42]. The pH of the initial mixture was in the range of 4.26–3.31 when this ratio fell in the range of 7.0–8.0. In addition to a 3D anionic aluminophosphate AlPO-CJ11/AlPO-CJB2 [43,44], an unidentified phase was obtained as well. Therefore, we only investigated the crystallization processes of AlPO-CJ9, AlPO-JU88, and AP2pip. The compositions of the initial

Table 1
The pH values of the initial mixtures with various P_2O_5/Al_2O_3 ratios and the corresponding products crystallized at 180 °C for 3 days*.

P_2O_5/Al_2O_3	1.0	2.0	3.0	4.0	5.0	5.5	6.0	7.0	8.0
pH	10.2	7.98	7.45	6.18	4.78	4.7	4.61	4.26	3.31
Products	□	□	♦	♦	♦ ○	○	○	▲ ●	▲ ●

[*] □: AlPO-CJ9; ♦: AlPO-JU88; ○: AP2pip; ●: AlPO-CJB2; ▲: unidentified phase.