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Molecular engineering of microporous crystals: (V) Investigation of the structure-directing ability of piperazine in forming two layered aluminophosphates

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ABSTRACT

The crystallization process of the layered aluminophosphates AP2pip and AlPO-CJ9 from initial mixtures with compositions of Al_2O_3:P_2O_3:1.1 piperazine:277 H_2O and Al_2O_3:P_2O_3:4.0 piperazine:277 H_2O, respectively, was investigated using multiple techniques. During the crystallization of AP2pip, the formation and dissolution of highly polymerized but structurally disordered fragments containing four-coordinated P sites to Al-centered polyhedra were observed. $^{27}Al \rightarrow ^{31}P$ CP/MAS HETCOR NMR analysis showed that the local P-site environment in the small building fragments formed in the initial mixture is same as that in the final crystal structure of AP2pip. The concentration of these small building fragments is very low. During the crystallization of AlPO-CJ9, the formation of small building fragments with the local P-site environment same or very similar to that observed in the final structure of AlPO-CJ9 were observed. The concentration of these small building fragments is high. These small fragments contained at least two complete coordination layers. The difference in the structure-directing role played by piperazine in the two synthesis systems was investigated in detail by designing several control experiments and analyzing the arrangements of the piperazine molecules in the interlayer region of AP2pip and AlPO-CJ9.

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1. Introduction

Zeolites and related microporous crystalline materials, which have periodic three-dimensional frameworks and well-defined pore structures, have attracted much interest due to their wide applications in catalysis, ion exchange, separation, and adsorption [1–7]. Besides mining, hydro/solvothermal synthesis is one alternative way to obtain this type of material. The introduction of organic species into the synthetic system and the extension of the composition from aluminosilicate to aluminophosphate significantly increase the structural diversity of such microporous crystalline materials and related open-framework materials [8–15].

The synthesis of microporous crystalline materials usually involves the mixing of inorganic ion sources, solvent, and, generally, an organic species, which is usually 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 weeks. The process variables (i.e., synthesis parameters) include the nature and the relative ratios of the chemicals used as source materials in the starting mixture, which are usually called the recipe of a batch synthesis, the heating temperature, and the heating time. During the formation of a specific structure, it has been proposed that organic molecules organize the oxide tetrahedral units into a particular geometric topology around themselves and thus provides the initial building blocks for the crystallization of a particular type of structure type, which has led to the concept of “template” of organic species. The organic species are encapsulated in the framework, stabilizing the system through non-bonding interactions [16].

During the synthesis of microporous crystalline materials, it has been found that some structures can only be synthesized within a very narrow crystallization field. However, some structures are not sensitive to changes in synthesis parameters and can be synthesized over a very broad crystallization field. Among the synthesis parameters, the “template” or “structure-directing agent” is the most important. The organic additive plays an important role in directing the formation of a specific structure during the synthesis of microporous crystalline materials [1]. Certain structures will not form in the absence of a specific organic additive. The template or structure-directing effect, particularly during the synthesis of microporous or open-framework aluminophosphates, has been attributed to the steric and electronic effects of these organic

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additives [1,17,18]. The charge distribution, size, and geometric shape of organic species are believed to be sources of these species' structure-directing ability. In previous studies, the templating or structure-directing ability of an organic additive with respect to a certain structure was measured and evaluated according to the non-bonding interactions established between the final inorganic host and the organic guest [19–25]. Compared to any given experimentally observed structure-directing agent, if a new organic species has a similar or lower interaction energy with an inorganic host, it is believed that this organic species will have a high possibility of directing the same structure. However, attempts to verify this hypothesis have achieved very limited success [26–28]. The reasons for this limited success include: (1) the chemical nature of the template or structure-directing agent is only one of the many important synthesis parameters that can determine the final structure and the presence of a specific structure-directing agent is sometimes necessary but not sufficient for the formation of a specific structure; (2) the calculated non-bonding interactions between the final inorganic host and the organic guest may not reflect the interaction between the organic species and the small inorganic species formed at the beginning of crystallization; and (3) compared to the first experimentally reported structure-directing agent, recently discovered structure-directing agents sometimes exhibit much lower or higher non-bonding interactions with inorganic hosts, suggesting that some important issues have been missed in calculating non-bonding interactions.

The experimental observations of "one-template/multiple-structure" and "multiple-templates/one-structure" frameworks have made the explanation of the template effect or structure-directing role of organic species by calculation of their non-bonding interactions with the final structure less convincing. To explain these phenomena, it was proposed that during the synthesis, both gel chemistry and organic species may play important roles in the formation of a specific structure but that templating becomes operative only within the environment of the right "gel chemistry" [16]. However, the exact definition of gel chemistry, what the right gel chemistry is, how organic additives affect the gel chemistry, and how the structure-directing role of an organic additive functions in the right gel chemistry are still not clear. Thus, the exact role of structure-directing agents is still far from being properly understood.

The difficulty in studying the structure-directing role of organic additives arises from the complexity of hydro/solvothermal crystallization, the lack of structural information regarding the species formed at different synthesis stages, and the lack of a complete understanding of the driving force for the formation of crystalline porous materials [7]. Therefore, enhanced efforts and new ideas are required to better understand the role of organic additives during the synthesis of microporous crystalline materials [29–45].

In this study, changes in the structure-directing ability of piperazine in directing two-layered aluminophosphates (AP2pip and AlPO-CJ9) was investigated to further elucidate the role of the organic template and its influence on the gel chemistry.

2. Experimental section

2.1. Synthesis of AP2pip and AlPO-CJ9

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 AP2pip (AlPO-CJ9) was conducted as follows: 12.42 g of 85% phosphoric acid was stirred with 270 g of water, and 7.56 g of boehmite was added. The mixture was stirred well for 1 h, and then 11.286 (41.04 for AlPO-CJ9) g of Piperazine hexahydrate was added with continuous stirring. The gel was further stirred for 1 h at ambient temperature to ensure homogeneity. The same pre-calculated amount (15 mL of mixture) of the reaction mixture with a molar ratio of Al_2O_3:P_2O_3:1.1 (4.0 for AlPO-CJ9) pip:277 H_2O was loaded into several Teflon-lined autoclaves (volume: 45 mL) using a 25-mL pipette while stirring. The autoclaves were then placed in a pre-heated oven at 180 °C. The recorded heating started when all of the autoclaves were loaded into the oven. The autoclaves were heated for different periods of time and quenched in cold water. The pH of the liquid phase was measured. The liquid and solid phases of the product were separated by centrifugation (9500 rpm or 8475 g), and the solid phase was dried under vacuum at ambient temperature without washing further with water. However, to obtain a pure and highly crystallized sample for NMR analysis, one product crystallized for 3 days was washed with water several times and was 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 ^{1}H decoupling were performed with a 90° pulse width of 4.6 μs, a 180 s recycle delay, and a ^{1}H 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.

A three-pulse *z*-filtered pulse sequence was used for the ^{27}Al 3Q MAS NMR experiments [46]. A 2.5 mm MAS probe with a spinning rate of 26 kHz was used. The rf field strengths of the first two hard pulses and the third soft pulse were set to approximately 100 and 10 kHz (calibrated with $Al(NO_3)_3$ solution), respectively. Forty-eight scans were accumulated, and the recycle delay was set to 18 s in the 3Q MAS experiment. The hypercomplex method was used for 2D data acquisition and processing.

The rotational echo adiabatic passage double resonance (REAPDOR) technique was used to measure the correlation between the spin-1/2 and spin->1/2 nuclei [47]. For the $^{31}P\{^{27}Al\}$ REAPDOR experiment, the π pulse length was 12 μs for ^{31}P and an adiabatic *rf* pulse with a length of Tr/3 (Tr: duration of one rotor period) was applied for ^{27}Al in the middle of the pulse sequence.

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 3300 DV spectrometer.

3. Results and discussion

Layered aluminophosphate AP2pip originally crystallized from a mixture of pseudoboehmite (Catapal B, Vista, 74 wt.% Al_2O_3), orthophosphoric acid (85 wt.% solution), piperazine hexahydrate, and water at 150 °C for 24 h [48]. The composition of the mixture was Al_2O_3:2.0 P_2O_5:2.0 pip:40 H_2O. The empirical formula of AP2pip is $[Al_3P_4O_{16}]_3 \cdot [C_4N_2H_{12}]_{4.5} \cdot 5H_2O$; the piperazine molecules

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