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Molecular engineering of microporous crystals: (IV) Crystallization process of microporous aluminophosphate $AlPO_4$-11

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ABSTRACT

The products of microporous aluminophosphate $AlPO_4$-11 crystallized for different periods of time were freeze-dried and characterized by XRD and NMR techniques. Six crystallographically distinct Al- and P-centered large fragments and 34 small fragments of dimer (Al–P), trimer (Al–P–Al and P–Al–P), tetramer (Al–P_3 and P–Al_3), pentamer (Al–P_4 and P–Al_4), and 4- and 6-membered rings were extracted from the framework of $AlPO_4$-11. Each of the six large fragments contained two completed coordination layers surrounding the centered atom. The shielding tensors of the Al and P atoms of the fragments were calculated using the quantum mechanics density functional theory. The experimentally observed chemical shifts of Al or P from the well-crystallized $AlPO_4$-11 were assigned to the shielding tensors of the center atoms of the six large fragments and were further used as references in the determination of the chemical shifts of the Al or P atoms in the small fragments. A comparison of the calculated chemical shifts of the Al and P atoms in the small fragments to the experimental data of the products isolated at different crystallization periods suggested that the fragments of dimers, trimers of the form Al–P–Al, tetramers of the form P–Al_3, and pentamers may exist in the crystallization process of $AlPO_4$-11. On the basis of these observations regarding the putative small fragments, a possible crystallization process of $AlPO_4$-11 was proposed.

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 [1–6]. Although numerous zeolitic structures have been successfully synthesized by using methods based on empirical findings or by exploring synthetic parameters through trial and error [7], it is of importance to rationally design and synthesize additional zeolitic structures with desired architectures and properties. This rational design requires a clear understanding of the reaction mechanism and crystallization process involved in zeolite synthesis. The previous study of the crystallization process is based on the crystal nucleation and growth theory [8–10]. This theory dictates that the formation of a crystalline entity from a solution starts through a nucleation process, and the increase in size is achieved by a growth process. Nucleation is usually defined as a series of atomic or molecular processes by which the atoms or molecules rearrange into a cluster of the product phase that is large enough to have the ability to grow irreversibly to a macroscopically larger size. The cluster is called a nucleus or critical nuclei. The crystal growth is a series of processes by which an atom, a molecule, or a fragment is incorporated into the surface of a nucleus, causing an increase in size. However, the structure of the nucleus has never been clearly described thus far, and the nuclei have never been separated during the synthesis of zeolites and related microporous crystalline materials.

The two main mechanisms appeared in the study of the reaction mechanism and crystallization process are the following: the solution-mediated transport mechanism and the solid hydrogel transformation mechanism [11–13]. The solution-mediated transport mechanism states that the crystallization process involves the dissolution of the hydrogel followed by the transport of the small fragments to the nucleation sites where the crystal growth takes place. However, the solid hydrogel transformation mechanism claims that the crystallization process involves the reorganization of the solid phase from an initially amorphous state to one with

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long-range ordering. In 2005, Cundy et al. summarized the previous studies on the reaction mechanism and crystallization process of zeolites in a comprehensive review [14]. In that review, the authors pointed out that the arguments about whether key events occur in the solid phase or in solution are sterile and unnecessary. At the end of the survey, Cundy et al. proposed a generalized mechanism for zeolite synthesis, which is based primarily on the solution-mediated transport mechanism.

In addition to the arguments on the solution- or solid-related reaction mechanisms, the studies of the reaction mechanism also focused on the investigation of the early stage of the crystallization process [15–38]. For example, Burkett et al. studied a D_2O-containing synthesis gel that produced pure-silica ZSM-5 with an NMR technique and found that the close contact between the protons of tetrapropylammonium (TPA) ions of the organic structure-directing agent and the silicon atoms of the inorganic moiety had been established before the long-range order of the crystalline pure silica ZSM-5 structure is formed [15,16]. Later, by combining the *in situ* wide-angle, small-angle, and ultra-small-angle X-ray scattering techniques, de Moor et al. studied the crystallization process of pure silica ZSM-5 templated by tetrapropylammonium ions [17]. On the basis of the collected data, de Moor et al. concluded that the key primary building unit composed of TPA and silicate is approximately 2.8 nm in size. The primary building units aggregated together to form entities up to 10 nm in size. These entities were called nuclei, which initiated the growth of pure silica ZSM-5. However, the exact structure of the primary building units and the larger entities was not described. A similar idea has also been developed by Martens and co-workers at Leuven [18–22]. By using a wide variety of experimental techniques, Martens and co-workers studied in detail the crystallization process of pure silica ZSM-5 templated by tetrapropylammonium ions. They identified slab-shaped particles (denoted as "nanoslabs") with dimensions of $1.3 \times 4.0 \times 4.0$ nm. The nanoslabs have the ZSM-5 structure with nine intersections per particle. Each of these intersections contains a TPA cation. The aggregation of such nanoslabs results in larger particles and, ultimately, in the crystalline product. However, there is no detailed information about how these nanoslabs formed, and this observation is questioned as well [23–25]. In contrast to the above studies, which were conducted under hydrothermal conditions, Tsapatsis and co-workers studied the crystallization process of pure silica ZSM-5 templated by tetrapropylammonium hydroxide (TPAOH) at room temperature [26–28]. They monitored the evolution of nanoparticles that formed spontaneously upon the hydrolysis of tetraethylorthosilicate in aqueous solutions of TPAOH at room temperature for more than one year up to and beyond pure silica ZSM-5 crystal formation. On the basis of their data, Tsapatsis and co-workers proposed that the crystalline pure silica ZSM-5 evolved from approximately 5-nm precursor nanoparticles through oriented attachment and that the nanoparticles actively participate in the nucleation and crystallization processes. However, the key step, i.e., the establishment of long-range order in the precursor nanoparticles, was not illustrated. Therefore, the detailed and exact structural information for the species formed in the early stage of the crystallization process is critical to understanding the reaction mechanism and crystallization process.

Recently, we developed a strategy for investigating the crystallization processes of microporous crystalline compounds and a method based on mathematical matrix and graph theories to describe the open framework of microporous crystals and the fragments that may be formed in the early stages of the crystallization process [39,40]. When the crystallization process starts, the complicated condensation reaction between Al and P sources under the conditions at the time will occur, forming the hydrogel with specific chemical composition and structure and the liquid phase located in the void of the hydrogel. Small fragments (species) of aluminophosphate with specific structure and configuration can be found in the liquid phase. Along with the crystallization process, the small fragments are assembled around the structure-directing agent. With our strategy, exact structural information for each species that formed during the period of crystallization or for a core unit from which a single crystal was grown could be obtained. The solid phase isolated at different crystallization periods can be characterized by various techniques. By comparing the simulated characterization information of these species with the experimental characterization data, it is possible to identify the fragments formed during the crystallization process. On the basis of these observations regarding the putative small fragments, we can further investigate and discuss the specific details of a possible crystallization process.

In this study, we investigated the crystallization process of $AlPO_4$-11. A method was developed to distinguish the possible and unlikely fragments formed in the crystallization process. The present study represents a step forward in understanding the crystallization of microporous aluminophosphates at the molecular level.

2. Experimental section

2.1. Synthesis

A typical procedure for the preparation of a reaction mixture is as follows: 1.94 mL of 85% phosphoric acid was stirred with 2.0 g of water, and 2.0 g of boehmite was added. The mixture was stirred well for approximately 10 min, and then 2.45 mL of di-(*i*-propyl)amine (D-iPA) was added dropwise with continuous stirring. The gel was further stirred for approximately 20 min at ambient temperature to ensure homogeneity. The reaction mixture with a molar ratio of Al_2O_3:P_2O_5:1.2 D-iPA:15 H_2O was loaded into a Teflon-lined autoclave (volume: 20 mL). The autoclaves containing approximately equal amounts of the reaction mixture were then placed in an oven pre-heated to 180 °C. The timing 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 product from each autoclave was divided into two parts. One-half of the product was freeze-dried (−60 °C), which ensured the complete collection of all small species formed during the crystallization process. The liquid and solid phase of the other half of the product was separated by centrifugation (9500 rpm or 8475g), and the solid phase to be used as a reference was dried at room temperature. The dried samples were sealed well for later characterization.

The powder XRD patterns were recorded on a Rigaku diffractometer equipped with a graphite monochromator using Cu Kα radiation (λ = 1.5418 Å) at 50 kV and 200 mA. The scanning angle (2θ, where θ is the Bragg angle) used ranged from 4° to 40° in steps of 0.02°, and the sampling interval was 0.1 s. TG analysis with a heating rate of 10 °C/min was performed in air using a TGA Q500 analyzer from TA Instruments in high-resolution mode.

2.2. NMR 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 at 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 s (corresponding to a $\pi/15$ flip angle) and a pulse delay of 1.0 s. The pulse length for ^{27}Al was