Microporous and Mesoporous Materials 147 (2012) 212–221

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Molecular engineering of microporous crystals: (III) The influence of water content on the crystallization of microporous aluminophosphate $AlPO_4$-11

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ARTICLE INFO

Article history:
Received 14 May 2011
Received in revised form 12 June 2011
Accepted 20 June 2011
Available online 28 June 2011

Keywords:
Aluminophosphate
$AlPO_4$-11
AEL
Crystallization
Zeolite

ABSTRACT

The influence of water content on the crystallization of the microporous aluminophosphate $AlPO_4$-11 was investigated by a combination of *in situ* UV Raman and *ex situ* XRD and NMR characterizations. Under high water content conditions (Al_2O_3:H_2O = 1:20–69), an $AlPO_4$-5 intermediated formed first and later co-existed with $AlPO_4$-11. In the last stage of crystallization, the crystalline $AlPO_4$-5 completely disappeared and well-crystallized $AlPO_4$-11 was obtained. The position of the three signals observed in the ^{31}P MAS NMR spectra of the isolated solid samples did not change during the hydrothermal treatment, suggesting that the fragments containing the P site in the junction of 6- and 4-membered rings of both $AlPO_4$-5 and $AlPO_4$-11 formed first and that the environments of the P sites were very similar to those in the final structure. A significant increase of Al concentration in liquid media was observed before the appearance of XRD detectable $AlPO_4$-11. Under low water content conditions (Al_2O_3:H_2O = 1:15), the $AlPO_4$-11 was directly crystallized from the initial mixture. *In situ* Raman spectra showed that the 10-membered rings were complete by the time the transformation of octahedral Al to tetrahedral Al was finished and that the conformation of the protonated di-(*i*-propyl)amine changed little during the crystallization. The present study showed that the composition of the liquid phase is critical to the formation of a specific structure.

1. Introduction

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 [1–5]. The structure of $AlPO_4$-*n* is built of alternating AlO_4 and PO_4 tetrahedra linked via oxygen atoms. $AlPO_4$-11 is one of these new microporous crystalline aluminophosphates. The structure of the calcined form of $AlPO_4$-11 has been solved by Rietveld refinement of neutron time-of-flight data [6]. The open framework of $AlPO_4$-11 comprises a one-dimensional channel system of elliptical 10-membered rings with a free diameter of approximately 6.7 × 4.4 Å and three distinct tetrahedral crystallographic sites for phosphorus and aluminum in a population ratio of 2:2:1. Because the 10-membered-ring pore opening is similar in size to many industrially important organic molecules, the literature contains several reports of the synthesis and characterization of this important molecular sieve [7–13].

In view of the important applications of the $AlPO_4$-11 and other aluminophosphate molecular sieves, a basic understanding of the crystallization mechanism at a molecular level coupled with the enormous body of existing empirical knowledge is absolutely necessary, which may lead to a more rational approach to the design and synthesis of aluminophosphate molecular sieves with new properties and architectures. Recently, the crystallization process of aluminophosphate molecular sieves of $AlPO_4$-5, $AlPO_4$-18, and $AlPO_4$-11 were studied by monitoring the crystallization process with *in situ* or *ex situ* characterization techniques [14–20]. Using an *in situ* UV Raman characterization technique, Fan et al. detected a chain-like intermediate composed of 4-membered rings for the channel formation during the crystallization of $AlPO_4$-5 and suggested a chain-to-open-framework transformation process [14]. Xu et al. have combined multinuclear solid-state NMR, powder X-ray diffraction (XRD), and infrared (IR) analyses to study the crystallization process of $AlPO_4$-5 in the presence of fluoride [15]. They found that, at the beginning of the reaction, the amorphous aluminophosphate species that formed immediately after the reactants and the template molecules were mixed did not interact, or

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doi:10.1016/j.micromeso.2011.06.018

interacted only weakly, with the initial gel-like solid, which could therefore be easily washed away from the solid. The evolution of the ^{13}C MAS NMR spectra of the solid separated from the hydrothermally treated mixture after different reaction periods suggested that the organic template existed primarily in the liquid phase of the initial mixture. The organic molecules were gradually occluded in the solid phase with reaction time, which indicated that the formation of $AlPO_4$-5 occurred in the liquid media and the insoluble $AlPO_4$-5 nanocrystals were embedded in or attached to the solid matrix during the separation process.

Huang and co-workers have reported extensive studies on the crystallization process of microporous aluminophosphates of $AlPO_4$-18, $AlPO_4$-5, and $AlPO_4$-11 formed from normal hydrothermal or dry-gel syntheses [16–19,21]. In the initial mixture for the crystallization of $AlPO_4$-18, the existence of an aluminophosphate species containing Al–O–P links, phosphate species, and the unreacted aluminum source of pseudo-boehmite was confirmed by $^{27}Al \rightarrow ^{31}P$ cross-polarization (CP) NMR experiments [16]. Continuous heating of the initial mixture resulted in the formation of a crystalline intermediate of $AlPO_4$-5. At the end of the crystallization stage, the intermediate of $AlPO_4$-5 completely disappeared and well-crystallized $AlPO_4$-18 formed [16].

Huang and co-workers have also reported studies on the crystallization process of $AlPO_4$-11 under normal hydrothermal and dry-gel conditions [17,18,21]. Under normal hydrothermal conditions, the initial mixture with a composition of $1.0Al_2O_3$:$1.0P_2O_5$:1.0*n*-Pr_2NH:$40H_2O$ was heated at elevated temperature for different time periods [17]. The liquid and solid phases were separated by centrifugation, which could lead to the loss of highly soluble species and extremely small fragments or particles of the product. Their results clearly show that a significant amount of amorphous aluminophosphate species were formed after the aluminum and phosphorus sources were mixed with a structure-directing agent at ambient temperature. Both tetrahedral and octahedral Al atoms were present in the amorphous aluminophosphate and both were connected to P atoms. The structure-directing agent neither incorporated tightly into nor interacted strongly with the amorphous aluminophosphate; these results have been confirmed in a recent study [15]. Under the dry-gel conditions, the composition of the autoclaved mixture was calculated as $1.0Al_2O_3$:$1.0P_2O_5$:1.0*n*-Pr_2NH:$10H_2O$ by taking into account the 15 wt.% water in the dry-gel and the 0.3 mL of pre-added distilled water per gram of dry-gel [18]. The crystallization process was followed by characterization of the samples that had been heated for different periods. Prior to the heat treatment at the crystallization temperature, the initial mixture with the composition of $1.0Al_2O_3$:$1.0P_2O_5$:1.0*n*-Pr_2NH:$40H_2O$ was heated at 80 °C to prepare the dry-gel. In the XRD patterns of as-prepared and dry-gel samples heated at the crystallization temperature for less than 8 h, Huang and co-workers observed a number of intense peaks in the resulting product's XRD pattern, although these peaks disappeared at the end of crystallization process [18]. Interestingly, these peaks did not appear in the XRD patterns of water-washed samples. The authors assigned these intense peaks to a semicrystalline intermediate aluminophosphate with a three-dimensional structure that bore some similarity to the structure of $AlPO_4$-11 [18].

In previous studies on the crystallization process of microporous crystals, the general study strategy has been to monitor the evolution of the species formed from mixed reactants with *in situ* or *ex situ* characterization techniques. On the basis of the information obtained about the structure of the species formed during the crystallization process, a possible crystallization process is then typically proposed. However, most of present characterization techniques cannot provide clear and unambiguous structural information at the molecular level for extremely small species due to their physical and time resolution limitations. In addition, the crystallization process of microporous crystalline materials is extremely complicated and involves the formation of numerous species via stoichiometric or nonstoichiometric reactions. Therefore, the current level of understanding of the crystallization process of microporous crystals such as microporous aluminophosphates at the molecular level is still insufficient, and the data are sometimes contradictory [22].

Recently, we developed a new strategy for investigating the crystallization processes of microporous crystalline compounds [23]. We have also developed a new method based on matrix and graph theories in mathematics to describe the open framework of microporous crystals and the possible fragments that form in the early stages of the crystallization process [24]. With the new strategy, exact structural information for each possible species that formed during the period of crystallization or for a core unit from which a single crystal was grown could be obtained. The collected information guided our study of the crystallization process of microporous crystals by providing clear structural information for the target species formed at the beginning of the crystallization process.

In this study, we investigated the influence of water content on the crystallization of $AlPO_4$-11 by combining the *in situ* and *ex situ* characterizations. New information has been obtained about the crystallization chemistry involving the formation of specific species and the crystallization pathway detailing the manner in which the formed species assemble together to form the open framework of $AlPO_4$-11. The present study represents a step forward in understanding the crystallization of microporous aluminophosphates at the molecular level.

2. Experimental Section

2.1. Synthesis

2.1.1. High water content conditions (diluted conditions)

The aluminum and phosphorus sources were boehmite (Catapal B, 72.7% Al_2O_3, Sasol) and phosphoric acid (85 wt.% H_3PO_4), respectively. Di-(*i*-propyl)amine (D-iPA) was used as the structure-directing agent. A typical procedure for the preparation of a reaction mixture is as follows: 17.5 g of 85% phosphoric acid was stirred with 80 g of water, and 28.2 g of boehmite was added. The mixture was stirred well for 3 h, then 8.78 g of D-iPA was added dropwise with continuous stirring. The gel was further stirred for 5 h at ambient temperature to ensure homogeneity. The same pre-calculated amount (9 mL of mixture) of the reaction mixture with a molar ratio of Al_2O_3:P_2O_5:1.2D-iPA:$69H_2O$ was loaded into several Teflon-lined autoclaves (volume: 20 mL) using a 10 mL syringe while stirring. The autoclaves were then placed in a pre-heated oven at 180 or 200 °C. The temperature of the oven dropped to about 140 °C when all of the autoclaves were loaded. The oven reached the target temperature after approximately 60 min. Timing started when all of the autoclaves were loaded into the oven. The autoclaves were heated for different periods and quenched in cold water. The liquid and solid phases of the product were separated by centrifugation (9500 rpm or 8475*g*), and the solid phase was dried at ambient temperature. The dried samples were sealed for later characterization.

2.1.2. Low water content conditions (concentrated conditions)

A typical procedure for the preparation of a reaction mixture is as follows: 1.94 mL of 85% phosphoric acid was stirred with 2 g of water, and 2 g of boehmite was added. The mixture was stirred well for approximately 10 min, then 2.45 mL of D-iPA was added dropwise with continuous stirring. The gel was further stirred for