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Synthesis of large single crystals of SAPO-47 in the presence of diethylamine using two-step temperature process

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ABSTRACT

By using diethylamine (DEA) as the structure-directing agent (SDA), large single crystals of SAPO-47 have been synthesized with a two-step temperature process. As a typical contaminant, the existence of SAPO-5 introduces a competing phase in the one-step temperature process. But our method shows that an initial temperature of 160 °C can successfully depress the SAPO-5 nuclei, facilitating the synthesis of pure SAPO-47 crystals in the finial crystallization process. Perfect rhombohedral-shaped SAPO-47 crystals with a size 230 × 230 μm are synthesized by optimizing crystallization temperature and duration, molar SiO_2/Al_2O_3 ratio, DEA and HF amount. Single-crystal X-ray diffraction measurement shows that the as-synthesized SAPO-47 crystals are of space group $R\bar{3}$ symmetry with lattice constants $a = b = c = 9.396$ Å, $\alpha = \beta = \gamma = 94.43°$, and their unit cell volume is $V = 821.7$ Å^3.

1. Introduction

Since the first report of crystalline microporous aluminophosphate ($AlPO_4$-n) in 1982 [1], many research works have been carried out on this new-type molecular sieve materials. Particular attention has been paid to the catalytic effect of metal-ion-containing $AlPO_4$-n-type molecular sieves in a variety of hydrocarbon reactions, such as cracking, hydrocracking, alkylation and isomerisation [2]. Recently, the application has been extended to the generation of new supra-molecular structures by intercalating guest molecules into the pores or cages of the molecular sieve templates [3–8]. The well-defined uniform pores or cages in 3D framework of $AlPO_4$-n crystals can selectively control the configuration of guest molecules based on their size and shape. Confinement exerted by the pores or cages can also stabilize some unstable structures in freestanding space [9,10].

$AlPO_4$-47 (CHA) is one kind of the $AlPO_4$-n crystals, with a framework consisting of alternating tetrahedral $(AlO_4)^-$ and $(PO_4)^+$, which form elliptical cages (6.7 × 10 Å) interconnected through 3.8 Å windows [11]. The substitution of silicon into the $AlPO_4$-47 crystals (SAPO-47) generates a negatively charged framework, and thus leads to an enhanced adsorption force between channel walls and guest molecules, which makes the formation of guest–host materials much easier. A pure SAPO-47 crystal is optically transparent in visible region and a good insulator with thermal stability up to 900 °C. These properties make it an excellent template for fabricating host–guest nanostructured composites. One recent example is to use SAPO-47 crystal as template to control the configurations of disperses red 1 dye molecules [12]. Moreover, SAPO-47 crystals provide a potential methodology to test the physical prosperities of guest materials in a controllable way. However, in most applications, the size and quality of SAPO-47 crystals can strongly affect their performance. Therefore, the synthesis of SAPO-47 crystals with large size and high quality is urgent for both fundamental research and practical application.

Several groups reported the methods of SAPO-47 crystals growth by using various structure-directing agents (SDA), including diethylethanolamine, methybutylamine, sec-butylamine, and isobutylamine, etc. [13–17]. However, most of the SAPO-47 products were powders. In this work, a two-step temperature process, nucleation stage at lower temperature (150–170 °C) and crystallization stage at higher temperature (200 °C), is used to synthesize SAPO-47 crystals in the presence of diethylamine (DEA). Compared with the one-stage method, the two-stage method is favor to synthesize the pure SAPO-47 crystals. By optimizing synthesis parameters, large single crystals of SAPO-47 with the size up to 230 × 230 μm have been synthesized. The crystals are of perfect rhombohedral morphology and high optical quality, and to our best knowledge, the largest SAPO-47 crystals reported so far.

2. Experimental

2.1. Synthesis

SAPO-47 crystals were synthesized using a hydrothermal process with a composite of $xSiO_2$:Al_2O_3:P_2O_5:yDEA:500H_2O:zHF as starting gels. Aluminum tri-isopropoxide (98 wt%, Aldrich),

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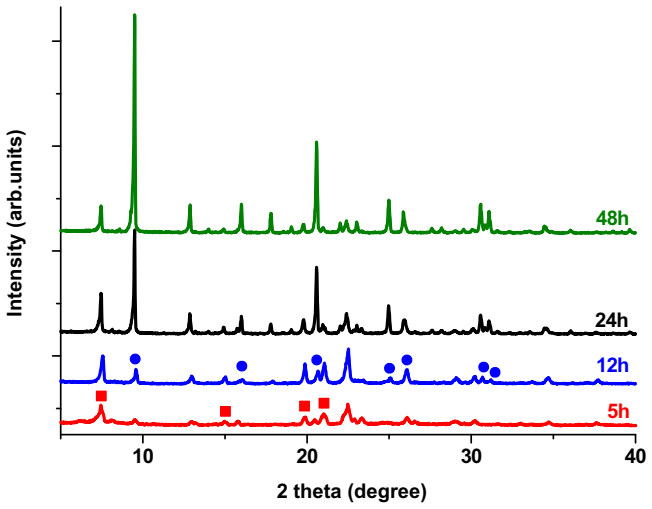

Fig. 1. XRD patterns of as-synthesized samples under different crystallization duration, where the solid square represents the peaks of SAPO-5 crystals, the solid circle represents the peaks of SAPO-47 crystals.

fumed silica (99%, Aldrich) and orthophosphoric acid (85 wt%, Aldrich) were used as sources of aluminum, silicon and phosphorus, respectively. DEA (99%, Aldrich) was used as the SDA. A typical synthesis procedure was as follows: (1) the aluminum tri-isopropoxide and fumed silica were first dissolved in distilled water and stirred vigorously for 10 h; (2) the diluted orthophosphoric acid was added dropwisely into the gel solution and stirred for 3 h; (3) the DEA was added into the mixed aluminophosphate gel and stirred for 3 h; (4) the diluted HF solution was slowly added into the homogeneous slurry and stirred for 3 h; (5) the gel formed from the reaction mixture was sealed into a Teflon-lined stainless-steel autoclave and heated to 160–200 °C under autogenous pressure for 5–125 h; (6) after crystallization, the solid products were filtered and washed with distilled water, then dried at 80 °C.

2.2. Characterization

As-synthesized crystals were characterized by X-ray powder diffraction (XRD) using a Philips PW1830 diffractometer at room temperature. The size and morphology of the crystals were investigated by scanning electron microscopy (JEOL Co., Model:JSM-6049LA) and optical microscopy. The single crystal X-ray diffractometry (Xcalibur, Eos, Gemini) was used to characterize the crystal structure at 20 °C. The X-ray source was enhanced Mo target (λ = 0.71073 Å). The working voltage was 50 KV and current was 35 mA. Lattice determination and data collection was carried out by using CrysAlisPro Version 1.171.34.49 software. Absorption correction was also performed by the same package with empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. Structure solution and refinement were performed by using SHELXS-97 software packages.

3. Results and discussion

3.1. One-step temperature process

SAPO-47 crystals were fabricated using the gel comprising $1.32SiO_2$:Al_2O_3:P_2O_5:2.7DEA:500H_2O:2.9HF. The gel formed from the reaction mixture was sealed in a Teflon-lined stainless autoclave and heated to 160–200 °C under autogenous pressure for 5–48 h.

3.1.1. Effect of the crystallization duration

In order to study the effect of crystallization duration on the quality and the size of SAPO-47 crystals, the crystallization temperature is first fixed at 200 °C, while the crystallization duration varies from 5 to 48 h. Fig. 1 shows the XRD patterns of as-synthesized products under different crystallization duration. The peaks appear at 7.4°, 14.9°, 19.8° and 21° (2θ marked by solid squares) when crystallization duration 5 h is adopted. These are characteristics of SAPO-5 (AFI) crystals [18]. It implies the presence of AFI phase. A similar phenomenon was reported in Ref. [19], which concluded that the co-product of SAPO-5 can be regarded

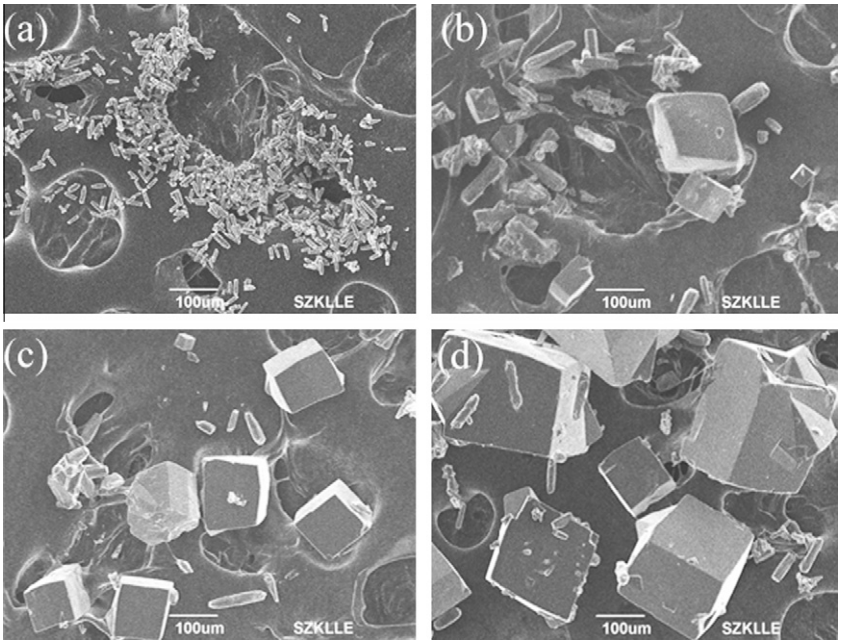

Fig. 2. SEM images of as-synthesized samples under different crystallization duration: (a) 5 h, (b) 12 h, (c) 24 h, and (d) 48 h.