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ScienceDirect
Microporous and Mesoporous Materials 114 (2008) 416–423
MICROPOROUS AND MESOPOROUS MATERIALS
www.elsevier.com/locate/micromeso

Synthesis of SAPO-34 templated by diethylamine: Crystallization process and Si distribution in the crystals

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Received 27 September 2007; received in revised form 22 January 2008; accepted 24 January 2008
Available online 1 February 2008

Abstract

The crystallization process of SAPO-34 molecular sieve with Si distribution in the crystals using diethylamine (DEA) as the template was investigated by XRD, SEM, IR, NMR, XRF, XPS and EDS techniques. It was found that the solution-mediated transport mechanism occurred during the crystallization, though the gel transformation cannot be completely excluded in the initial crystallization ($t \leqslant 1$ h). Si directly participated in the crystallization in the initial stage and incorporated into the framework of SAPO-34 by SM2 (P substitution by Si) and SM3 (pairs of Al and P substitution by 2Si) mechanisms. XPS analysis revealed the enrichment of Si on the surface of crystals. Based on the experimental results, a model of Si distribution in the crystals was proposed, which described a non-uniform distribution of Si in the crystals, with the increasing content from the core to the surface.

Keywords: SAPO-34; Diethylamine; Characterization; Crystallization mechanism; Si distribution

1. Introduction

SAPO-34, a silicoaluminophosphate molecular sieve with CHA structure, has exhibited excellent catalytic performance in methanol-to-olefin (MTO) reaction due to the contribution of small pore, medium acidity and good thermal/hydrothermal stability [1–4]. In recent years, MTO reaction has been attracting much attention because it is the key step as a non-oil route to produce ethylene and propylene [4–11]. Accordingly, researches on SAPO-34 – the active composition of MTO catalyst, have also received considerable interests. Many efforts have been focused on understanding the reaction mechanisms [12–15] and improving the catalytic performance. However, the investigation on the synthesis and crystallization mechanism of SAPO-34 is quite rare. As the catalytic performance of SAPO-34 is closely related to its acidic property and Si distribution, therefore, the detailed study on the synthesis mechanism would be helpful for controlling the framework composition and optimizing the acidic/catalytic property.

The crystallization of molecular sieves is a very complicated process influenced by reactants, mixing procedure, temperature, pH, etc. Two mechanisms regarding the crystallization process have been proposed [16–18]. One of which is the solution-mediated transport mechanism involving the dissolution of reagents followed by transport mechanisms to the nucleation sites where the crystal growth takes place, and the other is the solid hydrogel transformation mechanism involving the reorganization of the solid phase from amorphous components to crystalline. A combination of both mechanisms may also be possible; however, no general roles have hitherto been developed due to the complexity of crystallization process.

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1387-1811/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.micromeso.2008.01.030

It is recognized that there exist two kinds of Si substitution mechanisms in the crystallization of SAPO molecular sieves [19–25]. One is the substitution of P by Si (denoted as SM2), which would form Si(4Al) entities and lead to the formation of negatively-charged frameworks (balanced by protons attached to Si–O–Al bridges). The other is the double substitution of adjacent P and Al by two Si atoms (denoted as SM3), which gives rise to Si(nAl) ($n = 3 - 0$) structures and stronger Brønsted acid sites.

Some attempts have been made to explore the crystallization from the mixture gel to SAPO-34. The crystallization of SAPO-34 using morpholine as the template in the presence of HF was studied by Vistad et al., who suggested that the gel first dissolves into 4-rings (4R) units, further constituting a layered intermediate (the prephase), and that the next steps are redissolution, nucleation and crystallization of the prephase in different types of 4R building units [26–28]. However, no direct information about Si substitution was obtained, since ^{29}Si NMR was not applied in their studies. Therein, Si incorporation was proposed to proceed with the substitution of aluminum or phosphorus in the silicon-free 4R type-I units based on the elemental analysis results. Our group has reported the crystallization and Si incorporation mechanisms of SAPO-34 synthesized with triethylamine as the template [29], where the formation of SAPO-34 was possibly ascribed to the contribution of a gel conversion mechanism, with a two-stage crystallization process. In the first stage (less than 2.5 h), most of the crystallization (~80%) took place and the majority of Si (80%) incorporated into the framework of SAPO-34 by a direct insertion mechanism. In the second stage (longer than 2.5 h), the minority of Si (20%) inserted into the framework by the substitution of Si for P (SM2) as well as the substitution of 2Si for P + Al (SM3). Moreover, Huang et al. used cyclohexylamine as the template to investigate the synthesis of SAPO-44, which has the same structure as SAPO-34 but with different lattice symmetry [30]. They found that 2 h of hydrothermal treatment mainly generated an amorphous AlPO phase consisting of secondary building units, which would further assemble to half CHA cages, and that Si started to incorporate into the amorphous phase at later period. A layered material appeared after 6 h, and a further increase in heating time led to the formation of SAPO-44.

SAPO-34 can be synthesized with many templates, such as tetraethylammonium hydroxide (TEAOH) [1,10], dipropylamine [1], isopropylamine [1], piperidine [31], morpholine [20,26–28,32], triethylamine (TEA) [29,33] etc. However, only several investigations have involved in the synthesis of SAPO-34 templated by diethylamine (DEA) [34–37]. Our recent work indicated that DEA template could produce SAPO-34 with high purity and crystallinity [38]. Interestingly, the Si content of SAPO-34 synthesized with DEA was much higher than those with triethylamine (TEA) and tetraethylammonium hydroxide (TEAOH), even though the initial gel had similar compositions. The present paper reports detailed investigations on the crystallization mechanism of SAPO-34 synthesized with DEA template, and on the Si distribution by employing XRD, SEM, IR, XRF, NMR, EDS and XPS techniques.

2. Experimental

2.1. Sample preparation

SAPO-34 was hydrothermally synthesized from the gel with a composition of 2.0DEA:0.6SiO_2:1.0Al_2O_3:0.8-P_2O_5:50H_2O. Pseudoboehmite, phosphoric acid (85 wt%) and silica sol (25 wt%) were used as the sources of aluminum, phosphorus and silicon, respectively. Pseudoboehmite was added to the diluted phosphoric acid solution, which was then stirred for 2 h until a uniform gel was obtained. To the resultant gel silica sol and DEA were successively added, and the stirring was maintained for 1 h to form a uniform reaction mixture, which was then sealed in a 2000 ml autoclave (Fig. 1) and heated from room temperature to 473 K at a rate of 2 K/min. The crystallization was carried out at 473 K under autogenous pressure while stirring. Samples were withdrawn periodically from the autoclave during the crystallization. The crystallization time was recorded once the temperature of autoclave had reached 473 K. As-synthesized samples were obtained after centrifugation, washing, and drying at 393 K for 4 h, in which some samples underwent calcination in air at 823 K for 5 h to remove the template and water. Solid yield experiments were performed separately in 200 ml autoclaves with the same gel composition as described above.

2.2. Characterizations

The powder XRD patterns of the samples were recorded on an X-ray diffractometer (Rigaku D/MAX-RB) with Cu $K\alpha$ radiation ($\lambda = 0.15418$ nm). The crystal morphology was observed by scanning electron microscopy (KYKY-AMRAY-1000B). The chemical composition of the samples was determined with an X-ray fluorescence (XRF) spectrometer (Philips Magix-601), and those of some samples were also obtained by scanning electron microscope (JEOL-JSM-5600) equipped with an energy dispersive X-ray spectrometer (EDS, Oxford Link-ISIS-300). FT-IR spectra were measured using KBr-diluted pellet on an IR

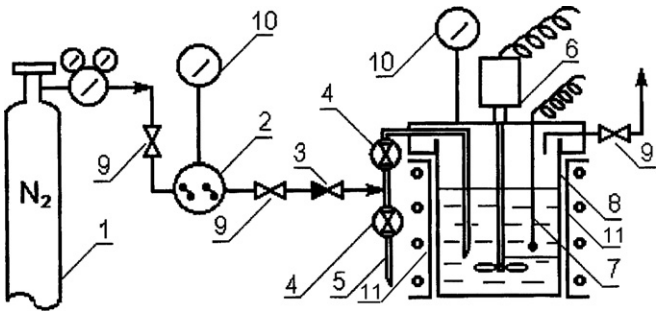

Fig. 1. Schematic diagram of the apparatus for SAPO-34 synthesis.