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Unraveling the non-classic crystallization of SAPO-34 in a dry gel system towards controlling meso-structure with the assistance of growth inhibitor: Growth mechanism, hierarchical structure control and catalytic properties

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ABSTRACT

Understanding silicoaluminophosphate formation mechanism lays the foundation for their structure manipulation via crystallization process control. Crystallization of SAPO-34 from a dry gel using tetraethyl ammonium hydroxide as structure-directing agent was monitored to unravel the formation mechanism. The initial gel was found to form a lamellar precursor first, which subsequently underwent phase transformation to discrete SAPO-34 nanocrystallites. The nanocrystallites thereafter mutually aligned with neighboring ones via a non-classic oriented attachment growth mechanism, affording large crystals as a result of grain boundary elimination. A new protocol to prepare hierarchical SAPO-34 was designed by hindering the aggregation of primary nanocrystallites with a growth inhibitor 1,2,3-hexanetriol. The structure of hierarchical SAPO-34 was characterized by XRD, N_2 physisorption, mercury intrusion, SEM, TEM, as well as ^{27}Al, ^{29}Si, ^{31}P MAS NMR spectra and compared with a conventional SAPO-34. More Si islands were formed via combined SM3 (Al+P pairs substitution by 2Si) and SM2 (P substitution by Si) mechanism for hierarchical SAPO-34 as Si was not fully incorporated into the precursor lamellar phase. NH_3-TPD showed that hierarchical SAPO-34 has comparable acidic strength to conventional SAPO-34. The obtained hierarchical SAPO-34 is comprised of <100 nm crystallites and possesses well-connected mesopores, both factors are crucial to mass transfer in zeotype materials. Hierarchical SAPO-34 exhibited a 1.5 times lifetime increase in catalytic chloromethane to olefin conversion with respect to a conventional counterpart.

1. Introduction

Aluminophosphates ($AlPO_4$) and silicoaluminophosphates (SAPOs) are regarded as an important subclass of molecular sieves that are nowadays widely used as solid acids catalyst in several important commercial processes. In particular, SAPO-34 with a chabazite (**CHA**) topology has arguably drawn the most important attention as it can be used as acid catalyst in methanol-to-olefin (MTO) process [1], CH_3Cl-to-olefin process [2], catalyst support for SCR-deNO_x [3], or as sorbent for CO_2/N_2 or CO_2/CH_4 separations [4,5]. The CH_3Cl-to-olefin process is proposed to be more economic than MTO, as CH_3Cl can be produced by direct oxidative chlorination of CH_4, henceforth bypassing the energy-intensive methane steam reforming to generate syngas and costly methanol synthesis processes [6]. In CH_3Cl-to-olefin catalytic conversion, the catalytic performances are dependent on both acidity and morphological features such as crystal size and porosity, quicker deactivation has been observed [2].

In SAPO-34, like in other SAPOs, the type of isomorphous substitution of Si atoms into framework can take place by SM2 and/or SM3 mechanisms [7]. In the SM2 mechanism, a P atom is

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substituted by a Si atom to generate an isolated Brønsted acid site. Whereas in the SM3 mechanism, a pair of Al–O–P are replaced by Si–O–Si, this mechanism will not generate acid site alone. To avoid generating Si–O–P bond that is prohibited by the Löwenstein's rule [8], SM3 mechanism should happen together with SM2, producing the so called Si island. Si atoms at the inner part of Si island are incorporated by SM3 mechanism, while the edge Si atoms substitute framework by SM2 mechanism [7]. Acid strength of sites at the margin of Si island increases with Si island size [7,9]. In general, the acid properties of SAPO-n depend on the content, location and distribution of Si atoms. The acidity can be affected by the choice of structure-directing agents (SDAs) [10] starting materials [11], crystallization processes [12] etc., controlling of which entails fundamental understanding of the crystallization mechanism.

Besides acidity, texture properties such as crystal size and porosity can also impact catalytic performances. SAPO-34 suffers from fast coking and rapid deactivation in MTO process [13]. Larger crystal size leads to fast deactivation that is associated with pore blocking caused by heavy aromatic species such as polyaromatics that retain in the **CHA** cavities [14]. These cokes are mainly products of side reactions that occur when primary products such as olefins cannot escape from intra-cavity sites quickly [15]. Chen et al. [13] pointed out that coking and deactivation can be alleviated by downsizing SAPO-34 crystal size that enhances diffusion, and have found that catalysts with a mean size of 400 nm showed the maximum lifetime. Lately, nanosized and hierarchically porous SAPO-34 has been developed to enhance catalytic lifetime [11,16]. Promoting the lifespan of SAPO-34 can significantly improve the profitability of MTO or CH_3Cl-to-olefin processes, and has been the most important research target in MTO catalyst design.

From the turn of the century, there is a surge of interest to synthesize hierarchically porous zeolites (HPZs) or nanozeolites as a means to promote mass transfer. However, most of them were aimed to prepare hierarchical aluminosilicates zeolites and the synthesis of hierarchical SAPO type materials has witnessed only limited success. In the case of SAPO-34, several synthetic strategies have thus far been established, which can be categorized into templating based strategy and crystallization based strategy. In templating synthesis, both soft templates (such as amphiphilic organosilanes [17], polymers [18]) and hard templates (such as carbon nanotubes [19]) have been utilized for the generation of SAPO-34 with auxiliary mesoporosity. On the other hand, in crystallization controlled synthesis, microwave assisted crystallization [11], colloid solution synthesis [20], sonochemical synthesis [21], post synthetic treatment [22], and dry gel conversion (DGC) [23] strategies have been proposed as possible means to decrease the crystal size of SAPO-34. Protocols such as organosilane or microwave based methods normally lead to reduced acid strength when the SAPO-34 crystal size is decreased or mesopores is generated [11,17]. Among the crystallization control strategies, DGC provides a facile, low cost and high-throughput means to control the particle size of SAPO-34 down to 100 nm that is demanding from an industrial viewpoint [1,23]. Besides, one should notice that not all mesopores are created equal, the efficiency of mesoporosity toward catalytic performance improvement is highly dependent on pore-connectivity [24].

As mentioned before, DGC has been recognized as an effective way to introduce mesoporosity and reduce the crystal sizes [23,25,26]. Particularly, in the case of SAPO-34, major attention is focused on the understanding of condition-dependent formation mechanism at the molecular level. For instance, Huang et al. [12,27,28] have employed a combination of techniques, especially with the assistance of ^{27}Al, ^{29}Si, ^{31}P MAS NMR to monitor the formation of several typical SAPOs using DEA, morpholine as SDAs. But less information has been provided on the morphology evolution at the meso-scale level.

Despite these efforts, the reason why crystallite size, Si incorporation and their distribution are highly dependent on synthetic parameters remains largely unknown for DGC systems. Unraveling the underlying crystal growth mechanism will not only shed light on its effect over SAPO-34 structure, but also allow us to achieve the control over structure via synthetic condition manipulations. Besides, there is still space to control the particle size distribution and crystallinity of the obtained SAPO-34, *cf.*, for comparison studies. Herein, we report the investigation of crystallization of SAPO-34 in a dry gel system using TEAOH as SDA, with an emphasis laid on the crystallization mechanism and the consequence over final structure of SAPO-34 thus obtained. We will show for the first time that the non-classic oriented attachment (OA) growth dominates in DGC of SAPO-34, despite that the process is complicated by the formation of a lamellar intermediates phase. The OA mechanism has not been reported for the synthesis of SAPO type materials before, to the best of our knowledge. This observation widens the knowledge on SAPO crystallization under high supersaturation conditions. Based on this new mechanistic understanding, a new synthetic route to generate hierarchical SAPO-34 with the help of a selected inhibitor will be proposed. The structure and texture properties of thus obtained hierarchical SAPO-34 will be disclosed by a suite of characterization techniques, such as X-ray diffraction (XRD), N_2 physisorption, ^{31}P, ^{29}Si, ^{27}Al MAS NMR etc. The acidity and catalytic performance of hierarchical SAPO-34 in CH_3Cl to olefins will be evaluated and compared with a conventional SAPO-34.

2. Experimental section

2.1. Synthesis

The reagents used were pseudoboehmite (75 wt% Al_2O_3, Aluminum Corporation of China), phosphoric acid (85 wt%, Shanghai Lingfeng Chemical Reagent Co. Ltd.), tetraethylammonium hydroxide (TEAOH) (35 wt%, Shanghai Cainorise Chemicals Co., Ltd), fumed silica (J&K Scientific Ltd., 99% + SiO_2), 1,2,3-hexanetriol (BIOXTRA, 98.0 wt %). The chemicals were used as provided without further purifications.

The condensed gel with molar ratio of 1.0 Al_2O_3:1.0 P_2O_5:0.6 SiO_2:2.0 TEAOH:50H_2O was prepared as following. A solution A was prepared by adding pseudoboehmite slowly to an aqueous solution of phosphoric acid after stirring for 7 h at room temperature. Concurrently, a solution B was synthesized by dissolving fumed silica in an aqueous solution of TEAOH. Next, solution B was added dropwise into solution A before continuous stirring for an additional 5 h. The reaction mixture was dried at 80 °C overnight to afford a sticky lump. The lump was transferred into a Teflon cup placed in a 100 mL Teflon-lined stainless steel autoclave and 0.50 g H_2O as stream source was separately added into the liner. The autoclave was heated to 200 °C for various durations in the crystallization study. The autoclave was quenched with cool water after removing from the oven. The product was dried at 80 °C for 6 h before characterizations.

The hierarchical SAPO-34 was synthesized from a reaction lump with molar ratio of 1.0 Al_2O_3:1.0 P_2O_5:x SiO_2:2.0 TEAOH:50H_2O:0.05 1, 2, 3-hexanetriol (x = 0.6, 0.3). The precursor lump was prepared as previously described for crystallization study. Precrystallization was conducted at 200 °C for 5 h to produce discrete crystallites. The crystallites were collected and dispersed in an aqueous solution of 1,2,3-hexanetriol of 10.0 mL. The solution was stirred for 5 h before drying at 80 °C to give a lump gel. The lump gel was treated with 3.00 g water as source of steam at 200 °C for 72 h. The as-synthesized product was centrifuged, washed thoroughly with