Catalysis Communications 103 (2018) 1–4

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Fabrication of nano-sized SAPO-11 crystals with enhanced dehydration of methanol to dimethyl ether

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ARTICLE INFO

Keywords:
Nano-sized
SAPO-11
Seed
Solvothermal
DME

ABSTRACT

Nano-sized SAPO-11 zeolite was successfully fabricated by a seed-induced quasi-solvothermal conversion (SIQSC) protocol without a secondary porogen that combined an in situ inoculating seed method (SI) and a quasi-solvothermal assisted conversion (QSC) process. The aggregation of SAPO-11 nanocrystals (20–30 nm) to give larger particles with an approximate 200 nm average size creates a lower acidity, larger surface area and higher inter-crystal mesoporosity than those in micro-sized SAPO-11 crystals. Importantly, the nano-sized SAPO-11 shows better performance in the dehydration of methanol to dimethyl ether (DME) than Al_2O_3 and micro-sized SAPO-11.

1. Introduction

SAPO-11 zeolites have been widely used in petrochemical industry. Recently, interest in the synthesis of SAPO-11 containing secondary mesopores has strongly increased [1,2]. These methods can enhance the surface area, especially of the external surface. It is widely accepted that the synthesis of nano-sized SAPO-11 is an effective route to improve the diffusion efficiency of this zeolite [1,3]. In order to obtain nano-sized zeolites, the key factors to control are the concentration and the supersaturation of the crystal nucleus.

Steam-assisted conversion (SAC) has recently attracted increased interest for the synthesis of hierarchical zeolites [4,5] and superfine zeolites [6,7] with larger surface areas, mainly due to the advantage of massive nucleation of zeolite in such a quasi-solid state. It is well-known that these routes are suitable for constructing zeolites with larger surface areas. Up until now, similar mechanisms and methods have been reported for a variety of morphologies of SAPO-11 [6–8]. Benefiting from massive nucleation and additives (such as fluoride ions [6] and CTAB [7]), these methods facilitate the synthesis of superfine SAPO-11 with excellent catalytic performance. However, for all of the examples mentioned above, a variable amount of additive is still needed, and the morphologies of the synthesized samples are not uniform. Therefore, the challenge for the synthesis of nano-sized SAPO-11 crystals with a larger surface area is to reduce the extra doping during the synthetic process, as this costly process restricts large-scale production in industry.

Recently, we synthesized a dandelion-like SAPO-11 by an in situ inoculating seed-induced steam-assisted conversion method (SISAC) [9]. In addition to providing the advantages of the SAC method, the seed-assisted method was introduced in situ. On the one hand, considering the low polarity of organic solvents, solvothermal synthesis is a promising technique for zeolite synthesis [10–12]. The predominant advantage of the solvothermal technique is that the crystallization growth rate can be greatly reduced with non-aqueous solvents [11]. Meanwhile, using zeolite growth modifiers (ZGMs), the kinetics of crystallization, the size and the morphologies of the MFI and LTL crystals can be effectively altered with ZGMs, as discovered by Rimer and co-workers [13–15]. Thus, different solvents may show a crystal growth modifier effect, providing unexpected control of the crystal size.

Conventional SAPO-11 synthesis yields micro-sized crystals, and their various applications depend heavily upon their physical characteristics, such as crystal size and morphology. Here, a uniformly nano-sized SAPO-11 zeolite was synthesized by a new strategy that combined the advantages of both solvothermal synthesis and ZGMs. This new method was denoted as “SIQSC”, which is different from the SISAC method described in our previous study [9]. The “SI” represents the in situ seed implanted method, where the initial gel was pre-treated at 433 K for 24 h. The “QSC” stands for the quasi-solvothermal assisted conversion by substituting the aqueous solution with ethanol in the second crystallization process, in which the dry gel was separated with ethanol during the crystallization process. It could be speculated that the roles of ethanol were 1) providing an environment for crystallization growth of the zeolite; and 2) binding to the crystal surfaces and thereby altering growth rate isotropically and/or inhibiting

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http://dx.doi.org/10.1016/j.catcom.2017.09.002
Received 16 July 2017; Received in revised form 5 September 2017; Accepted 6 September 2017
Available online 08 September 2017

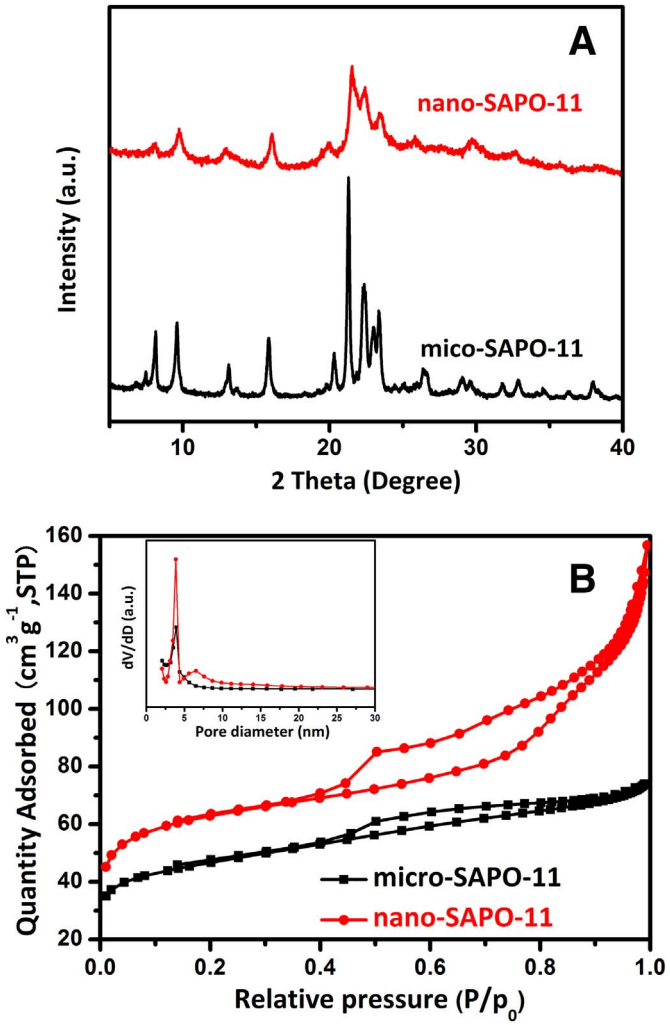

Fig. 1. XRD patterns (A) and nitrogen adsorption desorption isotherms (B) of SAPO-11 samples. The inset of B presents pore size distribution of SAPO-11 samples.

aggregation. We further studied the physical properties of nano-sized SAPO-11 by XRD, SEM, TEM, N_2 physisorption and Py-IR characterization, and their effect on the performance of dehydration of methanol to dimethyl ether using nano- and micro-sized SAPO-11.

2. Experimental section

Describing in **Supporting** information.

3. Results and discussion

The XRD patterns of nano- and micro-sized SAPO-11 are presented in Fig. 1A. Both show the typical SAPO-11 phase [1,3]. No diffraction peaks from impurities can be detected for nano-SAPO-11, which indicates that the SIQSC method can be used to synthesize SAPO-11. However, in comparison to micro-SAPO-11, nano-SAPO-11 shows decreased peak intensities and broadened linewidths, which are ascribed to the decreased crystal size in nano-SAPO-11 [16]. These results indicate that nano-SAPO-11 may have smaller crystals than micro-SAPO-11. The reference sample (C-DG-SAPO-11), which lacks the pre-crystallization step of the initial dry gel, was synthesized using a quasi-solvothermal assisted conversion, but no typical diffraction peaks attributable to the AEL structure could be identified in its XRD pattern (Fig. S1). These results suggest that the embryonic AEL structure plays a pivotal role in the formation of nano-SAPO-11 during the SIQSC process, which is in good agreement with our previous studies on the fabrication of dandelion-like SAPO-11 [9].

The N_2 adsorption and desorption isotherms are shown in Fig. 1B and the textural parameters are summarized in Table S1. The nano-SAPO-11 exhibits a type-IV isotherm with an H4 type hysteresis loop, indicating that it has a micro–meso hierarchical textural feature [9,17,18]. As shown in Fig. 1B, a pore diameter distribution of approximately 7 nm could be observed (inset in Fig. 1B). This phenomenon arises from the inter-void spaces between the particles. Compared with the micro-SAPO-11 (167.5 $m^2 g^{-1}$), the nano-SAPO-11 shows a larger BET surface area (217.6 $m^2 g^{-1}$). Moreover, it is worth noting that the external surface area for nano-SAPO-11 is nearly triple (100.5 $m^2 g^{-1}$) that of micro-SAPO-11 (36.9 $m^2 g^{-1}$) due to the nano-sized effect.

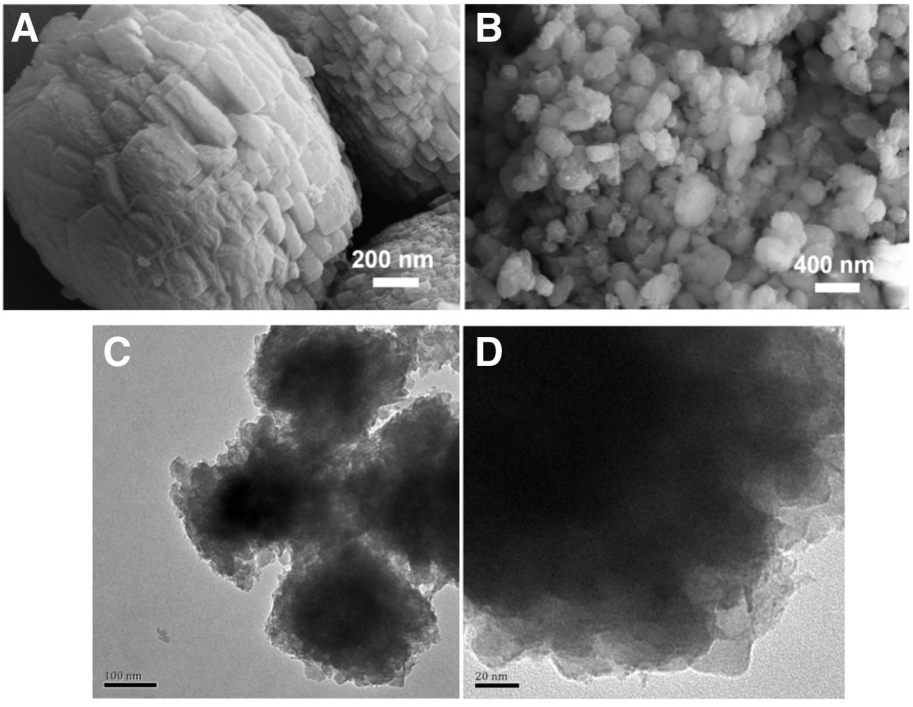

Fig. 2. SEM images of mico-SAPO-11 (A) and nano-SAPO-11 (B), TEM images of nano-SAPO-11 (C, D).