Catalysis Communications 108 (2018) 64–67

Contents lists available at ScienceDirect

Catalysis Communications

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

Short communication

Excellent catalytic performance for methanol to olefins over SAPO-34 synthesized by controlling hydrothermal temperature

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ARTICLE INFO

Keywords:
SAPO-34
Methanol to olefins
Silicon distribution
Mixed templates

ABSTRACT

A facile way to synthesize a series of SAPO-34 zeolites was developed by using the mixed templates of morpholine and TEAOH with changing the temperature. Among these samples, SAPO-34-210 exhibited with the longest lifetime and the highest selectivity to light olefin for methanol to olefin (MTO) reaction. The characterizations suggested that SAPO-34-210 has unique Si distribution due to much more amount of TEAOH introduced into structure, which resulted in the excellent catalytic performance.

1. Introduction

Methanol to olefins (MTO) process has been proposed as it builds a new route to produce light olefins. SAPO-34, as one of the famous zeolite catalysts, has shown high selectivity to C_2H_4 and C_3H_6 during MTO process on account of its moderate acidity and unique cages [1–6]. It has been used as the main catalyst in the industrialization of MTO in 2010 by Liu's group [1]. However, the restriction for mass transport of large molecule products for the 8 ring pore (3.8 × 3.8 Å) material is still a drawback, which leads to the formation of coke in the MTO process. This is one of the main reasons causing the short lifetime [5,7,8]. Previous works have confirmed that the intrinsic weakness of SAPO-34 can be overcome by reducing crystal size and acidity or synthesizing hierarchical structure, which can effectively prevent the coke deposition and enhance the catalytic performance in MTO reaction [9–11].

It is well established that the hydrothermal synthesis of SAPO-34 is a very intricate process which can be impacted by many parameters. One of the significant factors is the effect of the hydrothermal temperature, which may change the reaction process and cause diverse products and crystal sizes of SAPO-34 [12–14]. The sort of template also plays an important role in hydrothermal process. Nano-sized SAPO-34 catalysts can be prepared by the application of TEAOH used as a template [15,16], but it is not widely applied in industrial manufacture due to its exorbitant price [17]. Some nano-sized catalysts were also synthesized by mix-templates and these catalysts exhibited much better performance in MTO process [18–23]. Varying temperature systems, different ratios of mix SDAs systems and different sorts of SDAs systems for synthesizing SAPO-34 were well studied in recent literatures [15–23]. However, the mix SDAs with different hydrothermal synthesis of SAPO-34 was rare studied in the previous reports.

In this work, a series of SAPO-34 samples were synthesized by varying the hydrothermal temperature in the range of 190–220 °C and using morpholine and TEAOH as the mix templates. It was surprised that different amount of SDAs can be introduced into SAPO-34 with the varying temperature and the consequent changed the Si distribution in structure. The properties of prepared samples were fully studied and tested in the reaction of methanol to olefins.

2. Experimental section

2.1. Synthesis of SAPO-34

A series of SAPO-34 samples were fabricated by hydrothermal solvent way at different temperature (190, 200, 210 and 220 °C) in which morpholine and TEAOH were used as mixed templates. The molar composition of the synthesis gel was 1 Al_2O_3: 2.12 H_3PO_4: 1.08 SiO_2: 1 Morpholine: 1 TEAOH: 66 H_2O. The detail experiment method was described in the Supplementary information.

2.2. Characterization

XRD, SEM, XRF, TG, NH_3-TPD and Nitrogen adsorption/desorption were used in this work. The detail information of the measurements was presented in the Supplementary information.

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https://doi.org/10.1016/j.catcom.2018.01.033
Received 14 December 2017; Received in revised form 17 January 2018; Accepted 29 January 2018
Available online 31 January 2018

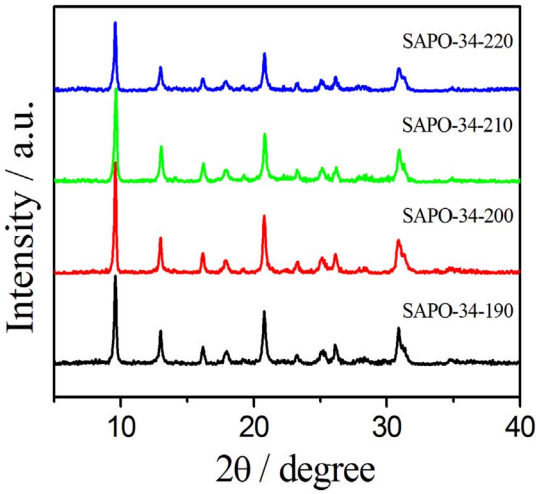

Fig. 1. XRD patterns of a series of SAPO-34 samples.

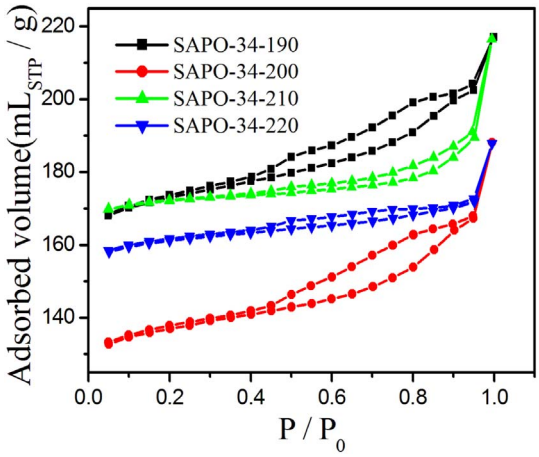

Fig. 2. N_2 adsorption-desorption isotherms of SAPO-34-190, SAPO-34-200, SAPO-34-210 and SAPO-34-220.

2.3. Catalytic activity evaluation

The catalysts were crushed and sieved into 0.4–0.6 mm particle size. 200 mg of catalyst was mixed with 2 g quartz and then put into the fix-bed reactor (8 mm inner diameter). The catalyst was pretreated at 540 °C with N_2 flow of 80 mL min^{-1} for 1 h before starting the reaction, and then the temperature was decreased to 400 °C. The flowing of N_2 (19 mL min^{-1}) was bubbled in methanol at 25 °C, which gave a WHSV of 2 h^{-1}. The products were analyzed every 16.2 min using an online gas chromatograph (Agilent GC 7820A) with a HP-PLOT/Q column (30 m × 320 μm × 20 μm) and a FID detector.

3. Results and discussion

3.1. Textural properties

A series of SAPO-34 zeolites was synthesized by using the mixed templates of morpholine and TEAOH and was denoted SAPO-34-190, SAPO-34-200, SAPO-34-210 and SAPO-34-220 according to the hydrothermal temperature at 190, 200, 210 and 220 °C, respectively. The XRD patterns of these samples clearly demonstrate typical CHA topology and high crystalline, which suggest that CHA structure can be obtained at different temperatures (Fig. 1). The sequence of the crystal size calculated by using the XRD results over the four samples is: SAPO-34-200 (55.1 nm) > SAPO-34-220 (49.5 nm) > SAPO-34-190 (48.2 nm) > SAPO-34-210 (45.3 nm) as shown in Table S1. The chemical compositions of all samples are displayed in Table 1. The atomic ratio of Si to Al (Si/Al) of all samples is similar about 0.40. As exhibited in Fig. 2, N_2 adsorption-desorption isotherms of SAPO-34-190, SAPO-34-200, SAPO-34-210 and SAPO-34-220 showed the samples possessed micropores and mesopores structures. But mesopores were formed due to the accumulation of particles. The BET surface area is 494, 416, 547 and 484 m^2/g for SAPO-34-190, SAPO-34-200, SAPO-34-210 and SAPO-34-220, respectively, which is related to their crystal size. Moreover, SAPO-34-200 had the lowest micropore volume (0.20 cm^3/g) among the four samples, which resulted in its lowest BET surface area.

3.2. SEM images

The SEM images are exhibited in Fig. S1. From the images, it was very surprising that the morphology obviously changed with the crystallization temperature. When the hydrothermal temperature was 200 °C, SAPO-34-200 exhibited the independent cubical shape (Fig. S1c and d), which was the conventional morphology of the SAPO-34. However, the other three samples displayed different size of spherical aggregates which comprised of nano-sized cube type SAPO-34 crystals. Generally, the sample with the spherical aggregate morphology showed much larger BET surface area than the sample with independent cubic morphology. This result also explained that SAPO-34-200 had the lowest BET surface area. In order to more clearly understand and confirm the above different morphology with temperature change, SAPO-34-200 and SAPO-34-210 samples were synthesized at different crystalline time such as 12, 24, 36 and 48 h, respectively. And their SEM images are shown in Fig. S2. For SAPO-34-200, it is obvious that the size became bigger with increasing the crystallization time. However, the size of SAPO-34-210 at different stages was almost unchanged and the crystal aggregated to spheres at 48 h. From these results, it can be seen that the temperature change can lead to different morphologies in the synthesis of SAPO-34 using mix templates, which may be attributed to the diverse growth of crystal nucleus at different hydrothermal temperatures.

Table 1
BET characterization results, chemical compositions and the total acidity of a series of SAPO-34 samples.

Sample	Product composition (atomic ratio)[a] Si/Al/P	Si/Al	S_{BET}[b] (m^2/g)	t-plot S_{ext}[c] (m^2/g)	S_{micro}[c] (m^2/g)	V_{micro}[c] (cm^3/g)	V_{meso}[c] (cm^3/g)	Acid amount (mmol /g)[d]
SAPO-34-190	0.185/0.457/0.358	0.40	494	47	447	0.25	0.08	0.44
SAPO-34-200	0.177/0.463/0.360	0.38	416	39	377	0.20	0.09	0.36
SAPO-34-210	0.189/0.456/0.355	0.41	547	16	531	0.26	0.07	0.39
SAPO-34-220	0.185/0.460/0.355	0.40	484	16	468	0.24	0.04	0.41

[a] Measured by X-ray fluorescence (XRF) spectromete.
[b] S_{BET} (total BET surface area) calculated by BJH method at the range of 0.05 < P/P_0 < 0.3.
[c] S_{micro} (micropore area) and V_{micro} (micropore volume) calculated using the t-plot method.
[d] Calculated from the two desorption peaks of NH_3-TPD profiles.