Facile synthesis of SAPO-34 with small crystal size for conversion of methanol to olefins

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ARTICLE INFO
Article history:
Received 23 January 2014
Received in revised form 10 April 2014
Accepted 21 April 2014
Available online 29 April 2014

Keywords:
Dry gel liquid-phase transport
SAPO-34
Methanol to olefins (MTO)
Morpholine
Tetraethylammonium hydroxide

ABSTRACT
SAPO-34 molecular sieves were fabricated by a dry gel liquid-phase transport method using morpholine (Mor) or morpholine-tetraethylammonium hydroxide (Mor–TEAOH) as the structure-directing agent (SDA). The prepared samples were characterized by scanning electron microscope (SEM), nitrogen adsorption–desorption, X-ray diffraction (XRD), ammonia temperature-programmed desorption (NH3-TPD), thermo-gravimetric analysis (TG) and Fourier transform infrared spectroscopy (FT-IR). The results indicated that the dry gel liquid-phase transport method is very effective to fabricate SAPO-34 molecular sieves with average crystal size about 0.6 μm using Mor–TEAOH as SDA and 3 μm using Mor as SDA, respectively. Moreover, the addition of TEAOH is beneficial to produce SAPO-34 with small crystal size. Methanol-to-olefin (MTO) reaction was chosen to test the catalytic performance of as-prepared SAPO-34 catalysts. The prepared SAPO-34 catalyst using Mor–TEAOH as SDA exhibited the excellent catalytic performance in MTO process owing to its small crystal size and high crystallinity. The conversion of methanol and selectivity of ethylene and propylene are up to 100% and 87.9%, respectively.

1. Introduction
Silicoaluminophosphate (SAPO) molecular sieves were firstly invented by Lok et al. in 1984 [1,2], as a new family of molecular sieves. The development of SAPO series provides a broad range of different frameworks and different compositions, some are analogous to available silica-dominant zeolites, such as SAPO-34 and SSZ-13. Among all SAPOs, SAPO-34 with small pore mouth (3.72 Å) is well known as the commercial and industrial catalyst for the application of methanol-to-olefins (MTO), which is mainly attributed to its mild acidity and shape selective catalysis by small pore entrance [3]. In terms of SAPO-34 synthesis, the nature and amount of the selected structure-directing agent (SDA) play a significant role in incorporating silicon into the aluminophosphate framework and the purity of structure and crystallinity of SAPO-34.

Hydrothermal method, as the conventional strategy, has been applied in the preparation of SAPO-34 by numerous researchers [4–15]. However, separation between solvents and solid products is required by filtration or centrifugation, and partial organic SDAs are inevitably preserved in the liquid phase, resulting in the wastewater pollutants and downstream purification system installation [16]. To overcome the current problems originating from hydrothermal method, dry gel conversion (DGC) method is alternative and effective towards the preparation of SAPO-34 [17]. DGC can be classified into two types: vapor-phase transport (VPT) and steam-assisted conversion (SAC). In fact, the VPT technique involves the crystallization of a dry silicoaluminophosphate gel in a vapor phase containing volatile SDA and water. The dry gel is placed in a sample holder located in the middle of an autoclave while a very small amount of the aqueous solution of SDA and deionized water is added to the bottom of the autoclave, the aqueous solution is physically separated from the dry gel powder, and the dry gel is converted to a zeolite in evaporated steam. Smaller amount of SDA is required in VPT method than that used in hydrothermal method [19]. The SAC approach is similar to VPT except that the SDA is contained in the initial dry gel, instead of the aqueous solution containing SDA, pure water is placed at the bottom of the autoclave as the steam source. However, the DGC method is more complex and has a high requirement towards the equipment, and the space efficiency of reactors is reduced. Therefore, the synthesis of zeolites by a simple and environmentally friendly method has been always a challenge.

Herein, we present a facile method to synthesize SAPO-34 via a dry gel liquid-phase transport method. The prepared samples were well characterized and their catalytic properties were evaluated by MTO reaction. Moreover, the relevant characterization and the catalytic performance comparison of samples fabricated by different synthetic methods were also reported.

2. Experimental

2.1. Synthesis of SAPO-34 samples

Pseudoboehmite (70 wt.% Al2O3, Chinalco, China), silicon sol (28 wt.% SiO2, Xi’an Chem., China) and orthophosphoric acid (85 wt.%, Bodi Chem., China) were used as sources of Al, Si and P, respectively.
Morpholine (Mor) (99 wt.%, Sinopharm Chemical Reagent Co. Ltd, China) and tetraethyammonium hydroxide (TEAOH) (25 wt.%, Sinopharm Chemical Reagent Co. Ltd, China) were used as the SDA in the preparation of SAPO-34.

SAPO-34 samples were synthesized using the dry gel liquid-phase transport method with a molar composition of 1.0SiO₂:1.5Al₂O₃:1.5P₂O₅:4H₂O:xR, where R and x represent SDA and the molar ratio of SDA, respectively. In a typical synthesis, 34.59 g of H₂PO₄ was mixed with 53.82 g of deionized water to form an orthophosphoric acid solution. 21.86 g of pseudoboehmite was then added to the above solution. After vigorous stirring, a homogenous solution was obtained. Subsequently, 21.43 g of silicon sol was added and the resulting mixture was stirred for another 2 h to get a homogeneous gel, and then followed by holding the gel at 80 °C with stirring until dry gel was formed. 20 g of as-prepared dry gel was ground and then added to the mixture of 50 mL of SDA and 50 mL of distilled water under stirring, the resulting solution was then transferred to a stainless-steel autoclave without Teflon, then heated and crystallized at 180 °C under autogenic pressure for 48 h. Finally, the products were filtered, washed with distilled water, and followed by drying at 120 °C for 4 h and calcination at 550 °C in air atmosphere for 5 h to remove the SDA. The obtained SAPO-34 samples in the presence of Mor and the mixture of 75% (volume) Mor-25% TEAOH were denoted as S34-L-M and S34-L-M-T, respectively.

For comparison, SAPO-34 was also prepared by hydrothermal method and VPT method using morpholine as SDA according to the procedures of Brent M. Lok and Hualan Zhou [2,20], the obtained samples were designated as S34-H-M and S34-V-M, respectively.

2.2. Characterization

The powder X-ray diffraction (XRD) patterns of as-synthesized samples were obtained on a Rigaku D/max-3C X-ray diffractometer with Cu Kα radiations under instrumental setting of 35 kV and 40 mA. The spectra were recorded from 5° to 40° with a step size of 0.02°. N₂ adsorption–desorption was performed at −196 °C using a Quantachrome AUTOSORB-1C instrument. Before the measurement, samples were degassed under vacuum at 300 °C for at least 10 h. The specific surface area (SBET) and the micropore volume were calculated according to Brunauer–Emmett–Teller (BET) equation and t-plot method, respectively. And the average pore diameter was estimated from the adsorption branches of the isotherms by the BJH method. Scanning electron microscope (SEM) images were recorded on a HITACHI S-570 scanning electron microscope. Prior to the image capture, each sample was placed onto a carbon membrane and Au sputtering coating was operating electron microscope. Prior to the image capture, each sample was washed with distilled water, and followed by drying at 120 °C for 4 h and calcination at 550 °C in air atmosphere for 5 h to remove the SDA. The obtained SAPO-34 samples in the presence of Mor and the mixture of 75% (volume) Mor-25% TEAOH were denoted as S34-L-M and S34-L-M-T, respectively.

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2.3. Catalytic evaluation

The catalytic tests of SAPO-34 for MTO reaction were carried out using an integral fixed-bed reactor (ϕ 32 mm × 650 mm) at atmosphere pressure. Catalyst (2 g, 40–60 mesh) was loaded into the stainless steel reactor. The sample was first pretreated in N₂ at 500 °C for 1 h and then the temperature of reactor was adjusted to 380 °C to start the MTO reaction. The weight hourly space velocity (WHSV) was 4.8 h⁻¹ for the feedstock of methanol. The reaction products were continuously analyzed using gas chromatograph (Wenlingfuli GC-9790) equipped with a flame ionization (FID) detector and an ATSE-30 capillary column.

3. Results and discussion

3.1. Crystalline structure and morphological features

Fig. 1 shows the wide-angle XRD patterns of the as-synthesized SAPO-34 molecular sieves. It can be seen that the representative diffraction peaks at 9.5°, 13°, 16.2°, 20.7°, 26° and 31° are observed in the XRD of all samples, corresponding to pure SAPO-34 with CHA-structure [19]. High peak intensity of XRD lines and absence of baseline drift indicate the high crystallinity without impurity for all samples. Of the four prepared samples, the intensity of these characteristic diffraction peaks for S34-L-M-T is the highest, indicating that the crystallinity and the phase purity of S34-L-M-T are better than that of the other three samples. Furthermore, the width of XRD diffraction peaks for S34-L-M-T is wider, illustrating that the crystallite size of S34-L-M-T is smaller.

SEM images of prepared SAPO-34 molecular sieves are shown in Fig. 2. Well-distributed cubic structures, typical for SAPO-34 crystal were observed. The average crystal size of S34-L-M-T sample is about 0.6 μm. While, S34-L-M, S34-H-M and S34-V-M samples have the similar average crystal size of about 3 μm. This finding is very consistent with XRD data. This is probably due to the addition of TEAOH during the synthesis of S34-L-M-T sample, and this is consistent with previous study showing that the crystals with larger size are obtained when only morpholine is used as the SDA [21]. The addition of TEAOH is beneficial to synthesize molecular sieves with small crystal size in the dry gel liquid-phase transport process. When the TEAOH is used as SDA, the TEAOH reacts easily with the pseudoboehmite, silica sol and orthophosphoric acid, therefore more nucleation centers are formed, and more molecular sieves with small crystal size are generated.

3.2. Nitrogen adsorption–desorption

The nitrogen adsorption–desorption isotherms and the pore structure characteristics of prepared SAPO-34 samples are illustrated in Fig. 3 and Table 1, respectively. All SAPO-34 molecular sieves display a type I isotherm with hysteresis loops originating from the mesopores formed between the crystal particles [22]. S34-L-M-T has the largest surface area and the smallest micropore volume among the four prepared samples, while the BET surface areas for S34-L-M, S34-H-M and S34-V-M samples using Mor as SDA are somewhat smaller because of their larger pore, and the micropore volumes of the three samples are approximately the same and in accordance with previous report [13]. The average pore diameters of S34-H-M and S34-V-M samples are larger
than that of the S34-L-M-T and S34-L-M samples because of the existence of more mesopores formed between their crystal particles.

3.3. NH$_3$-TPD

The NH$_3$-TPD profiles of the prepared SAPO-34 molecular sieves are presented in Fig. 4. Two desorption peaks in the TPD spectrum at 100–250 °C and 250–525 °C are primarily observed. In general, the desorption temperature represents the strength of acid sites, that is, the low temperature desorption peak at 100–250 °C is assigned to the weak acid sites, which corresponds to P–OH hydroxyl groups that are not fully coordinated by AlO$_4$ tetrahedra [6]. And the high temperature desorption peak at 250–525 °C is ascribed to the strong acidic sites which are generated by the incorporation of silicon into the framework of SAPO-34 molecular sieve [8]. As shown in Fig. 4, S34-L-M-T contains two temperature peaks centered at 176 °C and 428 °C, corresponding to the weak and strong acid sites, respectively. Compared with the S34-L-M-T, the peaks corresponding to weak acid sites of the S34-L-M and S34-V-M shift to the lower temperature, however, the peak of weak acid sites shifts to higher temperature for the S34-H-M. In terms of peaks at higher temperatures, the corresponding peaks of the S34-L-M, S34-H-M and S34-V-M all shift to the lower temperature. The desorption peak areas of the weak and strong acid sites for both S34-L-M-T and S34-L-M samples are almost the same, implying that they have the similar acid concentration for the weak and strong acid sites. S34-H-M contains more weak acidity and less strong acid acidity comparing to S34-L-M-T and S34-L-M samples. Regarding S34-V-M sample, the least acidity is observed in both weak acid sites and strong acid sites among the four prepared samples, and its intensity of strong acid sites is the weakest. According to the NH$_3$-TPD results, the catalysts synthesized by the dry gel liquid phase transport method have similar acid properties both in acid site concentration and strength no matter if the SDA is Mor or a mixture of Mor and TEAOH. The differences in the acid properties including acid site concentration and strength are observed when different synthesis methods are used with the same SDA. These properties will cause a different performance on the MTO process.

Fig. 2. SEM images of prepared SAPO-34 samples: (a) S34-L-M-T, (b) S34-L-M, (c) S34-H-M and (d) S34-V-M.

Fig. 3. The nitrogen adsorption–desorption isotherm of prepared samples.
Fig. 5. FT-IR spectra of prepared SAPO-34 samples.

Table 1
The pore structure characteristics of prepared SAPO-34 samples.

| Sample         | BET surface area \(\left(\text{m}^2 \text{ g}^{-1}\right)\) | Micropore volume \(\left(\text{cm}^3 \text{ g}^{-1}\right)\) | Average pore diameter (nm) |
|----------------|----------------------------------------------------------|----------------------------------------------------------|-----------------------------|
| S34-L-M-T      | 546.6                                                    | 0.26                                                     | 0.440                       |
| S34-L-M        | 463.2                                                    | 0.27                                                     | 0.435                       |
| S34-H-M        | 447.3                                                    | 0.28                                                     | 0.466                       |
| S34-V-M        | 425.3                                                    | 0.28                                                     | 0.473                       |

3.4. FT-IR spectroscopy

The FT-IR spectra of the prepared samples are given in Fig. 5. All characteristic peaks of the four molecular sieves are identical to those reported in the literature [23], according to which the basic framework vibration frequency region are as follows: the absorption peaks at 490 cm\(^{-1}\) and 632 cm\(^{-1}\) are \(\text{T}–\text{O}\) bending bands of \(\text{SiO}_2\) and \(\text{D}-\text{6}\) rings, respectively, and the bands at 730 cm\(^{-1}\) and 1095 cm\(^{-1}\) are the symmetric stretch vibration of \(\text{P}–\text{O}\) (or \(\text{Al}–\text{O}\)) and asymmetric stretch vibration of \(\text{O}–\text{P}–\text{O}\), respectively. Moreover, the peak at 1651 cm\(^{-1}\) corresponds to the vibration of hydroxyl groups from adsorbed water on samples. In addition, the broad peak centered at 3445 cm\(^{-1}\) corresponds to \(\text{Si}–\text{OH}\) and \(\text{P}–\text{OH}\) groups interacting through H-bonds [15]. In comparison of SAPO-34-H-M and SAPO-34-V-M samples, the intensity of all the vibration bands for SAPO-34-L-M-T and SAPO-34-L-M is stronger.

3.5. TG/DTG analysis

TG/DTG curves of the prepared SAPO-34 samples before calcinations are shown in Fig. 6. Four weight loss peaks are observed for S34-L-M-T precursor. It has two small weight loss peaks in the range of 100–243 °C and 243–322 °C [23], centered at 117 °C and 281 °C, respectively, which are attributed to the desorption of water from the molecular sieve with a weight loss of 0.34 wt.% and 0.46 wt.%, respectively, corresponding to desorption of physically and chemically adsorbed water. One significant weight loss (5.12 wt.%) in the temperature range of 322–490 °C centered at 432 °C is detected and could be related to the oxidative decomposition of morpholine. Meanwhile, another relatively gradual weight loss of 0.78 wt.% at 529 °C in the temperature range of 490–600 °C is observed, accompanied with a lower light olefins, aromatics and coke, therefore, the higher selectivity for ethylene and propylene is obtained. However, in terms of S34-L-M, S34-H-M and S34-V-M samples with larger crystal size, the methanol conversions are similar and reach to 100% after 400 °C. As temperature increases, the selectivity for ethylene increases, and the selectivity for propylene increases first and then decreases for all the three samples. The highest selectivity for ethylene is 45.72%, 52.43% and 45.7% at 440 °C, respectively. Moreover, the maximum of the selectivity for propylene on S34-L-M is 47.57% at 360 °C, while the selectivity on S34-H-M and S34-V-M is 44.47% at 340 °C and 45.1% at 360 °C, respectively. With temperature increases, the total selectivity for ethylene and propylene increases slowly first, reaches the maximum and then decreases, showing the same trend for the three samples. The highest total selectivity on S34-L-M is 84.37% at 400 °C, and that on S34-H-M and S34-V-M is 84.53% at 400 °C and 80.95% at 420 °C, respectively. For all prepared samples, the S34-L-M-T sample shows the most excellent performance for MTO process, this difference may arise from their different crystal morphologies and acid properties. The smaller the crystal size of S34-L-M-T is, the shorter the diffusion path is. The ethylene and propylene can diffuse out of the SAPO-34 pores easily before being converted to other additives such as higher olefins, aromatics and coke, therefore, the higher selectivity for ethylene and propylene is obtained. However, in terms of S34-L-M, S34-H-M and S34-V-M samples with larger crystal size, the diffusion path is longer, this presumably results in a second reaction along with a lower light olefin selectivity. The characteristic that both the intensity and amount of strong acid sites for S34-L-M-T are relatively high is another reason for the excellent performance in MTO process. It has been reported that the conversion of methanol to dimethyl ether
Fig. 6. TG/DTG curves of SAPO-34 samples: (a) S34-L-M-T, (b) S34-L-M, (c) S34-H-M and (d) S34-V-M.

Fig. 7. MTO performance over SAPO-34 catalysts at different reaction temperatures: (a) S34-L-M-T, (b) S34-L-M, (c) S34-H-M and (d) S34-V-M. (1) Methanol conversion. (2) Total selectivity for ethylene and propylene. (3) Selectivity for propylene. (4) Selectivity for ethylene. Reaction conditions: WHSV (MeOH) = 4.8 h⁻¹, P = 0.1 Mpa.
(DME) occurs mainly on the weak acid sites while the conversion of DME and methanol to light olefins occurs mainly on the strong acid sites [24]. It is worthy of noting that for all prepared samples, the selectivity for propylene is higher than that for ethylene at lower temperatures, and then decreases, while the selectivity for ethylene approaches the same at high temperatures. This may be ascribed to the change of pore size caused by coke deposition. When temperature is higher than 400 °C, the methanol conversion reaches 100%, the coke formation rate increases because more molecules are involved in the reactions, causing the reduction of the SAPO-34 pore size.

The methanol conversion and DME selectivity in products with time on stream over prepared SAPO-34 catalysts are shown in Fig. 8. S34-L-M and S34-V-M samples have 100% conversion of methanol at the initial stage and keep this activity without DME intermediate in products for 180 min and 150 min, respectively, and then DME increases rapidly. In the case of S34-H-M, only trace amounts of DME with a selectivity of 0.36% is detected after 180 min but then increases rapidly. Meanwhile, S34-L-M-T shows the longest catalyst longevity (the time when DME was observed from the beginning) for 240 min. This is mainly due to its smaller crystal size and more number of acid sites.

4. Conclusions

A dry gel liquid-phase transport method has been developed for synthesizing SAPO-34 molecular sieve. By using Mor and Mor–TEAOH as structure directing agents, SAPO-34 catalysts with regular cubic morphology and various crystal sizes were synthesized. The addition of TEAOH renders SAPO-34 with small crystal size. Compared to SAPO-34 prepared by conventional hydrothermal and VPT method, the SAPO-34 catalyst fabricated by dry gel liquid-phase transport method exhibits outstanding catalytic performance for MTO reaction. Among all catalysts, the S34-L-M-T catalyst displayed the best catalytic performance owing to its smaller crystal size and higher crystallinity. The conversion of methanol and selectivity to both ethylene and propylene reach 100% and 87.9%, respectively. The dry gel liquid-phase transport method could be extended to synthesize other molecular sieves due to its advantages, including the reusability of expensive structure directing agent, enhancing the efficiency of synthesis reactors, higher molecular sieve yield and reducing the use of structure directing agent.

Acknowledgments

The authors greatly thank the financial support from the Ministry of Science and Technology of the People’s Republic of China (Grant No. 2011BAD22B06), Chinese Academy of Sciences (XDA07070301 and Y2010022) and Postdoctoral Science Foundation of Qingdao, China. The authors also thank Dr. Zhanquan Zhang for his fruitful advices.

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