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Dry gel conversion as a suitable method for increasing the lifetime of SAPO-18 in MTO process

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ABSTRACT

The crystalline and pure SAPO-18 was synthesized by dry-gel conversion (DGC) methods (including steam-assisted conversion (SAC) and vapor phase transport (VPT)) and by conventional hydrothermal (CHT) method. The physicochemical properties of the catalysts were analyzed by XRD, FESEM, EDXS, and TPD techniques. It was found that the DGC methods have no significant effect on the crystallization time of SAPO-18. The catalysts with smaller crystallite size and in a higher solid yield were achieved by DGC methods. The results also revealed that DGC method changes significantly the acidic properties of SAPO-18 by affecting the amount and mechanism of silicon incorporation into the framework. The catalytic behavior of the samples was investigated in methanol-to-olefins (MTO) reaction. Although no considerable change was observed in light olefin selectivity over the samples, SAC method showed an increase of about 20% in useful lifetime of SAPO-18. It can be due to the smaller crystallite size and desirable acidic characteristic. Finally, the results were compared with those of DGC-synthesized SAPO-34 reported in the literature. It suggests that SAPO-18 synthesized by SAC method can be an acceptable alternative to SAPO-34 by exhibiting a comparable activity and longer lifetime in MTO process.

1. Introduction

The methanol-to-olefin (MTO) process is an economically attractive alternative for conversion of widely accessible raw materials such as natural gas to valuable and high-demand light olefins (Chen et al., 2005, 2004bib_Chen_et_al_2004; Wendelbo et al., 2002). Silicoaluminophosphate-34 (SAPO-34) has been researched widely as the most promising catalyst for MTO reaction due to the desired shape selectivity, moderate acidity and high hydrothermal stability (Wendelbo et al., 2002; Chen et al., 1999; Liang et al., 1990). Silicoaluminophosphate-18 (SAPO-18) is a crystalline microporous molecular sieve isostructural with aluminophosphate-eighteen (AEI) topology and structurally closely related to SAPO-34 (Chabazite topology) (Chen et al., 1994a). As found in the literature, it exhibits comparable catalytic performance to SAPO-34 in MTO process (Chen et al., 1994a, 1994bbib_Chen_et_al_1994b; Abdollahi et al., 2015; Nazari et al., 2015). SAPO-18 can be synthesized over wide range of Si/(Si + A1 + P) ratio (0–0.10) and has lower acid site concentration than SAPO-34 (Chen et al., 1994b). Because of the different shape of cages and the rigidity of the structure, its unit cells are more resistant to changing size under conditions of coke formation (Wragg et al., 2011). It has been also reported that the synthesis of SAPO-18 is more economical as compared to SAPO-34 due to the lower cost and consumption of the organic template in its synthesis gel (Aguayo et al., 2005). Given these positive characteristics, SAPO-18 can be a good alternative to SAPO-34 in MTO process.

Hydrothermal crystallization is the most well-known method for synthesis of the zeolites and zeotypes. Dry gel conversion (DGC) is a novel alternative technique for preparing of porous material, which was first suggested by Xu et al. (1990). This dry synthesis method can be further categorized into 1) steam-assisted conversion (SAC) and 2) vapor-phase transport (VPT) (Bandyopadhyay et al., 2002). The only difference between these two methods is how the template is added to the synthesis solution. The successful synthesis of several zeotypes of $AlPO_4$-5 (Bandyopadhyay et al., 2002; Chen et al., 2009), $AlPO_4$-11 (Chen et al., 2009), SAPO-34 (Askari et al., 2014; Zhang, 2013; Li et al., 2014; Yang et al., 2010;

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Hirota et al., 2010), SAPO-11 (Song et al., 2012) and MgAPO-36 (Saha et al., 2005) via SAC and VPT methods have been so far reported in the literature. DGC technique has outstanding advantages in comparison with conventional hydrothermal treatment (CHT). The uniform nanoparticles with high yield can be obtained by this method. It requires minimal template concentration, autoclave volume and energy (Bandyopadhyay et al., 2002). DGC is also suitable for investigating zeolite crystallization due to its simple reaction system where all the species are confined in the solid phase (Zhang, 2013).

SAPO-18, despite having a high potential for MTO process, has received less attention in the literature. To the best of our knowledge, there is no open report on the synthesis of SAPO-18 by dry gel conversion method. Therefore, in the present work, SAPO-18 molecular sieve was synthesized by CHT, SAC and VPT techniques. The effect of crystallization time on the synthesis of SAPO-18 by SAC method was investigated. Also physicochemical properties and catalytic activity of the DGC synthesized samples were studied and compared with those of the SAPO-18 prepared under hydrothermal conditions.

2. Experimental section

2.1. Synthesis of the catalysts

The synthesis of SAPO-18 by CHT was performed by following our previously reported procedure (Nazari et al., 2015). An appropriate amount of aluminum isopropoxide (98%, Merck) was first mixed with deionized water and was stirred strongly at room temperature for several hours. Then phosphoric acid (85%, aqueous solution, Merck) was diluted with deionized water and was dropwise added to the stirred mixture and was stirred vigorously for 1 h the silica sol (Ludox HS, 40% SiO_2, Aldrich) was dropwise added to the mixture and continued stirring for 1 h. Finally, N, N-diiso propylethylamine (98%, Merck) was gradually added to the solution. The resulting gel was allowed to be aged overnight under continuous stirring at room temperature and then was crystallized hydrothermally at 433 K in a 250 ml Teflon-lined stainless steel autoclave for 3 days.

In the SAC method, the synthesis solution was prepared as explained for the hydrothermal method. After aging, the resulting mixture was dried at 353 K in a paraffin bath with constant agitation to finally obtain a white dry gel. The solid sample was finely powdered and placed in a small Teflon cup (28 ml) located in the Teflon-lined stainless steel autoclave (250 ml). The amount of 0.4 g deionized water per gram of dried gel was put at the bottom of the autoclave so that there was no physical contact with dried powder. The samples were crystallized at 433 K for 2, 3 and 4 days. VPT method was carried out similar to SAC, but the synthesis gel did not contain the template. Instead, the template was mixed with small amount of water and is poured at the bottom of the autoclave. The dried powders were indirectly in contact with water and amine molecules via the vapor phase. Finally, crystallization was performed at 433 K for 3 days. The molar composition of initial hydrogel was $1Al_2O_3$:$0.9P_2O_5$:$0.4SiO_2$:$1.6C_8H_{19}N$:$50H_2O$ for CHT and SAC and $1Al_2O_3$:$0.9P_2O_5$:$0.4SiO_2$: $50H_2O$ for VPT. The as-synthesized catalysts were washed through distilled water and alcohol, dried at 363 K overnight and then calcined at 823 K for 6 h in order to completely remove the template.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on an Equinox 3000 diffractometer (Inel, France) using CuKa radiation ($\lambda = 1.5418$ Å). Field emission scanning electron microscope (FESEM) images was captured using a HITACHI S-4160 (China). The elemental composition of the catalysts was analyzed by energy dispersive X-ray spectrometer (EDXS). Temperature-programmed desorption of ammonia (NH_3-TPD) was conducted by a Pulsechemisorb 2705 apparatus equipped with a thermoconductivity detector. 0.2 g of sample was pretreated at 550 °C for 1 h and then cooled down to 100 °C under a dry He flow. The NH_3 gas stream was injected at the same temperature until adsorption saturation was reached. The sample was flushed with dry He to remove weakly adsorbed NH_3. Then the temperature was raised from 100 °C to 600 °C at a heating rate of 10 °C/min in the presence of helium flow.

2.3. Catalyst activity test

The catalytic reaction was performed at atmospheric pressure using a continuous downflow fixed bed microreactor with dimensions of 12 mm internal diameter and 20 cm length. A diagram of the reactor setup is schematically shown in Fig. 1. In this system, the aqueous methanol solution (Methanol/water weight ratio of 4:1) was first injected by a dosing pump (0.01–9.99 ml/min) and evaporated by a pre-heater at 473 K the gas feed was then directed to the reactor via a heat-traced tube. 2 g of the catalyst powder was diluted with quartz particles and loaded into the reactor. Previous to the reaction, the catalyst samples were pretreated under dry nitrogen flow at 723 K for 1.5 h. The reaction was carried out at the temperature of 698 K and constant weight hourly space velocity (WHSV) of 2 h^{-1}. A tube furnace was employed to heat up the reactor to the desired operating temperature. Two thermocouples were inserted in the middle of the catalytic bed and the reactor wall. Reactor temperatures were controlled by a proportional-integral-derivative (PID) controller and recorded by the time during the test automatically. The gas-phase products were analyzed on-line by gas chromatography using an Agilent 6890 equipped with flame ionization detector (FID) and HP-PLOT Q column.

The methanol conversion and the products selectivity were calculated from the carbon number of species. The light olefin selectivity was defined as the ratio of the sum of produced ethylene, propylene and butylene to all of the products. Also, product yield was calculated as the product of conversion and selectivity. The lifetime was defined as when light olefin selectivity began to drop down and the selectivity of dimethyl ether (DME) began to rise.

3. Results and discussion

3.1. Study of crystallization time in DGC method

Crystallization time played a key role in controlling the purity phase, crystal size and particles morphology. In order to study the optimum time for crystallization process of SAPO-18 in DGC method, three catalysts were synthesized at times of 2, 3 and 4 days by SAC method and effect of this parameter on the crystallinity, morphology and catalytic activity of the samples were investigated. Fig. 2 exhibits the powder XRD patterns of the calcined catalysts. As compared with AEI pattern, the patterns of all the samples confirmed the formation of a pure phase of SAPO-18. The low intensity of diffraction peaks of sample SAC(2days) suggests the poor crystallinity and coexistence of amorphous phase in the structure. The peak intensity and crystallinity rise with increasing the crystallization time to 3 days. Further increasing of the crystallization time did not reveal an appreciable change in the diffraction peaks.

Fig. 3 depicts the FESEM images of initial dry gel and the samples crystallized at 2, 3, and 4 days at two different magnifications (scale bars: 5 μm and 1 μm). The dry gel obtained via SAC method shows an uneven layered morphology. Irregular and non-uniform aggregates were observed after 2 days of crystallization. With prolonging