Particuology 27 (2016) 61–65

Contents lists available at ScienceDirect

Particuology

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

High-temperature synthesis of SAPO-34 molecular sieve using a dry gel method

Yazdan Rezaei[a], Rouein Halladj[a,*], Sima Askari[b], Ali Tarjomannejad[c], Tofan Rezaei[d]

[a] Department of Chemical Engineering, Amirkabir University of Technology (Tehran Polytechnic), P.O. Box 15875-4413, Tehran, Iran
[b] Department of Chemical Engineering, Science and Research Branch, Islamic Azad University, P.O. Box 14515.775, Tehran, Iran
[c] Department of Chemical Engineering & Petroleum, University of Tabriz, P.O. Box 51664-16471, Tabriz, Iran
[d] Chemistry Department, Islamic Azad University, Ilam Branch, P.O. Box 69319-86447, Ilam, Iran

ARTICLE INFO

Article history:
Received 10 November 2015
Received in revised form 30 January 2016
Accepted 4 February 2016
Available online 26 April 2016

Keywords:
SAPO-34
Rapid
High temperature
Dry gel method
Synthesis

ABSTRACT

SAPO-34 is one of the main catalysts used in the petrochemical industry. Various effective methods have been developed to synthesize SAPO-34 with optimal size and characteristics for such application. In the present study, SAPO-34 was synthesized using a dry gel method at high temperatures. Morpholine was used as an organic template. The products were characterized by X-ray diffraction, field-emission scanning electron microscopy, energy-dispersive X-ray spectroscopy, and gas sorption analysis. The results showed that application of the dry gel method at high temperatures successfully afforded a pure catalyst with high crystallinity. Small particles of less than 500 nm could be obtained within a short reaction time of 30 min.

Introduction

Silicoaluminophosphates, denoted as SAPO, are an important class of molecular sieves, wherein Brönsted acidic sites can be introduced upon substitution of Si into the neutral framework of AlPO4-*n* (Askari, Halladj, & Sohrabi, 2012b). Recently, SAPO-34 has attracted much attention because of its small pore size distribution, thermal/hydrothermal stability, medium acidity, and molecular sieving properties. Such characteristics enable good performance in the methanol-to-olefins process (MTO) (Dargahi, Kazemian, Soltanieh, Rohani, & Hosseinpour, 2011). Moreover, it is used as a membrane or an adsorbent in sorption reactions and as a catalyst in petrochemical reactions especially the MTO process (Bhawe et al., 2012). SAPO-34 exhibits high selectivity toward lower olefin production and affords complete conversion of methanol in the MTO reaction. However, owing to complete blockage of the internal channels of SAPO-34 crystals by coke, SAPO-34 is rapidly deactivated (Shalmani, Halladj, & Askari, 2012).

Recently, various synthesis methods have been successfully applied for the synthesis of nanoscale SAPO-34, resulting in a significant increase in its lifetime. Studies on the effect of crystal size of SAPO-34 on its selectivity and lifetime showed that crystals smaller than 500 nm have a longer lifetime in the MTO process than larger crystals (Askari, Halladj, & Sohrabi, 2012a; Jang, Min, Lee, Hong, & Seo, 2012; Nishiyama et al., 2009; Razavian, Halladj, & Askari, 2011; Wang, Lv, Hu, Xu, & Lu, 2011; Wang, Yang, Hu, Xu, & Lu, 2013). However, deactivation of nanoscale SAPO-34 with sizes less than 150 nm was rapid owing to coke generation (Jang et al., 2012). Among of the various synthesis methods, the hydrothermal method is a simple predominant strategy to synthesize SAPO-34 molecular sieves. The hydrothermal method is typically conducted in an autoclave at temperatures in the range of 180–200 °C. Furthermore, it requires an enclosed system and reaction times of approximately 24–72 h for the production of chabazite (CHA) and aluminophosphate-5 (known as AFI; the framework of the AFI single crystal consists of one-dimensional channels arrayed in a hexagonal structure). The formation of AFI, which is an impurity, is used as an indicator for confirming the formation of SAPO-5 (Dargahi et al., 2011).

The dry gel method has also been extensively studied (Hirota et al., 2010; Zhang, Bates, Chen, Nie, & Huang, 2011). Hirota et al. (2010) used the dry gel method in which tetraethylammonium hydroxide (TEAOH) was used as the organic template to synthesize particles of 75 nm in size. Additionally, the authors showed that the small catalysts possessed a long lifetime and that reducing the particle size improved the characteristics of the product.

* Corresponding author. Tel.: +98 64543151; fax: +98 21 66405847.
E-mail address: halladj@aut.ac.ir (R. Halladj).

http://dx.doi.org/10.1016/j.partic.2016.02.001

Typically, the dry gel method generates products containing 20–40% moisture (Zhang et al., 2011). In this method, high nucleation and low growth time lead to complete crystallization of SAPO-34 (Razavian et al., 2011). Dargahi et al. (2011) employed high temperatures to synthesize uniform SAPO-34 with high crystallinity at a temperature of 500 °C and a short reaction time of 45 min. The application of high temperatures ensures the synthesis of SAPO-34 only, thereby highlighting the high thermal stability of SAPO-34. Additionally, the X-ray results showed that using similar synthesis conditions, however, with varying percentages of organic template afforded SAPO-34 with varying sizes and levels of purity.

SAPO-34 can be synthesized through various templates. For instance, triethylamine (TEA) and TEAOH are suitable for the production of nano-sized particles. However, implementing TEA in the synthesis of SAPO-34 results in the formation of SAPO-5 as well. Moreover, TEAOH, which is the most commonly used template, is expensive, thereby increasing the cost of production (Shen et al., 2012; Wang, Wang, et al., 2011). Alternatively, to produce pure SAPO-34, morpholine is typically employed as the preferred template (Askari et al., 2012b); it can transform SAPO-5 into SAPO-34. However, its use commonly results in particle agglomeration, thereby generating large crystals of ~2 μm (Askari et al., 2012b).

In the present study, the synthesis of highly crystalline SAPO-34 with small crystal sizes was examined via a dry gel method at high temperatures using morpholine as the organic template.

Experimental

Sample preparation

SAPO-34 powder samples were synthesized by a dry gel method at high temperatures with the following gel molar composition of Al_2O_3:0.6SiO_2:P_2O_4:4morpholine:70H_2O. Al and P were supplied from aluminum isopropoxide (98% Al(O-i-Pr)$_3$, Merck, Germany) and H_3PO_4 (85 wt% aqueous solution, Merck), respectively. Morpholine (99 wt%, Merck) was used as the organic template, and tetraethylorthosilicate (TEOS) was used as the silica source.

In a typical experiment, Al(O-i-Pr)$_3$ was first mixed with morpholine and deionized water, and the mixture was stirred for 1 h. The silica source (TEOS or fumed silica) was then added to the mixture. Finally, with continuous stirring, H_3PO_4 solution was added dropwise to the above solution, followed by drying at 100 °C to obtain a dry gel. Six crystallization gel samples with the same molar composition were prepared and subjected to the different heating conditions listed in Table 1, as described subsequently.

The dry gel was then placed in a stainless steel autoclave. To investigate the effects of heating temperature and time on the final product, a small amount of water (g added water/g dried gel = 0.5) was added as the source of steam. After the heat treatment in autoclave, the solid product was recovered and washed three times by centrifuging with distilled water, followed by drying at 110 °C. The as-prepared crystals were then calcined at 560 °C in air for 5 h to remove the template. The final products are denoted as Samples 1–6 depending on the reaction temperatures and times employed (Table 1).

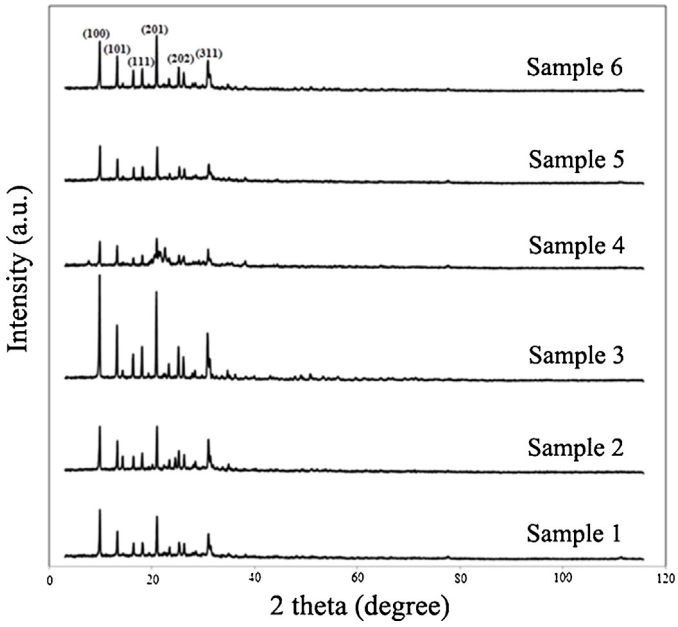

Fig. 1. XRD patterns of the synthesized samples. The reaction conditions employed for the different samples can be obtained from Table 1.

Characterization

Powder X-ray diffraction (XRD) patterns were recorded in a step-scanning mode on a PW3050 X-ray diffractometer (Philips, The Netherlands) using Cu-$K\alpha$ radiation (λ = 1.54 Å) operating at 40 kV and 40 mA. Particle morphology was analyzed by field-emission scanning electron microscopy (FESEM, ZEISS SIGMA VP, Germany). The particle size of the SAPO-34 samples was estimated by measuring the size of particles imaged during SEM analysis using a microstructure measurement software. The chemical composition of the calcined samples was determined by energy-dispersive X-ray spectroscopy (EDX, ZEISS SIGMA VP, Germany). The Brunauer–Emmett–Teller (BET) surface areas of the calcined samples were determined from the nitrogen adsorption isotherm data in the relative pressure (p/p_0) range of 0.05–0.30 obtained at 77.35 K using an Autosorb-1 (Quantachrome, USA) analyzer.

Results and discussion

XRD characterization

Fig. 1 illustrates the XRD patterns of the six SAPO-34 samples prepared at different reaction temperatures and times. All XRD patterns agreed with those of SAPO-34 structures reported in the literature (Askari et al., 2012b). The results indicated that using the high-temperature dry gel method, in general, afforded highly

Table 1
Synthesis conditions and analysis results of SAPO-34 samples.

Sample	Temperature (°C)	Time (min)	Particle size (nm)	Crystallinity (%)	Product	Si/Al	Surface area (m^2/g)
1	300	30	849–2000	52	SAPO-34	0.41	104.97
2	300	45	916–2300	55	SAPO-34	0.34	357.54
3	350	30	1504–3500	100	SAPO-34	0.37	192
4	350	45	1380–4200	38	SAPO-34, AlPO4	0.33	153.33
5	400	30	491–938	45	SAPO-34	0.42	44.5
6	400	45	634–1560	62	SAPO-34	0.63	402.53