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Synthesis and stability evaluation of hierarchical silicoaluminophosphates with different structural frameworks in the methanol to olefins process

Seyed Hesam Mousavi, Shohreh Fatemi*, Marjan Razavian

School of Chemical Engineering, College of Engineering, University of Tehran, P.O. Box 11365 4563, Tehran, Iran

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ABSTRACT

Silicoaluminophosphates (SAPOs) with different pore structures were synthesized through the implementation of polyethylene glycol (PEG) as a mesopores impregnation agent. Using PEGs with different molecular weights (MWs) and concentrations in the synthesis precursor, several samples were synthesized and characterized. Applying a PEG capping agent to the precursors led to the formation of tuned mesopores within the microporous matrix of the SAPO. The effects of the PEG molecular weight and PEG/Al molar ratio were investigated to maximize the efficiency of the catalyst in the methanol-to-olefin (MTO) process. Using PEG with a MW of 6000 resulted in the formation of both Zeolite Rho and chabazite structural frameworks (i.e., DNL-6 and SAPO-34). Pure SAPO-34 samples were successfully prepared using PEG with a MW of 4000. Our results showed that the PEG concentrations affect the porosity and acidity of the synthesized materials. Furthermore, the SAPO-34 sample synthesized with PEG (MW of 4000) and a PEG/Al molar ratio of 0.0125 showed a superior catalytic stability in the MTO reaction owing to the tuned bi-modal porosity and tailored acidity pattern. Finally, through reactivation experiments, it was found that the catalyst is stable even after several regeneration cycles.

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Introduction

Zeotype molecular sieves are the most widely used solid catalysts in industry owing to their microporous structures and the resulting unique shape selectivities. Silicoaluminophosphate-34 (SAPO-34), with the topological structure of chabazite (CHA), has been intensively studied as one of the best catalysts for the methanol-to-olefin (MTO) reaction. Such a process provides an alternate route to produce light olefins from non-petrochemical sources and has gained considerable attention in the last three decades (Sadeghpour & Haghghi, 2015).

The three-dimensional pore structure of the SAPO-34 molecular sieve consists of large cavities ($6.7 \times 10 \text{ \AA}$) separated by small windows ($3.8 \times 3.8 \text{ \AA}$). Its corresponding periodic building unit is the double 6-ring layer connected through 4-rings. In comparison with ZSM-5, the small entrances of the SAPO-34 molecular sieve cages located within 8-membered-rings (8-MR) only allow for the diffusion of linear hydrocarbons (Song, Fu, & Haw, 2001). Since aro-

matics and branched hydrocarbons are too large to pass through its 8-MR pores, light olefins are naturally predominant in the product streams. In addition, the cage shape and size of the SAPO-34 molecular sieve have been found to be suitable for preserving the reactive intermediates that selectively produce lower olefins (Rezaei, Halladj, Askari, Tarjomannejad, & Rezaei, 2016). Owing to the relatively moderate acidic strength and shape selectivity of the porous structure, high methanol conversion and selectivity toward light olefins can be achieved in the MTO reaction over the SAPO-34 catalyst (Dargahi, Kazemian, Soltanieh, Rohani, & Hosseinpour, 2011). The SAPO-34 catalyst, however, shows rapid deactivation arising from coke formation and encapsulation of the active sites, which completely blocks the internal channels of the structure during the MTO reaction. Such a phenomenon inhibits the access of reagents to the active sites located within the pores and wears out a huge part of the internal structure, which reduces the catalytic performance of SAPO-34 in the MTO process (Egeblad, Christensen, Kustova, & Christensen, 2007; Mozaffari et al., 2017).

Several attempts have been made to solve the issues related to the fast catalyst deactivation, such as synthesizing nano-sized zeolites (Tosheva & Valtchev, 2005), zeolite-ordered mesoporous materials (Laha et al., 2010), zeolites with secondary porosity made

* Corresponding author. Fax: +98 21 669667784.
E-mail address: shfatemi@ut.ac.ir (S. Fatemi).

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by steaming (Bernasconi, van Bokhoven, Krumeich, Pirngruber, & Prins, 2003), desilication (Groen, Peffer, Moulijn, & Pérez-Ramírez, 2004), procedures based on the confined space synthesis protocol (Schmidt, Madsen, & Jacobsen, 2000), and delaminated zeolites (Corma, Fornes, Martínez-Triguero, & Pergher, 1999). In this regard, hierarchical zeolitic structures are designated as zeolites with a bi/tri-modal pore size distribution, which exhibit reduced steric and diffusional restrictions (Cui, Zhang, He, Wang, & Wei, 2013; Serrano, Aguado, Escola, Rodríguez, & Peral, 2006).

Manipulating the nanocrystals into hierarchical nanoarchitectures using a self-assembly strategy is an efficient way to obtain structured catalysts with higher activities, longer life-times, and better selectivities (Zhao, Zhang, Huang, & Wei, 2012).

In recent decades, various methods have been developed to prepare hierarchical porous aluminosilicate zeolites, including post-treatment (Sommer et al., 2010), hard-templating (Jacobsen, Madsen, Houzvicka, Schmidt, & Carlsson, 2000), and soft-templating methods (Wu, Degirmenci, Magusin, Szyja, & Hensen, 2012). Notably, Choi, Cho et al. (2006) demonstrated a soft-templating synthesis of zeolites by introducing an organosilane surfactant as the mesoporosity impregnation agent into the conventional zeolite precursor. The authors further extended this strategy to synthesize mesoporous aluminophosphate molecular sieves (Choi, Srivastava, & Ryoo, 2006).

However, the development of an effective strategy for the formation of hierarchical SAPO-34 exhibiting excellent performance in MTO reactions is still a great challenge for the materials and chemical engineering, catalysis, and particuology communities.

In this contribution, a SAPO-34 molecular sieve with a tuned hierarchical nanostructure was synthesized through a facile one-step hydrothermal route using a combination of amine agents [i.e., tetraethyl ammonium hydroxide (TEAOH), diethyl amine (DEA)] and polyethylene glycol (PEG), as structure directing and meso-generating agents, respectively. As the addition of PEG polymer significantly affects the properties of the synthesis gel, the effects of the concentration and molecular weight (MW) of PEG on the physicochemical and structural properties of SAPOs were examined. Our investigations were focused on the introduction of tuned transport pores at the meso-scale to improve molecular diffusivity, enhance the accessibility of active sites within the cages, and reduce the intervention of small micropores (as they limit the diffusion of reactants and products). The proposed method would be inexpensive and easily reproducible for the high-yield production of SAPO-34 catalysts. The catalytic performance of the synthesized hierarchical SAPO samples in the MTO process was further investigated, with the aim to reveal the intrinsic correlation between the catalytic performance and the accessibility of the active sites, as well as the correlation between the accessibility and textural properties. Finally, the performance of different types of SAPO catalysts were compared with the conventional sample (free of PEG) to better understand the role of the tailored structure in the MTO process.

Experimental

Synthesis of catalysts

SAPO-34 molecular sieves were synthesized from a reaction mixture with a molar composition of 1 Al₂O₃: 0.5 SiO₂: 0.8 P₂O₅: 0.1 HCl: 1.8 DEA: 0.2 TEAOH: (*x*, MW) PEG: 60 H₂O, where *x* indicates the PEG/Al molar ratio and MW is the molecular weight of PEG. Initially, aluminum isopropoxide (98%, Merck, German) was dissolved in a mixed acidic solution (HCl: 37%, aqueous solution, Merck; and phosphoric acid: 85%, aqueous solution, Merck) under vigorous stirring. Tetraethyl orthosilicate (98%, Merck) was then

Table 1

Synthesis conditions for the as-synthesized hierarchical silicoaluminophosphate catalysts.

Sample name	PEG MW	PEG/Al molar ratio
4-0.025	4000	0.025
4-0.0125	4000	0.0125
6-0.025	6000	0.025
6-0.0125	6000	0.0125
Conventional	–	–

dissolved in a basic templates solution (TEAOH: 20%, Merck; and DEA: 99%, Merck) and the product was further added to the aluminum solution. In the next step, PEG (MW = 4000 and 6000, Merck) was added to the solution and the resulting gel was allowed to age and hydrolyze at room temperature for 24 h. Finally, the precursor gel was hydrothermally treated at 130 and 200 °C for 5 and 12 h, respectively. The solid product was recovered by centrifugation and washed four times, and then dried at 100 °C. To remove the organic template molecules from the material backbones, the samples were calcined at 550 °C for 5 h.

For comparison purposes, conventional SAPO-34 particles were synthesized through the same procedure without using the PEG soft template. The molecular weight of the used PEG and molar ratio of PEG to Al₂O₃ in the synthesized samples are presented in Table 1.

Characterization

X-ray powder diffraction (XRD) patterns were obtained using a D8 ADVANCE X-Ray (Bruker AXS, Germany) diffractometer (Cu K α radiation) in the 2 θ range of 2°–50°. The chemical composition of the solid samples was determined using a SPECTRO XEPOS X-ray fluorescence (XRF, Spectro, Germany) spectrometer. Field emission scanning electron microscope (FESEM) images were recorded using a Hitachi-S4160 microscope (Hitachi, Japan) operating at 30 kV. Nitrogen (N₂) adsorption–desorption isotherms were recorded using Bel-SORP MINI II apparatus (BEL, Japan). Textural properties, including total and micropore surface areas and volumes, were measured by the Brunauer–Emmett–Teller (BET) and t-plot methods. Micropore and mesopore size distributions were analyzed by micropore analysis (MP-plot) and Barrett–Joyner–Halenda (BJH) methods. Before the surface area measurements, the samples were degassed at 300 °C for 3 h. Fourier transform infrared (FT-IR) spectra were obtained using a PerkinElmer spectrometer (Spectrum GX, USA) in the frequency range of 4000–400 cm^{–1}. Temperature-programmed desorption (TPD) measurements were carried out with conventional apparatus (BELCAT-B analyzer, BEL). In a typical TPD measurement, 0.10 g of the sample was pretreated at 500 °C for 1 h under a helium flow to remove the adsorbed water. The sample was then saturated with ammonia (NH₃) at 100 °C for 1.0 h and then purged with a helium flow for 30 min to remove weakly adsorbed NH₃. The temperature was then increased at a heating rate of 10 °C/min ranging from 100 to 900 °C.

MTO reaction tests

The MTO reaction was carried out in a fixed-bed reactor at atmospheric pressure. 0.5 g of catalyst was loaded into the stainless-steel reactor. The reactor was 1.2 cm in diameter and 50 cm long. The temperature was measured by three thermocouples located above, below, and at the center of the catalyst bed. Furthermore, the temperature was controlled by three proportional–integral–derivative controllers (JOMO) with an accuracy of ± 1 °C. Before the MTO test, to activate the molecular sieve, the catalyst was pretreated in a N₂ flow at a reaction temperature of 400 °C for 1 h. Then a liquid mixture of methanol (30 wt%) in water was fed into the catalyst bed using a syringe pump accompanied with a N₂ stream (10 mL/min)

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