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Invited paper

DEA/TEAOH templated synthesis and characterization of nanostructured NiAPSO-34 particles: Effect of single and mixed templates on catalyst properties and performance in the methanol to olefin reaction

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ABSTRACT

A nanostructured NiAPSO-34 catalyst was hydrothermally synthesized and the effect of the template (diethylamine (DEA), tetraethylammonium hydroxide (TEAOH) and DEA/TEAOH) on the physicochemical properties and catalytic performance in the methanol to olefin (MTO) reaction was investigated. The samples were characterized by X-ray diffraction, field emission scanning electron microscopy (FESEM), particle size distribution analysis, energy-dispersive X-ray spectroscopy, Brunauer–Emmett–Teller analysis and Fourier transform infrared spectroscopy. The X-ray diffraction patterns indicated a higher crystallinity and larger crystallite size for the catalyst synthesized using the DEA template. The FESEM results indicated that the nature of the template could affect the morphology of the nanostructured NiAPSO-34 catalyst because of its effect on the rate of crystal growth. The catalytic performance of the samples was studied in the MTO reaction at atmospheric pressure and a space velocity of 4200 $cm^3/(g\,h^{-1})$ in a fixed bed reactor. The stability and activity of the NiAPSO-34 catalyst were improved using the DEA template because of its higher crystallinity, surface area and the greater extent of Ni incorporation into its framework. The possible stages of synthesis and the reaction mechanism for the MTO process over NiAPSO-34 are discussed in detail.

Introduction

The conversion of methanol to light olefins (the MTO reaction) has received much industrial attention because it reduces the dependency on the petroleum naphtha to produce highly desired ethylene and propylene products (Liu, Sun, Wang, Wang, & Cai, 2000; Travalloni, Gomes, Gaspar, & da Silva, 2008; Wei, Zhang, Liu, & Su, 2012; Xiang, Qian, Man, & Yang, 2014). Through the reforming process (Aghamohammadi, Haghighi, & Karimipour, 2013; Rahemi, Haghighi, Babaluo, Fallah Jafari, & Estifaee, 2013), natural gas readily produces a synthetic gas that can be converted to a number of liquid products such as methanol (Chu, Chen, Yu, Wang, & Fang, 2013; García-Trenco & Martínez, 2013; García-Trenco, Valencia, & Martínez, 2013; Li, Yuan, & Fujimoto, 2014). Methanol can be catalytically converted to various products such as gasoline and light olefins. This provides an indirect route for the conversion of fossil fuels to industrially valuable products (Dubois et al., 2003; García-Trenco & Martínez, 2013; Lunsford, 2000; Vora, Chen, Bozzano, Glover, & Barger, 2009).

The MTO reaction involves the formation of C—C bonds from C_1 fragments generated in the presence of acidic catalysts (Shen et al., 2012; Stocker, 1999). Among the devoted catalysts, the silicoaluminophosphate SAPO-34 molecular sieve with a pore size of 0.43–0.50 nm, 8-membered ring pores, high thermal stability, and relatively mild acidity exhibits the best performance in the production of light olefins (Aghamohammadi, Haghighi, & Charghand, 2014; Wang et al., 2011; Wu et al., 2013; Xu, Liu, Du, Wei, & Sun, 2004; Zhang, Bates, Chen, Nie, & Huang, 2011). SAPO-34 can only adsorb straight chain molecules, such as primary alcohols and

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linear olefins. The deactivation of this catalyst due to coke formation is a major disadvantage, which limits its lifetime in industrial processes (Álvaro-Muñoz, Márquez-Álvarez, & Sastre, 2013; Chen et al., 2014; Hulea et al., 2014; Lee et al., 2014; Liu, Tian, & Liu, 2012; Zhuang, Chen, Luo, & Xiao, 2014). Therefore, great effort has been made to improve the lifetime and selectivity of light olefins through modification of the SAPO-34 catalyst (Lee, Baek, & Jun, 2007; Stocker, 1999; van Niekerk, Fletcher, & O'Connor, 1996).

In particular, it has been shown that the isomorphous incorporation of heteroatoms into the SAPO-34 framework (MeAPSO-34) has a high selectivity toward ethylene and low selectivity toward methane formation. This occurs through the correction of catalyst acidity by creating new acid sites and framework distortions in the CHA-type material (Rajic, 2005; Tian, Ji, Lü, Bai, & Sun, 2013; Wei et al., 2008). The incorporation of heteroatoms into the SAPO framework can render them with a negative charge. If a divalent metal ion is substituted for Al(III), the framework will be rendered anionic, hence a Brønsted acid site is created in which the proton charge is balanced (Wei et al., 2008; Zhang et al., 2008). These Brønsted acid sites are formed only after removal of the positively charged organic template (through calcination) that resides in the framework pores (Rajic, 2005; Sena, de Souza, de Almeida, Cardoso, & Fernandes, 2011). It has been shown in this process that the organic species, especially amines and ammonium cations, play a key role during the synthesis of molecular sieve materials (Chae, Song, Jeong, Kim, & Jeong, 2010; Hu, Cao, Ying, Sun, & Fang, 2010; Zhu, Cui, Nawaz, Wang, & Wei, 2010). Besides acting as the structure-directing agent, space filling and charge compensating, they affect the degree of metal-ion substitution into the framework (Aghamohammadi et al., 2014; Alvaro-Munoz, Marquez-Alvarez, & Sastre, 2012). Therefore, in effective molecular sieve synthesis, the zeolite structure should adopt the electronic and geometric configuration of the template (Park et al., 2010).

A number of organic amines such as tetraethylammonium hydroxide (TEAOH), dipropylamine, morpholine, triethylamine (TEA), diethylamine (DEA), and mixed templates have been used in the synthesis of SAPO-34 (Alvaro-Munoz et al., 2012; Liu et al., 2008). Among these templates, DEA can produce SAPO-34 with high purity and crystallinity (Liu et al., 2008; Martínez-Franco, Moliner, Franch, Kustov, & Corma, 2012). In addition, TEAOH has shown excellent catalytic performance in the MTO reaction because of its appropriate particle size and has been widely investigated (Liu et al., 2012; Ye, Cao, Ying, Fang, & Sun, 2011). However, its relatively high cost may be a serious obstacle for commercial production. Consequently, the application of mixed templates rather than single templates may result in an increased catalyst lifetime while reducing the preparation costs (Lee et al., 2007; Liu et al., 2012).

The main objective of this paper is to use two different single templates and their combination (DEA, TEAOH, and DEA/TEAOH) for the synthesis of SAPO-34 with simultaneous Ni metal incorporation. According to previous reports, nickel-containing SAPO-34 exhibits high selectivity toward ethylene (Inoue, Dhupatemiya, Phatanasri, & Inui, 1999; Inui & Kang, 1997; Salmasi, Fatemi, & Taheri Najafabadi, 2011). In the literature, Ni incorporation has been reported only using one kind of template (Dubois et al., 2003; Inoue et al., 1999; Inui & Kang, 1997) that is different from that used in our procedure. In addition, the aim of this research (namely, the effect of the template on the degree of Ni substitution into the framework) and the experimental conditions differ from those reported in similar studies. In the present study, the effect of the template on the physicochemical properties of NiAPSO-34 catalysts is investigated. A number of techniques such as X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), particle size distribution analysis, energy-dispersive X-ray spectroscopy (EDX), Brunauer–Emmett–Teller (BET) analysis, and Fourier transform infrared spectroscopy (FTIR) are applied to characterize the obtained NiAPSO-34 catalyst. In addition, the catalytic performance of the samples in the MTO reaction is examined. The stages of catalyst synthesis and the MTO reaction mechanism over NiAPSO-34 are discussed in detail.

Materials and methods

Materials

Hydrothermal treatment was applied to prepare each of the Ni-substituted chabazite silicoaluminophosphate materials with DEA (Aldrich, 99%), TEAOH (Aldrich, 20%), and DEA/TEAOH (with a constant composition of 1:1) as the organic templates. Aluminum triisopropylate (Merck, 98%), fumed silica (Aldrich, 99.8%), phosphoric acid (Merck, 85%), and nickel nitrate hexahydrate (Merck) were used as the sources of aluminum, silicon, phosphorus, and nickel, respectively. Deionized water purchased from the Kasra Company was used to prepare the solutions.

Preparation and procedures

Three NiAPSO-34 samples with different single and mixed (DEA and TEAOH) templates were synthesized based on the hydrothermal method from a gel composition of $1Al_2O_3/0.6\,SiO_2/1P_2O_5/x\text{TEAOH}/y\text{DEA}/0.05\text{NiO}/70H_2O$ (x:y = 0:1, 1:0, 1:1). A typical preparation procedure of nanostructured samples with Ni incorporation is shown schematically in Fig. 1. The synthesized nanostructured NiAPSO-34 catalysts with the DEA, TEAOH, and DEA/TEAOH are denoted as NiAPSO-34(D), NiAPSO-34(T) and NiAPSO-34(DT), respectively.

The preparation procedure of the gel mixture is explained as follows: Aluminum triisopropylate and the TEAOH template (NiAPSO-34(T)) were dissolved in deionized water under stirring for 1.5 h. This was followed by the dropwise addition of an aqueous solution of phosphoric acid under stirring for 0.5 h. Fumed silica was then added to the solution and stirred for 0.5 h to achieve a uniform mixture. Next, nickel nitrate hexahydrate was added and the solution was stirred for 0.5 h. Finally, DEA was slowly added to the mixture as the template for NiAPSO-34(D) and NiAPSO-34(DT). At the beginning of the NiAPSO-34(T) catalyst synthesis, because of the high percentage of water in the TEAOH template structure (20 wt% TEAOH aqueous solution), weighted amounts of aluminum triisopropylate and TEAOH were dissolved and then the rest of the synthesis procedure was continued as previously described. The resultant gel was put in an autoclave where it was heated at 200 °C for 48 h. The solid product was removed by filtration, washed several times with distilled water and dried at 110 °C overnight. Finally, the nanostructured catalyst sample was calcined at 550 °C for 12 h to remove the organic template and the water trapped within the micropores.

Characterization techniques

The XRD patterns were recorded on a Bruker D8 Advance diffractometer (Cu Kα radiation 1.54178 Å) to identify the crystal phases in the range of $2\theta = 8°–50°$. The phase identification was made by comparing the measured data with the joint committee on powder diffraction standards (JCPDSs). The morphology of the nanostructured catalyst was investigated using a FESEM (Hitachi S-4160). The studied samples were covered with a thin gold film (deposited by ion sputtering) to improve their conductivity. The chemical composition of the nanostructured catalysts was determined using an SEM equipped with an EDX spectrometer for dot mapping (Scan

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