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Synthesis of highly selective and stable mesoporous Ni–Ce/SAPO-34 nanocatalyst for methanol-to-olefin reaction: Role of polar aprotic *N*,*N*-dimethylformamide solvent

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ABSTRACT

A series of mesoporous nanocrystalline silicoaluminophosphate (SAPO) zeolites (SAPO-34) were synthesized via an ultrasonic and microwave-assisted hydrothermal method in the presence of [3-(trimethoxysilyl)propyl]octadecyldimethylammonium chloride and cetyltrimethylammonium bromide surfactants as soft templates. Nickel and cerium were then doped on SAPO-34 using incorporation and impregnation methods, and all the catalysts were applied to the methanol-to-olefin (MTO) reaction. The catalysts were characterized using X-ray diffraction, field-emission scanning electron microcopy, inductively coupled plasma–atomic emission spectroscopy, transmission electron microscopy, Fourier-transform infrared spectroscopy, Brunauer–Emmett–Teller analysis, NH_3 temperature-programmed desorption analysis, and thermogravimetric analysis. For the impregnation method, the effect of using protic or aprotic solvents as impregnation media on the physico-chemical properties of the metal-based SAPO-34 was investigated. Water and *N*,*N*-dimethylformamide (DMF) were employed as the protic and aprotic solvents, respectively. The catalyst prepared using the aprotic DMF solvent exhibited higher dispersion and lower aggregation of metal species compared with that prepared using the protic water solvent. Furthermore, the sample synthesized using the incorporation method exhibited good catalytic performance; however, the Ni–Ce/SAPO-34 sample prepared using the impregnation method and aprotic DMF solvent exhibited superior catalytic performance in the MTO reaction.

Introduction

The increase in oil costs has drawn the attention of researchers to obtaining methanol from syngas as well as to the catalytic transformation process of this oxygenate compound. Moreover, public awareness of alternative energy sources such as coal, natural gas, and biomass that are used to provide fuels and raw materials is another issue associated with this enhanced attention (Aguayo, Gayubo, Vivanco, Olazar, & Bilbao, 2005). Since the 1970s, many researchers have been interested in methanol-to-olefin (MTO) conversion over microporous solid acid catalysts as an alternative process for olefin production (White, 2011). Various molecular sieves have been assessed for the MTO reaction in recent decades (Djieugoue, Prakash, & Kevan, 2000). Additionally, the roles of both the framework and acidity in controlling the performances of molecular sieves in the MTO reaction have been acknowledged (Chen, Bozzano, Glover, Fuglerud, & Kvisle, 2005). The aluminosilicate zeolite ZSM-5 and silicoaluminophosphate (SAPO) molecular sieve SAPO-34 are generally considered efficient catalysts for the MTO reaction. The use of SAPO-34 with chabazite cages and an eight-ring pore opening significantly improved the selectivity toward light olefins compared with the use of ZSM-5 (Liang et al., 1990; Wu, Guo, Xiao, & Luo, 2013). Aluminophosphate ($AlPO_4$)-based molecular sieves, however, are considered microporous materials and cannot be directly applied as acidic catalysts because of their neutral frameworks, which contrast with the negatively charged frameworks of zeolites. Nevertheless, a negatively charged framework can be produced by introducing Si into the $AlPO_4$ framework. Hence, the resulting SAPO-34 silicoaluminophosphates can be used as MTO reaction catalysts (Zhang, Bates, Chen, Nie, & Huang, 2011). However, the deposition of high-molecular-weight hydrocarbons at the pore entrances

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causes SAPO-34 catalysts to experience rapid deactivation and likely obstructs the internal cages of the SAPO-34 crystals (Chen, Moljord, Fuglerud, & Holmen, 1999; Qi et al., 2007).

Numerous researchers have proposed that the properties and applications of these catalysts would be greatly affected by the size and morphology of the crystallites. The diffusion limitations of the guest molecules in the micropores yield a strong correlation between SAPO-34 catalyst performance and its particle size (Chen et al., 1999; Hirota et al., 2010). Despite weakening the catalyst deactivation with the blockage of pore openings, nanozeolite crystals are still considered when a short inner diffusion path is adopted in MTO reactions. In addition, to improve the mass transfer property of the catalyst and increase the number of catalyst pore openings, mesopores with various forms obtained through HF etching (Xi et al., 2014), hard templating (Jacobsen, Madsen, Houzvicka, Schmidt, & Carlsson, 2000), and soft templating (Choi, Srivastava, & Ryoo, 2006) have been introduced into the zeolite crystal. These two features have positive effects on catalyst anti-deactivation. However, various approaches such as synthesis with mixed templates (Sadeghpour & Haghighi, 2015) or microwave-assisted and ultrasonic synthesis of SAPO-34 (Pajaie & Taghizadeh, 2015) have been employed to synthesize SAPO-34 with a smaller crystal size.

Another method involves modifying the zeolite with metal cations, leading to modification of the density and strength of the acid sites and, thus, increasing the selectivity toward light olefins and/or catalyst lifetime. Furthermore, the use of metal ions reduces the formation of methane. The type of modification method (incorporation, impregnation, or co-precipitation) and metal used thus appear to yield very different results.

Salmasi, Fatemi, and Najafabadi (2011) studied the incorporation of metal ions such as nickel and magnesium in the structure of SAPO-34 synthesized by mixing tetraethylammonium hydroxide (TEAOH) and morpholine templates. The introduction of metal ions affected the acidity and improved the catalytic activity of the SAPO-34 catalyst in the MTO process. The catalyst modified with nickel exhibited the best performance. Sun et al. (2012) investigated the catalytic performance of nano-Au/ZSM-5 in the methanol-to-propylene process. They observed that gold nanoparticles reduced the dehydrogenation reaction rate, leading to retardation of coke formation, thereby increasing the lifetime of the catalyst. The catalytic performance of ZSM-5 and SAPO-34 in the catalytic cracking of naphtha was also investigated by Varzaneh, Towfighi, and Mohamadalizadeh (2014). In their research, cerium and zirconium were used to modify the zeolite using the impregnation method. The catalytic performance of zeolite was also enhanced by introducing metal ions. Ce–Zr/ZSM-5 and Ce–Zr/SAPO-34 exhibited better catalytic performance than the other samples. Moreover, the effect of the metal chloride on the catalytic performance of SAPO-34 in the MTO reaction has been studied by Jiang et al. (2015). In their study, SAPO-34 was modified with metal cations using the impregnation method. They reported that different metal ions had completely different effects on the acidity of the catalysts. In addition, the sample modified with Fe exhibited lower acidity, and the catalyst had a longer lifetime than the other samples. Sedighi, Ghasemi, Sadeqzadeh, and Hadi (2016) studied the incorporation of Ni, Ce, Fe, and La into the framework of SAPO-34. They observed that introducing the metals led to improvement of the catalytic performance of SAPO-34. The sample modified with Ce exhibited better catalytic performance than the other samples.

In this study, the mesoporous SAPO-34 catalyst was synthesized by employing an ultrasonic and microwave-assisted hydrothermal method and [3-(trimethoxysilyl)propyl]octadecyldimethylammonium chloride ($[(CH_3O)_3SiC_3H_6N(CH_3)_2C_{18}H_{37}]Cl$ (TPOAC)) and cetyltrimethylammonium bromide (CTAB) surfactants as mesoporogen agents. The nickel and cerium oxides were loaded on mesoporous SAPO-34 using incorporation and impregnation methods. The impregnation process was performed using a protic and an aprotic solvent. Moreover, the effects of water and *N*,*N*-dimethylformamide (DMF) as the protic and aprotic solvents, respectively, on the physico-chemical properties of metal-based mesoporous SAPO-34 were studied. The synthesized catalysts were characterized using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), inductively coupled plasma–atomic emission spectroscopy (ICP-AES), transmission electron microscopy (TEM), Fourier-transform infrared (FT-IR) spectroscopy, Brunauer–Emmett–Teller (BET) analysis, NH_3 temperature-programmed desorption (NH_3-TPD) analysis, and thermogravimetric analysis (TGA). Finally, the catalytic performance of these catalysts in the MTO reaction was evaluated under the same operating conditions in a fixed bed reactor.

Experimental

Chemicals and regents

Tetraethylorthosilicate (TEOS, 98 wt%), orthophosphoric acid (H_3PO_4, 85 wt%), aluminum isopropoxide ($Al(i\text{-}C_3H_7O)_3$, AIP, 99 wt%), tetraethylammoniumhydroxide (TEAOH, 25 wt%), cetyltrimethylammonium bromide (CTAB, 99 wt %), $Ce(NO_3)_3{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and *N*,*N*-dimethylformamide (DMF, 99 wt%) were purchased from Merck. In addition, [3-(trimethoxysilyl)propyl]octadecyldimethylammonium chloride ($[(CH_3O)_3SiC_3H_6N(CH_3)_2C_{18}H_{37}]Cl$, TPOAC, 72 wt%) was purchased from Sigma–Aldrich. All the chemicals were used as received without further purification.

Catalyst preparation

SAPO-34 synthesis

Mesoporous SAPO-34 was synthesized hydrothermally with a molar composition of 1 Al_2O_3:1 P_2O_5:0.4 SiO_2:2 TEAOH:0.042 TPOAC:0.032 CTAB:70 H_2O. Briefly, certain amounts of AIP, TEAOH, and H_2O were mixed. After complete dissolution, the surfactants (including CTAB and TPOAC) were added to the suspension. Afterwards, TEOS and phosphoric acid were gradually added. Next, a microwave oven was used to heat the suspension at 200 W for approximately 1 h, followed by sonication for 15 min at room temperature. The gel obtained was transferred to a 200-mL Teflon-lined stainless-steel autoclave and then heated in an oven at 200 °C for 18 h. The resultant product was centrifuged and washed several times with deionized water. Finally, the product was dried at 110 °C for 12 h and calcined at 550 °C for 6 h.

Ni–Ce/SAPO-34 synthesis using incorporation method

Ni–Ce/SAPO-34 was synthesized using the incorporation method with a molar composition of 1 Al_2O_3:1 P_2O_5:0.4 SiO_2:2 TEAOH:0.042 TPOAC:0.032 CTAB:0.006 NiO:0.012 CeO_2:70 H_2O. The Ni–Ce/SAPO-34 sample was synthesized using a procedure similar to that used to the prepare SAPO-34. An aqueous salt solution was added to the gel only after complete preparation of the final gel of SAPO-34, and the suspension was stirred for 1 h. The subsequent steps were analogous to those described above. The catalyst synthesized using the incorporation method was called Ni–Ce/SAPO-34(IN).

Ni–Ce/SAPO-34 synthesis using impregnation method

Ni–Ce/SAPO-34 was prepared by sequential impregnation of cerium nitrate hexahydrate ($Ce(NO)_3{\cdot}6H_2O$) and nickel nitrate hexahydrate ($Ni(NO)_3{\cdot}6H_2O$). First, a calculated amount of calcined SAPO-34 was immersed in an aqueous solution of cerium nitrate. The concentration of metal nitrate in the aqueous solution was

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