Microporous and Mesoporous Materials 226 (2016) 331–343

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

One-pot hydrothermal synthesis of nanostructured ZrAPSO-34 powder: Effect of Zr-loading on physicochemical properties and catalytic performance in conversion of methanol to ethylene and propylene

Erfan Aghaei [a, b], Mohammad Haghighi [a, b, *], Zahra Pazhohniya [a, b], Sogand Aghamohammadi [a, b]

[a] Chemical Engineering Faculty, Sahand University of Technology, P. O. Box 51335-1996, Sahand New Town, Tabriz, Iran
[b] Reactor and Catalysis Research Center (RCRC), Sahand University of Technology, P. O. Box 51335-1996, Sahand New Town, Tabriz, Iran

ARTICLE INFO

Article history:
Received 21 March 2015
Received in revised form
30 January 2016
Accepted 1 February 2016
Available online 9 February 2016

Keywords:
ZrAPSO-34
Zr-loading
Methanol
Olefins
MTO

ABSTRACT

Nanostructured ZrAPSO-34 catalyst was successfully synthesized via hydrothermal method and Zr isomorphously was substituted into the framework of SAPO-34. The effect of various Zr loadings on the physicochemical properties and catalytic performance was investigated. The structure of the synthesized catalysts was characterized using XRD, FESEM, EDX, BET, FTIR, NH_3-TPD and DR-UV-Vis techniques. For samples with low Zr content, relative crystallinity increased and intact CHA structure produced. However, by further Zr loading, relative crystallinity strongly reduced. Acidity results confirmed that Zr incorporation led to increase in both acid sites concentration and strength. Characterization results confirmed the successful incorporation of Zr into SAPO-34 framework. ZrAPSO-34 and SAPO-34 catalysts were applied in methanol to olefins reaction. The Zr incorporation and Zr content have significant effects on the lifetime and product selectivity. For the samples with low Zr content, catalytic lifetime was prolonged compared to the sample synthesized without metal. However by increasing Zr loading, it was reduced and methane selectivity was increased.

1. Introduction

Light olefins are key chemical intermediates in the petrochemical industries that a lot of value added products produced from them. In recent decades, the increasing global demand for light olefins led to a gap between light olefins demand and supply. Generally, light olefins were produced from thermal and catalytic cracking of naphtha which require high temperature and have low light olefins yield [1,2]. Limitation for crude oil sources and the prediction of growth in oil prices in future are the reasons for the raised attention to the development of new technologies for production of light olefins from non-oil sources. Methanol to olefins (MTO) process could be one of the proper routes for production of light olefins in the future [3–5]. Methanol can be produced from non-oil sources such as natural gas, coal and biomass. Due to the importance of MTO process, research in various aspects of this process has been carried out in the last decades [6–8].

There are many solid acid catalysts such as ZSM-5, SAPO-11, SAPO-17, SAPO-18, SAPO-34 and SAPO-35 which have been employed in MTO process [9–15]. The SAPO-34 catalyst is the most promising catalyst for the MTO process giving up to 90% light olefins selectivity and complete methanol conversion at mild conditions [16–18]. SAPO-34 catalyst has the chabazite (CHA) structure with 8-member rings and entrance diameter of 0.38 nm [18,19]. It is the best catalyst for MTO process due to the small pore size, moderate acidity and well thermal/hydrothermal stability [20]. The main problem of SAPO-34 catalyst is the rapid deactivation by coke deposition that leads to the complete blockage of channels and cages [21]. Hence, SAPO-34 catalyst has short lifetime in MTO process. Therefore, lifetime enhancement of the SAPO-34 catalyst in MTO process seems to be necessary.

---

* Corresponding author. Reactor and Catalysis Research Center, Sahand University of Technology, P. O. Box 51335-1996, Sahand New Town, Tabriz, Iran. Tel.: +98 41 33458096, +98 41 33459152; fax: +98 41 33444355.
E-mail address: haghighi@sut.ac.ir (M. Haghighi).
URL: http://rcrc.sut.ac.ir

http://dx.doi.org/10.1016/j.micromeso.2016.02.009
1387-1811/

Up to now, many efforts have been made to promote the performance of SAPO-34 catalyst in the MTO process in several points of view like increasing light olefins selectivity, reducing methane formation and increasing lifetime [22–26]. Small particle size has strong effect on increasing lifetime and also reducing methane formation [24]. In our previous work, we synthesized SAPO-34 catalyst at moderate temperature with controllable particle size that the corresponding catalyst lifetime was significantly increased [16]. In another work in our group, SAPO-34 synthesized with ultrasound assisted hydrothermal method that indicated increased lifetime, remarkably [18]. Many metal ions have been incorporated into the framework of SAPO-34 including Ni, Mg, Mn, Zn, Co and Fe. Modified samples showed improved light olefins selectivity and/or longer lifetime [22,23,27–30]. Incorporation of metal ions is common method in order to improve the catalytic performance of SAPO-34 by reduction or controlling of methane and coke formation [28,31]. Isomorphs substitution of metal ions into the structure of SAPO-34 changes the density and strength of the acid sites, cage size and consequently catalytic performance of SAPO-34 [32]. Dubois et al. incorporated Co, Ni and Mn metals into SAPO-34 catalyst and reported that MnSAPO-34 has longer lifetime compared to SAPO-34 [30]. Salmasi et al. modified SAPO-34 with Ni and Mg metals and concluded that incorporation of Ni improved light olefins selectivity and lifetime due to the controlling of catalyst acidity [23]. In another work in our group, SAPO-34 lifetime increased by isomorphously substitution of Ce into the SAPO-34 structure templated by morpholine [33]. Metal incorporation has different effects on olefins selectivity and lifetime. Behbahani et al. reported that modified ZSM-5 with Sr showed shorter lifetime than the unmodified catalyst [34]. So, catalytic performance of MeAPSO-34 can be attributed to the type of metal and synthesis conditions. Zirconium due to high mechanical strength and proper thermal resistance has been used in thermal and catalytic cracking of naphtha [2]. Up to now, few researches have been reported concerning modification of SAPO-34 by zirconium [2]. Varzaneh et al. modified SAPO-34 and ZSM-5 by impregnation of ZrO_2 [2]. Results of XRD analysis showed that structure of SAPO-34 remained intact due to using impregnation method. By ZrO_2 impregnation concentration of middle and strong acid sites increased and catalyst lifetime promoted. It is expected that incorporation of Zr into the structure of SAPO-34 leads to the promotion of physicochemical properties and resultantly catalytic performance in MTO process.

To the best our knowledge, using Zr for the modification of SAPO-34 catalyst with isomorphous substitution in order to improve its catalytic performance has not been reported in the literature. In this investigation, we used Zr for the enhancement of catalytic properties of SAPO-34 in MTO process and isomorphously substituted into the framework of SAPO-34. Therefore, SAPO-34 catalysts were synthesized via hydrothermal method with using various Zr contents. Then complete study of the physicochemical properties of the synthesized catalysts was carried out by XRD, FESEM, EDX, BET, FTIR NH_3-TPD and DR-UV-Vis techniques. Finally, synthesized ZrAPSO-34 catalysts were used as an acid catalyst in MTO process. This work suggests optimum Zr content for the enhancement of SAPO-34 applied in MTO reaction.

2. Materials and methods

2.1. Materials

Aluminum triisopropylate (Merck, 98%), phosphoric acid (Merck, 85% aq. solution) and fumed silica (Aldrich, 99.9%) were chosen as precursor for Al, P and Si, respectively. The zirconium nitrate hexahydrate (Aldrich) was used as precursor for Zr. Tetraethyl ammonium hydroxide (Aldrich, 20% aq. solution) was used as organic structure directing agent (SDA). The deionized water was applied as synthesis medium.

2.2. Preparation and procedures

The schematic of preparation steps of ZrAPSO-34 is shown in Fig. 1. The precursor gel was prepared in three stages. At first, 10.90 g aluminum triisopropylate, 38.50 g TEAOH and sufficient amount of deionized water were mixed under stirring at room temperature. After 90 min, 0.95 g fumed silica was added to the obtained mixture and stirred for 1 h. Then, 6.03 g aqueous solution of phosphoric acid was added drop wise while stirring for 1 h. In the final step of gel preparation, sufficient amount of zirconium nitrate hexahydrate blended with the obtained gel. The resulting solution was aged at room temperature for 24 h under stirring to obtain a homogeneous white gel. In order to change Zr content in the synthesized catalysts, various contents of zirconium nitrate were selected and added to the initial gel. The molar composition of the synthesis gel was $1Al_2O_3:1P_2O_5:0.6SiO_2:xZrO_2:2TEAOH:70H_2O$. The implemented amounts of x were 0.0, 0.01, 0.05, 0.1, and 0.15. The obtained gel was transferred into a teflon lined stainless steel autoclave with a volume of 90 ml and kept in an oven at 200 °C for 48 h. After crystallization process and cooling to the room temperature, the solids product were washed with deionized water, filtered and dried at 110 °C. In order to remove the organic template and generation of the Brønsted acid sites, the dried samples were calcined at 550 °C for 12 h. All the synthesized catalysts powder were pelletized by tablet press machine and then crushed to particles with diameter of 1–2 mm. The synthesized samples were labeled according Zr loading. As an example, synthesized catalyst with 0.05 molar ratio of ZrO_2 denoted as $Zr_{0.05}$APSO-34.

2.3. Characterization techniques

X-Ray Diffraction (XRD) was performed on a Bruker D8 Advance diffractometer, using standard X-ray powder diffraction with a CuKα radiation source in the 2θ range of 8 to 50°. Morphology of synthesized catalysts was investigated using Field Emission Scanning Electron Microscopy (FESEM), HITACHI S-4160 analyzer. In order to improve conductivity and resolution of images, thin layer of gold covered on samples. The samples were prepared as thin self-supporting wafers with 10 wt. % of samples powder in KBr. The chemical compositions of the synthesized samples were analyzed by Energy Dispersive X-ray analyzer (EDX, Cam Scan MV2300). The Brunner–Emmett–Teller (BET) surface area was measured using nitrogen adsorption/desorption isotherms by a micrometric analyzer (Quantachrome ChemBET 3000). Fourier transform infrared spectra (FTIR) were recorded by a UNICAM 4600 FTIR spectroscopy. The spectrum was in the range of 400–4000 cm^{-1} in order to address surface functional groups. Catalysts acidity was measured by ammonia temperature programmed desorption using BELCAT analyzer with a TCD detector. Before analysis, 0.1 g of calcined sample was preheated at 550 °C for 60 min under a 50 cm^3/min helium gas flow. Ammonia adsorption was made from a mixture of 5% (molar basis) of ammonia in helium under total flow rate of 50 cm^3/min at 100 °C. After adsorption of ammonia, the samples were kept under a helium gas flow at 100 °C to remove physically adsorbed gases. Finally, the helium flow (50 cm^3/min) was passed through the sample with increasing temperature up to 700 °C at a rate of 10 K/min. Diffuse reflectance UV–Vis spectra of the synthesized samples were recorded using a Scino-S4100 UV–Vis spectrophotometer.