Molecular Catalysis 438 (2017) 86–92

Contents lists available at ScienceDirect

Molecular Catalysis

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

MCAT

Controlling size and acidity of SAPO-34 catalyst for efficient ethylene to propylene transformation

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ARTICLE INFO

Article history:
Received 7 February 2017
Received in revised form 22 May 2017
Accepted 22 May 2017

Keywords:
SAPO-34 catalyst
Ethylene to propylene reaction
Heterogeneous catalysis
Crystal size
Acidity

ABSTRACT

Acidity- and size-controlled SAPO-34 zeolites were prepared via a hydrothermal method by controlling the type and ratio of the structure-directing agents (SDA) such as tetraethylammonium hydroxide (TEAOH) and/or morpholine (MP). The SAPO-34 catalysts were applied and tested for their ability to convert ethylene to propylene (ETP) directly. The propylene formation from ethylene showed a volcano-type trend with a crystal size of 0.3–13 μm of the SAPO-34 zeolite by changing the ratio of TEAOH and MP. In addition, the propylene yield increased with an increase in the Si/(Si + P + Al) ratio from 0.042 to 0.105 and decreased at a Si/(Si + P + Al) ratio of 0.119. The results show that the proper size and acidity of the SAPO-34 catalyst with controlling the ratio of TEAOH and MP are required for an efficient ETP transformation process. The improved catalytic performance achieved while controlling the size and acidity may be related to number and strength of the active acid sites on the SAPO-34 zeolite.

1. Introduction

Propylene is an important raw material for the production of polypropylene, acrylonitrile, and propylene oxide [1–3]. Due to the greater levels of need for propylene derivatives such as polypropylene, the production of propylene has received much attention recently. To meet the increasing demand for propylene, several strategies, such as propane dehydrogenation and the metathesis of ethylene and 2-butene, have been developed for propylene production [4–9]. More recently, the direct conversion of ethylene to propylene (ETP) was proposed as a new process for the production of propylene [10–18]. This would be an interesting reaction process by which to produce propylene, particularly when it is combined with the industrial processes of ethane cracking to ethylene and the dehydration of ethanol/bio-ethanol to ethylene.

Several types of zeolites have been studied as potential ETP catalysts [10,13,15–17]. The acidity and the pore structure of zeolites were considered as the critical factors controlling the ETP reaction [16,17]. SAPO-34 and SSZ-13 zeolites with chabazite (CHA) cages connected via 8-ring windows for application to the ETP reaction have been reported in some studies, which show levels of high ethylene conversion and propylene selectivity [10,13,15,19,20]. The high propylene selectivity with CHA zeolites is related to shape selectivity caused by the small pores of the CHA zeolite [13,16]. It has been reported that the particle size of the SAPO-34 zeolite influences the degree of propylene selectivity and the production rate for the ETP reaction and that the acid strength of SAPO-34 is independent of the Si mole fraction, having little influence therefore on the degree of propylene selectivity [15]. The SSZ-13 zeolite had relatively high propylene selectivity compared to the SAPO-34 zeolite, but the catalyst was deactivated very rapidly [10]. We recently reported that the activity and selectivity for the ETP reaction were changed by controlling the SiO_2/Al_2O_3 ratios (silica/alumina ratios or SARs) of SSZ-13 catalysts [21]. Compared to the SSZ-13 zeolites, the SAPO-34, which is known as a methanol to olefins (MTO) catalyst, can be easily synthesized with relatively cheap templates. It also can be prepared in the wide range of crystal size and Si/(Si + P + Al) ratio. Therefore, CHA zeolite systems such as the SAPO-34 can provide a considerable amount of information to those attempting to design active and selective catalysts and to understand the reaction chemistry of the ETP reaction; however, very few studies have been devoted to direct ETP reactions using SAPO-34 zeolites.

In this work, a systematic study of the ETP reaction over a small-pore SAPO-34 molecular sieve was conducted in an effort to find

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http://dx.doi.org/10.1016/j.mcat.2017.05.021
2468-8231/

ways to increase the propylene yield and change the product distribution by controlling the crystal size and acidity. SAPO-34 zeolites with different crystal sizes and acidity levels were synthesized via a hydrothermal method by controlling the type and ratio of the structure-directing agent (SDA), after which they were characterized by various physicochemical analyses. The propylene yield and product distribution of other hydrocarbons were investigated when ethylene was reacted over the size- and acidity-controlled SAPO-34 catalysts.

2. Experimental

2.1. Preparation of acidity and size-controlled SAPO-34 catalysts

SAPO-34 zeolites with different crystal sizes and acidity levels were synthesized via a hydrothermal method while controlling the type and ratio of SDA. First, a gel solution was prepared with a gel molar composition of 0.3 SiO_2: 1 Al_2O_3: 2 SDA: 1 P_2O_5: 52H_2O with fumed silica (Aerosil 380) as a silica source, aluminium isopropoxide (Samchun Corp. 98%) as an alumina source, phosphoric acid (Samchun Corp. 85%) as a phosphorous source, and tetraethylammonium hydroxide (TEAOH, Sigma-Aldrich 25%) and/or morpholine (MP, Sigma-Aldrich 99%) as the SDA. The total molar ratio of SDA (including MP and TEAOH) was fixed at 2.0. To control the crystal size and acidity of the SAPO-34, the amount of MP was varied from 0 to 2.0. Note that MP 0, MP 1.0, MP 1.3, MP 1.5, MP 1.8 and MP 2.0 mean that the molar ratio of MP:TEAOH is 0.0:2.0, 1.0:1.0, 1.3:0.7, 1.5:0.5, 1.8:0.2 and 2.0:0.0, respectively. The prepared gel solution (MP 0–MP 2.0) was stirred for 24 h at room temperature. The solution was then transferred to a Teflon-lined autoclave with a rotary gear oven and crystallized at 180 °C for 24 h. After the crystallization process, the resulting solid samples were filtered, washed and then dried in an oven at 110 °C for 12 h. To remove the organic SDA, a calcination process was carried out at 550 °C for 6 h under an air atmosphere.

2.2. Catalyst characterization

The structure of the SAPO-34 catalyst was investigated by powder X-ray diffraction (XRD) patterns using a Rigaku Ultima IV diffractometer with Cu K_α radiation (λ = 0.15406 nm) at 40 kV and 30 mA. The crystal size and morphology were characterized by scanning electron microscopy (SEM) using a Tescan Mira 3 LMU FEG at 20 kV with a Pt coating. The chemical composition was analyzed by an inductively coupled plasma-atomic emission spectrometer (ICP-AES) using a Thermo Scientific iCAP 6500 duo. The surface area of the catalyst was determined by N_2 adsorption-desorption measurements using a Micromeritics ASAP2020 analyzer. The acidity of the catalyst was measured by the temperature-programmed desorption of ammonia gas (NH_3-TPD) using a BEL-CAT-B analyzer. Solid-state ^{27}Al MAS NMR spectra were obtained on a 400 MHz Avance II+ Bruker spectrometer operated at radio frequency of 104.26 MHz using a 90° pulse length of 1.8 μs and a cycle delay time of 3 s.

2.3. ETP reaction testing

The catalytic performance for the ETP reaction was tested with a 1/2" fixed-bed reactor, where 0.5 g of the SAPO-34 catalyst was loaded into the reactor, with the catalyst pretreated under a flow of nitrogen at 500 °C with 150 cc/min for two hours. After the pretreatment, ethylene gas was injected into the reactor and reacted at 400 °C with a weight hourly space velocity (WHSV) of 0.33 h^{-1} under ambient pressure, where the concentration of ethylene was fixed to 30 mol% under a nitrogen balance. The product gas was analyzed by an on-line gas chromatograph (GC, Younglin Corp. model 6100) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). The conversion of ethylene was calculated from the GC-TCD signal of nitrogen and ethylene. The hydrocarbon products generated from the reaction were analyzed by GC-FID. The columns used were a HP-PLOT Q (Agilent) capillary column and a Carboxen 1000 (Supelco) packed column. Conversion and selectivity were evaluated on a carbon mole basis and defined in Eqs. (1)–(2):

$$\text{Conversion}(\%) = [\{\text{carbon(mol) in initial ethylene} - \text{carbon(mol) in ethylene after reaction}\}/\{\text{carbon(mol) in initial ethylene}\}] * 100 \quad (1)$$

$$\text{Selectivity}(\%) = [\{\text{carbon(mol) in a product}\}/\{\text{carbon(mol) in all products}\}] * 100 \quad (2)$$

Based on GC analysis of products, the carbon balance was over 92 – 95% for each reaction performed.

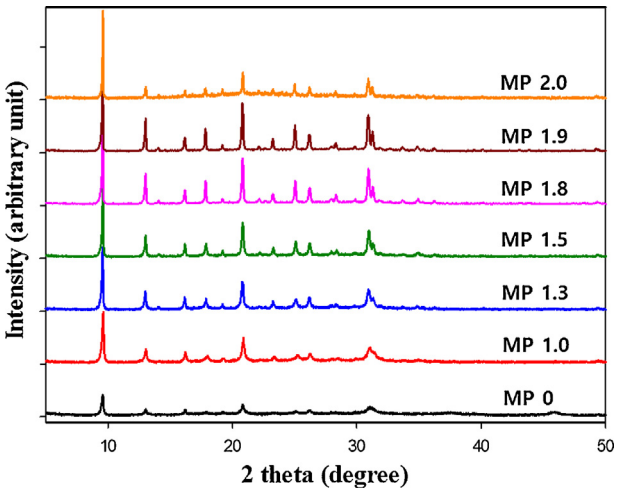

Fig. 1. X-ray diffraction patterns of the SAPO-34 catalyst prepared when controlling the amount of MP.

3. Results and discussion

3.1. Structural and chemical characterizations

Fig. 1 shows XRD patterns of the SAPO-34 prepared catalysts while controlling the ratio of MP and TEAOH with a SDA. The Si/(Si + P + Al) ratio was identical at 0.130 for all starting gels. The XRD result in Fig. 1 shows that the SAPO-34 catalysts prepared by changing the MP and TEAOH ratio have typical SAPO-34 crystalline characteristics [22–24] and that the XRD peak intensity gradually increases when increasing the amount of MP. This means that the crystallinity and size of the SAPO-34 catalysts increase with an increase in the amount of MP. It has also been reported that the crystalline phase and size change when MP is used as a template agent when also using TEAOH [22,23,25]. A change in the size of SAPO-34 was also demonstrated in the SEM analysis, as shown in Fig. 2 and in Table 1. The SEM images in Fig. 2 indicate that the crystalline size increases from 0.3 μm to 13 μm when controlling the MP and TEAOH ratio and when simultaneously increasing the amount of MP. The SEM analysis reveals that crystal size of the SAPO-34 is dependent on the nature and ratio of SDA used during synthesis [22,25]. It has been reported that Si atoms incorporate into the $AlPO_4$ framework through two different mechanisms [26,27]. One