Microporous and Mesoporous Materials 207 (2015) 9–16

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

Development of desilicated EU-1 zeolite and its application in conversion of dimethyl ether to olefins

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ARTICLE INFO

Article history:
Received 16 September 2014
Received in revised form
3 January 2015
Accepted 3 January 2015
Available online 13 January 2015

Keywords:
Desilication
EU-1
Alkaline treatment
Mesopore volume
Realumination

ABSTRACT

Creating mesoporosity in one-dimensional pore zeolites is still a challenging task in zeolite scientific community. Desilicated EU-1 (EUO), an one-dimensional pore zeolite, with Si/Al of 25 was developed using with different NaOH concentrations for different times to extract Si atoms from the framework and to form mesoporosity at fixed treatment temperature. Simple hexamethonium bromide was used as a template for EU-1 synthesis. The effects of concentration of NaOH and time of desilication on Si/Al, crystallinity, acidity and surface area have been investigated. A series of treated EU-1 samples was then applied for conversion of dimethyl ether to olefins (DTO). The sample treated with lower NaOH concentration (0.25 M) had the highest increase in mesopore volume with no significant change in acidity. An increase in mesopore volume contributed to higher selectivity toward propylene. The lower catalytic activity was observed over desilicated EU-1 as compared with the parent sample. The physicochemical properties of desilicated zeolites were analyzed using many characterization techniques. X-ray diffraction (XRD) was used to evaluate the effect of desilication on the crystallinity. Nitrogen adsorption–desorption isotherms and temperature-programmed desorption were used to evaluate the porosity and acidity, respectively. Morphology was analyzed using scanning electron microscope (SEM) and Transmission electron microscope (TEM).

1. Introduction

Practically, two main strategies are commonly used to enhance the mass transfer in the zeolite crystal and to prevent and suppress zeolite deactivation. The first strategy is to reduce the length of the diffusion path [1,2] by fabrication of nano-sized zeolites. Nano-zeolites had been synthesized for some types of zeolite frameworks like MFI, MTT and BEA [3–6] zeolites, but there are some limitations on this strategy such as difficult recovery from synthesis solution and engineering problem inside the packed bed reactor because of pressure drop across the column [7–9].

The second strategy to enhance the mass transfer is combining microporosity together with mesoporosity in the external surface of zeolite, which is also known as hierarchical zeolite. The existence of mesoporosity on the surface of zeolites facilitates better access to active sites inside the pores [10,11]. As a result, the zeolite activity will be increased and the reactant will have more available surface areas for reaction [12–16]. In addition, having more mesopores on the external surface will reduce the potency of pore blocking, which are the main cause of deactivation in typical hydrocarbon conversion such as catalytic cracking and methanol to hydrocarbon. Consequently, the life time of the zeolite will be increased [17–19]. So, generally in the case of hierarchical zeolites, the reactants and the products will have ease diffusion from the bulk phase into the pores and vice versa. In other words, introducing of mesopores will enhance the overall mass transfer [7,20]. However, in case of one-dimensional pore zeolites such as ZSM-22 (TON), which was reported by Perez-Ramirez et al. [21], desilication process decreased the surface area and suppressed the mass transfer diffusion. This detrimental effect was observed as the pore size of TON zeolite is too small and the Al species may leach from the framework and deposit on the pore mouth of zeolite. So it is not always true that the desilication will increase the surface area for the zeolite materials [22].

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http://dx.doi.org/10.1016/j.micromeso.2015.01.006
1387-1811/

The selection of appropriate Si/Al ratio is very important to create the mesoporosity [23–25], zeolites with too low Si/Al ratio will not easily contain mesoporosity after treatment because it is so difficult to extract the Si atoms from the structure. In the other case, when the Si/Al ratio is too high, desilication will end up with the dissolution of the zeolite. In the literature, it has been found that the optimum Si/Al to achieve good desilication and mesoporosity is between 25 and 50 [10], and in our case here EU-1 zeolite crystals with Si/Al of 25 have been used.

Selective conversion of dimethyl ether to olefins (especially propylene) has great market demand and become hot research topic. EU-1 zeolite showed high conversion of methanol to olefins (MTO) in previous works [26,27]. The MTO reaction produces DME as an intermediate product together with water [27], and then the DME converted to light olefins. Also for similar work of SAPO-34 (a 3-D zeolite), hierarchical structure of SAPO-34 gave higher selectivity toward propylene compared with the parent sample [20]. Therefore, the good catalytic results of EU-1 for methanol to olefins are expected to be observed again in DME to olefins.

2. Experimental

2.1. Parent zeolite

Pure and highly crystalline phase of EU-1 zeolite was synthesized based on the procedure described elsewhere [28,29]. The molar composition of the prepared gel was 9 Na_2O–10 $HMBr_2$–0.5 Al_2O_3–25 SiO_2–3000 H_2O. The synthesis started by preparing alkaline solution by adding 0.72 g of NaOH to 54 ml of deionized water. $Al(OH)_3$ (0.08 g) was added slowly to the solution as a source of aluminum followed by 3.62 g of hexamethonuim bromide as an organic structure directing agent. After the solution became homogeneous, 1.05 g of fumed silica was added as a source of silica. The above gel was prepared at room temperature and stirring speed of 500 rpm. After 12 h aging time, the gel was transferred to 100 ml PTFE autoclave and moved to conventional oven at 190 °C for 72 h. The autoclave reactor was quenched in a cold water to terminate the reaction quickly. The produced solids recovered by centrifugation and washed several times with deionized water to normalize the pH. The wet solids were transferred to 105 °C oven for drying overnight. The sample was then calcined at 550 °C for 12 h to remove the template. The Na-EU-1 was converted to NH_4-EU-1 by an ion exchange with 2 M of ammonium nitrate (NH_4NO_3) for 50 min in a microwave oven. The H-EU-1 was obtained by calcination at 550 °C for 12 h.

2.2. Alkaline treatment

Sodium hydroxide (NaOH) was selected to be the alkaline for the desilication treatment. The synthesized zeolite at 12 h aging time was treated with NaOH. The effect of NaOH concentration on the zeolite was investigated by using three different NaOH concentrations (0.25, 0.5 and 1 Molarity). The second crucial parameter was desilication time. The desilication contact time was varied at different periods (15, 30 and 60 min).

The treatment was carried out by adding 1 g the zeolite sample to 60 ml of NaOH solution while stirred at 400 rpm in 80 °C using a hot-plate.

Since the size of the micropores of EU-1 is classified as one of the medium-pore zeolites, the extraction of Si species from the framework is more difficult as reported for FER, TON and BEA frameworks [1,21,30]. Therefore, we applied high temperature (80 °C) during desilication for the all treated samples in order to get higher Si extraction. After treatment, the samples were washed several times until the neutral pH was obtained. Finally, the catalysts were dried at 105 °C for 12 h.

2.3. Characterization

Powder XRD patterns were recorded using a diffractometer (Miniflex, Rigaku) equipped with Cu Kα radiation (1.5405 Å). XRD patterns were recorded for 2θ from 5 to 50° using a scan of 0.02° per step and a counting time of 4 s for each step. Field-emission scanning electron microscopy (FE-SEM) as performed using LYRA 3 Dual Beam (Tescan) equipped energy dispersive X-ray spectrometry (EDX, Oxford Instruments) operated at an acceleration voltage of 30 kV. 2.2.5. N_2 adsorption was performed at −196 °C by a porosimeter (BELsorp mini, BEL Japan). Prior to the measurement, the powder was degassed at 350 °C for 12 h. The surface area, pore volume and pore size distribution were reported based on the BET calculation method. The acidity of parent and desilicated samples was analyzed by the NH_3 TPD instrument. The NH_3 was carried out by He with 1% balance. The heating rate was 5 °C/min and the final temperature was set at 700 °C.

2.4. Catalytic evaluations

DTO reaction over EU-1 (EUO) zeolites was performed using a fixed-bed reactor made of quartz glass (i.d. 4 mm) with a continuous-flow system under atmospheric pressure. The feed rates of DME and He were 1.3 and 19 mmol/h, respectively. The reaction temperature was set at 350 °C. The amount of EU-1 catalyst was about 0.05 g. The contact time (W/F: mass of the catalyst [kg] divided by the feed rate of methanol [mol/h]) was 0.039 kg h mol^{-1}. The product stream was analyzed with a Shimazu GC-14B gas chromatograph equipped with a flame ionization detector using an Al_2O_3 PLOT column (J&W scientific).

3. Results and discussion

3.1. Effect of desilication on EU-1 crystallinity

The XRD analysis was used to study the effect of desilication on the crystallinity. It was observed that as the desilication time increased, the crystallinity was initially decreased until reaching a steady-state condition, where the solution was saturated with Si species and the extraction of Si became more difficult. At this prolonged desilication, extractions had no more effect for long term treatment, and the dislocation reached a plateau. The three sets of XRD patterns in Fig. 1 (a, b and c) describe the implication of desilication on crystallinity.

The effect of NaOH concentration on the zeolite structure was almost similar to the effect of desilication time. Increasing the concentration of basic solution lowered the zeolite crystallinity. However, at high concentration, for instance, when 1 M of NaOH was applied for 60 min, severe extraction of Si species also impacted the removal of Al species from the frameworks as the Si–O–Al chains are interconnected. The XRD pattern of a sample treated with 1 M of NaOH for 60 min confirms that the zeolite crystal structure starts to change and collapse by the severe condition (harsh) Si removal. Instead of creating mesopores on the zeolite surface, large pores were created. In some cases at severe condition, the pores can reach hundreds of nanometers.

The XRD patterns are also very helpful to observe the effect of NaOH concentration as shown in Fig. 2.

The crystallinity of modified EU-1 is presented in Table 1. The crystallinity percentage was calculated according to the strongest XRD peaks for parent sample.