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Effect of synthesis parameters and ion exchange on crystallinity and morphology of EU-1 zeolite

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ABSTRACT

The effect of aging time, synthesis temperature and synthesis time on crystallinity and morphology of Na–EU-1 has been studied. Hexamethonium bromide was used as a template to synthesize Na–EU-1 zeolite with Si/Al of 25. In addition, the effect of modification using ion exchange with (NH_4^+, Ca^{2+}, Li^+ and Ni^+) nitrates to replace Na^+ was also studied. X-ray diffraction was used to study the phases and the crystallinity of zeolite crystals. Morphology of EU-1 crystals was observed using scanning electron microscope (SEM). Prolonged aging time up to 12 h favored pure phase and crystalline EU-1. It has been found that the optimum synthesis temperature to obtain highly crystalline EU-1 is 190 °C. The shortest synthesis time to obtain crystalline EU-1 at 190 °C is 72 h. Ion exchange reduced the crystallinity of EU-1 crystals. We anticipate that the metal-modified EU-1 is a potential catalyst in numerous reactions such as isomerization and methanol-to-hydrocarbon.

1. Introduction

One dimensional pore zeolites are very interesting materials for numerous applications in hydrocarbon conversions such as naphtha cracking [1–5], methanol to olefins [6] and isomerization of C8 aromatics [7–10]. EU-1 (EUO) is one of zeolites with one-dimensional channel system EU-1 (0.54 × 0.41 nm) by 10-MR (membered ring) opening and side-pocket by 12-MR (0.68 × 0.58 nm) [11–13]. Careful studies of synthesis parameters is required as different zeolitic phases can be produced from the same template [1–5], hexamethonium bromide [1–5]. The possibility to get impurities during the synthesis is large as the synthesis is very sensitive to temperature change, synthesis time and aging time (see Table 1). Giordano et al. reported the effect of Si/Al ratio, Si/template ratio and Si/OH^- ratio on EU-1 synthesis [2]. We used the optimum ratio of those parameters as the starting point to study the aging time, synthesis time and crystallization time.

Replacing the cation of zeolites material offers many advantages because this new cation has different chemical and physical properties, which are targeted at different catalytic applications. Zeolite structure will also be affected in such a way the dimensions of pores will change and this will directly affect the shape selectivity [6–9]. The surface acidity will also be changed because of the new atoms and the re-arrangement of the atoms in the structure. In this study, we also report effect of ion exchange on crystallinity and the morphology of EU-1 zeolite.

2. Experimental

EU-1 zeolite was successfully synthesized using procedure described by Giordano et al. [2]. In a typical synthesis, 0.72 g of sodium hydroxide (NaOH) was dissolved in 54 ml of deionized water. Then, 0.08 of Al(OH) and 3.62 g of hexamethonium bromide were added to the mixture. After stirring for 10 min, 1.05 g of fumed silica was added. The formed gel mixture was at 25 °C for 3 h with a stirring speed of 500 rpm. The mixture was transferred to 100 ml autoclave and heated to 190 °C for 72 h in a conventional oven. The molar composition was $9Na_2O–10HMBr_2–0.5Al_2O_3–25SiO_2–3000H_2O$. The product was washed with deionized water several times, until the neutral pH was reached. The sample was dried at 105 °C for 12 h.

2.1. Aging time

The most important parameter affecting the zeolite crystallinity is the aging time [10]. The aging time has been changed from 3 to 24 h at constant room temperature to achieve high crystallinity. EU-1 zeolites were synthesized with different aging times using similar composition.

2.2. Synthesis temperature and crystallization time

In order to study the effect of temperature on the zeolite crystallinity and morphology, the same procedure was applied at different synthesis temperatures (185 °C and 195 °C) and different crystallization times (24, 48 and 72 h) [11].

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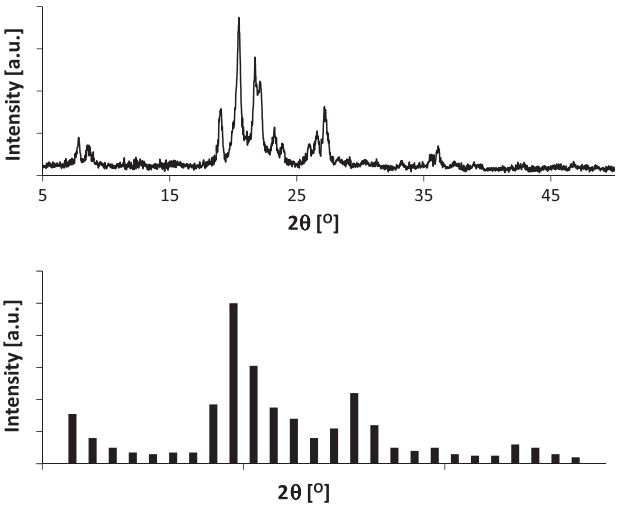

Fig. 1. XRD patterns of EU-1 zeolite in comparison with Ref. [4].

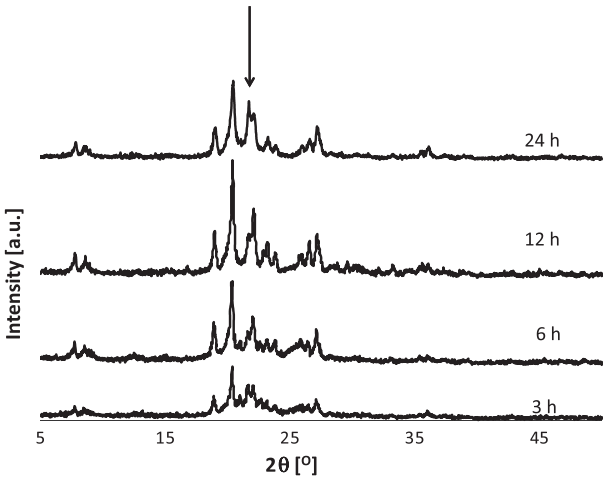

Fig. 2. XRD patterns of EU-1 synthesized with different aging times.

2.3. Ion exchange

Ion exchange was carried out using different cation nitrates (NH_4^+, Ca^{2+}, Li^+ and Ni^+). In a typical ion exchange, 33.3 ml solution of 2 M of these nitrates was prepared and then 20 g of this solution was added individually to 1 g of Na–EU-1 zeolite inside a PTFE holder. The ion exchange was performed using a microwave lab station. The PTFE holder was transferred to microwave. The microwave-assisted ion exchange was set at a temperature of 85 °C for 15 min with a stirring speed of 300 rpm. The solid product was separated from the solution by using a centrifuge and then the sample was dried at 110 °C for 12 h. Zeolite powder was calcined at 550 °C for 12 h in an oven.

2.4. 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. Fourier Transmission Infrared Spectroscopy (FTIR) was used to elucidate the properties of metal-exchanged EU-1. FTIR was performed with a Nicolet 6700 Spectrometer in transmission mode. Spectra were recorded at 4 cm^{-1} spectral resolution, an undersampling ratio of 4, and a speed of 20 kHz.

3. Results and discussion

The presence of as-synthesized Na–EU-1 was confirmed from XRD patterns as shown in Fig. 1. An XRD pattern reported by Xu et al. was used a standard [1].

3.1. Effect of aging time

Fig. 2 shows XRD patterns of Na–EU-1 synthesized with different aging times from 3 to 24 h. The crystallinity of samples was analyzed using XRD software (PDXL). By increasing the aging time, crystal size changes slightly in the nanometer range (see Table 2). Maximum degree of crystallinity was obtained after 12 h of aging time [12,13]. This EU-1 sample obtained after 12 h aging time was used as a standard for crystallinity calculation. Prolonged aging time contributed positively to crystallinity of EU-1. When the aging time was prolonged from 3 to 12 h, the crystallinity increased. However, when longer aging time (24 h) was applied, some impurities were observed at 2θ of 21.7, which overlapped on the EU-1 peak as shown in Fig. 2. This peak has been confirmed as a characteristic peak of cristobalite phase [2]. The impurities are shown by SEM micrographs in Fig. 3.

Table 2
Crystallinity and crystal size of EU-1 at different aging times.

Aging time (h)	Crystallinity (%)	Crystal size[a] (nm)
3	44.6	51.2
6	71.4	49.7
12	100	47.5
24	66.8	30.7

[a] The crystals size has been determined by XRD.

Fig. 3 shows the petal-like crystals, which were obtained with different aging times. The morphology is similar with other study on EU-1 as reported elsewhere [1]. The prolonged aging time affected crystal size, agglomeration rate and external morphology of EU-1. For aging time of 3 h, relatively large crystals of ca. 51 nm were observed. The nanocrystals formed large agglomerates of 2 μm and the presence of the amorphous phase was obvious. Increasing the aging time to 6 h reduced the crystal size to 49 nm with smaller portions of non-crystalline phase. Larger agglomerated particles (3–4 μm) were observed. In case of 12 h aging time, smaller nanocrystals of 47 nm were observed with highest crystallinity without amorphous phase. However, the agglomerates became larger (4–5 μm). When we further increased

Table 1
Effects of synthesis parameters on EU-1 properties.

Parameter	Synthesis condition	Template	Effect of parameters on EU-1 crystals	Ref.
Temperature	160 and 180 °C	Hexamethonium bromide	Phase purity was affected by temperature Co-crystallization of ZSM-48 and EU-1 was observed	Xu et al. [1]
Synthesis time	7, 9 and 11 days	Hexamethonium bromide	Phase purity and crystallinity were affected by crystallization time Formation of ZSM-48, cristobalite and quartz were reported	Giordano et al. [2]
Aging time	25–60 h	Benzyl dimethylamine and benzyl chloride	Zeolite crystallinity was affected by aging time	Rao et al. [4]