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Organotemplate-free and seed-directed synthesis of levyne zeolite

Haiyan Zhang [b], Chengguang Yang [b], Longfeng Zhu [b], Xiangju Meng [a], Bilge Yilmaz [c], Ulrich Müller [c], Mathias Feyen [c], Feng-Shou Xiao [a,*]

[a] Key Lab of Applied Chemistry of Zhejiang Province & Department of Chemistry, Zhejiang University, Hangzhou 310028, China
[b] College of Chemistry, Jilin University, Changchun 130012, China
[c] BASF SE, Ludwigshafen 67056, Germany

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ABSTRACT

Small-pore zeolite levyne has been successfully synthesized following an organotemplate-free route using RUB-50 zeolite as seeds with the aid of a small amount of alcohols. Physicochemical characterization with a combination of techniques including XRD, N_2 adsorption, FE-SEM, ^{27}Al and ^{29}Si NMR, and TPD-NH_3 shows that the zeolitic product from this seed-directed organotemplate-free synthesis approach (designated as LEV-SDS) has good crystallinity, high surface area, uniform crystals, tetrahedral Al^{3+} species, and abundant acidic sites. It is also found that alcohols play an important role in preparation of LEV-SDS zeolite by inhibiting the formation of MOR zeolite. Catalytic tests for the conversion of methanol-to-olefins (MTO) show that H-form of LEV-SDS zeolite exhibits good conversion of methanol and high selectivities for ethylene and propylene, which could be potentially important for using LEV-SDS zeolite as a catalyst in MTO reaction.

1. Introduction

Crystalline microporous zeolites have attracted much attention due to their uniform pore size, high surface area, controllable acidic sites, and designable redox species in the framework, which ensure their extensive applications in petrochemistry, fine chemical synthesis, adsorption, separation, and ion-exchange [1–7]. Particularly, considerable research interest has been focused on the synthesis and application of small pore zeolites such as SAPO-34 due to its unique shape selectivity for light olefins [8]. As a typical small-pore zeolite, levyne (LEV) zeolite has relative smaller pore size (3.6×4.8 Å) and low framework density (15.2 T/1000 Å^3), characterized by $4^9 6^5 8^3$ heptadecahedral cavity [9]. The natural levyne zeolite was first discovered in 1825, and its typical composition is $Ca_9(Al_{18}Si_{36}O_{108})\cdot 50H_2O$ [10,11] Synthetic LEV zeolite named ZK-20 was synthesized from an aluminosilicate gel using 1-methyl-1-azonia-4-azabicyclo[2.2.2]octane cation as a structure-directing agent (SDA) [12]. Subsequently, other aluminosilicate LEV zeolites were successfully prepared by using a series of organic compounds as SDAs, including N-methylquinuclidinium-cation [13,14], diethyldimethylammonium (DEDMA) [15,16], *N*,*N*′-bis-dimethylpentanediyldiammonium [17], *N*,*N*-dimethylpiperidine chloride [18], and choline hydroxide [19]. Additionally, phosphate-based LEV-type zeolites were also obtained in the presence of tropone hydroxide [20], quinuclidine [21], and 2-methyl-cyclohexylamine [22]; boron containing LEV-type zeolites were reported by using organic compounds of 3-azabicyclo[3.2.2]nonane and quinuclidine as templates [23,24]. Notably, it is necessary to use organic compounds as SDAs for normal synthesis of LEV zeolites, and the use of SDAs usually has shortcomings including high cost of organic templates, necessity for equipment that can withstand the pressure generated by the organic template and production of environmentally undesirable gases by high temperature calcination for removing these organic templates [25–27], which strongly hinder their wide applications in industry.

To avoid these problems, zeolite scientists have recently developed organotemplate-free routes to synthesize zeolites that previously required the use of organic templates in the synthesis, and successful examples include ECR-1 [28], ZSM-34 [29,30], Beta [31–35], high silica FER [36], and RTH [37] zeolites. In the present work, we have shown the details for organotemplate-free and seed-directed synthesis of LEV zeolite (LEV-SDS) in the presence of RUB-50 seeds and a small amount of alcohol. RUB-50, a LEV-type aluminosilicate zeolite was synthesized using diethyldimethylammonium (DEDMA) as an organic template [16]. The use of alcohols in the synthesis prevents the formation of MOR zeolite as an impurity, giving pure phase LEV zeolite, and catalytic tests show that H-form of the LEV-SDS zeolite is a good catalyst for selective formation of ethylene and propylene in methanol-to-olefins (MTO) reaction.

* Corresponding author. Tel.: +86 431 5168590.
E-mail address: fsxiao@zju.edu.cn (F.-S. Xiao).

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2. Experimental section

2.1. Materials

Fumed SiO_2 was purchased from Shenyang Chemical Co., sodium aluminate was supplied by Chinese Pharmic Group Chemical Co., sodium hydroxide, ammonium nitrate, methanol, ethanol, *n*-propanol, and *n*-butanol were obtained from Beijing Chemical Co., and RUB-50 zeolite with Si/Al ratio at 9.77 used as seeds in the synthesis was supplied by BASF SE.

2.2. Synthesis

Na-LEV-SDS zeolite was hydrothermally synthesized from the starting gels with molar ratio of SiO_2/0.35–0.38Na_2O/0.022–0.025Al_2O_3/35H_2O/1–2alcohol and seed crystals (1.5–5wt.% based on total silica amount). This synthesis mixture was hydrothermally treated at a temperature of 120 °C for 72 h in a poly(tetrafluoroethylene)-lined stainless steel autoclave under static conditions. In a typical preparation, 0.064 g of $NaAlO_2$ and 0.312 g of NaOH were dissolved in 7.56 mL of H_2O, followed by addition of 0.72 g of fumed SiO_2 and 0.554 g of ethanol. After the formation of the homogeneous aluminosilicate gel, 0.036 g of RUB-50 as seed was introduced into the gel under stirring at room temperature. After stirring for 5 min, the mixture was transferred into an autoclave for crystallization at 120 °C for 72 h. The solid product was collected by filtration, washed with deionized water, and dried at 80 °C for 12 h. In comparison, Na-LEV-SDS zeolites were also synthesized in the presence of other alcohols such as methanol, *n*-propanol, and *n*-butanol, respectively. When Na-LEV-SDS zeolite was used as seeds for synthesizing LEV-structure zeolite, the sample was designated as Na-LEV-SDS-2nd.

H-form of LEV-SDS was obtained by ion-exchange with 1 M NH_4NO_3 solution at 80 °C for 1 h (1 g of LEV zeolite in 50 mL of solution), followed by calcination at 550 °C for 3 h. This product was designated as 1H-LEV-SDS. When 1H-LEV-SDS was ion-exchanged with 1 M NH_4NO_3 solution at 80 °C for 3 h (1 g of 1H-LEV zeolite in 50 mL of solution), followed by calcination at 550 °C for 3 h. This product was designated as 2H-LEV-SDS.

ZSM-5 (Si/Al = 32) and SAPO-34 (Si/Al/P = 1:2.8:1.9) zeolites were synthesized according to the literature [38,39]. H-form of ZSM-5 and SAPO-34 were obtained by ion-exchange with 1 M NH_4NO_3 solution at 80 °C for 3 h, followed by calcination at 550 °C for 3 h, in addition this process was repeated for one time.

2.3. Characterization

X-ray diffraction (XRD) patterns were obtained with a Rigaku D/MAX 2550 diffractometer by using Cu Kα radiation. Nitrogen adsorption isotherms were measured at −196 °C using Micromeritics ASAP 2020 M. Samples were degassed at 200 °C for 12 h before the measurements. The morphology of the samples was observed by field emission scanning electron microscopy (FE-SEM) on a JSM-6700F electron microscope (JEOL, Japan). Sample composition was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) with a Perkin-Elmer 3300DV emission spectrometer. ^{27}Al and ^{29}Si NMR spectra were recorded on a Varian Infinity plus 400 spectrometer. Infrared (IR) spectra were recorded with a Bruker 66 V FTIR spectrometer. C/H/N elemental analysis was conducted on a Perkin–Elmer 2400 elemental analyzer. Temperature-programmed desorption of NH_3 (TPD-NH_3) was carried out with a TCD-detector. As a typical run, about 200 mg of H-form of LEV-SDS sample was placed in a quartz tubular reactor and pretreated at 500 °C in a nitrogen stream, followed by decreasing the temperature to 110 °C. After reaching to 110 °C, gaseous NH_3 passed though the sample for 30 min. After removal of excess NH_3 by flowing nitrogen for 2 h at 110 °C, the TPD-NH_3 curve of the sample was recorded by programmed heating from 110 to 620 °C with a heating rate of 10 °C/min.

2.4. Catalytic test

As a model reaction, methanol-to-olefins (MTO) reaction was carried out with a fixed-bed reactor at atmospheric pressure. 0.5 g of catalyst (20–40 mesh) was loaded into the reactor. The sample was pretreated under flowing nitrogen at 550 °C for 1 h, followed by decreasing the temperature of the reactor to 400 °C. Methanol with a weight hourly space velocity (WHSV) of 0.5 h^{-1} was pumped into the reactor under nitrogen. Products were analyzed online by an Agilent 6890 gas chromatograph equipped with an FID detector and a HP-PONA methyl siloxane capillary column.

3. Results and discussion

3.1. Organotemplate-free and seed-directed synthesis of Na-LEV-SDS zeolite

Fig. 1 shows the XRD patterns of the samples crystallized at 120 °C for 0–96 h. Prior to crystallization, weak peaks (major peak at 22.20°) can be observed in the XRD pattern (Fig. 1a), which is associated with the presence of RUB-50 seed crystals (Fig. S1) in the amorphous aluminosilicate gel. This result suggests that RUB-50 seeds are basically stable in the alkaline synthesis media. After crystallization for 36 h, the sample gives relatively low crystallinity at 41% (Fig. 1c), which is explained by the crystal growth from RUB-50 seeds in the amorphous aluminosilicate gel. Simultaneously, a slight shift of the major peak from 22.20° to 21.98° is also observed, which is due to Al-rich framework of LEV-SDS. A similar phenomenon has been reported for Al-rich Beta zeolite [32]. During the crystallization period between 36 and 72 h, there is almost no change in the major peak but the intensities of the XRD peaks significantly increase (Fig. 1c–f). For example, the sample crystallized at 48 h shows high crystallinity at 93.2% with the major peak at 21.94°. When the crystallization time is increased up to 96 h, there is no increase of the sample crystallinity, which suggests that the crystallization has been finished at 72 h already. Fig. 2 shows the dependence of sample crystallinity on

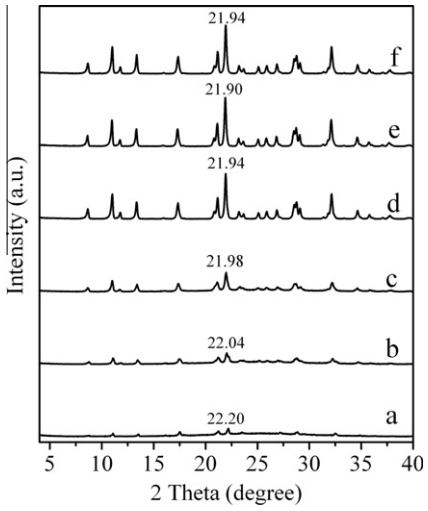

Fig. 1. XRD patterns of Na-LEV-SDS samples synthesized at (a) 0, (b) 24, (c) 36, (d) 48, (e) 72, and (f) 96 h in the presence of RUB-50 seeds.