



Synthesis and characterization of zeolite L prepared from hydrothermal conversion of magadiite



Yu Wang^{a,*}, Tianming Lv^a, Ye Ma^a, Fuping Tian^a, Li Shi^b, Xiaoyu Liu^a, Changgong Meng^a

^a School of Chemistry, Dalian University of Technology, Dalian 116024, China

^b Environmental Protection Research Institute of Light Industry, Beijing 100089, China

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ABSTRACT

Zeolite L has been synthesized by magadiite conversion method. The crystallization behavior and changes of medium-range structure during the crystallization were investigated by X-ray diffraction, scanning electron micrograph, vibrational spectroscopy and ²⁷Al magic angle spinning nuclear magnetic resonance. It is indicated that parts of 6 member-rings in magadiite still exist as secondary building units although the long-range order of magadiite was collapsed in the initial stage. The 4 member-rings and 8 member-rings were formed after the sample was heated for 3 h and 4 h, respectively. The influence of various parameters such as reaction temperature, time and substrate composition was examined. Highly crystallized and pure zeolite L could be prepared from the substrates with molar composition: 0.56M₂O–xAl₂O₃–SiO₂–49H₂O (M₂O = K₂O + Na₂O, x = 0.0033–0.04) by heating at 140 °C for 18 h, 160 °C for 12 h or 180 °C for 8 h.

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1. Introduction

Zeolite L (LTL) which is a crystalline microporous aluminosilicate was initially determined by Barrer and Villiger [1]. With a typical Si/Al ratio of 3.0, it possesses one-dimensional pore of about 0.71 nm aperture leading to cavities of about 0.48 × 1.24 × 1.07 nm, which is based on polyhedral cages formed by five six-membered rings (6Rs) and six four-membered rings (4Rs) [1,2]. After this disclosure, zeolite L has drawn a lot of attention as a promising material, including catalysis supports [3] and hosts of guest-host material. For example, it has been applied in industry in the aromatization of alkanes [4]. A monofunctional catalyst consisting of platinum on the non-acidic zeolite L has been reported to have high catalytic activity and high selectivity to benzene for conversion of n-hexane [5]. Zeolite L was used as the host material of artificial and loading suitable organic dye molecules in its one-dimensional channels was investigated by Calizaferrri's group [6].

Synthesis of zeolite L with or without using organic templates has been mostly reported by various investigators continuously. Some studies have been also conducted on the properties of zeolite

L by changing its crystal size, aspect ratio and so on. Joshi et al. reported the effects of crystallization kinetics on physicochemical characterization of zeolite L [7]. It was also obtained by Yong' group in a Na/K mixed alkali system [8]; furthermore the factors which influence on the synthesis outcome were investigated by them [9]. Zeolite L can be successfully prepared with minimum chemical waste containing much less silica, potassium and water than the conventional one [10]. The fly-ash and rice husk can be used to synthesize single crystal zeolite L and nanocrystalline zeolite L [11–13]. Aghabozorg et al. synthesized nanosized zeolite L with various synthesis times [14]. The morphology control of zeolite L was studied by some groups. According to Wortel, zeolite L with a cylindrical morphology was particularly valuable as a catalyst support. Its mean diameter was at least 0.5–1 μm [15]. The effects of various synthesis variables used on morphology were investigated and has been well documented [16–18]. Yoon et al. reported the influence of synthetic parameters on the long zeolite L crystals in hexagonal columnar structures with flat basal and side planes [19]. The zeolite L with an elongated to disc-shaped morphology was synthesized with various aspect ratios [20]. In the presence of diethylamine, trimethylamine catechol and acetylacetone the morphology of zeolite L could be tuned [21,22]. The zeolite L crystals with low aspect ratio were prepared by Cheng et al. [23].

* Corresponding author.

E-mail address: wangyu_200_2@dlut.edu.cn (Y. Wang).

Zeolite L with tunable size and morphology was also obtained by using a microwave synthesis method [24].

In general, zeolites are synthesized using an aluminosilicate gel as a starting material under hydrothermal conditions. The synthesis is usually gradual and has the following sequence: amorphous phase → less stable zeolite → most stable zeolite. On this basis, several research groups have proposed the high potential of an alternative method for zeolite synthesis, i.e., the recrystallization of layered silicate, magadiite, into zeolite. For example, P.A. Jacobs et al. firstly used magadiite as the silica source for synthesizing ZSM-5(MFI) and ZSM-11(MEL) [25]. Pál-Borbély et al. succeeded in the direct synthesis of MFI, MEL and FER zeolites from Al-magadiite via the hydrothermal layered silicate-zeolite transformation method [26,27]. Zones and Kooli et al. reported the conversion of magadiite into various zeolites such as ZSM-12, ZSM-39, ZSM-48, EU-2, FU-1 and SSZ-15 [28–30]. The detailed studies on the hydrothermal conversion of magadiite into silicalite-1 were investigated by Feng et al. [31]. Recently, our group has also succeeded in the synthesis of several types of zeolites such as OFF, FER, MOR, MAZ and MFI zeolites using magadiite as the starting material in the presence of various structure-directing agents (SDAs) such as tetramethylammonium bromide, ethylenediamine, cyclohexylamine, glycerol, and 1, 6-hexamethylenediamine [32–36]. This synthesis strategy means that the binderless preshaped zeolites can be prepared and have economical value [37,38]. Meanwhile, in the conversion process the locally ordered aluminosilicate species may exist which could be gave rise to a fast crystallization rate and a high selectivity to a particular zeolite [39–43].

Here, we report an alternative synthesis route to prepare zeolite L crystals by hydrothermal transformation of the magadiite method, and characterise the as-synthesis zeolite L (LTL). The effects of substrate composition, reaction time, reaction temperature sequence upon the crystallization of zeolite L were examined. Results in the crystallization kinetics along with those on the characterization of the products are reported here. The changes of medium-range structures during conversion were also investigated.

2. Experimental

2.1. Synthesis of magadiite

The starting material, magadiite was synthesized according to previous work in our laboratory [44]. In a typical procedure, 8 g diatomite (SiO₂ 96.7 wt %; Al₂O₃ 1.0 wt %; Na₂O 0.1 wt %) was dispersed in the mixture of 24 g water glass (SiO₂ 26.81 wt %; Na₂O 8.36 wt %) and 1 g deionized water, and then heated at 160 °C for 42 h. The resulting magadiite was filtered off, washed with deionized water until neutrality and dried at 100 °C overnight.

2.2. Conversion of magadiite

Conversion of magadiite into zeolites is of a similar fashion to other synthesis previously reported, where magadiite was used as the silica source. As-synthesized zeolites were obtained from a gel mixture at 160 °C with different compositional ratio. The reaction molar composition was as follow: $x \text{ M}_2\text{O} : \text{Al}_2\text{O}_3 : 25 \text{ SiO}_2 : y \text{ H}_2\text{O}$ ($\text{M}_2\text{O} = [z \text{ K}_2\text{O} + (1-z) \text{ Na}_2\text{O}]$ or Li_2O , Rb_2O). The mixture was thoroughly stirred at room temperature, and then transferred into a 100 mL stainless Teflon-lined steel autoclave to react different time. The resulting solid product was washed by deionized water until pH = 7–8, and dried at 100 °C overnight.

2.3. Characterization

The crystalline structures of solid products were determined by powder X-ray diffraction (XRD) patterns on a Panalytical X'Pert Powder diffractometer (CuK α). The diffractograms were recorded from 3 to 50° using a step size of 0.013° and at a scanning speed of 8° min⁻¹. In order to avoid the possible interference of the coexisting phases, such as zeolite W or NaP, the areas of the peaks appearing at $2\theta = 5.5, 19.4, 22.7, 28.0$ and 30.7 were used to estimate the crystallinity of the test sample. Scanning electron microscopy (SEM) was performed with a QUANTA450 microscope using an accelerating voltage 30 kV. The SiO₂/Al₂O₃ ratio of the products was measured by Inductively Coupled Plasma Mass Spectrometer (ICP, Optima 2000 DV, Perkin Elmer). Raman spectra were conducted using a Thermo Scientific spectrometry with a 532 nm excitation line. Spectra were recorded for 60 s and accumulated 5 times. IR spectra were recorded with a Nicolet 6700 FTIR spectrometer over the spectral region from 400 to 1200 cm⁻¹ with a resolution of 4 cm⁻¹ using the KBr disc technique. Raman and IR spectra were all normalized. ²⁷Al MAS NMR were carried out on a Bruker AVANCE III 600 spectrometer at a resonance frequency of 156.4 MHz using a 4 mm HX double-resonance MAS probe at a sample spinning rate of 15 kHz. The chemical shift of ²⁷Al was referenced to 1 M aqueous Al(NO₃)₃. ²⁷Al MAS NMR spectra were recorded by small-flip angle technique with a pulse length of 0.5 μs ($<\pi/12$) and a 1s recycle delay and 1000 scans.

3. Results and discussion

3.1. Influence of temperature and time

The crystallization kinetics are studied by comparing extents of crystallization of the mixture at different temperatures. The other synthesis conditions such as the substrates composition and rate of heating are kept constant. The details regarding the initial gel composition and characteristics of the samples are listed in Table 1. Fig. 1 shows the crystallization kinetics curves obtained at 140 °C, 160 °C and 180 °C from a substrate composition of 0.56M₂O–0.04Al₂O₃–SiO₂–49H₂O (M₂O = K₂O + Na₂O, K/K + Na = 0.9). It is interesting to note that the increase in reaction temperature caused a decrease in the induction period and resulted in reduction of the reaction time. This result elucidates that the rate of nucleation has been accelerated with an increase of crystallization temperature. For the zeolite L product prepared at 140 °C, the crystallinity of the zeolite reaches to 100% after 18 h. On the other hand, the maximum crystallinity of zeolite L crystal is synthesized in 8 h for 180 °C or in 12 h for 160 °C. Subsequently, the crystallization process of zeolite L is more closely investigated as a function of synthesis time at 160 °C. Fig. 2 exhibits the XRD patterns of the products prepared at varying crystallization periods. It is clear that the starting magadiite decomposes into an amorphous phase, and then the pure LTL-type zeolite crystallizes after 3 h of hydrothermal treatment. As the treatment time increased, the degree of crystallinity is developed progressively. The fully crystalline phase is obtained at 12 h. Upon further crystallization, the contribution due to metastable phase of zeolite L starts decreasing on account of its transformation into a more stable zeolite of type W. The corresponding SEM images of zeolite L are shown in Fig. 3. As shown in Fig. 3(a), magadiite exhibits a rosette-like shape. After 2 h of heating, the rosette-like shape is collapsed and small plates with agglomerate are shown. Upon heated for 3 h, small ice hockey puck-shaped crystals appear, indicating the zeolite L begins to grow. The amorphous material with plates shape gradually disappears as the crystallization progresses, and the amount of crystalline zeolite L phase increased. After 4 h amorphous material

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