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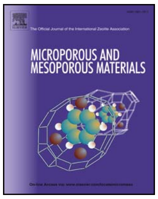

Mechanistic study on the synthesis of ZSM-5 from a layered silicate magadiite

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ABSTRACT

The transformation mechanism for zeolite ZSM-5 from magadiite in the present of tetrapropylammonium cations has been investigated. It is found that the transformation subjects no complete or extensive dissolution of magadiite. What's more, the transformation is beginning with the formation of linear channels rather than the zig-zag channels. On the basis of these observations, we proposed that the magadiite layers were reconfigured into linear chains with the structure direction of tetrapropylammonium cations in the initial stage, and then zig-zag channels were constructed by connection of linear channels. In this way, the framework of ZSM-5 was formed.

1. Introduction

Zeolites have attracted great interest in material and chemistry field because of their unique structure and properties. Synthesizing zeolites by conversion of magadiite, a cheap layered silicate with special structure, is considered to be one commercialization way [1–9]. Comparing to conventional silica source, faster crystallization rate can be obtained and the amount of structure directing agent can be decreased by use of magadiite as raw material for some cases [3]. To explanation this interesting finding, it is constructive to understand the formation mechanism for the zeolites from magadiite.

R. M. Barrer has proposed secondary building unit (SBU) theory in 1959, which involves zeolites can grow from the structural elements of their final framework [10]. Even so, understanding how they nucleate and grow remains one of the most challenging issues in modern zeolite science. M. B. Park et al. elucidated unequivocally the pathway for LTA zeolite from lta-cage in 2012 [11], the successful work of them has made breakthroughs in the field of zeolite grow mechanisms.

In our previous work, the crystallization process for zeolite omega from magadiite has been investigated in detail [12]. It has been proposed that although the long-range order of magadiite is collapsed in the initial stage, parts of 5-member rings (5Rs) and 6-member rings (6Rs) are still preserved as secondary building units (SBUs). Another work proposed that the formation pathway for mordenite from diatomite is different from that from colloidal silica reported by Dutta et al. [13]. Dutta et al. proposed that the 4-member rings (4Rs) initially present in the amorphous gel are undergoing accommodation of 5Rs around them in the synthesis of mordenite from colloidal silica [14], while we proposed that the 5Rs initially present in the diatomite are undergoing accommodation of 4Rs around them. The above works confirmed that some SBUs present in the silicate mineral materials could be used directly during the crystallization. To further investigate this issue, more investigations are still required to understand conversion process for zeolites from silicate mineral.

Zeolite ZSM-5 consists of 10-members ring (10R) linear channels along the [010] direction and intersected 10R zig-zag channels along the [100] direction. Tetrapropylammonium (TPA^+) cation is the most conventional structure directing agent (SDA) for synthesis of ZSM-5. The role of TPA^+ cations as SDA in the synthesis of pure-silica ZSM-5 has been investigated by M. E. Davis et al. [15–17]. It has been reported that the TPA^+ cations are located at the channel intersections with the propyl chains extending into both the linear channels and zig-zag channels. They also provide evidences for the mechanism of structure direction and self-assembly proposed for the TPA-mediated synthesis of Si-ZSM-5. Although the synthesis mechanism for ZSM-5 from amorphous silica source is proposed, the mechanism for ZSM-5 from layered silicate is also of interest because such transformation is special. Since zeolite crystallization is a complex process that may take place through different pathways depending on the composition and structure of raw materials, the gel composition and the synthesis conditions, the formation pathway for ZSM-5 from magadiite should be different from that from colloidal silica.

In this study, zeolite ZSM-5 was synthesized from magadiite in the presence of TPA^+ cations. The transformation mechanism was investigated by X-ray diffraction (XRD), scanning electron micrograph (SEM), Solid-state ^{1}H-^{13}C cross polarization magic angle spinning

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nuclear magnetic resonance (CP MAS NMR) spectra, Raman spectroscopy and high-energy X-ray diffraction (HEXRD). Here we present indirect but secure experimental evidence that this transformation is beginning with the formation of linear channels rather than the zig-zag channels.

2. Experimental

2.1. Preparation of magadiite

The starting materials include colloidal silica (30% SiO_2), sodium hydroxide and deionized water. The molar composition of the resultant mixture was SiO_2: 0.15 Na_2O: 4.22 H_2O. Hydrothermal treatment was carried out at 150 °C for 48 h. After crystallization, the solid products were separated and washed with deionized water till pH = 7–8. The products were then dried at 100 °C overnight.

2.2. Conversion of magadiite into ZSM-5

ZSM-5 was synthesized at 140 °C with the reaction molar compositon of SiO_2: 0.0025 Al_2O_3: 0.28 Na_2O: 35 H_2O: 0.2 TPABr. The reagents were mixed under stirring in the following order: deionized water, sodium aluminate, sodium hydroxide, tetrapropylammonium bromide, magadiite. Heating of the slurry was started after 3 h of further stirring. The autoclaves were removed from the oven after 18 h, 24 h, 36 h and 42 h, respectively, and cooled by water. The solid products were separated by vacuum filtration, washed with deionized water till pH = 7–8 and then dried at 100 °C overnight. Samples were marked as Z 18, Z 24, Z 36 and Z 42, according to the total time of hydrothermal treatment for 18, 24, 36 and 42 h, respectively.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were performed on a Panalytical X'Pert powder diffractometer at 40 kV and 40 mA.

The SiO_2/Al_2O_3 molar ratio of the as-synthesized zeolite ZSM-5 was determined by X-ray fluorescence spectrometry (XRF) using a JSX-3400R spectrometer.

The Brunauer- Emmet-Teller (BET) surface area of the calcinated zeolite ZSM-5 was determined by a Micromeritics ASAP-2020 porosity analyzer after being degassed at 350 °C for 4 h.

The acidity of H-ZSM-5 was investigated using the ammonia temperature-programmed desorption (NH_3-TPD). Sample was pretreated at 500 °C in He flow for 1 h, then cooled to 120 °C, exposed to a mixed gas of ammonia (7.88 vol %) with helium for 40 min. The physically adsorbed NH_3 was removed by He at 120 °C for 1 h. NH_3-TPD was performed on an automated chemisorption analyzer (ChemBET Pulsar TPR/TPD, Quantachrome, USA) from 120 to 650 °C at a temperature ramp rate of 10 °C/min. The desorbed NH_3 was detected continuously with a thermal conductivity detector (TCD).

Scanning electron micrograph (SEM) images were obtained with a NOVA NANOSEM 450 scanning electron microscopy.

Raman spectra were measured by a Thermo Scientific Raman spectrometer, with a 532 nm excitation line.

Solid-state NMR studies were performed on a Bruker AVANCE III 600 spectrometer at a resonance frequency of 150.9 MHz using a 4 mm MAS probe. ^1H-^{13}C CP MAS NMR spectra were recorded with a spinning rate of 8 kHz, a contact time of 2 ms and a recycle delay of 5 s. The chemical shifts of ^{13}C were externally referenced to TMS.

HEXRD experiments were carried out on a Panalytical Empyrean powder diffractometer using Ag Kα (λ = 0.55941 Å) and a scintillation detector, with incident photon energy of 22 keV. Data were collected from 2θ = 1.5° to 120°, with a step length of 0.02° (2θ) and counting times of 10 s/step. The collected data were subjected to well established analysis procedures including absorption, background and the Compton scattering corrections followed by normalization to the total scattering factor, $S(Q)$, which is related to the coherent part of the diffraction pattern, $I^{coh}(Q)$, as eq. (1):

$$S(Q) = 1 + [I^{coh}(Q) - \sum c_i |f_i(Q)|^2]/|\sum c_i f_i(Q)|^2 \tag{1}$$

where $I^{coh}(Q)$ is the measured coherent scattering intensity, and c_i and $f_i(Q)$ are the atomic concentration and X-ray atomic form factor, respectively, for atomic species of type i [23]. PDF, $G(r)$, is derived from eq. (2),

$$G(r) = \frac{2}{\pi}\int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1]\sin(Qr)dQ \tag{2}$$

Here, Q is the magnitude of the wave vector ($Q = 4\pi\sin\theta/\lambda$, where 2θ is the angle between the incoming and outgoing radiation and λ is the wavelength of the incident X-ray radiation). $Q_{\max}$ collected in this study is 19.4 $Å^{-1}$. In this study, the conversions of the HEXRD data to the PDFs were performed using the program PDFgetX2 [24].

3. Results and discussion

3.1. Characterization of as-synthesized zeolite ZSM-5

Powder XRD patterns of as-synthesized zeolite ZSM-5 is shown in Fig. 1(Z 42). The XRD pattern of Z 42 is in good agreement with the reported profiles for the MFI structure, indicating that a pure phase zeolite ZSM-5 is obtained. The SiO_2/Al_2O_3 molar ratio of the as-synthesized zeolite ZSM-5 is 63.5. After calcination of the as-synthesized zeolite ZSM-5 at 550 °C for 10 h, the sample shows a high BET surface area, 363 m^2/g, which is similar to the previous work [18], indicating that the as-synthesized zeolite ZSM-5 exhibits high crystallinity.

The calcinated zeolite ZSM-5 was converted to NH_4^+- ZSM-5 by applying conventional ion exchange procedures, and then H-ZSM-5 was obtained by thermal treatment. In the NH3-TPD curve of H-ZSM-5 as shown in Fig. 2, two peaks are generally observed in two temperature regions. The region-I (400–600 K) and region-II (600–800 K) temperature ranges represent weak and strong acid strength, respectively [19]. The area under the peaks represents relative acid-site density or the number of each acid-site [20]. The total acidity of as-synthesized H-ZSM-5 is 0.34 mmol (NH_3)/g).

3.2. Formation pathway for zeolite ZSM-5 from magadiite

XRD patterns of magadiite and the solid samples obtained at various time intervals during the transformation were shown in Fig. 1. Fig. 1(Z 18) shows that the intensity of peaks of magadiite is weaker after hydrothermal synthesis for 18 h. As the crystallization progresses, the intensities of the diffraction peaks of magadiite gradually reduce until

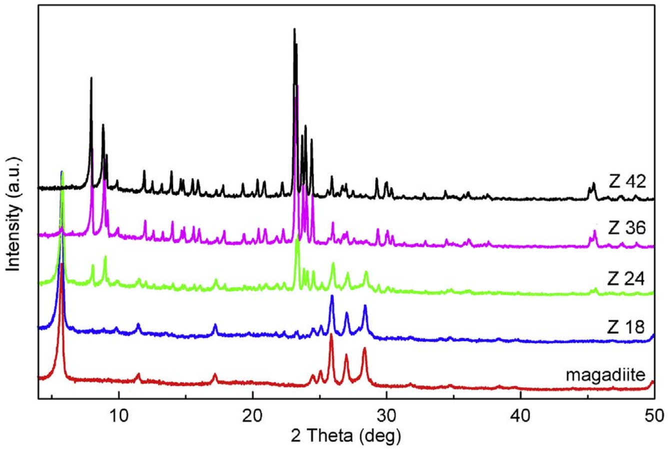

Fig. 1. XRD patterns of magadiite and the products obtained by heating the reactants for 18 h (Z 18), 24 h (Z 24), 36 h (Z 36) and 42 h (Z 42).