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Changes of medium-range structure in the course of crystallization of mordenite from diatomite

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ABSTRACT

Mordenite was synthesized from diatomite in a template-free system. The crystallization behavior and changes of medium-range structure during the crystallization were studied by X-ray diffraction, scanning electron micrograph, vibrational spectroscopy and high-energy X-ray diffraction. It is indicated that major 4-membered rings are formed at a stage later than that of 5-membered ring in the course of crystallization. Diatomite has also been demonstrated to consist of 5-membered rings and various rings lager than 5-membered ring. A formation pathway for mordenite from diatomite could be proposed that 5-membered rings formed initially are undergoing accommodation of 4-membered rings around them to form mordenite.

1. Introduction

Zeolites are crystalline aluminosilicates in which the aluminum and silicon atoms are present in the form of AlO_4 and SiO_4 tetrahedra. As it is reported in the previous study, the short-range order is represented by the local coordination polyhedra, while the medium-range structure can be regarded as the next highest level of structural organization beyond the short-range order [1]. Zeolites have attracted great interest in material and chemistry fields because of their unique structures and properties. To exploit efficient routes of zeolites, it is very necessary to understand their formation mechanism. In the past decades, many techniques have been used to study the formation mechanism of zeolite, and a number of mechanisms were proposed, such as solution transport [2,3] and solid phase transformation mechanisms [4,5]. However, the details on the atomic arrangement during the crystallization have not yet fully elucidated. These details are key issues in studying the formation pathway for zeolite. Vibrational spectroscopy is a useful technique to identify the structural elements of zeolites. Atomic pair distribution function (PDF) technique is another powerful method to determine the short and intermediate range structures of both disordered and crystallographic materials with the advent of high energy X-ray, neutron sources and fast computing. The PDF technique takes advantages of the Fourier relationship between measurable diffraction intensities and the real-space arrangement of atoms. It allows both the Bragg and diffuse scattering to be analyzed together without bias, revealing the short and intermediate range order of the material regardless of the degree of disorder [6]. Therefore, vibrational spectroscopy [7–10] and PDF analysis of high energy X-ray powder diffraction data [11–15] have been applied to study on the crystallization mechanisms of several zeolites.

Mordenite consists of parallel 12-membered ring (12R) channels and 8-membered ring (8R) channels along the [0 0 1] direction. It is an industrially important zeolite and is used in the separation and catalysis such as hydrocracking, hydroisomerization, alkylation, reforming dewaxing and dimethylamines synthesis [16,17]. Therefore, a lot of articles and patents concerning the synthesis of mordenite were reported [18–20]. However, there are relatively few reports on the detailed investigation of formation pathway for mordenite. To our knowledge, the only mechanism study reported in the literature is done by Dutta et al. They proposed that 4-membered rings (4Rs) initially present in the amorphous gel are undergoing accommodation of 5-membered rings (5Rs) around them in the synthesis of mordenite form colloidal silica [9]. In the present work, mordenite was synthesized from diatomite in a template-free system. Diatomite is a kind of siliceous biogenic sedimentary rock, which has been used as the raw material to prepare zeolites due to its relatively low cost and large reserves [21,22]. It consists of amorphous silica derived from skeletons of diatoms. Since zeolite crystallization is a complex process that may take place through different pathways depending on the structure being synthesized, the gel composition and the synthesis conditions. Clearly,

the formation pathway for mordenite from diatomite should be different from that for mordenite from colloidal.

In this study, the crystallization behavior and changes of medium-range structure during the crystallization of mordenite from diatomite were studied, for the first time, by X-ray diffraction (XRD), scanning electron micrograph (SEM), vibrational spectroscopy and high-energy X-ray diffraction (HEXRD). Synthesis of zeolites from cheap silicates, which little waste water and products are obtained with high yield, is considered to be one commercialization way in the future. This finding will promote to learn more about the formation mechanism and guide efficient synthesis of zeolites from silicates.

2. Experimental

2.1. Synthesis procedure of mordenite

The starting materials included diatomite (73.79% SiO_2, 11.30% Al_2O_3, Jilin province, China), water glass (26.81% SiO_2, 8.36% Na_2O, Liaoning province, China) and deionized water. The synthesis process was performed as follows: first, deionized water was placed into a 50 mL stainless steel autoclave; and then the water glass was added under stirring; last, diatomite was added. The molar composition of the resultant mixture was 23.20 SiO_2: 1.00 Al_2O_3: 3.65 Na_2O: 147.72 H_2O. Hydrothermal treatment began after 20 min of further stirring and carried out at 165 °C for 6–16 h. The autoclaves were removed from the oven after 6 h, 11 h, 13 h and 16 h, respectively, and cooled by water. The solid products were washed with deionized water till pH = 7–8 and dried at 100 °C overnight. Samples were named according of the total time of hydrothermal treatment: M 6, M 11, M 13 and M16, with times of heating for 6, 11, 13 and 16 h, respectively. Diatomite is named as M 0 in this study.

2.2. Characterization

The samples were identified by a Panalytical X'Pert powder diffractometer at 40 kV and 40 mA using Cu Kα radiation.

The Si/Al molar ratio of the as-synthesized mordenite was determined by X-ray fluorescence spectrometry (XRF) using a JSX-3400R spectrometer.

Solid-state ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) experiments were performed on a Bruker AVANCE III 600 spectrometer at a resonance frequency of 119.2 MHz. ^{29}Si MAS NMR spectra with high-power proton decoupling were recorded on a 4 mm probe with a spinning rate of 12 kHz, a π/4 pulse length of 2.6 μs, and a recycle delay of 120 s. The chemical shifts of ^{29}Si are referenced to TMS.

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. Infrared (IR) spectra were measured by a Nicolet 6700 FTIR spectrometer at 2 cm^{-1} resolution.

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):

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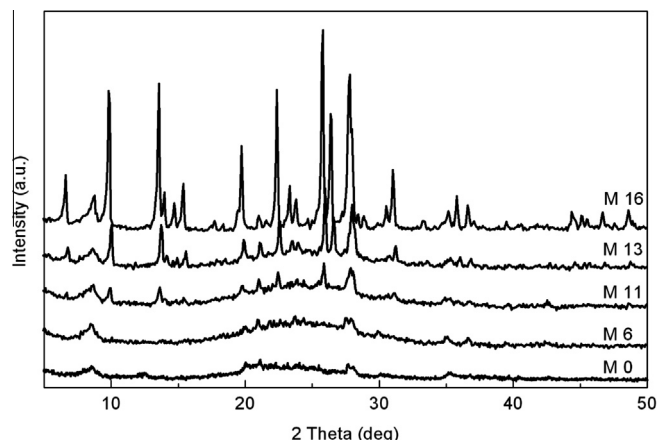

Fig. 1. XRD patterns of diatomite (M 0) and the solid samples obtained by heating the reactants for 6 h (M 6), 11 h (M 11), 13 h (M 13) and 16 h (M 16). All Bragg peaks seen in the sample M 16 are due to MOR structure.

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),

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

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

Powder XRD patterns of M 0, M 6, M 11, M 13 and M 16 are shown in Fig. 1. It is found that Bragg peaks due to mordenite are observed after 11 h of heating. The XRD pattern of M 16 is in good agreement with the reported profiles for the MOR structure, indicating that the crystallization is completed after 16 h of heating. The Si/Al molar ratio of the as-synthesized mordenite is 7.4.
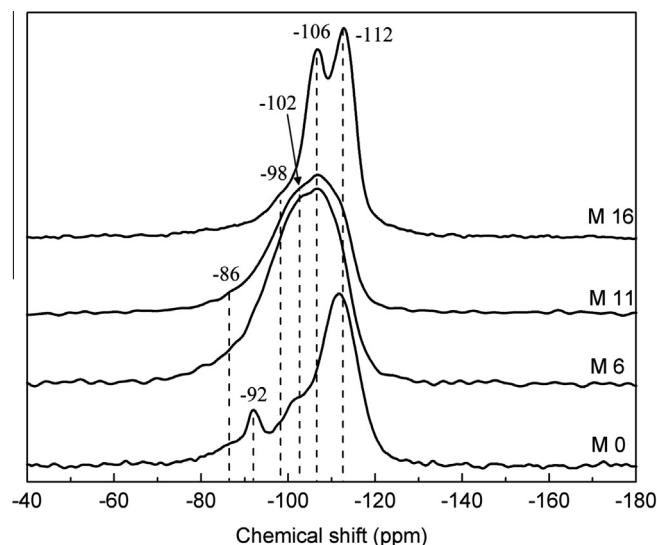

Fig. 2. Solid-state ^{29}Si MAS NMR spectra of diatomite (M 0) and the solid samples obtained by heating the reactants for 6 h (M 6), 11 h (M 11) and 16 h (M 16).