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Hydrothermal conversion of magadiite into mordenite in the presence of cyclohexylamine

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A B S T R A C T

Hydrothermal conversion of magadiite, in the presence of cyclohexylamine (CHA), into a commercially important mordenite (MOR zeolite) has been investigated. The effects of various parameters such as the reactant H_2O/SiO_2 ratio, CHA/SiO_2 ratio, reaction time, the presence of sodium ions and potassium ions are studied. Thermal and acid stability of the as-made MOR zeolite were examined. The pure MOR zeolite with high crystallinity, which is composed of parallelepiped crystals agglomerate, was obtained at 140 °C for 28 h with the molar composition: $0.14M_2O:SiO_2:xAl_2O_3:54H_2O:16CHA$ ($M_2O = K_2O + Na_2O$, K/K + Na = 0.3, $x = 0.028$ and 0.04). The structure of the sample was totally destroyed at 1100 °C and the product is exceptionally stable towards strong acid.

1. Introduction

Magadiite, with the ideal chemical composition $Na_2Si_{14}O_{29}·9H_2O$ [1], is a crystalline layered silicate existing in nature as mineral and can be easily synthesized in the laboratory under hydrothermal condition [2–8]. The interlayer space of magadiite contains oxygen ions which are compensated by sodium ions between the layers. Magadiite is a promising material as a catalyst and novel adsorbent owing to its high charge density and reactivity between its silicate sheets. Another application has recently been developed by conversion of magadiite into porous materials.

Magadiite used as starting precursor to synthesize porous materials has been attracting widespread interest due to its scientific significance and industrial application. The advantages of this approach are that the binderless preshaped zeolites can be prepared and gain economical profits. The recrystallization and/or conversion of magadiite into several known zeolites are well documented in the literature. Magadiite was first used as the silica source in the synthesis of ZSM-5 (MFI) and ZSM-11 (MEL) zeolites without going into details [9]. The controlled full or partial hydrothermal recrystallization of aluminum-substituted magadiite varieties to MFI and MEL zeolites was elucidated by Gabriella [10]. Feng et al. compared magadiite with fumed silica and reported that magadiite showed a higher reactivity for the formation of silicalite-1 [11]. The MOR sample was also obtained in the presence of tetraethylammonium hydroxide [12,13]. The synthesis of ferrierite by hydrothermal transformation of magadiite by using piperidine as the intercalating and/or structure directing agent has also been reported [14,15]. Using Mn^{2+} ion-exchanged magadiite precursor, Mn-silicalite-1 was obtained by Ko et al. [16]. Many types of zeolites made from magadiite, including ZSM-11, ZSM-39, ZSM-48, EU-2, FU-1, SSZ-15 [17] and FLS-1 [18], were investigated by using various templates. In our effort to broaden the diversity of synthesis zeolites from magadiite, we have presented a considerable amount of work on the recrystallization of magadiite into zeolites such as offretite and ferrierite by using structure agents like tetramethylammonium bromine and ethylenediamine, respectively [19,20]. The influence of short-chain tetraalkylammonium cations on the recrystallization of magadiite into zeolites were also studied in detail in our previous work [21].

MOR zeolite, which is a high-silica zeolite with two-dimensional pores, has been considered for applications as the adsorptive separation of gas or liquid mixtures and catalysis owing to its high thermal and acid stabilities [22]. It can also be used as hosts of semiconductor materials, chemical sensors and nonlinear optical materials [23–25]. For the first time, the present paper deals with the conversion of magadiite to MOR zeolite using cyclohexylamine as the template and/or structure directing agent. This conversion is achieved via hydrothermal treatment in a CHA–H_2O system. The purpose of this paper was to investigate the parameters affecting the conversion and to identify the products by different techniques.

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2. Experimental

2.1. Synthesis of magadiite

Magadiite was prepared from a gel having the molar composition $0.15Na_2O:4.22H_2O:SiO_2$ at 160 °C for 42 h according to the previous reported study in our laboratory [6]. A typical procedure was as follows: 24 g water glass was stirred with 1 g deionized water at room temperature, followed by adding 8 g diatomite. After being stirred 10 min, the mixture was transferred into a 100-mL Teflon-lined autoclave and heated under autogenous pressure. The resulting crystalline product was washed with deionized water and dried at 100 °C overnight.

2.2. Hydrothermal conversion of magadiite into mordenite

The hydrothermal conversion of magadiite into MOR zeolites was performed as follows. $NaAlO_2$ (45% Al_2O_3) was dissolved in deionized water, and then NaOH, KOH and magadiite was added into the above solution. The synthesis mixture was stirred for 2 h at room temperature. After stirring, CHA was added into the mixture. The resultant synthetic solution had the chemical composition of $0.14M_2O:SiO_2:xAl_2O_3:54H_2O:16CHA$ ($M_2O = K_2O + Na_2O$, K/K + Na = 0.3, $x = 0.028$ and 0.04).

The mixture was charged into 100 mL stainless steel autoclaves equipped with a Teflon liner and then crystallization was conducted at 140 °C for 12 h to 7 d. After crystallization, the autoclave was cooled to room temperature, and the sample was filtered and washed with deionized water till pH = 7–8. The product was dried at 100 °C overnight. The sample was calcined at 550 °C for 10 h in order to remove the organic species.

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 (CuKα). The diffractograms were recorded from 3° to 50° using a step size of 0.013° and at a scanning speed of 8° min^{-1}. Scanning electron microscopy (SEM) was performed with a QUANTA450 microscope using an accelerating voltage 30 kV. Thermogravimetric analysis (TG) features were measured on a TA Instruments, Q50, under nitrogen flow heated from 50 to 800 °C, at a heating rate of 10 °C min^{-1}. The adsorption and desorption isotherms were obtained by an automated nitrogen adsorption analyzer (Micromeritics, ASAP 2020), and the sample was outgassed at 350 °C for 4 h prior to the measurements. Specific surface area was calculated by using the Brunauer–Emmet–Teller (BET) method. The IR spectra were recorded in transmission mode on a Nicolet 6700 FTIR spectrometer over the spectral region from 400 to 4000 cm^{-1} with a resolution of 4 cm^{-1} using the KBr disc technique. ElementarvarioEL III elemental analyzer was applied to determine the carton and nitrogen content in the synthesized MOR sample. The SiO_2/Al_2O_3 ratio was measured by inductively coupled plasma MassSpectrometer (ICP, Optima2000DV, PerkinElmer). The ^{27}Al MAS NMR spectra were recorded on a Varian Infinity Plus 400 spectrometer.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 depicts the XRD patterns of the starting material magadiite and products obtained at various crystallization times. All the diffraction peaks are indexed to those of magadiite which indicates that the product is free from impurities (curve (a) in Fig. 1). The typical peaks corresponding to magadiite decreases drastically at the reaction time of 12 h (Fig. 1(b), sample 1) and those corresponding to MOR zeolite are initially observed at the heating time of 16 h (Fig. 1(c), sample 2). This indicates that the nucleation of MOR zeolite occurs during the first 16 h after heating. After 28 h of reaction the highly crystalline and pure MOR zeolite could be obtained (Fig. 1(d), sample 3). It implies that magadiite is not directly transformed into MOR zeolite. The magadiite crystals decompose in alkaline media of NaOH and KOH firstly. Then "the building units" of magadiite rearrange and thus assemble into MOR zeolite framework. The crystallinity is not altered at the heating time of 72 h (Fig. 1(e), sample 4). Upon heating 168 h, MOR zeolite along with analcime (ANA) and α-quartz are obtained (Fig. 1(f), sample 5). This trend indicates that less stable species (MOR zeolite) nucleate more rapidly than the more stable ones (ANA and α-quartz) [23].

The effects of various parameters such as the reactant SiO_2/Al_2O_3 ratio, H_2O/SiO_2 ratio, CHA/SiO_2 ratio, the presence of sodium cations and potassium cations on the conversion of magadiite into

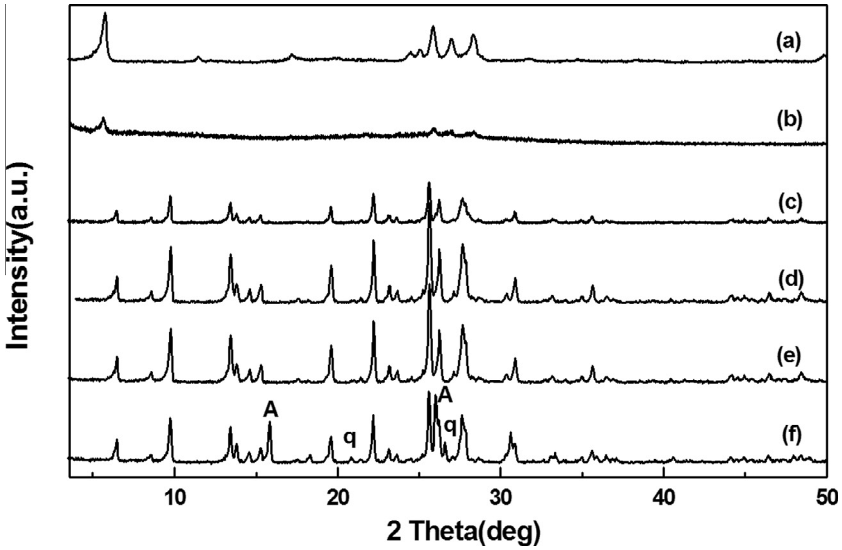

Fig. 1. X-ray powder diffraction patterns of (a) magadiite and the samples withdrawn at various intervals of hydrothermal conversion of magadiite into MOR zeolite at 140 °C for (b) 12 h, (c) 16 h, (d) 28 h, (e) 72 h and (f) 168 h (Nos. 1–5, Table 1).