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Mechanism of zeolite X crystallization from diatomite

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ABSTRACT

Here we systemically investigated the crystallization process of zeolite X using diatomite, a natural cost-effective silica precursor by the hydrothermal method. To decipher the mechanism, solids were separated from the mixtures at various stages of crystallization and were characterized by XRD, SEM, solid state NMR, FT-IR, UV-Raman and XRF. The XRD patterns revealed that the crystallization started between 3 and 3.5 h and ended by 5 h. The SEM images showed that the intermediate species of zeolite X appear on the surface of particles. The FT-IR and UV-Raman spectra suggested the presence of double six-membered rings (D6R) in the framework of zeolite X and they played a critical role in the crystallization process. Furthermore, the UV-Raman spectra indicated that the secondary building units of β cages formed the intermediate species and they were interconnected via double six-membered rings to form the framework of zeolite X.

1. Introduction

Zeolites are microporous crystalline materials made up of corner sharing TO4-tetrahedra (T stands for tetrahedral atom, in classical zeolites, they are Si or Al). The structure is the result of spatial connection between SiO4 and AlO4 tetrahedra in three-dimensional system and there are channels and cages with well defined dimensions making them interesting for industrial applications, such as catalysis [1], adsorption [2,3], ion exchange [4,5] and membranes [6].

Generally, zeolites are synthesized via hydrothermal method from chemical reagents as starting materials. Over recent years, natural aluminosilicate and silicate minerals and industrial solid wastes such as coal fly ash [7–9], metakaolin [10–12], solid wastes [13–15], rice husk [16] and diatomite [17–19] have also been explored as silica and/or alumina sources to synthesize zeolites. Among them, diatomite is an interesting natural material due to its relatively low cost, large reserves and highly reactive amorphous state derived from silica skeletons of diatoms making it an alternative low-cost precursor to processed chemicals in order to synthesize zeolites. However, the formation of a particular zeolite structure strongly depends on the chemical composition and nature of species present in the precursor gel [20,21]. In addition, the limited understanding of the zeolite formation mechanism from natural minerals is one of the challenges for most researchers to rationally control the synthesis process. Because most of the published research [1,9,22–24] about the formation of zeolites from natural minerals was related to the optimization of synthesis conditions or practical applications after synthesis instead of the formation mechanism. Therefore, A detailed and deeper understanding of nucleation and crystal growth of zeolite from natural minerals will not only help in controlling and predicting the best conditions but will also unmask the cooperative relationships between the chemical composition of natural minerals and zeolite structure.

Many techniques have been used to obtain the fundamental understanding of nucleation and crystal growth of zeolite and then arrive at its formation mechanism. Solid state NMR and UV-Raman are the most powerful tools for the characterization of zeolites. The solid state NMR technique can gain detailed information about speciation in both solid and liquid phase, which will identify the changes in the connectivity of Si and Al atoms in the solid phase, as well as the structure of silicate and aluminosilicate anions present in the liquid phase at various stages of crystallization. UV-Raman techniques can be applied to the study of zeolite synthesis and provide structural information of intermediate species during the crystallization process

In the present work, we report on the synthesis of zeolite X from diatomite under hydrothermal conditions. In order to understand the crystallization process and species involved in nucleation and crystal growth, the solids separated from the mixtures at various stages of crystallization were characterized by XRD, SEM, solid state NMR, FT-IR,

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UV-Raman and XRF. Finally, the crystallization mechanism was systematically explored and discussed.

2. Experimental

2.1. Materials

Diatomite (Dt) is obtained from Linjiang City, Jilin Province, China. Its main chemical composition by wt% is: SiO_2: 63.77%; Al_2O_3: 18.97%; Fe_2O_3: 1.48%; CaO: 0.48%; K_2O: 0.16%; Na_2O: 0.04%. It was ground to a size smaller than 30 mesh and dried at 105 ℃. Sodium hydroxide, aluminum hydroxide and the other chemicals used in the experiments were purchased from Xilong Reagent Co. (Xilong, China). All chemicals were of analytical reagent grade and used without any further purification. Deionized water was used throughout this study.

2.2. Synthesis of zeolite X

The zeolite X was synthesized from diatomite according to our previous work, which includes three processes as follows: gel formation, aging and crystallization. It was carried out under different crystallization times, while other preparation conditions including crystallization temperatures, aging temperature and time, Na_2O/SiO_2 and H_2O/Na_2O ratio were kept constant. The following conditions were used: 110 ℃ of crystallization temperature, 30 ℃ of aging temperature, 30 min of aging time, 40 of H_2O/Na_2O ratio and 1.4 of Na_2O/SiO_2 ratio. Initially, 10.83 g diatomite and 4.84 g $Al(OH)_3$ were dispersed in 116 mL of NaOH solution (2.78 mol/L) under vigorous magnetic stirring for 30 min to form a homogeneous dispersion at room temperature. Then, the mixed solution was put into a Teflon-lined stainless steel autoclave. Finally, the container was closed and maintained at 110 ℃ for different crystallization times. After that, the autoclave was cooled to room temperature naturally, and then the solid phase and the supernatant solution were obtained by separating the synthesized slurry before further measurement.

2.3. Characterization

The surface morphology of samples was observed by S-4800 scanning electron microscope (Hitachi, Japan). X-ray diffraction measurements (XRD) were performed on a D8 advance X-ray diffractometer (Bruker, Germany) equipped with Cu-Kα radiation (λ = 0.154056 nm) to identify the crystalline phases of the obtained adsorbents. The samples were scanned in the range of 2θ from 10° to 80° with a 0.02° step at a scanning speed of 4°/min. Chemical composition of samples were determined using wavelength dispersive X-ray fluorescence spectrometry (XRF) on a Shimadzu XRF-1800 apparatus. Solid-state ^{29}Si and ^{27}Al MAS NMR experiments were performed on a Bruker DRX-400 spectrometer. ^{29}Si NMR spectra were recorded at 79.5 MHz using a 1.6 μs π/4 pulse with a 4 s recycle delay and 2000 scans. The samples were spun at 4 kHz and chemical shifts were referenced to 4, 4-dimethyl-4-silapentane sulfonate sodium (DSS). ^{27}Al NMR spectra were recorded at 104.3 MHz using a 0.75 μs π/12 pulse with a 0.5 s recycle delay and 800 scans. The chemical shift was referenced to aluminum nitrate. UV Raman spectra were measured with a Jobin-Yvon T64000 triple-stage spectrometer at a resolution of 2 cm^{-1} in the range between 100 and 4000 cm^{-1}. And the excitation line was 324 nm. Fourier-transform infrared spectroscopy was also applied in this work, and the spectra were obtained using a Thermofisher Nicolet 6700 spectrometer. The samples were prepared by mixing with potassium bromide (KBr) followed by making pellets.

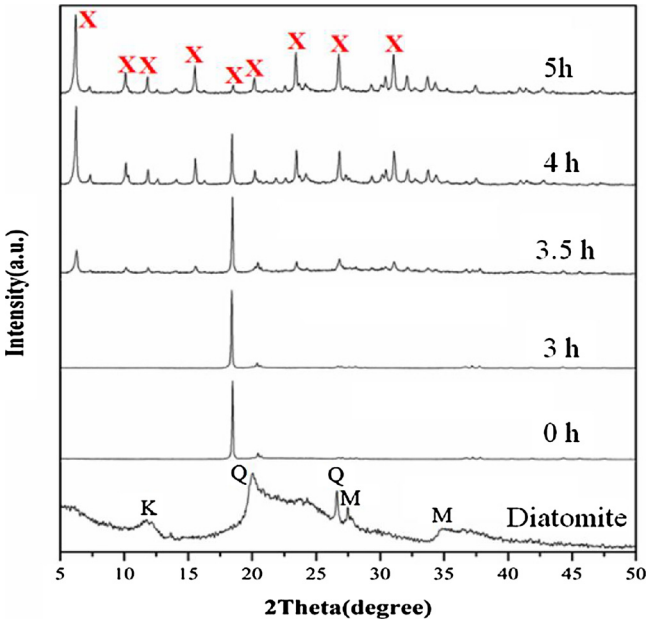

Fig. 1. XRD patterns of diatomite precursor and samples synthesized at different crystallization times of 0 h, 3 h, 3.5 h, 4 h and 5 h. X = zeolite X; Q = quartz; M = montmorillonite; K = kaolinite.

3. Results and discussion

3.1. XRD analysis

The XRD patterns of diatomite and samples synthesized at different crystallization times are shown in Fig. 1. According to the XRD patterns of diatomite, the broad reflection centered at 2θ = 15–30° is attributed to the amorphous silica, and the peaks at 2θ = 20.08° and 26.65° are ascribed to quartz. The peaks at 11.88°, 27.35° and 35°–40°, which are characteristic to kaolinite-montmorillonite [25,26]. It can be seen from Fig. 1 that no product of zeolite X was obtained at crystallization time from 0 h to 3 h, but after 3.5 h the characteristic diffraction peaks of zeolite X (JCPDS 38-0237) were detected at 2θ = 6.10°, 9.97°, 15.39°, 23.24°, 26.58° and 30.86° and these reflections were observed to grow as time increased up to 5 h. Meanwhile, the typical diffraction peak of aluminum hydroxides at 2θ = 18.35 can also be found, which might be due to the incomplete reaction of diatomite and aluminium hydroxides. Then it decreased from 3.5 h to 5 h and finally disappeared when the crystallization time was 5 h. The XRD analysis pointed out that the crystallization in the system may start between 3 and 3.5 h with the hydrothermal treatment.

3.2. FT-IR analysis

It is well known that spectroscopic methods provide useful information about the structure of intermediate species during the crystallization process. The FT-IR spectra with wavenumbers from 1800 to 4000 cm^{-1} of diatomite and samples synthesized at different crystallization times are shown in Fig. 2. As for diatomite, the bands at 3700 and 3620 cm^{-1} are assigned to the OH stretching of inner surface hydroxyl [27] and stretching mode of the OH-group coordinated to Al cations [25,26], respectively. And the broad band at 3437 $cm^{-1}$is due to the stretching vibration of the OH groups on the surface [28]. When the crystallization time was from 0 h to 3.5 h, there appeared a new band at 3525 cm^{-1}, which is attributed to the hydrogen bonded O—H···groups [29]. The appearance of hydrogen bonded O—H···groups may be due to the gel transformation in alkaline solutions. When the crystallization time was from 4 h to 5 h, there was only one broad band at 3475 cm^{-1} attributing to the water molecules and the OH groups on