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Investigation on the effect of zeolite precursor on the formation process of MCM-41 containing zeolite Y building units

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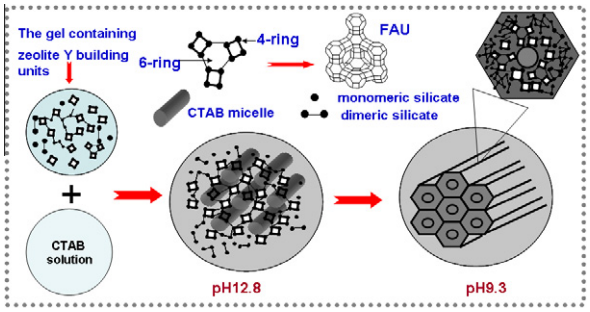
HIGHLIGHTS

- Zeolite Y secondary building units promotes a metastable mesopore formation.
- Low-polymerized silicates cannot induce mesopore formation at high pH.
- Well-crystallized zeolite crystals cannot induce mesopore formation at high pH.
- During the synthesis process the structure and locations of CTAB changes.

GRAPHICAL ABSTRACT



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ABSTRACT

The formation process of MCM-41 containing zeolite Y building units has been investigated by UV Raman spectroscopy, ^{29}Si and ^{27}Al MAS NMR spectroscopy, X-ray diffraction (XRD), N_2 adsorption and electron microscopy (SEM and TEM). It is found that the precursor containing zeolite Y secondary building units promotes the formation of a metastable mesopore structure just after mixing the zeolite precursors with CTAB. In contrast, the low-polymerized aluminosilicates and well-crystallized zeolite crystals cannot be assembled with CTAB at this stage. The result supports that the zeolite secondary building units should promote to the formation of the mesopore wall. This has been ascribed to its high anionic charge density as well as the appropriate multidentate coordination. Lowering down the pH value to 9.3 facilitates the further polymerization of the aluminosilicate species to build up a stable mesoporous phase.

Introduction

Mesoporous materials such as M41S, SBA and MSU have been synthesized since early 1990 [1–4]. These materials possess larger pore size and facilitate the diffusion of bulky molecules. They have been extensively applied in many fields such as catalysis, adsorption, environment, medicine and biotechnology [5–12]. At the same time the studies on the synthesis mechanism of mesoporous materials also received extensive attention. Several mechanisms have been proposed for the synthesis of the MCM-41-type materials [12–26]. Each mechanism provides the useful information for understanding the formation process and guides the synthesis of new mesoporous materials.

However, the molecular sieves such as MCM-41 show relatively low acidity and hydrothermal stability due to the amorphous nature of the pore walls. Therefore, various methods have been proposed to improve the hydrothermal stability and acidity of MCM-41-type materials [27–44]. One of the most common approaches is the self-assembly of protozeolitic nanoclusters or 'zeolite seeds' with surfactant micelle [27–41]. The first step is the crystallization of the aluminosilicate gel to obtain zeolite seeds. Then the gel containing zeolite seeds is assembled with surfactant micelle to form mesopore structure. In our previous work, the effect of zeolite precursor on the formation of MCM-41 molecular sieve containing zeolite Y building units have been investigated [45]. The paper focused on the effect of zeolite precursor crystallization process

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and pH adjustment on the final structure of the product. More recently, Shi et al. [46] reported the preparation of hierarchical mesoporous zeolites by self-assembly with CTAB. Their work focused on the kinetic control over zeolite seed formation. Considering that the protozeolitic nanoclusters/zeolite seeds are different from the amorphous aluminosilicate source, the cooperative interactions between the different precursors and CTAB micelles should be another important issue.

Surfactant such as cetyltrimethylammonium bromide (CTAB) is commonly used as the template for the preparation of the MCM-41-type materials. The micelle configuration of CTAB is a key issue for the understanding of the mesopore formation. Depending on the cooperative self-assembly formation mechanism, the preorganized surfactant arrays may be rearranged according to the charge density matching and shape requirements after adding the silica species. The final configurations are dependent on the silica-surfactant liquid–crystal phases [17–23]. However, to the best of our knowledge, there is few detailed work focusing on the interaction of the zeolite precursors and CTAB micelles during the self-assemble process.

Raman spectroscopy has been extensively used to study the cationic, anionic, and nonionic surfactants [47–53]. The surfactants such as CTAB form micelles in aqueous solution when concentration is above the certain critical micelle concentration (cmc). The transformation from all-trans to gauche conformation can be identified by the Raman bands in the range of 1000–1200 cm^{-1}. The disorder/order parameter (I_{2850}/I_{2890}) and environment polarity parameter (I_{2930}/I_{2850}) are used to estimate the degree of disorder and the polar/apolar character of the hydrocarbon chains. [50–52]. In particular, UV Raman spectroscopy avoids fluorescence interference, and has been proved to be a powerful tool for characterization of zeolite and zeolite building units in mesoporous material [45,54–65].

In this study, the formation process of the MCM-41 molecular sieve using zeolite Y synthesis gel as the silicate source has been investigated by UV Raman spectroscopy, ^{29}Si and ^{27}Al MAS NMR spectroscopy, X-ray diffraction, N_2 adsorption and electron microscopy (SEM and TEM). This work focused on the effect of the precursors on the intermediate structure of the assembled aluminasilicates before the pH adjustment, and the changes in the structure and configuration of CTAB micelles induced by the self-assembly process.

Materials and methods

Synthesis of the material

Chemical reagents included sodium hydroxide (AR, Shenyang xinxing reagent plant), Ludox (30% SiO_2 Qingdao Haiyang Chemical Co., Ltd), Sodium silicate nonahydrate (Tianjin Bodi Chemical Holding Co., Ltd), Sodium aluminate (AR, Tianjin Jinke Fine Chemical Research Institute) and Cetyltrimethylammonium bromide (CTAB) (AR, Tianjin guangfu fine chemical research institute).

MCM-41 was prepared as follows: the sodium silicate solution was prepared by mixing 5.12 g sodium silicate nonahydrate with 28.34 g deionized water. Then CTAB aqueous solution composed of 1.46 g CTAB and 20 g deionized water was added to the sodium silicate solution. The pH value was lowered down by dropwise adding the sulfuric acid to the mixed solution, and then the gel was formed. MCM-41 containing zeolite building units was prepared according to the previous paper [45]. Zeolite Y was prepared as follows: 1.18 g sodium aluminate was added to the aqueous sodium hydroxide solution, which is composed of 3.12 g sodium hydroxide and 14.15 g deionized water. Then 18 g Ludox was added to the basic sodium aluminate solution under vigorous stirring until a homogeneous white gel was formed. The gel was crystallized at 100 °C for different times. After that CTAB aqueous solution composed of 7.82 g CTAB and 228.6 g deionized water was added to the colloidal zeolite Y and the pH value was adjusted to 9.3 by dropwise adding the sulfuric acid to the mixed solution. The hydrothermal crystallization samples were prepared by transferring the gels to a stainless-steel autoclave, and kept it in an oven and heated at 100 °C for 44 h. Finally, the solid and liquid phases of the gels were obtained by centrifuging.

Characterization

X-ray powder diffraction patterns of the samples were taken on a Rigaku D/Max 2400 diffractometer (Shimadzu Co.) using nickel-filtered Cu Kα X-ray source at a scanning rate of 0.02 over the range between 1.0° and 20.0°.

UV-Raman spectra were recorded on a DL-2 Raman spectrometer. A 244-nm line of LEXEL LASER was used as the excitation source. Acton triple monochromator was used as a spectrometer for Raman scattering. The spectra were collected by a Prinston CCD detector. The power of the laser line at the sample was 5 mW. The heights of the Raman bands were measured after the baseline was corrected by using the origin 7.0 baseline correction function.

Transmission electron microscopy (TEM) images were recorded on a Tecnai $G^2$20 S-Twin electron microscope operating at 200 kV. Samples for analysis were suspended and dispersed on a grid.

Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 with the acceleration voltage of 3.0 kV. The samples were mounted using a conductive carbon double-sided sticky tape. A thin coating of gold sputter was deposited onto the samples to reduce the effects of charging.

^{29}Si and ^{27}Al MAS NMR spectra were recorded on a Bruker AVANCE III 500WB spectrometer with a recycle delay time of 1 s and a spinning speed of 12 kHz.

N_2 adsorption–desorption isotherm was measured at liquid nitrogen temperature using an AUTOSORB-1-MP system. The pore-size distribution for mesopore was analyzed from the adsorption branch of the isotherm by BJH (Barrett–Joyner–Halenda) method.

Results and discussion

Fig. 1 shows the powder X-ray diffraction (XRD) patterns of the zeolite Y systhesis gels which was used as the precursor for the synthesis of MCM-41. The aluminosilicate gels after crystallizing for 0 and 2 h (the samples a and b) are amorphous since no diffraction peak is present. When the crystallization time is increased to 4 h, the sample c exhibits the weak peaks at 6.2, 10.2, 15.6, 23.6, 26.9 and 31.3°, which are characteristic of faujasite structure. Further, as the crystallization time is extended to 6 h and 12 h, the peak intensities of faujasite zeolite are enhanced significantly. Apparently, zeolite Y crystal begins to form and grow after crystallizing for 4 h.

The zeolite Y synthesis gel was used as the aluminosilicate source to prepare the MCM-41. In the second synthesis step the synthesis gel of zeolite Y was mixed with CTAB solution. It should be noted that the pH value of the mixture is not adjusted and kept at ca. 12.8. Fig. 2 provides the X-ray diffraction patterns of the solid phase of the mixture prepared by mixing CTAB solution with zeolite Y synthesis gels after different crystallization times. The sample a shows no diffraction peak. In contrast, a peak at $2\theta = 2.1°$ is observed in Fig. 2b–d. The d spacing of these samples is about 41 Å. It has been reported that the layered (lamellar) material shows a primary d spacing (repeat distance) of 31(±1) Å and the