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Direct synthesis of mesoporous ZSM-5 zeolite by a dual-functional surfactant approach

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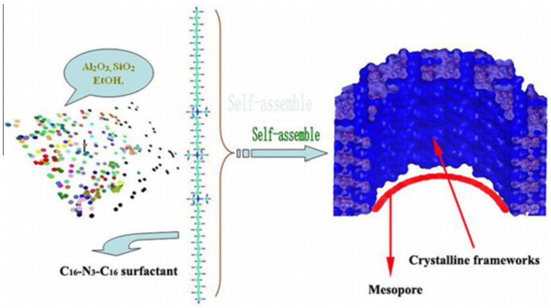
HIGHLIGHTS

- ▶ A dual-functional surfactant has been synthesized.
- ▶ The synthesized mesoporous zeolite possesses crystalline microporous walls.
- ▶ Employing Gaussian DFT method for study of the dual-functional cationic surfactant.
- ▶ The mesoporous ZSM-5 zeolite shows superior catalytic activities.

GRAPHICAL ABSTRACT



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ABSTRACT

Mesoporous molecular sieves with crystalline microporous walls of ZSM-5-like frameworks was directly prepared by a dual-functional triquaternary ammonium-type surfactant. Mesopores are generated by surfactant aggregates and crystalline microporous zeolite frameworks within the mesopore walls are directed by quaternary ammonium functional groups of surfactant. The mesoporous zeolite sample was characterized by a complementary combination of X-ray diffraction, scanning electron microscopy, transmission electron microscopy, nitrogen adsorption isotherms, Fourier transform infrared spectroscopy, ^{27}Al MAS NMR spectra and density functional theory calculation. The results suggest that present method is suitable as a direct synthesis route to highly mesoporous zeolites. Due to the short diffusion routes and strong acidity, the mesoporous ZSM-5 zeolite displayed a clear advantage on catalysis reactions involving large molecules compared to commercial zeolites and mesoporous amorphous materials. The present approach provides an efficient route to synthesize other related mesoporous zeolites in the future.

1. Introduction

Zeolites and related crystalline molecular sieves have shown great (or potential) applications in many modern industrial processes related to catalysis, adsorption, and separation, especially in the field of petrochemical industry due to the fact that these materials possess high surface area, adjustable pore size, high thermal and chemical stability [1,2]. However, in many catalytic applications, the main drawback of zeolites is their intricate pore and channel systems in the molecular size ranging from 0.3 to 1.5 nm [3]. It makes large molecules cannot react effectively over these microporous materials because of the limitation of their small pore sizes.

To solve the diffusion problems of guest species in zeolites, mesoporous aluminosilicate materials with adjustable larger pore sizes, such as MCM-41 [4] and SBA-15 [5] have been successively invented since the 1990s. These materials can overcome the pore size constraint of microporous zeolites and allow the diffusion of lager molecules. However, as compared with conventional zeolites, these mesoporous materials exhibited insufficient hydrothermal

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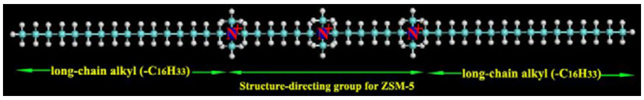

Fig. 1. The molecular structure of 'bifunctional' cationic surfactant (C_{16}–N_3–C_{16}) (white spheres, hydrogen; cyan spheres, carbon; blue spheres, nitrogen). For simplification, counter anions (Br^-) for quaternary ammoniums are omitted.

stability and acidity, which limits their use as catalysts in a wide range of industrial processes and reactions. During the past several years scientists endeavored to improve the framework crystallinity for practical applications, but the hydrothermal stability and framework acidity were still far from the properties of crystalline zeolites.

In order to overcome the limitations of single micro- or mesoporous materials and to combine the advantages of these two types of molecular sieves, Various attempts to synthesize mesoporous aluminosilicate materials with improved framework crystallinity were reported. Among them, the typical ones include the assembling of zeolite seeds or zeolite hydrolysis products to an ordered mesoporous phase [6–10], alkaline or acid leaching [11–15], carbon materials [16,17], the partial recrystallization of preassembled walls of mesoporous materials into zeolitic frameworks [18], treating the mixture of microporous and mesoporous precursor simultaneously [19,20], coating the zeolite primal building unites on the pore walls of pre-synthesized mesoporous silica [21,22]. However, these synthesized products were either microporous zeolite crystals or amorphous mesoporous materials or phase-separated mixtures of them [23]. In a typical approach, molecular templates for zeolites were applied to the synthesis composition for ordinary mesoporous zeolites [24,25]. To get the single-crystal(-like) mesoporous zeolites with the direct synthesis method, mesoscale template and/or synthesis processing should be well designed to control the interactions between the template and zeolitic species during crystallization [26]. In this respect, Ryoo and co-workers had made great progress [27–30]. Herein, extending their work, we report the results obtained by employing a bifunctional triquaternary ammonium-type surfactant (as shown in Fig. 1) that could generate micropores and mesopores simultaneously. Besides, we study the molecular properties of the surfactant by means of the DFT method. The mesoporous ZSM-5 zeolite combined the advantages of mesoporous materials and zeolite crystals made it more desirable for catalytic reactions of large molecules as catalyst, and catalytic activity was investigated.

2. Experimental

2.1. Synthesis of organic surfactant

The gemini-type triquaternary ammonium surfactant is synthesized according to the literature procedures [29]. First 0.0113 mol of N,N-Dimethylhexadecylamine (98%, J&K) and 0.113 mol of 1,6-Dibromohexane (98%, J&K) were dissolved in 50 mL toluene/acetonitrile mixture with v/v = 1:1, then the mixture was refluxed with stirred for 8 h at 65 °C, after cooling to room temperature and solvent evaporation, the precipitated product was $[C_{16}H_{33}–N^+(CH_3)_2–C_6H_{12}–Br]Br^-$. The precipitate was collected by filtration and washed with diethyl ether, and dried in a vacuum oven at 50 °C for 8 h. Second, 0.01 mol of 1-Bromohexadecane (98%, J&K) and 0.1 mol of N,N,N′,N′-Tetramethyl-1,6-hexanediamine (99%, J&K) were dissolved in 50 mL toluene/acetonitrile mixture with v/v = 1:1, then the mixture was refluxed with stirred for 8 h at 65 °C, after cooling to room temperature and solvent evaporation, the precipitated product was $[C_{16}H_{33}–N^+(CH_3)_2–C_6H_{12}–N(CH_3)_2]Br^-$. The precipitate was collected by filtration and washed with diethyl ether, and dried in a vacuum oven at 50 °C for 8 h. Finally, 0.005 mol $[C_{16}H_{33}–N^+(CH_3)_2–C_6H_{12}–Br]Br^-$ and 0.005 mol $[C_{16}H_{33}–N^+(CH_3)_2–C_6H_{12}–N(CH_3)_2]Br^-$ were dissolved in 40 mL acetonitrile, then the mixture was refluxed with stirred for 8 h at 75 °C. After cooling to room temperature and solvent evaporation, the precipitate was filtered and washed with diethyl ether, and dried in a vacuum oven at 50 °C for 8 h to obtain the final product, the $[C_{16}H_{33}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_{16}H_{33}][Br^-]_3$ surfactant, it is designated as C_{16}–N_3–C_{16}. The purity of the final solid product was analyzed by ^1H NMR measurements in $CDCl_3$ solution with a Bruker Avance Digital 400 spectrometer (^1H NMR ($CDCl_3$) δ 0.86 (t, 6H, $[CH_3–(C_{15}H_{30})]_2$); 1.03–1.56 (m, 68H, $[CH_3–(C_{15}H_{30})]_2$, $[N^+–(CH_2)_2–(CH_2)_2–(CH_2)_2–N^+)]_2$); 2.23–2.33 (m, 12H, $[CH_2–(CH_2–N^+–CH_2)–CH_2]_3$); 3.21–3.51 (m, 12H, $[N^+–(CH_2)_2]_3$); 3.76 (s, 18H, $[N^+–(CH_3)_2]_3$)).

2.2. Direct synthesis of the mesoporous zeolite

In a typical synthesis of the hexagonally ordered mesoporous molecular sieve, a homogeneously mixed solution was first prepared from tetraethylorthosilicate (TEOS, 98%, J&K), C_{16}–N_3–C_{16} surfactant, $NaAlO_2$ (44.7 wt.% Na_2O, 52 wt.% Al_2O_3, J&K), NaOH, ethanol and H_2O with a molar ratio of 5.43 Na_2O:24 SiO_2:0.6 Al_2O_3:1.2 C_{16}–N_3–C_{16} surfactant: 192 EtOH: 1706 H_2O. The resultant gel mixture was aged under magnetic stirring at 65 °C for 12 h. The final gel obtained was transferred into 50 mL Teflon-lined stainless steel autoclave and heated at 423 K for 5 d. After crystallization, the product was collected by filtration, dried in air, and calcined at 550 °C for 5 h to remove the template. The resulting mesoporous zeolite sample is denoted by MZS, For comparison, conventional ZSM-5 and mesoporous amorphous aluminosilicate Al-MCM-41 samples were prepared in this study following the literature reports [31,32].

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 ADVANCE diffractometer system equipped with Ni filtered Cu target K_α radiation (peration at 40 kV, 40 mA, wave length $\lambda = 0.15418$ nm). N_2 adsorption–desorption isotherms were measured with a Micromeritics ASAP 2010 system at 77 K. The samples were outgassed for 12 h at 150 °C before the measurements. The specific surface areas of materials were calculated from the adsorption branch of the isotherm using the Brunauer–Emmett–Teller (BET) equation. Mesopore size distribution was analyzed by using the Barrett–Joyner–Halenda (BJH) method, and micropore size distribution was analyzed by applying Horvath–Kawazoe equation. Scanning electron microscopy (SEM) images were obtained with a Carl Zeiss, ZEISS Ultra 55 at a low landing energy (5.0 kV). Transmission electron microscopy (TEM) was performed with a JEM-2100HR electron microscope operated at 200 kV. ^{27}Al MAS NMR measurements were preformed on a Bruker Avance AV 400 spectrometer at 104.26 MHz. The chemical shifts were referenced to a saturated aqueous aluminum sulfate solution ($\delta = 0$ ppm). IR spectra of samples in he form of KBr pellets were recorded on an FT-IR spectrometer (Bruker Vector 33) with a resolution of 1 cm^{-1}.

2.4. Calculations

We used density functional theory (DFT) calculations throughout, which provides a very useful tool for understanding molecular properties and for describing the behavior of atoms in molecules [33]. Surfactant geometry optimization was performed at the DFT B3LYP level theory using 6-31G* basis set with Gaussian 03 program. This basis set provided accurate geometry and electronic