



# Synthesis of hierarchically porous silicate-1 and ZSM-5 by hydrothermal transformation of SiO<sub>2</sub> colloid crystal/carbon composites

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## ABSTRACT

Hierarchically porous silicate-1 and ZSM-5 zeolites were successfully prepared by a hydrothermal crystallization process in the presence of SiO<sub>2</sub> colloid crystal/carbon composite. The inter-crystalline mesopores and macropores were successfully created inside these zeolite materials. The effect of synthesis conditions including hydrothermal reaction temperature, reaction time, silica source and aluminum source on the morphology and porous structure were studied in detailed. All the samples were characterized by XRD, SEM, N<sub>2</sub> adsorption-desorption analysis and NH<sub>3</sub>-TPD. The advantage of hierarchically porous structure was evaluated by the catalytic application. The hierarchically porous ZSM-5 as a catalyst displayed higher catalytic activity than the conventional ZSM-5 when using the acetalization reaction of cyclohexanone as a model reaction.

## 1. Introduction

Zeolites are highly ordered microporous materials, which possess excellent properties including open crystalline frameworks, well-defined micropores (typically 0.25–1.5 nm), high surface area, strong acidity, and good hydrothermal stability. They have been widely applied in heterogeneous catalysis [1]. Lots of reported work indicated that the catalytic sites mainly locate in the inner surface of zeolite micropores. Unfortunately, the severe diffusion limitation caused by the small pore size and long micropore length of conventional zeolites restricts not only the catalytic activity and but also the lifetime of the catalysts [2]. Although ordered mesoporous materials with amorphous frameworks facilitate the diffusion of reactant and product molecular, their weak acidity and low hydrothermal stability hinder their catalytic application [3–5].

Two promising strategies for fast mass transfer have been proposed to solve this problem. One is the preparation of nanozeolites, which facilitates to decrease the mass transfer limitation by shortening the intracrystalline diffusion path length. However the nanozeolites suffer from several severe problems, such as low preparation yield, low thermal stability and difficult separation from the reaction mixture [6]. The other is the synthesis of hierarchically porous zeolites, which are gaining more and more attention because of their unique properties including short diffusion length, high external surface area and large pore volume, while promoting the catalyst separation due to their larger secondary particle sizes.

The dealumination method is able to create large pores in zeolite

materials through the acid leaching or under the steaming condition [7–12]. For the desilication method, the selective extraction of silicon from the zeolite framework can be realized by alkali treatment [13]. Despite large pores could be created in zeolite materials by these two powerful methods, a decrease in crystallinity and hydrothermal stability were observed, which significantly decrease their catalytic performance in the practical application.

A novel and efficient strategy, called template method, has been widely developed using carbon materials (porous carbon, CNTs, active carbon, etc.), organic aerogels, CaCO<sub>3</sub> nanoparticles and surfactant molecular as templates to synthesize hierarchically porous zeolites. Viswanadhm *et al.*, prepared hierarchical ZSM-5 by using glucose as a template precursor through a steam-assisted crystallization process [14]. Kim *et al.*, used TPAOH impregnated mesoporous materials containing carbon nanotubes in the pores to synthesize hierarchical ZSM-5 structure [15]. Zhou *et al.*, used three short-chain organosilanes to prepare hierarchically micro-/mesoporous ZSM-5 zeolite by steam-assisted crystallization of dry gels [16]. Despite these reported work successfully created large pores inside ZSM-5 zeolite, the expensive template materials, low preparation yield, pore collapse, tedious preparation process and ununiform morphology limit the further application of the template method [17–23]. Therefore, achieving an ideal hierarchically porous structure within zeolite materials is still a great challenge.

Herein we developed a novel strategy to prepare hierarchically porous silicate-1 and ZSM-5 zeolites by *in situ* assembling of nanozeolites through hydrothermal crystallization process. Using a SiO<sub>2</sub> colloid

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crystal/carbon composite as the silica source resulted in the optimum hierarchically porous structure of silicate-1 and ZSM-5 zeolites. The effect of silica source, aluminum source, hydrothermal reaction temperature and reaction time on the morphology and hierarchically porous structure were investigated in detailed. The catalytic performance of the hierarchically porous ZSM-5 was studied through the acetalization of cyclohexanone with methanol. It showed higher catalytic activity than the conventional ZSM-5.

## 2. Experimental section

### 2.1. Materials

Tetra-n-propylammonium hydroxide (TPAOH, 40 wt. %) were purchased from Alfar Aesar. Tetraethyl orthosilicate (TEOS), sucrose, sodium hydroxide (NaOH), ammonium hydroxide ( $\text{NH}_3\cdot\text{H}_2\text{O}$ ), cyclohexanone, ethanol (EtOH), sodium aluminate, aluminium chloride and aluminium nitrate nonahydrate ( $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ) were obtained from Sinopharm Chemical Reagent Co., Ltd. Methanol was obtained from Shanghai Yunli Economic and Trade Co., Ltd.

### 2.2. Synthesis

#### 2.2.1. Synthesis of $\text{SiO}_2$ colloid crystal

The  $\text{SiO}_2$  colloid crystal was prepared by a reported method with a little modification [24]. The  $\text{SiO}_2$  spheres were first synthesized by adding 6 mL of TEOS in a solution containing 10 ml of deionized water, 74 ml EtOH and 3.14 ml of  $\text{NH}_3\cdot\text{H}_2\text{O}$  under continuous stirring. After 6 h, the white  $\text{SiO}_2$  spheres were collected and washed with deionized water 3 times. Then the  $\text{SiO}_2$  spheres were redispersed in a solution containing 34 ml of EtOH and 34 ml of deionized water by ultrasonic treatment. The  $\text{SiO}_2$  colloid crystal was obtained by evaporating the solution at room temperature and then calcining at 850 °C for 3 h in a muffle furnace.

#### 2.2.2. Synthesis of $\text{SiO}_2$ colloid crystal/carbon composite

1.4 g of  $\text{SiO}_2$  colloid crystal was soaked with a mixture containing 1.75 g of sucrose, 7 ml of  $\text{H}_2\text{O}$  and 0.105 ml of concentrated  $\text{H}_2\text{SO}_4$  under stirring. After 1 h, the wet solid sample was heated at 100 °C for 6 h and then 160 °C for 6 h in an oven. This process was repeated three times. The black  $\text{SiO}_2$  colloid crystal/carbon composite was obtained by carbonizing at 550 °C with a heating rate of 2 °C/min in  $\text{N}_2$  for 2 h.

#### 2.2.3. Synthesis of $\text{SiO}_2$ /carbon composite

The  $\text{SiO}_2$  spheres, instead of  $\text{SiO}_2$  colloid crystal, were directly used to prepare  $\text{SiO}_2$ /carbon composite. The typical preparation process of  $\text{SiO}_2$  spheres/carbon composite is similar to that of  $\text{SiO}_2$  colloid crystal/carbon composite. The SEM image of this composite is shown in Fig. S1.

#### 2.2.4. Synthesis of hierarchically porous silicate-1

In a typical synthesis process, the  $\text{SiO}_2$  colloid crystal/carbon composite which contains 0.1 g of  $\text{SiO}_2$ , 0.5083 g of deionized water, 0.0106 g of NaOH and 0.3383 g of TPAOH (40 wt. %) were mixed under stirring for 1 h at room temperature, and then heated in a Teflon-lined autoclave at 160 °C for 24 h. After the autoclave naturally cooled to room temperature, the solid product was collected, washed with deionized water 3 times and dried at 110 °C in an oven. Finally, the template inside silicate-1 was completely removed by calcining it at 550 °C with a heating rate of 5 °C/min in air for 5 h. In a series of control experiments, various  $\text{SiO}_2$  sources were used to prepare silicate-1 to study their effect on the morphology and porous structure.

#### 2.2.5. Synthesis of hierarchically porous ZSM-5

The synthesis procedure of hierarchical porous ZSM-5 (H-ZSM-5) with a Si/Al ratio of 50 was similar to that of silicate-1 except the addition of 0.0124 g of  $\text{Al}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ . The resultant ZSM-5 was calcined

to remove the template at 550 °C with a heating rate of 5 °C/min in air for 5 h.

The conventional ZSM-5 (C-ZSM-5) with a Si/Al ratio of 50 was synthesized according to the previously reported method [25]. 0.065 g of  $\text{NaAlO}_2$  and 8.35 g of TEOS were added into 12.25 g of  $\text{H}_2\text{O}$ . Then 1.644 g of TPAOH (40 wt.%) was added in the above under stirring. After stirred at room temperature for 3 h, the mixture was transferred into an autoclave and heated at 170 °C for 24 h. The resultant Con-ZSM-5 was calcined at 550 °C in air for 5 h to remove the template.

ZSM-5 samples were treated through ion exchange with 15 ml of 1 mol/L  $\text{NH}_4\text{NO}_3$  aqueous solution at 80 °C for 3 h. This process was repeated 3 times. Then the solid product was collected by centrifugation, washed with deionized water and dried at 110 °C overnight in an oven. The final products were converted to H-form by calcination at 550 °C for 5 h [26].

### 2.3. Adsorption experiments

The adsorption of methylene blue on the ZSM-5 zeolite materials was studied to investigate the effect of hierarchically pores on the diffusion of organic molecular. 30 mg of ZSM-5 zeolite materials were added into 10 ml of methylene blue solution with a concentration of  $3.566 \times 10^{-6}$  mol/L. After that, these suspensions were stirred vigorously at room temperature. The concentration of methylene blue was measured by a Shimadzu UV-1800 spectrophotometer.

### 2.4. Acetalization of cyclohexanone

The acetalization reaction of cyclohexanone was carried out in a three-necked flask connected with a condenser [27]. In a typical reaction, 0.05 g of ZSM-5 catalyst was dispersed in a solution containing 10 mL of methanol and 0.098 g of cyclohexanone. The solution was stirred at 50 °C. The reaction mixture was separated at intervals by centrifugation and then analyzed by a Shimadzu GC-2014 gas chromatography with a Rtx-5 column and FID detector.

### 2.5. Characterization

The powder XRD patterns were recorded on a Rigaku D/Max-2550PC X-ray diffractometer with Cu K $\alpha$  radiation. The material morphologies were characterized by scanning electron microscopy (SEM, Hitachi S-4800). Nitrogen adsorption-desorption analysis was performed at -196 °C using a JWGB-JK122W sorption analyzer. The specific surface area was calculated by the BET (Brunauer-Emmett-Teller) method. The average pore size was calculated from the adsorption branch using the BJH (Barrett-Joyner-Halenda) method. The molar ratio of Al/Si was determined by using energy-dispersive X-ray (EDS) spectroscopy. The temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD) was performed by using an automated chemisorption analyzer (ChemStar, Quantachrome).

## 3. Results and discussion

### 3.1. Morphology of $\text{SiO}_2$ colloid crystal/carbon composite

Fig. 1a and b shows the typical SEM images of monodisperse  $\text{SiO}_2$  spheres with an average diameter of 208 nm. As shown in Fig. 1c and d,  $\text{SiO}_2$  colloid crystal has a closely packed, ordered three-dimensional structure, which was constructed by numerous  $\text{SiO}_2$  spheres. The large ordered pores were clearly observed inside the  $\text{SiO}_2$  colloid crystal. These pores, the interstitial voids between  $\text{SiO}_2$  spheres in the colloid crystal, were filled with carbon materials after soaking a mixture of sucrose and concentrated  $\text{H}_2\text{SO}_4$  and then calcining at high temperature in  $\text{N}_2$ . Fig. 1e and f shows that the ordered structure  $\text{SiO}_2$  colloid crystal remained well.

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