



Short communication

Synthesis and catalytic cracking performance of mesoporous zeolite Y



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ABSTRACT

Mesoporous zeolite Y (denoted as meso-Y) was synthesized using hydrothermal synthesis method using pluronic P123 block copolymer as template. Furthermore, stabilized Y (USY) was prepared through ion exchange and ultra-stabilization process of the meso-Y. The catalysts were prepared and characterized by XRD, SEM, TEM, N₂ adsorption–desorption, NH₃-TPD and Py-IR. These catalysts were evaluated by determining the micro-activity using the light diesel oil as sample. The results showed that the Meso-CAT-3 catalyst had the highest micro-activity and lowest coke yield. It could be ascribed to the mesoporous structure which is known to improve the mass transfer of the larger molecules.

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1. Introduction

Zeolites are widely used as catalysts in industry. Zeolite Y is a crystalline microporous aluminosilicate with a typical framework pore of 0.74 nm and a supercage of 1.3 nm [1]. The microporosity of zeolite Y plays an important role in its shape selectivity [2–4]. However, in reactions involving large molecules, these micropores limit the diffusion of bulky reactants/products and reduce the catalytic activity. This problem has received increasing attention as the quality of crude oil becomes gradually more inferior. To resolve such a problem, many efforts have been devoted to mesoporous materials with large pores.

A considerable number of traditional approaches to introduce mesopores in zeolite Y have been reported, and it can be roughly divided into two approaches. First, a non-template approach is a post-treatment method to introduce mesopores in microporous zeolite Y through, such as desilication and dealumination [5–9] treatment in acid or alkali conditions. However, the post-treatment might induce a lower crystallinity, and this method is destructive. The second strategy uses templates and creates large pores by introducing various templates into the zeolite during the synthesis process. But, it is difficult to avoid the phase separation between the templates and silicate species [10,11]. Therefore, the synthesis of mesoporous zeolite Y continues to be a challenge.

Block copolymers have excellent aggregation properties and can form hydrogel in solution playing as space limitation agent. Zhou et al. [11] used block copolymers and directly synthesized mesoporous ZSM-5 zeolites with the assistance of steam-assisted crystallization process. They found that block copolymer compounds no longer acted as a meso-template role but served as a type of scaffold. Block copolymers offered a “confined space” to guide the aluminosilicate gel growing into zeolite crystals and led the silica sources into ordered and interconnected mesoporous structures through the self-assembly process. Zhou et al. [12] used copolymer F127 and cationic surfactant cetyltrimethyl ammonium bromide as co-templates to synthesize mesoporous ZSM-5 zeolite through hydrothermal treatment. They observed that the large channels were highly oriented in the direction of the b axis, owing to the prior aggregation of F127.

In this work, mesoporous zeolite Y was prepared using pluronic P123 (PEO₂₀PPO₇₀PEO₂₀) as template. This method has been rarely reported in previous studies. Pluronic P123 is a nonionic surfactant, which is available on the market and has excellent aggregation properties. In the aqueous solution of the zeolite precursor, the pluronic P123 performed as a space limitation agent, and directed the zeolite precursor species to grow with a mesoporosity. The characterization results showed that the introduction of mesopores did not reduce the crystallinity of the zeolite Y, and large mesopore volume was successfully created. Therefore, this strategy is a novel and feasible approach for generating mesopores in zeolite Y. The concentration of the block copolymers has an effect on the formation of micro/mesostructure in synthesis process. Thus, the influence of P123 was examined by changing the additional amount.

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2. Experimental section

2.1. Preparation of mesoporous zeolite Y

Zeolite Y was prepared as described previously [13]. In this work, the templates were added to the aluminosilicate gel. The entire aluminosilicate gel had a molar ratio of $0.42\text{Na}_2\text{O}:0.074\text{Al}_2\text{O}_3:\text{SiO}_2:17.13\text{H}_2\text{O}:\text{xP123}$ (where x represents the molar ratio of P123:SiO₂, in this study, $x = 0.000, 0.001, 0.003$ and 0.005). The precursor gel was transferred to a stainless steel autoclave and hydrothermally treated at 102 °C for 24 h. The samples were dried and calcined in air at 550 °C for 6 h to remove the templates. The final mesoporous zeolites Y with different template amounts were denoted as NaY, Meso-NaY-1, Meso-NaY-3, and Meso-NaY-5, respectively.

The ultra-stable zeolites Y were obtained through ion exchange process with 1.0 M (NH₄)₂SO₄ solution three times and then ultra-stabilization treatment was carried out in a continuous flow system in 100% steam flow of 25 mL/h at 600 °C for 2 h. The resulting samples were denoted as USY, Meso-USY-1, Meso-USY-3, and Meso-USY-5, respectively.

The catalysts were obtained from kaolin (50%), alumina gel (15%), and USY samples (35%). They were calcined at 550 °C for 1 h, crushed, and sieved to 40–60 mesh. The aging of the catalysts (5 g) was carried out in water vapor at 800 °C for 4 h. The final aged catalysts were denoted as CAT, Meso-CAT-1, Meso-CAT-3, and Meso-CAT-5, respectively.

2.2. Physical and chemical characterization

X-ray diffraction (XRD) patterns of the prepared zeolites were recorded on a Bruker AXSD8 using nickel-filtered Cu K α X-ray radiation at 40 kV and 30 mA. The 2 θ range was scanned from 15° to 35° with a scanning rate of 2°/min. The framework Si/Al ratios of all the Y type zeolites involved in this work were obtained from the unit cell parameter of the zeolites (a_0) by equation [14], a_0 taken in Å.

$$\text{Si/Al ratios} = \frac{25.858 - a_0}{a_0 - 24.191}$$

A Axios mAX X-ray fluorescence (XRF) spectrometer was used for the measurement of the bulk silicon-to-aluminum ratio of the zeolites.

The isotherms of nitrogen were measured using a BilderSSA-4300 system at liquid nitrogen temperature. The total specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) equation. The total pore volumes were calculated from the amounts of nitrogen adsorbed at $P/P_0 = 0.98$. The micropore volumes were calculated by the t-plot method.

Scanning electron microscopy (SEM) was performed on a Quanta 200 (FEI Co., Netherlands) apparatus. Transmission electron microscopy (TEM) was recorded by JEOL JEM-2100 electron microscope operating at 200 kV.

The pyridine IR (Py-IR) was obtained on Magna-IR 560 ESP spectrophotometer. The wafers (diameter 12 mm) were purged in the IR cell at 350 °C for 2 h under a vacuum, and then cooled down to room temperature for pyridine adsorption. Py-IR spectra were recorded in the range of 1700 to 1400 cm⁻¹ at 200 and 350 °C.

Temperature-programmed ammonia desorption (NH₃-TPD) of the samples was studied on a TPD/TPR 5079 analyzer. The previously heated samples were exposed to ammonia for 15 min to ensure adsorption saturation. After injecting pure nitrogen at 100 °C for 1 h, the NH₃-TPD profile was recorded from 100 to 600 °C at a heating rate of 10 °C min⁻¹.

2.3. Catalytic cracking performance tests

Catalytic cracking tests of the catalysts were carried out in a micro-activity test (MAT) unit. The details about the experimental conditions for the catalytic cracking can be found in supporting information.

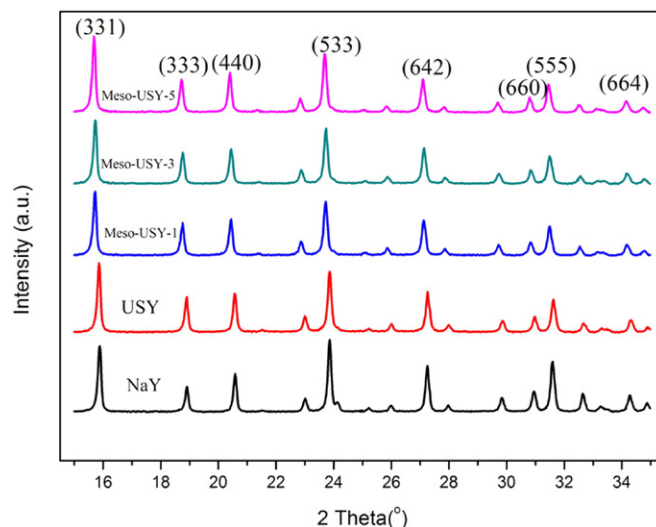


Fig. 1. XRD patterns of the zeolites.

3. Results and discussion

3.1. Crystallinity and chemical composition analysis

The similarity in the XRD patterns of zeolites (Fig. 1) indicates that the original zeolite structure was mostly retained. All the Meso-USY zeolites still have good crystallinity and close framework (SiO₂/Al₂O₃)_{XRD} (Table S1), indicating that the addition of P123 has negligible damaging effect on the framework of the USY zeolite. The bulk (SiO₂/Al₂O₃)_{XRF} (Table S1) of USY is a little lower than that of Meso-USY, supporting the existence of more aluminum atoms [15]. Low Na₂O concentration indicates the little detrimental on the catalyst activity.

3.2. Textural property analysis

As shown in Fig. 2 USY and Meso-USY samples exhibited Type IV isotherms with H-IV hysteresis loops. Among these samples, USY and Meso-USY-5 display similar form of hysteresis loops, while the hysteresis loops of Meso-USY-1 and Meso-USY-3 are steeper, especially Meso-USY-3, suggesting that more textural mesopores are present in these two samples than that in USY and Meso-USY-5. According to the data of surface area, pore volume and average porous diameter are calculated from nitrogen adsorption–desorption isotherms as seen from Table 1,

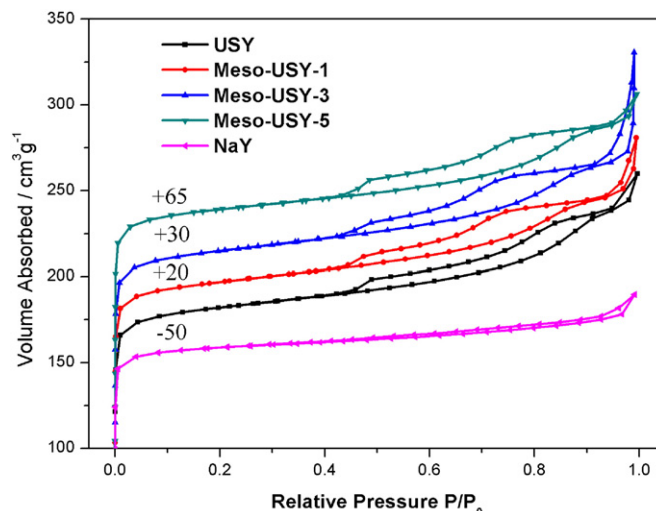


Fig. 2. N₂ adsorption–desorption isotherms of zeolites.

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