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Synthesis of flammulina-like mordenite using starch as template and high catalytic performance in crack of wax oil

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HIGHLIGHTS

- Flammulina-like zeolite mordenite (MOR-ST) is synthesized by using starch template.
- MOR-ST possesses higher thermal stability and smaller crystalline size.
- MOR-ST exhibits much higher catalytic activity in cracking of wax oil.
- MOR-ST provides better products distribution than MOR-TEA.

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ABSTRACT

In this study zeolite mordenite (MOR-ST) was directly synthesized by hydrothermal method using starch as template successfully. The morphological characterization of the samples was fulfilled by XRD, SEM and BET. SEM showed that the as-synthesized MOR-ST displayed a flammulina-like morphology and smaller crystalline size in comparison with the conventional mordenite (MOR-TEA) synthesized by TEAOH template. Additionally MOR-ST presented bigger BET surface area, smaller bulk density and higher hydrothermal stability. The catalytic performance of MOR-ST and MOR-TEA were studied using Daqing wax oil in a quartz micro-reactor at 500 °C. The results revealed that MOR-ST provided remarkably enhanced activity and higher gasoline yield in crack of wax oil in sharp contrast to MOR-TEA (conversion 85.70 wt.% vs. 69.00 wt.%).

1. Introduction

Mordenite (MOR) is one of the zeolites which have been widely used in adsorptive separation of gas or liquid mixtures and more importantly in catalysis such as hydrocracking, hydroisomerization, alkylation, reforming, dewaxing and dimethylamine synthesis [1–5]. The framework of MOR consists of two-dimensional porosity of 6.5 × 7.0 Å (12-membered ring) main channels and 2.6 × 5.7 Å (8-membered ring) tortuous pores [6]. Due to the small size of 8-membered ring and bad accessibility, the structure of MOR is generally regarded as one-dimensional, which causes diffusion limitations in catalytic converting of macromolecules [7–9]. Therefore small crystals, especially nano crystals of MOR are preferred to promote diffusion compared with micrometer-sized ones [10,11]. A number of synthetic processes have been developed to synthesize MOR. However most of the reported methods have involved organic or inorganic templates such as ammine, ammonium salt, alcohol, carbon black and fluoride ions which resulted in high costs and environmental pollution [12–20]. On the other hand, the synthesis of MOR with desired morphology, especially with nano size is still a challenge.

Recently starch as an environmentally friendly and easily available natural resource has been used as template to synthesize porous materials such as silicalite monoliths [21], aluminosilicates [22], ZSM-5 [23,24], AlPO-n [25], TS-1 [26] and Al_2O_3 [27]. To the best of our knowledge, facile, low-cost and environmentally benign method to synthesize small MOR crystals is rarely reported [28–31]. In this work we would like to present a convenient approach to synthesize flammulina-like MOR using harmless, biodegradable and cheap starch as template. The MOR exhibits an excellent catalytic activity when it was employed in cracking of wax oil.

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2. Experimental

2.1. Synthesis of MOR

All starting materials such as sodium aluminate (industry grade, Al_2O_3: 41 wt.%), water glass (industry grade, SiO_2: 26.83 wt.%, Na_2O: 8.2 wt.%), TEAOH (AR, 10% aqueous solution), cationic starch (industry grade, DS 0.02–0.03, pH 6–8), $Al_2(SO_4)_3$ (AR, 98%) and NaOH (AR, 98%) are commercially available and directly used without further purification. Sodium aluminate (1.64 g) and water glass (118 g) were added into NaOH aqueous solution (100 mL, 1.0 mol/L). The mixture was stirred (300 rpm) at room temperature (about 20 °C) for 30 min and then further aged at 30 °C for 3 h to give a directing agent. Then TEAOH (10 g), or cationic starch (21 g) as template was added to a mixture containing the directing agent (10 g), $Al_2(SO_4)_3$ (1.5 g), water glass (50 g) and distilled water. The composition of the resulting gel was 23 Na_2O: Al_2O_3: 53 SiO_2: 1.58 template: 1295 H_2O. The gel was transferred to a Teflon-lined autoclave and crystallization was carried out at 150 °C under autogenous pressure for 48 h. The products were recovered by filtration, washed thoroughly and dried at 120 °C overnight, and then calcined in air at 600 °C (heating rate 10 °C/min) for 4 h to remove organic templates. The samples were named MOR-TEA, and MOR-ST respectively.

2.2. Characterizations

Power X-ray diffraction (XRD) patterns of the samples were recorded on a SHIMADZU Lab XRD-6000 X-ray diffractometer with monochromatised Cu Kα radiation (40 kV, 30 mA). Fourier transform infrared spectra (FTIR, MAGNA-IR 560 E.S.P) were recorded in the wavenumber range 4000–400 cm^{-1} at room temperature using the KBr pellet method. Scanning Electron Microscopy (SEM) images were recorded using a JEOL JEM-2100 electron microscope operating at 200 kV. The porosity of each sample was determined by measuring the N_2 adsorption–desorption isotherm at −196 °C with a Micromeritics ASAP 2020 automated system. The total surface area was calculated according to the BET isothermal equation. The micropores volume, mesoporous volume, and external surface area were evaluated by the t-plot method. The bulk phase molar Si/Al ratio of the materials was determined by a Rigaku ZSX-100e X-ray fluorescence (XRF) spectrometer.

2.3. Preparation of catalysts

The samples were ion-exchanged three times with a 1 mol/L NH_4Cl aqueous solution at 60 °C for 12 h under stirring (300 rpm) and then calcined in air at 540 °C (heating rate 10 °C/min) for 4 h to obtain H-MOR-TEA, and H-MOR-ST. H-type samples were mixed with kaoline and alumina-sol in a ratio of 35: 50: 15 and calcinated 540 °C (heating rate 10 °C/min) for 4 h. Then the powder samples were tabletted in a mould and crushed to 40–60 mesh particles to afford the corresponding catalysts.

2.4. Catalytic performance evaluation

The Daqing wax oil catalytic experiments were performed in a fixed bed reactor at atmospheric pressure. The catalyst loading was 5.0 g, the weight hourly space velocity (WHSV) was 19.35 h^{-1}. Reaction products were analyzed using an Agilent 7890 N GC equipped with a flame ionization detector (FID) and a capillary column INNOWAX, 60-m cross linked polyethylene glycol with an internal diameter of 0.32 mm. The analysis conditions for gas products were as follows: carrier gas N_2 20 mL/min, H_2 25 mL/min, air 300 mL/min, inlet temperature 200 °C, detector temperature 200 °C, column temperature raised from 50 °C to 180 °C during 50 min, injection 0.1 mL. For liquid products: carrier gas N_2 20 mL/min, H_2 25 mL/min, air 300 mL/min, inlet temperature 300 °C, detector temperature 300 °C, column temperature controlling from initial 40 °C for 2 min, to 150 °C at 9 °C/min for 4 min, and then to 300 °C at 16 °C/min for 15 min, injection 0.1 μL.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of mordenite samples of MOR-TEA and MOR-ST synthesized by the hydrothermal

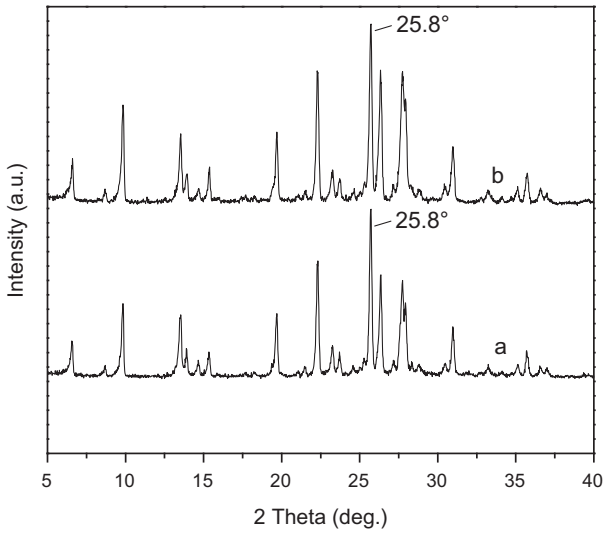

Fig. 1. XRD patterns of (a) MOR-TEA and (b) MOR-ST.

Table 1
Bulk density and hydrothermal stability of MOR-TEA and MOR-ST.

Sample	Bulk density (g/mL)	Relative crystallinity (%)	Retention of crystallinity (%)[a]
MOR-TEA	0.94	77	25
MOR-ST	0.86	100	72

[a] Hydrothermal treatment was carried out under a 100% steam at 750 °C for 4 h.

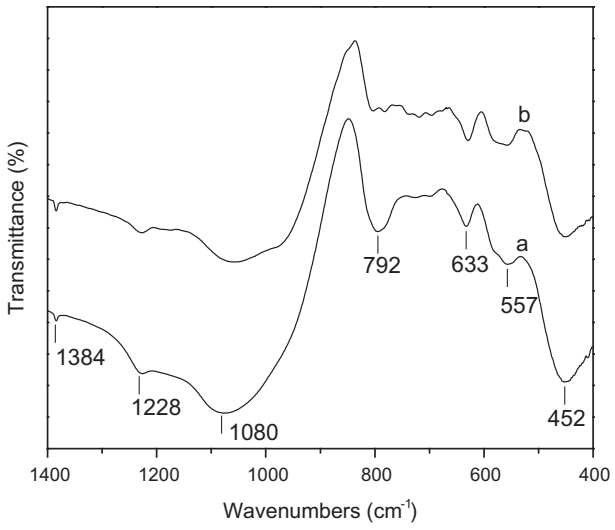

Fig. 2. FT-IR spectra of (a) MOR-TEA and (b) MOR-ST.