Short communication

Urea solution treatment: A facile and moderate approach to achieve hierarchical zeolite beta

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ABSTRACT

Hierarchical zeolite beta is successfully obtained via treating microporous zeolite beta with urea solution. Desilication takes place in a mild and stable alkaline media provided by the hydrolysis of urea solution. The hierarchy can be easily controlled by adjusting treatment temperature and time, the amount of urea solution and Si/Al ratio of the starting zeolite without loss of crystallinity. The resultant hierarchical zeolite beta can be directly used in acid catalytic reactions without tedious ammonium exchange, and it exhibits improved catalytic performance in nopol synthesis.

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1. Introduction

Microporous zeolites have been widely used in industry as heterogeneous catalysts due to their superior thermal and hydrothermal stability and strong acidity [1–2]. However, the relatively small micropores in zeolites impose diffusion limitations and restrict the accessibility for bulky molecules to the active sites located within micropores [3]. Therefore, it became highly desirable to synthesize hierarchical zeolites to overcome the limitations of traditional microporous zeolites. In recent years, significant attention has been paid on the synthesis and application of hierarchical zeolites [4–5], which have been reported to display many advantages due to the improved mass transport and tuneable active sites.

Typical strategies to achieve hierarchical zeolites are generally classified into three categories: the preparation of nanocrystalline zeolites [6], the employment of hard/soft templates in zeolite synthesis [7–8] and post-synthesis treatment, i.e., treating zeolites by steaming [9], acidic [10–11] or alkaline solution [12–18]. The last method involves desilication from zeolite framework and has proven to be a simple and efficient method to create intracrystalline mesopores [19–20]. NaOH solution is the most widely used alkaline media, while organic alkalies are sometimes employed to avoid the collapse of the framework when the framework Al is less stable [21] or the framework Si/Al ratio is extremely high [22]. A mixture of NaOH and organic alkali is reported to be

effective for better preserved intrinsic zeolitic properties [14–15]. However, when hierarchical zeolite derived from NaOH treatment is used as acidic catalysis, it has to be followed by tediously repeated ammonium exchange to transform it into protonic form. On the other hand, though hierarchical zeolite originated from sole organic alkali treatment can be directly used in protonic form in acid-catalyzed reactions, the relatively expensive cost limits its usage on large scale.

Herein, we report a facile and moderate method to achieve hierarchical zeolite beta, where urea solution is employed to provide a mild, stable and homogeneous alkaline media (pH = 9.25–9.58). The alkalinity was provided by ammonia, the product of the hydrolysis reaction of urea solution under controlled conditions. It's worth noting that the crystallinities of urea solution treated zeolites are perfectly preserved and the mesoporosity can be successfully developed. The resultant hierarchical zeolite beta displayed improved catalytic performance in nopol synthesis.

2. Experimental

2.1. Preparation of samples Bx

Parent zeolite H-beta (Nankai University Catalyst Factory, Si/Al = 12.5, coded as B0) was predealuminated by 0.3 or 2.0 mol/L citric acid solution with a liquid to solid ratio of 20 mL/g at 85 °C under continuous stirring for 4 h. After that, the zeolite was filtered, washed, dried at 120 °C overnight and calcined at 550 °C for 5 h. Then the dealuminated zeolites were treated with urea solution (5–20 wt%) at 80 °C or refluxing

Table 1
Si/Al ratios, crystallinities and textural properties of zeolites beta treated by urea solution under different conditions.

Sample	Si/Al ratio[a]	RC[b]/%	S_{BET}[c]/m² g⁻¹	S_{meso}/m² g⁻¹	V_{total}/cm³ g⁻¹	V_{meso}/cm³ g⁻¹	V_{micro}[d]/cm³ g⁻¹
B0	12.5	100	524	97	0.30	0.10	0.20
B1	–	100	503	105	0.34	0.16	0.18
B2	32	102	481	116	0.34	0.18	0.16
B3	–	97	451	124	0.35	0.19	0.16
B4	–	105	473	102	0.33	0.16	0.17
B5		105	493	139	0.39	0.23	0.16
B6	31	104	498	157	0.41	0.25	0.16
B7	–	110	490	110	0.35	0.17	0.18
B8	–	111	493	110	0.35	0.17	0.18
B9	–	102	482	132	0.36	0.20	0.16
B10(12.5)[e]	–	107	500	108	0.33	0.15	0.18
B11(75)[e]	60	105	444	120	0.37	0.22	0.15

[a] measured by XRF.
[b] RC = Relative Crystallinity.
[c] BET method.
[d] t-plot method.
[e] the data in parentheses refer to the Si/Al ratios of the zeolites before urea solution treatment.

temperature for 1–8 h, the resulting samples were filtered, washed, dried and calcined as the above mentioned procedure and designated as B1–B9. The sample notation and detailed treatment conditions are listed in Table S1.

2.2. Characterization

X-ray diffraction patterns were collected on X'pert diffractometer operated at 40 kV and 40 mA using Cu K_α radiation ($\lambda = 1.5418$ Å). N₂ adsorption-desorption isotherms were measured on an ASAP-2020 apparatus at −196 °C. Prior to the measurements, the samples were evacuated at 300 °C for 4 h. The total surface areas were determined by BET method. The micropore volumes were obtained by t-plot method. The BJH model applied to the adsorption branch of the isotherm was used to obtain the mesopore size distribution. Transmission electron microcopy (TEM) was carried out in a Hitachi HT7700 microscope operated at 100 kV with a AMT41B camera. Scanning electron microscopy (SEM) was carried out in a Hitachi S-5500 microscope operated at an accelerating voltage of 20 kV. The Si/Al ratio was determined by X-ray fluorescence (XRF). Temperature-programmed desorption of ammonia (NH₃-TPD) was measured in a homemade quartz reactor, which was connected to an gas chromatograph (Tianmei 7900) equipped with a thermal conductivity detector. Pyridine-IR was performed on Nicolet Avatar 360 spectrometer by scans of 64 with a resolution of 4 cm⁻¹. The quantities of Brønsted and Lewis acid sites of zeolites were calculated according to the equations in the literature [23].

2.3. Catalytic performance measurements

The prins condensation of β-pinene with paraformaldehyde was carried out in a 10 mL flask equipped with a reflux condenser and a magnetic stirrer, using toluene as solvent. In a typical run, 0.75 mmol

β-pinene, 1.5 mmol paraformaldehyde, 1.4 mL toluene and 20 wt% catalyst (pretreated at 400 °C for 4 h in air) were mixed together and stirred magnetically at 70 °C for 1 or 5 h. After the reaction, the mixture was centrifuged and analyzed by GC (7890 F, SE-54 capillary column 30 m × 0.32 mm × 0.5 μm, FID detector). The ingredients of all products were analyzed with HP 6890N-5975B (GC–MS) equipped with EI ion source and quadrupole detector.

3. Results and discussion

As displayed in Table S1, besides the treatment conditions (such as temperature, time, the amount and concentration of urea solution), the influence of Si/Al ratio on the hierarchy of modified zeolite was also investigated. The SEM image of parent beta shown in Fig. S1a suggested that the starting zeolite is composed of secondary particles aggregated from many small crystals in the range of 50–150 nm. This kind of morphology usually corresponds to the existence of some irregular interparticle voids [16], which was also confirmed by a clear hysteresis loop in the N₂ sorption isotherm (Fig. S2). As illustrated by Fig. S2a–e and the data in Table 1, compared with parent zeolite B0, all modified samples displayed more pronounced hysteresis loop and evidently improved mesopore volumes (from 0.10 to 0.25 cm³ g⁻¹) but slightly decreased micropore volumes (from 0.20 to 0.15 cm³ g⁻¹) under various conditions, indicating that urea solution treatment is a very gentle and efficient method to develop mosoporosity in zeolite beta by providing a homogeneous and stable alkaline media through hydrolysis reaction of urea solution under heating. The crystallinities of all urea-treated samples were well preserved or even slightly improved (Table 1), exhibiting a quite different tendency from that of NaOH-treated samples [13,16]. No zeolite debris was observed in the SEM image of sample B6 (Fig. S1b). The almost unchanged morphology of sample B6 is in good accordance with its crystallinity (Table 1). The comparison of the
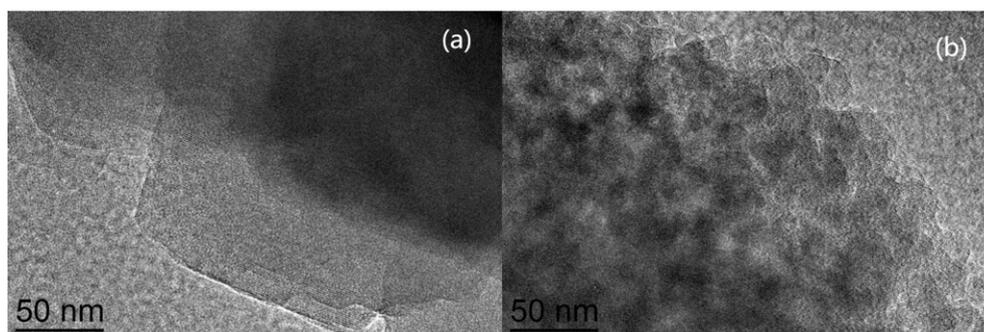

Fig. 1. TEM images of parent (a) and urea treated zeolite beta B6 (b).