Hierarchical ZSM-5 Zeolite Synthesized from Natural Rectorite Mineral without a Secondary Template

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Abstract: This paper reports a novel and economic strategy to synthesize a hierarchical micro-mesoporous ZSM-5 zeolite from the sub-molten salt (SMS) activated rectorite without using any secondary mesopore template. The physicochemical properties of the synthesized zeolite was characterized extensively. The results show that the synthesized ZSM-5 is of pure-phase MFI with larger BET surface area and higher mesopore volume than those of commercial ZSM-5, whose intercrystalline mesopores are attributed to the interstitial spaces assembled by nanorods.

Keywords: ZSM-5 zeolite, Natural rectorite mineral, Hierarchical pore structure, Submolten salt activation.

1. Introduction

The uniform micropores, strong acidity and unique crystal structure of ZSM-5 zeolite enable its superior catalytic performance in various chemical reactions. However, the traditional microporous ZSM-5 zeolite has encountered severe diffusion restriction and consequent pore blocking issues when applied to the reactions involving bulk molecules, as a result of its narrow three-dimensional 10-membered-ring channel structure. Fortunately, the hierarchical zeolite combining both the outstanding thermal and hydrothermal stability of microporous zeolite and better diffusion properties of mesoporous zeolite exhibits the ability to overcome the above problem. Recently, our team proposed a novel sub-molten salt (SMS) media to activate natural aluminosilicate minerals efficiently, so that they could be used as whole aluminum and silica source of zeolite synthesis[1, 2]. Furthermore, the zeolites synthesized from natural minerals entirely owned hierarchical micro-mesoporous structure with large external surface area and mesopore volume, but the crystalline size is slightly big and the increment of crystallinity was difficult. Herein, we report an economical and environmental friendly route to synthesize hierarchical ZSM-5 zeolite from the SMS activated natural rectorite without using any secondary mesopore template so as to expose more active sites and improve the diffusion efficiency.

2. Experimental

Referred to our previous study[2], the rectorite-NaOH-H_2O mixture was put into an oven exposed to air at 250 ^oC for 2 h to perform the SMS depolymerization.In a typical synthesis, the SMS activated rectorite, tetrapropylammonium bromide (TPABr), waterglass (27.6% SiO_2, 8.9%N_2O), H_3PO_4 and deionized water were mixed with a molar composition of 1 Al_2O_3:2.9 TPABr:25 Na_2O:60 SiO_2:2200 H_2O:16.8 H_3PO_4. Then, the resultant mixture was hydrothermally crystallized in a Teflon-lined stainless steel autoclave at 120 ^oC for 36 h. The obtained solid product was recovered by filtrated, washed, dried, and calcined at 550 ^oC for 6 h in air to decompose the organic template. Finally, HZSM-5 zeolite was acquired by successive ion exchanges with 0.5 M HCl aqueous solution and calcinations at 520 ^oC for 4 h.

3. Results and discussion

Fig. 1a shows the XRD patterns of the synthesized and commercial ZSM-5 zeolite. It clearly indicates that the synthesized ZSM-5 zeolite has a typical MFI topology with a relative crystallinity of 99% (higher than 91% of the ZSM-5 zeolite synthesized from natural minerals entirely[2]). As shown in Fig. 1b, the N_2 adsorption-desorption isotherm of synthesized ZSM-5 has an IV-type hysteresis loop with the relative press

P/P_0 ranging from 0.4 to 0.9, corresponding to the capillary condensation of N_2 in mesopores. In addition, the size of the mesopores is estimated to be 10-15 nm using the Barrett-Joyner-Halenda (BJH) method (inset in Fig. 1b). According to the textural parameters showed in Table 1, the synthesized ZSM-5 has a much higher BET surface area (371 m^2/g) and external surface area (141 m^2/g) as compared with a commercial ZSM-5 zeolite (329 and 72 m^2/g, respectively). Moreover, the total pore volume and mesopore volume are also larger than those of the commercial one. The FESEM images in Fig. 1d and 1e show that the synthesized sample has a uniform spheroidal morphology of *ca.* 1 μm in size (smaller than 4μm of the zeolite synthesized from natural minerals entirely[2]), and each particle is composed of a bundle of nanorods, suggesting that the synthesized ZSM-5 zeolite has plenty of intercrystalline mesopores that are actually attributed to the interstitial spaces assembled by those nanorods. The temperature-programmed desorption of ammonia (NH_3-TPD) curves of the two zeolites in H-forms are shown in Fig. 1c. The peaks corresponding to the weak and strong acid sites of the synthesized ZSM-5 centered at 240-260 °C and 470-490 °C, respectively, and the less peak area indicates the synthesized ZSM-5 zeolite owns a lower amount of both weak and strong acid sites compared with the commercial ZSM-5 zeolite.

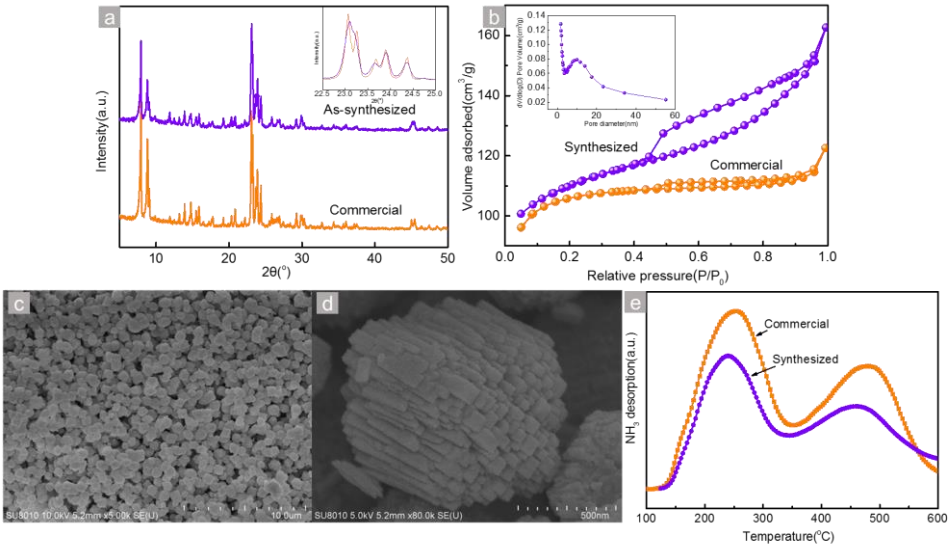

Figure 1. (a, b and c) XRD patterns, N_2 adsorption-desorption isotherms, BJH pore diameter distribution curve (inset in b) and NH_3-TPD curves of the different ZSM-5 zeolites, (c and d) FESEM images of the synthesized ZSM-5 zeolite.

Table 1. The textural parameters of different ZSM-5 zeolites.

Sample	Synthesized ZSM-5 zeolite	Commercial ZSM-5 zeolite
BET surface area, m^2/g	371	329
Micropore surface area, m^2/g	230	257
External surface area, m^2/g	141	72
Pore volume, cm^3/g	0.25	0.18
Micropore volume, cm^3/g	0.11	0.13
Mesopore volume, cm^3/g	0.14	0.05

4. Conclusions

A hierarchical ZSM-5 has been successfully synthesized from the natural rectorite mineral through one-step hydrothermal crystallization method without using any secondary template. The characteristic results showed the synthesized ZSM-5 had a high crystallinity, large external surface area and abundant mesopore volume, which made contribution to exposing more active sites and improving diffusion efficiency.

References

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