Melting-assisted Synthesis of Hierarchical SSZ-13 Zeolite

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Abstract. In order to reduce the diffusion resistance of the reactants and products in the traditional microporous SSZ-13 zeolite, a hierarchical SSZ-13 zeolite was synthesized with melting-assisted method. The hierarchical SSZ-13 zeolite was easily and quickly synthesized by ammonium fluoride solid-phase grinding under solvent-free condition. The obtained SSZ-13 samples were characterized by XRD, SEM, BET and EDS. The results clearly indicate that the etched zeolite contains micropores and mesopores, and in addition, no significant decrease of crystallinity is observed for the sample etched with ammonium fluoride. Using this method, other zeolites with CHA, MFI, and TON topologies were etched successfully.

1. Introduction
In recent years, with the development of the petrochemical industry, the demand for light olefins such as ethylene and propylene has increased dramatically worldwide[3]. The methanol-to-olefins (MTO) reaction is a new route to produce light olefins from non-petroleum sources and has received extensive attention and conducted in-depth research in the past few years[2].

Among the catalysts for MTO reaction, SSZ-13 zeolite has attracted wide attention due to its ordered pore structures, high hydrothermal stability, large surface area, suitable surface acidity and exchangeable surface cations[3]. However, the traditional SSZ-13 zeolite is easy to deactivate and possess low mass transfer efficiency due to its diffusion resistance of reactants and products in the micropores[4]. Therefore, one of the hot issues in the research of microporous zeolites is how to reduce the mass transfer diffusion resistance caused by the micropore structures[5]. To overcome this drawback, the introduction of meso-macropores to synthesize zeolites with hierarchical pores structure has caused widespread concern in the past few years. The hierarchical SSZ-13 has different pore structure, which has the shape-selective catalytic performance of the microporous zeolite and the diffusion transport property of the mesoporous zeolite. It can not only decrease diffusion resistances to accelerate transport rates, but also regulate the acid property distribution to overcome the problem of weak acidity of ordered mesoporous zeolite [6].

In recent years, hierarchical SSZ-13 zeolites have attracted extensive attention from researchers. There are two main methods to synthesize hierarchical SSZ-13 zeolites, in-situ synthesis methods and post-synthesis approaches. Hense et al.[7,8] used N,N,N-trimethyl-1-adamantanoammoniumhydroxide(TMAdaOH) with mono- or diquaternary ammonium-type surfactant as dual-template to synthesize hierarchical SSZ-13 zeolites and also combined TMAdaOH and C_{22,4,4}Br_2 to synthesize mesoporous SSZ-13 zeolites. The catalyst lifetime was improved due to the high interconnectivity of micropores and mesopores in the zeolite. Nevertheless, this method requires the addition of a surfactant to synthesize the hierarchical zeolites, and the synthesis of the surfactant is complicated and time-consuming. And the soft template also has the disadvantage of easily blocking
the channel. F⁻ ions have been found to interact with the organic structure directing agent to promote the synthesis of zeolite[9]. Zhu et al.[10] synthesized bimodal microporous SSZ-13 zeolite by adding small amount of fluoride in alkaline hydrothermal conditions. Another method to synthesize hierarchical SSZ-13 zeolite is post-synthesis approaches. Unni Olsbye et al.[11] used sodium hydroxide solution to synthesize the H-SSZ-13 zeolite with a Si/Al ratio of 14 by desilication post-treatment to form mesoporous. But alkaline treatment would decrease the surface area and acid sites, which would decrease the catalytic MTO performance[12]. The method of fluoride etching to synthesize hierarchical zeolites is very flexible, which can not only adjust the density and size of the secondary pore system, but also not damage the zeolite structure[13]. However, it has been reported that the fluoride post-treatment requires water as a solvent, and the acid or alkali post-treatment requires heating at high temperature, which causes sewage pollution and a certain amount of energy waste.

Herein, we have developed a simple, fast and solvent-free route to synthesize hierarchical SSZ-13 by a melting-assisted post-synthesis method, where solid ammonium fluoride was used as an etchant. In addition, this solid-phase ammonium fluoride etching method is also applicable to other zeolites. The solvent-free etching method not only reduces the waste of water resources, but also improves the output of hierarchical SSZ-13 and the etching effect is uniform. The hierarchical SSZ-13 includes microporous and mesoporous.

2. Results and Discussion

2.1 XRD results analysis and discussion

Fig. 1 XRD patterns of SP13 and SP13-0.2-25-1

Fig. 1 shows XRD patterns of SP13 and SP13-0.2-25-1. Both samples exhibit characteristic diffraction peaks of typical SSZ-13 zeolites with high crystallinity (2θ = 9.5, 16.28, 20.95, 25.12, 30.95°), and no impurity phase peaks appeared[14]. It is worth mentioning that the XRD patterns of the samples before and after the etching showed similar peak intensities, and the crystallinity of the hierarchical SSZ-13 zeolite after fluoride etching has not significantly decreased. This means that NH₄F etching does not significantly damage the crystallinity of the parent zeolite.

2.2 SEM images analysis and discussion

The SEM images of SP13-X samples, meaning different amounts of solid ammonium fluoride treated at 160°C for 6 h, are shown in Figure S1. The surface of the SP13-0.5 sample treated with 0.5g of ammonium fluoride (Figs.1d and h) showed cracks, while the surface of the SP13-0.05 sample treated with 0.05g of NH₄F (Figs.1a and e) was smooth without etch marks, indicating too little or too much amount of NH₄F cannot achieve the desired etching effect. Both of the SP13-0.1(Figs.1b and f) and SP13-0.2 (Figs.1c and g) samples treated with NH₄F obtained the desired hierarchical structure, but the SP13-0.2 sample (Figs.1g) shows a more uniform etching effect. Figs.2 shows the images of SP13-
0.2-T samples exploring the effect of different temperatures on the etching effect. From the Figs.2, it can be seen that within a certain temperature range (25-140°C), temperature was not a significant factor that caused different etching effects. Subsequently, the factor of time on the etching effect was explored. The SP13-0.2-25-0 sample (Figs.3a and c) represents washing immediately after ground with solid ammonium fluoride, the SSZ-13 could also be etched, but as the reaction time increased, the pores began to become more uniform. It can be completely etched in about 1h, and there is not much difference in the etching effect after 1h.

Fig. 2 shows SEM images of SSZ-13 zeolites before and after solid ammonium fluoride post-treatment. As shown in Fig. 2a and c, the parent SP13 zeolite displayed a cubic structure with smooth surface and the particle size was about 9-12 μm. Obvious etch marks on the surface of the sample treated with ammonium fluoride could be observed through Fig. 2b and d, and holes of various sizes appeared, that is, hierarchical pore structure.

2.3N\textsubscript{2} adsorption/desorption results analysis and discussion

Fig. 3 shows the N\textsubscript{2} adsorption/desorption isotherms of the SP-13 and SP13-0.2-25-1 samples. The curves of the two samples increase sharply when the relative pressure is 0 < \(p/p_0\) < 0.01, which is due to the formation of micropores. The sample SP13 does not have distinct hysteresis loop and shows type I isotherms, that means the parent SSZ-13 zeolite was microporous. The sample SP13-0.2-25-1 shows H\textsubscript{IV} hysteresis loop, indicating the existence of the mesopores formed after the etching of ammonium fluoride in the hierarchical SSZ-13 zeolite\textsuperscript{[15]}. The textural property of the samples are listed in Table 1. The SP13-0.2-25-1 sample had similar microporous pore volume with that of the SP13 sample. But the SP13-0.2-25-1 sample had larger mesoporous volume compared with the SP13 sample. This was because the SP13-0.2-25-1 sample contained more mesopores with that of the SP13 sample. Thus, this indicated that the SSZ-13 zeolite treated with solid ammonium fluoride formed a certain number of mesopores, and the original micropores of the zeolite were not significantly damaged.
2.4 EDS results analysis and discussion

Table 2 shows that the Si and Al contents of the NH₄F etched sample are reduced a certain extent. However, the Si/Al of the etched SSZ-13 was greatly increased as compared with that of the parent SSZ-13, indicating that NH₄F can remove a certain amount of silicon and aluminum, but more inclined to dealumination. And SSZ-13 zeolite with higher Si/Al ratio could be obtained by this strategy.

2.5 Discussion on other zeolite etching results

This melting-assisted synthesis route has also been employed to prepare other zeolites with CHA, MFI, and TON structures. Fig. 4 shows the SEM images of other zeolites before and after post-treatment with solid ammonium fluoride. It can be seen that the morphology of SAPO-34, ZSM-5, and ZSM-22 zeolites had all changed. The etched debris and pores appeared on the surface of SAPO-34 zeolite (Fig. 4d), and the surface of etched ZSM-5 zeolite (Fig. 4e) became rough. The ZSM-22 zeolite was etched from long rods to short rods, and the surface changed from smooth to rough. We can speculate that the solid ammonium fluoride post-treatment etching method is suitable for most zeolites, since SAPO-34, ZSM-5, and ZSM-22 zeolites belong to the topologies of CHA, MFI, and TON, respectively.
3. Conclusions

In summary, an effective process was developed for synthesis of hierarchical SSZ-13 zeolites through a novel melting-assisted post-synthesis route using solid ammonium fluoride at room temperature. Compared with conventional post-treatment synthesis of hierarchical zeolites, the solid ammonium fluoride etching has the following advantages: (1) the process is simple and only requires grinding; (2) the etched pores are uniform; (3) it eliminates the need to formulate chemicals as solvents, reducing water waste; (4) it do not need to heat, reducing energy resource waste; (5) post-processing materials are easily to obtain and inexpensive. Moreover, this method has successfully etched other zeolites, such as SAPO-34, ZSM-5, and ZSM-22 with CHA, MFI and TON topologies, respectively, so we believe that most zeolites are also suitable for this method to synthesize hierarchical pores.

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References

[1] Stephen W, Paul B. (1999) The characteristics of SAPO-34 which influence the conversion of methanol to light olefins. J. Microporous & Mesoporous Materials, 29(1-2):117-126.
[2] Liu Z, Sun C, Wang G, et al. (2000) New progress in R&D of lower olefin synthesis. J. Fuel Processing Technology, 62(2): 161-172.
[3] Fickel D W, Lobo R F. (2010) Copper coordination in Cu-SSZ-13 and Cu-SSZ-16 investigated by variable-temperature XRD. Journal of Physical Chemistry C,114(3): 1633-1640.
[4] Borodina E, Meirer F, Lezcano-Gonzalez I, et al. (2015) Initial Carbon-Carbon Bond Formation during the Early Stages of the Methanol-to-Olefin Process Proven by Zeolite-Trapped Acetate and Methyl Acetate. ACS Catalysis, 5(2): 992–1003.
[5] Pérez-Ramírez J, Christensen C H, Egeblad K, et al. (2008) Hierarchical zeolites: enhanced utilisation of microporous crystals in catalysis by advances in materials design. Chemical Society Reviews, 37(11): 2530-2542.
[6] Chal R, Gerardin C, Bulut M, et al. (2011) ChemInform Abstract: Overview and Industrial Assessment of Synthesis Strategies Towards Zeolites with Mesopores. ChemCatChem, 3(1): 67-81.
[7] Wu L, Degirmenci V, Magusin P C M M, et al. (2013) Mesoporous SSZ-13 zeolite prepared by a dual-template method with improved performance in the methanol-to-olefins reaction. Journal of Catalysis, 298: 27-40.
[8] Wu L, Degirmenci V, Magusin P C M M, et al. (2012) Dual template synthesis of a highly mesoporous SSZ-13 zeolite with improved stability in the methanol-to-olefins reaction. Chemical Communications, 48 (76): 9492.

[9] Pulido A, Corma A, Sastre G. (2006) Computational Study of Location and Role of Fluoride in Zeolite Structures. The Journal of Physical Chemistry B, 110 (47): 23951-23961.

[10] Zhu X, Kosinov N, Hofmann J P, et al. (2016) Fluoride-assisted synthesis of bimodal microporous SSZ-13 zeolite. Chemical Communications, 52 (15): 3227-3230.

[11] Sommer L, Mores D, Svelle S, et al. (2013) Mesopore formation in zeolite H-SSZ-13 by desilication with NaOH. Microporous & Mesoporous Materials, 132 (3): 384-394.

[12] Zhu X, Kosinov N, Kubarev A V, et al. (2017) Cover Feature: Probing the Influence of SSZ-13 Zeolite Pore Hierarchy in Methanol-to-Olefins Catalysis by Using Nanometer Accuracy by Stochastic Chemical Reactions Fluorescence Microscopy and Positron Emission Profiling. ChemCatChem, 9: 3432.

[13] Qin Z, Gilson J P, Valtchev V. (2015) Mesoporous zeolites by fluoride etching. Current Opinion in Chemical Engineering, 8: 1-6.

[14] Kumar M, Luo H, Román-Leshkov Y, et al. (2015) SSZ-13 Crystallization by Particle Attachment and Deterministic Pathways to Crystal Size Control. Journal of the American Chemical Society, 137 (40): 13007-13017.

[15] Wu L, Degirmenci V, Magusin P C M M, et al. (2013) Mesoporous SSZ-13 zeolite prepared by a dual-template method with improved performance in the methanol-to-olefins reaction. Journal of Catalysis, 298 (1): 27-40.