Template-Free Synthesis and Catalytic Application of Hierarchical Zeolites from Natural Aluminosilicate Mineral: A Multi-Scale Approach

Xiaojun Bao,[a,]* **Yuanyuan Yue**[a]

[a]*National Engineering Research Center of Chemical Fertilizer Catalyst, College of Chemical Engineering, Fuzhou University, Fuzhou, 350002, P. R. China.*

**Corresponding author: +86 (0)591 22865220, baoxj@fzu.edu.cn*

Abstract: Herein, we report a template-free approach to synthesize both microporous and hierarchical zeolites from natural aluminosilicate mineral. The results show that the synthesized zeolites own more open pore channels and less strong acid sites compared with the conventional one and thus demonstrate superior catalytic activity in hydroisomerization of n-octene. Significantly, compared with the traditional synthesis process, the material and energy consumptions and pollutant discharges are greatly reduced while the utilization efficiency of the raw materials is significantly increased by using our proposed approach, highlighting the economic- and eco-sustainability and industrial prospects of the methodology we present.

Keywords: Template-free, hierarchical zeolites, Natural aluminosilicate minerals.

1. Introduction

Hierarchically structured zeolites, which integrate microporous crystalline framework and auxiliary mesoporous structure, has attracted great interest. The current preparation methods of hierarchical zeolites can be divided into two categories: direct synthesis and post-synthetic modifications. However, these methods unavoidably give rise to serious emission to the environment due to the use and subsequent removal of various templates or/and the discharge of waste alkalis/acids used for zeolite dealumination/desilication. Moreover, all of them exclusively involve the use of synthetic Al- and Si-containing chemicals whose production processes associated with huge waste generation and extensive energy consumption. Therefore, the current practices for fabricating hierarchical zeolites are not green.

Herein, we present a multi-scale approach to synthesize hierarchical zeolites that starts from natural aluminosilicate mineral rather than chemicals, excludes the use of any organic template, and does not discharge waste alkali or acid liquor. The hydroisomerization activity of the resultant hierarchical zeolite was also investigated.

2. Experimental

Take the synthesis of ZSM-5 zeolite as an example, the submolten salt (SMS) activated kaolin[1], was mixed with distilled water, water glass and seeds under vigorous stirring. After being aged, the resulting mixture was hydrothermally crystallized at 170 ºC for 48 h. The resultant solid product was recovered by filtration, washing and drying to obtain a microporous ZSM-5. The mother liquid was collected during filtration and reused for generating mesopores in the synthesized microporous ZSM-5. The hierarchical ZSM-5 was prepared by putting a certain amount of the synthesized microporous ZSM-5 into the mother liquid, stirring the slurry at 65 ºC for 2 h, cooling the slurry to room temperature, filtrating the slurry, washing the filter cake obtained with deionized water, and drying the cake overnight. The alkali liquid was collected for reuse. The synthesized hierarchical NaZSM-5 was converted to H-form one by successive ion-exchange with a 0.1 mol/L HCl solution. The acidic liquid was neutralized with the obtained alkali liquid yielded during the generation of mesopores by the mother liquid and then the thus-obtained solid was recycled as silicon source.

3. Results and discussion

The X-ray diffraction (XRD) pattern of the synthesized hierarchical sample in Figure 1A confirms the high purity and crystallinity of the synthesized sample. The representative field-emission scanning electron microscope (FESEM) image (inset in Figure 1A) shows that the sample is present in the form of flat-prism particles with rough surface on which there appear abundant pinholes, and accordingly many intra-crystalline cavities are observed in the hierarchical ZSM-5, as seen from the TEM images in Figure 1B. The nitrogen adsorption-desorption isotherm indicates the coexistence of micropores and mesopores in the sample. The pore size distribution (inset in Figure 1C) reveals the mesopores in the hierarchical ZSM-5 are distributed between 4 and 10 nm. The temperature-programmed desorption of ammonia (NH_3-TPD) measurement in Figure 1D displays that the strength of both weak and strong acid sites of the synthesized hierarchical ZSM-5 is weaker than that of the reference ZSM-5 that is a typical microporous zeolite. Moreover, the hierarchical zeolite simultaneously possesses the lower amounts of strong acid sites and total acid sites when compared with the reference ZSM-5. To test the catalytic performance, two NiMo/HZSM-5-γ-Al_2O_3 catalysts, denoted as CAT-Ref-Z and CAT-Hir-Z, respectively, were prepared. The catalytic results in Figure 1E and 1F show that both of the two catalysts give a 100% conversion ratio of n-octene, but the product distributions are distinctively different. CAT-Hir-Z displays the higher selectivity to di-branched and mono-branched isomers while giving the lower selectivity to cracking products, attributed to the weaker acid strength and the hierarchical pore structure of the hierarchical ZSM-5.

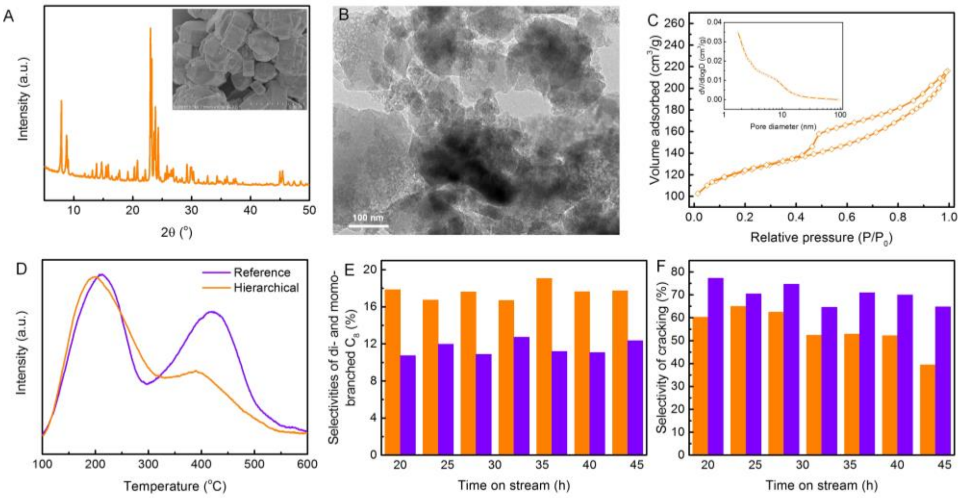

Figure 1. XRD pattern (A), FESEM (inset in A) and TEM (B) images, N_2 absorption-adsorption isotherm (C), BJH pore size distribution (inset in C) and NH_3-TPD curve (D) of the hierarchical ZSM-5 zeolite, and the selectivities to di- and mono-branched C_8 (E) and cracking products (<C_8, F) over CAT-Ref-Z (violet) and CAT-Hir-Z (orange).

4. Conclusions

In summary, we have successfully developed a sustainable route to generating mesopores in ZSM-5 zeolite. Our approach is achieved by using inexpensive raw materials instead of synthetic inorganic chemicals as feedstock, by employing the mother liquid instead of a fresh alkaline solution to generate mesopores, and by reusing Si-rich alkali liquor and the ion-exchanging solution to reduce the waste discharge. The resultant hierarchical ZSM-5 zeolite shows outstanding performance in converting n-octene into high octane mono- and di-branched isomers because of its suitable acidity property and unique pore structure.

Acknowledgements

We gratefully acknowledge the financial supports from the National Natural Science Foundation of China (grants U1462203, 91434206 and 21506034).

References

1. Y. Yue, H. Liu, P. Yuan, C. Yu, X. Bao, Sci. Rep. 5 (2015) 9270.