

# Templated Synthesis of Hierarchically Mesoporous Zeolites from Cationic Polymers and Their Excellent Catalytic Properties

Feng-Shou Xiao\*, Chengyang Yin, Tiandi Tang, and Lifeng Wang

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun 130012, China, E-mail address: fsxiao@mail.jlu.edu.cn

## Introduction

Zeolites with intricate micropores have been widely applied in industry at present, but the relatively small micropores in zeolites significantly influence the mass transport in many catalytic reactions. Recently, mesoporous zeolites from carbon templates have been successfully synthesized [1,2], but their industrial applications are still limited, because of the cost of template, the complexity of synthetic procedures, and the difficulty for dispersion of templates into gels. In this work, at first we describe templated synthesis of a series of hierarchically mesoporous zeolites such as Beta [3] and MFI from the use of mesoscale cationic polymers, then we investigate their catalytic properties in alkylation, cracking, hydrogenation [4], and hydrodesulfurization [5].

## Experimental

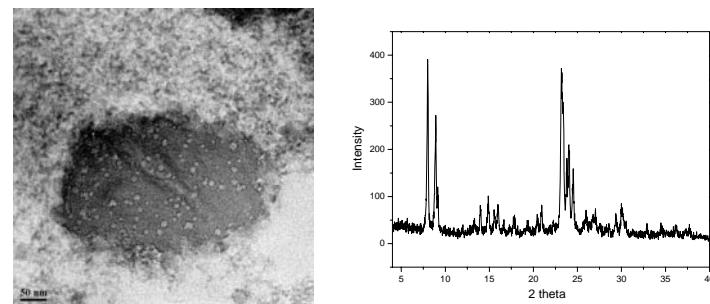
The samples of hierarchically mesoporous Beta (Beta-H) and mesoporous ZSM-5 (ZSM-5-H) were hydrothermally synthesized from a mixture template of tetraethylammonium hydroxide (TEAOH) and tetrapropylammonium hydroxide (TPAOH) with cationic polymer at 140 °C and 180 °C, respectively. H-form of samples was ion-exchanged twice with  $\text{NH}_4\text{NO}_3$  solution (1M) at 70 °C for 3 h, followed by calcination at 500 °C for 4 h. Zeolite-supported palladium catalysts were prepared by ion-exchange with  $[\text{Pd}(\text{NH}_3)_4]^{2+}$  solution, followed by calcination and reduction procedures. The alkylation of benzene with isopropanol was carried out at a reaction temperature of 200 °C with benzene/isopropanol molar ratio of 4/1, reaction pressure of 2.0 MP, and WHSV of  $10 \text{ h}^{-1}$ ; Cracking of bulky 1,3,5-triisopropylbenzene was performed at 300 °C by pulse injections (0.4  $\mu\text{l}$ ) with 50 mg of catalyst; Pyrene hydrogenation was carried out in an autoclave at a temperature of 250 °C, hydrogen pressure of 40 bar, and 3.5 g of pyrene in 120 mL of tridecane; Hydrodesulfurization (HDS) of 4,6-dimethyldibenzothiophene (4,6-DMDBT, 0.2 g) was carried out using tridecane (110 mL) as solvent with a catalyst amount of 300 mg, total pressure of 65 bar, and 250 °C

## Results and Discussion

The X-ray diffraction (XRD) patterns of mesoporous zeolites templated from cationic polymer templates show characteristic peaks associated with zeolites such as Beta and ZSM-5. Furthermore, nitrogen isotherms of these samples exhibits pore size distribution ranged from 4-40 nm, indicating the presence of mesoporosity in these samples. Interestingly, both scanning electron microscopy (SEM) and transmission electron microscopy (TEM) techniques confirm the presence of mesoporosity in these samples. When palladium species are loaded into mesoporous Beta zeolite (Beta-H), TEM images show that Pd particles are located in both mesopores and micropores. The presence of mesoporosity in these zeolites is favorable for the catalytic conversion of bulky molecules and the mass transport in catalysis.

In alkylation of benzene with isopropanol, mesoporous Beta (Beta-H) exhibits high activity and selectivity as well as long catalyst life, compared with conventional Beta. For example, after reaction for 6 h, Beta-H shows near 99 % conversion for propanol and about 97 % selectivity for cumene. In contrast, conventional Beta gives the conversion at 86 % and the selectivity at 88 % under the same conditions. Considering the similarities of Beta-H to conventional Beta for Si/Al ratio, aluminum distribution, acidic strength, and crystal size, the higher catalytic activity over Beta-H than that over conventional Beta should be directly assigned to the contribution of mesoporosity in the Beta-H. In cracking of bulky 1,3,5-triisopropylbenzene, mesoporous ZSM-5 (ZSM-5-H) shows very high activity (90 %), while conventional ZSM-5 shows relatively low conversion (46 %). These results indicate that the presence of the mesoporosity in zeolites is very important for the conversion of bulky molecules and the mass transport of reactants and products in catalysis.

As a model catalytic reaction for increasing fuel quality, deep saturation of bulky aromatics such as pyrene in the presence of 200-ppm sulfur has been investigated, showing that mesoporous Beta supported Pd catalyst (Pd/Beta-H) exhibits much higher conversion of pyrene and selectivity for products of deep hydrogenation of pyrene as well as better sulfur tolerance than those of conventional Beta zeolite supported Pd catalyst (Pd/Beta) and mesoporous materials supported Pd catalyst (Pd/MCM-41). Furthermore, the tests in hydrodesulfurization of 4,6-DMDBT show that Pd/Beta-H is much more active than Pd/Beta. The difference in catalytic activities of Pd/Beta-H and Pd/Beta is attributed to the difference in mesoporosity of the samples. The good sulfur tolerance in deep hydrogenation of bulky aromatics and high activity in HDS of 4,6-DMDBT would be very helpful to design and prepare highly active hydrotreating catalysts for the production of ultra clean fuels.



**Figure 1.** SEM image and XRD pattern of mesoporous ZSM-5 (ZSM-5-H). The mesopores in a crystal of ZSM-5 are clearly observed, which are very helpful for mass transfer.

## References

1. C. J. H. Jacobsen et al., J. Am. Chem. Soc. 122 (2000) 7116.
2. Y. Tao, H. Kanoh, K. Kaneko, J. Am. Chem. Soc. 125 (2003) 6044.
3. F.-S. Xiao, et al., Angew. Chem. Int. Ed. 45 (2006) 3090.
4. T. D. Tang, C. Y. Yin, L. F. Wang, Y. Y. Ji, F.-S. Xiao, J. Catal. 249 (2007) 111.
5. T. D. Tang, C. Y. Yin, L. F. Wang, Y. Y. Ji, F.-S. Xiao, J. Catal. 257 (2008) 125.