

# Summary

Light olefins are extremely essential raw materials in petrochemicals because they are building blocks for various end products, such as polyethylene and polypropylene. Recently, market analysis showed that the demand for light olefins is desperate and the current supply cannot match the demand. Considering energy savings and flexibility of operation, fluid catalytic cracking (FCC) process is expected to maximize the production of light olefins. Hexane cracking reaction has always been considered as a model reaction to produce light olefins. Except for that, with the increasing demand for olefins, dimethyl ether (DME)-to-olefins (DTO) process as a non-petroleum route to make olefins has also attracted considerable attention. It is of great significance to develop a new catalyst that has high chemical stability as well as high catalytic activity and selectivity to light olefins. YNU-5 is a large-pore zeolite recently discovered in Yokohama National University, containing a distinguishable three-dimensional channel system: 2-dimensional 12-ring ( $0.78\text{ nm} \times 0.59\text{ nm}$ ; large micropore) with channel intersection connected with 8-ring channel ( $0.44\text{ nm} \times 0.34\text{ nm}$ ; small micropore), thus forming a large space around  $7.97\text{ \AA}$  that are accessible through 12-ring windows. Besides, there is an isolated 8-ring channel ( $0.40\text{ nm} \times 0.29\text{ nm}$ ; small micropore) in the framework. The application of YNU-5 zeolites has not been well studied so far. With the aim of investigating the catalytic performance, YNU-5 zeolite was used as solid catalyst over DTO reaction and cracking reaction after successful framework stabilization. However, the rapid deactivation of YNU-5 zeolites limited its application. To enhance the catalytic ability, I also intended to prepare hierarchical zeolites. The hierarchical structure was successfully introduced to the YNU-5 structure by appropriate treatments to form mesopores. Compared to conventional YNU-5 zeolites confronting with severe mass transfer constraints of reactants or products due to the intrinsic micropores, hierarchical materials successfully showed higher catalytic activity and selectivity. In addition, shape-selectivity of the YNU-5 was examined and scientifically useful information was obtained.

This thesis targeted an improved understanding of the novel YNU-5 zeolite with YFI framework in three aspects: the preferable synthetic conditions, introducing of mesopores, and evaluation of its catalytic performance over various reaction systems. YNU-5 zeolites were synthesized, characterized, and applied to various catalytic reactions, DTO reaction, alkane cracking, and alkylation. During the synthesis investigation, it was found that a very slight amount of an impurity phase tended to be formed along with the desired product YNU-5. This minor phase was very often MFI. The presence of this nanoparticle contaminant phase evidently improved the

performance of the catalytic system during the DTO reaction. Based on the product distribution obtained using highly dealuminated, very pure YNU-5 as a solid acid catalyst, this material behaves more like a 12-ring zeolite. The highly dealuminated YNU-5 also shows increased selectivity for high value C3 and C4 olefins, which suggests potential practical applications. Properly dealuminated YNU-5 catalyst exhibits high resistance to coking and good catalytic stability even at high temperature of 650°C. More importantly, it also has high selectivity of light olefins C3= and C2=. Based on these results, YNU-5 is a useful cracking catalyst. For further improvement of catalytic properties, there are two methods: (a) synthesis of nanosized YNU-5 zeolites; (b) introducing mesopores system to YNU-5 framework. The former strategy is difficult to realize. However, hierarchical YNU-5 zeolites were successfully obtained by base treatment. Additionally, I found that introducing the hierarchical structure further improved the catalytic performance of YNU-5 mainly by maintaining the mass transfer through the intra-particle mesopores. In the isopropylation reaction, dealuminated YNU-5 zeolites shows high shape selectivity of  $\beta,\beta$ -DIPN.

The achievements in this work open up the possibility of YNU-5 for various catalytic applications, enhancing the industrial feasibility of this new zeolite as a stable solid-acid catalyst.