

Hierarchical zeolites with tailored mesoporosity by partial detemplation and desilication

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Introduction

The dark side of zeolites in heterogeneous catalysis arises from their purely microporous nature, which often causes diffusion constraints due to restricted access and slow intracrystalline transport to/from the active sites. Different approaches (nanosized crystals, composites, mesoporous crystals) have been recently pursued to enhance the accessibility and molecular transport over these systems [1]. Desilication by treatment in alkaline medium (typically NaOH) has been demonstrated as an attractive top-down non-templating route to prepare hierarchical zeolites, integrating in a single material the unique catalytic properties of the native micropores and the facilitated access and improved transport consequence of a complementary mesopore network. Methods to synthesize hierarchical zeolites in general and desilication in particular do not have a precise control of the amount and location of the newly created mesopores. Well-defined hierarchical systems are required for diffusion and catalytic studies, ultimately leading to solid structure-function relationships.

Herein we report a novel synthetic methodology to tailor the degree of mesoporosity in hierarchical zeolites, consisting of the combination of partial detemplation and silicon extraction. This approach will be illustrated for different zeolite frameworks, including beta, ZSM-5, and ITQ-4 zeolites. The functionality of the introduced mesoporosity in the hierarchical zeolites is demonstrated in various diffusion-limited catalytic reactions.

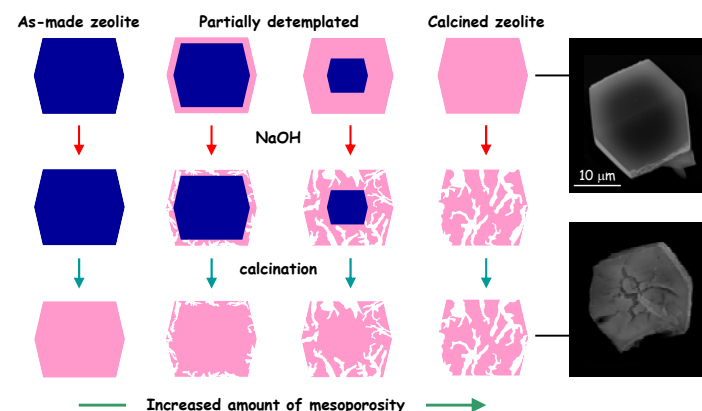
Materials and Methods

Beta, ZSM-5 and ITQ-4 zeolites (Si/Al = 35) were synthesized hydrothermally in fluoride medium using TEA⁺, TPA⁺, and N-benzylquinuclidinium ions as the templates, respectively. The as-made zeolites were calcined at different temperatures to obtain samples with different template content. Alkaline treatments were performed in 0.2 M NaOH at 65°C in the range 10–60 min. The samples were finally calcined at 550°C for 5 h. The composition, structure, morphology, and porosity of the parent and treated materials were characterized in detail. The materials were tested in pyrolysis and acylation reactions.

Results and Discussion

So far, demetallation treatments (desilication, dealumination, detitanation) have been conducted over calcined zeolites [1,2]. Our approach is based on the fact that the template-containing zeolite is virtually inert to Si leaching upon treatment in aqueous NaOH solutions. The structure-directing agent occluded in the micropores hinders the contact between hydroxyl groups from NaOH and Si-O-Si linkages, thereby lowering the amount of Si leached. Partial removal of the structure directing agent from the micropores (Scheme 1) creates regions in the crystal which are susceptible to mesopore formation by subsequent desilication, while template-containing regions are fully protected from silicon leaching. Adjusting the degree of template removal by variation of the calcination temperature in the range 230–550°C, it is

possible to regulate the amount of mesoporosity upon subsequent alkaline treatment and final calcination. The results show that a higher degree of detemplation induces a larger increase in mesopore surface area upon NaOH treatment, and this is accompanied by a decrease of the micropore volume. Consequently, this approach enables precise control of the extent of mesopore formation in the range 20–250 m² g⁻¹ in various families of zeolites.



Scheme 1. Representation of the partial detemplation and desilication treatment to tailor mesoporosity development in zeolites. Right: SEM micrographs of calcined (purely microporous) and alkaline-treated (hierarchical) beta crystals.

The introduced mesoporosity leads to catalysts with higher catalyst effectiveness due to the improved accessibility of the molecules to the active sites and shorter diffusion path lengths. This will be illustrated for the pyrolysis of plastics and the acylation of aromatics. This combined treatment permits to design in an elegant manner the hierarchical zeolite with the desired ratio of micro- and mesoporosity, widening the applicability of desilication to other framework types and compositions.

Significance

Partial detemplation followed by desilication in alkaline medium is a powerful and elegant approach to design hierarchical zeolites with tailored degree of mesoporosity. This achievement is based on the distinct capability of NaOH to extract silicon in template-containing or template-free regions of the zeolite. The introduced mesoporosity enhances the effectiveness of the materials in catalysis.

References

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2. Groen, J.C., Moulijn, J. A., and Pérez-Ramírez, J. *J. Mater. Chem.* 16, 2121 (2006).