

POST-SYNTHESIS MODIFICATION OF ZEOLITES BY FLUORIDE MEDIUM TREATMENT

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ABSTRACT

The present study explores the fluoride road to prepare hierarchical zeolite crystals. Equilibrium in fluoride containing solutions and the formation of very reactive species, which are not Al/Si selective, will be discussed. After a proper adjustment of the concentration in a fluoride solution, non-selective chemical etching of the zeolite framework occurs. The possibilities offered by this dissolution approach is exemplified by controlled modification of most important industrial zeolites.

Keywords: zeolite, hierarchical, modification, fluoride treatment

INTRODUCTION

Zeolites able to process bulkier molecules are highly desired by the petrochemical industry.^[1] A number of zeolitic materials containing pores larger than 1 nm have been synthesized, however there is still not a material offering an industrial perspective. An alternative approach is the expansion of pore dimensions at the expense of partial dissolution of zeolite framework. Introduction of larger meso- and/or macropores in conventional zeolite crystals leading to size reduction of crystalline domain containing solely micropores is also expected to improve zeolite performance. The latter method has a better potential to meet the technological challenges in terms of cost and stability. The present work explores the fluoride road to prepare hierarchical zeolite crystals, with an ultimate goal of rational control of zeolite properties.

EXPERIMENTAL

Micron-sized well shaped ZSM-5 crystals were used for the preparation of hierarchical materials. Fluoride media treatments were carried out with HF and NH₄F-HF mixed aqueous solutions. HF treatments were performed as follows: i) 0.5 g of the parent ZSM-5 zeolite was dispersed in 15 ml of 0.5 mol L⁻¹ HF solution and reacted at 338 K for 15 min under stirring; and ii) 0.5 g of the parent ZSM-5 zeolite was dispersed in 15 ml of 1.0 mol L⁻¹ HF solution and reacted at 298 K for 6 min under stirring. Mixed NH₄F-HF treatment was performed as follows: 2.5 g NH₄F was dissolved in 15 ml of 0.2, 0.5 or 1.0 mol L⁻¹ HF aqueous solution first, then, 0.5 g of the parent ZSM-5 zeolite was dispersed in the mixed solutions and react at 298 K for different periods of time under stirring. All the samples were thoroughly washed using distilled water after the fluoride medium treatment. The H-forms of the parent and acid modified zeolites were obtained by calcination in static air at 823 K for 2 h with a heating rate of 4 K min⁻¹.

RESULTS AND DISCUSSION

Buffering HF solutions with NH₄F shifts the equilibrium to the most reactive species (HF, FHF⁻), which are not Al/Si selective.^[2] Thus, after a proper adjustment of HF and NH₄F concentrations, non-selective chemical etching of the zeolite framework occurs. The resulting materials combine a secondary porosity with retention of the native compositional and structural characteristics of the parent zeolite. The NH₄F-HF treated materials display a

substantially better catalytic activity than HF treated ones. This increased activity for m-xylene conversion is due to a retained zeolite acidity coupled with improved transport through the crystals.

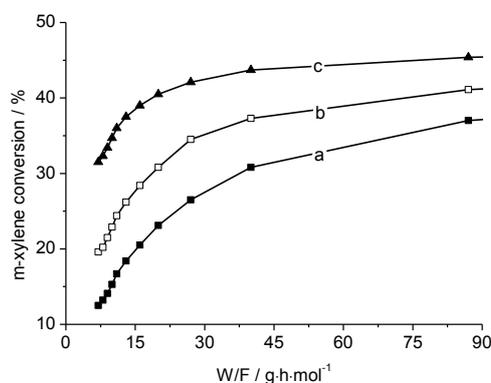


Figure 1. Conversion of m-xylene on the parent (a), 10 (b) and 45 (c) min treated ZSM-5. Temperature: 623 K; W/F: 7 – 87 g h mol⁻¹.

The surface area, porosity properties, aluminum content, number and distribution of acid sites of NH₄F-HF-treated zeolites are similar to the parent ZSM-5. The most plausible explanation for the increased activity of the NH₄F-HF treated zeolites is an increased accessibility to the zeolite micropores. Small parts of the crystals are removed by a selective dissolution of defect zones. In addition, large pores penetrating deep in the crystals are created. The zeolite crystals consist of intergrown building blocks. The interfaces of these individual segments act as diffusion barriers due to a local mismatch in the alignment of the micropore network, making some portions of the zeolites inaccessible to reactant molecules and affecting their adsorption capacity and catalytic activity. The small intergrowth domains on the zeolite surface are disintegrated during fluoride treatment. As a result, the diffusion of molecules in and out becomes easier, which certainly influence the catalytic conversion of m-xylene.

CONCLUSION

The preparation of hierarchical zeolites with a chemical composition similar to their parent is an important step in the rational design of zeolite catalysts. It provides also a key to unravel the respective contributions of improved diffusion and controlled acidity on the overall catalytic performance.

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