

The effect of mesoporosity in ZSM-5 and Y zeolites on the conversion of aromatic hydrocarbons

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Introduction

Zeolites are widely used in industry for many different applications. One of the main areas of use is catalysis, especially related to oil refining, hydrocarbon conversion, and other petrochemical processes. They are chosen for these processes because of their high acidity and pore shape selectivity. However, due to the small diameter of the pores—usually no larger than 12 Å—they often impose diffusion limitations and limited accessibility for larger molecules, which cannot fit into the pores and reach the active sites. One method to solve this problem is to introduce mesoporosity into the zeolite structure. A network of mesopores and micropores would reduce diffusion limitations and access issues while still providing the acidity that makes zeolites so active [1].

In this study ZSM-5 and Y zeolites were tailored using two “top-down” methods: desilication by alkaline treatment and desilication with a surfactant. Desilication introduces mesopores by Si extraction and creates mainly mesopores with a wide pore size distribution. Desilication with a surfactant leads to a dramatic increase in surface area while better preserving the crystal structure [2].

Materials and Methods

Commercially available zeolites were used as starting materials, purchased from Zeolyst International. ZSM-5 (CBV8014) and Y (CBV780) were selected for use in this study. For mesoporosity by desilication, the following procedure was used: zeolite was first stirred with NaOH for 30 minutes at 65 °C. It was separated by centrifuging, then washed with deionized water and dried overnight at 80 °C. It was then stirred with HCl for 6 hours at 65 °C. The same separation, washing and drying procedure was followed. Three successive ion exchanges with NH_4NO_3 were performed. The zeolite was then dried for 5 hours at 120 °C and calcined for 5 hours at 550 °C [3].

For the desilication with surfactant method, the zeolite was treated with a solution of NaOH and CTAB. It was then stirred with HCl, and three ion exchanges performed. Finally it was dried for 5 hours at 120°C and calcined for 5 hours at 550°C.

Characterization was performed using: Nitrogen adsorption to understand the pore structure changes, x-ray diffraction and TEM to investigate changes in the crystal structure, and FTIR to monitor changes in Brønsted and Lewis acidities.

The catalytic conversion of aromatic hydrocarbons was tested in a PyGC/MS reactor using the microporous and mesoporous zeolites.

Results and Discussion

The nitrogen adsorption isotherm (Figure 1, a) shows that both the desilication and desilication with surfactant techniques introduce mesoporosity. However, the average pore size of the ZSM-5 desilicated with a surfactant (10-60 nm) is much larger than that of the

desilicated ZSM-5 (5-15 nm). The reason for this may be the higher alkaline concentration used for the desilication with surfactant technique. The effect of both the alkaline and surfactant concentrations on pore size and volume will be presented.

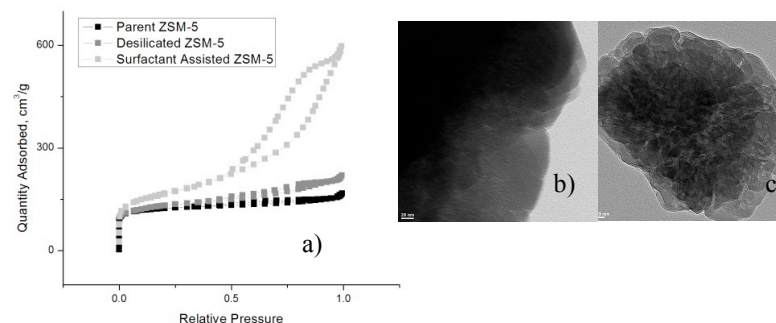


Figure 1: a) Nitrogen adsorption isotherm of parent and mesoporous ZSM-5; b) TEM image of parent ZSM-5; c) TEM image of desilicated ZSM-5.

The TEM image (Figure 1, b&c) corresponds to the desilicated ZSM-5. The more open structure is apparent, while the crystal does not lose much of its original integrity.

The catalytic conversion of aromatic hydrocarbons (e.g. naphthalene, toluene, etc.) using mesoporous ZSM-5 tailored by these techniques was investigated and will be presented.

Significance

Introducing mesoporosity into ZSM-5 and Y zeolites would decrease the diffusion and access limitations of large aromatic molecules, allowing them to be converted into smaller, more valuable products. The size and volume of the mesopores can be tailored by changing the concentration of the alkaline solution and the surfactant.

References

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