

OLEFINS SYNTHESIS FROM ACETONE OVER SIZE-CONTROLLED ZEOLITE NANOCRYSTALS -EFFECT OF CRYSTAL SIZE ON CATALYTIC ACTIVITY AND STABILITY -

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Summary

Mono-dispersed MFI-type zeolite nanocrystals were successfully prepared in water/surfactant/oil solution. The surfaces as well as bulk phase of the nanocrystals with a diameter of approximately 50 nm were well-crystallized without amorphous SiO₂. HZSM-5 zeolites with different crystal sizes of 1.0 μm and 50 nm were used as catalysts to synthesize olefin from acetone, in order to investigate the effect of crystal size on the catalytic performance. The decrease in the crystal size led to the increase in the catalytic stability. Moreover, the production of aromatics could be restricted by using HZSM-5 zeolite nanocrystal, which exhibited the high olefin selectivity.

Keywords

Rational design of catalysts, Novel functional materials, Nanotechnology applications

Introduction

Zeolites are crystalline aluminosilicates that possess strong activity, high surface area, high thermal stability, and a high adsorption capacity for hydrocarbons. Moreover, since each kind of zeolite has a micropore of a specific diameter almost equal to the diameters of lighter hydrocarbons, zeolites exhibit a remarkable molecular sieving effect for these hydrocarbons. Hence, they have been widely used as shape-selective catalysts in various types of hydrocarbon processing.

In general, the sizes of zeolite crystals are usually very large, approximately 1-3 μm, as compared with micropores exhibiting a molecular-sieving effect. The relatively small micropore causes a low diffusion rate of the hydrocarbon reactants as compared with the reaction rate. Moreover, the pore mouths are easily plugged due to coke deposition under diffusion-controlled condition, leading to a short lifetime for the catalysts. To overcome this problem, it will be necessary to achieve faster mass transfer of the reactants in the crystals; to this end, nanometer-sized zeolite crystals would be a promising solution. We have successfully prepared MFI^{1,2)} and MOR³⁾ zeolite nanocrystals via hydrothermal synthesis in water/surfactant/organic solvent (emulsion method). The nanometer-sized zeolite is expected to be a promising material for increasing the outer surface area as well as decreasing the diffusion resistance of the organic reactant within the micropore, which improves the catalytic activity and lifetime.

In this study, the MFI-type zeolite (ZSM-5) nanocrystals were applied to selective olefins synthesis from acetone, where olefins such as ethylene and propylene are obtained by cracking of iso-butane produced from aldol-condensation products of acetone⁴⁾. In this olefin synthesis, the condensation and cracking reaction proceed over the acid sites of zeolite, which are located on the surface of inside pore as well as the outersurface of crystal. First, the selective deactivation of the acid sites located near the outersurface of the zeolites were examined by the catalytic cracking of silane (CCS) method, in which SiO₂ units are formed selectively on the acid sites of the zeolite using organic silane compounds⁴⁾. Finally, the size-controlled preparation of MFI zeolite nanocrystals was carried out by the emulsion method, and the effects of crystal size on the catalytic activity and stability were investigated for the selective production of lighter olefins from acetone.

Experimental

Preparation of MFI-type zeolite nanocrystals

MFI zeolite nanocrystals were prepared via hydrothermal synthesis in water/surfactant/organic solvent (emulsion method¹⁻³⁾). Water solution containing Si and Al sources were obtained by hydrolyzing each metal alkoxide with a dilute tetrapropyl-ammonium-hydroxide/water solution. The water solution thus obtained was added to a surfactant-organic solvent solution. Polyoxyethylene-(15)-

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oleylether and cyclohexane were employed as a surfactant and organic solvent, respectively.

Deactivation of acid sites of zeolite by CCS method

Di-phenyl silane (DPS) was used as the silane compound. Powdery MFI-type zeolites were exposed to the silane compound vapor at 373 K in a nitrogen stream. The sample was heated up to 773 K to decompose DPS molecules on acid sites, and was calcined in air stream at 823 K to form SiO₂ unit on each acid site. The acid sites where the silane compound chemically adsorbed were deactivated by the formation of SiO₂ unit⁴.

Olefin synthesis from acetone over ZSM-5 zeolite

Acetone to olefin reactions were carried out using a fixed bed type reactor under N₂ stream at an atmospheric pressure. ZSM-5 zeolites prior to and after CCS treatment using TPS were used as catalysts. The reaction conditions were as follows: a reaction temperature of 623~773k, W/F of 0.5~1.0 kg-cat/(kg-acetone/h). The reaction products were analyzed using online gas chromatography

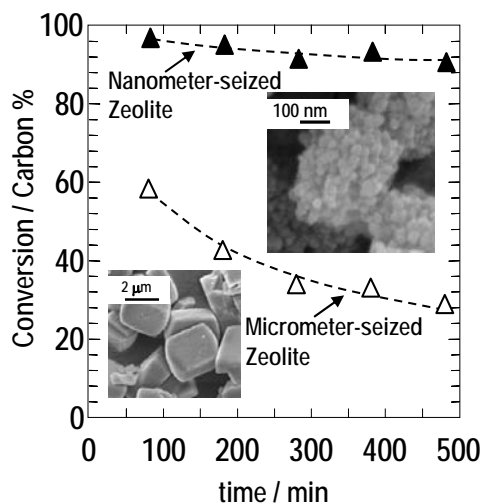


Fig. 1 FE-SEM photographs of micro and nanometer-sized ZSM-5 zeolites and acetone conversion in olefins synthesis.

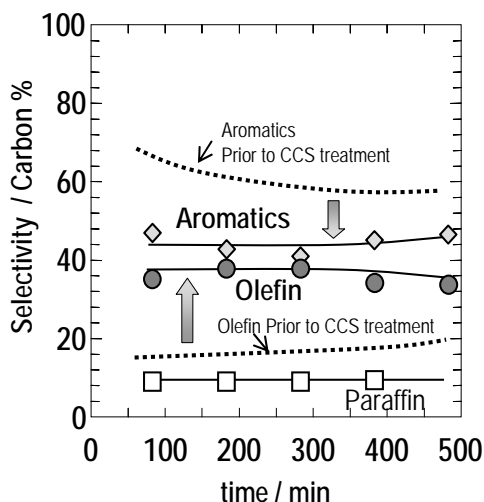


Fig. 2 Products selectivity on nano-size ZSM-5 zeolite. Acid sites of the zeolite were deactivated by CCS treatment. The dashed lines represented the products yields using the zeolite catalyst prior to CCS treatment.

(Shimadzu Co. Ltd., GC-14A) with a porapak-Q column.

Results and Discussion

ZSM-5 zeolite with the crystal size of 1.0 μm and 50 nm were prepared by the emulsion method. The acid sites located near the outersurface of these zeolites were selectively de-activated by the CCS method and selective olefins synthesis from acetone over these zeolite catalysts were carried out. Figure 1 shows the FE-SEM photographs of the prepared ZSM-5 zeolites and the acetone conversion in olefins synthesis. From the X-ray diffraction analysis and NH₃-TPD method, it was confirmed that these zeolites possessed the almost same crystallinity and acidity. As shown in the figure, though these zeolites possessed almost the same properties including the crystallinity, micropore volume and acidity, the catalytic performances were quite different from each other. In the micrometer-sized zeolite, the acetone conversion decreased with time on stream, and the value was much lower than that in the nanometer-sized zeolite. The differences in the catalytic performance resulted from the crystal sizes. As the crystal size of zeolite decreased, the diffusion length for reactant hydrocarbons within the zeolite decreased, leading to the reaction-rate-controlling condition.

Figure 2 shows the product selectivity in the olefins synthesis using the nanometer-sized zeolite as a catalyst. In the nanometer-sized zeolite, high olefins selectivity as well as low aromatics selectivity were achieved. As shown in Figs. 1 and 2, the catalytic performance was stable as compared with the micrometer-sized zeolite. As a result, the zeolite nanocrystal was effective catalyst for olefins synthesis from acetone.

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