

Catalytic activities and structures of silicalite-1/H-ZSM-5 zeolite composites

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Received 4 July 2007; accepted 3 December 2007

Available online 19 February 2008

Abstract

Polycrystalline silicalite layers were formed on H-ZSM-5 with different crystal sizes of 5–30 μm . The silicalite-1/H-ZSM-5 composite with a crystal size of 5 μm showed high catalytic activity and excellent of *para*-xylene selectivity. But, *para*-selectivity slightly decreased with increasing the crystal size, indicating that the surface of the large H-ZSM-5 crystals was not fully covered by the silicalite-1 layer. The toluene conversion over the catalyst with a small crystal size (5 μm) was very stable with reaction time, while the catalysts with large crystal sizes were rapidly deactivated. The crystalline structure of the interface between silicalite-1 and H-ZSM-5 crystals was studied by FE-SEM and TEM observations. The silicalite-1 crystals were epitaxially grown on the surface of the H-ZSM-5 crystals and their pores must be directly connected to the pores of H-ZSM-5.

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Keywords: Silicalite-1; ZSM-5; Composite; Alkylation; Overgrowth; Diffusivity; *para*-Selectivity; Toluene conversion

1. Introduction

Medium pore size MFI zeolites have found to be suitable for the production of *para*-dialkyl aromatics because their pore size is similar to the molecular dimensions of these aromatics. To enhance *para*-selectivity, a number of modification techniques have been reported such as chemical vapor deposition [1,2] and chemical liquid deposition of silicon alkoxides [3,4] and impregnation of phosphorous, MgO or boron [5,6]. Although these modification techniques could increase *para*-selectivity, the conversion was decreased significantly because a diffusion resistance of products increased by narrowing of the pore-opening size. Rollmann had reported a combined ZSM-5 with silicalite-1 to provide high *para*-selectivity and conversion [7]. Dou-

ble structured MFI films, which are called zoned MFI, were synthesized on silicon [8], quartz [8–10] and alumina [10]. A single crystal of ZSM-5 coated with silicalite-1 has also been synthesized by Lee et al. [11] who reported the catalytic properties of the composite catalysts on alkylation of toluene. Li et al. [12] investigated the crystalline structure of the dealuminated ZSM-5 crystals coated with silicalite-1. They implied that the silicalite-1 might be grown epitaxially on the ZSM-5. But, the crystalline structure in the interface between silicalite-1 and ZSM-5 was not investigated.

According to the reports on silicalite-1 layers grown on ZSM-5 [8,11,12], the structure and thickness of the silicalite layer depend on the Si/Al ratio, crystal size and shape of the substrate H-ZSM-5. In our previous reports [13,14], silicalite-1 overgrowth on H-ZSM-5 with different Si/Al ratios and their catalytic behaviors were discussed. The silicalite/H-ZSM-5 composite catalysts showed both high toluene conversion and high *para*-selectivity in the alkylation of toluene with methanol. The silicalite-1 coating

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significantly increased the *para*-selectivity to nearly 100%. In this study, silicalite layers were formed on H-ZSM-5 catalysts with different crystal sizes. The influence of the crystal size on the catalytic activity and deactivation behavior for the alkylation of toluene was investigated. In addition, the crystalline structure of the interface between silicalite-1 and H-ZSM-5 was observed carefully. The reasons for the high *para*-selectivity and high toluene conversion were discussed from the viewpoint of the structure of the composite.

2. Experimental

2.1. Preparation of HZSM-5

ZSM-5 zeolites were synthesized under hydrothermal conditions with a Si/Al ratio of 70. The reactant materials used for the synthesis were tetraethylorthosilicate (TEOS; $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$; Wako Pure Chemical Industries Co., Ltd.) and colloidal silica (CS; Nissan Chemical Co., Ltd.) as silica sources, aluminum nitrate $(\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$; Wako Pure Chemical Industries Co., Ltd.) as an alumina source, tetrapropylammonium bromide (TPABr; Wako Pure Chemical Industries Co., Ltd.), deionized water (H_2O), and sodium hydroxide (NaOH). The molar ratios of the solution was 2.5 SiO_2 (TEOS): 1.0 SiO_2 (CS): 0.025 Al_2O_3 : 0.5 TPABr: 0.25 Na_2O : 120 H_2O .

The synthesis solution was mixed for 30 min at 303 K. The crystallization was carried out in closed Teflon-lined stainless steel vessels under autogenous pressure at 453 K for 24 h. To stir the solution during the hydrothermal synthesis, the vessel was rotated in an oven. The crystalline size of ZSM-5 zeolites was controlled by changing a rotating speed and a volume of the closed vessel. The products were then calcined at 873 K for 5 h to remove TPA cations remaining in their structures. A proton-exchange process was carried out by using an ammonium chloride (NH_4Cl , 1 N) aqueous solution. The ZSM-5 crystals were mixed with the NH_4Cl aqueous solution for 12 h at ambient temperature. The crystals were then calcined again at 873 K.

2.2. Preparation of silicalite-1/HZSM-5

H-ZSM-5 with different crystal sizes was used as a core zeolite for the silicalite coatings. The precursor solution consisted of TEOS, tetrapropylammonium hydroxide (TPAOH), ethanol (EtOH) and deionized water with the molar ratios of 0.5TPAOH: 120 H_2O : 8EtOH: 2 SiO_2 . Approximately 1.0 g of H-ZSM-5 crystals was immersed in 15 g of the precursor solution. The crystallization was carried out under hydrothermal conditions at 453 K for 24 h in a stainless steel vessel with agitation. The coating was repeated twice. The products were rinsed repeatedly by deionized water and dried at 363 K overnight, then calcined in air at 873 K for 5 h with a heating rate of 1 K min^{-1} . The products were gathered by using filtration. Here, the mass changes after coating were measured after both the first and second coating.

2.3. Characterization

The products were characterized by X-ray diffraction (XRD) recorded on a Rigaku Miniflex using $\text{Cu K}\alpha$ radiation and scanning electron microscope (SEM) on a Hitachi S-2250N.

The crystalline structure of the silicalite-1/H-ZSM-5 composite was observed by the field emission scanning electron microscopy (FE-SEM) on a Hitachi S-5000L microscope at an acceleration voltage of 21 kV and the transmission electron microscope (TEM) on FEI Tecnai 20 at 120 kV and 200 kV.

2.4. Catalytic testing

Alkylation of toluene with methanol over the ZSM-5 and silicalite/ZSM-5 catalysts with different crystal sizes was performed using a fixed bed reactor at 673 K. The space time W/F is 0.14 kg-cat h mol^{-1} and the molar ratio of methanol/toluene was 1.0. The products of alkylation were analyzed by a gas chromatograph GC-2014 (Shimadzu Co.) equipped with a flame ionization detector (FID) using a Xylene Master column PRC 7791 (50 m, 0.32 mm).

3. Results and discussion

3.1. Morphology of H-ZSM-5 and silicalite-1/H-ZSM-5 composites

The XRD patterns of the uncoated and coated samples (data not shown) did not include reflection peaks for amorphous silica and impurities other than an MFI structure. Fig. 1 shows the SEM images of H-ZSM-5 crystals with different crystal sizes. The samples are labeled as S1-S4. The crystal sizes of the S1-S4 HZSM-5 crystals are 5, 10, 20 and 30 μm , respectively. The crystal sizes changed at different rotating speeds of the vessels. The stirring conditions seem to influence a nucleation rate of H-ZSM-5.

The SEM images of the S1-S4 HZSM-5 after the silicalite coating are shown in Fig. 2. The top layer seems to consist of randomly oriented crystals after the second coating. But, we have reported that the silicalite-1 crystals after the first coating are oriented in the same direction as the substrate ZSM-5 crystal surface [14]. The structure of the interface between H-ZSM-5 and silicalite-1 will be discussed in the Section 3.3. An overgrowth of a silicalite-1 layer on the H-ZSM-5 crystals (S1) was observed clearly. The coatings were composed of silicalite-1 polycrystals with a size of 1 μm . The crystal size did not increase so much even after the second coating. The thickness of the silicalite-1 layer must be less than a few μm .

Fig. 3 shows mass gain of zeolites after the first and second coatings. The mass gain, was slightly increased with decreasing crystal size because of an increase in an external surface area of H-ZSM-5. The mass gain after the silicalite-1 coating was too large for all the samples, considering that the silicalite-1 layer formed on the H-ZSM-5 surface was

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