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Selective formation of *para*-xylene over H-ZSM-5 coated with polycrystalline silicalite crystals

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Abstract

H-ZSM-5 crystals with various Si-to-Al ratios were coated with polycrystalline silicalite-1 layers by a repeated hydrothermal synthesis. The thus-formed silicalite-1 layers were affected by the morphology of the substrate H-ZSM-5 crystals. Applied to the alkylation of toluene with methanol, the silicalite coating significantly enhanced *para*-selectivity up to 99.9% under all reaction conditions. The enhanced *para*-selectivity may originate from diffusion resistance through the inactive silicalite layer on the H-ZSM-5, resulting in increased diffusional length. The silicalite coating on the H-ZSM-5 catalysts not only improved *para*-selectivity, but also prevented catalyst deactivation.

Keywords: ZSM-5; Silicalite-1; Toluene; Xylene; Alkylation; Overgrowth

1. Introduction

The selective formation of *p*-xylene is a challenging process, because *p*-xylene is one of the most valuable aromatic compounds required for the raw materials of terephthalate and polyester. The selective formation of *p*-xylene in the disproportionation of toluene, as well as the alkylation of toluene with methanol and transalkylation of methylbenzenes, has been studied over acidic zeolites such as ZSM-5 [1–6], mordenite [7], zeolite Beta [8,9], zeolite X [10], zeolite Y [11–13], and MCM-22 [14,15], as well as mesoporous aluminum silicate Al-MCM-41 [16]. ZSM-5 in particular is very interesting because its pore size is suitable for separating *p*-xylene from a mixture of xylene isomers. The last few decades have brought many reports concerning pore modification of ZSM-5 to enhance *para*-selectivity [1,2,12–26] and techniques for impregnation of phosphorous, MgO, or boron [1,2]; deposition of inert silica on the pore mouth by chemical vapor deposition (CVD) [19,20,22,25]; chemical liquid deposition (CLD) [6,17,18,20]; and others. However, further improvement of *para*-selectivity with high toluene conversion is still a challenging target, because a decrease in toluene conversion is inevitable after the pore modification.

Recently, we developed a porous catalyst covered with a permselective microporous membrane [27–29]. Silica–alumina catalyst particles coated with silicalite-1 membranes [27] showed higher *para*-selectivity (about 90%) than the thermodynamic equilibrium value (23%), because of a selective removal of the produced *p*-xylene through the silicalite-1 membrane. However, the reaction rate decreased largely due to the diffusion resistance of reactants and products thorough the thick silicalite-1 layer. Consequently, we have developed a novel composite catalyst consisting of a zeolite crystal of H-ZSM-5 with an inactive thin silicalite-1 layer in the hope of solving this problem [30].

A number of cases of zeolite overgrowth on different framework structures, including FAU on LTA [31], MCM-41 on FAU [32], and FAU on EMT zeolite [33], have been reported to date. In contrast, silicalite-1 has the same structure as the H-ZSM-5 substrate, resulting in the formation of a single-crystal-like silicalite/H-ZSM-5 particle [30].

However, as several researchers have reported, in the silicalite-1 layer grown on the ZSM-5, the so-called “zoned” MFI [34–36], the structure and thickness of silicalite layer depend on the Si/Al ratio, crystal size, and shape of the substrate H-ZSM-5. In the present study, silicalite overgrowth on H-

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ZSM-5 with different Si/Al ratios was studied. In addition, the catalytic activity of H-ZSM-5 depends on the Si/Al ratio, which may affect the overall activity and deactivation behavior on silicalite-coated H-ZSM-5. The thickness, structure, and quality of the silicalite layer, as well as catalytic performance, are discussed here.

2. Experimental

2.1. Synthesis of H-ZSM-5

ZSM-5 crystals with various Si-to-Al ratios were prepared by hydrothermal synthesis at 453 K for 24 h. The synthesis solution consisted of tetraethyl orthsilicate (TEOS), aluminum nitrate [$Al(NO_3)_3 \cdot 9H_2O$], sodium hydroxide (NaOH), and tetrapropylammonium bromide (TPABr). The molar composition was 1.5–3.5 SiO_2:0.025 Al_2O_3:0.5 TPABr:0.25 Na_2O:120 H_2O. The synthesis solution was mixed for 30 min at 303 K. This solution was poured into a Teflon-lined stainless steel vessel for hydrothermal treatment. The resulting ZSM-5 powders were calcined at 773 K for 5 h. A proton-exchange process was carried out using an ammonium chloride (NH_4Cl, 1 N) aqueous solution after the hydrothermal synthesis. The ZSM-5 crystals were mixed with the NH_4Cl aqueous solution for 12 h at ambient temperature, and the crystals were calcined again at 773 K. Hereinafter, the H-ZSM-5 samples synthesized using precursor solutions with Si/Al ratios of 30, 50, and 70 are designated H-ZSM-5(30), H-ZSM-5(50), and H-ZSM-5(70), respectively.

2.2. Silicalite coating

Silicalite coatings on H-ZSM-5 crystals were deposited as follows. A starting sol for synthesis of silicalite-1 coatings consisted of TEOS as a silica source, tetrapropylammonium hydroxide (TPAOH) as a structure-directing agent (SDA) and alkali source, ethanol, and deionized water. The H-ZSM-5 crystals were immersed in the precursor solution with a molar ratio of 2 SiO_2:0.5 TPAOH:8 ethanol:120 H_2O. The crystallization was carried out at 453 K for 24 h in a stainless steel vessel by hydrothermal synthesis with no agitation. The coating process was repeated twice. The products were rinsed with deionized water and dried at 363 K overnight, then calcined in air at 773 K for 6 h at a heating rate of 1 K/min. The products were characterized by scanning electron microscopy (SEM), using a Hitachi S-2250, and X-ray diffraction (XRD) recorded on a Rigaku MiniFlex using Cu$K\alpha$ radiation.

2.3. Alkylation

The catalytic activity and selectivity of silicalite/H-ZSM-5 were investigated on alkylation of toluene. Alkylation of toluene with methanol was performed using a fixed-bed reactor. The products were introduced directly into a Shimadzu GC-14B FID gas chromatograph with a Bentone34 + DNP column. Details of the experiments are described elsewhere [30].

3. Results and discussion

3.1. Morphology of the zeolite composites

Fig. 1 shows XRD patterns of the uncoated and coated samples. Even after coating, the XRD patterns did not include reflection peaks for amorphous silica and impurities other than an MFI structure, suggesting that the products are silicalite/ZSM-5 composites. Fig. 2 shows SEM images of synthesized H-ZSM-5 and silicalite/H-ZSM-5 with varying Si-to-Al ratios. H-ZSM-5(70) crystals were of hexagonal cylindrical shape and approximately 12 µm in size. After the first silicalite coating, small silicalite-1 crystals were formed on the H-ZSM-5 crystal. A silicalite-1 layer was grown along the external surface of the H-ZSM-5 crystal. The silicalite-1 crystals are oriented in the same direction as the substrate ZSM-5 crystals, and the silicalite-1 crystals grow on the ZSM-5 crystal surfaces perpendicular to the a- and b-axes. The silicalite/H-ZSM-5 has a single-crystal-like structure [30]. On the other hand, in the present study, the formed silicalite-1 layer comprised oriented polycrystals. Finally, a large amount of silicalite-1 crystals (<3 µm in diameter) was formed on the first silicalite-1 layer.

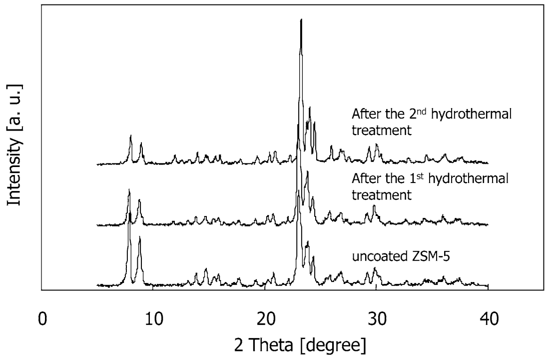

Fig. 1. XRD patterns of uncoated and coated H-ZSM-5(70) crystals.

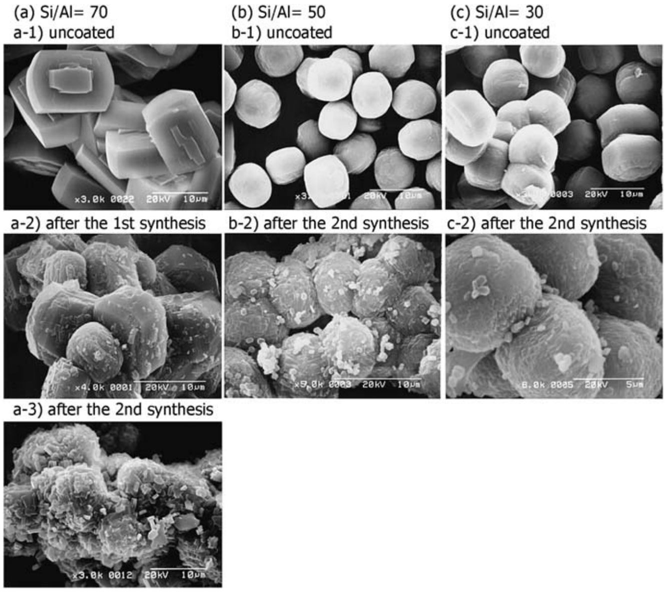

Fig. 2. SEM images of H-ZSM-5 and silicalite/H-ZSM-5 crystals.