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High utilization of methanol in toluene methylation using MFI zeolite nanosponge catalyst

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ABSTRACT

A highly mesoporous MFI zeolite nanosponge, which was composed of a disordered assembly of 2.5-nm thick zeolite frameworks, was synthesized using a meso- and micropore dual structure-directing surfactant. The zeolite nanosponge was investigated as a catalyst for toluene methylation by methanol. The results showed remarkably high toluene conversion and xylene yield, in comparison with the bulk zeolite counterparts. The high catalytic performance was attributed to the suppression of side reactions that could convert methanol to linear hydrocarbons. This suppression can be attributed to the fact that the dealkylation of polymethylbenzenes, which must take place before linear hydrocarbon formation, did not occur significantly in the zeolite nanosponge as compared to the case of bulk zeolites. In addition to the aforementioned high performance, the MFI zeolite nanosponge was also superior to the bulk MFI in terms of catalytic longevity.

1. Introduction

Benzene, toluene, and xylene (BTX) are basic raw materials for various petrochemical products [1]. One of the largest sources of BTX is from the catalytic reforming of heavy naphtha. However, in this process, toluene is overproduced relative to current market demand. The surplus toluene should be converted to a more valuable xylene via transalkylation or methylation processes [1–3]. Among the toluene-to-xylene conversion processes, methylation using methanol [2–5] has been a focus of attention in recent years after methanol became available at low cost from shale gas processing [6]. In recent decades, the toluene methylation process has been extensively studied using various zeolite catalysts with common names, such as Y [7], ZSM-5 [3,5,8,9], mordenite [5,9], beta [5,9], MCM-22 [10], and SSZ-33 [3]. Among the investigated zeolites, high silica ZSM-5 turned out to be the most suitable catalyst. The main feature of this zeolite is its pores, which are composed of 10-membered oxygen rings (*i.e.*, 10-MR). The 10-MR pores are wide enough for the first alkylation reaction to take place, but cause steric hindrance to further reactions to polymethylbenzenes (*e.g.*, hexamethylbenzene). Thus, high xylene selectivity is an advantage of these 10-MR zeolites [5,9]. Furthermore, the narrow 10-MR zeolite pores exhibit shape selectivity for *p*-xylene over the *o*- and *m*- isomers. Since *p*-xylene is more valuable than *o*- and *m*-xylenes, there have been very extensive studies on ways to increase the shape selectivity [11–13]. These 10-MR zeolites were modified in various ways with oxides of boron, magnesium, silicon, and phosphorus to achieve high *p*-xylene selectivity. However, these modifications led to a decreased toluene conversion owing to the inherent trade-off relationship, which implied a low first-pass yield and high recycling flow in the conventional zeolite-based catalytic processes. Consequently, this strategy could increase both the investment and operational costs and reduce the economics and efficiency of aromatic plants.

In the present work, we focus our attention on the toluene methylation approach that pursues high toluene conversion and xylene yield rather than high *p*-xylene selectivity. We note that this methylation process is normally carried out in a temperature range of 623 ~ 723 K. If we use a conventional ZSM-5 zeolite as a catalyst under such high-temperature conditions, the toluene conversion is usually less than 40%. This low toluene conversion is attributed to the consumption of methanol in side reactions [5,9,14], typically producing multi-methylated toluenes (*e.g.*, tri- and tetra-methylbenzenes) and linear hydrocarbons (*e.g.*, ethylene and propylene). Ahn et al. [5] investigated the methanol usage for side reactions using medium pore (10-MR) zeolites (*e.g.*, ZSM-5 and ZSM-11) and large pore (12-MR) zeolites (*e.g.*, MOR and BEA). They showed that the low production of multi-methylated toluenes and the high yield of linear hydrocarbons in ZSM-5 zeolites are due to a pore size effect. They also reported the effect of the zeolite crystal size on methanol usage, but predicted that the effect would be modest for the zeolite crystals of < 100 nm.

ZSM-5 zeolite is built with an MFI structure type aluminosilicate

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