Direct and Selective Conversion of Methanol to *para*-Xylene over Zn ion doped ZSM-5/Silicalite-1 Core-Shell Zeolite Catalyst

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Abstract

We successfully designed Zn ion doped ZSM-5/silicalite-1 core-shell zeolite catalyst. On methanol to *para*-xylene (MTpX) over the core-shell catalyst, *p*-xylene yield was 40.7 C-mol% and *para*-selectivity (*para*-xylene selectivity in xylene isomers) was higher than 99 C-mol%, which substantially exceeds the other results reported in the literature.

Introduction

p-Xylene is the most important isomer of xylenes for chemical industries since it can be converted into terephthalic acid which is one of the precursors of

polyethylene terephthalate (PET). Currently, *p*-xylene has been mainly produced from petroleum resources through multistep processes including reaction and separation processes. There is a serious problem in these processes; petroleum resources will be exhausted in the future. Furthermore, there is another problem that separation of *p*-xylene from xylenes is energy intensive due to the repetitive adsorptive separation and isomerization.

To solve the first problem, methanol to hydrocarbons (MTH) process using zeolite catalysts has attracted the attention because methanol can be produced from nonpetroleum resources and the catalysts for methanol synthesis have been widely studied ^[1-21]. As for improvement of selectivity to aromatic compounds, doping Zn, Ga and Ag species into zeolite catalysts has been found to be effective ^[12-21].

Meanwhile, to solve the second problem, the development of MFI zeolite membrane for the separation of xylenes ^[22-25] and surface modified MFI zeolite catalysts for toluene disproportionation or methylation have been promising ^[26-37]. In the former approach, xylenes were separated using the difference in the diffusivity in the MFI type zeolite pores (shape selectivity). In the latter approach, although shape selectivity is also used, the existence of acid sites on the external surfaces of ZSM-5 catalysts tends to inhibit the selective production of *p*-xylene due to undesirable xylene isomerizations there as a result of the lack of shape selectivity. To overcome this drawback, surface modification methods have been developed; e.g., impregnation of phosphorous, magnesium, or boron, deposition of

inert silica by chemical vapour deposition (CVD) or chemical liquid deposition (CLD) and so on ^[26-37].

However, many reaction and separation processes are still required to obtain high-purity *p*-xylene. Thus, more simple processes to produce *p*-xylene from nonpetroleum resources is strongly desirable. Direct *p*-xylene synthesis from methanol is one of the most promising candidates to solve both problems.

In our previous work, silicalite-1 (Al-free MFI type zeolite) coated catalysts showed much higher catalytic performance on various reaction systems ^[38-46]. Especially, ZSM-5/silicalite-1 core-shell structured zeolite catalyst showed both high *para*-selectivity in xylene isomers and catalytic activity in case of using methanol as a fuel ^[38]. In this study, to improve *p*-xylene yield, we designed Zn ion doped core-shell zeolite (Zn/ZSM-5/silicalite-1), which consists of Zn ion doped MFI zeolite with acid sites (Zn/ZSM-5) in the core and MFI zeolite without acid sites (silicalite-1) in the shell. Then, we evaluated the catalytic property of Zn/ZSM-5/silicalite-1 on methanol to *p*-xylene (MTpX).

Results and Discussion

We prepared Zn/ZSM-5 (Zn ion exchanged ZSM-5) and Zn/ZSM-5/S (Zn ion exchanged and silicalite-1 coated ZSM-5) using commercial ZSM-5 (Toso, SiO₂/Al₂O₃=39, **H-form**). More detailed procedures were listed on the experimental section in Supplementary Information.

Fig. 1 shows the XRD patterns of ZSM-5, Zn/ZSM-5 and Zn/ZSM-5/S. The peaks from MFI zeolite structure were detected on all samples, which shows that

the MFI structure remained even after ion exchange and silicalite-1 coating. Then, no peaks derived from Zn species were detected, which implied that Zn contents were very small and bulky Zn species were not present. Furthermore, from the results of ICP measurement (Table 1), Zn/Al ratios were not changed after silicalite-1 layer coating. These results implied that Zn species were present mainly as counter cation of zeolite. It was reported that this state of Zn species was favourable for enhancement of aromatics yield on MTH ^[21].

BET specific surface areas (Table 1) also were similar on all samples, which indicating that bulky Zn species and amorphous SiO₂ were not formed and blocked zeolitic pores. Moreover, from the FE-SEM images (Fig. 2), silicalite-1 overgrowth was observed. In addition, Al species signals (around 75 eV) on Zn/ZSM-5/S were not observed by XPS measurement (Fig. 3), indicating that Al species were not present on the surface of Zn/ZSM-5/S. From the above discussion, Zn/ZSM-5/S was Zn ion doped core-shell zeolite consisting of Zn ion doped MFI zeolite with acid sites (Zn/ZSM-5) in the core and MFI zeolite without acid sites (silicalite-1) in the shell.

Fig. 4 and Table 2 shows the results of reaction test (MTpX). Xylenes yield increased with increase of *W/F* values on all samples. Then, xylenes yield increased by doping Zn, which was in accord with previous works ^[13, 14, 20, 21]. Uncoated samples (ZSM-5 and Zn/ZSM-5) showed trade-off relationship regarding xylenes yield and *para*-xylene selectivity in xylenes (*para*-sel.). Meanwhile, as for Zn/ZSM-5/S, high *para*-sel. (>99%) maintained even in case of

high W/F values (high xylenes yield), which indicated that the undesired reactions on the external surface were inhibited even in case of high W/F values (high xylenes yield). Moreover, in optimum condition, Zn/ZSM-5/S showed *para*-xylene yield (40.7 C-mol%) with high *para*-sel. (>99%). To our knowledge, these results were best on MTpX reaction in previous works ^[47, 48].

The above results of MTpX reaction tests were summarized in Fig. S1-3. As for uncoated samples, *para*-sel. is high to some extent in case of low W/F values since the effect of undesired reactions on the external surface was small. However, the effect of undesired reactions on the external surface was stronger with increase of W/F values, which results in approaching **thermal equilibrium** (low *para*-sel.). On the other hand, as for Zn/ZSM-5/S, the effect of undesired reactions on the external surface is very small due to silicalite-1 coating. Owing to this, high *para*-sel. (>99%) maintained even in case of high W/F values (high xylenes yield).

Time courses of xylenes yield and *para*-selectivity are shown in Fig. 5. Although xylenes yield slightly decreased from the initial states as for all catalysts, xylenes yield were constant from 2 h to 4h. High *para*-sel. (> 99 %) maintained from 1 h to 4 h on Zn/ZSM-5/S. As for uncoated catalysts, *para*-sel. slightly increased with increase of Time On Stream (TOS). A possible reason is that acid sites on the external surfaces were partially covered with coke, which results in decreasing the effect of undesired reactions. There is no great difference of coke deposition rate between ZSM-5 and Zn/ZSM-5 as shown in Fig. 6. Meanwhile, the coke deposition rate of Zn/ZSM-5/S was smaller than uncoated catalysts. Coke is

rapidly formed by acid sites on the external surfaces[[1](#)]. It is suggested that coke formation was suppressed by inert silicalite-1 coating on the external surfaces.

Conclusion

In this communication, we successfully designed Zn ion doped core-shell zeolite (Zn/ZSM-5/silicalite-1) which consisted of Zn ion doped MFI zeolite with acid sites (Zn/ZSM-5) in the core and MFI zeolite without acid sites (silicalite-1) in the shell. We also demonstrated that this catalyst showed both *p*-xylene yield and *para*-sel. on MTpX reaction.

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Table 1 BET surface areas and chemical composition of catalysts.

catalysts	S_{BET} [m ² /g]	Al [wt%]	Zn [wt%]	Zn/Al [-]
ZSM-5	470	2.14	-	-
Zn/ZSM-5	454	2.05	0.81	0.395
Zn/ZSM-5/S	452	0.87	0.35	0.402

Table 2 Xylenes yields and *para*-selectivity.

catalysts	<i>o</i> -Xylene [C-mol%]	<i>m</i> -Xylene [C-mol%]	<i>p</i> -Xylene [C-mol%]	<i>para</i> -Sel. [C-mol%]
ZSM-5	7.4	16.3	7.6	24
Zn/ZSM-5	11.0	25.2	12.9	26
Zn/ZSM-5/S	< 0.1	0.3	40.7	> 99

* $T = 673$ K, $W/F = 23.7$ g h/mol, Time On Stream (TOS) = 1 h

Fig. 1 XRD patterns of catalysts.

Fig. 2 FE-SEM images of (a) ZSM-5, (b) Zn/ZSM-5 and (c) Zn/ZSM-5/S.

Fig. 3 XPS spectrums on Al species.

Fig. 4 Results of MTpX reaction tests : (a) yields of xylene isomers and (b) *para*-selectivity in xylene isomers.

Fig. 5 Time courses of (a) yields of xylene isomers and (b) *para*-selectivity in xylene isomers.

Fig. 6 Coke deposition rate of catalysts.

Graphical Abstract