

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.

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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, be-

cause 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 through 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 orthosilicate (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 ($<3 \mu m$ in diameter) was formed on the first silicalite-1 layer.

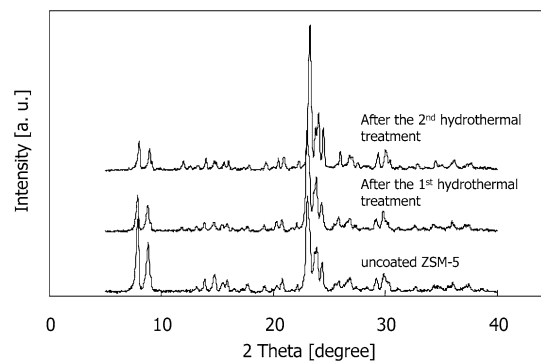


Fig. 1. XRD patterns of uncoated and coated H-ZSM-5(70) crystals.

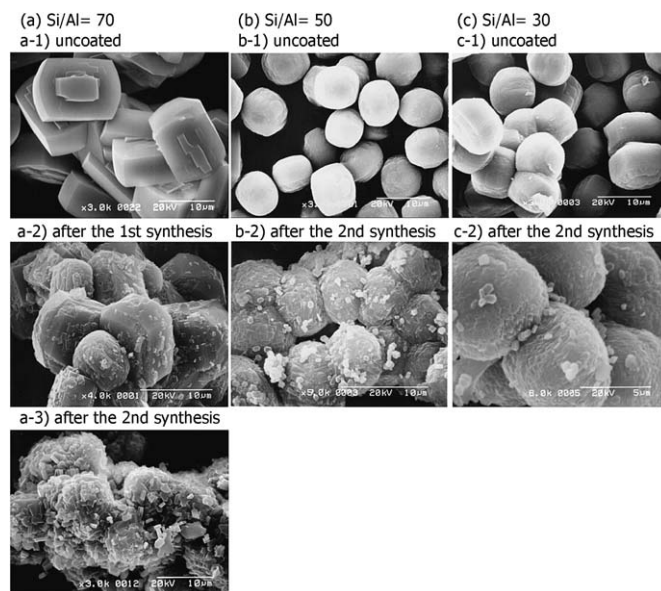


Fig. 2. SEM images of H-ZSM-5 and silicalite/H-ZSM-5 crystals.

The different morphology of the silicalite layer must be due to the different Si-to-Al ratio of the substrate H-ZSM-5. The Si-to-Al ratio in the present study is lower than that in our previous report (Si/Al = 108). The presence of Al in the H-ZSM-5 must have affected the formation of the polycrystalline layer.

The H-ZSM-5(50) and H-ZSM-5(30) crystals were near-spherical in shape and had a crystal size of approximately 7 and 10 μm , respectively. The morphology of these two silicalite/H-ZSM-5 crystals was very similar regardless of the Si-to-Al ratio of the H-ZSM-5 substrate. The morphologies of the silicalite layers on H-ZSM-5(30) and H-ZSM-5(50) were also very similar. This indicates that the morphology of the formed silicalite-1 layer is affected by the shape of the H-ZSM-5 substrate crystals. The silicalite layer on H-ZSM-5(50) seems to consist of a closely-packed layer of 1- μm silicalite crystals of hexagonal cylindrical shape. In addition, the silicalite layers grew in the same direction of H-ZSM-5 crystals, as in the case of the silicalite/H-ZSM-5(70) after the first hydrothermal synthesis. The deposited polycrystals after the second synthesis were randomly oriented and were not densely packed. However, the silicalite layer in the vicinity of the external surface of H-ZSM-5 seemed to be oriented and compact. A study of the epitaxial growth of the silicalite layer at the silicalite-ZSM-5 interface using TEM measurements will be reported in the future.

The Si/Al molar ratios of the H-ZSM-5 crystals were analyzed by EDX. The actual Si/Al ratios of all the samples were 18 for H-ZSM-5(30), 28 for H-ZSM-5(50), and 52 for H-ZSM-5(70), lower than the Si/Al ratios of the precursor solutions.

3.2. Alkylation of toluene

Alkylation of toluene with methanol was carried out over uncoated H-ZSM-5 and silicalite/H-ZSM-5 catalysts. The molar fraction of produced *p*-xylene in all of the xylene isomers is defined as the *para*-selectivity. Table 1 lists the toluene conversion, the aromatic product distribution, and the fraction of xylene isomers before and after silicalite coating of H-ZSM-5(70). The toluene conversion and *para*-selectivity over H-ZSM-5 and silicalite/H-ZSM-5 with varying Si-to-Al ratios are given in

Table 1
The alkylation of toluene with methanol over H-ZSM-5(70) and silicalite/H-ZSM-5(70)

| | Silicalite/H-ZSM-5(70) | H-ZSM-5(70) |
|---------------------------|------------------------|-------------|
| Conversion of toluene (%) | 49.9 | 53.7 |
| Product composition (%) | | |
| Benzene | D.L. | 0.2 |
| <i>p</i> -Xylene | 46.1 | 23.9 |
| <i>m</i> -Xylene | D.L. | 16.3 |
| <i>o</i> -Xylene | D.L. | 7.5 |
| Ethyl toluenes | 3.7 | 0.6 |
| Trimethyl benzenes | 0.1 | 4.1 |
| Fraction of xylenes (%) | | |
| <i>p</i> -Xylene | 99.9 | 50.1 |
| <i>m</i> -Xylene | <0.05 | 34.2 |
| <i>o</i> -Xylene | <0.05 | 15.7 |

Note. Reaction temperature: 673 K, reaction time: 60 min, $W/F = 0.20$ kg-catalyst h mol⁻¹, D.L.: below detection limit.

Table 2. The *para*-selectivity increased significantly after silicalite coating in all of the samples. The toluene conversion over silicalite/H-ZSM-5 was high even after the silicalite coating. The fraction of trimethyl benzenes decreased from 4.1 to 0.1% after silicalite coating. In contrast, the yield of ethyl toluenes increased after silicalite-1 coating. In our previous work [30], the silicalite coating not only decreased the production of *o*- and *m*-ethyl toluenes and trimethyl benzenes, but also increased the fraction of *p*-ethyl toluene. Because the molecular sizes of *o*- and *m*-ethyl toluenes are larger than the pore size of silicalite-1, the ethyl toluenes produced over silicalite/H-ZSM-5 must be *p*-ethyl toluene.

Mirth et al. [4,5] studied toluene alkylation and isomerization on a H-ZSM-5 catalyst and suggested that the high *para*-selectivity obtained above 573 K is because the rate of reaction is governed by a diffusion limitation at high temperature. Above 573 K, the rate of isomerization is higher than that of methylation, resulting in the accumulation of *m*-xylene and *o*-xylene in the pores. The ratio of diffusivities of three xylene isomers was determined to be *p*:*m*:*o* = 1000:1:10 [4]. In our reaction conditions, the *para*-selectivity is higher than that of the thermodynamic equilibrium value (23%) for even the uncoated catalyst. Thus, the rate of reaction must be controlled by a diffusion limitation for both the uncoated and coated catalysts. The effectiveness of the catalyst is low for even the uncoated catalyst. Even though *p*-xylene forms selectively in H-ZSM-5 in the diffusion control region, the isomerization on acid sites on the external surface reduces the *para*-selectivity for the uncoated catalyst. But the silicalite layer could remove the acid sites on the external surface of H-ZSM-5 and inhibit isomerization of *p*-xylene. Enhancement of *para*-selectivity through a pore mouth modification using CVD [19,20,22,25] and CLD [6,17,18,26] methods has been reported by several groups. But all of the acid sites on the external surface are difficult to remove by surface modifications, such as silylation. The silicalite coating is an excellent technique for covering the ZSM-5 crystals with an inactive layer; furthermore, in this method, the pore opening size does not decrease after coating. This is the reason why the toluene conversion over silicalite/H-ZSM-5 was also high even after the silicalite coating.

The toluene conversion over silicalite/H-ZSM-5(30) was much lower than that over the other two silicalite/H-ZSM-5 catalysts. The silicalite-1 layer on H-ZSM-5(30) must be thicker than that of the other two H-ZSM-5 crystals, because toluene conversion and selectivity could be significantly affected by the quality and thickness of the silicalite-1 layer [27–29].

Fig. 3 shows changes in toluene conversion and *para*-selectivity over the uncoated H-ZSM-5(70) catalysts and silicalite/H-ZSM-5(70) with reaction time. The reaction temperature was 673 K, and the space time (W/F) was 0.12 kg-catalyst h mol⁻¹. Toluene conversion and *para*-selectivity at the early period over the uncoated H-ZSM-5(70) catalyst were >40 and >65%, respectively. Toluene conversion decreased rapidly to <20% after 240 min, but the *para*-selectivity increased slightly with reaction time, reaching about 70% after 300 min. Compared with the uncoated H-ZSM-5, silicalite/H-ZSM-5(70) showed excellent *para*-selectivity (>99.9%).

Table 2
The alkylation of toluene with methanol over H-ZSM-5 and silicalite/H-ZSM-5

| | Silicalite/H-ZSM-5(30) | | Silicalite/H-ZSM-5(50) | | Silicalite/H-ZSM-5(70) | |
|---------------------------------|------------------------|------------------------------|------------------------|------------------------------|------------------------|------------------------------|
| | Toluene conversion (%) | <i>Para</i> -selectivity (%) | Toluene conversion (%) | <i>Para</i> -selectivity (%) | Toluene conversion (%) | <i>Para</i> -selectivity (%) |
| Uncoated H-ZSM-5 ^a | 63 | 40 | 65 | 38 | 65 | 49 |
| Silicalite/H-ZSM-5 ^b | 42 | >99.9 | 52 | >99.9 | 55 | >99.9 |

Note. Reaction temperature: 673 K, reaction time: 60 min.

^a $W/F = 0.09 \text{ kg-catalyst h mol}^{-1}$.

^b $W/F = 0.15 \text{ kg-catalyst h mol}^{-1}$.

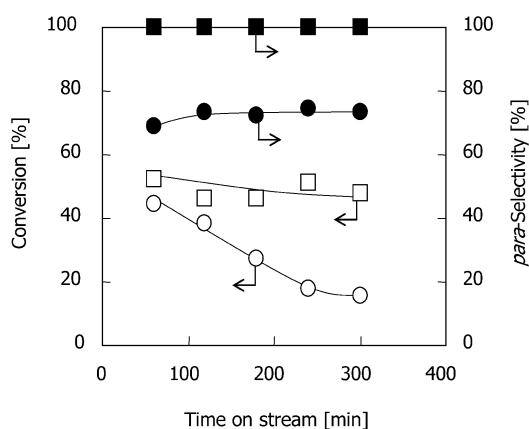


Fig. 3. The alkylation of toluene with methanol over the uncoated H-ZSM-5(70) and silicalite/H-ZSM-5(70) catalysts at 673 K. $W/F = 0.12 \text{ kg-catalyst h mol}^{-1}$, methanol/toluene = 1.0. Open symbol: toluene conversion, filled symbol: *para*-selectivity. H-ZSM-5(70): circle, silicalite/H-ZSM-5(70): square.

The toluene conversion was >40%, greater than that of the uncoated H-ZSM-5(70), because the toluene conversion was constant during the reaction. This result indicates that the silicalite coating inhibited coke formation caused by the reaction. Coke formation has been one of the most significant issues in solid acid catalysts. The silicalite coating not only enhanced *para*-selectivity, but also prevented catalyst deactivation. This result indicates that coke formation occurred near the external surface of the H-ZSM-5 crystals. Because of diffusion resistance, the reaction occurred mainly near the surface of H-ZSM-5. Thus, coke formation significantly affected the reaction rate for the uncoated catalyst. The high stability of the coated catalyst under reaction can be explained by the removal of acid sites on the external surface of H-ZSM-5.

Fig. 4 shows the activity of the alkylation of toluene with methanol over silicalite/H-ZSM-5(70) at different methanol-to-toluene ratios. The silicalite/H-ZSM-5 catalysts retained excellent *para*-selectivity (>99.9%) for 300 min under all reaction conditions. At a methanol/toluene molar ratio of 0.5, the maximum toluene conversion was theoretically 50%. Because the toluene conversion was approximately 40, 80% of the methanol could be used for alkylation of toluene. In other words, the relative toluene conversion was 80%. At a methanol/toluene molar ratio of 1.0, the toluene conversion was approximately 55%. This result shows that methanol could be consumed for alkylation more efficiently at the lower molar ratio of methanol/toluene.

Fig. 5 shows the toluene conversion and *para*-selectivity over the silicalite/H-ZSM-5(70) and uncoated H-ZSM-5(70)

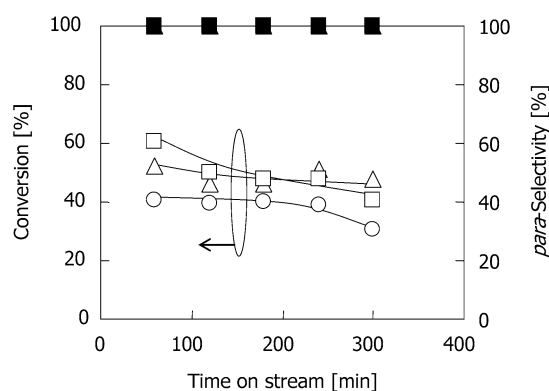


Fig. 4. Activity of the alkylation of toluene with methanol over silicalite/H-ZSM-5(70) with different methanol/toluene feed ratios at 673 K. $W/F = 0.12 \text{ kg-catalyst h mol}^{-1}$. Open symbol: toluene conversion, filled symbol: *para*-selectivity. Methanol/toluene = 0.5: circle, 1.0: triangle, 2.0: square.

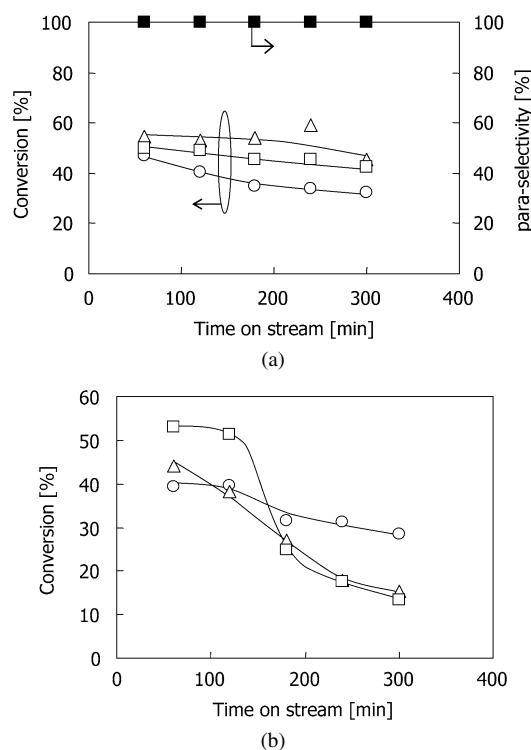


Fig. 5. Activity of the alkylation of toluene with methanol over (a) silicalite/H-ZSM-5(70) and (b) uncoated H-ZSM-5(70) at different reaction temperature. $W/F = 0.15 \text{ kg-catalyst h mol}^{-1}$, methanol/toluene = 1.0. Open symbol: toluene conversion, filled symbol: *para*-selectivity. 623 K: circle, 673 K: triangle, 773 K: square.

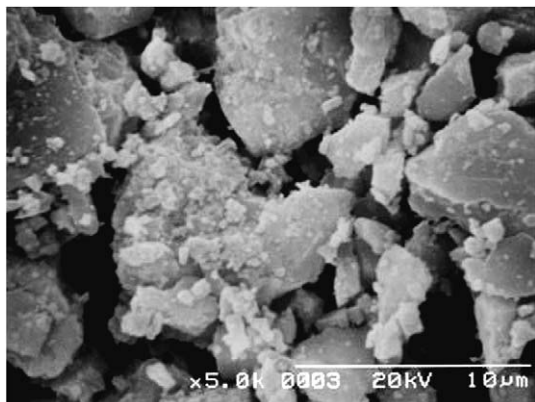


Fig. 6. An SEM image of crushed silicalite/H-ZSM-5 crystals(70).

Table 3
The alkylation of toluene with methanol over crushed silicalite/H-ZSM-5(70)

| | Crushed silicalite/H-ZSM-5(70) |
|---------------------------|--------------------------------|
| Conversion of toluene (%) | 64.3 |
| Fraction of xylenes (%) | |
| <i>p</i> -Xylene | 48.0 |
| <i>m</i> -Xylene | 39.9 |
| <i>o</i> -Xylene | 12.0 |

Note. Reaction temperature: 673 K, reaction time: 60 min, $W/F = 0.20$ kg-catalyst h mol⁻¹.

catalyst at different reaction temperatures. The *para*-selectivity was >99.9% at all temperatures and remained stable for 300 min during the reaction. The toluene conversion at 673 K was higher than that at 623 K, but the toluene conversion at 773 K was lower than that at 673 K. Both the diffusion rate and reaction rate of toluene would be expected to increase with increasing reaction temperature. Hence, catalyst deactivation might occur at the earlier stage of the reaction at 773 K. The toluene conversion over the uncoated H-ZSM-5 decreased significantly at high temperatures, indicating that deactivation of the uncoated H-ZSM-5 occurred rapidly at high temperatures. The deactivation rate was still low over the silicalite-coated catalyst at high temperatures.

We investigated the alkylation of crushed silicalite/ZSM-5 crystals. Fig. 6 shows an SEM image of the crushed silicalite/ZSM-5. The silicalite coating layer must have been broken completely by grinding. Table 3 summarizes the activity and selectivity on the alkylation of toluene over the crushed silicalite/ZSM-5. The *para*-selectivity over the crushed silicalite/ZSM-5 was decreased to the same level as that of the uncoated ZSM-5. This result strongly suggests that a compact silicalite layer plays an important role in enhancing *para*-selectivity.

Fig. 7 compares the toluene conversion and *para*-selectivity over the silicalite/H-ZSM-5 catalyst with those over various reported H-ZSM-5 catalysts modified by silylation and impregnation. Normally, the *para*-selectivity has a trade-off relationship with conversion; here, however, the silicalite/H-ZSM-5 catalyst showed high *para*-selectivity even at high toluene conversion, indicating that the silicalite coating on the external surface of ZSM-5 crystals is an effective technique for inhibiting the iso-

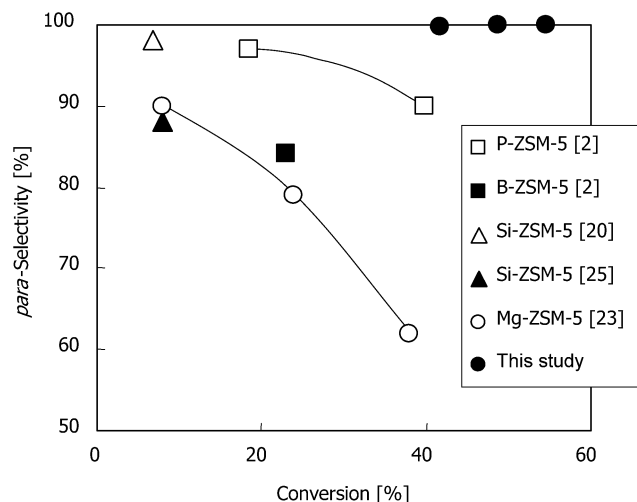


Fig. 7. The alkylation of toluene with methanol over various modified H-ZSM-5 catalysts and silicalite/H-ZSM-5(70).

merization from *p*-xylene to the other xylene isomers near the external surface of ZSM-5.

The enhanced *para*-selectivity may originate from diffusion resistance through the inactive silicalite layer on the H-ZSM-5, resulting in increased diffusional length. This mechanism is similar to that reported for the surface-modified zeolites by silylation [6,17,19]. The excellent *para*-selectivity (higher than the reported values) suggests that silicalite coating under hydrothermal conditions is an effective way to remove acid sites from the external surface of zeolites.

4. Conclusions

H-ZSM-5 crystals with varying Si/Al molar ratios were coated with silicalite-1 layers by hydrothermal synthesis. The silicalite layers thus formed comprised oriented polycrystallites of a few μm thickness that grew on the surface of the substrate H-ZSM-5 in the early stage of synthesis. The presence of Al in the H-ZSM-5 must have affected formation of the polycrystalline layer.

When applied in the alkylation of toluene with methanol, the silicalite/H-ZSM-5 catalysts showed excellent *para*-selectivity, >99.9% under all of the reaction conditions. The toluene conversion over the silicalite/H-ZSM-5 catalyst was almost constant, indicating that the silicalite coating inhibited coke formation on the external surface of H-ZSM-5. Its development as a new multifunctional catalyst is expected.

Acknowledgments

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References

- [1] N.Y. Chen, W.W. Kaeding, F.G. Dwyer, J. Am. Chem. Soc. 101 (1979) 6783.

- [2] W.W. Kaeding, C. Chu, L.B. Young, B. Weinstein, S.A. Butter, *J. Catal.* 67 (1981) 159.
- [3] M.A. Uguina, J.L. Sotelo, D.P. Serrano, *Appl. Catal. A* 76 (1991) 183.
- [4] G. Mirth, J. Cejka, J.A. Lercher, *J. Catal.* 139 (1993) 24.
- [5] G. Mirth, J.A. Lercher, *J. Catal.* 147 (1994) 199.
- [6] J. Cejka, N. Zilkova, B. Wichterlova, G. Elder-Mirth, J.A. Lercher, *Zeolites* 17 (1996) 265.
- [7] R. Mantha, S. Bhatia, M.S. Rao, *Ind. Eng. Chem. Res.* 30 (1991) 281.
- [8] T. Yashima, H. Ahmad, K. Yamazaki, M. Katsuta, N. Hara, *J. Catal.* 16 (1970) 273.
- [9] T. Yashima, K. Sato, T. Hayasaka, N. Hara, *J. Catal.* 26 (1972) 303.
- [10] A.E. Palomares, G. Elder-Mirth, J.A. Lercher, *J. Catal.* 168 (1997) 442.
- [11] E. Dumitriu, V. Hulea, S. Kaliaguine, M.M. Huang, *Appl. Catal. A* 135 (1996) 57.
- [12] P. Ratnasarmy, R.N. Bhat, S.K. Pokhriyal, *J. Catal.* 119 (1989) 65.
- [13] J. Das, Y.S. Bhat, A.B. Halgeri, *Catal. Lett.* 23 (1994) 161.
- [14] P. Wu, T. Komatsu, T. Yashima, *Micropor. Mesopor. Mater.* 22 (1998) 343.
- [15] P. Prokesova, N. Zilkova, S. Mintova, T. Bein, J. Cejka, *Appl. Catal. A* 281 (2005) 85.
- [16] S. Zheng, H.R. Heydenrych, A. Jentys, J.A. Lercher, *J. Phys. Chem. B* 106 (2002) 9552.
- [17] S. Zheng, H. Tanaka, A. Jentys, J.A. Lercher, *J. Phys. Chem. B* 108 (2004) 1337.
- [18] S. Laforge, D. Martin, J.L. Paillaud, M. Guisnet, *J. Catal.* 220 (2003) 92.
- [19] M. Niwa, M. Kato, T. Hattori, Y. Murakami, *J. Phys. Chem.* 90 (1986) 6233.
- [20] T. Hibino, M. Niwa, Y. Murakami, *J. Catal.* 128 (1991) 551.
- [21] M.A. Uguina, D.P. Serrano, R. van Grieken, S. Vènes, *Appl. Catal. A* 99 (1993) 97.
- [22] J.-H. Kim, A. Ishida, M. Okajima, M. Niwa, *J. Catal.* 161 (1996) 387.
- [23] Y.-G. Li, W.-H. Xie, S. Yong, *Appl. Catal. A* 150 (1997) 231.
- [24] L.-Y. Fang, S.-B. Liu, I. Wang, *J. Catal.* 185 (1999) 33.
- [25] A.B. Halgeri, J. Das, *Catal. Today* 73 (2002) 65.
- [26] S. Zheng, H.R. Heydenrych, H.P. Röger, A. Jentys, J.A. Lercher, *Topics Catal.* 22 (2003) 101.
- [27] N. Nishiyama, M. Miyamoto, Y. Egashira, K. Ueyama, *Chem. Commun.* (2001) 1746.
- [28] N. Nishiyama, K. Ichioka, D.-H. Park, Y. Egashira, K. Ueyama, L. Gora, W. Zhu, F. Kapteijn, J.A. Moulijn, *Ind. Eng. Chem. Res.* 43 (2004) 1211.
- [29] N. Nishiyama, K. Ichioka, M. Miyamoto, Y. Egashira, K. Ueyama, L. Gora, W. Zhu, F. Kapteijn, J.A. Moulijn, *Micropor. Mesopor. Mater.* 83 (2005) 244.
- [30] M. Miyamoto, T. Kamei, N. Nishiyama, Y. Egashira, K. Ueyama, *Adv. Mater.* 17 (2005) 1985.
- [31] E.D. Burchart, J.C. Jansen, H. van Bekkum, *Zeolites* 9 (1989) 432.
- [32] K.R. Kloetstra, H.W. Zandbergen, J.C. Jansen, H. van Bekkum, *Micropor. Mesopor. Mater.* 6 (1996) 287.
- [33] A.L. Yonkeu, V. Buschmann, G. Miehe, H. Fuess, A.M. Goosses, J.A. Martens, *Cryst. Eng.* 4 (2001) 253.
- [34] C.S. Lee, T.J. Park, W.Y. Lee, *Appl. Catal. A* 96 (1993) 151.
- [35] Q. Li, J. Hedlund, J. Sterte, D. Creaser, A.-J. Bons, *Micropor. Mesopor. Mater.* 56 (2002) 291.
- [36] Q. Li, Z. Wang, J. Hedlund, D. Creaser, H. Zhang, X. Zou, A.-J. Bons, *Micropor. Mesopor. Mater.* 78 (2005) 1.