High Utilization of Methanol in Toluene Methylation Using an MFI Nanosheet Catalyst

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Benzene, toluene, and xylene are the basic raw materials for various petrochemical products. Industrially, surplus toluene is usually converted into a more valuable xylene via either a transalkylation or methylation process. Among toluene-to-xylene processes, toluene methylation using methanol has been extensively studied owing to its high catalytic selectivity towards xylene. Nevertheless, the toluene conversion is ca. 40% over various conventional zeolite catalysts and further improvement is demanded for the prevalent commercialization of this process.

The present work was able to determine that the diffusion path–length of a zeolite catalyst could strongly affect the toluene conversion. Thus, the effect of the zeolite catalyst's crystal thickness on the catalytic performance has been investigated in detail. Several MFI zeolites with various crystal thicknesses were hydrothermally synthesized using appropriate structure-directing agents [1, 2] and these were characterized using various techniques. Fig. 1 shows representative SEM and TEM images for MFI zeolite samples with different crystal thickness in the range 2.5–200 nm, which were evaluated as the catalysts for toluene methylation using methanol. Fig. 2 shows toluene conversions plotted as functions of the reaction temperature and WHSV. The catalytic performances of the MFI zeolite catalysts were observably enhanced progressively as the zeolite's thickness decreased. A toluene conversion as high as 72% could be obtained over the MFI nanosheet catalyst with a crystal thickness of 2.5 nm, which was the best result reported thus far.

The catalytic performance was greatly dependent on the zeolite crystal thickness according to the above results, because the toluene methylation using methanol often competed with the methanol-to-hydrocarbon (MTH) conversion, which was an undesirable side reaction [3]. Thus, the remarkable high catalytic performance of the nanosheet catalyst was attributable to the low selectivity of the side products via the MTH route. The relationship between the catalyst's performance and the zeolite crystal's thickness was also supported by density functional theory (DFT) and molecular dynamics (MD). Therefore, regulation of the crystal thickness in the zeolite could be considered a viable means of enhancing the catalytic performance for toluene methylation using methanol.

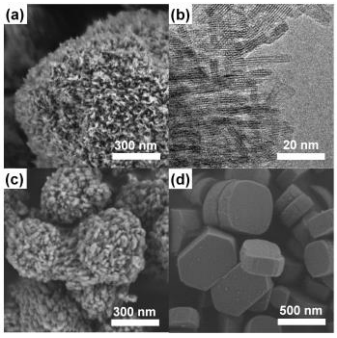

Fig.1 SEM and TEM images for the MFI zeolites with crystal thicknesses of (a, b) 2.5 nm, (c) 20 nm, and (d) 200 nm.

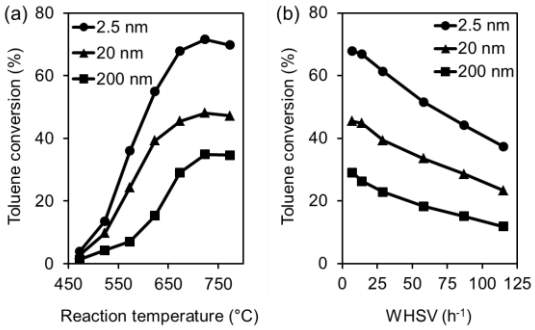

Fig. 2 Toluene conversion for the MFI zeolite catalysts with different crystal thicknesses plotted as functions of (a) the reaction temperature and (b) WHSV.

REFERENCES

[1] M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki and R. Ryoo, Nature, 461 (2009) 246.
[2] W. Kim and R. Ryoo, Catal. Letters, 144 (2014) 1164.
[3] U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T.V.W. Janssens, F. Joensen, S. Bordiga, K.P. Lillerud, Angew. Chem. Int. Ed., 51 (2012) 5810.