

Consecutive Bio-oil Upgrading Process via Two-Stage Reaction

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Hydrodeoxygenation (HDO) is known to be an effective method to convert biomass pyrolysis oil to high-quality fuel oil [1]. Use of acidic zeolites such as H-FER, H-MOR and H-MFI is essential for effective HDO since they can provide acidity required for efficient cracking and dehydration reactions during HDO. HZSM-5, a representative commercial catalyst widely used in oil refining and petrochemical synthesis process, has been vastly applied to HDO reaction. However, it undergoes fast deactivation due to limited diffusion of large molecules into its micro-scale channels. To increase the diffusivity of large molecules inside catalyst, mesoporous materials have been successfully applied to catalytic HDO reaction [2]. However, overall HDO efficiency over mesoporous materials was limited due to their low acidity.

In this study, a two-stage reactor consisting of catalytic pyrolysis and catalytic HDO reaction was used for the first time. Desilicated HZSM-5 catalyst having larger pore size than commercial microporous HZSM-5 was prepared by desilication of HZSM-5. The effects of desilication and acidity of HZSM-5 on HDO reaction were examined by comparing the product distributions achieved from consecutive catalytic pyrolysis-catalytic HDO reaction of miscanthus.

Fig. 1 shows the product distributions obtained from the consecutive catalytic pyrolysis-catalytic HDO reaction of miscanthus over different Ni-based catalysts. With similar SiO₂/Al₂O₃, desilicated HZSM-5 (D. HZSM-5) was more effective than commercial HZSM-5 for hydrocarbon production. This indicates the advantage of

mesoporosity of desilicated HZSM-5 for the upgrading of bio-oil. Meanwhile, compared to desilicated HZSM-5(30), desilicated HZSM-5(80) was more efficient for formation of hydrocarbon via HDO of miscanthus pyrolysis oil. This might be due to its higher SiO₂/Al₂O₃ ratio which reduced the cracking reaction of oil and led to high oil production with low yield of gas. Up to 10 sequential reactions over desilicated HZSM-5 were also performed (data are not shown); the results indicated that the deactivation of desilicated HZSM-5 during sequential use of catalyst was not severe compared to commercial HZSM-5. Based on the results mentioned above, it could be concluded that desilicated HZSM-5 can be a promising catalyst which not only provides higher hydrocarbon production but also has longer life time compared to commercial microporous HZSM-5.

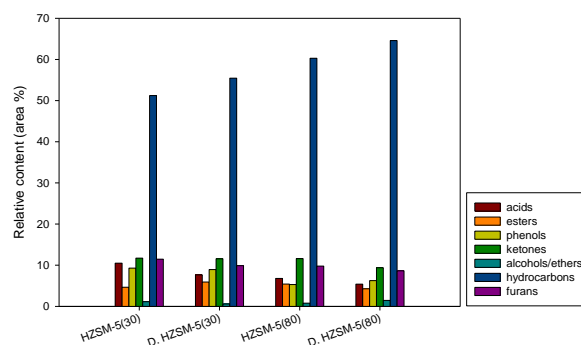


Fig. 1. Product distribution from consecutive catalytic pyrolysis-catalytic HDO of miscanthus over Ni/HZSM-5 and Ni/desilicated HZSM-5.

ACKNOWLEDGEMENTS We would like to acknowledge the financial support from the R&D Convergence Program of NST (National Research Council of Science & Technology) of Republic of Korea (CAP-16-05-KIMM).

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