Fine-Tuning Texture of Highly Acidic HZSM-5 Zeolite for Efficient Ethanol Dehydration

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Abstract

Converting carbon-consuming biomass and its derived-compounds into fine chemicals is a promising solution for decarbonization. One of the promissing strategy for the conversion of biomass-derived compounds is dehydration of (bio)ethanol to produce ethylene – the largest consumed chemical for plastics manufacturing.[1] Typically, a high acidic zeolite offers excellent ethylene yield from (bio)ethanol dehydration; however, maintaining stable ethylene production remains challenging due to undesired side-reactions. To overcome this issue, the fine-tuned textural property of the highly acidic HZSM-5 catalyst with a hierarchical structure is crucial to improve diffusion restrictions and prevent undesired side-reactions. Herein, tetrabutylammonium hydroxide as a meso- and micropore directing agent and the controlled molar ratio of NaF-to-Al_2O_3 were employed to fine-tune the texture of high acid catalysts using the hydrothermal synthesis.[2] The hierarchically designed HZSM-5 with the tiny nanosheet size of 6.5 nm exhibits a high external surface area and mesoporosity, eventually enhancing the catalytic performance of ethanol dehydration up to 95 % ethylene yield as well as inhibiting the formation of heavy hydrocarbons. Insights into the mechanistic points of view by the *in-situ* DRIFTS study revealed that ethylene could be produced through ethoxy-mediated mechanism or decomposition of diethyl ether (DEE). The catalyst deactivation caused by polyaromatics obtained from side-reactions is the main reason for low ethanol conversion and high DEE selectivity. Reducing the crystal size of highly acidic zeolite to ultra-thin nanosheet can shorten the residence time of ethanol, intermediates, and products in porous structures, substantially suppressing the transformation of coke precursors into heavy hydrocarbons to achieve high and stable ethylene yield. These findings open up perspectives for the development of a heterogeneous catalyst for the alternative way of monomer production without CO_2 emission.

References

[1] IEA, Paris, **2018**.
[2] P. Pornsetmetakul, S. Klinyod, C. Rodaum, S. Salakhum, P. Iadrat, E. J. M. Hensen, C. Wattanakit, *ChemCatChem* **2023**, *15*, e202201387.