

Insights into the Deactivation and Product Formation Behavior of ZSM-5 Zeolite Catalysts in the Conversion of Ethanol to Small Aromatics

M. Seifert, M.S. Marschall, T. Gille, O. Busse, W. Reschetilowski, J.J. Weigand
Technische Universität Dresden, Dresden, Germany

Abstract

Conversion of ethanol to hydrocarbons over porous acidic zeolite H-ZSM-5 (ETH process) is considered according to hydrocarbon pool mechanism in methanol-to-olefin catalysis (MTO process). An increase in durability and yield of small aromatics during the ethanol conversion are main challenges to improve industrial relevance for prospective application in refining. But this is prevented by a simultaneous increasing formation of undesired ethylene and as a consequence of the pore-blocking by nano-sized coke molecules.

Trends of durability changes and yields of small aromatics are explained not only by developing an understanding of bicyclic hydrocarbon pool mechanism using mechanistic approaches. They are also described by molecular processes near active sites particularly with the constellation of special site multiplets.

Deactivation behavior is correlated to different n^{th} order kinetics and the formation of center-controlled reactive intermediates (CRI) to solid-state material properties. The synthesis of ZSM-5 and its post-synthetic modification together with the adaption of process parameter in ethanol conversion aims to overcome challenges in log time stability of catalysts used. Moreover, it will give insights in the formation mechanism towards small aromatics inside and outside the zeolite pores of ZSM-5 (0.52 – 0.56 nm). Special focus was directed to change typically applied methods for zeolite modification by new treatments including acid and base washing or steaming in combination with the variation of residence time and feed flow.

Zeolite powder characterization of fresh and modified ZSM-5 by Clariant (structure (XRD), surface property and acidity (TPAD), elemental composition (ICP-OES), framework and extra-framework structure species (NMR), particle size analysis (REM, LDA)) is combined with the product analysis (GC, GC-MS) of catalytic test reactions in a fixed-bed reactor setup and discussed. By means of the models for deactivation kinetics and the formation of CRI the obtained catalytic results are verified.

Comparative discussion of catalytic results, solid-state properties (e.g. Si/Al, crystallinity, BET surface) and imaginary experiments on catalytic active multiplet centers together with local conversion pathways from ethanol to products and coke give hints to distinct dominant multi-site formation pathways towards olefins, small aromatics and poly-aromatic coke precursors.

The authors sincerely thank the German Research Foundation (DFG) for funding the research project RE 906/11-1.