

Understanding Coke Formation Mechanism in MFI Zeolites during Methanol-to-Hydrocarbons Conversion

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We investigated coke formation in methanol-to-hydrocarbons reaction over the MFI zeolites having different crystallite sizes. As the mass transfer of hydrocarbons was increased with decreasing zeolite crystallite size, an aromatic-based catalytic cycle became dominant compared to an olefin-based cycle. Consequently, methylated benzene intermediates accumulated within the zeolite micropores could act as coke precursors and polymerize to form internal coke. Aromatic products that diffuse out of zeolite micropores could be condensed at the external surface of zeolite crystallites. Once the carbon deposits were formed at the external zeolite surface, external coke continued to grow even non-catalytically by the thermal reaction with methylated benzenes. Different zeolite catalysts and reaction times affected only the relative amounts of internal and external cokes, but not their chemical natures. Internal coke is likely to have the polymeric structures of methylated acenes connected via methylene bridges. External coke is highly polyaromatic with many fused rings. In terms of catalyst deactivation, internal coke proved to be much more detrimental than external coke.