Heterogeneous Catalysis in Nanopores: Enhancing the Accessibility of Active Sites by Hierarchical Pore Systems

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Nanoporous catalysts are applied in a broad range of chemical conversions. Often, however, low catalyst effectiveness factors may result, if mass-transfer limitations exist, e.g., due to large substrate molecules. Additional pore systems with larger dimensions in the macro- and mesoporous range may, thus, help to increase accessibility and mass-transfer to and away from the catalytically active sites within nanoporous catalysts. This presentation will highlight two examples of nanoporous catalytic systems demonstrating the beneficial effect of an additional system with larger pores. In particular, the enhancement of accessibility of active sits with respect to diffusion improvements by a hierarchical pores system will be discussed

The first example treats titanium silicalite-1 (TS-1) for the epoxidation of the unsaturated fatty acid methyl esters (FAMEs) of biodiesel with hydrogen peroxide. To enhance the accessibility of the catalytically active Ti sites for FAME epoxidation in TS-1-based catalysts, nanocrystals of TS-1 are applied into which an additional mesopore system is introduced to alleviate transport hindrances. Also, nanosheets and pillared TS-1 catalysts provide highly accessible Ti sites. The combination of TS-1 crystals and activated carbon beads in composite catalysts represents another way to design active epoxidation catalysts using both high accessibility and the sorptive functionality for reactant enrichment in the vicinity of the active Ti sites.

In a second example, it is shown that two enzymes, i.e., glucose oxidase and horseradish peroxidase, can be co-immobilized on a monolithic silica materials exhibiting a hierarchical system of mesopores with two different widths. The smaller pores (ca. 3-5 nm) can accommodate the enzyme with the smaller diameter, while the enzyme with the larger diameter only fit into the larger mesopores (ca. 30-50 nm). The hierarchy and interconnectivity of the pores as well as the location of the enzymes within the pore systems are confirmed by PFG NMR diffusometry. Moreover, the enzymes remain active when immobilized on the hierarchical silica support.