

# Contribution of mesopores of hierarchically structured titanium silicalite-1 to the catalytic activity towards the methyl oleate epoxidation

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In micro- and mesoporous materials, transport of fluids with molecules of dimensions comparable with those of the pores often determines the overall rate of processes such as adsorption or catalysis as a result of diffusion limitations. While the vast majority of self-diffusion studies are focused on transport characteristics of low molecular-weight species, in particular short-chain hydrocarbons, far less diffusion data are reported for higher molecular-weight compounds with molecular dimensions of up to several nanometers, such as proteins, fats and oils or long-chain hydrocarbons.

The present contribution demonstrates first successful experimental results on molecular self-diffusion coefficients of methyl oleate (MO) confined to mesopores of catalytically active molecular sieves with a hierarchical micro-/mesopore system [1]. The pore hierarchy has been introduced into the initially microporous titanium-containing silicalite-1 (TS-1) catalyst by alkaline treatment and by pseudomorphic transformation.

The self-diffusion processes of MO in pelletized TS-1-based catalysts containing mesopores of 3-40 nm pore width as a result of a post-synthetic treatment were investigated by means of pulsed field gradient (PFG) NMR. Three different diffusion regimes in the treated catalysts were observed: i.) intra-crystalline diffusion within mesopores, ii.) long-range diffusion in the mesopore and in the inter-crystalline space of a pellet, and iii.) bulk-like diffusion in the voids between and outside the pellets. The intra-crystalline diffusivities are approximately two orders of magnitude lower compared to those of diffusion in the bulk phase at the same temperature. In the parent microporous TS-1, no diffusion of MO within the crystallites was observed (as expected).

The experimental data suggest that the mesopore network of the hierarchical micro-/mesoporous TS-1-based catalysts is well interconnected and accessible for MO molecules at room temperature. This, however, does not rule out possible existence of isolated mesopores being not accessible for methyl oleate. In such case, introduction of mesopores might not facilitate the intra-crystalline transport, as reported in Ref. [2]. The obtained self-diffusion coefficients allow the estimation of the time required for MO to diffuse through the entire pellet at room temperature. Moreover, the diffusivities differ for the materials with different width fractions of intra-crystalline mesopores.

In addition to the diffusion experiments, water sorption studies were performed. These were aimed at addressing the possible change in the surface hydrophobicity of the studied catalysts after application of alkaline treatment and pseudomorphic transformation. This, in turn, might influence the activity of the catalyst for MO epoxidation. Thus, the observed differences in activity of the hierarchical TS-1-based catalysts reported in Ref. [3], will be discussed in the context of the mesopore accessibility and the surface hydrophobicity.

## References

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