Sol-gel routes to Ti-SiO_2 epoxidation catalysts with tailored properties

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The simultaneous control over texture and active site speciation is an important challenge in catalysis. The titanosilicalite-1 (TS-1) zeolite is a good illustration. This microporous crystalline material shows very high Ti dispersion and high performance *e.g.* in olefin epoxidation. However, its use in industrial applications is limited to lower olefins as the microporosity strongly hampers the diffusion of the reactants and products in and out the pores. Besides, the framework Ti content is limited to 2.5 mol. %. There are therefore strong incentives to find new titanosilicate catalysts, combining large pores and high Ti loading and dispersion, in order to extend the versatility of epoxidation catalysts to larger olefins (*e.g.* cyclohexene) [1]. However, these solids are often amorphous, bringing an additional challenge in order to stabilize the active species in the presence of water. Also, the catalysts are often obtained in the form of small powders, requiring further steps to shape the materials before they could be used in flow processes. Herein, we present three examples of sol-gel strategies which successfully address the above-mentioned challenges.

As a first example, we use the unique features of the aerosol-assisted sol-gel chemistry to prepare – in an easy and scalable way – hierarchically porous materials (4 mol. % Ti) with a sphere-like shell morphology (Fig. 1 a). The porosity is controlled at the three micro-, meso- and macro- levels by the use of the evaporation-induced self-assembly (EISA) of a surfactant in the presence of tetrapropylammonium hydroxide (TPAOH), combined with polymer beads as hard templates. The high specific surface area (up to 890 $m^2.g^{-1}$) and the pore architecture of these materials account for their high performance compared to TS-1 (Fig. 1b) [2].

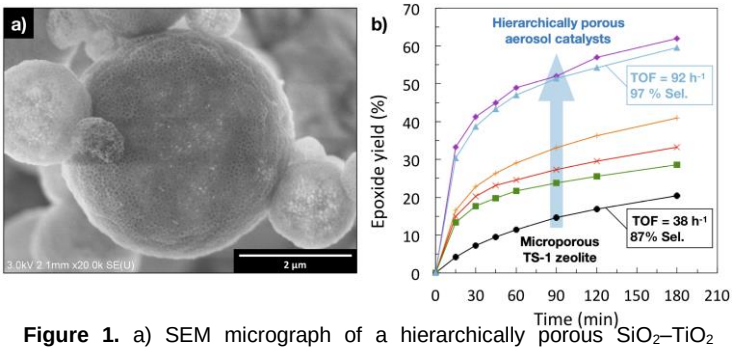

Figure 1. a) SEM micrograph of a hierarchically porous SiO_2–TiO_2 catalyst made by aerosol; b) Activity in the epoxidation of cyclohexene

Moving further, we synthesize a macrocellular titania-silica monolith foam using an emulsion-based templating technique. These monoliths are shown to possess high void fractions (*ca.* 85–90%) and mechanical properties comparable to Si(HIPE), but also high Ti dispersion, allowing not only to reach outstanding epoxidation activities compared to TS-1 (~ 14 times higher TOF with 98% sel.), but also to perform epoxidation in continuous flow mode (Fig. 2). This study paves the way to process intensification in olefin epoxidation [3].

Finally, since amorphous SiO_2–TiO_2 mixed oxides are sensitive to the presence of water, we investigate the role of surface hydrophobicity – through the grafting of methyl groups – on the performance of a mesoporous catalyst (6 mol. % Ti, 1020 $m^2.g^{-1}$) prepared by a non-hydrolytic sol-gel route. We show that, in the presence of a large excess of water in the solvent (25% vol.), we can increase not only the activity, but more importantly the selectivity of the catalyst (Fig. 3) [4].

Thus, we present an overview of innovative preparation methods that lead to efficient SiO_2–TiO_2 catalysts with tunable texture, pore architecture, Ti loading, surface properties, and also with possible scale-up and use in flow processes.

References

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