Hierarchically porous (organo-) silica species as supporting materials for selective oxidation Ti-based catalysts

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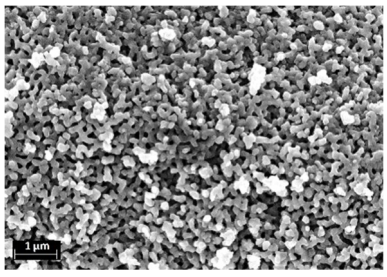
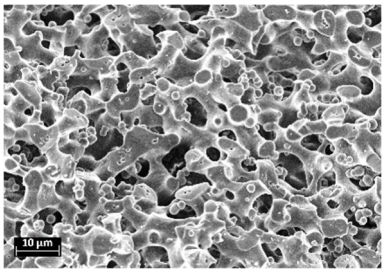
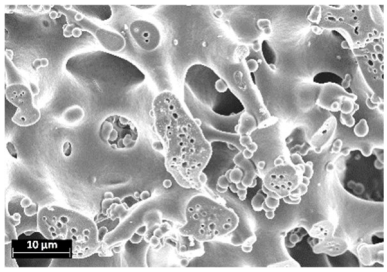
Tetrahedrally coordinated titanium(IV) is an active site, inter alia, for the selective oxidation of olefins. A famous catalyst using this kind of active site is the titanium silicalite-1 (TS-1),[1] which is used, for example, within the HPPO (propylene-to-propylene-oxide) process. This catalyst works under mild conditions and shows high yields and selectivity, but is hindered by slow diffusion pathways, due to the small pores of the TS-1.[2]

One idea to tackle such diffusion limitations is the usage of materials with hierarchical porosity. In our group, we use different types of macroporous starting materials to synthesize such hierarchical porous supporting materials **(Table 1)**. The main focus is on so-called *controlled pore glasses* (CPG), which are silica materials with an amorphous pore structure and a narrow pore size distribution with controllable pore sizes between 0.3 and 1000 nm. They can be synthesized in various geometric shapes and show a high mechanical, chemical and thermal stability.[3,4] Another potentially suited material, which are used in our group, are silica monoliths synthesized by spinodal decomposition (SDS).[5] These class of materials extends the range of the

Table 1: Scanning electron microscopy (SEM) images, macropore volume (P_{V_macro}) and diameter (d_{macro}) of the different starting materials.

CPG	PMO	SDS
		
0.9 cm³/g	1.1 cm³/g	0.9 cm³/g
140 nm	≈ 5 µm	≈ 10 µm

macropore size and is easier to synthesize than CPGs. A third class of materials used in our group are periodic mesoporous organosilicas (PMO). For the synthesis of these materials the 1,4-Bis(triethoxysilyl)benzene (BTEB) was used as precursor.[6] The advantage of these materials is that besides the pore size, the hydrophobicity can also be adjusted.[7,8]

In order to generate a hexagonal ordered mesoporous MCM-41 system within the pore walls of the macropores and thereby synthesize a hierarchical porous supporting material, the above-mentioned starting materials were pseudomorphically transformed. This step has already been successfully performed for all mentioned starting materials by using a cetyltrimethylammonium hydroxide (CTAOH) solution.

To insert tetrahedrally coordinated titanium(IV) into the framework of the supporting materials, they were impregnated before the pseudomorphic transformation with a titanium(IV) precursor, *e.g.* titanium isopropoxide (TTIP), in accordance with the incipient wetness process. This synthesis step we have already successfully performed for CPGs. The insertion of titanium into the SDS and the PMO is part of our current work.

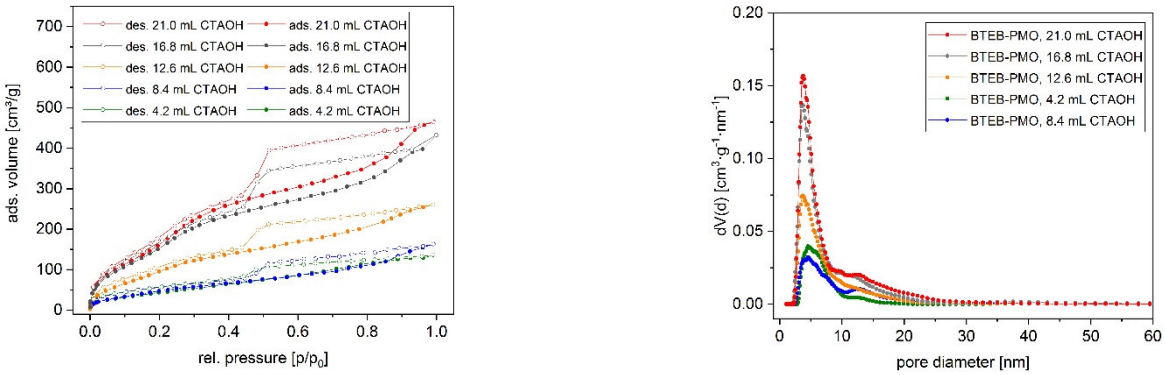


Figure 1: Adsorption-desorption isotherms and pore size distributions calculated from nitrogen physisorption (77 K, kernel: *N2 at 77 K on silica, cylindr. pore, NLDFT ads.*) of pseudomorphically transformed BTEB-PMOs with different volumes of CTAOH solution. The data of the CPGs were already shown on a previous poster, the data of the SDS are not yet completely available.

References:

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