Local pore size control within carbon particles

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Already in 1980 Hegedus postulated optimized pore structures for pelleted catalysts [1], which is also true for other applications like e.g. electrocatalysis, energy storage or adsorption. Hegedus pioneering work and more detailed recent optimization studies showed that optimized pore networks are a combination of micro- and mesopores, which vary in composition within a catalyst particle [2]. While catalyst supports with a homogeneous combination of bi- and multimodal pore structures are readily available for application, locally tuned structures within the particle are rarely reported. Within this work the local pore structure tuning of carbon supports from core-shell-like towards gradually changing structures is studied. Basis for the synthesis of local optimized pore structures in this study is the conformal conversion of carbides to carbide-derived carbons (CDC) by a chlorination reaction [3, 4]. The resulting carbon pore structure can be controlled by the process conditions and a parallel partial oxidation with carbon dioxide [5, 6].

Synthesis of CDC took place in a horizontal tubular reactor heated between 600 to 1200 °C by an external electrical resistance furnace. Titanium carbide powder (mean diameters: 3 and 50 µm) was placed in a graphite crucible and treated with a mixture of Cl_2, CO_2 and He for several hours to achieve full conversion of carbide to carbon. During the reaction the concentrations of the reactants in the gas feed and the temperature were varied. The obtained materials were analyzed by N_2- and CO_2-sorption, XRD, Raman, FTIR and TEM.

The local tuning of the pore structure can be demonstrated best with a core-shell support synthesized. Thereby the outer 36% of the particle volume show micro- and mesoporous character, while the inner core consists solely of micropores. In Fig. 1 a comparison of the pore size distribution of the shell and the shell and core is given.
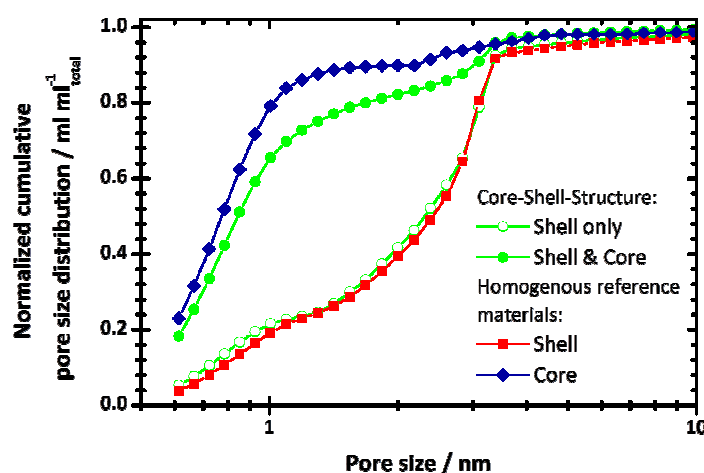

Fig. : QSDFT (N2) pore size distribution of a carbon support core-shell structure.

While in this example a sharp transition in the pore structure within the particle occurs, supports with gradual change in pore size along the radius of the particle could also be implemented. The pore size distribution of the final structure is between the limiting cases shown in Fig. 1.

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