

Impact of Confinement in Core@Shell Arrangements on Particle Size Effects in the Fischer-Tropsch synthesis

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The design of supported porous solid catalysts is of great importance for maximizing catalytic activity and controlling product selectivity. Generally, the interaction between metal species and the support strongly influences the performance of the catalysts.^[1] One attractive option to steer the metal-support interaction is the encapsulation of dispersed metal nanoparticles referred to as a strong metal-support interaction.^[2] So far, most efforts approached core@shell structures from a materials chemistry perspective, focusing on establishing synthetic control and on stabilization of the metal nanoparticle core via embedding in a protective shell. There has been little attention paid to the exploitation of the confinement effect from a reaction engineering point of view, and thus also to the control of access to the catalytic core by selective transport of reactants through the shell.^[1]

The concept of confinement has already been reported for metal nanoparticles encapsulated in hollow mesoporous structures.^[3] The tuneable structure of the core@shell configuration can influence the selectivity of reactions.^[2,4] Due to selective transport of reactants and products through the porous shell the faster diffusing reactants and the slower diffusing products are enriched within the inner void space in proximity of the active nanoparticle. Consequently, a different composition in the proximity of the active nanoparticle compared to the bulk is promoted leading to an overall more desirable product spectrum. As of now, there is no scientific work investigating the impact of the confinement effect on the particle size effect for Fischer-Tropsch (FT) synthesis, despite that this effect is well known for conventional FT catalysts.^[5]

For the investigation of the impact of confinement on the particle-size effect, we varied the cobalt particle sizes in the range of 6.5 to 30.0 nm and compared Co@SiO₂ core@shell structures to conventional Co/SiO₂ catalysts with the same particle size. Respective experiments were carried out in a fixed-bed reactor under isothermal conditions at 260 °C, 20 bar and a H₂/CO feed ratio of 2.

Figure 1 shows that the optimal turnover frequency (TOF) and cobalt time yield (CTY) shifts to larger particle sizes in the core-shell structure compared to conventional catalysts reported by Bezemer et al.^[5]

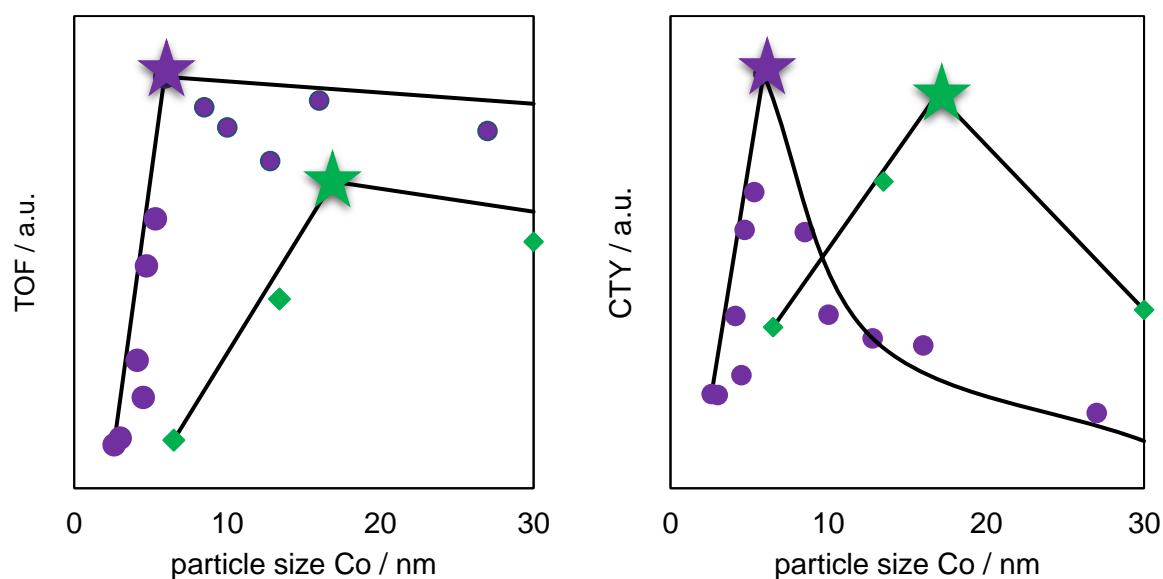


Figure 1: Turnover frequency (TOF), left, and Cobalt time Yield (CTY), right, of the Co@SiO₂ catalysts (green) compared to the conventional catalyst reported by Bezemer et al.^[5] (violet).

Initial observation of the experiments indicates a confinement effect, which has an influence on dependency of turnover frequency and cobalt time yield on the particle size effect and thus leads to a shift in the optimal particle size. Presumably, the microenvironment in proximity to the active core is changed by the selective transport through the shell. This creates a CO-rich and H₂-lean microenvironment, thus reducing the hydrogenation ability of metallic Co and promoting the desorption of olefins as well as inhibiting its re-adsorption and secondary hydrogenation.^[6] These hypotheses are in agreement with the product spectrum of the Fischer-Tropsch experiments, where not only a shift from long to medium chain lengths can be seen, but also an increased fraction of olefins and isomers.

References

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