

Cobalt-Based CO₂ Hydrogenation: Link Between Particle Size, Oxidation State and Product Selectivity

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Introduction. The effect of particle size on the reactivity of cobalt nanoparticles in Fischer-Tropsch chemistry is well established, but less is known about the impact on cobalt-based CO₂ hydrogenation.^[1] To study this, we used Surface Organometallic Chemistry (SOMC) to synthesize well-defined cobalt nanoparticles (Co-NPs) on SiO₂, varying particle size by adjusting treatment temperature.^[2] This contribution advances the understanding of particle size effects in cobalt-based CO₂ hydrogenation.

Experimental/methodology. An SOMC-based protocol was established to synthesize supported Co-NPs using Co(Alkyl)₂tmeda as precursor, yielding highly dispersed Co-NPs on SiO₂. Characterization of the SOMC-derived materials was carried out using microscopy and spectroscopy to assess surface cleanliness and particle formation. The catalytic behavior of the materials was studied in CO₂ hydrogenation and found to change with particle size. This change was investigated using in situ XAS under CO₂ hydrogenation conditions.

Results and discussion. The SOMC-based protocol was established and used to synthesize supported Co-NPs with Co(Alkyl)₂tmeda as molecular precursor, yielding highly dispersed Co-NPs on SiO₂. Characterization revealed particle formation (Fig. 1a) and complete removal of organic moieties. In CO₂ hydrogenation, the catalytic behaviour was found to change with particle size (Fig. 1c), which was further studied using in situ XAS under CO₂ hydrogenation conditions (Fig. 1b). Results link particle size, oxidation state, and reactivity in cobalt-based CO₂ hydrogenation.

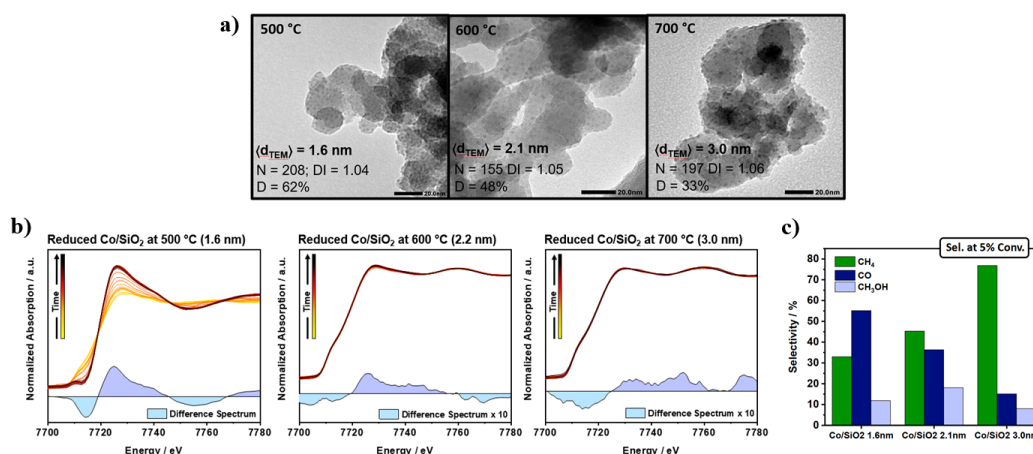


Figure 1: a) Bright-field transmission electron micrographs, b) in situ XANES and c) product selectivities in CO₂ hydrogenation at 5% conversion of SOMC-derived Co/SiO₂ at 1.6 nm, 2.0 nm and 3.0 nm.

[1] G. L. Bezemer, J. H. Bitter, H. P. C. E. Kuipers, H. Oosterbeek, J. E. Holewijn, X. Xu, F. Kapteijn, A. J. van Dillen, K. P. de Jong, *J. Am. Chem. Soc.* **2006**, *128*, 3956-3964.

[2] C. Copéret, *Acc. Chem. Res.* **2019**, *52*, 1697-1708.