Cobalt-Based CO_2 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 SiO_2, 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 $Co(Alkyl)_2$tmeda as precursor, yielding highly dispersed Co-NPs on SiO_2. 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 CO_2 hydrogenation and found to change with particle size. This change was investigated using in situ XAS under CO_2 hydrogenation conditions.

Results and discussion. The SOMC-based protocol was established and used to synthesize supported Co-NPs with $Co(Alkyl)_2$tmeda as molecular precursor, yielding highly dispersed Co-NPs on SiO_2. Characterization revealed particle formation (Fig. 1a) and complete removal of organic moieties. In CO_2 hydrogenation, the catalytic behaviour was found to change with particle size (Fig. 1c), which was further studied using in situ XAS under CO_2 hydrogenation conditions (Fig. 1b). Results link particle size, oxidation state, and reactivity in cobalt-based CO_2 hydrogenation.

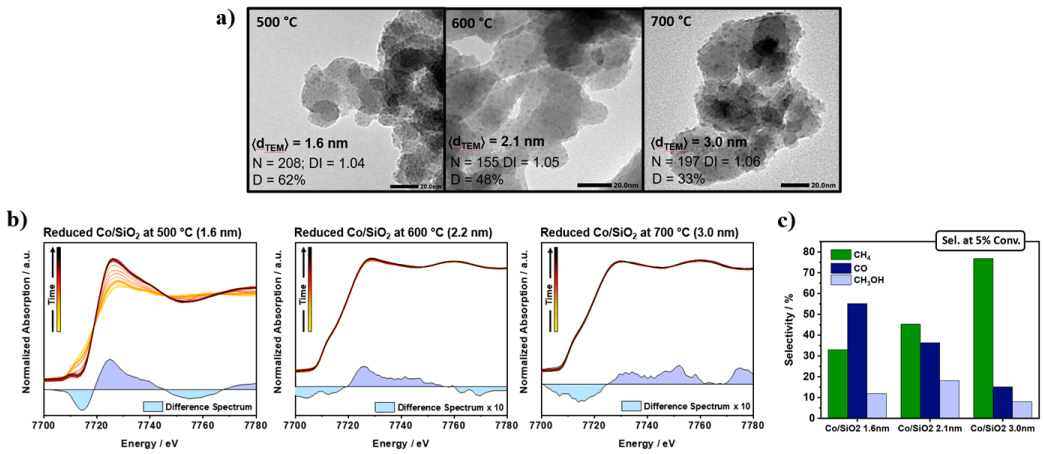


Figure 1: a) Bright-field transmission electron micrographs, b) *in* situ XANES and c) product selectivities in CO_2 hydrogenation at 5% conversion of SOMC-derived Co/SiO_2 at 1.6 nm, 2.0 nm and 3.0 nm.

[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.