

X-ray nanoscopy of cobalt Fischer–Tropsch catalysts at work†

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Transmission X-ray microscopy has been used to investigate individual Co/TiO₂ Fischer–Tropsch (FT) catalyst particles in 2-D and 3-D with 30 nm spatial resolution. Tomographic elemental mapping showed that Co is heterogeneously concentrated in the centre of the catalyst particles. In addition, it was found that Co is mostly metallic during FT at 250 °C and 10 bar. No evidence for Co oxidation was found.

The Fischer–Tropsch (FT) process is the second step in the production of liquid fuels from natural gas, biomass or coal. The process converts synthesis gas (a mixture of CO and H₂) into long-chain hydrocarbons. Industrially, this is usually carried out using a cobalt- or iron-based catalyst. Of these two, cobalt is considered to be more favourable for processing synthesis gas derived from natural gas.¹

In the past, active and selective (towards liquid product, C₅₊) Co catalysts have been prepared using different support materials.² However, deactivation of the catalyst is still a major challenge. Possible causes for deactivation include sintering, reoxidation of cobalt and mixed metal-support compound formation (e.g. CoTiO₃).^{3,4} Characterization studies of deactivation are complicated by the presence of waxes and by changes in the Co oxidation state upon exposure to air.³ To address these difficulties, it is desirable to perform the characterization under reaction conditions. Indeed, several studies have been performed using *in situ* X-ray Absorption Spectroscopy (XAS) and/or *in situ* X-Ray Diffraction (XRD) on Co FT catalysts.^{5–8} No Co oxidation of mixed compounds was reported. However, these studies were not spatially resolved. This means that any effects on the single catalyst particle level could not be observed.

Local information can be obtained by soft X-ray microscopy and spectroscopy.^{9–11} However, the low penetration power of the soft X-ray radiation has limited the sample thickness to approximately 2–3 μm, even away from an absorption edge. Specially designed nanoreactors must be used to minimize attenuation by the windows.¹² More importantly, the gas pressure is limited to about 1 bar, whereas industrial operating conditions are often at higher pressures (e.g., 10 to 30 bar).

To perform *in situ* characterization of Co FT catalysts at the nanoscale and under realistic conditions, we have turned our attention to Transmission X-ray Microscopy (TXM) using hard X-rays at beamline 6-2c of the Stanford Synchrotron Radiation Lightsource (SSRL).¹³ In TXM, monochromatic X-rays from the synchrotron source are focused by a capillary condenser onto the sample, which is mounted on an *x,y,z,θ* movable and rotatable stage. The transmission image is formed by a zone plate onto a CCD camera. The image has a field of view of about 25 μm × 25 μm, and a spatial resolution of about 30 nm.

By changing the energy during imaging, X-ray Absorption Near-Edge Spectra (XANES) for each pixel data are collected. These spectra give information about the local chemical environment and oxidation state of the element(s) of interest.¹³ In addition, it is possible to collect tomography data above and below an absorption edge, resulting in a 3-D elemental distribution within an individual catalyst particle.¹⁴

We have recently designed and constructed a reactor that can be mounted on this beamline.¹⁵ The reactor consists of a capillary (outer diameter: about 100 μm, wall thickness: about 10 μm) that is attached to a holder with high-temperature epoxy. He, H₂ and CO were flowed through the capillary at pressures of up to 20 bar. The capillary can be heated to temperatures up to 350 °C. The temperature is controlled using a thermocouple mounted at the same height as the capillary. The *in situ* set-up was tested using a mass spectrometer in a separate experiment, showing the formation of C₁–C₃ products (Fig. S2†).

The catalyst under study consists of dispersed Co nanoparticles on TiO₂. Two materials have been prepared by incipient wetness impregnation, with Co loadings of 10 wt% and 15 wt%,

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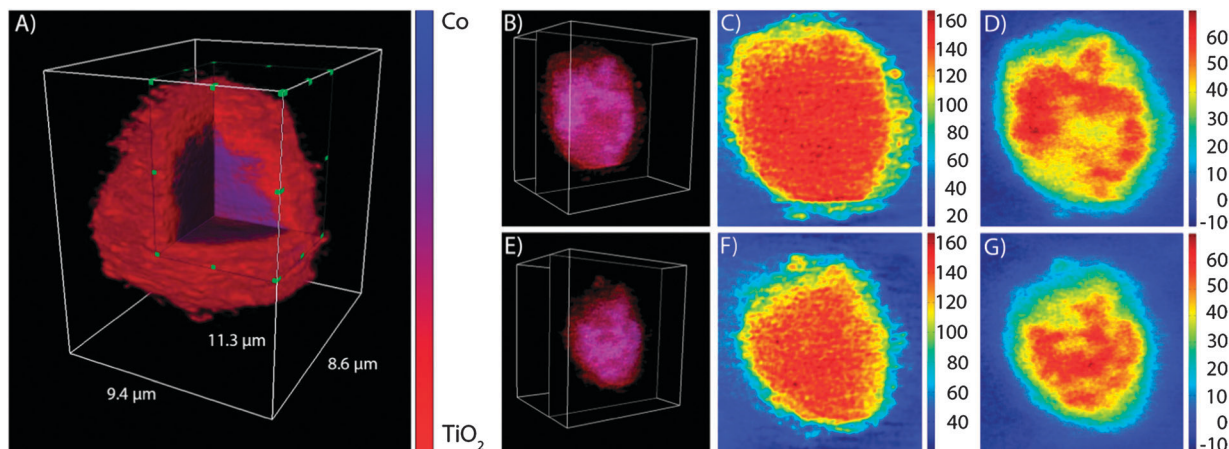


Fig. 1 (A) 3-D representation of a fresh, calcined individual 15 wt% Co/TiO₂ catalyst particle as measured using transmission X-ray microscopy at the Co K-edge. Contributions from TiO₂ are shown in red (data collected at 7650 eV); contributions from Co are shown in blue (difference between data collected at 7650 eV and 7750 eV). (B)–(D) and (E)–(G) Details of two different slices through the volume of the particle. (C) and (F) Contributions of TiO₂. (D) and (G) Distribution of cobalt over the slice.

respectively.¹⁶ The preparation procedure is detailed in the ESI.† XRD revealed that Co is present as Co₃O₄ particles with an average size of about 18 nm (Fig. S1).† Temperature Programmed Reduction (TPR) profiles of the catalysts (Fig. S6)† show no peaks above 500 °C, so SMSI effects do not play a big role during reduction in H₂.¹⁷ Catalytic testing (Fig. S7)† shows strong deactivation during the first 45 h on stream.

Fig. 1 shows the tomographic reconstruction (Movie S1†) of a fresh 15 wt% Co/TiO₂ catalyst particle at the Co K-edge. Fig. 1A shows the 3-D rendering of the catalyst particle, with a section cut out to show the inside of the particle. From the slices through the particle (B–D and E–F), it can be seen that the cobalt is not homogeneously distributed over the TiO₂. Instead, the cobalt is concentrated in areas in the centre of the particle.

Co K-edge XANES spectra of Co reference materials (Co₃O₄, CoO, CoTiO₃ and Co) were measured (Fig. 2A). These spectra were used in the least-squares fits of the data.¹⁸ To compromise between data quality and scan time, energy points were selected so that each scan took about 30–45 min. To start the *in situ* experiment, the 10 wt% Co/TiO₂ catalyst was crushed and loaded into a capillary. The catalyst was first characterized at room temperature under a He atmosphere. The gas was switched to 1 mL min^{−1} H₂, and the temperature was raised to 350 °C in 20 min. After about 2 h, the

temperature was lowered to 250 °C in 10 min and the gas was changed to CO and H₂ in a ratio of 1 : 2 (total flow: 1 mL min^{−1}). The system was then pressurized to 10 bar.

Examples of the *in situ* Co K-edge XANES spectra of the catalyst particle are shown in Fig. 2B, together with least square fits (dashed lines). The spectra are averaged over all pixels of the TXM image stacks. Spectrum (a) was measured at room temperature. The fitting procedure shows that the chemical composition is 100 ± 2% Co₃O₄, 0 ± 4% CoO and 0 ± 4% CoTiO₃, confirming the XRD results. Spectrum (b) was measured after 90 min at 350 °C under H₂. The metallic pre-edge feature and the disappearance of the white line are notable. The fit indicates that Co₃O₄ was reduced to the metallic phase. The chemical composition was 4 ± 3% CoO, 0 ± 0% CoTiO₃ and 95 ± 1% Co. The absence of CoTiO₃ confirms that SMSI effects do not play a role at this stage. Spectra (c)–(e) were measured under FT conditions (250 °C, 10 bar pressure of CO–H₂ in a ratio of 1 : 2), after 0 h, 3 h and 9.75 h respectively. Again, the pre-edge and absence of a white line indicate metallic cobalt. The fits show that the catalyst is metallic (within experimental error) during the FT reaction.

The average chemical composition of the particle during the experiment is plotted in Fig. 2C. Immediately after starting the reduction the contribution from metallic cobalt increases.

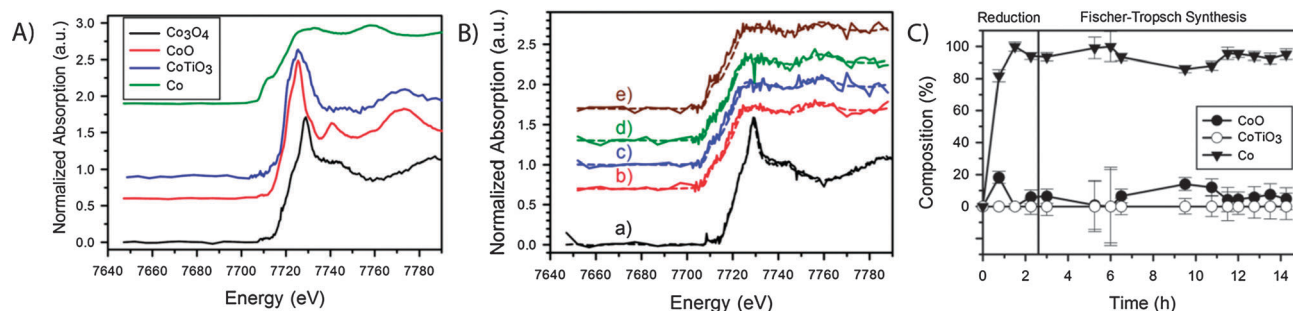


Fig. 2 (A) X-ray Absorption Near Edge Spectra (XANES) of Co₃O₄, CoO, CoTiO₃ and Co reference materials. (B) Examples of spectral fits of the average XANES spectra as measured at (a) room temperature; (b) after reduction in H₂ at 350 °C and 1 bar for 90 min; (c) during Fischer-Tropsch synthesis at 250 °C and 10 bar pressure in CO–H₂ in a ratio of 1 : 2 for 0 h on stream; (d) after 3 h on stream; (e) after 9.75 h on stream. (C) Compositional changes of a 10 wt% Co/TiO₂ catalyst particle as a function of time and the different treatments applied; i.e., reduction in H₂ at 350 °C and 1 bar; and during Fischer-Tropsch synthesis at 250 °C and 10 bar pressure for 11.25 h in CO–H₂ in a ratio of 1 : 2. Co₃O₄ is excluded from this plot, because it was only detected in the first fit. Each data point is plotted at the start of the XANES scan. Each scan took about 30–45 min.

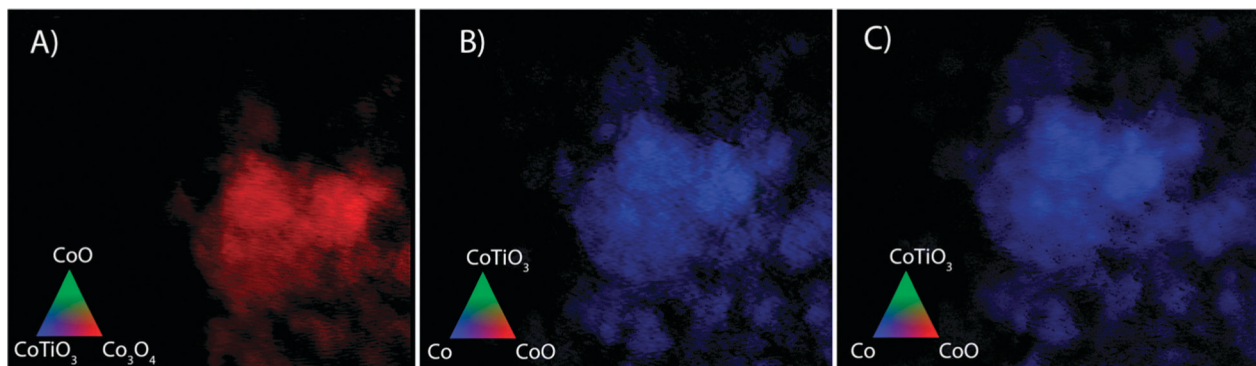


Fig. 3 A series of 2-D Transmission X-ray Microscopy (TXM) images of a 10 wt% Co/TiO₂ catalyst particle as a function of the different treatments applied: (A) room temperature; (B) after reduction in H₂ at 350 °C and 1 bar for 90 min; (C) during Fischer-Tropsch synthesis at 250 °C and 10 bar pressure in CO-H₂ in a ratio of 1 : 2 for 9.75 h on stream.

Only during the first scan is CoO observed, consistent with previous studies.^{5–8} After 90 min we observed 100% metallic Co, within experimental error. During the FT reaction the contribution of metallic Co stayed at 100%, with only statistically non-significant contributions from CoO and CoTiO₃.

The same conclusions are drawn from the 2-D TXM images (Fig. 3, all 2-D chemical maps obtained during the experiment are shown in the ESI†). At room temperature (Fig. 3A) the entire fresh particle consists of Co₃O₄. After the hydrogen reduction treatment (Fig. 3B), only metallic Co is found. After 9.75 h of FT reaction, we observed almost only metallic Co (Fig. 3C). In the chemical maps, we show that even on a local scale, oxidized cobalt (CoO or CoTiO₃) is present only as statistically non-significant species. We also found that the morphology of the particle was stable during 10 h of FT reaction.

In conclusion, *in situ* Transmission X-ray Microscopy (TXM) has been used to chemically image a single TiO₂-supported Co catalyst particle with a spatial resolution of 30 nm in 2-D as well as the elemental image in 3-D. This has been performed after calcination, during reduction in H₂ and during Fischer-Tropsch synthesis at 10 bar for 11 h. After calcination, the supported Co₃O₄ nanoparticles are heterogeneously distributed within the TiO₂ support. Most of the cobalt nanoparticles are located in the centre of the catalyst particle. Reduction in H₂ leads to an immediate (*i.e.* during the first XANES scan) formation of Co metal nanoparticles, with only small contributions of CoTiO₃ and CoO, and no change in the chemical state of Co was observed during Fischer-Tropsch synthesis. In other words, under the applied FTS conditions in the *in situ* TXM setup, no experimental evidence for potential re-oxidation or metal-support compound formation of supported Co nanoparticles was found, even on a local scale.

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