

 <b>ESRF'</b>	<b>Experiment title:</b> In situ XAS studies on unpromoted and rhenium promoted cobalt Fischer-Tropsch catalysts	<b>Experiment number:</b> CH-440
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**Report:**

In situ XAFS spectroscopic studies have been carried out at 450 °C on the hydrogen reduction of a rhenium-promoted Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. Reductions carried out using 100% hydrogen and 5% hydrogen in helium gave different results. Whereas the reduction using dilute hydrogen yielded bulk-like metallic cobalt particles (hcp or fcc), the reaction with pure hydrogen led to a more dispersed system with smaller cobalt metal particles (<40 Å) the crystal form of which could not be established so that the recently reported metastable nonclose-packed body-centred cubic form cannot be excluded.

Reoxidation of a similar catalyst in water-containing gas mixtures has been reported in the literature; it is suggested that the different outcome in the case of the 100% hydrogen protocol may be due to a similar mechanism. This would involve the in situ water produced by the reduction with reoxidation/reduction of cobalt metal particles in the water vapour - hydrogen mixture. However, this mechanism cannot be established by the present study.

Additionally, in both reduction protocols a small fraction (3 - 4 wt. %) of the cobalt content is randomly dispersed over the tetrahedral vacancies of the alumina support with Co-O bondlengths of  $1.96 \pm 0.01$  Å. This dispersion occurs during reduction and not calcination. The cobalt in these sites cannot be reduced at 450 °C, a temperature that is too low to permit formation of the spinel CoAl<sub>2</sub>O<sub>4</sub>.

This work has been accepted for publication in Journal of Materials Chemistry.