

IN-SITU SPECTROSCOPY OF MONODISPERSED COBALT NANOPARTICLES DURING REDUCTION AND CARBON MONOXIDE HYDROGENATION

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Changes in the electronic structure and surface composition of monodispersed cobalt nanoparticles (NP) with different sizes have been followed using *in situ* X-ray absorption spectroscopy (XAS) in the Advance Light Source (Berkeley). Their catalytic performance in the carbon monoxide hydrogenation reaction has been tested also in a conventional fixed bed reactor.

The NP have been synthesized by colloidal chemistry, obtaining monodispersed metallic cobalt crystals covered mainly by oleic acid [1]. Those NP were deposited on a flat support (gold foil), using the Langmuir-Blodgett technique, obtaining an ideal 2-D model of a cobalt catalyst. The as-synthesized particles were in the metallic state (Co⁰), but oxidized during the transferring process.

A specially designed gas-flow cell was used in order to perform *in situ* soft X-ray absorption measurements (Figure 1) [2]. This cell allows us to work in atmospheric pressure (1 atmosphere) and to follow simultaneously the Co L-edge and O K-edges of the cobalt NP. The treatment of the samples in pure hydrogen at temperatures up to 350°C causes the reduction of the cobalt oxide and the removal of the surfactant layer covering the particles, as evidenced by changes observed in the oxygen K-edge spectra. Scanning electron microscopy pictures of the samples after the reducing treatments show that the morphology of the samples has not been changed. After reduction, carbon monoxide (CO) and mixtures of CO and H₂ were flown over the particles at different temperatures to study the CO adsorption and test the CO hydrogenation reaction. During the reaction the Co nanoparticles remain in the metallic state and are covered by carbon monoxide (CO). If the reaction is performed in batch mode, water (a byproduct of the reaction) is also adsorbed over the surface (Figure 2).

The catalytic performance reveals that the samples become active after the reduction treatment and that they are significantly more resistant to deactivation than a standard sample. Their reactivity is different depending on the Co particle size. Specifically, the methanation turnover frequency of silica supported nanoparticles was found to be proportional to their diameter which varied from 3 to 10 nm. Oxidation by water vapour produced during reaction was proposed to be the cause of the different reactivity (as Co oxide is inactive for the CO hydrogenation reaction) [3]. However, *in situ* XAS experiments demonstrated that Co nanoparticles remain metallic even

with water adsorbed. Hydrogen-Deuterium (HD) exchange experiments indicated that it is the dissociation of H_2 that is responsible for the observed decrease in activity with size.

References

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Figures:

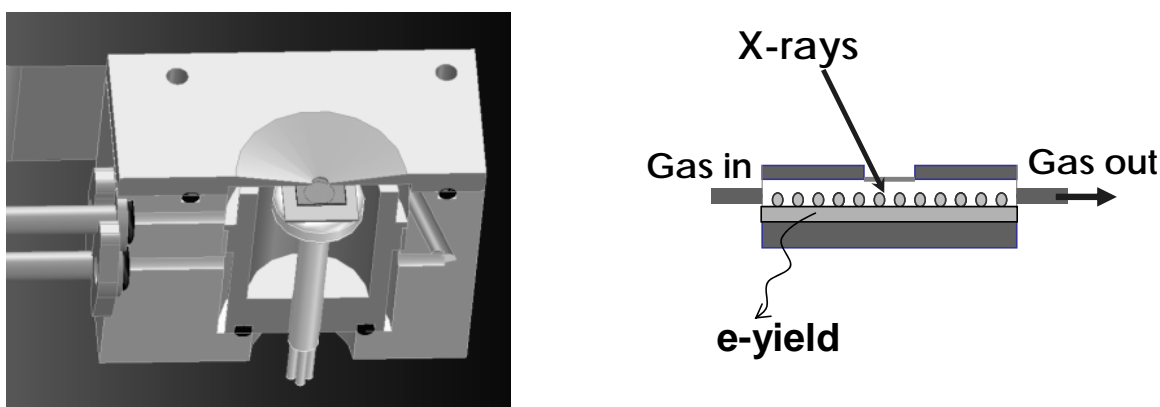


Figure 1. Drawing and schematic diagram of the gas-flow cell used for *in-situ* X-ray absorption measurements.

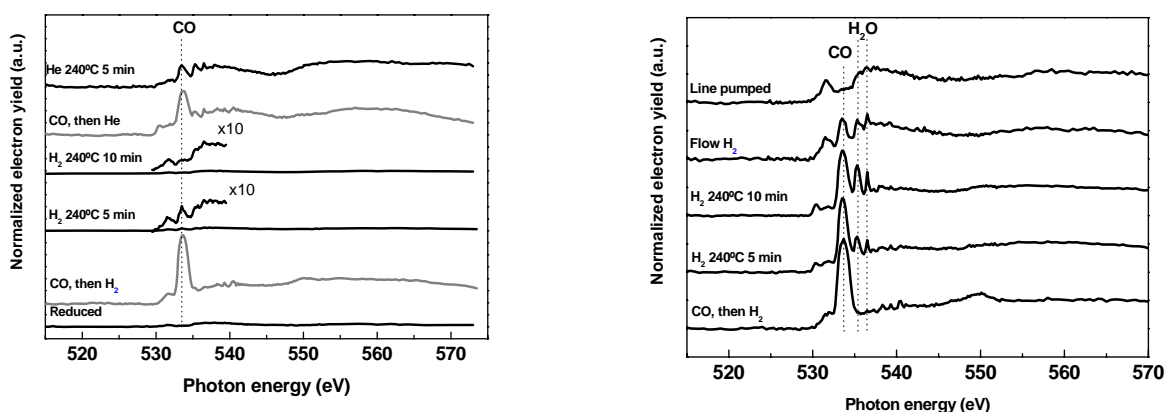


Figure 2. O K-edge of 4.2 nm cobalt NP after exposing to CO and heating in H_2 and He. First, CO was flown and then the sample was heated at 240°C either in H_2 or He in a flow mode (a) or in H_2 in a batch mode (b).