



**In-situ studies of one-pot fabrication of cobalt - cobalt oxide hybrid materials for energy application**

**Experiment number:**  
CRG 01-01-954

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<b>Shifts:</b> 15	<b>Local contact(s):</b> Wouter van Beek	

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1. "Puzzling Mechanism behind a Simple Synthesis of Cobalt and Cobalt Oxide Nanoparticles: In Situ Synchrotron X-ray Absorption and Diffraction Studies"

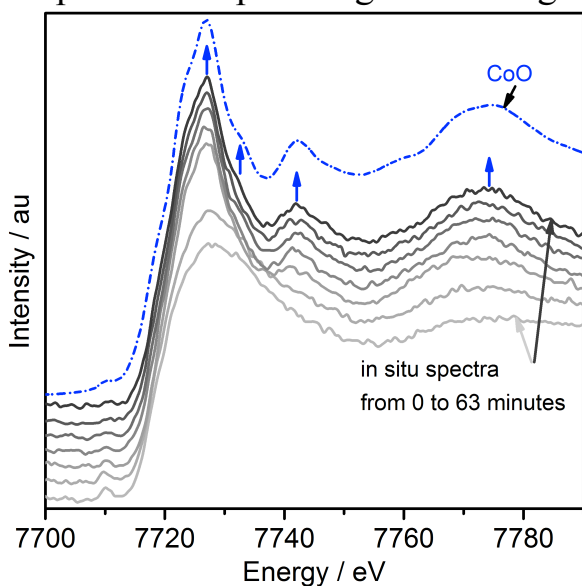
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**Abstract** "Here, we show a simple approach to synthesize cobalt and cobalt oxide nanoparticles in an organic solvent. We find that the cubic  $\text{Co}_3\text{O}_4$  nanoparticles can be easily obtained, even at temperatures as low as 80 °C. Moreover, exactly the same reaction at 180 °C leads to metallic Co nanoparticles. Thus, in addition to the synthetic efforts, we study the mechanism of occurrence of oxidation and reduction of a  $\text{Co}^{2+}$  precursor in benzyl alcohol. Remarkably, the in situ X-ray absorption and diffraction measurements of the synthesis at 140 °C reveal that oxidation of  $\text{Co}^{2+}$  to  $\text{Co}^{3+/2+}$  and reduction of  $\text{Co}^{2+}$  to  $\text{Co}^0$  reactions take place simultaneously. It is followed by a rapid formation of  $\text{Co}_3\text{O}_4$  nanoparticles and its consecutive solid-state reduction to  $\text{CoO}$ . In parallel, metallic Co nanoparticles begin to grow. In addition, Multicomponent Curve Resolution–Alternating Least Squares (MCR-ALS) analysis of X-ray absorption spectroscopy (XAS) data efficiently reveals the nontrivial interdependence between four different reactions. Our strategy to control reduction and oxidation of Co-based nanoparticles as they grow opens up an elegant pathway for the one-pot-synthesis of the hybrid materials for energy-related applications."

2. The analysis of the data obtained in-situ during the synthesis of Co-poly(ionic liquid)s hybrid structure is in progress.

The main finding is that the presence of the polymer matrix in the reaction solution strongly influences the Co-synthesis at the different stages. This point out the importance of understanding of the role of polymeric matrix on the chemistry and will help to develop strategies to design complex structures.

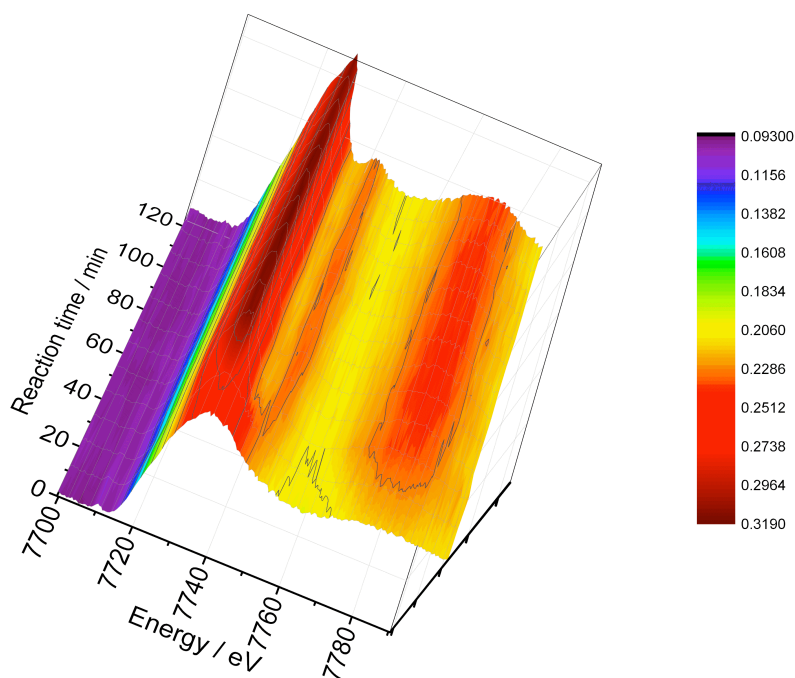


**Figure 1.** Selected XAS spectra of reaction solution and their comparison with the reference spectrum of CoO nanoparticles.

- **Pre-nucleation stage:** the kinetics of transformation from precursor to pre-monomer is changed. The reduction of the dissolved  $\text{Co}^{2+}$  species in benzyl alcohol is not observed (Figure 1).

- **Nucleation and growth stage:** In the synthesis without polymer several parallel reactions are taking place in the solution and the temperature and time of reaction are determining the final composition of the nanoparticles (see abstract and reference 1 above).

In the case of Co-PILs hybrids the nanoparticles are nucleating and growing direct at the surface of polymeric matrix. Remarkably, the presence of polymer favor (catalyze) the direct nucleation of CoO nanoparticles and other parallel reactions like reduction to Co or oxidation to  $\text{Co}_3\text{O}_4$  even after reacting for 2 hours are not observed (XAS shown in Figure 2, PXRD not shown here).



**Figure 2.** In-situ XAS spectra recorded during in-situ synthesis of CoO at the surface of polymeric matrix at Co K-edge. MCR-ALS analysis is in progress.