

# Oxidation of Cobalt Hydroxide

## Keywords

Cobalt hydroxide, heterogeneous catalysis, catalysis cell, oxidation

## Application Note MO402(1)

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## Overview

The Catalysis Cell is used to study the oxidation of Cobalt Hydroxide in a pressurised oxygen environment.

## Introduction

Cobalt compounds are used in a variety of applications within both the chemical and petrochemical industries. Cobalt hydroxide  $\text{Co}(\text{OH})_2$  is especially interesting due to its exceptional physical properties which means it is widely applied in the fields of Li-ion batteries, gas sensing and heterogeneous catalysis. It is also used as a precursor for the production of  $\text{Co}_3\text{O}_4$  and  $\text{CoO}(\text{OH})$ . In particular, the development of inexpensive  $\text{Co}(\text{OH})_2$  catalysts to replace Pt in fuel cell electrodes for the oxygen reduction reaction (ORR) has been an area of increasing interest.<sup>1</sup>

Here we demonstrate the use of the high temperature catalysis cell for investigating the processes taking place on a novel catalyst surface. Silica supported  $\text{Co}(\text{OH})_2$  was analysed before and after calcination in an oxygen atmosphere of 3 bar.

## Experimental

Measurements were performed using the state-of-the-art Kratos AXIS photoelectron spectrometer. The catalysis cell mimics the conditions of a normal reactor vessel allowing the operator to recreate reactor conditions and analyse the chemical changes taking place on the surface of the catalyst. A schematic of the catalysis cell is shown in Figure 1. The cell consists of a fused quartz reactor vessel contained within a stainless steel vacuum chamber. A simple transfer mechanism allows the user to perform experiments and analysis without exposing the sample to the atmosphere.

## Discussion

After the sample was prepared, mounted and *in-situ* transferred to the sample analysis chamber (SAC), survey and high-resolution spectra were acquired. Cobalt and oxygen were clearly visible with a small amount of adsorbed carbonaceous material. Figure 2 shows a peak fitted high-resolution spectrum acquired for the Co 2p region before reaction. The most intense peak is at 780.8 eV which is characteristic of  $\text{Co}(\text{OH})_2$ .

Since both components of the Co 2p region show the same qualitative information only the higher intensity Co 2p<sub>3/2</sub> core level, including the shake-up satellites, were fitted. The additional spectral lines at higher binding energy have been related previously to either coupling between unpaired electrons in the atom or to multiple electron excitation.<sup>3</sup>

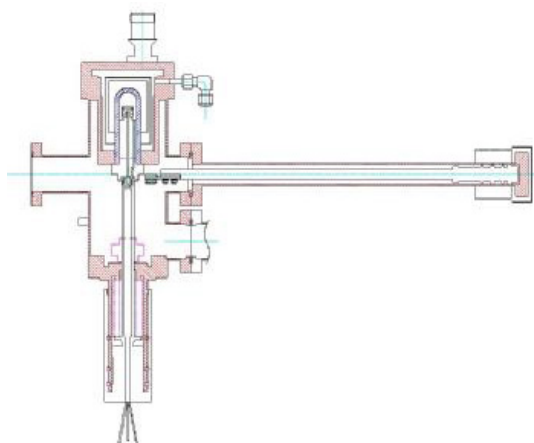


Figure 1: Schematic of the catalysis cell.

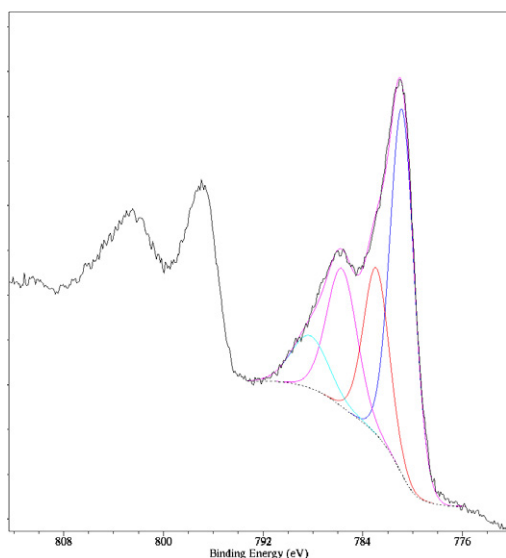


Figure 2: Co 2p spectrum of prepared cobalt hydroxide catalyst.

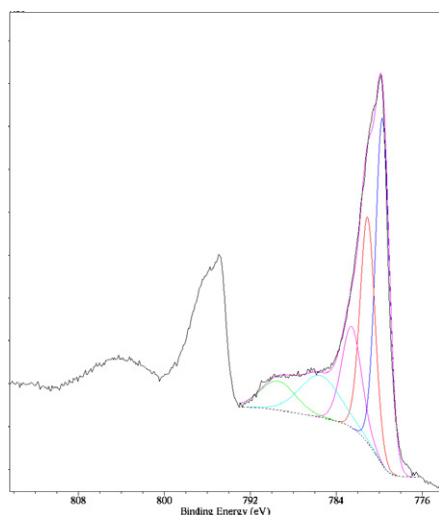


Figure 3: Co 2p spectrum of oxidised cobalt hydroxide.

Having established the oxidation state of the prepared catalyst, successive heating treatments were performed in the cell. Each treatment involved heating the sample and introducing O<sub>2</sub> gas to a known pressure of 3 bar. After 10 minutes, the catalyst was removed and analysed to see any changes in the chemistry of the surface. After heating to 150°C and 200°C, no changes were observed in the Co 2p region. There was a decrease in the observed C 1s signal which was most likely oxidation and desorption of adventitious carbon as CO and CO<sub>2</sub>. Once the sample was heated to 250°C however, a distinct change in the Co 2p envelope was observed (see Figure 3).

For the oxides of Co it is not possible to confidently identify the oxidation state simply by using the peak position of the Co 2p<sub>3/2</sub> peak. Instead, using a recent publication by Biesinger *et al.*, the true oxidation state may be identified by the shake-up structure.<sup>4</sup> This is common for many top-row transition elements and actinides. Here the high binding energy shake-up feature, fitted with two components at 785.6 eV and 789.5 eV, acts as a fingerprint in identifying the oxide as Co<sub>3</sub>O<sub>4</sub>.

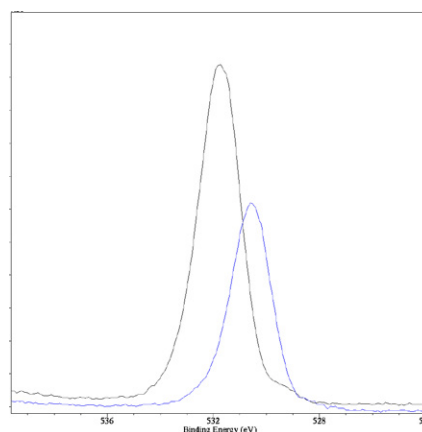


Figure 4: O 1s spectra of oxidised cobalt hydroxide catalyst before (black) and after (blue) oxidation reaction

Figure 4 shows the O 1s spectra before and after reaction in oxygen. A shift in the peak position of the O 1s orbital was clearly observed. This shift from 531.7 eV to 530.3 eV is characteristic of the change in oxygen environment from hydroxides to low oxides. The small low binding energy shoulder on the untreated sample may be due to some surface contamination from adsorbed carbon or low percentages of oxyhydroxide species.

## Conclusions

Here we investigate the oxidation of Co(OH)<sub>2</sub> using the catalysis cell. The catalysis cell allowed us to treat the sample under high temperature high pressure conditions similar to those found in industrial reactors. Careful analysis of the XPS spectra generated after each successive treatments shows that once calcined above 200°C the surface of the catalyst changes from hydroxide to oxide. Peak fitting the Co 2p region identified Co to be present as Co<sub>3</sub>O<sub>4</sub>.

## References

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