



Experiment title: *In situ* XRD/XAS/Raman investigation of the active phases and interactions of copper-ceria catalysts during preferential CO oxidation

Experiment number:
01-01-845

Beamline: BM01B	Date of experiment: from: 01.09.10 to: 07.09.10	Date of report: 01.01.2011
Shifts: 18	Local contact(s): Hermann Emerich	<i>Received at ESRF:</i>

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Report:

Fuel cell technologies are seen as possible sustainable future solutions for meeting the increasing energy demand. Hydrogen is usually produced through steam reforming or partial oxidation of hydrocarbons or alcohols together with CO₂, CO, H₂O and N₂, followed by the water-gas shift reaction. However, for proton exchange membrane fuel cells (PEMFC) applications, CO levels in the hydrogen feed will have to be reduced to below 100 ppm to avoid poisoning of the Pt anode. This can be obtained by preferential oxidation of CO (PROX), methanation or by use of selective membranes [1]. PROX of CO in the H₂-rich gas stream obtained from reforming/partial oxidation has been recognised as one of the most straightforward and cost effective methods to achieve acceptable CO concentrations (< 100 ppm) [2]. The main challenge with the PROX is to find a catalyst that is active and selective at low temperatures (fuel cell operating temperature). Au-based catalysts and bimetallic catalysts (e.g. Pt-Ni) on different supports are promising materials. However, the durability of these catalyst materials is insufficient. Several metal oxide catalysts have been proposed where the Cu-CeO₂ system has been shown to be a promising candidate. The catalytic activity for preferential CO oxidation by this catalyst system is depending on the loading and preparation methods [3]. The wide application of CeO₂ in heterogeneous catalysis is mainly due to two features; the redox couple of Ce(IV)/Ce(III) and the high oxygen storage capacity. The activity of these catalysts have been attributed to thermal stability and the oxygen vacancies of the ceria support [4]. The presence of these oxygen vacancies due to the Ce³⁺ ions in the CeO₂ lattice can be observed by use of Raman spectroscopy [5]. The selectivity towards CO₂ formation is dominant in the low temperature range and decay is often observed at higher temperatures due to increased activity of the H₂ oxidation reaction. The temperature-sensitive selectivity to CO is mostly related to the presence of hot-spots in the PROX fixed bed reactor, which is caused by the highly exothermic CO and H₂ oxidation in PROX. Thus, minimized heat transport resistance could efficiently suppress the undesired reactions mentioned above. Furthermore, it has also been found that the heat transport resistance is mostly related to the interparticle heat transfer [6,7]. Therefore, increasing the thermal conductivity of the catalyst system and reducing the interparticle heat conduction distance would

improve the selectivity to CO oxidation. This can be obtained by supporting the active phase on a carbon support. The PROX reaction has been proposed to follow a Mars van Krevelen reaction mechanism where copper oxide co-exists together with copper metal. The selectivity of the oxidation of H₂ and CO has been claimed to follow two different adsorption steps [8]. The presence of metallic copper and copper in a higher oxidation state have been claimed to be a parameter that needs to be controlled to be able to achieve a catalyst with high selectivity towards the CO oxidation reaction [3].

Experimental method:

An in situ cell was used in order to combine the X-ray techniques and Raman. The cell consist of a stainless steel base and two linear motion guides. A quartz capillary tube was used as a reactor and was fixed with swagelok fittings to the base. The catalysts bed was kept in place in the quartz tube by quartz wool plugs. The sample was heated by a vertical hot air blower.

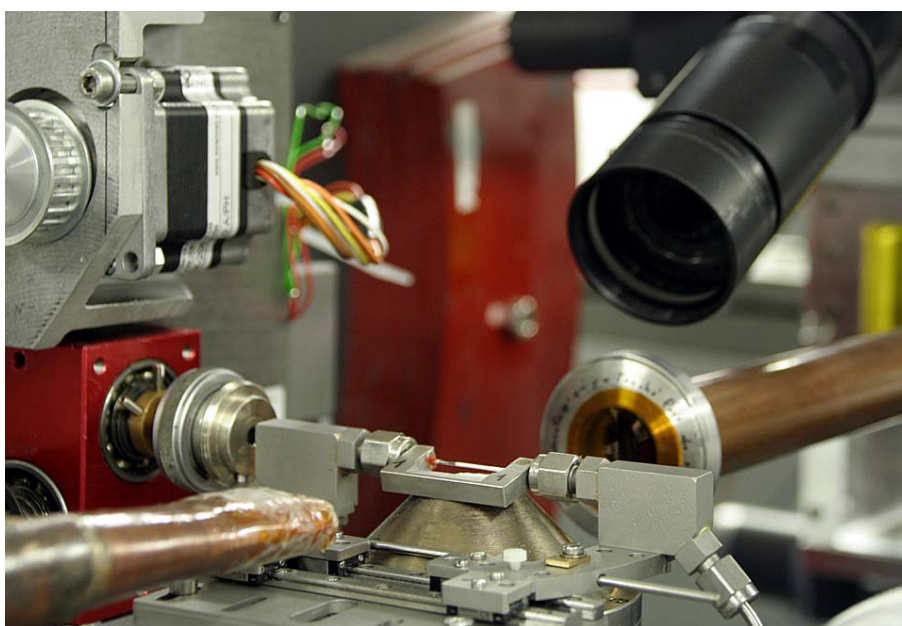


Figure 1: Cell setup for *in situ* PROX measurement

The catalysts were heated to 250°C with a heating rate of 2°C/min in the reaction mixture and the temperature was held for 4 hours and thereafter cooled down to room temperature. The total flow to the reactor was 5.6 ml/min (CO:O₂:H₂:He 2:2:36:60). Short scans of the Cu edge profiles were collected together with Raman and XRD during the reaction. The XRD data were collected with the standard setup, using a wavelength of 0.5 Å. The exit gas was analysed by a mass spectrometer for determination of the conversion and selectivity.

Results:

To follow the oxidation state of copper the Cu k-edge XANES spectra were monitored during the PROX reaction in the earlier mentioned temperature interval. Figure 2 shows the changes in the energy of the absorption edge for CuCeO₂ supported on carbon during selective oxidation of carbon monoxide in presence of hydrogen. The edge position described by the first inflection point in the edge jump, shifts to lower energies at approximately 150°C indicating a decrease in the effective charge of copper. Relative to CuO, the edge position is shifted by ~1.2 eV at 180°C and continuing temperature ramping leads to further shifts to a lower edge position. A quantitative picture of the oxidation states of copper can be obtained by determining the amounts of the three phases detected during the reaction. Linear combination of the XANES spectra and the respective model compounds, Cu(0), Cu(I) and Cu(II) reveal that the initial oxidation state of copper in the catalysts is +II. By increasing the temperature during the reaction a reduction of the valence state of copper occurs and it goes through a intermediate where all the three oxidation states are present. The main compound at 250°C is metallic copper.

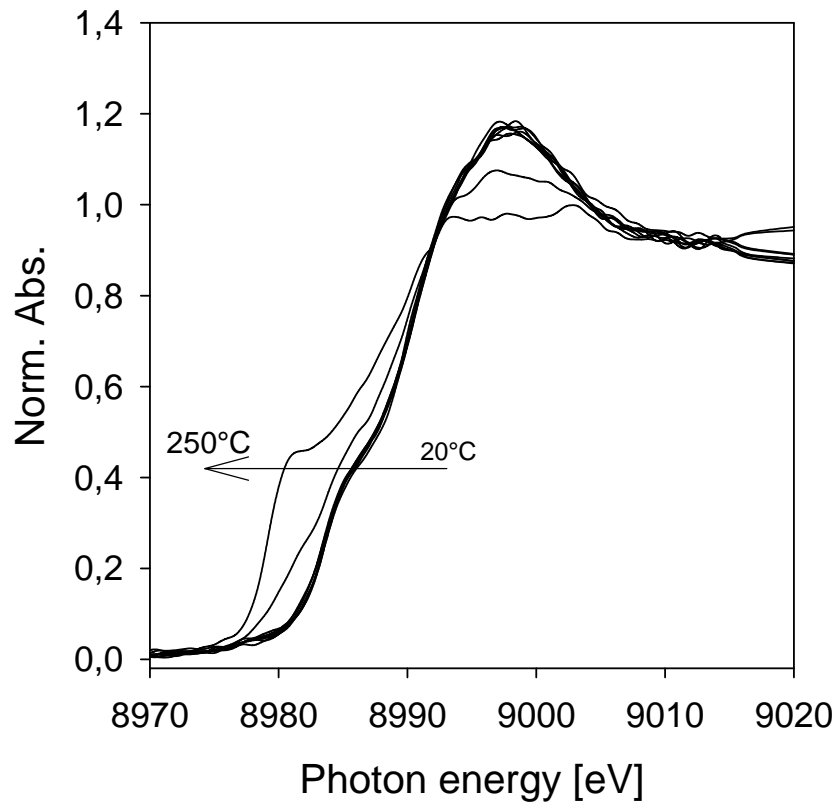


Figure 2: Temperature evolution of the Cu K-edge XANES spectra during oxidation of CO in the presence of hydrogen in the temperature interval 20-250°C.

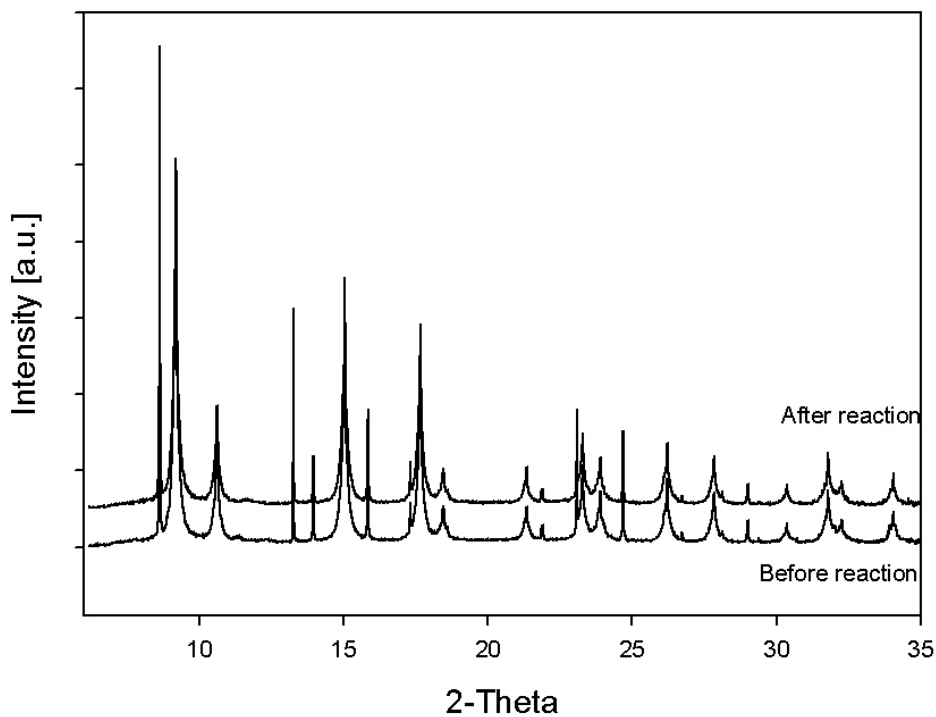


Figure 3: Diffractograms of CuCeO_2 supported on carbon prior to and after the PROX reaction.

However, inspection of the inflection point after the sample is cooled down to room temperature reveal an increase in energy of approximately 1 eV. This indicates that the oxidation state of copper during the reaction

is a function of the temperature. The highest selectivity towards oxidation of CO was found in the lower temperature range (60-180°C) where the XANES results show that the copper phase is partially reduced.

The XRD data detected at room temperature prior to and after the PROX reaction is presented in Figure 3. XRD reflections characteristic of the FCC fluorite structure of CeO₂ are present in the pattern of the catalyst. Diffraction lines due to CuO and Cu₂O were not detected. The absence of peaks related to copper may be attributed to highly dispersed Cu species on the surface of ceria or the formation of a Cu-Ce-O solid solution or a combination of these two phenomena. However, comparison of the two diffractograms reveals that no structural and/or phase changes can be observed during the reaction.

References

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