



	Experiment title: Study of deactivating effect of CO ₂ and H ₂ O in CuxO/CeO ₂ CO-PROX catalysts by DRIFTS/XAS/MS	Experiment number: CH-4671
Beamline: BM23	Date of experiment: from: 27 July 2016 to: 01 August 2016	Date of report: 02/09/2016
Shifts: 15	Local contact(s): Manuel MONTE CABALLERO	<i>Received at ESRF:</i>
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Report:

Copper-ceria based catalysts have been proved to be good alternatives to precious metals (Pt, Au, Rh, etc.) for hydrogen purification. However, they present, as a difference with precious metals, an important structural dependence for the processes involved which imposes a deep knowledge of the catalyst nanostructure in order to achieve optimum performance through rational design. In turn, most relevant aspects for practical application of ceria-related catalysts are related to their durability in the presence of CO₂ and H₂O in the reactant stream.

In this experiment we investigated the effects in structure (with XAS) and activity of copper-ceria catalysts under a CO-PROX mixture (H₂+CO+O₂, 50:1:1.25) with high CO₂ concentration (15 %). The set-up was also test with a water-rich flow (10 %); however, minor but unavoidable problems (beam loss, temperature stability at some point) together with a lack of time (fifteen instead of eighteen shifts allocated) make impossible to complete the full experiment. Infrared spectra could not be taken as the DRIFTS fluorescence cell was not available last run.

Catalysts consist on small amounts of copper (~ 1 % in weight with respect to the total weight of the catalyst) dispersed over nanostructured ceria, which distinguish each support. The ceria nanospheres present higher surface area and exposed, mainly, the most stable ceria faces, (111); while the ceria nanocubes exposed (100) faces and have a lower specific surface. Three catalysts were studied: 1 % of copper over ceria nanospheres, 1 % of copper over ceria nanocubes and 0,16 % of copper over ceria nanocubes. The first and the last have the same surface density of copper. Details of the catalysts could be found in these articles: D. Gamarra et al. Applied Catalysis B-Environmental 130:224-238, 2013 and M. Monte et al. Catalysis Today 229:104-113, 2014.

The catalysts were place in a capillary and under a 60 ml/min flow and XAS spectra were recorded after the output gases detected by the mass spectrometer reach the stabilization. Initially, samples were exposed to 20 % oxygen in helium and heated (10 °C/min) until 400 °C for one hour. After cooling, they were exposed to CO-PROX mixture (H₂+CO+O₂, 50:1:1.25, in He) first, and CO-PROX+CO₂ mixture (H₂+CO+O₂+CO₂, 50:1:1.25:15) then, at room temperature, 180, 240 and 270 °C. XAS spectra (up to k=16) were recorded at each temperature under each mixture.

As expected, the presence of CO₂ in the flow reduce the activity and the selectivity in all catalysts. These changes are higher at moderate temperatures, in which the catalysts show the better behaviour in absence of CO₂ (see picture below, left panel). Also, the effects of CO₂ are higher in the nanocubes catalysts, which show a different nature of the carbonates generated over each support (as previously founded). From which could be extracted that the carbonates created over nanocubes are in contact or close to the interphase between the copper particles and the ceria support, as this is the active centre for CO oxidation in this type of catalysts. Preliminary analysis of EXAFS signals (see picture below, right panel) point to a compaction of the copper particles and a disorganization of first oxygen shell when CO₂ is present in the flow. Changes, which increase with the temperature.

