ESRF	**Experiment title:** Operando XAS analysis of visible light assisted CO2 reduction on mono- and bi-metallic (Ni, Cu, Fe)/ CeO2 catalysts	**Experiment number**: MA 5036
Beamline: BM23	**Date of experiment**: from: 25/01/2022 to: 31/01/2022	**Date of report**: 7. 8. 2022
Shifts: 18	**Local contact(s)**: Dr. ATZORI Cesare, Dr. LOMACHENKO Kirill	*Received at ESRF:*

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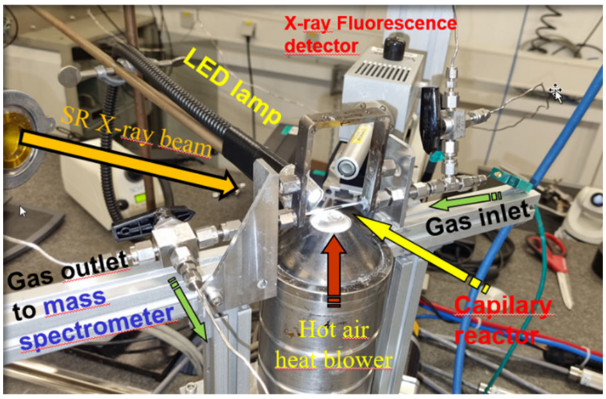
Report:

We performed *operando* X-ray absorption spectroscopy (XAS) on a set of catalysts (2 wt. % Ni dispersed as sub-nanometer clusters on CeO_2 synthesized in air, H_2 or Ar atmosphere, and 2 wt. % Cu or Fe dispersed on Al_2O_3) during the activation and successive (photo)catalytic CO_2 reduction reaction. We monitored the oxidation state and changes in local atomic structure of the constituent elements (Ni, Cu, Fe and Ce). The operando XAS experiment was coupled with mass spectrometer of BM23, for the analysis of the gas phase to provide the interconnection between structural changes and macroscopic kinetic performance (activity and selectivity). The dynamic structure of the catalyst was analyzed in thermally driven and light assisted mode in a quartz capillary micro-reactor cell, coupled with MS of BM23. These results will provide information on the valence and structure of the active metallic species to elucidate the reaction mechanism, which is necessary for the rational design of new, active and robust transition metal@semiconductor catalysts relevant to the sustainable and efficient conversion of solar to chemical energy.

A Si(111) double crystal monochromator was used with energy resolution of about 1 eV at 8 keV. Higher-order harmonics were effectively eliminated by the flat mirror installed in front of the monochromator. The beam size on the sample was 4 mm horizontal and 0.2 mm vertical. The intensity of the monochromatic X-ray beam was measured by three consecutive ionization detectors, filled with appropriate nitrogen or argon gas mixtures to obtain 15% absorption in the first cell and 70% in the second and third cell (for Cu, Ni K-edge: first filled with 300 mb Ar, second and third filled with 1400 mbar N2, for Fe K-edge: first filled with 220 mb Ar, second and third filled with 1000 mbar N2, for Ce L3-edge: first filled with 220 mb Ar, second and third filled with 1000 mbar N2, in all cases all cells were filled-up with He to the total pressure of 2 bars).

The catalyst samples were prepared in the form of homogeneous micronized powder mixed with BN powder and inserted in the quartz capillary with 1.5 mm diameter. The total absorption thickness (μd) of about 2.5 was obtained above the investigated metal K-edge. The quartz capillary with the sample was mounted on the micro-reactor holder (Fig. 1), placed in the monochromatic beam between first two ionization detectors. For fluorescence measurements, a solid state SDD detector was used. The capillary was attached to the gas inlet, providing a constant flow of appropriate gas mixture for the reduction of the catalyst or catalytic reaction, while gas outlet was connected to the MS of BM23 to continuously monitor reaction products during operando XAS experiments.



During the operando XAS experiment the catalysts was activated in 10% H_2/He stream (flowrate of 27 ml/min) at 1 bar at 350°C or 500°C, prior to (photo)catalytic experiments. During photo-catalytic reaction under controlled conditions, the catalyst is exposed to He, H_2 and CO_2 gas mixture (flowrate: 7ml/min of H_2, 3ml/min of CO_2 and 20 ml/min in of He) at 1 bar at 350°C or 500°C in thermally and light assisted mode. The catalyst was heated with a hot air -blower and illuminated with visible LED source with 790 mW/cm^2 irradiance (Fig. 1). The temperature of the catalyst was monitored with thermocouple inserted in the quartz capillary.

Figure 1. *Experimental set-up for the operando XAS experiment at BM23.*

The absorption spectra were measured in fluorescence and/or transmission detection mode in the energy region from -150 eV to +1000 eV relative to the investigated Cu, Ni or Fe K-edge, and -150 eV to 500 eV for Ce L3-edge. In XANES energy region 0.3 eV steps were used and equidistant k steps of 0.03 Å^{-1} in EXAFS region, with an integration time of 5 s/step. XAS spectra were measured in initial state on as prepared catalyst in He at RT, and then at each intermediate stationary state during catalyst activation and during catalytic reaction (consecutive scans were performed with light on and light off). Two or more repetitions of each scan were measured and superimposed to improve the signal-to-noise ratio. Exact energy calibration was provided by simultaneous measurements of absorption spectra on respective Cu, Ni or Fe metal foil, or on crystalline CeO_2, placed between second and third ionization detectors.

We analyzed XAS spectra with IFEFFIT (Demeter) program package exploiting LCA and PCA analysis of series of XANES spectra and multi-edge parallel fitting of EXAFS spectra, using FEFF6 program code to construct *ab initio* EXAFS models. Preliminary Ni K-edge XANES and EXAFS results (Fig. 2) clearly show that Ni cations in as prepared catalysts at RT are present as mixture of Ni^{2+} and Ni^{3+} oxide nanoparticles on CeO_2 support. The relative ratio of the two valence states depends on the synthesis path (calcination in air, H_2 or Ar atmosphere). During activation in H_2/He at 500°C, all Ni cations are reduced to small metallic Ni nanoparticles (size below 1nm), attached to CeO_2 support, with different structures, depending on the synthesis path, which explains differences in their catalytic performance (activity). Small structural changes in Ni nanoparticles during the light-on experiment are indicated. DFT calculations of electronic energy of possible active sites in the catalysts, based on the XAS structural data, are in progress. Conversion and selectivity are calculated from continuous gas phase MS analysis. We expect that the information on structure and oxidation state of the metallic sites and macroscopic catalytic performance will reveal the active site structure and reaction mechanism differences in thermo and light assisted catalysis. Manuscript writing, containing also data acquired during this beamtime is in progress.

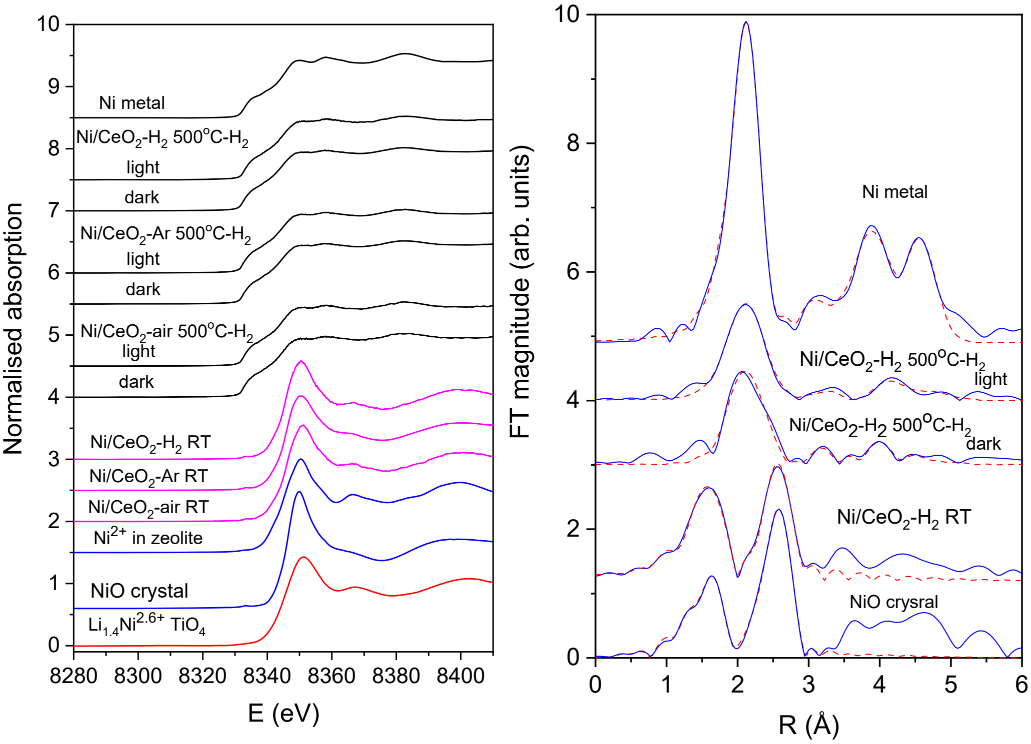


Figure 2. Left) *Operando Ni K-edge XANES spectra measured on of Ni/CeO2 photo-catalysts and reference Ni compounds.* ***Right)*** *Fourier transform magnitude of k^2-weighted Ni K-edge EXAFS spectra of the Ni/CeO2-H_2 photo-catalysts measured operando on initial state at RT and during reduction in He at 500°C (light off and on). Solid line – experiment; dotted line – best fit EXAFS model.*