ESRF	**Experiment title:** **In situ XAS visualization of the formation of the active sites in Ni-Nx-C catalysts for the hydrogen reduction reaction**	**Experiment number**: CH-6246
Beamline: BM08	**Date of experiment**: from: 21/06/22 to: 27/06/22	**Date of report**: 11/09/22
Shifts: 18	**Local contact(s)**: Michela Brunelli, Francesco D'Acapito	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Enrico Berretti* – CNR ICCOM (Florence, Italy)

Alessandro Lavacchi– CNR ICCOM (Florence, Italy)

Carlo Santoro* – University of Milano Bicocca (Milan, Italy)

Mohsin Muhyuddin* – University of Milano Bicocca (Milan, Italy)

Seyed Ariana Mirshokraee* - University of Milano Bicocca (Milan, Italy)

Report:

The aim of the experiment was to acquire XAS spectra of a Ni-N-C catalyst based on Ni Phtalocyanine (NiPc) during pyrolisis at Ni k-edge. The objective was to unravel Ni-N-C evolution during the heat treatment, and to correlate it with changes in electrocatalyst performances. The core of the experiment was similar to our previous experiment (A08-1 1084) performed on a similar catalyst based on FePc. It was divided in two series of measurements:

1) In-situ XAS acquisitions of the sample during pyrolisis (performed during daytime);
2) Ex-situ XAS acquisitions of Ni-N-C samples previoulsy heat-treated in our labs (performed during nighttime).

This time we were able to use a novel Microtomo gas flow cell for the heating. The cell was easily able to achieve 875°C in Ar/H2 95%/5% environment, enabling us to sample the temperatures (between 600 and 800 °C) at which electrochemical changes in the catalytical powder occurred. Moreover, we were able to test both the slightly reducing atmosphere (Ar/H2 95%/5%) usually adopted for the production of the electrocatalytical powders, and a complete inert atmosphere (Ar 100%) for the in-situ tests. With the new flow cell, the first part of the experiment was devoted to the definition of the best conditions do achieve the best temperature conditions.

In-situ acquisitions were performed for temperature steps, in which the temperature was left constant for about 3 hours for each step, alternating fast scans (C-Scans) during the heating ramps, and slow scans (k-scans) during the temperature plateau. A number of acquisitions was performed on the same formulation in order to be sure of the reproducibility of the results.

We were able to track noticeable changes in the XAS spectra:

a) Inside the single ex-situ series (from 25°C to 1000°C, performed only for Ar/H2 samples);
b) Inside the in-situ series (from 25°C to 850°C);
c) Between the ex-situ and in-situ series (Figure 1);
d) Between in-situ NiPc pyrolized in Ar/H2 95%/5% and in Ar 100% (Figure 2)

e) We were able to determine also a shifting towards the ex-situ spectra of the samples subjected to the in-situ treatment. This very intresting phenomena was initially attributed to the reversible occupancy of the Fe active site from the oxigen when the sample was left outside in air after the pyrolisis (Figure 3), but further modelistic studies will be needed to confirm this.

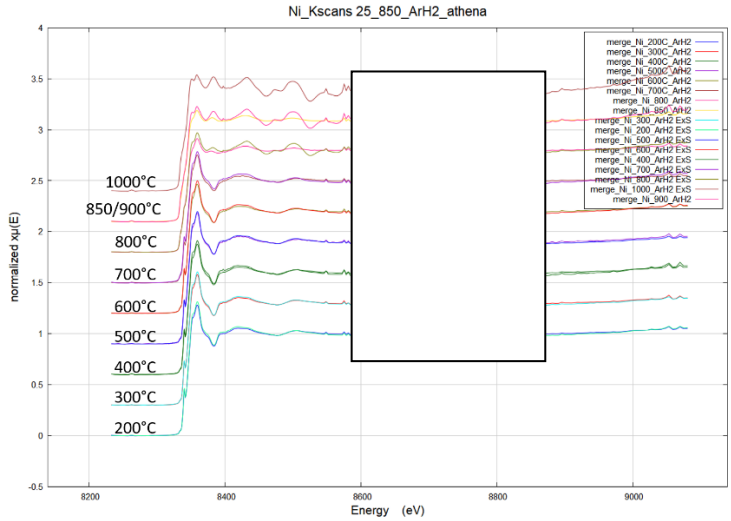

Figure 1 – Comparison between XAS from ex-situ (-EXS samples in the legend) and in-situ NiPc in KB samples, pyrolized in Ar/H2 atmosphere

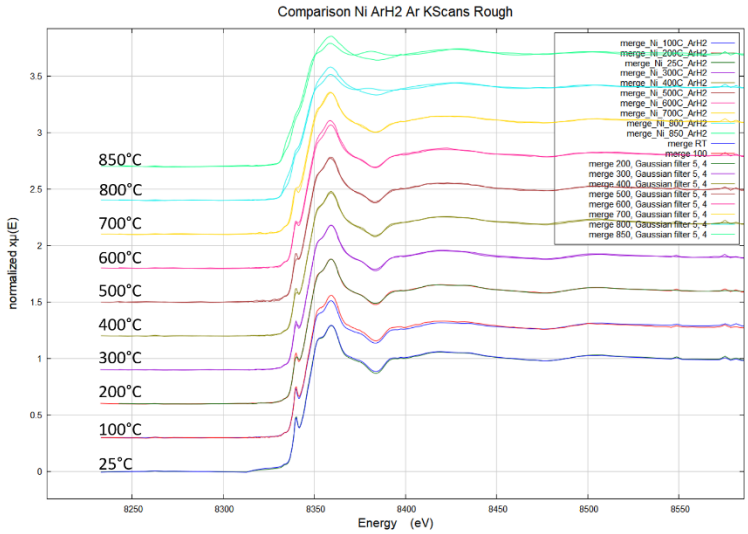

Figure 2 - Comparison between XAS from in-situ NiPc in KB samples, pyrolized in Ar/H2 atmosphere and pure Ar atmosphere

Moreover, we were able to acquire a new set of in-situ spectra for the FePc samples exploiting the bigger temperature range of the new microtomo cell, thus completing the set of data of the previous experiment othe iron (A08-1 1084, Figure 3).

In conclusion, during this turn we were able to acquire a consistent set of data on the evolution of NiPc both in-situ and ex-situ, using two different reactive environments (Ar/H2 and Ar), and to complete the dataset from the previous experiment on FePc, acquiring new insights on what is happening in these systems.