



	Experiment title: Combined XRS-XES study of trifunctional materials for super-dry reforming	Experiment number: CH-6500
Beamline: ID20	Date of experiment: from: 02/11/2022 to: 07/11/2022	Date of report: 23/1/2023
Shifts: 15	Local contact(s): Dr. Alessandro Longo	<i>Received at ESRF:</i>
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Report: Summary

A bifunctional Ni-based catalyst, Ni/MgFeAlO₄, was found to be highly carbon resistant in methane dry reforming (DRM). As next research step, Ca was introduced for sorption functionality to make a trifunctional material, Ni/CaMgFeAlO for chemical looping super-dry reforming. In this campaign, H₂-TPR, CO₂-carbonation and -decarbonation have been performed and followed by *in-situ* XRS-XES. The light elements O and Ca were recorded by XRS to investigate the effect of incorporated CaO in carbonation-decarbonation, while the transition elements Ni and Fe were followed by XES to study the NiFe alloy formation and the influence of Ni on the CO₂ capacity of CaO. The data analysis has been started by the PhD, joint between LCT, Ghent University, and ID20, ESRF.

Experimental conditions

We made use of an ESRF reactor cell with a spherical Kapton dome (Fig. 1 left), allowing x-ray access over a 2π solid angle. To admit reaction gases, a gas feed rig with mass flow controllers and switching valves was brought by the users and installed inside the hutch, next to the gas bottles (Fig 1. right).

The main sample for this in-situ investigation is 5%Ni/CaFeMgAlO. This was placed as a pellet in the

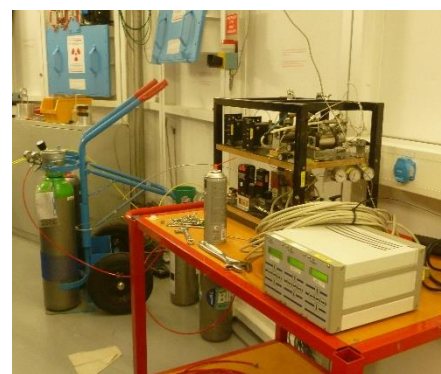
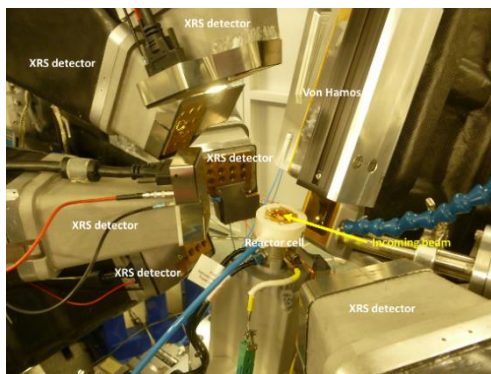


Figure 1 left: reactor cell amidst the XRS and XES detectors; right: gas feed rig

reactor cell and heated to reaction temperature (~830°C) in H₂, to induce Ni-Fe alloying. After H₂-TPR, CO₂ was introduced (~650°C) to induce CO₂ sorption by CaO (transforming to CaCO₃) and possible oxidation of Ni and Fe. Hereafter, the temperature was raised to ~830°C to track CO₂ desorption/CaCO₃ decomposition.

Experiments performed and first results for Ca and O K signals

Ca L_{2,3} edge: Ca L_{2,3} edge spectra of 5%Ni/CaFeMgAlO recorded at RT in He for fresh, reduced (after H₂-TPR), re-oxidized (after CO₂-carbonation) state and after decarbonation at 830°C are shown in black, red, green and violet, respectively (Figure 2A). The peaks at 349.5 eV (P2) and 353 eV (P4) correspond to the L₃ and L₂ edge, originating from transition from 2p_{3/2} and 2p_{1/2} to the unoccupied conduction d band, respectively. The shoulder peaks P1 and P3 were generated due to the crystal field that arose from the symmetry of atoms around Ca²⁺. A clear change at the L_{2,3} edge is observed after treatment (Figure 2A). The intensity of the L_{2,3} peaks decreases after reduction, but increases above the fresh state upon CO₂ re-oxidation. After decarbonation, the L_{2,3} intensity decreases below the fresh one, even deeper than for the reduced state. Differences between the sample and reference Ca L_{2,3} spectra of CaCO₃ and Ca(OH)₂ are shown in Figure 2B. The intensity of the shoulder peaks in the treated sample lies significantly below the ones for the references, which indicates a different local environment around Ca²⁺. Further analysis is needed to quantify and interpret these changes.

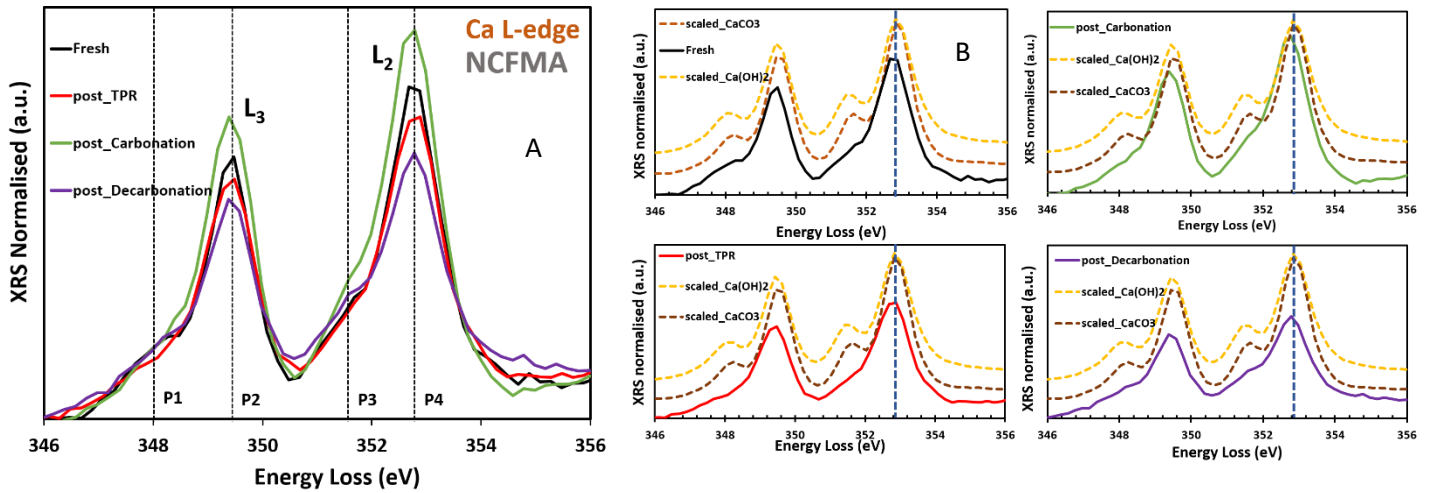


Figure 2: (A) in-situ measurement of Ca L_{2,3} edge of 5%Ni/MgCaFeAlO in fresh, reduced, re-oxidized state and after decarbonation. (B) Recorded experimental spectra for different treatments plotted with references CaCO₃ and Ca(OH)₂. Scaled = given a vertical offset.

O K-edge: The O K-edge recorded at RT in He is shown in black, red, green and violet for the fresh, reduced, re-oxidized state and the one after decarbonation, respectively (Figure 3A). A pre-edge is observed at 532 eV, whereas the main feature of the K edge is at 541 eV. The edge intensity increases gradually after carbonation and decarbonation treatment. In addition, a distinguishable shoulder is observed at 537.5 eV, which becomes more prominent/distinct after treatment.

The O K-edge spectra obtained from CaCO₃ and Ca(OH)₂ are very different from what is observed for the 5%Ni/CaFeMgAlO sample. The spectral features P1, P2, P3, P4 in CaCO₃ (Figure 3B) arise due to Ca—O and Ca—C hybridization. As the oxygen environment in Ni/MgCaFeAlO is different from pure CaCO₃ or Ca(OH)₂, containing also a contribution from the spinel phase CaFeMgAlO, the pure CaCO₃ or Ca(OH)₂ references cannot describe the O K edge of 5%Ni/CaFeMgAlO accurately.

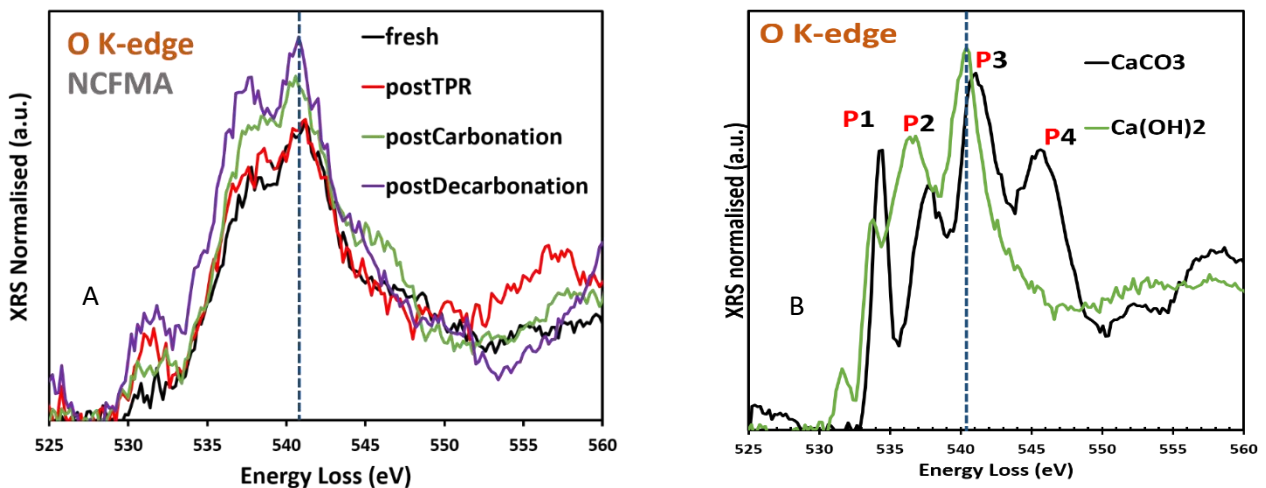


Figure 3: (A) in-situ measurement of O K edge of 5%Ni/MgCaFeAlO in fresh, reduced and re-oxidized state and after decarbonation. (B) O K edge spectra of ex situ reference samples CaCO₃ and Ca(OH)₂.

Unfortunately, the heating supply of the in-situ reactor dome failed on Friday evening, after which high temperature control was lost (max temperature was then limited to 550°C, i.e. insufficient for adequate reduction). Despite some help from the EHO, much appreciated, the problem could not be solved and hence experiments could not be continued as planned over the entire weekend. For instance, no measurements could be performed with a trifunctional material of different composition or with physical mixtures. Some ex-situ and low T measurements were performed instead.

Concluding, we have performed combined XRS and XES measurements on one trifunctional material during in-situ reduction/carbonation/decarbonation treatment at 830°C. The sample examined should allow us to understand its behavior under reduction, CO₂ oxidation and decarbonation. These results will be used in a publication with working title 'In-situ XRS-XES study of trifunctional materials for super-dry reforming.'