



	Experiment title: In-situ XAS study of trifunctional Ni-Ca-Fe materials for super dry reforming	Experiment number: CH-6418
Beamline: BM08	Date of experiment: from: 13/09/2022 to: 19/09/2022	Date of report: 18/11/2022
Shifts: 18	Local contact(s): D' ACAPITO Francesco	<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/CaMgFeAlO₄ for chemical looping super dry reforming. In this campaign, H₂-TPR, CO₂-TPO, and RWGS have been performed by means of in-situ XAS to investigate the effect of incorporated CaO on the FeO_x reduction-oxidation activity, the NiFe alloy formation and to study the influence of Ni on the CO₂ capacity of CaO. As Ca could unfortunately not be measured due to experimental set-up restrictions, only Ni and Fe signals have been followed. The data analysis has been started by the joint Ph.D. between LCT, Ghent, and ID20, ESRF.

Experimental conditions

The sample was diluted with fumed silica (~ 95% dilution) to get a good signal and a pellet was made for the reactor cell. 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 appropriate gas bottles (Fig. 1). The two main samples for in-situ investigation were: 5wt.% Ni/CaFeMgAlO₄ and CaFeMgAlO₄, referred to as 5NCFMA and CFMA. A pellet was placed in the reactor cell and heated to reaction temperature (~830 °C) in H₂, to induce Ni-Fe alloying. After H₂-TPR, CO₂ was introduced (~830 °C) to follow the effect upon Ni and Fe of 1/ CO₂ oxidation, 2/ CO₂ sorption by CaO (transforming to CaCO₃) and 3/ of subsequent CO₂ desorption/CaCO₃ decomposition (under inert ~830 °C). After another reduction RWGS was run with gas flow ratio H₂:CO₂ = 1:1 at 650 °C, followed by a temperature rise to 750 °C in He to decompose CaCO₃. In all steps, Ni and Fe were followed by means of in-situ XANES (continuous scans during treatment) or EXAFS (at RT after treatment).



Fig. 1: gas feed rig in hutch BM08.

Experiments performed and results

Fresh, reduced and oxidized states of 5NCFMA and CFMA are shown in blue, green and red, respectively (Fig. 2A and 2C). For both samples, a clear change in intensity of pre-edge and post-edge is observed after subsequent reduction-oxidation. After reduction, the edge is shifted towards the left, close to the Fe metal, while re-oxidation shifts it back towards the right, though not entirely to the original position. These edge positions reflect the mean oxidation state of the sample after each treatment. In addition, the white-line (WL) position and intensity change after TPR-TPO for both samples. A slight difference appears between the WL of both samples in reduced state, likely due to the presence of Ni in 5NCFMA.

A Fourier transform yields the pseudo-radial distribution around the absorber (Fig. 2B, D), which will provide information about bond distances and neighboring ions after modelling. Reduced 5NCFMA slightly differs from CFMA around 3-4 Å, whereas the oxidized state mostly differs at ~1-2 Å, pointing to the influence of Ni.

After RWGS with H₂:CO₂=1:1 at 650 °C, the temperature was raised to 750 °C in He to decompose the formed CaCO₃. The released CO₂ can oxidize Fe to FeO_x, which is confirmed in Fig. 3. In the case of 5NCFMA, more

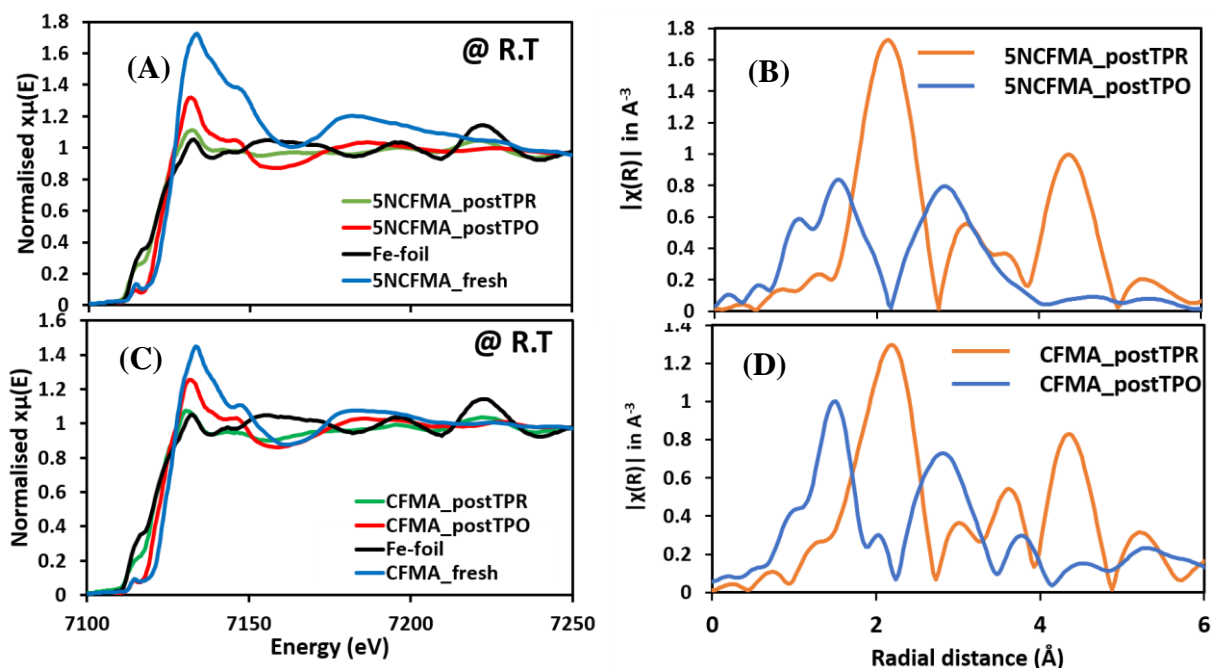


Fig. 2: Fe K-edge XANES at RT for 5NCFMA (A) and CFMA (C) after different treatments, together with Fe foil as reference; **B, D:** R space EXAFS of 5NCFMA (B) and CFMA (D) for TPR-TPO.

iron is getting oxidized after the second RWGS showing a further increase in WL, whereas CFMA has close to equal signal after RWGS1 and RWGS2, indicating that most of the Fe is already oxidized after the first cycle.

At the Ni K-edge, H₂-TPR reduces NiO to Ni, but CO₂ re-oxidation is unable to re-oxidize Ni and this is confirmed by the obtained spectra in Fig. 4A. In case of post-RWGS treatment at 750°C, Ni remains in a reduced state, which indicates that the released CO₂ during decomposition of carbonate cannot oxidize Ni.

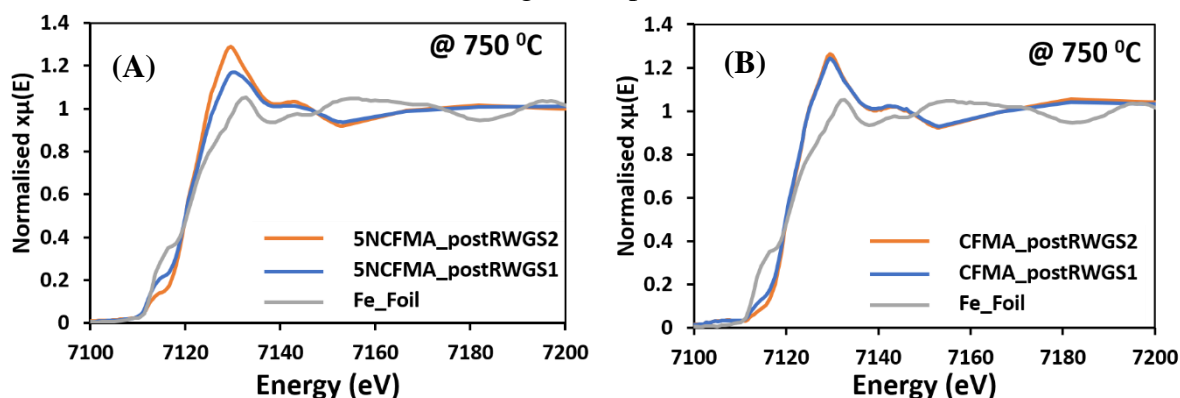


Fig. 3: Fe K-edge at 750°C in He after 2 cycles of RWGS with H₂:CO₂=1:1 for (A) 5NCFMA and (B) CFMA.

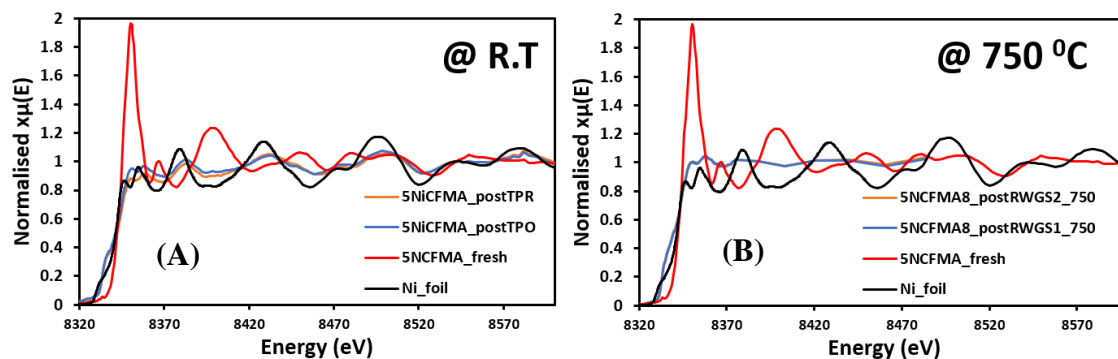


Fig. 4: Ni K-edge of 5NCFMA fresh, after (A) TPR-TPO and (B) at 750°C in He after two consecutive RWGS with H₂:CO₂=1:1. Ni foil spectrum retrieved from another campaign.

Concluding, we have successfully performed in-situ XAS of trifunctional materials during treatment at 830°C. The two samples examined will allow for a rigorous comparison of their behavior under reduction, CO₂ oxidation, and reverse water gas shift, to assess the effect of the CaO presence. These results will be used in a publication with working title ‘In-situ XAS study of trifunctional Ni-Ca-Fe materials for super dry reforming.’