	Experiment title: **In situ XRS characterization of Ni-Fe restructuring during methane dry reforming**	**Experiment number:** CH-6020
Beamline: ID20	**Date of experiment:** from: 27/9/2021 to: 5/10/2021	**Date of report:** 25/2/2022
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Remark: a new joint PhD between LCT-Ghent University and ID20-ESRF, Soumya Kumar Das, has started in November 2021 at ID20. This PhD student will take up the data analysis of this campaign as part of his work. This report could therefore only be drafted after obtaining his preliminary analysis.

Report: Summary

Ni is a common, efficient catalyst for methane dry reforming (DRM). To mitigate its tendency to deactivation (by carbon deposition and sintering), Fe is a good promoter, suppressing carbon and increasing catalyst activity. When Fe is incorporated into $MgAl_2O_4$, this $MgFeAlO_4$ support has surprisingly good performance and carbon resistance. In a previous campaign, XRS was used on *ex situ* supports $MgAl_2O_4$ and $MgFeAlO_4$ (9wt% Fe) in calcined and reduced state to identify their restructuring from the perspective of each constituent element. Now, $NiO + Fe_2O_3$ or NiO only were impregnated onto these supports, yielding Ni-Fe nanoalloys upon reduction, with catalyst and metal oxide sites for DRM. In this second beamtime, this bifunctionality was examined in situ during redox and DRM reaction, for which data analysis is currently taken up by the newly joined PhD.

Experimental conditions

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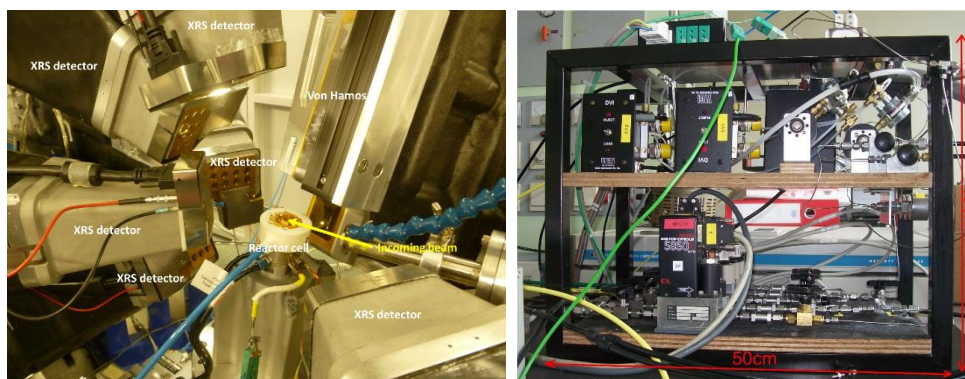

Fig. 1 left: reactor cell amidst the XRS and XES detectors; right: gas feed rig

The two main samples for in situ investigation were: $NiFe/MgAl_2O_4$ and $Ni/MgFeAlO_4$. These were placed as pellet in the reactor cell and heated to reaction temperature (~800°C) in H_2, to induce Ni-Fe alloying. All elements, O, Al, Ni, Fe, as well as C, were followed by means of the XRS detectors (Mg overlaps with an Fe signal). In addition, Fe and Ni XES were measured in parallel using a Von Hamos detector placed aside the cell.

Experiments performed and results

For each sample, the set of experiments started with an in situ reduction by means of H_2-TPR or CH_4-TPR up to 800°C and a 1h dwell at high T. Then, isothermal reactions were performed at 800°C, e.g. CO_2 oxidation, with eventually an isothermal H_2 reduction to bring the sample back to reduced state for DRM. DRM was
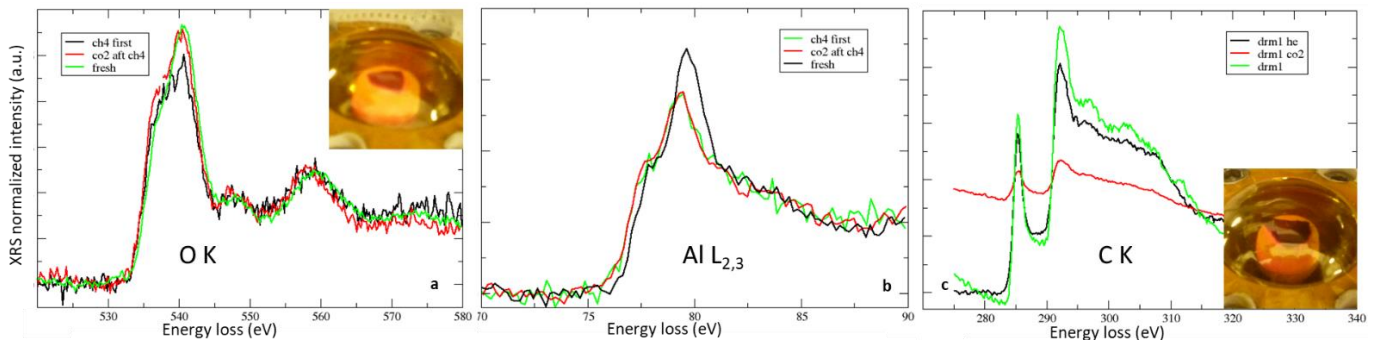
Fig. 2: **a**: *O K and* **b**: *Al $L_{2,3}$ for Ni/MgFeAlO$_4$, fresh, after in situ CH$_4$-TPR and isothermal CO$_2$ exposure;* **a** *inset: fresh sample;* **c**: *C K signal from NiFe/MgAl$_2$O$_4$, after DRM with 1:1 ratio,* **c** *inset: coked sample after DRM with ratio 1:1.*

performed with different ratios CH$_4$:CO$_2$, e.g. 1:3 and 1:1, to assess the balance between reducing and oxidizing reactants.

For the Ni/MgFeAlO$_4$ material, CH$_4$ reduction and subsequent CO$_2$ oxidation lead to changes in the O and Al signal, especially in the ratio of shoulder to main peak (Fig 2a and b). For O K, both spectral features are associated with excitation of O1s electrons above the Fermi level into the Mg/Al3sp and the Fe4sp band hybridized with O2p states. Similarly, the Al L$_{2,3}$ signal shows a change in ratio of its shoulder vs. main peak upon reduction. The latter holds information on the inversion parameter of the spinel phase.

The NiFe/MgAl$_2$O$_4$ showed massive coke formation after DRM with CH$_4$:CO$_2$ = 1:1 ratio (inset of Fig. 2c). The corresponding C K signal shows several features that pertain to different transitions (π* ~285eV, σ* > 290eV). In contrast, the Ni/MgFeAlO$_4$ material exposed to the same harsh coking conditions, did not suffer from C deposition, yielding no C signal at all (not shown).

At the Ni and Fe K edges, XES was recorded in parallel to the multi-element XRS acquisitions. Comparison with Ni and Fe references showed that for NiFe/MgAlO$_4$ Ni cycled back and forth between a metallic state (~Ni foil) after reduction, while going towards Ni^{2+} after CO$_2$ oxidation (~Ni(NO$_3$)$_2$) (Fig 3a). The Fe Kβ$_{2,5}$ signal varied more subtly (Fig 3b). After DRM exposure using CH$_4$:CO$_2$ = 1:1 as ratio, the Ni signal took up a position inbetween metal and oxide state (Fig 3c). As for Fe, there a clearly different signal was obtained during DRM, with lower main intensity in Kβ$_{2,5}$ and a sloping pre-edge towards Kβ" (Fig 3d). Again, in contrast, the Ni/MgFeAlO$_4$ material showed variation in the main peak shape and intensity but no sloping pre-edge (not shown).

All signals from XRS and XES will be further analyzed and compared to point out the resemblances and differences. Where possible,
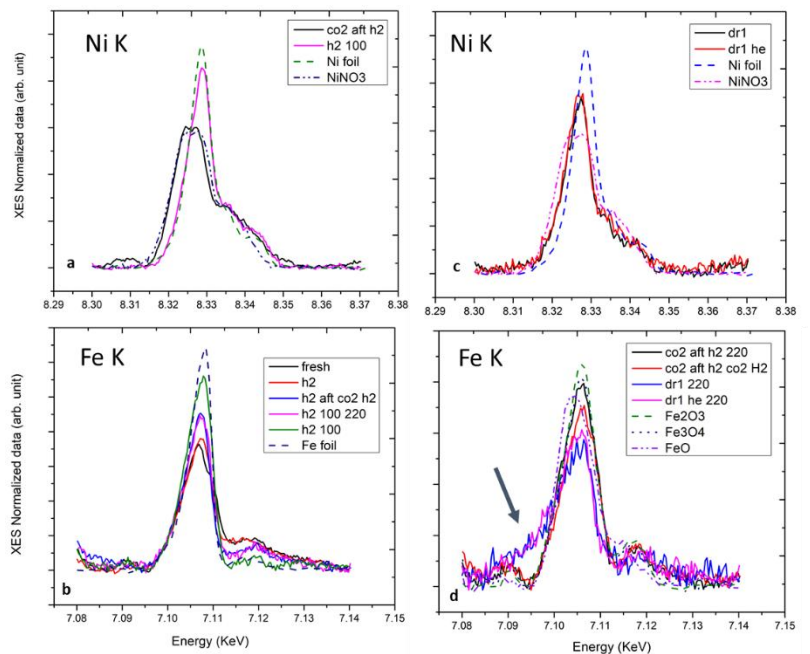

Fig. 3: NiFe/MgAlO$_4$ in situ XES at Ni and Fe edge after several treatments. Left frames: after reduction and/or oxidation, right frames: after DRM reaction.

an LCF analysis will be pursued based on reference spectra to identify the contribution of different species in the overall signal. In addition, simulation of signals is also envisaged as a means for spectral identification in relation to the performed treatment.

Concluding, we have performed successfully for the first time combined XRS and XES measuements during in situ catalytic treatment at 800°C. The two samples examined will allow for a rigorous comparison of their behaviour under reduction, CO$_2$ oxidation and dry reforming of methane. These results will be used in a publication with working title '*In situ XRS-XES characterization of Ni-Fe restructuring during methane dry reforming.*'