	Experiment title: Nature of Ni-Fe-Rh sites under reducing/oxidizing environment studied by in-situ XAS	**Experiment number**: **IH-CH-1213**
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Shifts: 6	**Local contact(s)**: A. Longo, D. Banerjee	

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Summary

Nickel-based catalysts are attractive alternatives for noble metals in reforming reactions. Adding Fe to Ni helps to reduce deactivation by suppressing carbon accumulation and increasing catalyst stability, depending on the Fe:Ni ratio. Rh is added as promoter to further stabilize the Ni-Fe alloy under reforming conditions. During this in-house DUBBLE beam time, insight was pursued on the rearrangements that take place in two catalysts, 10Ni-5Fe ('Ni-Fe') and 10Ni-5Fe0.5Rh ('Ni-Fe-Rh') supported on $MgAl_2O_4$, under reducing, oxidizing, as well as isothermal redox cycling conditions.

Experiments performed

Both materials were pelletized without dilution and mounted in the micro-tomo reactor cell available at DUBBLE. After room temperature EXAFS, XANES spectra were collected during temporal and cycling treatments at high temperature, while EXAFS scans were recorded after cool-down from each treatment to room temperature for better signal/noise ratio. For a complete view on the rearrangements, measurements were repeated at the Fe K, Ni K and Rh K edge.

TPR: A reduction is required to bring the materials in their alloyed, i.e. active state. The XANES variation during TPR at the Ni edge looks very similar for both materials (not shown). At the Fe K edge on the other hand, clear differences occur in the R-space graphs. From XRD, Ni is expected to alloy with Fe upon reduction of Ni-Fe. The presence of Rh seems to induce changes in this evolution: whereas the starting point is the same in both samples, i.e. as-prepared (calcined) phases supported on $MgAl_2O_4$, the evolution for Ni-Fe-Rh is less smooth and the final state has a somewhat different appearance.
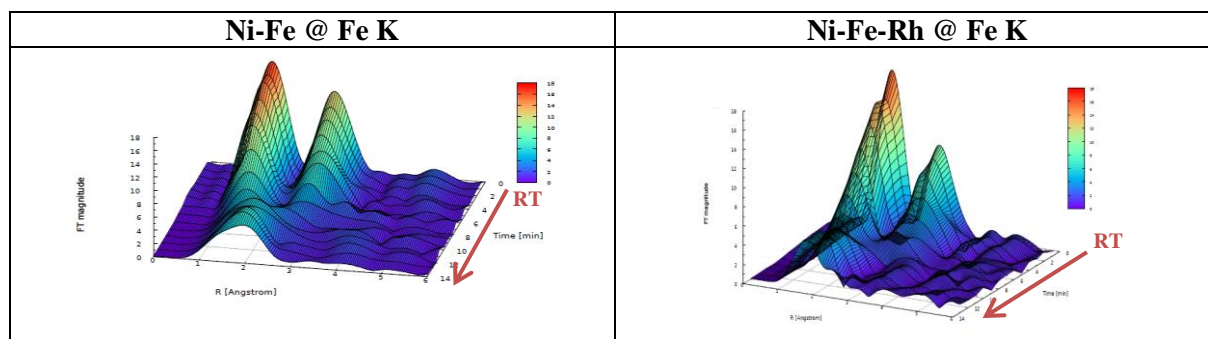

TPO: upon reoxidation with CO_2, Ni-Fe is known to segregate into Ni and Fe which is subsequently oxidized to Fe_3O_4. At the Fe K edge, the final state for both samples does not appear the same: Ni-Fe presents 2 neighbour shells at ~2 and ~3Å, while in Ni-Fe-Rh, only the first one is present. The reason for this difference could be the presence of Rh, which will be clarified by means of detailed modelling. In this respect, the TPO data recorded at the Rh edge can be of value, as these indicate what happens with this element upon CO_2 oxidation. The Ni edge again doesn't show major differences.

Fe-Ni @ Fe K	Fe-Ni-Rh @ Fe K	Fe-Ni-Rh @ Rh K
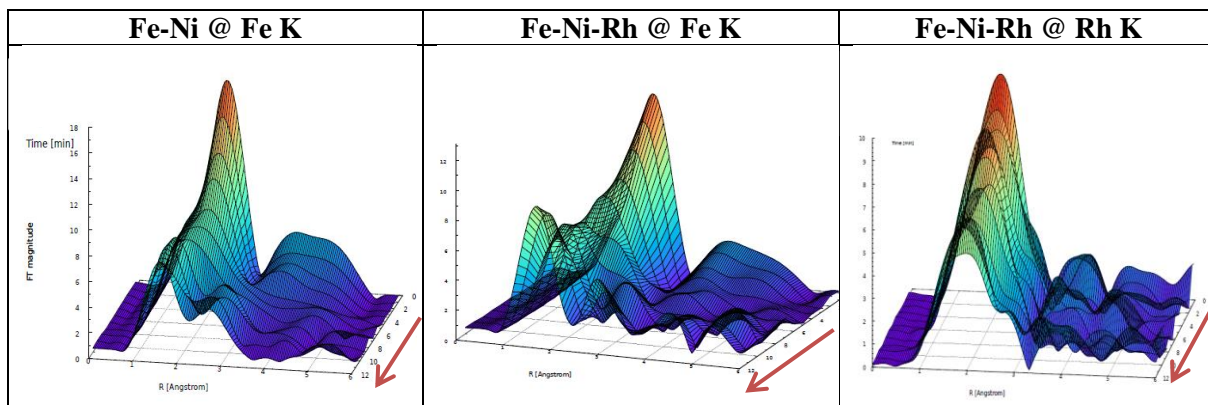
Isothermal redox cycling: to assess the stability of the structure obtained after reduction of the Ni-Fe-Rh material, three redox cycles were performed alternating between H_2 reduction and CO_2 oxidation with an additional 4th H_2 reduction at 750°C. The latter treatment was repeated for XANES recording at the Fe and Ni K edge. At the Fe edge, gas switching has a clear effect: the white line position and intensity move back and forth between a reduced and more oxidized state. This translates in switching positions of the R space maximum (i.e. the first neighbour shell) as a function of cycling time (see inset figure; red arrow indicates reduced position). Ni is far less affected by the cycling, showing only slight white line variations with time and no real first shell shift in R space (see inset figure). Whether upon cycling irreversible rearrangements take place, will follow from a modelling analysis of both XANES and EXAFS.

Ni-Fe-Rh @ Fe K	Ni-Fe-Rh @ Ni K
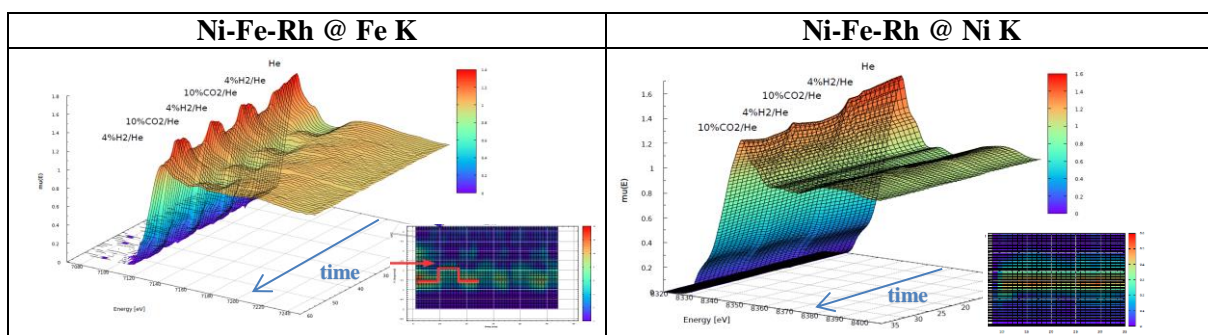
Ni, Rh and Fe overall evolutions in Ni-Fe-Rh: The evolution of Ni and Rh R space signals for Ni-Fe-Rh are represented in the figures here below. For Ni, the calcined state is clearly oxidized (blue signal), but after TPR, TPO or cycling a metal-like state is observed, without much difference. At the Rh edge, the calcined state is equally oxidized (green signal). After TPO or after cycling (ending with a reduction) the local Rh environment is also metal-like, suggesting that the CO_2 oxidation cannot restore the oxidized state. As for Fe, The local environment evolves from oxidized in the calcined state (blue) towards metal-like after TPR (red), back to oxidized after TPO (green) and again metal-like after cycling (purple).

Ni K evolution	Rh K evolution	Fe K evolution
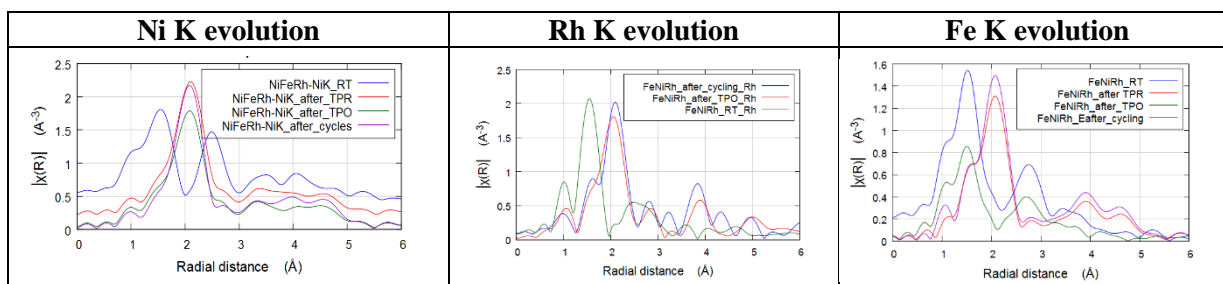
Clearly, among the three elements Fe adapts most easily to a change in the gas environment. More subtle changes, like in particle size or neighbouring atoms, will appear after detailed analysis. In this respect, modelling will be pursued for both XANES (symmetry) and EXAFS spectra (coordination), while for Fe also the XAS pre-edge feature can deliver information (electronic).

Conclusion: the XAS results will allow to establish the nature of the active sites, the role and location of Rh in the Ni-Fe-Rh catalyst. The effect of Rh on the Ni-Fe alloy stability as a function of the environment (reducing/oxidizing), as a model composition of the reforming reactions, will be assessed from the XANES evolution. These results will be used in a publication with working title 'Nature of Ni-Fe-Rh sites under reducing/oxidizing environment studied by in-situ XAS'.