ESRF	**Experiment title:** Unravelling the role of alloys in Ni-Fe/SiO_2 and Ni-Cu/SiO_2 CO_2 hydrogenation catalysts by operando XAS	**Experiment number:** CH-6115
Beamline: BM23	**Date of experiment:** from: 29/09/2021 to: 05/10/2021	**Date of report:** 03/01/2022
Shifts: 18	**Local contact(s):** Kirill Lomachenko	*Received at ESRF:*

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Report:

Short description of the actual experiment

The aim of this beamtime was to unravel the role of metal alloys in Ni-Fe/SiO_2 and Ni-Cu/SiO_2 CO_2 hydrogenation catalysts by *operando* XAS. To gain insights into metal alloy formation and evolution, dependent on both varying metal ratio and metal, we performed *operando* XAS experiments at the Fe, Ni, and Cu K edge first during reduction where metal alloy formation takes place and subsequently during CO_2 hydrogenation. Hereby, we collected XAS during both ramping and holding steps (Fig.1). Importantly, the holding steps were adjusted to the possibilities at BM23, i.e., we considered the possible time resolution and a reasonable number of scans for a sufficient data quality. These *operando* experiments were conducted in a self-supplied setup, which was inserted at BM23. Our setup comprised a capillary cell with integrated IR-heaters, a gas rig with various MFC's and gas filters, a temperature controller, and a gas chromatograph to simultaneously conduct product analysis. Eventually, we will combine the XAS results with those from product analysis to deduce a fundamental understanding of synergistic effects in bimetallic catalysts and their influence on catalytic performance in CO_2 hydrogenation. This is particularly important for the rational design of next generation bimetallic catalysts for CO_2 valorization and our journey towards a more circular economy.

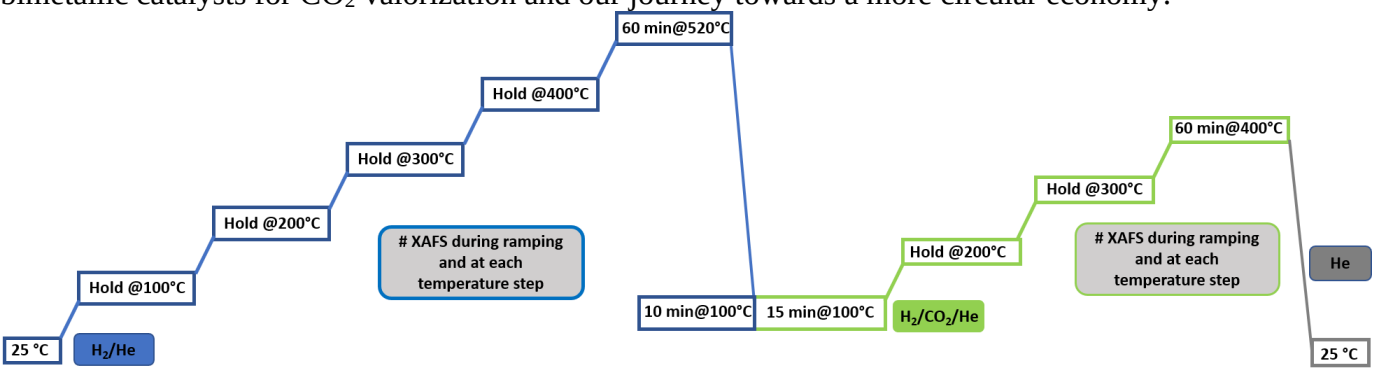

Fig.1: Scheme of the performed *operando* experiments at BM23.

Difficulties encountered during the experiment

We had to find a compromise for the beam size in y-direction (height) to account for the curvature of the capillary (0.96 mm inner diameter) and to minimize the influence of possible inhomogeneities of the sample. Moreover, while heating (max. 520°C), the glass capillary bends, which induces a decrease of the data quality and the necessity to re-align. As this was already know before the experiment, we included an automatic re-alignment step in the measurement macro, however, this automated process did unfortunately not work sufficiently at higher temperatures. Hence, we manually re-aligned at each temperature step.

During the complete beamtrip, we had several issues with Bliss and NexusWriter. Unfortunately, software errors (software crash) occurred multiple times. Although Kirill Lomachenko and Cesare Atzori were very supportive and always approachable when these errors occurred, they couldn't solve these issues as it was not BM23-related. Always when these software errors occurred, the XAS scans were no longer saved, and we had to pause the experiment. Unfortunately, during several measurements, these pausing times took hours and we had to abort the experiment, which was very time-intensive (one *operando* experiment took approx. 11 h). In view of the limited time, we had to adjust our plans and decided to focus on the Ni-Fe/SiO_2 system, i.e., to investigate varying Ni/Fe ratios and corresponding monometallic counterparts. Hence, the influence of metal alloys on Ni-Cu/SiO_2 catalysts could not be investigated in this beamtime. To do so, we would need an additional beamtime.

Exemplary results

In order to gain insight into both metals of the bimetallic catalysts, we scanned alternating the Fe and Ni K edge. Fig. 2 exemplarily depicts some distinct changes in the XAS spectra when comparing the starting point at 23°C during reduction conditions, the reduced state at 520°C, and the catalytically active state at 400°C during CO_2 hydrogenation conditions.

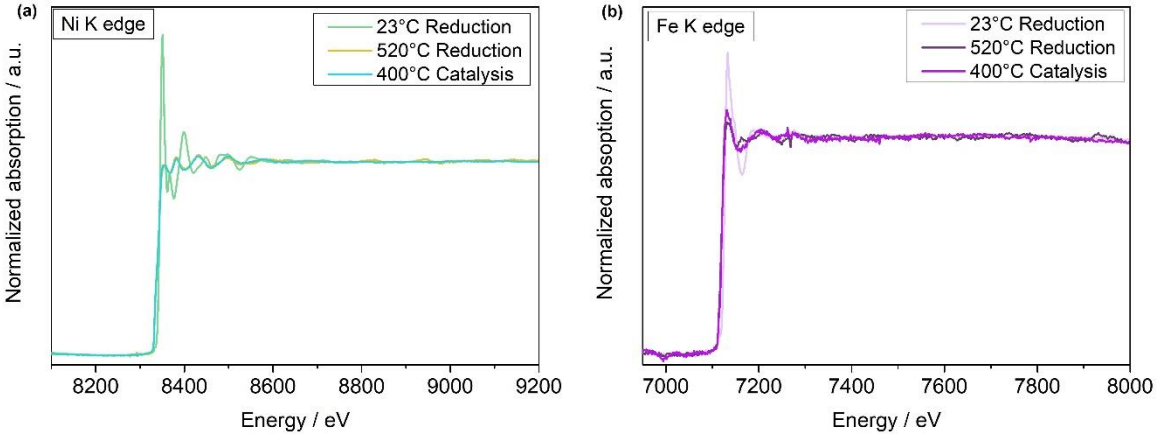

Fig.2: Normalized Ni (a) and Fe (b) K edge XAS spectra at different temperatures and gas compositions. Reduction: H_2:He = 1:1, Catalysis: H_2:CO_2:He = 4:1:5, 1 bar.

Fig. 3 shows the evolution of the Ni and Fe K edge XAS spectra together with the CO_2 conversion and selectivity towards main reaction products (methane and CO) as function of time on stream at 400°C during CO_2 hydrogenation. Currently, we are still in the process of data analysis, nevertheless we can already conclude that this beamtime enabled the detailed investigation of a complete set of Ni-Fe bimetallic catalysts.

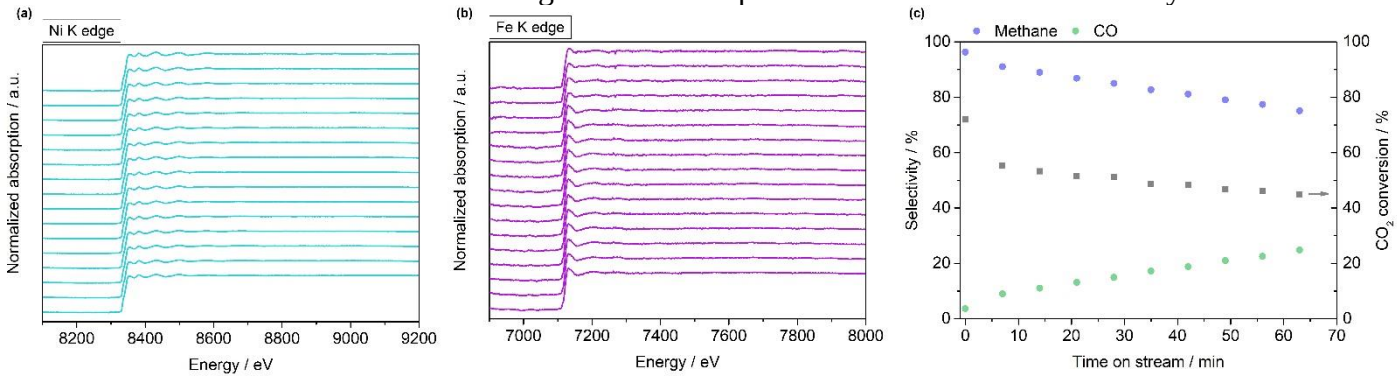

Fig.3: Normalized Ni (a) and Fe (b) K edge XAS spectra at 400°C during CO_2 hydrogenation together with CO_2 conversion and selectivity towards main reaction products as function of time on stream extracted from the simultaneously measured chromatograms (c).