ESRF	**Experiment title:** Gaining Insights into Alloy Formation and Evolution of Ni-Fe/SiO_2 and Ni-Cu/SiO_2 CO_2 Hydrogenation Catalysts by Operando Anomalous Small Angle X-ray Scattering	**Experiment number**: CH-6161
Beamline: BM02	**Date of experiment**: from: 28/10/2021 to: 02/11/2021	**Date of report**: 28/01/2022
Shifts: 15	**Local contact(s)**: Frederic De Geuser, Marina Appel, Nils Blanc	*Received at ESRF:*

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Report:

Short description of the actual experiment

The aim of this beamtime was to gain insights into the metal alloy formation and evolution of Ni-Fe/SiO_2 and Ni-Cu/SiO_2 CO_2 hydrogenation catalysts by *operando* ASAXS. To realize ASAXS, we performed *operando* SAXS experiments at 5 different energies around the Fe, Ni, and Cu K edge first during reduction where metal alloy formation takes place and subsequently during CO_2 hydrogenation. Hereby, we measured ASAXS during both ramping and holding steps (Fig.1). Importantly, the holding steps were adjusted to the possibilities at BM02, i.e., we considered all motor movements and recording times for the images both with and without kapton. These *operando* experiments were conducted in a self-supplied setup, which was inserted at BM02. 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. Before starting the experiments, we decided to slightly modify the planned *operando* ASAXS experiments by additionally adding a WAXS detector so that we finally performed *operando* ASAXS-WAXS experiments at BM02. The addition of the WAXS detector did not affect the ASAXS experiments but rather enabled to yield additional information on the catalysts. Eventually, we will combine the ASAXS-WAXS 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.

Difficulties encountered during the experiment

We had several beam losses and one very long beam loss of 9 h due to issues of the storage ring. These beam losses induced problems for the *operando* experiments as we had to pause the current program step. However, pausing such a complex reaction program (total time ~11 h) is not possible at each step. Hence, we had to abord several measurements and restart the experiment after the beam was back with a new sample, which was very time-intensive. In view of the limited time, we had to adjust our plans and decided to focus on the influence of varying additional metal, i.e., replacing Fe by Cu, by measuring 2 Ni-Fe/SiO_2 and the corresponding Ni-Cu/SiO_2 catalysts. Hence, the influence of varying metal ratio on both Ni-Fe/SiO_2 and Ni-Cu/SiO_2 catalysts could not be investigated *operando* in this beamtime. To complete the proposed study by measuring *operando* ASAXS-WAXS at the Ni-Fe/SiO_2 and Ni-Cu/SiO_2 catalysts with varying metal ratio, additional beamtime would be needed.

All catalysts are SiO_2-supported metal(oxides) with only 6wt% total metal loading. Therefore, we expected that the signal from SiO_2 and the metal particles cannot be entirely deconvoluted and we decided to perform a complete *operando* ASAXS-WAXS experiment with a capillary filled only with SiO_2. Moreover, as all catalysts were located inside a glass capillary, we additionally performed a complete *operando* experiment with an empty capillary as background measurement. In view of the complexity of the supported bimetallic catalysts, we decided together with the local contacts that it is worth to spend a comparatively long time on measuring possible backgrounds, which might become beneficial for the data analysis after the beamtrip.

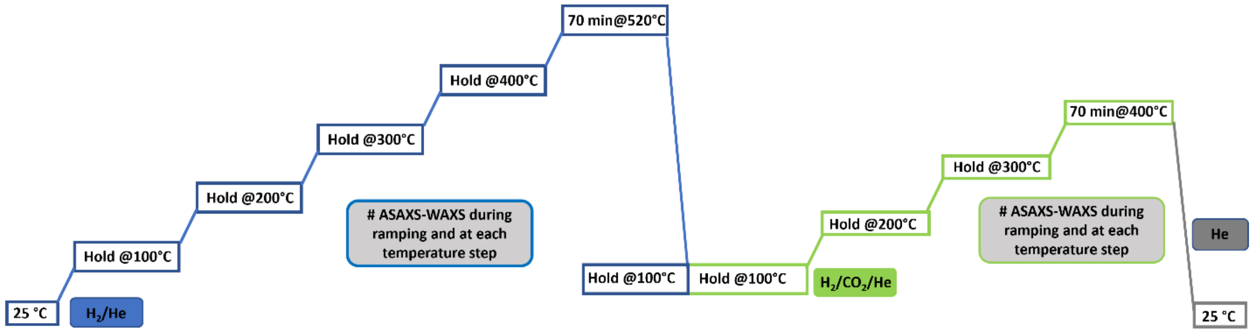

Fig.1: Scheme of the performed *operando* experiments at BM02.

Exemplary results

Currently, we are still in the process of data analysis. As the normalization is crucial for ASAXS, N. Genz is in close contact with F. De Geuser to optimize the data analysis. Fig. 2a exemplarily depicts some slight changes (intensity and slope) in the scattering curves dependent on both Ni energy and sample, i.e., varying Ni/Fe ratio (Ni/Fe higher for pink curves). From Fig. 2b it is evident that (1) SiO_2 shows the same scattering curves independent of temperature and gas composition (2) Ni-Fe/SiO_2 shows slightly different scattering curves compared to SiO_2 (3) Ni-Fe/SiO_2 shows a temperature- and gas composition-dependency. Based on the preliminary data processing, we can already conclude that we reveal both changes in the scattering curves between the different samples, i.e., varying additional metal and varying metal ratio (note although we could only conduct *operando* experiments for 2 different metal ratios being not sufficient for profound conclusions, various metal ratios were measured *ex situ* to get a first impression about metal ratio dependent differences in preparation for a future beamtime), and during the *operando* experiments, i.e., varying temperature and gas composition which is related to the reduction (metal alloy formation) and CO_2 hydrogenation.

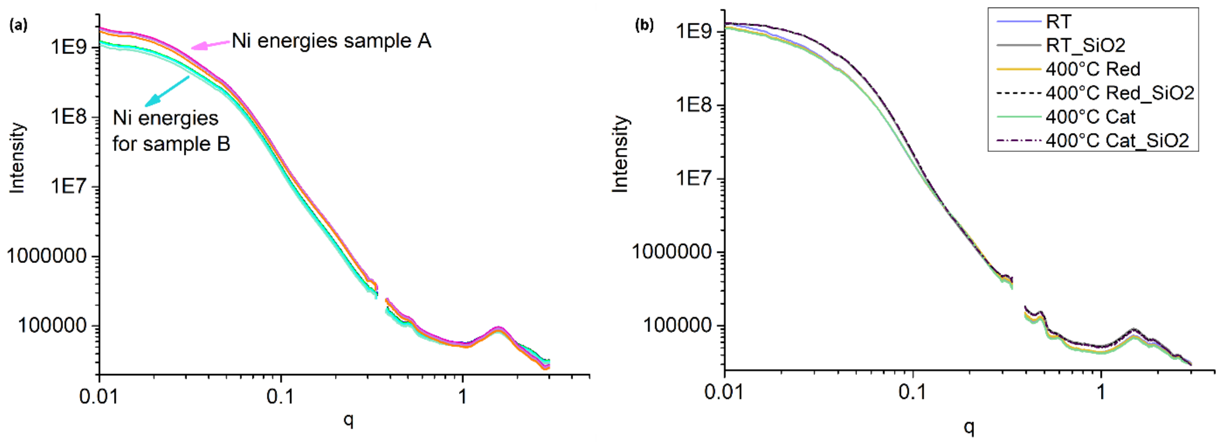

Fig.2: Comparison of the scattering curves at all Ni energies at 25°C for 2 Ni-Fe/SiO_2 catalysts (a) together with the scattering curves at one specific Ni energy (8.263 keV) during an *operando* experiment for Ni-Fe/SiO_2 and pure SiO_2 (b) (Red: H_2:He = 1:1, Cat: H_2:CO_2:He = 4:1:5, 1 bar). The depicted scattering curves are not yet background subtracted and normalized.