EUROPEAN SYNCHROTRON RADIATION FACILITY

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Experiment Report Form

ESRF	**Experiment title:** In situ PDF study on MOF-derived Nickel methanation catalysts under dynamic operation conditions	**Experiment number**: CH6069
Beamline: ID15A	**Date of experiment**: from: 18.01.22 to: 22.01.22	**Date of report**: 05.09.2022 *Received at ESRF:*
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Report:

With this proposal, we wanted to investigate how a dynamic gas feed during the reaction $4H_2 + CO_2 \leftrightarrow CH_4 + 2H_2O$ influences the structure of a Ni_3Fe catalyst. For this purpose we performed 3 experiments with changing gas feed, namely: Full hydrogen dropouts (activation of the catalyst in 100% H_2, followed by 30 min catalysis with 8 mL/min H_2 and 2 mL/min CO_2 followed by 30 min dropout with 0 mL/min H_2, 2mL/min CO_2, 8 mL/min He, overall 7 cycles), partial dropouts (activation, 30 min catalysis followed by 30 min dropout with 4 mL/min H_2, 2 mL/min CO_2, 4 mL/min He, overall 7 cycles), stochiometric dropouts (activation, 30 min catalysis followed by 30 min dropout with 4 mL/min H_2, 1 mL/min CO_2, 5 mL/min He, overall 7 cycles).

We collected the data using a Dectris Pilatus 3 CdTe 2M with an X-ray energy of 65 keV, which led to a Q-range of 0.7-30.8 $Å^{-1}$. We knew from earlier beamtimes with this detector, that strong scattering samples can produce a memory/ghosting effect. Therefore, we reduced the measuring time to 1 s, followed by 30 s sleep. The full dropouts revealed an interesting phase behavior of the Ni_3Fe alloy catalyst. At room temperature, the sample consisted of mostly Ni_xFe_y alloy fcc structure, with sidephases of the corresponding oxides. This was expected, as the samples were stored under air. During the experiments the ratios of the sidephases changed (see Figure1).

The conversion of CO_2 to CH_4 decreased with time on stream, visible in the decreasing MS signal of CH_4.

The experiments with partial and stochiometric dropouts of H_2 showed a less harsh response in the phase transition and the CO_2 conversion. We think that these results are of great value, especially for the catalysis community, that is trending towards catalysts that are comprised of more than one metal.

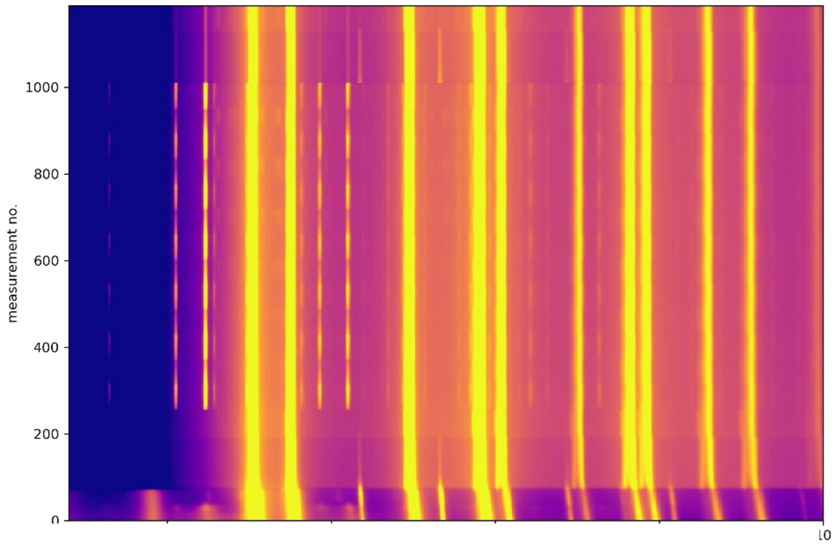

***Figure 1**: Heatmap of the PXRD patterns during full H_2 dropouts.*

To study the structural behavior right after the gas feed change with a higher time resolution, we conducted a 4th experiment under full H_2 dropout conditions, where we reduced the frames per image to 100 ms, with a total 600 frames after the gas feed change. This resulted in several ten thousand datasets, which are still under investigation. The above experimental results will be connected to complementary XAS and XES data measured at DESY Petra III beamline P65 and P64, and the goal is to submit a publication during the second funding phase of the DFG priority program SPP2080.

Another experiment that we conducted was the tracking of structural deviations inside the catalyst bed, by applying a horizontal scan along the catalyst bed. We took 1 s measurements at 11 points with 1 mm distance and a 150x150 micron beam size. This data is still under study.

A reference catalyst consisting of NiO on an Al2O3 support synthesized by an urea precipitation method was also measured. We applied the same gas feed conditions as for the full H_2 dropouts described above.