ESRF	**Experiment title: Test of a new hypothesis on the structure of a Ni catalyst during the catalyzing of the methanation reaction.**	**Experiment number**: CH-2508
Beamline: ID03	**Date of experiment**: from: October 3rd 2007 to: October 9th 2007	**Date of report**: 27 Feb. 2009
Shifts: 18	**Local contact(s)**: Olivier Balmès	*Received at ESRF:*

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Report:

The aim of the experiment was to investigate the structure and morphology of the nickel carbide which appears on the (111) surface of a Ni single crystal when heating the UHV-prepared surface under a $CO+3.H_2$ mixture at near-atmospheric pressure. This carbide decomposes when heating further. Its decomposition is accompanied by a strong increase of the rate of the Ni-catalyzed methanation reaction $CO + 3\ H_2 => CH_4 + H_2O$.

In the proposal, it was suggested that the carbide may form vertical nanowires. This would have important consequences on the mechanism of the methanation reaction : in particular, the decomposition of the carbide would provide a "redispersion" of the catalyst as small particles, even though the initial geometry of the catalyst is that of a flat (111) surface.

Technical developments were done specially for this experiment, in order to improve the compatibility of the UHV-HP chamber with GISAXS measurements, by reducing the background signal due to the small-angle-scattering by the Be windows. First, a xz-motorized beam stop was mounted outside the reactor, to block both the beam specularly reflected by the sample and the scattering arising when this beam crosses the exit Be window. To be effective, such a system needs to be as close as possible to the exit Be window.

Secondly, a manually-actuated slit was mounted inside the reactor, with z-translation and theta-rotation motions, to block the scattering produced when the incident beam crosses the entrance Be window (upstream of the sample). This second system was installed but not used due to a mechanical problem. To be effective, such a slit needs to be as far as possible from the window, whichs bring the slit quite close to the sample (10 mm) due to the small diameter of the chamber (80 mm).

There was however another strong and unforeseen source of SAXS background in the experiment, due to scattering by beam-induced-oxide accumulated on the exit Be window of the KB microfocussing system. This signal needs to be removed for future experiments.

Also, for future experiments it would be preferable to focus the beam vertically with the KB instead of using the toroidal mirrors, to confine the incident beam to the sample surface. The lead pipe between the slits on the detector arm also needs to be remounted, to reduce the overall background, which limited the sensitivity for detection of carbide peaks. Working at incidence near the critical angle (0.17°) instead of the usual 1° will also improve the sensitivity for detecting thin carbide, as shown during the last days of the experiment.

Three weeks were taken before the experiment to add the new parts for the GISAXS on the reactor, and to do catalysis tests.

On the sample preparation side, a pre-requisite for this experiment was to reproduce the results of Ref [1] with respect to catalyst activity for the methanation. The idea being to investigate a possible link between the final carbide morphology and the reaction rate after carbide removal.

This unfortunately failed : the reaction rate at 400°C was at least 100 times below the value observed in the experiments of Ref. 1 (May 02 and Nov 02). Instead of producing methane, the methanation reaction produced "coke" on the catalyst surface, visible as black dust particles.

The carbide of interest, which is the one forming under the stoechiometric $CO+3H_2$ mixture, could not be obtained : we had to expose the sample to a stronger treatment (pure CO + higher temperature) to form carbide. Also, we had to change the surface preparation to render the surface reactive with respect to CO : high pressure treatments were needed, with O_2 oxidation followed by H_2 reduction. The UHV-prepared surface (using sputter-anneal treatments) was exceptionally unreactive with respect to gas exposures, be it CO or O_2. It was so passivated that the formation of a 2D diamond layer was evocated, as a possible result of a too high partial CO pressure (due to sample outgassing) during the high temperature anneal.

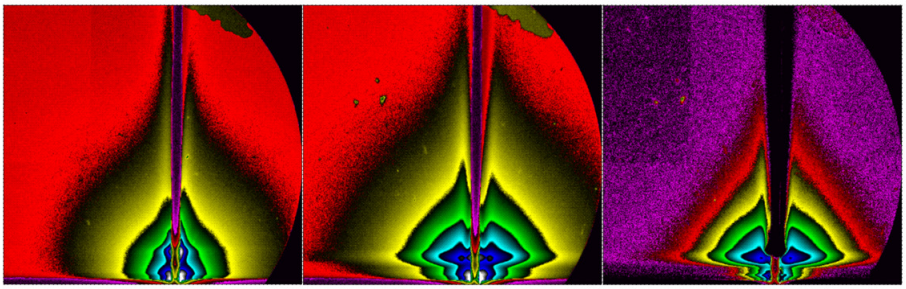
Tests are under way in order to understand why the catalyst failed. Current focus is on UHV surface preparation and gas line contamination.

Ex-situ FEG-SEM after repreparing the surface by sputter-anneal showed numerous unexpected micron-sized particles, which may act as sources of impurities that would cover the surface during high temperature anneal. The reaction will therefore first be tested using a dummy polycrystalline Ni sample.

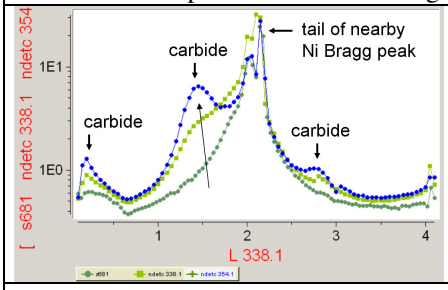
Also, a greasy compound was found in the regulator of the Ar bottle connected to the gas line, raising suspicion about a contamination of the gas line. A simpler gas line will therefore be assembled temporarily for the purpose of testing. Also a new syngas bottle will be used. In Nov 07, a bottle beyond the expiry date (i.e. with unwarranted purity) had to be used due to a delay in delivery.

Catalytic activity will be tested in the reactor using mass spectrometry for gas analysis. Post-reaction surface morphology will be examined by SEM.

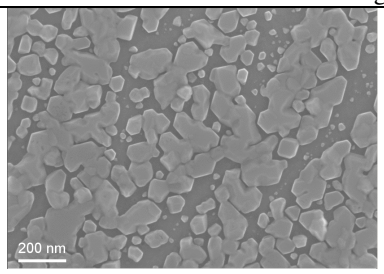
In spite of the problems encountered in Nov. 07, a number of encouraging results could be collected from the experiment : on the carbide-covered surface, nano-islands were observed, both in situ using GISAXS and ex situ using FEG-SEM.



in situ GISAXS pattern : from left to right : clean Ni surface / with Ni carbide islands / difference image



in situ surface diffraction : L-scan along a carbide rod, on the clean Ni and during the carbide growth



ex situ image of the islands by FEG-SEM

The "GISAXS" signals presented here are in fact better described as off-specular reflectivity. Indeed, GISAXS would correspond to a small perturbation of the reflectivity from a surface that remains mostly flat, while here the specular rod is strongly affected : the final carbide-covered is notably rougher than the initial Ni(111) surface. Therefore, the interest of the beam-stop system just downstream of the chamber is limited to thin carbide : at this stage low Be-scattering background and high sensitivity are needed to detect the GISAXS signal from the thin islands. For thicker carbide, a significant part of the reflectivity goes off-specular, and this can be detected even on top of Be-scattering.

Concerning the carbide crystallographic structure, the L-scans along the carbide rods were found to present not only HCP peaks but also FCC peaks, with an increasing HCP / FCC ratio during growth. Further reciprocal space mapping is however needed to confirm the existence of FCC carbide.

Comparison with the previous experiments showed that the "pure CO" carbide differs from the "CO + H2" carbide. First the in-plane lattice parameter of the "CO+H2" carbide is closer to the one of Ni, by about 2%. Second, exposure to $CO+H_2$ gives only carbide, while exposure to pure CO also gives graphite powder. The graphite formation is clearly favored by the x-ray beam : a beam footprint is clearly visible. The SEM image shown here is taken outside of the beam footprint.

To get the carbide structure and morphology relevant to the real conditions for methanation, the study of carbide growth needs to be repeated under CO+H2. One can expect that the smaller lattice mismatch with Ni will change the lateral size of the islands. Also, the graphite formation will be avoided, which is desirable as it may partially block the carbide growth.