ESRF	**Experiment title: Structure sensitivity of hydrogenation of CO over Ru nanoparticles**	**Experiment number**: MA-1715
Beamline: ID03	**Date of experiment**: from: 10-04-2013 (8:00) to: 13-04-2013 (8:00)	**Date of report**: 26-02-2014
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Report:

The goal of the experiments was to investigate structure sensitivity of Ru nanopearticles during the hydrogenation of carbon monoxide. Previous experiments with mass selected Ru nanoparticles on SiO_2/Si substrates showed increasing turn over frequencies for the hydrogenation of carbon monoxide with increasing particle size. The reaction is believed to be catalyzed by strongly under-coordinated surface sites and will therefore strongly depend on the particle morphology. Transmission electron microscopy (TEM) of the mass selected Ru nanoparticles, produced in a cluster source located in the Physics Department at DTU, indicated larger particles to be aggregates of smaller subunits with morphologies far away from their equilibrium shape, while smaller particle showed morphologies close to the equilibrium shape. Furthermore, higher deactivation of the larger Ru particles compared to their smaller counterparts was observed. With a combination of grazing incidence X-ray diffraction (GIXD), grazing incidence X-ray small angle scattering (GISAXS) and mass spectroscopy we expected therefore to observe a transformation of the larger polycrystalline Ru nanoclusters to single crystalline particles, accompanied by changes in the particle morphology and a decrease in the turn over frequency for the hydrogenation reaction. Additional grazing incidence X-ray absorption near edge spectroscopy (GIXANES) was planned to resolve the oxidation state of the particles in oxidizing atmosphere.

The experiment was a first time proposal and unfortunately we encountered several difficulties during the allotted beam time. With the energy of 22 keV (slightly below the Ru K-edge) proposed for the experiments and with a focused beam, we were not able to obtain any GIXD or GISAXS signal. Only after decreasing the energy of the incident beam to 11 keV and expanding the beam, we were able to acquire GIXD patterns for samples with high surface coverage. We do not know the reason for it, but radiation damage of the sample might be an explanation. The GISAXS, acquired with an additional Pilatus 300K detector placed about 2 m behind the sample, was too weak to distinguish it from the background scattering from air and the Be doom of the flow cell, provided by the ID03 beam line. We performed the experiment in continuous gas flow. Even at the lowest possible flow rates were the conversion levels of CO to methane not sufficient for a proper detection.
In plane GIXD was acquired during heating in a flow of CO in H_2 (2:98) from room temperature to 427C from two samples with particles with masses corresponding to a diamter of 7 and 10 nm, assuming spherical morphology. From analysis of the FWHM of the Ru(100), (002) and (101) reflection of the fresh samples a mean lateral crystallite size of d_{7nm} = 3.9 nm +/- 0.2 nm for the 7 nm particle and d_{10nm} = 10.4 nm +/- 0.7 nm for the 10 nm particles was determined. The mean crystallite sizes obtained from GIXD matching well with previous observations by TEM. In fact the particles with an expected diameter of 7 nm seemed to consisting to a large extend of tetramers from subunits with a diameter of 4 nm, see figure. However, the GIXD data indicates that the particles with an expected diameter of 10 nm seem to a large extend to be single crystalline. The determined mean lateral crystallite diameter for both particle sizes remained constant during the heating to 427C in a reactant gas, revealing that the deactivation observed in our laboratory experiments may not be explained by particle sintering or the formation of single crystalline particles.

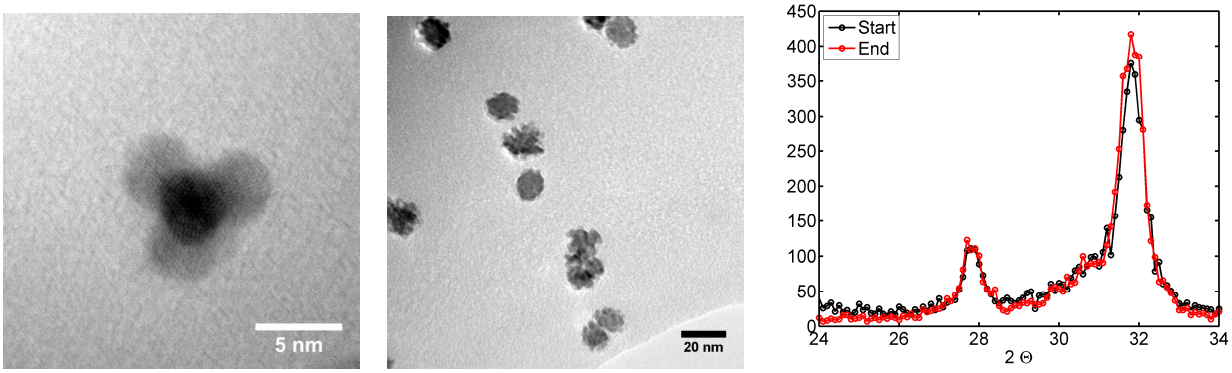

Figure: TEM of Ru nanoparticle with a masses corresponding to a diameter of 7 nm (left) and 10 nm (middle) and GIXD from a 10 nm Ru sample at the start (black) and after 2 heating cycles from RT to 427C during a hydrogenation of CO experiment.

Though we were not able in this first time proposal to achieve the expected data from all different proposed techniques, we are certain that experiments with similar prepared model catalyst systems from our cluster source at ID03 are feasible, but they will require further optimization in respect of beam size and energy, sample and sample environment.
We would like to express our gratitude to the beam line scientist in charge, who spent a substantial amount time identifying the optimum conditions to obtain the GIXD data.