INDUSTRIAL PILOT PROJECT

X-ray Absorption Spectroscopy for in-depth understanding of NiMo catalysts used for biofuel production

THE INDUSTRIAL CHALLENGE

Lignin is a biproduct from the pulp and paper industry that has a large potential as a renewable feedstock to produce value-added chemicals, biofuels, and aromatics. One of the important steps in the production of biofuel from lignin is the catalytic hydrotreatment processes. For this process Sun Carbon has developed a tailored $NiMo/Al_2O_3$ catalysts. A key requisite for designing and optimizing the catalytic process is to be able to link the catalytic properties with the detailed characteristics of the catalysts.

WHY USING A LARGE SCALE FACILITY

Due to the thin layer of active metals (Ni and Mo) on the support (Al_2O_3), the characterisation of the catalyst is a challenge. Synchrotron-based X-ray absorption spectroscopy (XAS) was identified as a very promising technique – both for characterising the catalysts itself but also for in-situ studies of redox reactions and of the activation of the catalyst. The technique would, theoretically, also allow operando studies of relevant catalytic processes. One major advantage is that vacuum is not needed when performing XAS at photon energies above ~2000 eV. This allows studies at high pressures, as well as minimal sample preparation (avoiding introduction of potential artefacts).

HOW THE WORK WAS DONE

The XAS experiments took place at the Balder beamline, MAXIV Laboratory. Two different types of material systems were studied: *i*) industrial catalysts ($NiMo/Al_2O_3$) and *ii*) model systems composed by NiMo nanoparticles (NPs). The NP model system was designed with the attempt to perform operando studies in the future. Both types of samples were produced with two Ni:Mo molar ratios (1:2 and 2:1) and the measurements were performed for samples 'as produced' in ambient atmosphere (ex-situ) and in-situ. In the in-situ measurements, the redox reactions of Ni and Mo was studied using two different chamber set-ups in which the samples could be heated up to 500- 600 °C while flowing either 5% O_2 in N_2 or and 5% H_2 in N_2 over the samples. Primarily XANES (the energy region just above the absorption edge) were used, but also EXAFS were measured for a selected number of sub-samples ex-situ. The measurements were performed both in transmission mode and in fluorescence mode to allow correction for self-absorption.

THE RESULTS AND EXPECTED IMPACT

High quality XANES and EXAFS spectra could be retrieved ex-situ, revealing information of the chemical state of Ni and Mo before and after activation. The measurement reveal that the initial oxidation state of the industrial catalyst was different to the NPs but that after reduction during heating, the samples look very similar. The in-situ studies allowed to follow the redox reactions as a function of temperatures in either an oxidizing or reducing atmosphere. Critical information of the on-set temperature of material transformations could be retrieved. As an example, initially the Ni and Mo in the industrial catalyst did not seem to form a real alloy. This was first formed when heated in a reducing environment.

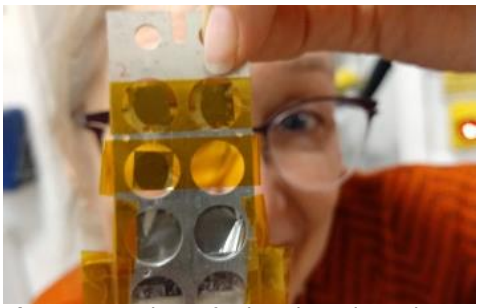

Figure. A variety of NiMo based catalysts were tested with XAS at the Balder beamline at MAX IV.

Based on the learnings about the model particles and the possibilities and limitations with XAS, we conclude that the technique could allow future operando studies during catalytic reaction using a chamber for high pressure experiments.

SunCarbon

Contacts: Christian Hultenberg, SunCarbon, christian@hulteberg.com
Sara Blomberg, Lund University, sara.blomberg@chemeng.lth.se
Jenny Rissler, Research Institutes of Sweden (RISE), jenny.rissler@ri.se

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