

In-situ Scanning Transmission X-ray Microscopy of catalytic materials under reaction conditions

Emiel de Smit¹, J. Fredrik Creemer², Henny W. Zandbergen³, Bert M. Weckhuysen¹ and Frank M.F. de Groot¹

¹Inorganic Chemistry and Catalysis group, Debye Institute for Nanomaterials Science, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, Netherlands

²DIMES-ECTM, Delft University of Technology, 2600 GB Delft, Netherlands

³Kavli Institute of NanoScience, National Centre for High Resolution Electron Microscopy, Delft University of Technology, 2600 GA Delft, Netherlands,

*e.desmit@uu.nl

Abstract. In-situ Scanning X-ray Transmission Microscopy (STXM) allows the measurement of the soft X-ray absorption spectra with 10 to 30 nm spatial resolution under realistic reaction conditions. We show that STXM-XAS in combination with a micromachined nanoreactor can image a catalytic system under relevant reaction conditions, and provide detailed information on the morphology and composition of the catalyst material. The nanometer resolution combined with powerful chemical speciation by XAS and the ability to image materials under realistic conditions opens up new opportunities to study many chemical processes.

1. Introduction

Scanning X-ray Transmission Microscopy (STXM) beamlines are being developed at many synchrotron radiation sources worldwide. A recent overview of STXM beamlines is provided by Hitchcock et al¹. The STXM technique uses a focused soft X-ray beam to make a two dimensional raster scan of a sample at a specified energy. X-rays are absorbed by the sample and the transmitted signal is detected. By changing the energy of the incident X-ray beam, images can be acquired over a range of energies, yielding a full X-ray Absorption Spectrum (XAS) per measured point. The resulting spectromicroscopic technique is called STXM-XAS, in analogy to Scanning Transmission Electron Microscopy (STEM) in Electron Energy Loss Spectroscopy (EELS) mode. STXM-XAS and STEM-EELS provide access to the same soft X-ray absorption spectra, where the spatial resolution of STEM-EELS is in the range of, typically, 0.5 nm versus the 10 to 30 nm resolution provided by STXM-XAS beamlines^{2,3}.

The main difference X-ray and electron microscopy is the reduced interaction cross section of X-rays with matter, yielding the possibility to measure thicker samples in transmission mode. The maximum thickness is a few hundred nm in STEM-EELS versus ~10 micron for STXM-XAS, depending on the material and X-ray absorption edge energy. In addition, the reduced cross section yields less/different

sample damage¹. STXM-XAS can, in principle, be measured in a number of detection modes, including electron yield that turns the technique into a (vacuum) surface probe. Fluorescence yield allows macroscopic samples and also low detection limits for dilute systems. We have used the STXM in transmission mode. A major experimental challenge was to overcome the strong attenuation of soft X-rays in gaseous atmospheres, which makes the technique difficult to apply under realistic reaction conditions.

The first in-situ STXM-XAS experiments on a working catalyst have been published in 2008. The reduction of an iron-based Fischer-Tropsch catalyst was carried out in H₂ at 1 bar, between 50 and 450 °C while imaging the catalyst with a spatial resolution of 35 nm. The Fischer-Tropsch reaction enables the production of high-purity chemicals and transportation fuels from sources other than conventional crude oil, most notably natural gas, coal and biomass. The STXM-XAS experiments have been performed under actual Fischer-Tropsch conditions, using a mixture of CO and H₂ gas. The correlations of the carbon K edge of the substrate with the iron L edge of the catalyst indicates that carbon is mainly formed at the iron nanoparticles, whereby the nature of carbon is different at sites away from the iron nanoparticles⁴. As such, this nanoscale chemical imaging technique provides insights into the *local* morphologically and chemically dependent reduction behavior of a complex Fischer-Tropsch catalyst system. The extent and rate of reduction of the iron oxide phase were shown to depend on its chemical surroundings and the extent of interaction with the underlying support material⁵.

2. Experimental

STXM experiments were performed at beamline 11.0.2⁶ of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory in Berkeley, CA, USA and beamline 10ID-1 (SM) at the Canadian Light Source (CLS) in Saskatoon, SK, Canada. Images were recorded with a step size of 35 nm. To minimize the interaction between X-ray light and gas phase molecules, we applied a specially designed nanoreactor⁷ which reduced the gas path length to 50 μm. The nanoreactor consists of a reactor chamber of about 500 x 500 x 50 μm³ which was supplied with gasses by micrometer-sized gas channels and fitted with a resistive Pt heater element, allowing heating up to 500 degrees Celsius. The nanoreactor contains 5 x 5 micron areas that have a window thickness of 10 nm. The transmission through the 20 nm SiN_x windows, the 50 micron 1 bar gas atmosphere and a 100–5000 nm thick sample allows for excellent in-situ STXM-XAS experiments.

3. Results

We have performed in-situ STXM on magnetite Fe₃O₄ nanoparticles. Figure 1 shows the Fe₃O₄ nanoparticles under 1 bar of hydrogen at 150 °C. The average iron L edge spectrum at 150 °C is essentially a pure magnetite spectrum, which indicates that the whole sample consists of the magnetite Fe₃O₄ phase. At 250 °C, the iron L edge has changed and now appears as a combination of iron oxide and iron metal. The iron L edge is measured in each 35x35 nm pixel and the spectral shape of each pixel is simulated as a linear combination of Fe₃O₄, a divalent iron oxide and iron metal. Figure 1 shows the reduction at 250 °C, where the sample is reduced in a very inhomogeneous manner with regions that remain essentially Fe₃O₄ (blue) next to regions that are largely reduced to iron metal (red). At higher temperatures the whole sample reduces to iron metal. An important finding is that the reduction of iron oxides is extremely inhomogeneous, with metal existing next to oxide regions on a scale of 50 nm.

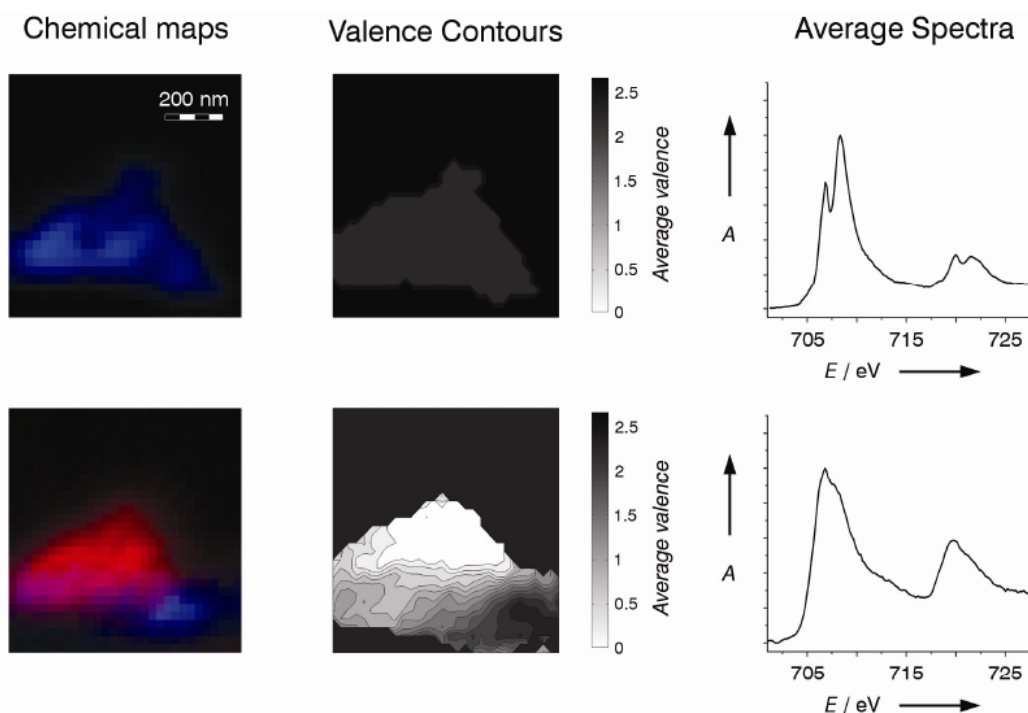


Figure 1: Chemical maps (left), Valence contour maps (middle) of the iron-oxide particle and Fe L_{2,3}-edge spectra averaged over the entire particle (right) for reduction in H₂ at 150 °C (top) and 250 °C (bottom). Blue pixels indicate the presence of Fe₃O₄; red pixels indicate the presence of Fe⁰. The pixel dimensions of the chemical map are 35 x 35 nm². The valence contours maps indicate the distribution of the average valence of iron species over the particle. The iron phase is significantly reduced to Fe⁰ at 250 °C.

This Fe₃O₄ reduction experiment shows the possibility to map materials under active conditions with a spatial resolution of 30 nanometres. This type of in-situ STXM-XAS could also be used to study other systems in specialized or extreme environmental conditions. This is not limited to catalysts, and it can also be used for many other applications, such as detecting airborne (pollution) particles, studying structural changes in hydrogen storage materials, or examining the distribution of medical nanoparticles in cells.” In addition, one can imagine in-situ tomographic imaging of catalytic solids under working conditions, including the in-situ study of the material synthesis and activation.

The examples show the possibility to map materials under working conditions with a spatial resolution of 30 nanometres. This type of in-situ STXM-XAS could also be used to study other systems in specialized or extreme environmental conditions. This is not limited to catalysts, and it can also be used for many other applications, such as detecting airborne (pollution) particles under various atmospheric conditions, studying structural changes in hydrogen storage materials under hydrogen removal, studying the charging of batteries.

It is evident that there is a bright future for nanoscale chemical imaging using in-situ STXM experiments. The goal is to improve the temperature and pressure range up towards 1000 °C and 10 bar, thereby extending the range of feasible materials science and catalysis experiments. In addition to the present type of nanoreactors, we are working to extend the range of in-situ STXM experiments and a number of new routes are being investigated. An in-situ reactor cell will be developed for liquid state transmission experiments, which implies the reduction of the X-ray optical path to a few microns. X-

ray tomographic experiments need the possibility to rotate the sample. Because the nanoreactors use 10 nm thick windows of a few micron diameter, it is not possible to rotate the complete nanoreactor. An option would be to develop a nano-rotation stage for the sample, maintaining the nanoreactor itself in a fixed position. STXM at low concentrations (down to 100 ppm) are not possible in transmission mode, implying that Fluorescence yield detection must be used. Such fluorescence yield based experiments would allow the mapping of impurities/promoters in heterogeneous catalyst and in materials science in general. In-situ STXM will likely never reach the 0.1 nm spatial resolution as obtained from electron microscopy. STEM-EELS experiments on the other hand will be unfeasible for many samples and for many sample conditions⁸. A useful solution would be to combine in-situ STXM-XAS experiments with ex-situ STEM-EELS experiments on the same sample positions. One could imagine measuring a catalyst ex-situ with STEM-EELS, performing some treatment in-situ with a STXM nanoreactor and performing a second STEM-EELS experiment after reaction.

4. Concluding remarks

We have demonstrated that STXM-XAS can image a catalytic system as complex as an iron-based Fischer–Tropsch system under catalytically relevant reaction conditions, and deliver detailed information on the morphology and composition of the catalyst material.

The STXM nanometer resolution combined with powerful chemical speciation by XAS and the ability to image materials under realistic conditions in a nanoreactor opens up opportunities to study many chemical processes taking place on solids.

Acknowledgements

E.d.S., B.M.W and F.d.G. acknowledge financial support from the Netherlands National Science Foundation (NWO).

References

1. A. P. Hitchcock, J. J. Dynes, G. Johansson, J. Wang and G. Botton, *Micron* **39**, 741 (2008).
2. D. A. Muller, *Nat. Mater.* **8**, 263 (2009).
3. J. M. Thomas and J. C. Hernandez-Garrido, *Angewandte Chemie* **48**, 3904 (2009).
4. E. de Smit, I. Swart, J. F. Creemer, G. H. Hoveling, M. K. Gilles, T. Tylizczak, P. J. Kooyman, H. W. Zandbergen, C. Morin, B. M. Weckhuysen and F. M. F. de Groot, *Nature* **456**, 222 (2008).
5. E. de Smit, I. Swart, J. F. Creemer, C. Karunakaran, D. Bertwistle, H. W. Zandbergen, F. M. F. de Groot and B. M. Weckhuysen, *Angewandte Chemie* **48**, 3632 (2009).
6. T. Warwick, K. Franck, J. B. Kortright, G. Meigs, M. Moronne, S. Myneni, E. Rotenberg, S. Seal, W. F. Steele, H. Ade, A. Garcia, S. Cerasari, J. Delinger, S. Hayakawa, A. P. Hitchcock, T. Tylizczak, J. Kikuma, E. G. Rightor, H. J. Shin and B. P. Tonner, *Rev. Sci. Instrum.* **69** (8), 2964 (1998).
7. J. F. Creemer, S. Helveg, G. H. Hoveling, S. Ullmann, A. M. Molenbroek, P. M. Sarro and H. W. Zandbergen, *Ultramicroscopy* **108**, 993 (2008).
8. J. M. Thomas and J. C. Hernandez-Garrido, *Angewandte Chemie* **48**, 3904 (2009).