

# Nanoscale Chemical Imaging of a Working Fischer-Tropsch Catalyst by *in situ* Scanning X-ray Transmission Microscopy

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## Introduction

Microscopy is a widely applied tool in the characterization of heterogeneous catalysts. From infrared light to electron beams, contemporary microscopists apply the full wavelength spectrum to image catalytic materials on different microscopic scales. Modern microscopes often integrate spectroscopy with imaging techniques to simultaneously obtain morphological and quantitative chemical information on a sample (for example by STEM-EELS, Infrared, UV-VIS or Fluorescence Microscopy) under catalytically relevant conditions.

Scanning X-ray Transmission Microscopy (STXM) [1], with its current 15 nm spatial resolution and high chemical speciation potential by X-ray Absorption Spectroscopy (XAS), is a recent promising addition to the field. The technique uses a focused soft X-ray (200 – 2000 eV) beam to make two dimensional raster scans of a sample. X-rays are absorbed by the sample and 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 absorption spectrum per measured point.

The main experimental challenge is to overcome the strong attenuation of soft X-rays in gaseous atmospheres, which makes the technique difficult to apply under realistic reaction conditions. Here, we use a specially designed nanoreactor [2] to overcome this challenge and study the distribution and chemical identity of iron and carbon species in an Fe<sub>2</sub>O<sub>3</sub>/CuO/K<sub>2</sub>O/SiO<sub>2</sub> Fischer-Tropsch Synthesis (FTS) catalyst during reduction in H<sub>2</sub> at 350°C and FTS in CO/H<sub>2</sub> at 250°C [3].

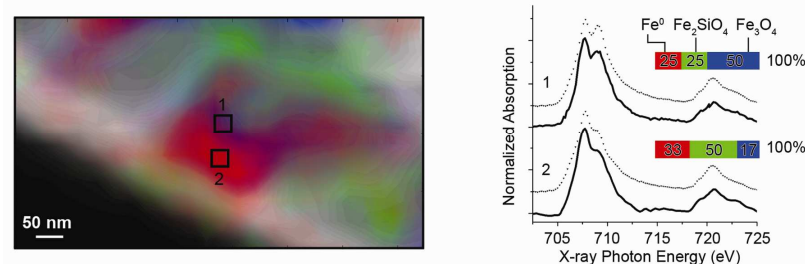
## Materials and Methods

The promoted Fischer-Tropsch catalyst was synthesized by precipitation from an iron nitrate solution [3]. All experiments were performed at STXM beamline 11.0.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory in Berkeley, CA,

USA. Images were recorded with a (x, y) step size of 35 nm. The nanoreactor [2] reduced the gas path length to 50 μm, minimizing the interaction between X-ray light and gas phase molecules. The reactor consists of a reactor chamber of about 500 x 500 x 50 μm which is supplied with reactant gasses by micrometer-sized gas channels and is fitted with a resistive Pt heater element, allowing heating up to 500 °C.

## Results and Discussion

Studying the catalyst material during reduction and FTS revealed 35 nm spatial variations in the iron valence and its metal/carbide/oxide nature. After reduction, the catalyst material consisted mainly of iron (II) silicates, iron oxide and small amounts of α-Fe. During FTS remaining iron oxide was converted into iron (II) silicate species and Fe<sup>0</sup> (Fig. 1). Both sp<sup>2</sup> and sp<sup>3</sup> hybridized carbon species were observed. Sp<sup>2</sup> species were found to be almost exclusively located near Fe<sup>0</sup> species, indicating the conversion of α-Fe into iron carbides. Sp<sup>3</sup> species were also found unassociated from the Fe<sup>0</sup> species indicating the formation and spreading of FTS products over the support material.



**Figure 1:** Spatial distribution map (left) of iron species over the SiO<sub>2</sub> support (white) and Fe L<sub>2,3</sub>-edge XAS spectra (right) after reduction in H<sub>2</sub> at 350°C for 2 h.

## Significance

STXM was applied under *in situ* conditions to study the physicochemical properties of a complex iron-based FTS catalyst. It was illustrated that STXM is a versatile tool in the characterization of catalytic solids. Its nanometer resolution combined with powerful chemical speciation by XAS and the ability to image materials under realistic catalytic conditions opens up opportunities to study many chemical processes taking place on solids – including, but certainly not limited to heterogeneous catalysis.

## References

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