

Nanoscale Chemical Imaging of a Working Catalyst

The heterogeneous catalysts used in most chemical processes typically consist of nanoscale metal or metal oxide particles dispersed on high-surface-area supports. While these particles are the active elements of the catalyst, the overall performance depends not only on their size and composition but also on their multiple interactions with the support, reactants, and products. Probing this chemical soup in real time under realistic reaction conditions is such a tall order that in some cases even the catalytically active chemical species is not known. A Dutch team working at the ALS has combined scanning transmission x-ray microscopy with a reaction chamber adapted from electron microscopy to identify the chemical species present for an iron-based Fischer–Tropsch synthesis catalyst and to image their distribution on the nanoscale. When developed further, this new tool may give chemists the ability to design and tailor catalysts for maximum selectivity and efficiency in a wide range of chemical processes.

In the Fischer–Tropsch process, synthesis gas, a mixture of CO and H₂, is converted through a surface polymerization reaction into liquid hydrocarbons of various forms that can then be used in the production of high-purity chemicals and transportation fuels without the need for crude oil.



Artist's conception of the Fischer–Tropsch synthesis reaction in which a carbon–hydrogen chain molecule is generated from synthesis gas (CO and H₂) with the help of a catalyst comprising an iron oxide phase dispersed on silicon oxide (SiO₂) with water and carbon dioxide as by-products. In the drawing, carbon is gray, hydrogen is white, and oxygen is red.

The most common catalysts are based on iron and cobalt. For its in-situ soft x-ray scanning transmission microscopy (STXM) study at ALS Beamline 11.0.2, the Dutch team used an iron-based catalyst consisting of an iron oxide phase dispersed on

silicon oxide (SiO₂), with copper oxide and potassium oxide promoters added to improve its selectivity, activity, and stability. The lack of in-situ data under reaction conditions makes it difficult to control phase transformations in the complex iron–

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Research conducted by E. de Smit, I. Swart, C. Morin, B.M. Weckhuysen, and F.M.F. de Groot (Utrecht University, The Netherlands); J.F. Creemer, G.H. Hoveling, P.J. Kooyman, and H.W. Zandbergen (Delft University of Technology, The Netherlands); and M.K. Gilles and T. Tyliczszak (ALS).

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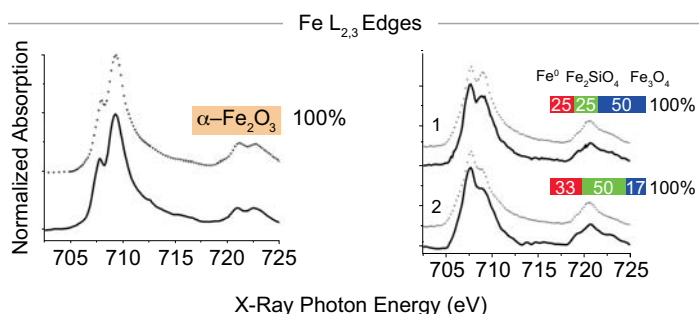
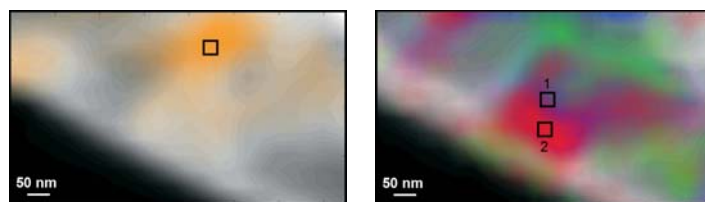
oxygen–carbon system, which can be important in maintaining catalyst performance.

Use of STXM to study this catalyst under reaction conditions solves the nanoscale part of the problem but suffers from the transmission-limiting high gas pressures (one atmosphere or higher) typically encoun-

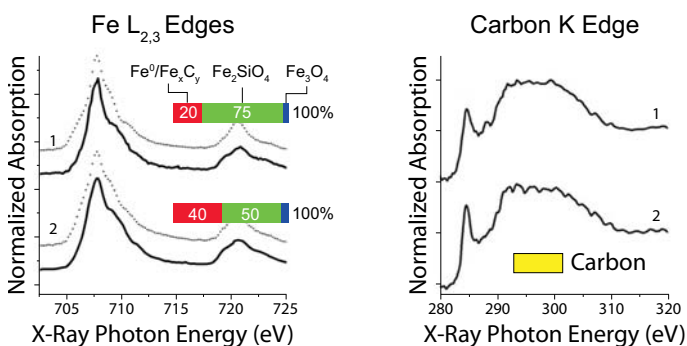
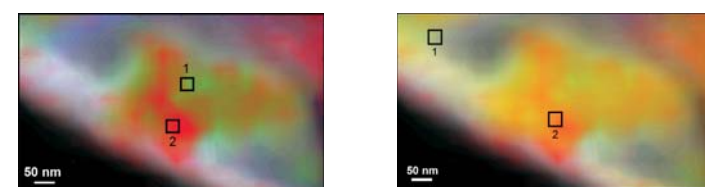
Watching Catalysts at Work

Catalysts—substances that speed up chemical reactions without themselves being consumed—are essential to the production of many industrially important chemicals. They also play a large role in environmental chemistry, most famously exemplified by the catalytic converters that reduce toxic emissions from vehicle tailpipes. Because of their importance, researchers all over the world are working to better understand how catalysts work and how to improve them, a stiff challenge both because many catalysts come in the form of tiny nanometer-sized particles and because they operate in gaseous atmospheres at high temperature that complicate probing. As a result, such nanoscale catalysts could until recently only be observed before and after, but not during, a reaction.

The Fischer–Tropsch synthesis of hydrocarbon chains for use in the production of high-purity chemicals and transportation fuels from sources other than crude oil is a case in point. The complex chemistry associated with the iron-based catalyst has made even the identity of the active catalyst at work an unsolved mystery. At the ALS, de Smit et al. have used an x-ray microscopy technique with a special sample chamber to probe tiny catalyst particles under working conditions. This new ability to identify the chemical species present and map their spatial distribution could provide the insight needed to guide the design of improved or novel catalysts for a range of important chemical processes.



Iron species contour maps of the catalyst material before catalysis. Maps (top row) of a 400 nm × 750 nm region were constructed from corresponding iron L₃- and L₂-edge (bottom row) and oxygen K-edge (not shown) spectra taken at room temperature in helium before treatment (left) and after 2 h in hydrogen at 350 °C (right). The dotted lines in the L-edge spectra are fits by a linear combination of reference spectra. The bar graphs represent the calculated relative percentage contributions of the different iron phases at the sampling points.



Chemical contour maps of the 400 nm × 750 nm region after Fischer–Tropsch reaction for 4 h in synthesis gas at 250 °C. Left: Iron species map and corresponding iron L₃- and L₂-edge spectra. Right: Composite contour map, showing the distribution of carbon species overlaid on the iron species map and the corresponding carbon K-edge spectra for the indicated sample regions.

tered. To obtain high-quality data, the researchers adapted a “nanoreactor” originally designed for in-situ electron microscopy. The small distance through which the soft x rays traveled in the reaction chamber together with thin silicon nitride windows allowed measurements at atmospheric pressure, and an embedded platinum spiral heater produced temperatures up to 500 °C.

The experiment itself comprised three series of STXM measurements with a spatial resolution of 40 nm: first, in initial characterization at room temperature in helium; then, after two hours at 350 °C in reducing hydrogen gas; and lastly, after a further 4 hours at 250 °C in synthesis gas. To identify the valence and coordination of iron species, spectra were taken

for each pixel at the iron L₃ and L₂ edges; for oxygen-containing species, at the oxygen K edge; and for carbon-containing species, at the carbon K edge. The measurements generated chemical contour maps for the species present. Quantitative analysis of the spectra yielded calculated proportions for the various phases present at each point.

In brief, initially there was a heterogeneous distribution of predominantly α-Fe₂O₃ (the catalyst precursor) and SiO₂ (the support) with no evidence of carbides. After the reducing treatment in hydrogen, significant changes included the appearance of a heterogeneous distribution of Fe₃O₄, FeSiO₄, and an Fe⁰ species. During catalysis, the proportion of FeSiO₄ grew at the expense of Fe₃O₄. Carbon K-edge spectra indicate the

preferential presence of carbon with the Fe⁰, suggesting the formation of iron carbides, a finding consistent with prior knowledge that during a reaction, iron oxide and metallic iron (α-Fe) usually coexist, with the iron

phases largely converted into iron carbide. These measurements demonstrate that STXM can provide details about the morphology and composition of complex catalytic systems under realistic conditions.