

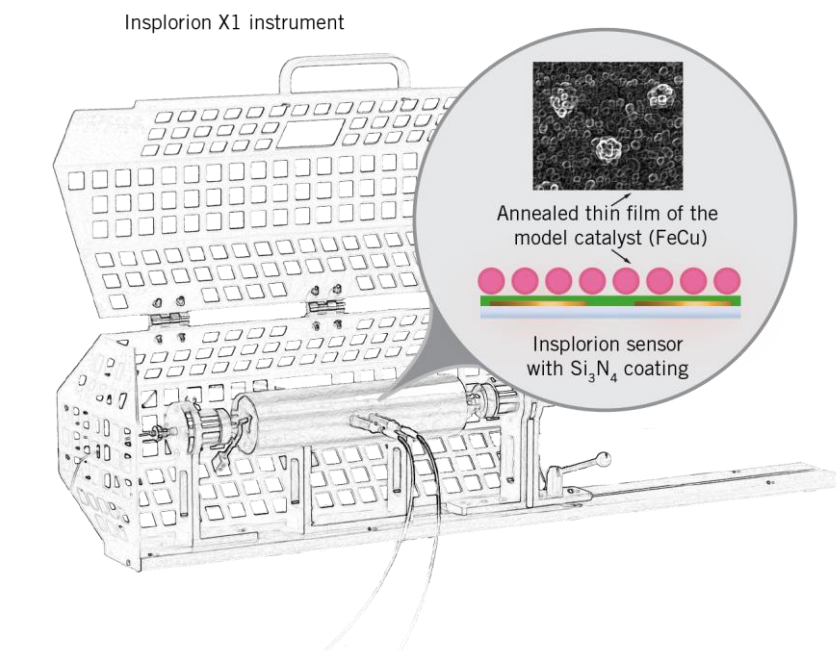
## Reduction of Cu-Promoted Fe Model Catalysts

Insplorion's Nanoplasmonic Sensing (NPS) technology enables measurements of the oxidation and reduction of metal nanoparticles in situ and in real time. In this application note it is shown how NPS can be used to study the reduction of Cu-promoted Fe model catalysts.

### Introduction

The performance of a catalyst is often strongly dependent on its oxidation state. Under reaction conditions, it is common that the catalyst materials take on different oxidation states at different positions in a catalytic reactor due to gas-phase gradients, diffusion limitations and resulting spatial variations. This poses a difficulty when trying to isolate the importance of various catalyst properties for its performance. By using flat, supported model catalysts such problems can be circumvented.

In addition, on flat, supported catalysts, all of the catalytically active material is accessible for characterization by surface sensitive techniques, such as X-ray photoelectron spectroscopy (XPS) and NPS. This opens up the possibility for in situ investigations of the catalyst surface properties, instead of the commonly used pre- and post-use analysis. Since various catalyst phases are only stable at elevated temperatures and in precisely controlled environments, in-situ investigations of catalysts can yield information that otherwise would have been missed and straighten out misconceptions and



**Figure 1:** Insplorion system setup. The inset shows a schematic illustration of the sensor and sample used in this application example (not to scale!). The AFM image shows the catalyst particles (small dark regions) covering the gold nanodisks (brighter regions).

erroneous interpretations deriving from post-reaction changes in the catalyst.

In this application note in situ NPS is used in combination with quasi in situ XPS to study the effect of Cu promotion on Fe catalyst reduction.

### Experimental Procedure

The catalyst material was deposited on Insplorion sensors with  $\text{Si}_3\text{N}_4$  coating. The sensors were annealed to form a terminating  $\text{SiO}_2$  layer. Four different samples were produced by evaporating thin metal films on top of the sensors; (i) Pure Fe, (ii) Pure Cu, (iii) Fe and 20 wt% Cu, (iv) Fe and 2 wt% Cu. After annealing the Fe particles were ca. 20 nm in diameter.

The samples were first fully oxidized in pure  $\text{O}_2$  at  $400^\circ\text{C}$  for 1 hour. Subsequently, the temperature was decreased to  $30^\circ\text{C}$  and the measurement chamber was purged in order to remove all  $\text{O}_2$  before changing the gas to pure  $\text{H}_2$ . In pure  $\text{H}_2$ , two subsequent temperature ramps from  $30^\circ\text{C}$  to  $400^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$  were run. The sample was reduced during the first temperature ramp, while the second temperature ramp served as a control.

For XPS measurements, pre-treatments, as similar as possible to the conditions used during NPS measurements, were performed in a high-temperature gas reaction-cell

and the samples were transferred in-vacuum to the measurement chamber.

## Results

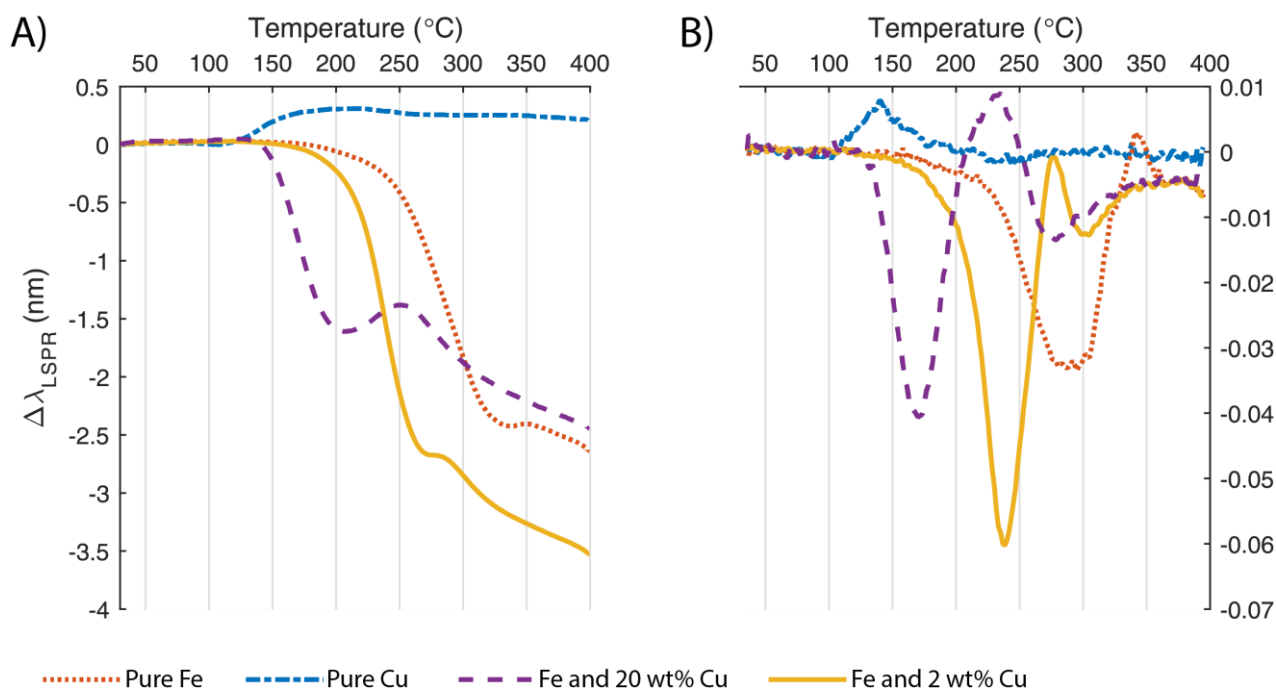
The catalysts on all samples were found to switch reversibly between the oxidized and reduced states. Figure 2a shows the data obtained during the first temperature ramp from 30°C to 400°C in dry H<sub>2</sub> after subtracting the NPS signal originating from the increasing reactor temperature. The derivatives of these signals are shown in figure 2b. A red-shift is seen for the Cu-catalyst (blue dash-dotted line) starting at ~130°C and ending around 180°C. This is manifested as a broad, positive peak in the derivative, shown in figure

2b. For the Fe-containing catalysts the characteristic response is a blue-shift with an intermediate region with a slower or even a reverse shift. By comparison with the results from the XPS experiments these shifts were determined to be associated with reduction of the catalysts. The XPS data (not shown) indicates that the Fe-catalysts are reduced in three distinct steps; Fe<sub>2</sub>O<sub>3</sub>→Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>→FeO, and FeO→Fe/FeO. The LSPR shift during reduction of Fe catalyst also occur in three distinct steps each of which corresponds to one of the three reduction processes. From the temperature dependent LSPR wavelength shifts it can be seen that Fe<sub>2</sub>O<sub>3</sub> reduction starts at

~230°C with a rate peak at around 290°C (red dotted curve). Furthermore, the presence of Cu lowers the starting temperature for FeO<sub>x</sub>-reduction by about 120°C for 20wt% Cu (purple dashed curve) and 50°C for 2wt% Cu (solid orange curve).

## Conclusions

NPS is a useful method for *in situ* detection and characterization of the temperature dependent oxidation/reduction of catalyst nanoparticles. With NPS it is possible to find the temperature at which a change in the oxidation state takes place and to compare the rates of this change.



**Figure 2:** LSPR signal during reduction in dry H<sub>2</sub> (10 ppmV H<sub>2</sub>O) for four different model catalysts. A) shows the peak shifts during heating from 30 to 400 °C and B) the corresponding derivative.

## References

[1] Reduction of Cu-Promoted Fe Model Catalysts Studied by In Situ Indirect Nanoplasmonic Sensing and X-ray Photoelectron Spectroscopy, Hans O.A. Fredriksson et al., *J.Phys.Chem. C*. 119(8) 2015 4085-4094.