

# Nanoparticle Sintering

## Introduction

Catalyst sintering is a major cause of catalyst deactivation, which yearly causes billions of dollars of extra cost associated with catalyst regeneration and renewal.

In order to develop more sintering-resistant catalysts, a detailed understanding of the sintering kinetics and mechanisms is required. It is therefore of great importance to investigate sintering in situ, in real time and under realistic catalyst operation conditions (i.e. at high temperatures and pressures in reactive gas atmospheres). Today there is a lack of available techniques that allow such studies.

Using Pt/SiO<sub>2</sub> as model catalyst, this Application Note illustrates that Indirect Nanoplasmonic Sensing (INPS) has the potential to fill this gap and provide novel real time data at low cost and with high throughput.

## Experimental

The INPS sensor consists of Au nanodisks (average diameter 80 nm, height 20 nm) deposited on a glass substrate and covered by a 10 nm thick SiO<sub>2</sub> spacer layer (Fig. 1a). The spacer layer serves several functions, including (i) protection of the Au nanodisks from the environment and from structural re-shaping, (ii) providing tailored surface chemistry (i.e. catalyst support material) for

the catalyst to be studied, and (iii) preventing the catalyst from directly interacting with the Au nanodisks by e.g. alloy formation.

The Pt model catalyst is formed onto the sensor chip by evaporating a 0.5 nm thick (nominal thickness) granular film. This results in individual Pt nanoparticles with an average diameter of  $\langle D \rangle = 3.3 \text{ nm}$  ( $\pm 1.1 \text{ nm}$ ), which mimics the size range of real supported catalysts.

The change of the localized surface plasmon resonance (LSPR) centroid wavelength,  $\Delta\lambda$ , is monitored during Pt nanoparticle sintering at different temperatures ( $< 610^\circ\text{C}$ ) in inert (Ar) or oxidizing (4% O<sub>2</sub> in Ar) environment at atmospheric pressure. The remote nature of the INPS approach (optical transmission measurement through the INPS chip) makes measurements at high temperatures and pressures easily possible. All experiments are performed in an Insplorion X1 gas flow reactor, and the optical spectra are collected and analyzed using the Insplorer® software.

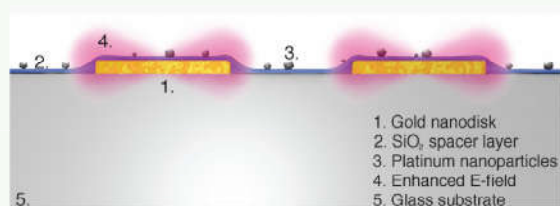
## Results

Exposing the Pt nanoparticles to O<sub>2</sub>, a well-known sintering promoter for Pt, causes the LSPR centroid position,  $\lambda$ , to shift towards shorter wavelengths and, simultaneously, a decrease in the optical absorbance

is observed (Fig. 2a). Analysis of  $\Delta\lambda$  during the course of the experiment, shows that the LSPR shifts fast in the beginning and then more slowly towards the end of the experiment (Fig. 2b, black curve). In contrast, when the same experiment is performed in pure Ar (or in 4% O<sub>2</sub> on a "blank" sensor without Pt) no significant shift during the entire experiment is observed (Fig. 2b, blue curve). These results indicate that INPS can be used to monitor the sintering of nanoparticle catalysts (since O<sub>2</sub> is a known sintering promoter for Pt).

The sintering of the Pt particles is confirmed by TEM imaging after 5 min and 6 hours in Ar and 4% O<sub>2</sub>/Ar, respectively (Fig. 2c-f). Slow sintering is observed in Ar at 610°C, causing  $\langle D \rangle$  to increase from 3.12 nm to 3.48 nm after 6 hours. However, already after 5 min in 4% O<sub>2</sub> the Pt nanoparticles have sintered more ( $\langle D \rangle = 3.6 \text{ nm}$ ) than after 6 h in Ar and after 6 h sintering in O<sub>2</sub>,  $\langle D \rangle$  has increased to 8.9 nm.

To further demonstrate the direct correlation between the plasmonic signal from the INPS sensor and sintering of Pt nanoparticles, experiments are performed where the sintering process is interrupted after different exposure times of the Pt particles to 4% O<sub>2</sub> atmosphere at 550°C (Fig. 3a). TEM imaging is performed after each sintering time



**Figure 1:** Schematic cross-section of the Indirect Nanoplasmonic Sensing (INPS) chip. The sensing structure consists of an array of gold nanodisks (1) deposited on a conventional glass slide (5) and covered by a SiO<sub>2</sub> spacer layer (2) onto which the Pt model catalyst particles (3) are deposited through thermal evaporation. Sintering of the Pt nanoparticles is sensed through the locally enhanced plasmonic field (4, "nanoantenna") surrounding the Au nanodisks.



interval (Fig. 3b-g). Plotting  $\Delta\lambda$  as a function of sintering time for the six different experiments ( $t = 10$  min, 30 min, 1 h, 3 h, 6 h, and 12 h) (Fig. 3a) shows that the signal is completely reproducible during overlapping sintering intervals for different samples. This demonstrates the robustness and reproducibility of the INPS measurement method. Furthermore, when comparing the optical response with particle size distributions (PSDs) obtained from TEM image analysis, an unambiguous correlation is found between the optical response (i.e. the centroid shift  $\Delta\lambda$ ) of the INPS sensor and the Pt catalyst particle density during the sintering process. The latter relation is used to calculate an average particle diameter, which

is subsequently used for theoretical modeling and curve fitting to the experimental data. The results indicate Ostwald ripening as the dominant sintering mechanism (see Larson et al. for details).

## Conclusions

Indirect Nanoplasmonic Sensing (INPS) was applied to study sintering kinetics of a supported catalyst in situ with a temporal resolution in the sub-second range under fairly realistic catalyst operation conditions.

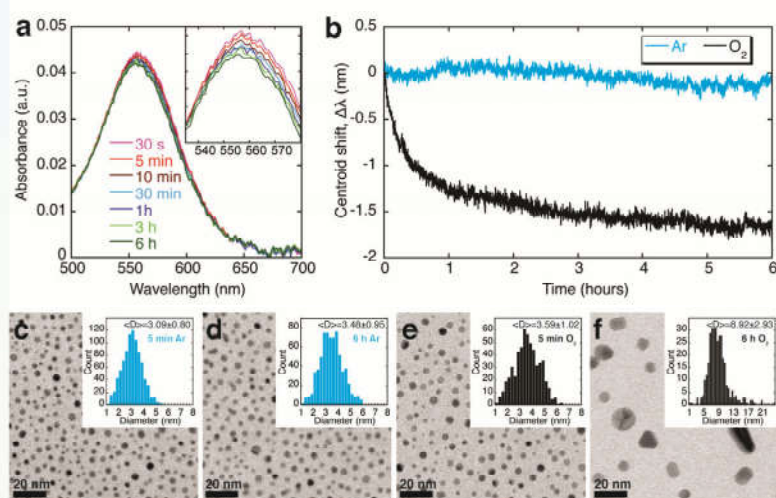
Due to the superior time resolution, the INPS sintering kinetics described above are more detailed than those obtained by other techniques (the latter kinetics often

contain only a few data points), which provides a unique tool for real time in situ sintering studies.

## References

Real Time Indirect Nanoplasmonic in situ Spectroscopy of Catalyst Nanoparticle Sintering, Elin M. Larson, Julien Millet, Stefan Gustafsson, Magnus Skoglundh, Vladimir P. Zhdanov, Christoph Langhammer, ACS Catalysis, DOI: 10.1021/cs200583u (2011).

More information about catalyst sintering: Mechanisms of Catalyst Deactivation, C.H. Bartholomew, Applied Catalysis A: General 212 (2001) 17-60.



**Figure 2 (above):** (a) Absorbance spectra obtained at different times during the sintering of the Pt model catalyst in 4% O<sub>2</sub>/Ar at 610°C. The LSPR peak of the INPS sensor spectrally shifts to shorter wavelengths and, simultaneously, a decrease in the optical absorbance is observed. (b) Graph showing the LSPR peak centroid shift vs. sintering time in 4% O<sub>2</sub>/Ar (black) and 100% Ar (blue) atmosphere. Clearly, in O<sub>2</sub>, which is known to promote the sintering of supported Pt catalysts, the centroid shifts fast in the beginning and then more slowly, almost linearly, towards the end. In contrast, in pure Ar only a very small centroid shift is seen. TEM pictures and corresponding PSD histograms of the Pt nanoparticles after 5 min (c) and 6 h (d) in pure Ar at 610°C reveal that the particle size is nearly constant with time, indicating almost total absence of sintering. TEM images and PSD histograms after 5 min (e) and 6 h (f) in 4% O<sub>2</sub>/Ar at 610°C clearly show significant Pt catalyst particle sintering, in agreement with the INPS measurement.

**Figure 3 (right):** (a) Real time plasmonic sintering kinetic curves obtained for 6 different samples and sintering times under identical experimental conditions (4% O<sub>2</sub>/Ar atmosphere at 550°C) demonstrate reproducibility between experiments and illustrate the robustness of the INPS platform. Corresponding TEM micrographs obtained after each sintering time interval, i.e. 10 min (b), 30 min (c), 1 h (d), 3 h (e), 6 h (f) and 12 h (g), with respective PSD histograms and average particle diameters  $\langle D \rangle$  illustrate the significant sintering of the Pt model catalyst, as registered by the INPS sensor.

