

Optical Nanocalorimetry of Catalytic Reactions

Introduction

Dissipated heat from an exothermic catalytic reaction is a critical parameter for phenomena like catalytic ignition and light-off in catalytic converters for e.g. car emission cleaning. This application note illustrates the possibility to use the Insplorion's Indirect Nanoplasmonic Sensing (INPS) platform to measure nanoscale local temperature changes and to exploit this for a novel optical nanocalorimetry of reactions on supported nanoparticle catalysts under realistic temperature and pressure conditions.

In the experiment presented here the exothermic $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$ reaction over Palladium (Pd) nanoparticles is used as model reaction.

The INPS Technology

INPS employs the Localized Surface Plasmon Resonance (LSPR) excitation in gold sensor nanodisks to study processes and changes on/in adjacent functional nanomaterials through the coupling of the locally enhanced plasmonic near-field to the latter or through the intrinsic temperature sensitivity of the LSPR

(optical calorimetry). INPS can be used to quantitatively, in real time ($< 10^{-2}$ s time resolution) and *in situ*, study physical and chemical properties and processes involving metallic and non-metallic nanostructures and thin films.

Experimental

The experimental setup consists of an arrangement of two optical fibers for optical transmission measurement through a quartz flow-reactor in which the INPS sensor chip is mounted (Fig. 1a). The INPS chip

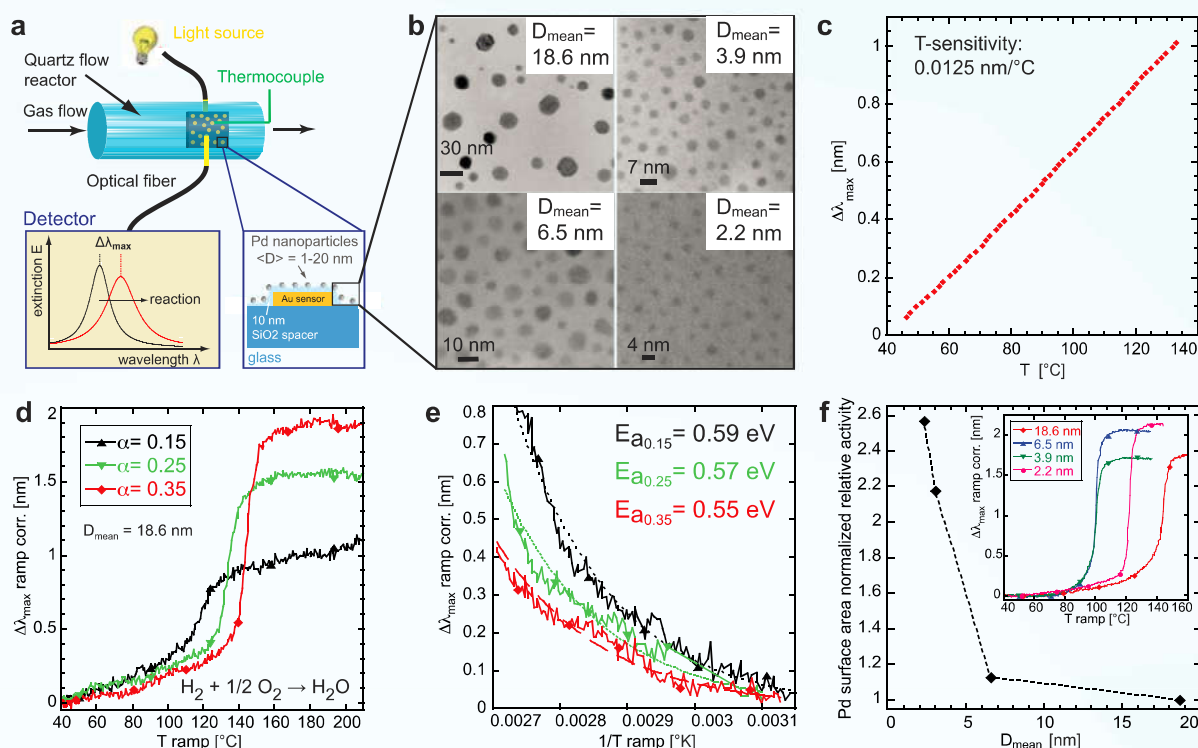


Figure 1: Fig. 1. Optical calorimetry of a catalytic reaction. (a) Schematic depiction of the experimental setup used for this study. It consists of a simple arrangement of two optical fibers for optical transmission measurement through a quartz flow-reactor in which the INPS chip, decorated with Pd nanoparticles, is mounted. (b) TEM images of four different investigated Pd nanoparticle sizes after structural stabilization by catalytic annealing. (c) Depiction of the linear T-dependence of the INPS LSPR, yielding a temperature sensitivity of $\Delta\lambda_{\text{max}} = 0.0125 \text{ nm}/^\circ\text{C}$. (d) Catalytic light-off traces obtained for the hydrogen oxidation on Pd with $D_{\text{mean}} = 18.6 \text{ nm}$ for $\alpha = 0.15, 0.25, 0.35$ in Ar carrier gas at 4% total reactant concentration. (e) Arrhenius analysis of LSPR temperature traces below light-off (the dotted/dashed lines correspond to Arrhenius-function fits to the LSPR data). (f) Light-off traces for four different Pd particle sizes (inset) and a measure of the relative activity for each Pd catalyst particle size. An approximately 3-fold increase of the catalyst activity per surface area for the smallest catalyst particles, relative to the largest ones, is observed.



consists of an array of nanofabricated plasmonic Au disks (76 nm diameter, 30 nm high) deposited on a glass substrate and covered by a thin (≈ 10 nm) film of SiO_2 (Fig. 1B). The sensor chip surface is decorated with Pd nanoparticles 18.6 – 2.2 nm in diameter (Fig. 1b).

The chemical power generated by the exothermic $\text{H}_2 + \text{O}_2$ reaction on the Pd nanoparticles causes a temperature rise on the sample surface and of the sensing Au nanodisks, which results in a measurable shift of the spectral peak position ($\Delta\lambda_{\text{max}}$) of the LSPR of the Au sensing nanoparticles.

Results

For calibration purpose, $\Delta\lambda_{\text{max}}$ was first measured as a function of T in inert gas atmosphere without catalytic reaction, resulting in a linear T-dependence and a temperature sensitivity of $\Delta\lambda_{\text{max}} = 0.0125 \text{ nm}/^\circ\text{C}$ (Fig. 1c).

Fig. 1d shows catalytic light-off traces obtained for Pd nanoparticles with $D_{\text{mean}} = 18.6 \text{ nm}$ for three different relative H_2 and O_2 concentrations in Ar carrier gas $\alpha = [\text{H}_2]/([\text{H}_2]+[\text{O}_2])$, and a total reactant concentration of 4%. The reactor heating-rate was $4^\circ\text{C}/\text{min}$ and the constant gas flow rate 1000 mL/min. The $\Delta\lambda_{\text{max}}$ values displayed in Fig. 1d are corrected for the spectral shift induced by external heating of the reactor (calibration curve in Fig. 1c).

If there were no other heating/power source than the external heating, the three curves ($\alpha = 0.15, 0.25,$ and 0.35) would all lie flat on the abscissa. The rise over the abscissa is attributed to an LSPR peak shift induced by local heating of the Au sensor nanodisks, due to the dissipated heat from the exothermic $\text{H}_2 + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O}$ reaction ($\Delta H = 250$

kJ/mol) on the Pd catalyst particles. Thus, this measurement provides an absolutely unique local measurement of the temperature rise, extremely difficult to obtain by other means.

The general form of the curves (for the three α values) is a first slow rise of temperature (i.e., of the reaction rate), until a fast rise begins (transition from kinetic limitation to mass transport limitation) and then a flattening, when the reaction reaches the mass transport limited regime, and therefore becomes rather insensitive to further temperature rise.

Since a Pd hydride phase is not formed at the temperatures considered here, the potential contribution to the LSPR signal originating from hydrogen in solid solution in the metallic Pd is completely negligible.

The observed trend, that the light-off is occurring at higher temperatures for higher α values, is as expected and has its origin in the detailed kinetics of the reaction, which can be related to hydrogen poisoning and that the reaction activation energy can be associated with hydrogen desorption. To quantify these measurements and demonstrate the direct correlation between measured LSPR shift and local catalyst temperature, an Arrhenius analysis of the low-temperature (below light-off and the kinetic phase transition) regime is shown in Fig. 1e. The obtained apparent activation energies for three different reactant concentrations are in excellent agreement with the literature.

The inset in Fig. 1f shows light-off traces for four different Pd particle sizes (Fig. 1b) at $\alpha = 0.35$. Fig. 1f shows a very clear trend towards higher relative activity with decreasing particle size. With the activity of the largest particles ($D_{\text{mean}} = 18.6 \text{ nm}$) as reference (i.e., activity = 1), an almost 3-fold increase of

the catalyst activity per surface area is observed for the smallest catalyst particles ($D_{\text{mean}} = 2.2 \text{ nm}$).

Conclusions

These results demonstrate how Insplorion's INPS platform can be used for calorimetric studies of reactions on supported nanoparticle catalysts by optically measuring local catalyst temperatures (i.e., the temperature of the catalyst nanoparticles, not the average temperature of the entire catalyst system, including the support structure) under realistic (T, p) reaction conditions.

This offers a unique nanocalorimetric way of measuring catalytic reactions on small amounts of catalytically active nanoparticles, including size-dependent activity.

References

Indirect Nanoplasmonic Sensing: Ultrasensitive Experimental Platform for Nanomaterials Science and Optical Nanocalorimetry, Christoph Langhammer, Elin M. Larsson, Bengt Kasemo, and Igor Zoric, Nano Letters 10 (2010) 3529-3538.

