Indirect Nanoplasmonic Sensing in Catalysis: Sintering, Reactant Surface Coverage Changes and Optical Nanocalorimetry

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We report four different application areas, within catalysis, of a new “nanoplasmonic” (localized surface plasmon resonance, LSPR) method, Indirect Nanoplasmonic Sensing (INPS), which uses a remarkably simple optical transmission (or reflection) measurement. The method can with high sensitivity follow catalytic reactions in real time in-situ and can be applied to both model catalysts and real supported catalysts at realistic catalyst working conditions (i.e. high pressures and temperatures).

A catalyst is a substance that increases the rate of a reaction without itself being destroyed or consumed. Many industrial processes as well as the environmental and energy sectors depend on catalysis. Some of the most important uses for catalysts are to decrease the need for energy and raw materials and to clean industrial and automotive exhausts. To understand and improve heterogeneous catalyst systems it is important to be able to monitor the catalyst’s state and to follow the reaction in real time. However, there is still a need for new experimental probes that allow such investigations to be made on the often complex catalyst structures and under realistic catalyst working conditions. Here we present a technique that has the potential to partly fill this need. We show that INPS can be used to monitor changes in adsorbed species on nanoparticle catalysts or chemical changes in a thin film [1], for optical nanocalorimetry[2] and to monitor sintering[3]. Sintering is the deactivation of a catalyst by the coalescence of catalytically active nanoparticles to form larger less active particles. Catalyst sintering causes large economic and environmental costs associated with catalyst regeneration/renewal.

The principle is “nanoplasmonic” sensing, which has been intensely investigated for biosensing. A LSPR is a coherent resonance oscillation of the conduction electrons, a plasmon resonance, in a metal nanoparticle, which can be excited by near-visible light with an appropriate color/wavelength. The wavelength at which the resonance occurs depends e.g. on the dielectric properties of the particle’s nanoenvironment and can, therefore, be use for sensing where dielectric changes are to be detected [4]. INPS applies a patent searched [5] sensor chip design (see figure 1A) which allows events such as sintering, surface coverage changes[1], and hydrogen storage[2, 6] in/on nanoparticles/clusters/thin films to be monitored using the plasmon resonance of other nanoparticles in their close vicinity. The INPS technology is being commercialized by Insplorion AB that markets and sells research instruments.

Figure 1B shows real-time data from the storage (8 to 38 minutes) and release (from 38 minutes, induced by adding hydrogen) of nitrogen oxides (NOx) in/from a barium compound[1]. The data shows that the reaction can be monitored with high sensitivity and time resolution and that the obtained signal is concentration dependent. The reaction studied here is relevant in NOx storage and release catalysts extensively researched for lean burn automotive engines and shows that INPS can be used to study such reactions or as a nitrogen oxide sensor. We also show that a change in surface adsorbate from oxygen to hydrogen/carbon monoxide can be monitored with sub-monolayer sensitivity using INPS[1].

For optical nanocalorimetry it is utilized that the plasmon resonance is sensitive to temperature changes. Figure 1C shows light off traces obtained for Pd nanoparticles (average diameter 18.6 nm) deposited on an INPS sensor chip. The Pd particles were exposed to mixtures of hydrogen and oxygen (α= relative hydrogen concentration, total reactant concentration was kept constant) and the external temperature was increased linearly. Figure 1C shows the data after correction for the external temperature change. The data shows a rapid increase in the catalyst temperature at catalytic light off. The peak shift obtained at high temperatures depends on the α-value as expected (different α values give different maximum reaction rates). We also demonstrate that INPS can be used to study particle size dependent reactivity[2].

In the last application, it is demonstrated that INPS can be used for real-time and intermittent monitoring of catalytic cluster sintering. Sintering of Pt clusters, similar to those in the car exhaust catalyst, was monitored in different gas environments at atmospheric pressure on SiO_2 surfaces. Substantially increased sintering rate were observed in 4% O_2 (in Ar) as compared to in pure Ar. As expected, the sintering rate was also found to increase with increasing temperature (see figure 1D). The optical signal obtained during sintering was calibrated using post-mortem TEM imaging of TEM-window samples, identical to the optical/glass samples, which were run in parallel with the optical measurements.

The obtained data show that INPS is a promising novel technique for real-time measurements of the catalyst state and nanocalorimetry using a low cost, optical transmission/reflection measurement.

References

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