

NO_x Storage Kinetics of Barium Oxide

Introduction

NO_x storage/release catalysts, in which NO_x is temporarily accumulated in the catalyst before being reduced to N₂, play a key role in automotive emission cleaning. They rely on an active material, for example barium oxide (BaO), which upon NO_x storage is converted to Ba(NO₃)₂ or related compounds. Pt (and in practice usually also Rh) is needed for the reduction step and also for oxidation of NO (when present) to NO₂ during the storage phase.

In this application note, the NO_x con-

version to N₂ on a Pt/BaO model catalyst is monitored in real-time using the Insplorion's Indirect Nanoplasmonic Sensing (INPS) platform.

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 material 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

An optical transmission measurement is made through a quartz reactor in which an INPS sensor chip is mounted (Fig. 1A). The sample con-

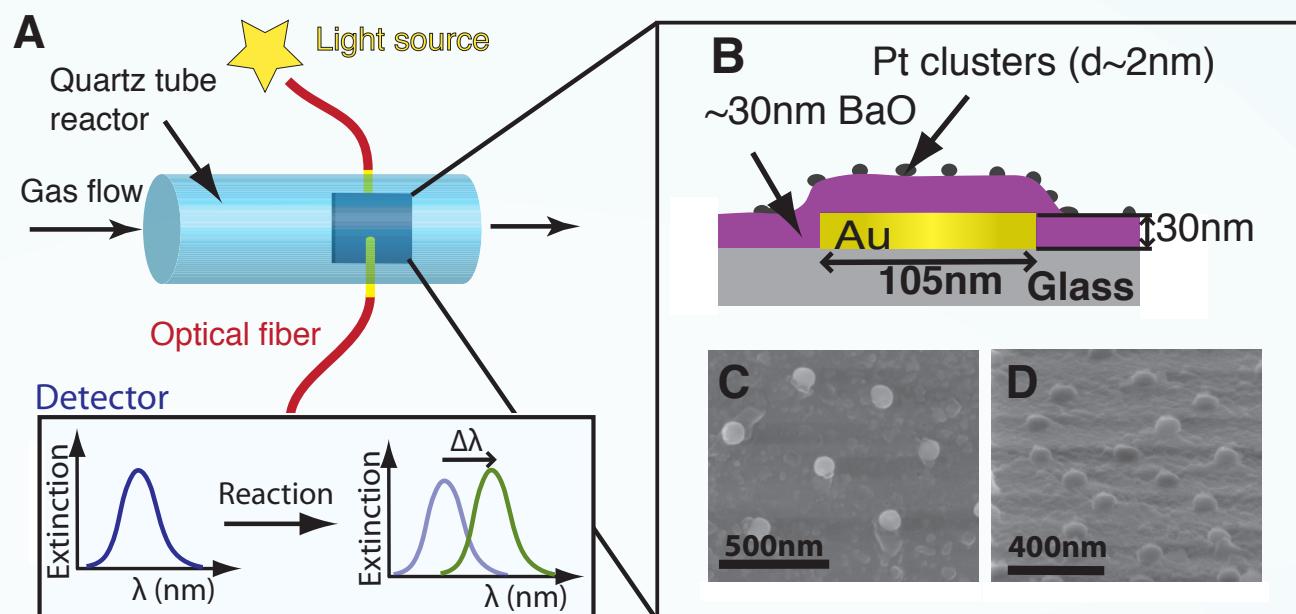


Figure 1: Experimental setup and sensing structures. (A) Flow reactor arrangement and (bottom) optical readout principle. (B) Sensing structure used to monitor the NO₂ storage/release kinetics from BaO. (C and D) Top-view (C) and 70° tilt (D) SEM images of the sensing structure in (B).

sists of an array of nanofabricated plasmonic gold disks (140 nm diameter, 30 nm high) deposited on a glass substrate and covered by an evaporated 30 nm thick film of NO_x-active BaO (Fig. 1, B to D). The catalyst Pt nanoparticles are deposited on the BaO surface.

The transmission of white light through the sample, via the reactor walls, is detected as a function of wavelength by use of a fiber-coupled array spectrometer. The shift of the LSPR peak, $\Delta\lambda_{\max}$, provides the sensing function.

The experiment was performed by continuously recording $\Delta\lambda_{\max}$ during NO_x storage and subsequent release. To mimic the NO_x storage period, the sample was exposed for 30 min to a gas mixture of 30 to 1000 ppm NO₂ + 6% O₂ in Ar carrier gas at atmospheric pressure. It was subsequently exposed to 2% H₂ to mimic the reduction period in which the catalyst is restored to be able to store NO_x again.

Results

The results of both the storage period ($t = 8$ to 38 min in Fig. 2) and the reduction step are shown in Fig. 2A. For all curves, there is an initial rapid upward shift of $\Delta\lambda_{\max}$ within 20 s after exposure to NO₂ and O₂ and then a slowly continuing increase, which is greater for higher NO₂ concentrations. This is interpreted as LSPR detection of the BaO + NO_x storage reaction, converting a thin surface layer of BaO to Ba(NO₃)₂, which changes the effective refractive index and volume. These changes are then detected by the LSPR sensor and read out as a peak shift, $\Delta\lambda_{\max}$. The larger signals for larger NO₂ concentrations (quantified in Fig. 2B) are caused by a combination of reversible and irreversible NO_x storage, both increasing with increasing NO_x concentration. Exposing the sample to H₂ (at 38 min in Fig. 2A) results as expected in a

shift of $\Delta\lambda_{\max}$ back to the original value before the NO₂ exposure because of the hydrogen reduction of stored NO_x to N₂ and consequent Ba(NO₃)₂ → BaO conversion (creating partly reduced BaO). The immediate shift also at 0 ppm NO₂ is due to the oxidation of the partially reduced BaO in the presence of O₂ after the hydrogen treatment.

Conclusions

In this application note, the Pt/BaO/Au-LSPR structure senses changes in the dielectric constant near the Au particles, which is caused by incorporation of NO_x in the BaO layer. The results show that Insplorion's INPS technique is a very sensitive and fast method for NO_x sensing.

References

Nanoplasmonic Probes of Catalytic Reactions, Elin Larsson, Christoph Langhammer, Igor Zoric, Bengt Kasemo, Science 326 (2009) 1091-1094.

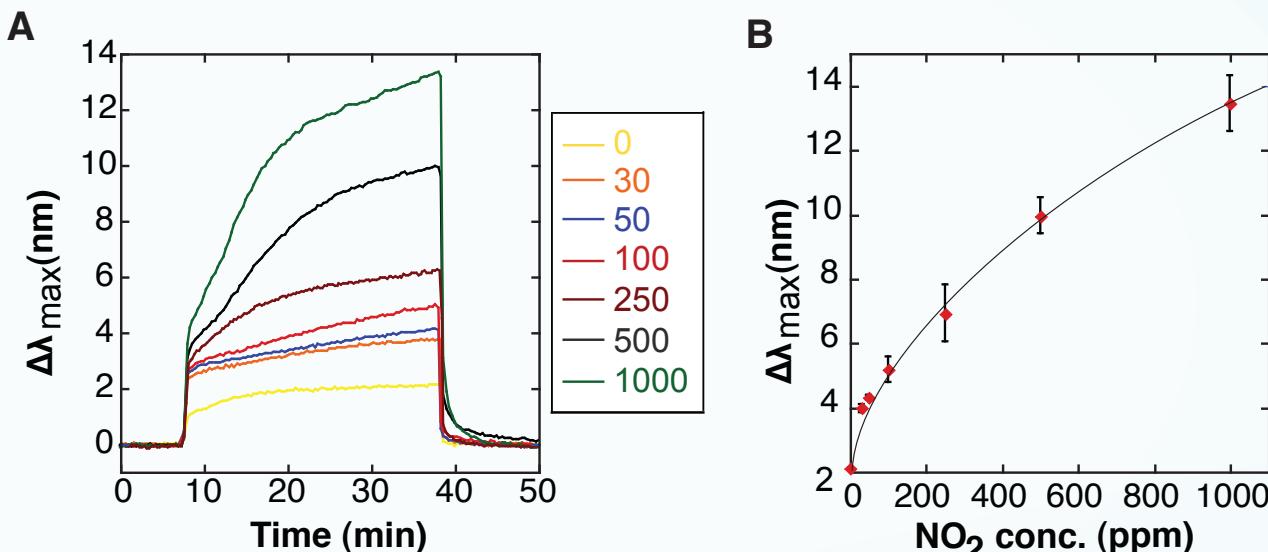


Figure 2: NO_x storage and release (as N₂) from BaO measured with the sensor-catalyst model structure in Fig. 1, B to D. (A) Plasmon peak shift during 30 min NO₂ storage (at $t = 8$ to 38 min), at seven different concentrations (0, 30, 50, 100, 250, 500, and 1000 ppm), and subsequent release by exposure to 2% H₂ (at $t = 38$ min). (B) Total Plasmon peak shift after 30 min of NO₂ exposure as a function of NO₂ concentration [same concentrations as in (A)].