Sintering of platinum nanoparticle catalysts in a mesoporous alumina support

Insplorion's Nanoplasmonic Sensing (NPS) technology enables sensitive detection of e.g. structural and chemical changes within a sensing volume that extends a few tens of nanometers from the NPS sensor surface. In this application example, NPS studies of catalytic processes on catalyst nanoparticles dispersed in a three dimensional mesoporous washcoat matrix are demonstrated. The use of the experimental platform is illustrated by measuring sintering kinetics of Pt nanoparticles inside a mesoporous alumina matrix under oxidizing conditions at atmospheric pressure and at temperatures up to 625 °C.

Introduction

The science and technology of catalysis is of great significance as it affects our daily life. Four major sectors of the world economy; petroleum and energy production, chemicals and polymer production, food industry and pollution control, involve catalytic processes.

Catalysis is commonly divided into homogenous and heterogeneous catalysis. In heterogeneous catalysis, solids catalyse reactions of molecules in gas or solution. To use the often expensive catalyst materials (e.g. platinum) in an economical way, catalysts are usually nanometer-sized particles (which have a large surface area), supported on an inert, porous structure.

Catalyst sintering causes a loss of active surface area due to the agglomeration of catalyst nanoparticles and is an important cause of catalyst deactivation during industrial operation.

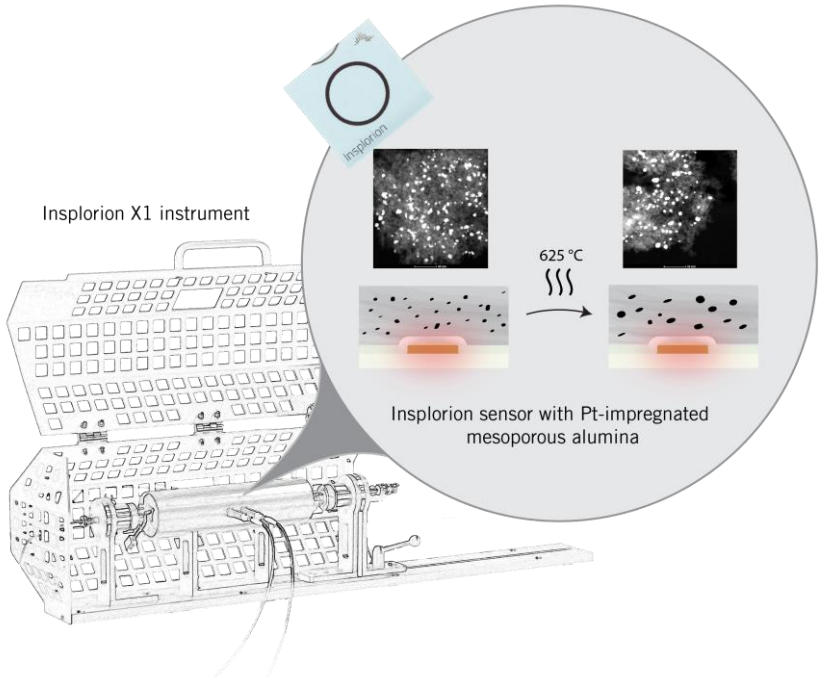

Figure 1: Insplorion system setup. The inset shows a schematic illustration of the sensor and sample configuration used in this application example (not to scale).

Experimental Procedure

NPS sensors with gold nanodisks (diameter = 140 nm and height = 20 nm) were heat treated at 800 °C for 43 hours to stabilize the plasmonic gold nanoparticles structurally before sputter deposition of a 10 nm thick alumina coating. A second heat treatment was then performed at 700 °C for 36 hours to stabilize the entire assembly. The mesoporous alumina was prepared by spin coating a böhmite slurry on the NPS chip surface and then transforming the böhmite to mesoporous γ alumina through calcination in air at 650 °C. The resulting mesoporous washcoat matrix had a uniform thickness of ca. 400 nm.

Pt nanoparticles were, subsequently, formed in the pores of the alumina matrix by wet impregnating the washcoat layer with Pt

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catalyst precursor and subsequent calcination.
The sintering measurements were performed by heating the samples in Ar to the designated temperature. After the temperature had been allowed to stabilize completely, Pt sintering was promoted by exposing the samples to O_2 diluted in Ar for 10 hours. The shift in spectral position of the plasmon resonance peak, $\Delta\lambda_{peak}$, was measured continuously during oxygen exposure.

Results

Figure 2a shows the time evolution of $\Delta\lambda_{peak}$ measured at different temperatures (550-625 °C). A red shift, with a magnitude that scaled with the applied sintering temperature was observed. This is in good qualitative agreement with previous studies on flat model systems, and the signature of Pt particle rearrangement within the sensing volume of the gold particles due to ripening. As $\Delta\lambda_{peak}$ is larger for the measurements at higher temperature, it indicates a more severe sintering, in agreement with the known temperature dependence of nanoparticle sintering processes.
Sintering experiments were also performed in different oxygen concentrations at 600 °C (figure 2b). It was found that the NPS peak shift upon exposure to 4% O_2 was almost three times larger compared to 1% O_2 in Ar. This shows a significant concentration dependence of the sintering process, which is in agreement with previous experimental investigations and theoretical calculations.

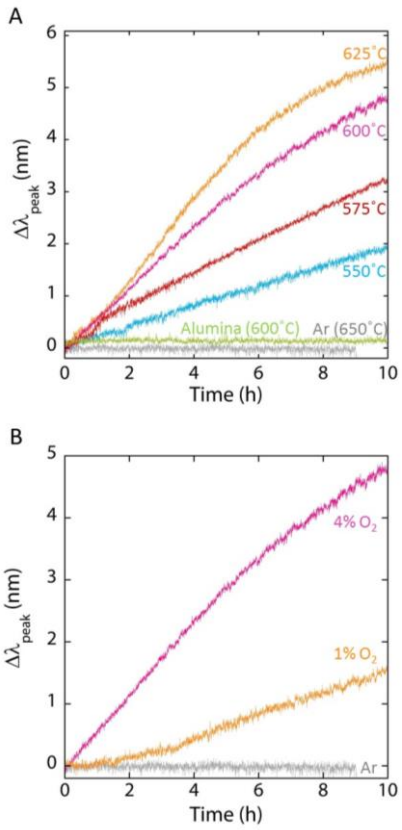

Figure 2: Real time sintering kinetics of Pt particles supported on a mesoporous alumina washcoat. A) Measured at 550, 575, 600 and 652°C in 4% O_2 in Ar. Data from control experiments for a sample without Pt (bare alumina) measured at oxidizing conditions at 600°C, as well as a Pt-impregnated sample exposed to pure Ar at 650°C is also shown. B) Measured in different gas environments pure Ar at 650°C, 1% O_2 in Ar at 600°C and 4% O_2 in Ar at 600°C.

Conclusions

NPS studies of catalytic processes on catalyst nanoparticles dispersed in a three dimensional mesoporous alumina washcoat matrix was demonstrated. Traditional recipes for the fabrication of mesoporous catalyst washcoat materials and wet impregnation with Pt catalyst precursor was used to obtain a realistic catalyst structure. The possibility to use such a structure to monitor catalytic processes in the gas phase at high temperatures was demonstrated by monitoring the sintering kinetics of the Pt nanoparticles inside the mesoporous alumina washcoat layer under oxidizing conditions at temperatures up to 625 °C.

Reference

P. Tabib Zadeh Adibi et al. *Plasmonic Nanospectroscopy of Platinum Catalyst Nanoparticle Sintering in a Mesoporous Alumina Support,* **ACS Nano 2016**, *DOI: 10.1021/acsnano.5b07861*

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