Real time in situ monitoring of catalyst sintering on different support materials

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Introduction
Heterogeneous catalysts are often realized as nanometer sized metal particles dispersed on high surface area oxides, such as Al₂O₃. However, due to large surface to volume ratio of small metal particles they are prone to sinter (i.e. coalesce into large particles) under operating conditions. This is a major cause of catalyst deactivation and leads to additional costs associated with either metal overloading or regeneration procedures [1]. In this work, indirect nanoplasmonic sensing (INPS) [2] is used to monitor the sintering kinetics of Pt nanoparticles on different support materials in real time, in situ and under operating conditions. Recently, INPS in combination with transmission electron microscopy (TEM) has proven to be a powerful tool to explore sintering of Pt nanoparticles on SiO₂ [3].

Materials and Methods
Platinum nanoparticles with average size of about 3.5 nm were grown on three different flat support materials by means of thermal evaporation of an ultrathin granular Pt film. The considered support materials are 10 nm thick sputtered silica (mesoporous), PECVD-deposited silica (dense), and sputtered alumina. The experiments were performed in a gas flow reactor with optical access for transmission measurements (white light). In the INPS sintering experiment, the sintering of nanoparticles was tracked by monitoring the shift in the plasmonic signal. Comparing the INPS sintering kinetic curves with intermittent TEM data yielded a correlation between INPS plasmonic shift and Pt nanoparticle size. Hence, it was possible to obtain sintering kinetics with very high time resolution, which, in turn, facilitates the identification of a dominant sintering mechanism.

Results and Discussion
Normalized INPS sintering kinetics obtained at identical conditions for three different support materials are shown in Figure 1. A blank sample (without Pt) is shown for comparison, which exhibits a negligible INPS signal shift. This indicates that the shifts observed in other curves are caused by the sintering of the Pt particles on the INPS sensor. Figure 2 shows TEM pictures of Pt nanoparticles along the monitored sintering process.

Significance
In situ Monitoring of sintering under operating conditions with very high temporal resolutions is important for understanding sintering mechanisms. Scrutinizing the role of support materials is critical because (i) it can shed light on the importance of support-particle interactions and (ii) as it could pave the way to minimize sintering effects. We will also show how the INPS method allows for studying sintering of nanoparticles on three-dimensional mesoporous support material that resembles realistic washcoat material.

Figure 1. Normalized INPS signal related to sintering of Pt nanoparticles at 592°C in O₂/Ar on different support materials. The curve for a sample without Pt (blank) is included.

Figure 2. TEM images of (a) fresh Pt/SiO₂ and evolution of Pt nanoparticles supported on sputtered silica at 597°C in 4% O₂/Ar after (b) 10 min, (c) 1 h and (d) 6h sintering time intervals. The size of scale bar is 20 nm.

References