

## The Role of Nucleation Sites on the Stability of Catalytic Nanoparticles

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Gold (Au), an otherwise inert metal, becomes a very active catalyst when present in the form of nanoparticles, 2-5 nm in diameter [1-3]. However, there are challenges in using Au as a catalyst, because it sinters readily under reaction conditions. This leads to a growth in particle size, and loss of catalytic activity. Based on the evidence so far, it appears that Ostwald ripening is the dominant mechanism for Au nanoparticle sintering [4]. Ripening involves emission of adatoms from smaller particles and their capture by larger particles.

Au is known to be more stable on some supports than on others. For example, Au/TiO<sub>2</sub> is more stable than Au/SiO<sub>2</sub>. This is thought to be due to stronger interactions between Au and the TiO<sub>2</sub> support that stabilize the Au nanoparticles [5]. However, over time, both catalysts lose activity due to particle growth. We have found in our lab that under certain conditions Au can be more thermally stable on a mixed oxide support such as TiO<sub>2</sub>-SiO<sub>2</sub> than on the single component oxide supports SiO<sub>2</sub> and TiO<sub>2</sub>. The reasons for this improved stability are not fully understood. In this work, we have explored the role of nucleation sites, and specifically whether the mixed oxide supports provide more nucleation sites than those available on the single component oxide supports. Furthermore, the nucleation sites initially present when the catalyst was prepared may become inactive or unavailable as the catalyst is subjected to elevated temperature treatments. This causes the catalyst to have limited sites for the binding of adatoms, causing catalyst sintering. Understanding the nature of the nucleation sites and developing methods to reactivate these sites could provide a new approach to control catalyst sintering and is the focus of this work.

The stability of Au nanoparticles was investigated by varying the nature of TiO<sub>2</sub>/SiO<sub>2</sub> mixed oxide supports. The goal was to systematically vary the morphology and chemistry of TiO<sub>2</sub> on SiO<sub>2</sub> in order to create nucleation sites that will remain active throughout the course of reaction, specifically sites that can be reactivated. Physical vapor deposition (PVD) and hydrolysis of an alkoxide precursor were the methods used for the deposition TiO<sub>2</sub> onto SiO<sub>2</sub>. The morphology of the TiO<sub>2</sub> was controlled by varying the degree of hydrolysis of the TiO<sub>2</sub> precursor. The morphology was also varied by controlling the coverage of TiO<sub>2</sub> from sub-monolayer to multiple layers. The deposition precipitation method was used to deposit Au onto the mixed oxide support. Electron microscopy was used to monitor the size distribution of the Au nanoparticles before and after calcinations treatments.

Two TiO<sub>2</sub> deposition methods were found to stabilize Au nanoparticles at temperatures up to 700°C. The mechanisms for stabilization are still under investigation, but we suspect that the Au stabilization may be due to the presence of amorphous TiO<sub>2</sub> as opposed to crystalline TiO<sub>2</sub>. Micrographs of the stabilized Au particles in these samples are shown in Figure 1 and contrasted with micrographs of sintered Au nanoparticles. The corresponding particle size distributions are shown in Figure 2. Further characterization of these samples is in progress to identify the Au nucleation sites on the TiO<sub>2</sub>/SiO<sub>2</sub> support. This will lead to new insights on the stability and control of sintering in heterogeneous catalysts.

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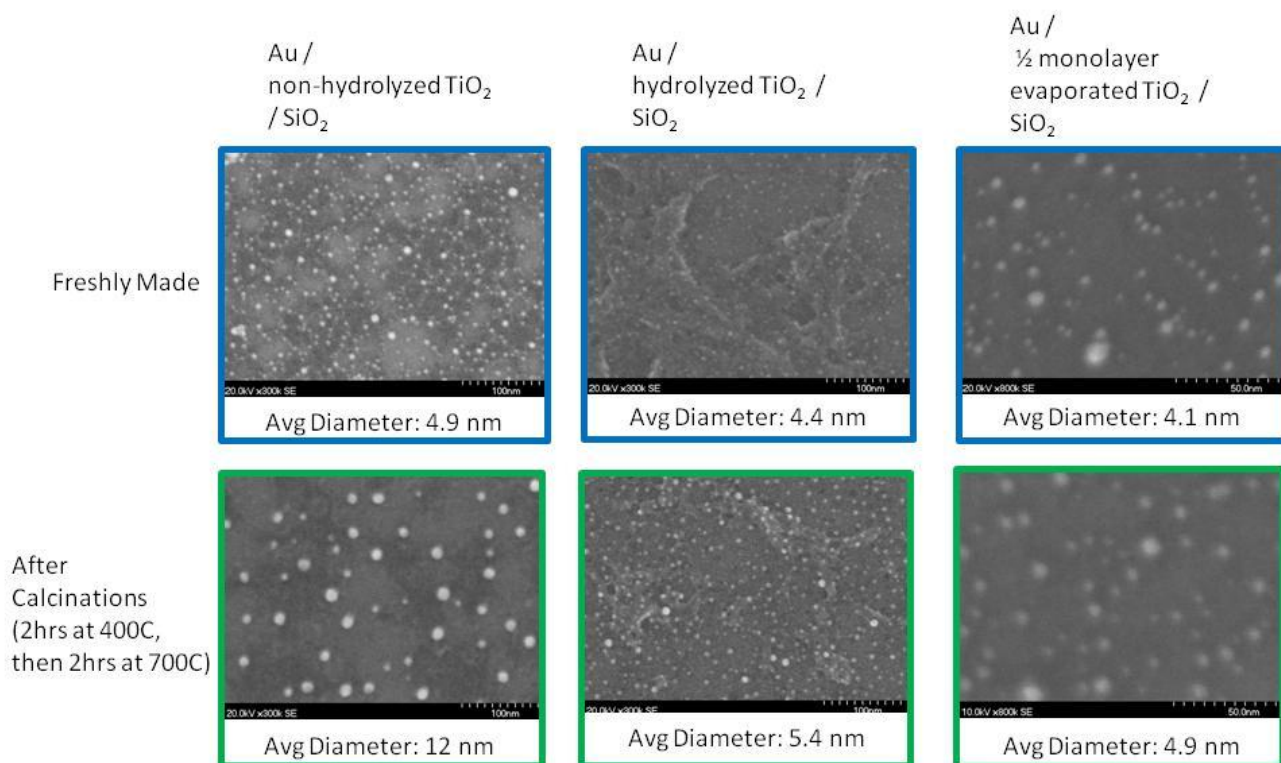


Figure 1. Micrographs show Au nanoparticles can be stabilized by varying support

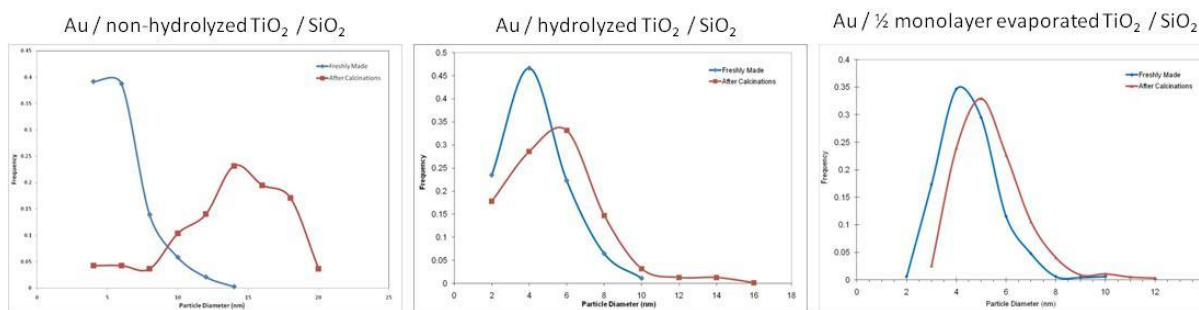


Figure 2. Particle Size Distributions for Samples in Above Micrographs