Essential Role of Solution Processing for the Stabilization and Catalytic Activity of TiO₂-Supported Gold Nanoparticles

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Introduction
The activity, durability, and properties reported for gold catalysts vary widely due to differences in nanoparticle synthesis methodology, catalyst treatments, support properties, and the difficulty in reproducibly preparing gold catalysts [1,2]. Of all the support types used for gold catalysts the most commonly investigated one is TiO₂ [3]. Of the various TiO₂ sources Degussa P25 is the most commonly used for bulk Au/TiO₂ studies and is substrate for the World Gold Council Au/TiO₂ reference catalyst. In this paper we report on the vapor phase synthesis of gold nanoparticles supported on Degussa P25 and identify a key, previously unrecognized, variable for the production of active and structurally stable Au/TiO₂ catalysts [4].

Materials and Methods
The Au/TiO₂ catalysts were prepared using a magnetron sputtering technique which has been described in several previous publications [5-7]. Briefly, ~1 gram of titania and two-1 inch Teflon® coated stir bars were placed inside a set of stainless steel (SS) cups attached to a vacuum compatible motor. A high purity gold target (Engelhard, 99.995%) was sputtered by direct current (dc) magnetron sputtering in a Ar atmosphere. The SS cups were rotated causing the powders to tumble constantly exposing a new region of the titania for the sputtered gold to deposit onto. The P25 was used in the natural form from Degussa or after solution phase processing. Solution phase processing entailed reproducing the steps used to prepare supported gold catalysts by the deposition-precipitation (DP) technique without the auric acid [8].

Results and Discussion
Gold nanoparticles grown on natural P25 have a very uniform distribution of particle sizes with an average diameter of 2.4 nm. The catalysts have a low activity relative to the WGC reference catalysts (0.008 vs 0.34 mole CO/mole Au•sec respectively). After 6 days of storage in the dark, but at atmospheric conditions, all the gold nanoparticles rapidly and irreversibly agglomerate into large 16-23 nm gold particles resulting in the loss of all catalytic activity. However, the clusters were stable under UHV conditions.

The gold particles grown on the treated supports are significantly more uniform and smaller (Au/pH 10 TiO₂ = 1.2 nm; Au/pH 4 TiO₂ = 1.3 nm) than the catalysts grown on the natural P25 (2.4 nm). The gold particle coarsening is virtually eliminated for the treated TiO₂ supported nanoparticles stored under atmospheric conditions. Catalysts supported on treated TiO₂ were significantly more active than the non-treated analogs (Au/pH 10 TiO₂ rate = 0.28 and Au/pH 4 TiO₂ rate = 0.16 mole CO/mole Au•sec respectively), Figure 1. These catalysts are approximately 20 to 40 times more active than the Au/natural P25 catalyst and comparable to the most active gold catalysts reported in the literature [9]. Extensive characterization studies reveal no measurable change in surface defects or surface chemistry with solution processing except for the formation of strongly bound surface hydroxyls.

Figure 1. Catalytic activity data for Au nanoparticles on TiO₂ treated under different conditions.

Significance
Employing the vapor deposition technique allows us to deconstruct solution phase synthesis techniques to identify how the chemical processing influences catalytic properties of the resulting metal clusters. These results show that the coincidental addition of hydroxyls to the surface of the TiO₂ during the solution phase synthesis of gold catalysts are a key variable for the production of stable and catalytically active gold catalysts.

References