Preparation of Small, Monodisperse Supported Au Nanoparticles via Strong Electrostatic Adsorption of Au Ethylenediamine

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Introduction
Au nanoparticles have a high potential in catalysis and have been studied extensively for years beginning with Haruta’s discovery in 1987 that gold nanoparticles are highly active in CO oxidation reactions at sub-ambient conditions ¹. Gold nanoparticles have also been shown to be catalytically active for several chemical reactions including selective oxidation of hydrocarbons, reduction of NO and acetylene hydrochlorination to form vinyl chloride monomer (VCM).

In this work we demonstrate a simple, scalable synthesis of small (1-3 nm) Au nanoparticles on a variety of supports using strong electrostatic adsorption (SEA). SEA is used to create highly dispersed nanoparticles that are strongly bound to a support by controlling the pH of the solution. By controlling the pH of the solution relative to the support point of zero charge, the surface of the support becomes protonated or deprotonated resulting in an electrostatic interaction with an oppositely charged ionic precursor complex. The strongly interacting Au precursors, after thermal reduction, yield highly dispersed metal particles.

Materials and Methods
These experiments employed numerous support materials; SiO₂ (amorphous A90 and A300 and mesoporous SBA-15), γ-Al₂O₃, TiO₂, Nb₂O₅, ZrO₂, and graphitic carbon were used directly from the manufacturers. CeO₂ was obtained through calcination of cerium(III) acetate hydrate at 500 °C for 4 hours. Nb₂O₅ was achieved by calcination of niobic acid at 500 °C for 2 hours. Gold ethylenediammine, [Au(en)₂]³⁺ was prepared as described by Block and Blair².

Fresh [Au(en)₂]³⁺ was prepared at 200 ppm and a wide range of initial pH values. Each support was then weighed out for a surface loading of 1000 m²/L and added to 30 ml of pH adjusted Au solution. After 1 hour of shaking and contact the solid support material was filtered and dried at room temperature for 72 hours. ICP-OES was used to measure gold concentration in the parent solutions and after adsorption, and the difference was used to compute the Au uptake.

Significance
The ability to synthesize ultra-small Au nanoparticles onto a variety of supports with a wide range of zero charge points is demonstrated. This method is extendable to many other supports with low or mid-range points of zero charge.

STEM images of a) 1.4% Au/A90, b) 5.1% Au/A300, c) 8.2% Au/SBA-15. Scale bar is 20 nm.

References
2- B.P. Block, and J.C.B. Jr., Journal of the American Chemical Society 73 (1951) 4722-4725.

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