

Synthesis, characterization and evaluation of Au bimetallic catalysts prepared by electroless deposition methods

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Introduction:

Electroless deposition (ED) has been used for the preparation of continuous, thin film metal coatings, but also has the potential for the preparation of novel, bimetallic catalysts by adjustment of the deposition parameters [1]. Unlike traditional methods for the preparation of bimetallic catalysts, ED permits the selective deposition of a secondary metal (e.g., Au) on the surface of a catalytically active, primary metal surface (Pt, Pd). In order to prepare catalysts using this technique it is necessary to design a reactive, yet stable ED solution by the proper selection of the secondary metal salt and reducing agent(s), as well as the pH and temperature of the ED bath [2].

Synthesis:

Two gold electroless baths (EB) were developed to synthesize a series of Au-Pt/SiO₂ and Au-Pd/SiO₂ catalysts. The first bath was formulated using AuCl₄⁻ as the metal source and HCHO as the reducing agent, while the second employed Au(CN)₂⁻ as the Au source and hydrazine as the reducing agent. UV-Visible spectroscopy was used to evaluate the stability of Au electroless baths. In order to determine specificity and stability of the bath, the ED solution was exposed to the SiO₂ support to ensure that neither metal salt adsorption nor spontaneous reduction and precipitation of the secondary metal from solution occurred. Finally, the optimum stable conditions (pH and concentrations of Au source and reducing agent) for electroless gold deposition were established.

Table1: Optimum stable conditions for Au electroless deposition

EB 1 ([AuCl ₄] ⁻ , HCHO)	EB 2 ([Au(CN) ₂] ⁻ , H ₂ N-NH ₂)
[AuCl ₄] ⁻ < 0.126 mmoles/L	[Au(CN) ₂] ⁻ < 0.212 mmoles/L
[HCHO] < 0.466 mmoles/L	[H ₂ N-NH ₂] < 4.07 mmoles/L
[HCHO]/[AuCl ₄] ⁻ = 2/1 to 1.5/1	[H ₂ N-NH ₂]/[Au(CN) ₂] ⁻ = 30/1 to 20/1
pH = 8-10 and T=25°C	pH = 8-10 and T=25°C

Characterization:

For both systems, variable, sub-monolayer coverages of Au on Pt were achieved by adjusting the parameters for deposition. Thus, a series of Au-Pt/SiO₂ and Au-Pd/SiO₂ catalysts were prepared and characterized using H₂-O₂ titration (i.e., hydrogen titration of oxygen-precovered sites) and transmission Fourier-transform infrared (FT-IR) spectroscopy of CO adsorption. The H₂-O₂ titration results showed a decrease in H₂ uptake on Pt (or Pd) as Au was added, indicating Au deposition on Pt (or Pd) had occurred. However, the deviation of H₂

uptake from theoretical mono-dispersed coverage indicated both catalytic and autocatalytic deposition regimes. Changes in the population of adsorbed CO species with increasing Au content also corroborated this finding. The observed negative shifts in binding energy of Au 4f_{7/2} e⁻ and positive shifts of Pd 3d_{3/2} e⁻ in Au-Pd/SiO₂ catalysts from their monometallic counterparts suggests bimetallic interaction (i.e., the transfer of electrons from Pd to Au). In addition, XRD, EDX and HRTEM techniques were used to measure the particle size distribution and compositions of the Au-Pd catalysts.

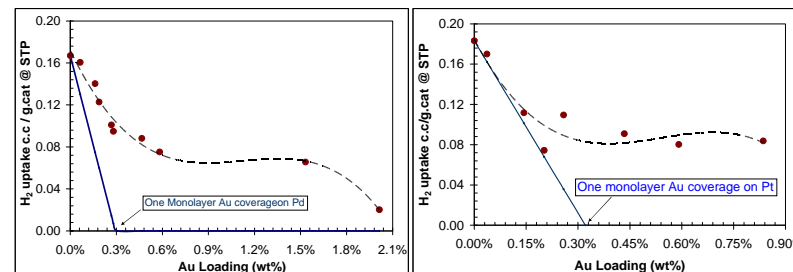


Figure1: H₂-O₂ titration results Left: Au-Pd/SiO₂ synthesized in EB 2, Right: Au-Pt/SiO₂ synthesized in EB 1

Evaluation:

The Au-Pt/SiO₂ catalysts have been evaluated for propylene hydrogenation to test for bimetallic ensemble effects. For this reaction Au is considered to be inactive. The reactions were performed at T = 10°C, P=1 atm, feed = 400 SCCM (5% C₃H₆, 20% H₂, 75% He). This hydrogenation reaction was found to be structure insensitive as shown by the Pt-based, constant TOF values achieved for the different Au loadings.

Secondly, oxidation studies of isopropyl alcohol to acetone over Pd/SiO₂, Au/SiO₂, and Au-Pd/SiO₂ have been initiated to evaluate the selectivity and activity of the Au-Pd bimetallic system. Preliminary results for the effects of Pd on the stability and activity of Au will be presented. The results for this probe reaction will be used develop optimum compositions for the selective, liquid phase oxidation of glycerol to form valuable chemical intermediates, such as glyceraldehyde, glyceric acid, hydroxyacetone, hydroxybutyric acid, oxalic acid, and glycolic acid.

References:

1. Okinaka, Y.O, Tetsuya, *Electroless deposition processes: Fundamentals and applications*. Advances in Electrochemical Science and Engineering, 1994. **3**: p. 55-116.
2. I. Ohno, O. Wakabayashi, and S. Haruyama, *Anodic oxidation of reductants in electroless plating*. Electrochemical Society, 1985. **132**(10): p. 2323

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