

## Preparation, Characterization, and Kinetic Evaluation of Ag-Pt Bimetallic Catalysts Prepared by Electroless Deposition

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### Introduction

Many monometallic catalysts used in industrial chemical processes have been replaced by bimetallic or multimetallic catalysts, which often provide enhanced selectivity, stability, and/or activity [1,2]. These bimetallic catalysts are typically prepared by either co-impregnation or successive impregnation of both metal salts onto the catalyst support [3]. In both methods, it is virtually impossible to ensure formation of truly bimetallic particles; instead formation of separate monometallic particles can and does occur [4]. The resulting complex mixture of bimetallic and monometallic particles results in poor control over the final catalyst performance, complicates catalyst characterization [5], and makes it very difficult to directly correlate the relationship between catalyst composition, characterization, and performance. An alternate, industrially-feasible method for the preparation bimetallic catalyst is the electroless deposition (ED) of reducible metal salts onto other metals. ED is a catalytic or auto-catalytic process for the selective deposition of metallic components onto catalytically active sites through a controlled chemical reaction that is catalyzed by the pre-existing metal (catalysis) or the metal which is being deposited (auto-catalysis) [6].

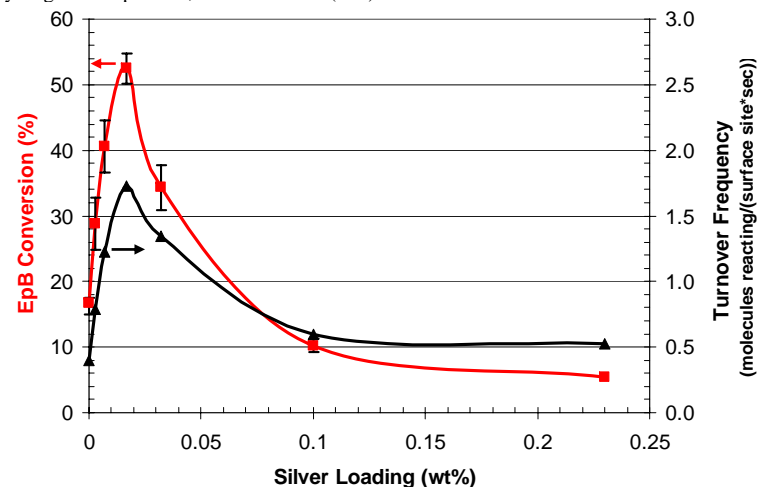
### Materials and Methods

A series of Ag-Pt catalysts have been prepared by the electroless deposition of Ag onto the Pt component of a Pt/SiO<sub>2</sub> catalyst at room temperature using an aqueous solution containing HCHO (reducing agent), NaOH (adjust pH to 9), and AgNO<sub>3</sub> (Ag<sup>+</sup> source). These bimetallic catalysts have been characterized using atomic absorption, selective H<sub>2</sub> chemisorption, XPS, and FTIR of <sup>12</sup>CO and <sup>13</sup>CO adsorption. Finally, gas-phase kinetic studies have been conducted using the selective hydrogenation of 3,4-epoxy-1-butene (EpB - a multifunctional olefin containing both a C=C bond and an epoxide ring) in a fixed bed reactor at atmospheric pressure and 100°C using a feed of 2.5% EpB, 20% H<sub>2</sub>, balance He at GHSV = 8500hr<sup>-1</sup>. Feed and product streams were analyzed using an in-line GC equipped with both TCD and FID detectors. Reaction data are reported after 900min online to obtain steady state conditions.

### Results and Discussion

Hydrogen chemisorption, XPS, FTIR, and the reaction studies all verify that Ag is deposited on Pt (not on the SiO<sub>2</sub> support) and indicate that both the catalytic deposition of Ag on Pt and autocatalytic deposition of Ag on Ag are present. Results for FTIR of CO adsorption indicate that Ag is preferentially located on the Pt(111) sites based on the strong reduction of the linear CO-Pt(111) peak at approximately 2090cm<sup>-1</sup>. These results have been corroborated by FT-IR of <sup>13</sup>CO adsorption and will be discussed using preliminary theoretical studies.

As seen in the figure below, the addition of a small amount of Ag to Pt-containing catalysts results in a 3-fold increase in both TOF and intrinsic activity. Higher Ag loadings result in lower activities presumably due to coverage of the Pt sites by Ag atoms, although TOF of the residual Pt sites remain essentially constant. The unexpected increase in catalytic activity is attributed to a Ag induced reduction in the interaction of EpB with the Pt surface, consistent with the kinetics and energetics of this reaction. Changes in product selectivity have also been observed; unsaturated C<sub>4</sub>-oxygenates (3-buten-1-ol, crotonaldehyde, and crotyl alcohol) are apparently formed on corner and edge sites and butylene oxide, the selective C=C hydrogenation product, is formed on Pt(111) sites.



**Figure 1.** Effect of Ag loading on the EpB hydrogenation conversion and TOF (calculated using H<sub>2</sub> chemisorption data). Ag/SiO<sub>2</sub> is inactive for this reaction.

### Significance

The ED process provides a controlled, industrially feasible method for the production of bimetallic catalysts. Additionally, the controlled placement of the secondary metal using ED should aid fundamental studies in the correlation of catalytic activity and composition.

### References

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