

# Synthesis of Supported Pd/Au Dilute Limit Alloy Nanoparticles

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## Introduction

Useful chemicals are widely synthesized by homogeneous transition metal-catalyzed reactions. However, the aggregation and precipitation of atomically dispersed catalysts causes considerable loss of activity [1]. For example, palladium-based catalysts, while being some of the most versatile, are known to aggregate to form Pd black [2]. This has spurred interest in the heterogenization of atomically dispersed Pd catalysts to impart stability and facilitate recyclability.

In this study, we demonstrate the synthesis of a supported, dilute limit alloy of Pd in Au. Using the simple method of co-electrostatic adsorption [3] with small amounts of Pd precursor relative to Au, Pd sites are isolated in the surface of silica supported Au nanoparticles. Site isolation is confirmed with in situ CO adsorption in a FTIR flow cell as well as measurements of catalytic reactivity.

Iwasawa et al. investigated Pd based homogeneous catalysts to decrease metal aggregation and precipitation in alcohols oxidation processes [1]. Later, Enache et al. studied oxidation of primary alcohols to aldehydes using a heterogeneous bimetallic Au-Pd supported catalyst [2]. Here we employ the partial oxidation of 1-phenylethanol, for which the selective product acetophenone will only occur over isolated Pd sites [1], [2].

## Materials and Methods

The catalyst was prepared using the simple and scalable method of strong electrostatic adsorption (SEA) [3], [4]. Aerosil 300 amorphous silica (280 m<sup>2</sup>/g, PZC 3.6) was used as support. Catalysts with different molar Pd:Au ratio of 3:1, 1:1, 1:5, 1:14, 1:28, 1:53, and monometallic Pd and Au catalysts were synthesized. The Au precursor was synthesized using hydrogen tetrachloroaurate (III) hydrate 99.9% to make trichlorobis(ethylenediamine)gold(III). Tetraamminepalladium(II) chloride was used as Pd precursor.

## Results and Discussion

The FTIR data in Figure 1 show the CO spectra and deconvoluted peaks of various types of CO adsorption on the catalysts. CO adsorption favors three-fold and bridge adsorption on the surface of Pd. The linear CO adsorption is more favored when the surface is saturated with CO or there are only isolated Pd sites on the surface. On Au surfaces, CO adsorption is almost negligible at room temperature. The CO adsorption on monometallic Pd was used as a reference to fit the position and shape of peaks attributed to Pd. Au shows only a very small CO adsorption peak at 2130 cm<sup>-1</sup>. In the bimetallic catalyst, the position and intensity of the peaks changed significantly the amount of Pd in the catalysts was decreased, while keeping the Au loading constant. Figure 2a shows the linear to nonlinear peak area by decreasing the Pd:Au molar ratio. This analysis confirms that almost all multi-coordinated forms of CO adsorption on Pd disappeared at the dilute limit of Pd/Au.

Preliminary results of the probe reaction are shown in Figure 2b. Significant amounts of acetophenone were produced at a Pd/Au ratio of 1:5, and this amount (per Pd site)

increased further as the ratio of Pd/Au decreased. Evaluation of the complete series is underway.

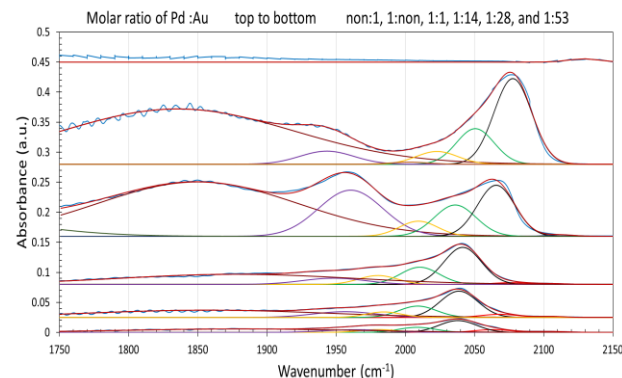


Figure 1. FTIR spectra of in situ CO adsorption on monometallic and bimetallic catalysts.

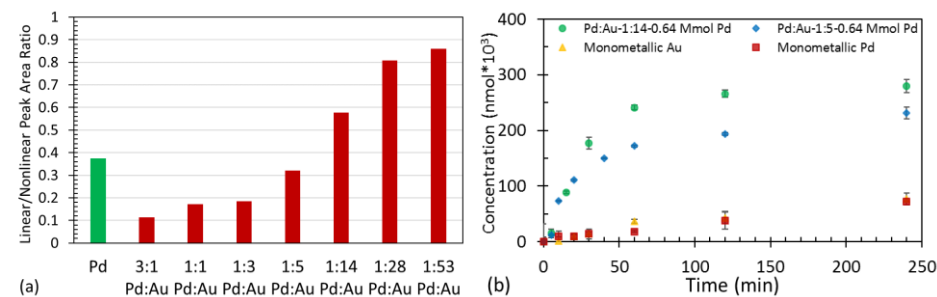


Figure 2. (a) linear to nonlinear CO adsorption FTIR peak area ratio, (b) reaction product acetophenone concentration vs. time.

## Significance

Stable isolated site catalysts could be a bridge between homogeneous and heterogeneous catalysis promising well-defined and highly selective active centers.

## References

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