

Novel fabrication and catalytic application gold–palladium alloy nanoparticles

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Introduction

The increasing demand for clean and energy-efficient chemical processes requires the catalysts of tomorrow to deliver greater activity and selectivity at lower temperatures. Alloys have proven superior to single metal catalysts in this respect for many applications. Alloy catalysts can offer greater reaction-specific catalyst tunability, lower cost, and higher performance than their monometallic counterparts.¹⁻⁵ Au-Pd catalysts have been of particular interest not only because of the wide range of reactions in which they can be used but also because of their relative simplicity.⁶ Au and Pd are soluble at all compositions, so that the effects of different phases need not be considered.^{7,8}

Results and Discussion

The gold–palladium alloy were prepared by the citrate-reduction procedure. 2.1 ml 2.4 mM HAuCl₄/K₂PdCl₄ of different molar ratios was mixed with 47.9 ml H₂O in a quartz beaker. The solution was stirred and heated to boiling, and then 1.0 ml 35mM sodium citrate solution was added to the boiling solution. The solution was further boiled for 40 min and was then left to cool to room temperature.

Figure 1a shows UV-vis spectra of Au, Pd, and Au-Pd bimetallic nanoparticles. Au nanoparticles show a characteristic surface plasmon absorption at 520 nm, and Pd nanoparticles show broad absorption over the entire spectral range. The absorbance behavior of the bimetallic nanoparticles is found to be different from those of the individual and physical mixture of monometallic nanoparticles. The characteristic absorbance band of Au nanoparticles that appears at 520 nm is absent in the case of the Au-Pd bimetallic nanoparticles, while it is present in the case of the physical mixture. This clearly indicates that dispersions of Au-Pd nanoparticle systems do not contain monometallic clusters but contain clusters with bimetallic structure.

Figure 1b shows the plot of $\ln(A_t/A_0)$ against reaction time for alloy nanoparticles in the catalytic reduction of 4-nitrophenol into 4-aminophenol in the presence of NaBH₄. In the catalytic reaction, a good linear fitting of $\ln(A_t/A_0)$ versus the reaction time was obtained. The rate constant of the reduction calculating from the slope, increases from pure Au to

pure Pd as the Pd content increased in Au-Pd alloy particles, indicating that Pd could be much more efficient than Au for the electron transfer from BH₄⁻ ion to 4-nitrophenol.

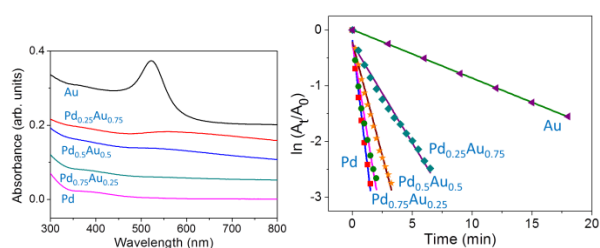


Figure 1 (a) UV-vis spectra of Au-Pd nanoparticles with different molar ratios. (b) Plot of $\ln(A_t/A_0)$ against reaction time for alloy nanoparticles in the catalytic reduction of 4-nitrophenol.

Conclusions

The Au-Pd alloy NPs with various compositions were synthesized by a facile synthesis process. only sodium citrate was used and only one step heating process was needed. UV-vis spectroscopy confirmed the formation of homogeneous alloy NPs. the Au-Pd alloy nanoparticles including pure Au and Ag samples were exploited as catalysts for the reduction of 4-nitrophenol in the presence of NaBH₄. As the Pd content was increased in the AuPd alloy nanoparticles, the rate constant of the reduction was exponentially increased from pure Au to pure Pd.

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¹Alexeev, O. S.; Gates, B. C. *Ind. Eng. Chem. Res.* **2003**, 42, 1571.

²Han, Y.-F.; Wang, J.-H.; Kumar, D.; Goodman, D. W. *J. Catal.* **2005**, 232, 467.

³Scott, R. W.; Sivadinarayana, C.; Wilson, O. M.; Yan, Z.; Goodman, D. W.; Crooks, R. M. *J. Am. Chem. Soc.* **2005**, 127, 1380.

⁴Besenbacher, F.; Chorkendorff, I.; Clausen, B. S.; Hammer, B.; Molenbroek, A. M.; Nørskov, J. K.; Stensgaard, I. *Science* **1998**, 279, 1913.

⁵Huber, G. W.; Shabaker, J. W.; Dumesic, J. A. *Science* **2003**, 300, 2075.

⁶Coq, B.; Figueras, F. J. *Mol. Catal. A: Chem.* **2001**, 173, 117.

⁷Ferrer, D.; Torres-Castro, A.; Gao, X.; Sepúlveda-Guzmán, S.; Ortiz-Méndez, U.; José-Yacamán, M. *Nano Lett.* **2007**, 7, 1701.

⁸Gao, F.; Goodman, D. W. *Chem. Soc. Rev.* **2012**, 41, 8009.