

Title	Effects of Preparation Methods and Electronic States of the AuPd Bimetallic Nanoparticles on the Activity for Aerobic Oxidation of Alcohols
Author(s)	Nishimura, S.; Yakita, Y.; Katayama, M.; Higashimine, K.; Ebitani, K.
Citation	Nanotech 2013, 1: 448-451
Issue Date	2013-05
Type	Conference Paper
Text version	publisher
URL	http://hdl.handle.net/10119/11433
Rights	© 2013 NSTI http://nsti.org . Reprinted and revised, with permission, from Nanotech 2013, pp. 448-451, May 12-16, 2013, Washington DC, U.S.A.
Description	

Effects of Preparation Methods and Electronic States of the AuPd Bimetallic Nanoparticles on the Activity for Aerobic Oxidation of Alcohols

S. Nishimura, Y. Yakita, M. Katayama, K. Higashimine and K. Ebitani*

School of Materials Science, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Nomi, Ishikawa 923-1292, Japan, ebitani@jaist.ac.jp

ABSTRACT

Correlations between nanostructure of AuPd active sites synthesized with different preparation methods and their catalytic activities for the oxidation of alcohols were investigated. The catalytic activity strongly depend on the morphology and Au/Pd molar ratio of the AuPd active site, these were attributed by the differences in preparation methods. The Au₆₀Pd₄₀-PVP/HT catalyst prepared with a simultaneous reduction method exhibited the highest activity for aerobic oxidation of alcohol; *ex.* TON = 395,700, TOF = 207,000 h⁻¹ for 1-phenylethanol oxidation.

Characterizations with TEM, XPS, XAFS and other analytical techniques suggested that the highly active Au₆₀Pd₄₀-PVP/HT catalyst possessed uniform AuPd nanoalloys and the largest amount of electrons in Au 5*d* states. These results proposed that formation of the uniform AuPd nanoalloys allowed a big electron transfer from Pd to Au atoms, and which played an important factor for the significant activity of the Au₆₀Pd₄₀-PVP/HT.

Keywords: AuPd nanoalloy, alcohol oxidation, preparation method, morphology, electronic negativity.

1 INTRODUCTION

Oxidation reaction of primary and secondary alcohols into the corresponding aldehydes or carboxylic acids and ketones, respectively, has a crucial role in organic syntheses. Traditionally, the stoichiometric inorganic oxidants such as potassium permanganate (KMnO₄) and potassium chromate (K₂CrO₄) reagents were widely used in the industrial processes, however, they produced a lot of salts as the by-product after their performances as an oxidant. With increasing the concerns on environmental and economic issues, the “green” oxidants such as molecular oxygen (O₂) and hydrogen peroxide (H₂O₂) have been attempted to use for alcohol oxidation, they remains only a quantity of water as a by-product equal to the performing oxidant after the oxidation reaction.

These movements promote the development of metal supported heterogeneous catalyst which can achieve both an effective activation of such green oxidants for the alcohol oxidation and a decrease of the cost for separation of catalyst from reaction mixture and purification of the product. For instance, metal supported and/or incorporated

hydrotalcite (HT) catalysts such as Ru/HT, Au/HT, Pd/HT, and Pt/HT were reported as novel heterogeneous catalyst for alcohols oxidation using O₂ oxidant [1-4]. In these catalysts, the HT acts as not only the support for active metal sites but also its surface basic site for accelerating the proton abstraction process of alcohol to form metal-alcoholate intermediates.

Herein, we synthesized the Au_xPd_y bimetallic NPs stabilized onto HT with different preparation methods, and compared their catalytic activities for aerobic oxidation to study the effect of physical/chemical properties of Au_xPd_y NPs as active site. Heterometallic nanoparticles (NPs) have made great impacts for development of the advanced new materials because of their unique behaviors different from those of monometallic NPs [5-7]. Especially, the AuPd bimetallic NPs were well known as the good nanocatalyst for oxidations, hydrogenations, acetoxylation, the direct synthesis of H₂O₂, the oxygen reduction in electrodes, and so on [8-12].

2 EXPERIMENTAL

The PVP-protected bimetallic Au_xPd_y NPs were prepared with various Au:Pd (*x*:*y*) molar ratios in a polyol reduction method [13,14] with some modifications. The ethylene glycol (EG) and poly(*N*-vinyl-2-pyrrolidone) (PVP, Mw = 58,000) were used as reductant and capping agent, respectively, for syntheses of Au_xPd_y-PVP NPs from PdCl₂ and HAuCl₄ sources.

Briefly, the simultaneously reduced Au_xPd_y NPs (Au+Pd) were examined that an aqueous mixed solution of PdCl₂ (*y* mmol), KCl (0.1 g), HAuCl₄·4H₂O (*x* mmol), PVP (0.58 g) and EG (50 ml) was refluxed for 2 h. The sequential reduced Au_xPd_y NPs (Au→Pd) were carried out as follows: an aqueous mixture of HAuCl₄·4H₂O (*x* mmol), PVP (0.29 g) and EG (25 ml) was refluxed for 1 h, thereafter, another aqueous mixture of PdCl₂ (*y* mmol), KCl (0.1 g), PVP (0.29 g) and EG (25 ml) was added and continuously refluxed for totally 2 h. The sequential reduced Au_xPd_y NPs (Pd→Au) was produced by the similar methodology to the (Au→Pd) method with a converse order of refluxing metal. These synthesized Au_xPd_y NPs were deposited onto the solid base HT, then three different types of Au_xPd_y-PVP/HTs denoted as (Au+Pd), (Au→Pd) and (Pd→Au), respectively, were prepared.

The catalytic activities were evaluated by the aerobic oxidations of benzyl alcohol and/or 1-phenylethanol. The products were analyzed by GC-FID (DB-FFAP or DB-1 column). Characterization of those Au_xPd_y NPs were investigated by Energy-dispersive X-ray (EDS) and the scanning TEM-high angle annular dark field (STEM-HAADF) (Kyoto-Advanced Nanotechnology Network; No. 2011-JAIST-9 and 2011-JAIST-33), a X-ray photoelectron spectroscopy (XPS) and/or a X-ray-absorption fine structure spectroscopy (XAFS; BL01B1, SPring-8, Japan, 2011A1607, 2012B1610) analytical techniques.

3 RESULTS AND DISCUSSIONS

Figure 1 shows catalytic activities for the aerobic oxidation of benzyl alcohol over the each type of Au_xPd_y -PVP/HT catalysts synthesized with different Au/Pd mole ratios. It was indicated that preparation method and Au/Pd molar ratio effected to their catalytic activities for the aerobic oxidation of benzyl alcohol. Interestingly, even under the differences in Au/Pd ratio, the activities were in order: (Au+Pd) > (Pd→Au) > (Au→Pd) methods. The $Au_{60}Pd_{40}$ -PVP/HT (Au+Pd) were found to be the highest active catalyst among them. Under the same condition, the Au_{100} -PVP/HT and Pd_{100} -PVP/HT prepared with the same simultaneous reduction method indicated 0% and 34% yields, respectively.

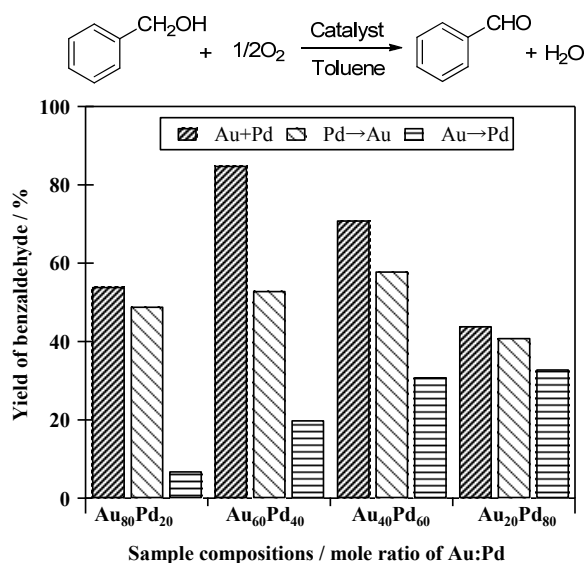


Figure 1 Aerobic oxidation of benzyl alcohol over the Au_xPd_y -PVP/HT catalysts prepared with different methods. *Reaction conditions:* Benzyl alcohol (2 mmol), catalyst (0.2 g, Au + Pd = 0.02 mmol), toluene (5 mL), 50 °C, O_2 flow.

In order to investigate the nanocomponents in $Au_{60}Pd_{40}$ -PVP/HTs, TEM analyses were examined. As shown in the Figure 2, AuPd alloy in the $Au_{60}Pd_{40}$ -PVP NPs (Au+Pd) and Pd@Au core-shell in the $Au_{60}Pd_{40}$ -PVP NPs (Pd→Au) method were observed. Average sizes of the $Au_{60}Pd_{40}$ -

PVP/HT estimated by 500 NPs were 2.6 nm in the (Au+Pd) method and 4.6 nm in the (Pd→Au) method. On the other hand, the $Au_{60}Pd_{40}$ -PVP/HT (Au→Pd) catalyst was composed with the mixture of Au and Pd particles, Au agglomerates and isolated Pd NPs. Additionally, Au agglomerates in the Au_{100} -PVP/HT catalyst and monodispersed Pd NPs with 2.6 nm as the average size of 500 NPs in and Pd_{100} -PVP/HT catalyst were determined in TEM images.

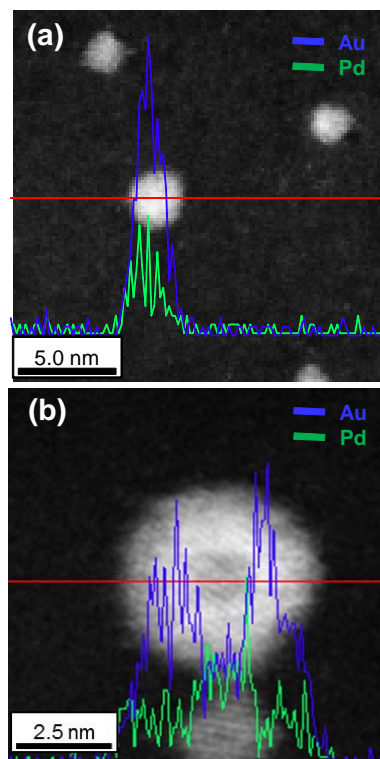


Figure 2 STEM-EDS line analysis of $Au_{60}Pd_{40}$ NPs prepared by (a) (Au+Pd) and (b) (Pd→Au) methods.

A further experiment for structure analysis, the extended X-ray absorption fine structure (EXAFS) analyses was studied. Fourier-transforms (FTs) of k^3 -weighted Au L_{3} -edge EXAFS spectra of samples and references were shown in Figure 3(a). The |FT|s of Au_{100} -PVP/HT and $Au_{60}Pd_{40}$ -PVP/HT (Au→Pd) were similar to the Au foil. While the $Au_{60}Pd_{40}$ -PVP/HTs of both (Pd→Au) and (Au+Pd) methods possessed a two-humped peak in the range of 2-3 Å, this peak was attributed to the presence of AuPd in core-shell and alloy [15-17]. The |FT|s of k^3 -weighted Pd K -edge EXAFS spectra were also shown in Figure 3(b). The $Au_{60}Pd_{40}$ -PVP/HT (Au→Pd) and Pd_{100} -PVP/HT were composed with Pd metal. The $Au_{60}Pd_{40}$ -PVP/HTs of (Pd→Au) and (Au+Pd) included the similarities around 2-3 Å with AuPd alloy [15,16]. The peak around at 1.5 Å in |FT|s obtained in all samples is fitted as the Pd-O, which is likely due to partially oxidized Pd and/or PVP coordination to the particle surface.

These results from TEM and EXAFS analyses suggested that the preparation methods of (Au+Pd), (Pd→Au) and (Au→Pd) in Au₆₀Pd₄₀-PVP/HTs influenced to the morphology of active sites, and AuPd alloy, Pd@Au core-shell NPs, and isolated Au and Pd NPs were formed, respectively.

The highly active Au₆₀Pd₄₀-PVP/HT (Au+Pd) was also applied for aerobic oxidation of 1-phenylethanol to acetophenone. The 2 mmol of 1-phenylethanol was easily converted (100% conv.) to >99% yield of acetophenone at 40 °C for 1 h under O₂ flow (20 ml·min⁻¹). Use of lower

temperature (O₂ flow, 27 °C, 3 h) or milder oxidant (air purge, 40 °C, 12 h) also achieved the high activity (>99% yield). Traditionally, the catalytic activity for aerobic oxidation has been elucidated with 250 mmol scale of 1-phenylethanol. The turnover number (TON) and turnover frequency (TOF) of the oxidation of 1-phenylethanol (250 mmol) into acetophenone over the Au₆₀Pd₄₀-PVP/HT (Au+Pd) catalyst were up to 395,700 and 69,100 h⁻¹, respectively, at 423 K for 24 h in the absence of solvents with 35% yield and 95% selectivity. These high activities were comparable to the various types of heterogeneous catalysts reported previously [2, 18-21].

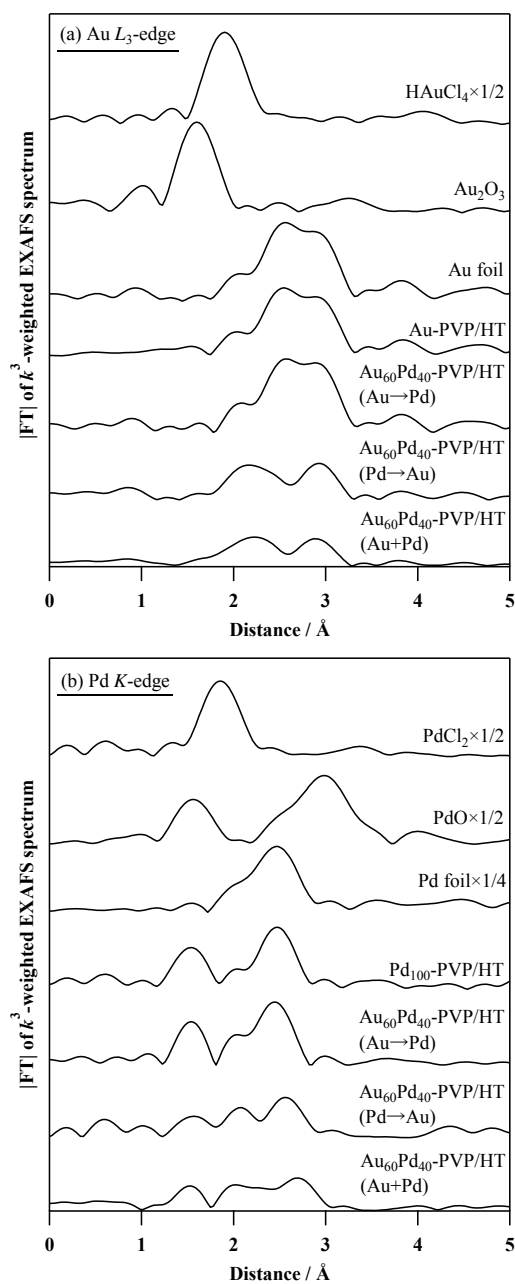


Figure 3 Fourier-transforms (FTs) of k^3 -weighted (a) Au L_3 -edge and (b) Pd K -edge EXAFS spectra of the Au₆₀Pd₄₀-PVP/HTs, Au₁₀₀-PVP/HT and references.

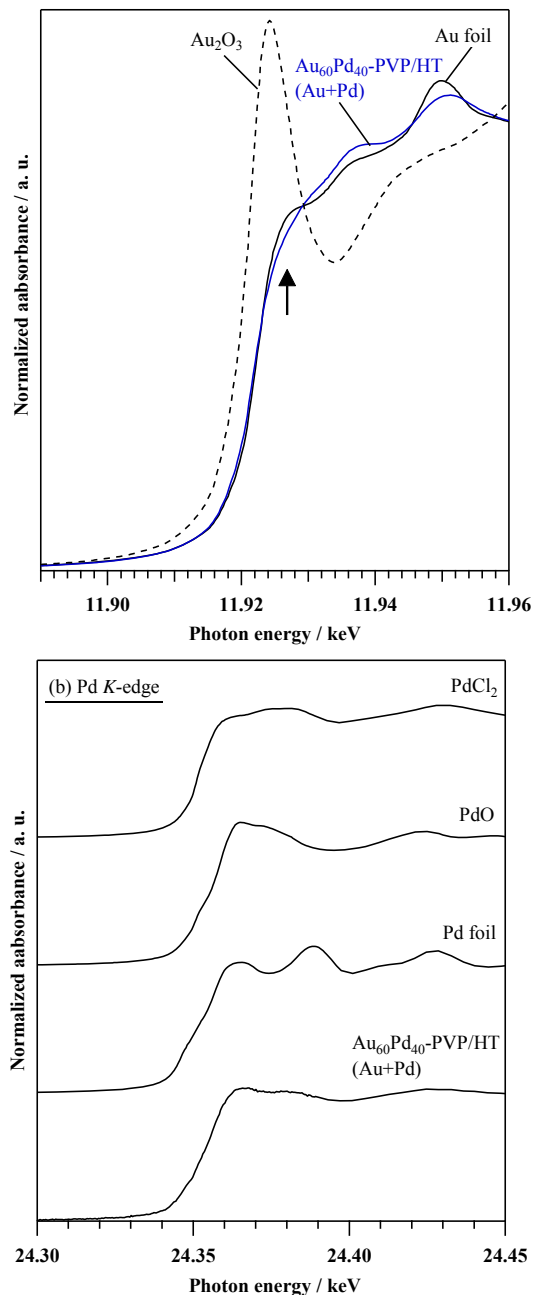


Figure 4 XANES spectra in (a) Au L_3 -edge and (b) Pd K -edge of the Au₆₀Pd₄₀-PVP/HT (Au+Pd) and references.

In order to investigate the significant novelty acquired by Au₆₀Pd₄₀-PVP/HT (Au+Pd) catalyst, the electronic condition was discussed by a X-ray absorption near-edge structure (XANES). It was observed that the Au₆₀Pd₄₀-PVP/HT showed a lower intensity than Au foil (Figure 4(a)) in the white-line (WL) area of Au L₃-edge XANES spectrum, this related to the frequency of electron transition from 2*p* to 5*d* state; *i.e.* the Au₆₀Pd₄₀-PVP/HT (Au+Pd) possessed more 5*d* electron density than Au bulk. On the other hand, the Pd *K*-edge XANES indicated that the Pd state in Au₆₀Pd₄₀-PVP/HT (Au+Pd) was not metallic but cationic including ionic and/or oxidized Pd atoms (Figure 4(b)). Thus, it was suggested that the negatively charged Au atoms and electronically poor Pd atoms were presence in the Au₆₀Pd₄₀-PVP/HT (Au+Pd), these supposedly derived from the electron transfer from Pd to Au atoms according to Pauling's electronegativity protocol. Presence of the negatively charged Au atoms also supported by a X-ray photoelectron spectroscopy (XPS) (not shown). The well correlations between the negativity in Au atoms and catalytic activity for aerobic oxidation was reported previously [22].

4 CONCLUSION

We discussed the effects of preparation methods and electronic states of the AuPd bimetallic NPs on the activity for aerobic oxidation of alcohols. The Au₆₀Pd₄₀-PVP/HT catalyst prepared by a simultaneous reduction method (Au+Pd) showed the higher activities for aerobic oxidation of benzyl alcohol than that prepared by sequential reducing methods, (Pd→Au) and (Au→Pd). The highly active Au₆₀Pd₄₀-PVP/HT (Au+Pd) possessed AuPd nanoalloy active sites containing the electronic rich Au and poor Pd atoms.

According to these results, we suggested that the electron transfer from Pd to Au atoms in AuPd NPs differed by preparation method and Au/Pd molar ratio played an important factor for the significant activity of aerobic oxidation reactions. The simultaneous reducing method prepared the Au₆₀Pd₄₀-PVP/HT catalyst composed uniform AuPd alloy NPs and high numbers of negatively-charged Au atoms, these characters contributed to a significant activity for alcohol oxidation reactions [23].

REFERENCES

[1] A. Takagaki, M. Takahashi, S. Nishimura, and K. Ebitani, *ACS Catal.*, 1, 1562, 2011.
 [2] T. Mitsudome, A. Noujima, T. Mizugaki, K. Jitsukawa, and K. Kaneda, *Adv. Synth. Catal.*, 351, 1890, 2009.
 [3] N. Kakiuchi, Y. Maeda, T. Nishimura, and S. Uemura, *J. Org. Chem.*, 66, 6620, 2001.
 [4] A. Tsuji, K.T.V. Rao, S. Nishimura, A. Takagaki, and K. Ebitani, *ChemSusChem*, 4, 542, 2011.
 [5] H. Zhang, T. Watanabe, M. Okumura, M. Haruta, and N. Toshima, *Nature Mater.*, 11, 49, 2012.

[6] G.L. Brett, Q. He, C. Hammond, P.J. Miedziak, N. Dimitratos, M. Sankar, A.A. Herzing, M. Conte, J.A. Lopez-Sanchez, C.J. Kiely, D.W. Knight, S.H. Taylor and G. J. Hutchings, *Angew. Chem., Int. Ed.* 50, 10136, 2011.
 [7] N.K. Chaki, H. Tsunoyama, Y. Negishi, H. Sakurai, T. Tsukuda, *J. Phys. Chem. C*, 111, 4885, 2007.
 [8] M.H.A. Rahim, M. M. Forde, R. L. Jenkins, C. Hammond, Q. He, N. Dimitratos, J.A. Lopez-Sanchez, A.F. Carley, S.H. Taylor, D.J. Willock, D.M. Murphy, C.J. Kiely, and G.J. Hutchings, *Angew. Chem. Int. Ed.*, 52, 1280, 2012.
 [9] N. Toshima, M. Haruta, Y. Yamazaki, and K. Asakura, *J. Phys. Chem.*, 96, 9927, 1992.
 [10] M. Chen, D. Kumar, C.W. Yi, and D.W. Goodman, *Science*, 310, 291, 2005.
 [11] J.K. Edwards, B. Solsona, N.E. Ntainjua, A.F. Carley, A.A. Herzing, C.J. Kiely, and G.J. Hutchings, *Science*, 323, 1037, 2009.
 [12] J.H. Shim, J. Kim, C. Lee, and Y. Lee, *Chem. Mater.*, 23, 4694, 2011.
 [13] D. Ferrer, A. Torres-Castro, X. Gao, S. Sepúlveda-Guzmán, U. Ortiz-Méndez, and M. José-Yacamán, *Nano Lett.*, 7, 1701, 2007
 [14] M. Harada, K. Asakura, and N. Toshima, *Shokubai*, 34, 432, 1992.
 [15] P. Dash, T. Bond, C. Fowler, W. Hou, N. Coombs, and R.W.J. Scott, *J. Phys. Chem. C*, 113, 12719, 2009.
 [16] L. Guzi, A. Beck, A. Horvath, Zs. Koppány, G. Stefler, K. Frey, I. Sajo, O. Geszti, D. Bazin, and J. Lynch, *J. Mol. Catal. A: Chem.*, 204-205, 545, 2003.
 [17] F. Liu, D. Wechsler, and P. Zhang, *Chem. Phys. Lett.*, 461, 254, 2008.
 [18] A. Abad, P. Concepcion, A. Corma, and H. Garcia, *Angew. Chem., Int. Ed.*, 44, 4066, 2005.
 [19] A. Abad, C. Almela, A. Corma, and H. Garcia, *Tetrahedron*, 62, 6666, 2006.
 [20] K. Mori, T. Hara, T. Mizugaki, K. Ebitani, and K. Kaneda, *J. Am. Chem. Soc.*, 126, 10657, 2004.
 [21] D.I. Enache, J.K. Edwards, P. Landon, B. Solsona-Espriu, A.F. Carley, A.A. Herzing, M. Watanabe, C.J. Kiely, D.W. Knight, and G.J. Hutchings, *Science*, 311, 362, 2006.
 [22] S. Nishimura, Y. Yakita, M. Katayama, K. Higashimine, and K. Ebitani, *Catal. Sci. Tech.*, 3, 351, 2013.
 [23] S. Nishimura, K. Ebitani, and Y. Yakita, JP Patent submitted; 2013-037206.

ACKNOWLEDGEMENT

This research is partly supported from Intellectual Property Highway Promotion of the Japan Science and Technology Agency (JST), Japan.