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## Preparation and Evaluation of Bimetallic Au Nano-Catalyst with Aerobic Oxidation of 1-Phenylethanol

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### ABSTRACT

Contributions of electronic (or ligand) and geometric (or ensemble) effects on the AuM bimetallic nano-catalyst were elucidated by using a simple aerobic oxidation of 1-phenylethanol to acetophenone on the basis of difference in the ionization energy values ( $E_i$ ) between Au and M elements. The poly(*N*-vinylpyrrolidone) (PVP)-protected Au<sub>60</sub>M<sub>40</sub> bimetallic NPs (M = Ag, Cu, Pd, Pt and Ir) were prepared with a polyol reduction method, and stabilized onto the solid base hydrotalcite support affording the Au<sub>60</sub>M<sub>40</sub>-PVP/HT catalysts. The yields for acetophenone were observed as the following order; Au<sub>60</sub>Pd<sub>40</sub>-PVP/HT (>99%) >> Au<sub>60</sub>Ag<sub>40</sub>-PVP/HT (17.4%) > Au<sub>60</sub>Cu<sub>40</sub>-PVP/HT (13.8%) > Au<sub>60</sub>Pt<sub>40</sub>-PVP/HT (7.1%) > Au<sub>60</sub>Ir<sub>40</sub>-PVP/HT (5.5%), at 343 K for 6 h. Differences in the  $E_i$  between Au and M ( $E_{iAu}-E_{iM}$ ) indicted that the yields over the Ag, Cu, Pt, and Ir incorporated Au catalysts were well-understood on the ligand effects theory, though geometric factors such as differences in nanostructure around Au atom in Au<sub>60</sub>M<sub>40</sub> NPs on HT should be further considered as other contributed factors. The significant activity on Au<sub>60</sub>Pd<sub>40</sub>-PVP/HT was studied in terms of the electron density of Pd atoms. It was observed that the Pd 4d density was varied by the amount of Au loading. According to these observations combined with our previous studies, we suggest that the advantages in AuPd bimetallic catalyst are not only in the ligand effect serving negatively-charged Au but also the ensemble effect of neighbor Pd, and they synergistically contribute to the novel activity for aerobic alcohol oxidation over AuPd catalyst.

### INTRODUCTION

Gold-Palladium (AuPd) bimetallic catalyst has much attracted by many research groups and it is well-known as the most extensively studied bimetallic Au-based catalyst because of its highly catalytic performance for various reactions [1]. For instance, the novelty of AuPd bimetallic catalysts was reported in aerobic alcohol oxidation [2-4], hydrogenation of dienes [5], direct synthesis of H<sub>2</sub>O<sub>2</sub> from H<sub>2</sub> and O<sub>2</sub> gas [6], hydrogenation of biomass-based furaldehydes [7], low-temperature CO oxidation [8] and so on, though the favorable nanostructure was much difference in each study. Novel catalytic performances and various preparation methods have been surveyed well for Au-based nano-catalysts, however, the reasons for such significant and widely-capable performances over them, *ex.* novel AuPd bimetallic catalysts, are still unclear.

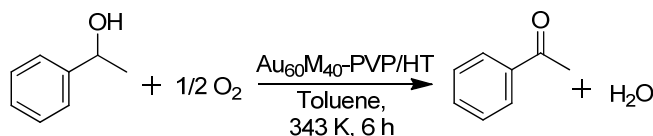
Herein, in order to clarify the extraordinary catalytic property on AuPd active center, we synthesized the poly(*N*-vinylpyrrolidone)-protected AuM bimetallic NPs supported hydrotalcite (AuM-PVP/HT) catalysts and compared their catalytic performance in the aerobic oxidation of 1-phenylethanol. We thought such simple alcohol oxidation without side- and over- reactions in comparison with commonly studied benzyl alcohol oxidation might help the rational consideration for the effects of secondary element on AuM catalyst, especially on AuPd catalyst.

## EXPERIMENTS

The Au<sub>60</sub>M<sub>40</sub>-PVP/HT catalysts were prepared by a simultaneous polyol reduction method using ethylene glycol (EG) (or 2-ethoxyethanol) and PVP as a reducing and a capping agent, respectively [3-4]. The Ag, Cu, Pd, Pt and Ir were selected as the second element of M because of both their low surface segregation energy with Au [9] and the presence of reports for such kind of AuM-alloy formations. Briefly, an aqueous mixed-solutions (50 ml) of HAuCl<sub>4</sub> and PdCl<sub>2</sub>, CuCl<sub>2</sub>, H<sub>2</sub>PtCl<sub>6</sub>, H<sub>2</sub>IrCl<sub>6</sub> or AgNO<sub>3</sub> (all served by Wako) were prepared. The amount of Au and M was 0.06 mmol and 0.04 mmol, respectively (Au/M = 60/40 (mol/mol)). KCl (0.1 g, Kanto) was also added for just Pd case. Then, 0.58 g of PVP (ACROS, Mw = 58,000) and 50 ml of EG (Wako) were mixed with the above solution, following by a reflux treatment for 2 h. Thereafter, 1.0 g of HT (Tomita, Mg/Al = 5.3) was added into the solution, and then an additional reflux treatment for 1 h was operated. The emulsion was filtered off, washed with 2 L of deionized water, and dried *in vacuo* at room temperature. For the synthesis of AuAg catalyst, 2-ethoxyethanol (Wako) with a same procedure was used instead of EG for modification because the typical EG method could produce only Au<sub>60</sub>Ag<sub>40</sub> NPs with wide size distributions ( $\sigma = 2.05$ ).

As-prepared Au<sub>60</sub>M<sub>40</sub>-PVP/HT catalysts were characterized by Uv-vis (JEOL V-670), ICP-AES (Shimadzu ICPS-7000 ver.2) and TEM (Hitachi H-7650, 100 kV). XAS studies were performed at a BL-9A for Pd-L<sub>3</sub> edge and a BL-9C for Au-L<sub>3</sub> edge (Proposal No. 2013G586) and a BL-NW10 for Pd-K edge (Proposal No. 2012G763) in KEK-PF (Tsukuba, Japan).

In general procedure for the aerobic oxidation (Scheme 1), 1-phenylethanol (4 mmol), toluene (5 mL), and the as-prepared Au<sub>60</sub>M<sub>40</sub>-PVP/HT catalyst (0.2 g) were mixed at 343 K for 6 h under O<sub>2</sub> flow (20 mL•min<sup>-1</sup>) with vigorous stirring (400 rpm). The products were analyzed by GC-FID (Shimadzu GC-2014) using naphthalene (TCI) as an internal standard.

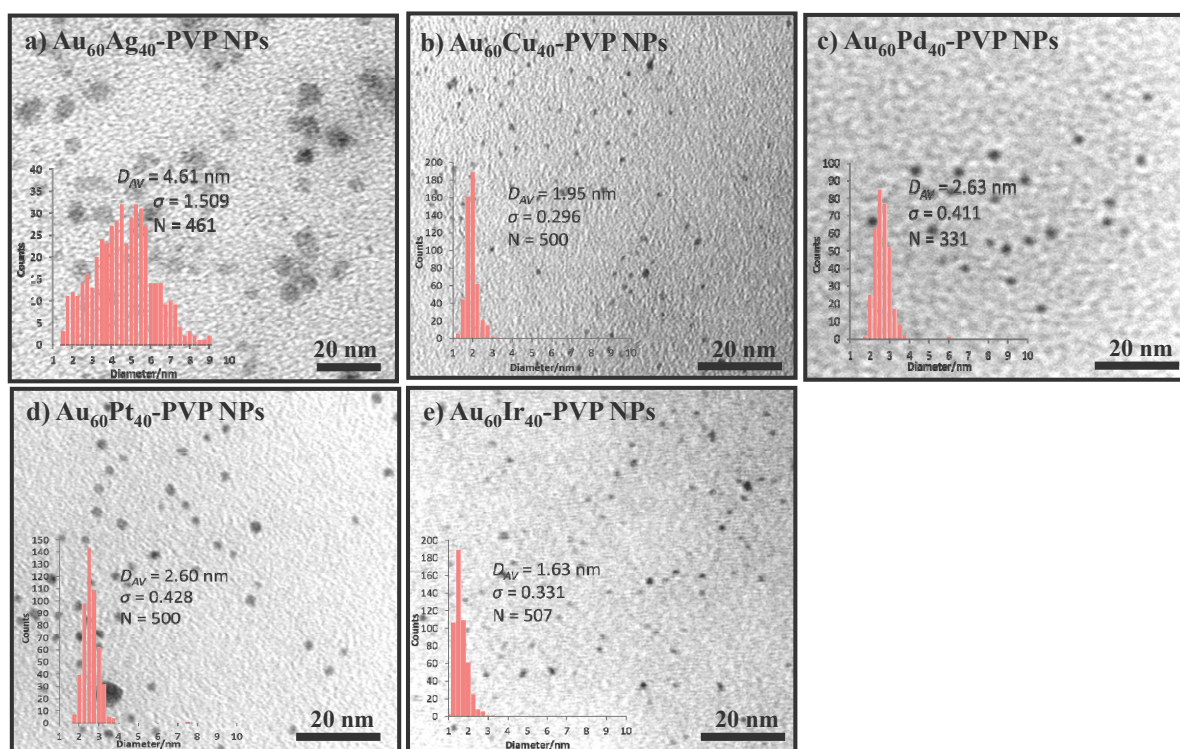


**Scheme 1.** Aerobic oxidation of 1-phenylethanol to acetophenone.

## DISCUSSION

TEM images of the as-prepared Au<sub>60</sub>M<sub>40</sub>-PVP NPs are illustrated in Figure 1 with particle size distributions in diameter. The Cu, Pd, Pt and Ir incorporated Au NPs exhibited very narrow size distributions ( $\sigma = 0.30\sim 0.43$ ) whereas the AgAu showed a wide distribution ( $\sigma = 1.5$ ). It indicated that the synthesis of AuAg bimetallic NPs with a narrow size distribution seemed to be difficult even though the modified preparation method was applied for this case.

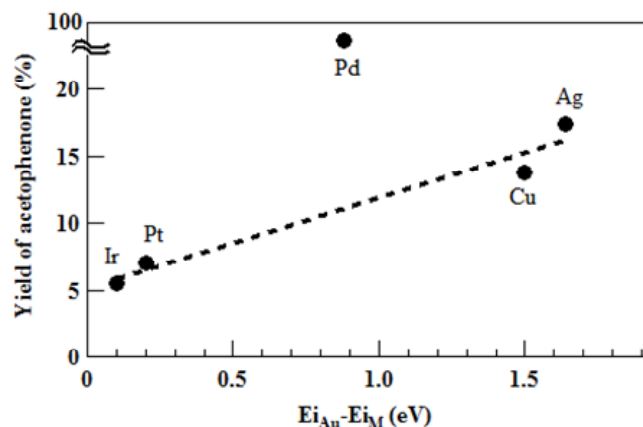
Activities for 1-phenylethanol oxidations over Au<sub>60</sub>M<sub>40</sub>-PVP/HT catalysts are listed in Table 1. The yield for acetophenone exhibited the following order: AuPd (>99%) >> AuAg (17.4%) > AuCu (13.8%) > AuPt (7.1%) > AuIr (5.5%), at 343 K for 6 h. In Au-based aerobic oxidation in a solution reaction, a significant impact on catalysis derived from the presence of negatively-charged Au atoms has been observed [2, 10-11]. When the electron net-charge from M toward Au atoms (the ligand effect of neighbor atom onto Au center) is a dominant factor for the above reactivity, the differences between Au and M in the ionization energy value (one of elucidation factors for electron transfer phenomenon [12]) may lead the way for understanding of the activity. According to this hypothesis, the yields for acetophenone are tentatively plotted as



**Figure 1.** TEM images and size distributions of Au<sub>60</sub>M<sub>40</sub>-PVP NPs.

**Table 1.** Activities of AuM-PVP/HT catalysts for aerobic oxidation of 1-phenylethanol.

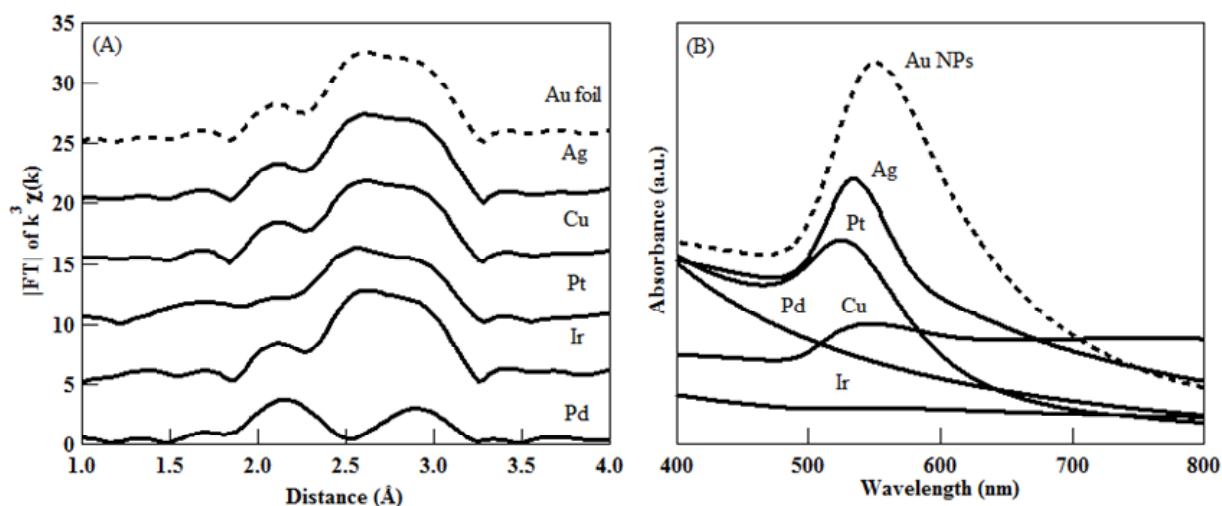
Catalyst	Ei <sub>Au</sub> -Ei <sub>M</sub> (eV)	Conv. (%)	Yield (%)	Aver. Size (nm)	Metal amount (Ratio in mol%)	
					Au (mmol·g <sup>-1</sup> )	M (mmol·g <sup>-1</sup> )
Au <sub>60</sub> Ag <sub>40</sub> -PVP/HT	1.64	16.7	17.4	4.6	0.056 (67)	0.028 (33)
Au <sub>60</sub> Cu <sub>40</sub> -PVP/HT	1.50	14.8	13.8	2.0	0.058 (50)	0.057 (50)
Au <sub>60</sub> Pd <sub>40</sub> -PVP/HT	0.88	>99	>99	2.6	0.064 (52)	0.062 (48)
Au <sub>60</sub> Pt <sub>40</sub> -PVP/HT	0.20	9.1	7.1	2.6	0.061 (62)	0.037 (38)
Au <sub>60</sub> Ir <sub>40</sub> -PVP/HT	0.10	6.8	5.5	1.6	0.036 (54)	0.031 (46)



**Figure 2.** Plot of the activity as a function of the difference in ionic energy value.

the function of difference in ionization energy value between Au and M element [13], as shown in Figure 2. Interestingly, except for AuPd catalyst, there was nice linearity ( $R^2 = 0.959$ ) between the yield and the difference in ionization energy value among Ag, Cu, Pt and Ir for Au ( $E_{iAu}-E_{iM}$ ). Thus, the ligand effect seemed to be the dominant factor for the aerobic oxidation of 1-phenylethanol over Au<sub>60</sub>M<sub>40</sub>-PVP/HT catalysts.

However, the nanostructures around Au atoms in each catalyst estimated by the |FT| of  $k^3$ -weighted Au-L<sub>3</sub> edge EXAFS and UV-vis spectroscopies (Figure 3) strongly suggested that the coordination between Au-M and/or the ratio of exposed Au cluster in Au<sub>60</sub>M<sub>40</sub>-PVP NP on HT was not same. Nanostructures around Au atom incorporated Ag, Cu, Pt or Ir bimetallic NP were similar to Au foil suggested by a broad peak at 2.2-3.3 Å in |FT| whereas the incorporated Pd produced uniform alloy in AuPd determined by the humped peak at 1.5-3.5 Å in |FT| [3-4]. In the SPR resonance peak, the shift to lower wavelength at around 500-600 nm was attributed to the decreases in a diameter of Au NPs [14]. The shift to lower wavelength with diminishment of absorbance observed in Figure 3 proposed that not only the size but also the ratio of exposed Au surface in AuM NPs were changed by the kind of secondary element M; *i.e.* the cases of Ag and Pt possessed a larger size and a ratio of Au surface than Cu and Ir cases, while the Pd case showed much difference in SPR peak owing to the formation of fully miscible AuPd alloys. It is likely that the simple evaluation among Au<sub>60</sub>M<sub>40</sub>-PVP/HT catalysts on the basis of ionization energy values between Au and M supported the strong contributions of ligand effects, however, further studies on the geometric structures and mixing patterns of Au<sub>60</sub>M<sub>40</sub>-PVP alloys have to be considered to understand the whole catalysis on Au-base bimetallic nano-catalyst during aerobic alcohol oxidation.



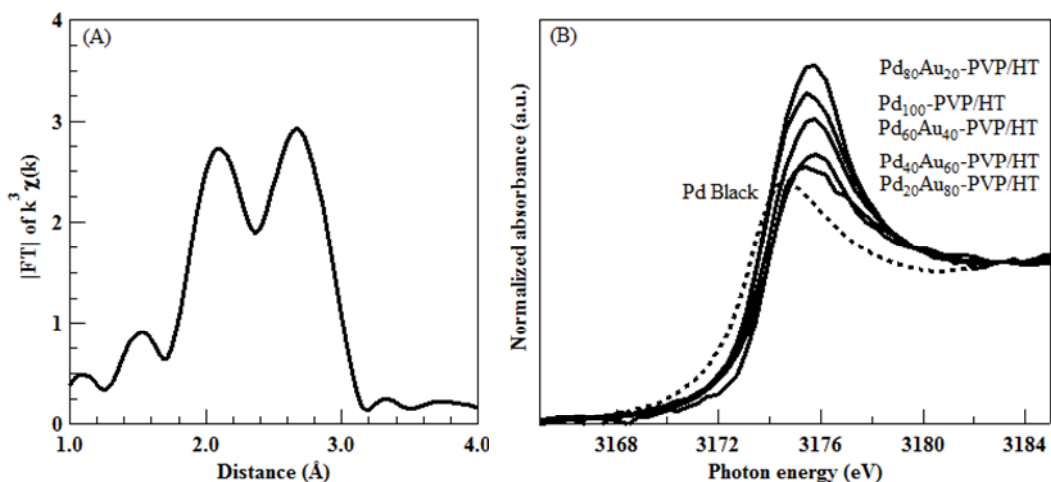
**Figure 3.** (A) |FT| of  $k^3$ -weighted Au L<sub>3</sub>-EXAFS and (B) UV-vis spectra of Au<sub>60</sub>M<sub>40</sub>-PVP/HT(s).

On the other hand, we wondered why the Au<sub>60</sub>Pd<sub>40</sub>-PVP/HT catalyst showed such an exceptional significant activity among Au<sub>60</sub>M<sub>40</sub>-PVP/HT catalysts, as shown in Figure 2. As result in Pd-K edge EXAFS (Figure 4A), the humped peaks were also appeared in both |FT|s at 1.5-3.5 Å in good agreement with Au-L<sub>3</sub> edge (Figure 3A), indicating the presence of well-interacted Au-Pd alloy [7, 15] which helps to bring out the synergetic effects derived from alloying. In our previous reports in Au<sub>x</sub>Pd<sub>y</sub>-PVP/HT with various Au/Pd ( $x/y$ ) mol ratios [3], it was observed that with increase of Pd contents till 40% into Au in Au<sub>x</sub>Pd<sub>y</sub>-PVP/HT, the yield was drastically increased, thereafter, gradual decrease in the yield was observed in the range of

40-100% Pd content. The highest activity for 1-phenylethanol oxidation was obtained at Au<sub>60</sub>Pd<sub>40</sub>-PVP/HT (TOF = 69,100 h<sup>-1</sup>, TON = 395,700). We proposed that a large electron transfer from Pd atoms to Au 5d state played an important factor for the formation of highly active AuO<sup>2+</sup> and/or AuO<sub>2</sub><sup>2+</sup> species, which leads to the significant activity in the reaction. These proposals based on the ligand effect were supported by XPS and Au-L<sub>3</sub> XANES analyses.

To further study the catalysis over AuPd catalyst, we tried to monitor the neighbor Pd state in Au<sub>x</sub>Pd<sub>y</sub>-PVP/HT by using Pd-L<sub>3</sub> edge XANES analyses because it was well-known that the only monometallic Pd site also exhibited a high activity (*ex.* TOF = 9,800 h<sup>-1</sup>, TON = 236,000, in PdHAP) for aerobic oxidation of 1-phenylethanol [16-17]. The height in Pd-L<sub>3</sub> XANES contributes to the possibility for electron transmission from 2p to 4d state in Pd atom; *i.e.* lower height in the WL means smaller number of holes in 4d (more electrons in 4d). The obtained Pd-L<sub>3</sub> edge XANES of Au<sub>x</sub>Pd<sub>y</sub>-PVP/HT are shown in Figure 4B. The heights in WL were increased from 0% to 20% Au doping into Pd, and then gradually decreased with increase in Au concentrations (20-80%). In the main, the Au substitution into Pd supposedly induced to gain the net-electron in 4d states of Pd. The phenomenon, Pd gains d charges owing to alloying with Au, was also reported in previous literature [18-19], whereas the proposed charge redistributions in AuPd-alloy were a little difference from our observations in d charges of Au and Pd atoms. According to this observation, we would like to suggest here that the changes of electron density in not only Au atom but also Pd atom in PVP-capped AuPd-alloy NPs might play important roles synergistically for the aerobic alcohol oxidation reaction.

To reveal the whole catalytic behavior over AuPd-PVP/HT catalyst, the investigations on the electronic redistribution behavior in Au-Pd alloy in the presence of PVP, an electron donating agent, are ongoing study.



**Figure 4.** (A) |FT| of k<sup>3</sup>-weighted Pd-K EXAFS of Au<sub>60</sub>Pd<sub>40</sub>-PVP/HT and (B) Pd-L<sub>3</sub> edge XANES of Au<sub>x</sub>Pd<sub>y</sub>-PVP/HT(s).

## CONCLUSIONS

The PVP-protected Au<sub>60</sub>M<sub>40</sub> bimetallic NPs (M = Ag, Cu, Pd, Pt and Ir) supported HT catalyst (Au<sub>60</sub>M<sub>40</sub>-PVP/HT) were prepared and applied for a simple aerobic oxidation of 1-phenylethanol to acetophenone. The yields over AuAg, AuCu, AuPt and AuIr well suggested the

strong contributions of ligand effect on the basis of difference in ionization energy value, however, the effects of nanostructure of these catalysts still remained unclear. An exceptional high catalytic activity of Au<sub>60</sub>Pd<sub>40</sub>-PVP/HT was also discussed in terms of the electron density in Pd 4d state. It suggested that the density in not only Au 5d but also Pd 4d was differed by Au/Pd ratios. We supposed that the synergy effect between Au and Pd strongly contributed the novelty of AuPd catalyst for aerobic alcohol oxidation reactions.

## ACKNOWLEDGMENTS

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