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Description
Role of Negatively Charged Au State in Aerobic Oxidation of Alcohols over Hydrotalcite Supported AuPd Nanoclusters

Shun Nishimura, Yusuke Yakita, Madoka Katayama, Koichi Higashimine and Kohki Ebitani

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The PVP-protected bimetallic gold/palladium nanoclusters (Au$_x$Pd$_y$-PVP NCs) were prepared onto the solid base hydrotalcite (HT) with various Au:Pd (x:y) molar ratios. Transmission electron microscopy showed narrow particle size distributions of Au$_x$Pd$_y$-PVP NCs with a mean diameter in the range of 2.6-3.0 nm regardless of Pd contents. Aerobic oxidations of 1-phenylethanol over the Au$_x$Pd$_y$-PVP/HT catalysts exhibited that their catalytic activities were significantly affected by the Pd contents. Correlations between charge transfer between Au and Pd and catalytic activity of the Au$_x$Pd$_y$-PVP/HT catalyst were investigated with X-ray photoelectron spectroscopy (XPS), X-ray absorption near-edge structure (XANES), Michaelis-Menten kinetic studies for alcohol oxidation, and other analytical techniques. The peaks of Au 4f in the XPS spectra were shifted to lower energy side with increase of Pd contents, indicating the electron transfer from Pd to Au atoms according to the Pauling’s electronegativity protocol. The electron densities in Au 5d orbital in the Au$_x$Pd$_y$-PVP/HT catalysts estimated by the Au L$_3$-XANES spectra correlated well with their catalytic activities. Moreover, the kinetic studies also proposed that the electron rich Au 5d states, resulted from the intermetallic electron transfer from Pd atoms, strongly contributed to the rate-determination step in the alcohol oxidation. It was concluded that the electronic negativity in the Au 5d states controlled by the Pd contents accelerated the rate-determination step in alcohol oxidation through highly active radical-like intermediates.

Introduction

Bimetallic nanoparticles (NPs) have attracted great interests and potentials in advanced materials science because they achieved unique performances different from those of monometallic NPs. Since the catalytic activities of nano-sized Au particles were reported by Haruta in 1980s, it makes breakthroughs in series of Au and incorporated second element NPs as catalysts such as Au cluster, AuPd, AuPt, AuAg and so on. However, the contribution of these advanced catalysts on the reaction kinetics over the bimetallic catalyst is still questionable. In general, (i) the each element promotes different elementary reaction steps (bifunction effect), (ii) the electron transfer among two elements improve reactivity (ligand effect), and (iii) the specific group of surface atoms developed by geometric growth (ensemble effect), were considered as driving forces for significant performances of heterometallic assemblies. The difficulties in the synthesis of uniform bimetallic NPs with various mixing ratio and/or morphologies become a barrier to discuss and compare their performances in the reaction mechanism.

From the viewpoint of energy and environmental issues, aerobic oxidation of alcohols for the synthesis of fine chemicals over a highly active heterogeneous catalyst has been investigated. It leads to environmentally-friendly synthesis routes comparing to the stoichiometric oxidations over transition metal complexes. Additionally, the traditional process produces a large amount of undesirable salts and needs energy for separation of the product from reaction mixture. Therefore, the notable protocols for the active sites synthesis on a nanoscale has a great impact for development of highly functionalized heterogeneous catalyst in next advantage. In this regard, supported polymer capped highly dispersed bimetallic NPs catalysts, ex. Au@Pd-PVATiO$_2$, AuPd-PVA/MgO, and AuPd-PVA/C have been extensively studied for alcohols oxidation into carbonyl compounds.

Herein, we examined the aerobic oxidation over the PVP-protected AuPd bimetallic (Au$_x$Pd$_y$-PVP) NCs deposited onto the hydrotalcite (HT) catalysts with similar size distributions of Au$_x$Pd$_y$-PVP NCs. The AuPd NCs are well-known as one of the most attractive active site for the catalyst for various reactions such as not only alcohol oxidation, but also hydrogenation of 1,3-cyclooctadiene, the direct synthesis of H$_2$O$_2$, acetoxylation of ethylene, and oxygen reduction in electrode. The HT has been known as an effective support for various reactions such as deoxygenation, chemoselective reduction, and oxidation reactions because it exhibits turnable surface base sites on the HT, achieving highly catalytic performance through proton abstraction and uniform depositions of active metal on the surface. It is supposed that the combination with AuPd NCs and HT become a significant heterogeneous catalyst for the alcohol oxidation. In addition, both
the careful synthesis of bimetallic NCs and study on their reaction mechanism may give the clarification of their novelties in the reaction.

Effect of the doping hetero atoms to Au nanocluster (NC) for catalytic activities has been widely focused on by several researchers. Notably, Toshima et al. reported that the degree of electron transfer in the bimetallic core/shell NCs is proportional to the visible-light-induced hydrogen generation from water in the system of EDTA/[Ru(bpy)]$_2$Cl$_2$/MV$^{3+}$/metal NC. They clarified that the bimetallic NC can accept electrons more easily than the monometallic one, and which accelerated the rate-determining step; production of methyl viologen cation radical. They also suggested that differences of the ionic potential between Pd and Pt could provide an uneven distribution of electrons, and the formed positive Pd shell in the Pt@Pd-PVP NCs favored the C=C double bond of diene substrate and provided good catalytic activity. It has been said that the intermetallic electron transfer in the bimetallic NCs seem to play an important role in the acceleration of rate-determination step.

In this study, we succeeded in the synthesis of extremely active Au$_{x}$Pd$_{y}$-PVP/HT possessing the highest turnover number (= 395,700) for aerobic oxidation of 1-phenylethanol (250 mmol). Thereafter, transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray absorption spectroscopy, Michaelis-Menten kinetic studies for alcohol oxidation and other analytical techniques were employed in order to realize the novelty of the synthesized Au$_{x}$Pd$_{y}$-PVP/HTs. By taking advantages of morphological and electronic analysis of Au-Pd-PVP NPs with kinetic studies in aerobic oxidation of alcohols with and without radical scavenger, it was also revealed that the remarkable activity of the Au$_{x}$Pd$_{y}$-PVP/HT catalyst was strongly contributed by the electron rich Au 5$d$ states, since the formed negative Au species induces the active radical-like peroxo-species formation which accelerated the rate-determination step of the alcohol oxidation.

Experimental

Chemicals and Materials

Hydrogen tetrachloroaurate tetrahydrate (HAuCl$_4$·4H$_2$O), palladium chloride (PdCl$_2$), potassium chloride (KCl), ethylene glycol (EG), sodium carbonate decahydrate (Na$_2$CO$_3$·10H$_2$O) and benzyl alcohol were supplied by Wako Pure Chemical Ind., Ltd. Benzyl alcohol were supplied by Wako Pure Chemical Ind. Co. Ltd. 2,6-Di)butyl)phenol (EG), sodium carbonate decahydrate (Na$_2$CO$_3$·10H$_2$O) and toluene were purchased from Kanto Chem. Co. Ltd. 2,6)Di)butyl)phenol and toluene were purchased from Kanto Chem. Co. Ltd.

Transmission electron microscopy (TEM) was taken by Hitachi H-6500 at 100 kV. An energy-dispersive X-ray analysis (EDS) attached to the scanning TEM-high angle annular dark field (STEM- HAADF) was performed with JEOL JEM-ARM200F at 200 kV. Under vacuum and visible (UV-vis) spectra were measured by Perkin-Elmer Lambda35 spectrometer. X-ray photoelectron spectroscopy (XPS) was measured on Shimadzu Kratos AXIS-ULTRA DLD spectrometer using Al target at 15 kV and 10 mA. The binding energies were calibrated with the C 1$s$ level (284.8 eV) as the internal standard reference. Induced couple plasma spectroscopy (ICP) was recorded with Shimadzu ICP-AES-7000 Ver.2. The contents of Pd and Au on the catalyst were estimated by the standard curve method. X-ray absorption near edge structure (XANES) measurement was performed at the BL01B1 in SPring-8 of Japan Synchrotron Radiation Research Institute (JASRI). The Au L$_3$-edge XANES spectra was recorded at room temperature using a Si(111) monochromator.

Aerobic Oxidation of Alcohols

Aerobic oxidations of 1-phenylethanol to acetophenone were carried out in the glass tube attached with a reflux condenser. In general procedure, 2 mmol of alcohol in 5 ml of toluene and the Au$_{x}$Pd$_{y}$-PVP/HT catalyst were added to the glass tube, and purged with an O$_2$ flow before reaction under stirring (500 rpm). Subsequently, the mixture was stirred at desired temperature for a given time under an O$_2$ flow (20 ml•min$^{-1}$) in atmospheric pressure. After the reaction, resultant solution was filtered off the solid catalyst using Millex syringe filter (0.20 µm). The products were analyzed by GC equipped with a DB-FFAP (30 m length, 0.25 mm i.d.) or a DB-1 (30 m length, 0.25 mm i.d.) column with FID detector using the internal standard curve method. The naphthalene was used as an internal standard to determine the conversion and yield.

Characterizations

Aerobic oxidations of 1-phenylethanol to acetophenone were carried out with Au$_{x}$Pd$_{y}$-PVP/HTs with various Pd contents. The results are summarized in Table 1. Size distributions of the Au$_{x}$Pd$_{y}$-PVP/HTs were also listed in the Table 1, and these values were similar among Au$_{x}$Pd$_{y}$-PVP/HTs except for Au$_{100}$-PVP/HT (aggregation) (See electronic supporting information (ESI), Figure S1). The Au$_{100}$-PVP/HT showed no activity (entry 1). The bimetallic Au$_{x}$Pd$_{y}$-PVP/HTs exhibited difference activities, and the Au$_{100}$Pd$_{y}$PVP/HT achieved the most significant activity among Au$_{x}$Pd$_{y}$-PVP/HTs (entries 2-5). The excellent yields of the Au$_{100}$Pd$_{y}$PVP/HT were also performed even at 300 K (>99% yield, entry 3) and under air condition (>99 yield, entry 3). It is likely that the Pd contents in the Au$_{x}$Pd$_{y}$-PVP/HTs have a strong influence on catalytic activity for aerobic oxidation of 1-phenylethanol. We also
tested its reusability in aerobic oxidation of 1-phenylethanol, then it could be reused without significant loss of activity and selectivity after washing with acetone followed by a 10 wt% Na₂CO₃ aqueous solution and drying in vacuum (Figure S2). The reaction over the Pd₁₀₀-PVP/HT catalyst was rarely proceeded regardless of the small particle size (2.6 nm) whereas the bare Au NPs stabilized on HT (Au/HT) catalyst with a similar size distribution (2.6 nm) and metal amount (0.075 Au mmol·g⁻¹) showed little activity (entry 7). It is supposed that the Au atoms in Au₃₋₄-PVP NPs mainly play as an active site for the alcohol oxidation. Furthermore, scope for the Au₃₋₄-PVP/HT in aerobic oxidation of various alcohols to the corresponding aldehydes or ketones under mild reaction condition was also examined. Though the presence of substituents such as p-H, CO₂-, and p-Cl- on the aromatic ring affect the yield of the product (vide infra), the Au₃₋₄-PVP/HT catalyst allows adaptive oxidation for various alcohol substrates (Table S1).

The turnover number (TON) and turnover frequency (TOF) of the oxidation of 1-phenylethanol (250 mmol) into acetophenone were at 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 values are comparable to the previous reports (detailed information is listed in Table S2); i.e., Au/HT (93% yield, TON = 200,000, TOF = 8,300 h⁻¹), 36 Au/CeO₂ (TON = 250,000 (after three recycles), TOF = 12,500 h⁻¹), 12,13 PdHAP (37.8% yield, TON = 236,000, TOF = 9,800 h⁻¹), 49 and Au@Pd/TiO₂ (TON = 269,000 h⁻¹). 19 These results clearly show that the present Au₃₋₄-PVP/HT is excellent catalyst for oxidation of alcohol. Investigation of different supports with Au₃₋₄-PVP NPs also provided the novelty of the combination of AuPd bimetallic NCs and HT as a catalyst for alcohol oxidation reaction (Table S3). To clarify the reaction pathway over the Au₃₋₄-PVP/HT, investigations using radical scavenger were performed. As the results shown in Figure 1, the TEMPO moderately influenced the oxidation rate of 1-phenylethanol. It has been reported that the alcohol oxidation over the monometallic metal supported catalysts proceed the metal-alcoholoxde formation mechanism and which is not affected by the radical scavengers. 16,18,37,49 Interestingly, our finding is different from the such previous studies over monometallic catalyst (via infra). Additionally, if the dominant reaction mechanism involving the formation of carbon-centered free radicals intermediates over the Au₃₋₄-PVP/HT catalyst, the yield of acetophenone should be unchanged by such a small amount of TEMPO radical scavenger (0.0032 mmol). The 2,6-di-tert-butyl-p-cresol (0.0454 mmol) also influenced the oxidation rate of 1-phenylethanol (67% yield after 1 h reaction). These results implied that another radicalic intermediates were seemed to be formed during the reaction (vide infra).

From comparison of the reaction rate between primary and secondary alcohols, the oxidation of 1-phenylethanol (TOF = 755 h⁻¹) was faster than that of benzyl alcohol (TOF = 552 h⁻¹),

### Table 1 Aerobic oxidation of 1-phenylethanol under base free conditions using Au₃₋₄-PVP/HT catalysts with various Pd contents.*

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conv. (%)</th>
<th>Yield. (%)</th>
<th>Particle size (nm)</th>
<th>Metal amount (mmol·g⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Au₃₋₄-PVP/HT</td>
<td>2</td>
<td>0</td>
<td>Agglomerate</td>
<td>0.075</td>
</tr>
<tr>
<td>2</td>
<td>Au₃₋₄Pd₃₋₄-PVP/HT</td>
<td>100, 92</td>
<td>99, 92</td>
<td>3.1</td>
<td>0.115</td>
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<tr>
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<td>Au₃₋₄Pd₃₋₄-PVP/HT</td>
<td>100, 100, 100, 100</td>
<td>&gt;99, &gt;99, &gt;99, &gt;99</td>
<td>2.6</td>
<td>0.054</td>
</tr>
<tr>
<td>4</td>
<td>Au₃₋₄Pd₃₋₄-PVP/HT</td>
<td>58</td>
<td>57</td>
<td>2.6</td>
<td>0.052</td>
</tr>
<tr>
<td>5</td>
<td>Au₃₋₄Pd₃₋₄-PVP/HT</td>
<td>19</td>
<td>19</td>
<td>2.6</td>
<td>0.023</td>
</tr>
<tr>
<td>6</td>
<td>Pd₃₋₄-PVP/HT</td>
<td>2</td>
<td>0</td>
<td>2.6</td>
<td>0.154</td>
</tr>
<tr>
<td>7</td>
<td>Au₃₋₄/HT</td>
<td>18</td>
<td>18</td>
<td>2.6</td>
<td>0.075</td>
</tr>
</tbody>
</table>

*Reaction conditions: 1-phenylethanol (2 mmol), catalyst (0.2 g; Au + Pd = 0.02 mmol), mole ratio of alcohol / (Au+Pd) = 100, toluene (5 ml), 313 K, 1 h, O₂ flow (20 ml·min⁻¹).  
† Analyzed by GC using an internal standard technique.  
‡ Determined by TEM measurement about 500 NPs for each sample.  
§ Estimated with ICP analysis.  
*Reduced by KBH₃.  
†1-phenylethanol (4 mmol).  
||300 K, 3 h.  
Air purge, 12 h.

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**Fig. 1** Time-course of aerobic oxidation of 1-phenylethanol in the absence (closed circle) or presence (open circle) of TEMPO. Reaction conditions: 1-phenylethanol (2 mmol), Au₃₋₄Pd₃₋₄-PVP/HT catalyst (0.2 g), TEMPO (0 or 0.5 mg), toluene 5 ml, 313 K, O₂ flow (20 ml·min⁻¹).
individually (Figure S3). In contrast, benzyl alcohol (TOF = 315 h⁻¹) was faster oxidized than 1-phenylethanol (TOF = 69 h⁻¹) using an equimolar mixture of alcohols (intermolecular competitive oxidations) (Figure S4). These observations were also reported, previously.¹⁴,¹⁷ It is said that the faster oxidation of primary alcohol than secondary alcohol in competitive oxidation presumably supported the formation of metal-alcoholate intermediate species through the ligand exchange.⁵⁰-⁵² To determine the presence of a carbocationic character in the transition state of the reaction, the logarithm of the rate constants, \( \log(\frac{k_X}{k_H}) \), against substituent constant (\( \sigma \)) reported by Hammet were plotted in the aerobic oxidation of \( p \)-substituted benzyl alcohols. As shown in the Figure 2, there is a reasonable linearity between \( \log(\frac{k_X}{k_H}) \) and the \( \sigma \) parameter in the following order of the reactivity: \( p \)-CH₃O > \( p \)-CH₃ > \( p \)-H > \( p \)-Cl > \( p \)-NO₂. The Hammet \( \rho \) value was -0.240 (R² = 0.96). The negative value indicates that a carbocationic character on the benzylic carbon is an intermediate specie in the transition state of the alcohol oxidation over the \( \text{Au}_{60}\text{Pd}_{40}\text{PVP/HT catalyst}. Consequently, it is likely that the oxidation of alcohols over the \( \text{Au}_{60}\text{Pd}_{40}\text{PVP/HT catalyst is progressed via the alkoxyide intermediate.}

In order to understand the superiority of the \( \text{Au}_{60}\text{Pd}_{40}\text{PVP/HT catalyst for alcohols oxidation, their morphologies and electronic states were also investigated. Figure 3 shows the STEM-HAADF image and STEM-EDS line analysis of the \( \text{Au}_{60}\text{Pd}_{40}\text{PVP NCs. Since the STEM-HAADF analysis technique offers enhanced contrast proportional to } Z^2, \text{the heavier Au atoms (atomic number; } Z = 79) \text{ give rise to a brighter image than the lighter Pd atoms (} Z = 46 \text{). However, the STEM-HAADF image of } \text{Au}_{60}\text{Pd}_{40}\text{PVP NCs looks uniform contrast (Figure 3A). As the result of quantitative analysis of EDS profile, the } \text{Au}_{60}\text{Pd}_{40}\text{PVP NCs was likely composed with homogeneous mixed 60.2% Au and 39.8% Pd atoms (Figure 3B). These values agreed well with the stoichiometric ratio in } \text{Au}_{60}\text{Pd}_{40} \text{ NC. Moreover, other components of } \text{Au}_{x}\text{Pd}_{y}\text{PVP NCs show similar images in the STEM-HAADF images and the STEM-EDS line analysis (Figure S5), and the later proposed that their Au/Pd ratios also suits to the stoichiometric ratio of Au/Pd for each. The detailed morphologies of } \text{Au}_{x}\text{Pd}_{y}\text{PVP NCs could not be resolved due to the extremely small size of the NCs and the difficulty in obtaining electron beam diffraction. The } \text{UV-vis spectra of the } \text{Au}_{x}\text{Pd}_{y}\text{PVP NCs dispersed solutions show no specific surface plasmon (SPR) absorption of the Au NPs.}

Fig. 2 Hammet plots for oxidation of benzyl alcohol and \( p \)-substituted benzyl alcohols. Reaction condition: alcohol (0.5 mmol), toluene (5 ml), \( \text{Au}_{\alpha}\text{Pd}_{\beta}\text{PVP/HT catalyst (10 mg), 313 K, 5 min, } \text{O}_2 \text{ flow (20 ml•min}^{-1}\)).

Fig. 3 (A) STEM-HAADF image and (B) STEM-EDS line analysis of the \( \text{Au}_{60}\text{Pd}_{40}\text{PVP NCs. The blue and green lines are corresponding to the presences of Au and Pd elements, respectively.}

Fig. 4 (A) XPS spectra of (a) \( \text{Au}_{20}\text{Pd}_{80}\text{PVP}, (b) \( \text{Au}_{40}\text{Pd}_{60}\text{PVP}, (c) \( \text{Au}_{60}\text{Pd}_{40}\text{PVP and (d) } \text{Au}_{80}\text{Pd}_{20}\text{PVP NCs around Au 4f components, and (B) plots of the peak positions of Au 4f}_{7/2} \text{ as a function of Pd contents.}
around 520-580 nm whereas the Au$_{1@PVP}$ NPs shows the SPR feature at 527 nm (Figure S6). As mentioned above, the unimodels and narrow size distributions among Au$_{1@PVP}$ NCs in various Pd contents were observed (Figure S1). If the alloy is not formed, the size related to the isolated Au NPs will be also obtained. Therefore, distribution would lead to a broad or bimodal one due to different growth rates for the two metal NPs and the SPR phenomena. According to these results, it was suggested that the compositions of the Au$_{1@PVP}$-PVP NCs were different from that of Au or Pd mother clusters and the mixtures of isolated Au and Pd NCs, which indicates that each particle contains both Au and Pd elements in the form of alloy phase. It seems to be possible to form the alloy via the spontaneous alloying mechanism even under the low temperature.

The XPS spectra of Au$_{1@PVP}$-PVP NCs were measured in order to discuss the charge transfer between two metals. The peaks around Au 4f components are shown in Figure 4(A). The humped peaks were contributed to the Au 4f$_{7/2}$ (around at 83 eV) and 4f$_{5/2}$ (around at 87 eV). All Au$_{1@PVP}$-PVP NCs exhibited negative shifts in the both Au 4f binding energies compared to that of pure Au foil (84.0 and 88.0 eV). Importantly, increasing the Pd contents induced more shifts in binding energy to the lower energy side (Figure 4(B)). Thus, it is supposed that the charge transfer from Pd to Au atoms was facilitated by increase in Pd contents of Au$_{1@PVP}$-PVP NCs. The largest negative shift in Au 4f$_{7/2}$ was -1.96 eV in the case of Au$_{1@Pd_{100}}$-PVP NCs. The negative shifts of binding energy in the Au 4f$_{7/2}$ peak were also reported in the crown-jewel-structured Au$_{12}$Pt$_{47}$-PVP NCs (-1.5 eV), Au$_{100}$Ag$_{100}$-PVP alloy NCs (-1.4 eV), Au$_{100}$Pt$_{100}$-PVP NCs (-0.15 eV), and Au$_{100}$Pt$_{100}$-PVP NCs (-1.4 eV). The large number of negative shift in Au 4f peak supposed that the Au$_{1@Pd}$-PVP NCs have a lot of agglutinations between Au and Pd atoms, which increased the opportunity for electron transfer from Pd to Au atoms. While, the XPS peaks in Pd 3d were hard to analyzed because of weak intensities and XPS overlapping at 335.0 eV corresponding to Pd 3d$_{5/2}$ and Au 4d$_{5/2}$ (Figure S7).

was reported that the Pd NCs with a diameter less than 2.0 nm have an amorphous structure whereas that with a diameter more than 2.5 nm have crystalline structures. It is indicated that the phase transfer of Pd NCs was found between 2.5 and 4.0 nm. In our case, the average size of Au$_{1@Pd_{100}}$-PVP NCs were below 2.7 nm. Therefore, the Pd atoms in the Au$_{1@Pd}$ cluster supposedly composed the amorphous structure of Pd aggregates and/or the less ordered AuPd structure, and which makes the Pd related peaks broadening. From XPS analysis, the electron transfer from Pd to Au was elucidated, however, the correlation between the electron transfer and their catalysis still remains unclear.

To confirm the presence of the electronic negative Au atoms in Au$_{1@Pd_{100}}$-PVP NCs, Au L$_{3}$-edge XANES spectra were also measured for Au$_{1@Pd}$-PVP/HTs, as shown in Figure 5(A). The white-line (WL) feature in the L$_{3}$-edge spectrum is related to the transition of 2p electron to unoccupied 5d electron states. Though the unperturbed Au atom possesses no holes in 5d orbital (electron configuration [Xe]6s$^{1}$4f$^{14}$5d$^{10}$), the Au bulk L$_{3}$-edge XANES spectra exhibits the WL feature due to the s-p-d hybridization which lead to the small amount of electron transformation from 5d to s-p states.

The WL features around 11.925 eV in the Au$_{1@Pd}$-PVP/HTs indicated lower intensities than Au foil (Figure 5(A)). Therefore, it was supposed that the Au$_{1@Pd}$-PVP/HTs contained more 5d electrons than Au foil. To further elucidate the differences in the 5d electron densities among Au$_{1@Pd}$-PVP/HTs, the areas of WL features in Au$_{1@Pd}$-PVP/HTs were calculated. Because the width in the WL feature depends on the lifetime of core hole, the dipole-transition matrix element, and the distribution of the density of states of unoccupied $d$ band at the Fermi level of the element, the range from 10 eV below the X-ray absorption edge ($E_{a}$) to 13 eV above the $E_{a}$ was applied for calculation. Here, $\mu_{a} = 107.7$ cm$^{-1}$ g$^{-1}$ and $\rho = 19.32$ g cm$^{-3}$ are the X-ray absorption cross section at L$_{3}$-edge jump and the density of Au, respectively. The areas as a function of Pd contents were plotted with the yield of acetophenone in Figure 5(B). The area of Au L$_{3}$-edge XANES spectrum was

![Fig. 5](image_url) (A) The changes in Au L$_{3}$-edge XANES spectra and (B) Correlations between the area in the range of -10 eV < $E_{a}$ < 13 eV among Au$_{1@Pd}$-PVP/HT catalysts with various Pd contents.
5) Formation of Au-hydroperoxide species + δ-Pd-PVP/HT in AuPd NPs.

\[ \text{formation of (AuPd))OOH + RCOCH}_3 \]

6) Reoxidation by O₂, Formation of water

\[ \text{formation of water} \]

1) Formation of negatively charged Au atom

2) Activation of O₂. Formation of Au coordinated peroxy species (Au-O'O²⁻ species)

3) Formation of Au-Alcoholate intermediate

4) β-hydride elimination Rate-Determining step

5) Formation of Au-hydroperoxide species

Fig. 6 Proposed reaction mechanism of alcohol oxidation over Au-Pd-PVP/HT catalysts.

Fig. 7 Lineweaver-Burk plot and Michaelis-Menten kinetics in the aerobic oxidation of 1-phenylethanol over the Au-Pd-PVP/HT (solid line) and bare Au/HT (dash line) catalysts. Reaction conditions: 1-phenylethanol (0.25-3 mmol), catalyst (10 mg), toluene 5 mL, 313 K, 5 min, O₂ flow (20 mL·min⁻¹).

\[ \text{formation of (AuPd))OOH + RCOCH}_3 \]
In the case of the Au_{100}Pd_{40}-PVP/HT catalyst, K_{M} and k_{2} were calculated to be 3228 mM and 0.152 mM s^{-1}, respectively, whereas over the bare Au_{100}/HT catalyst, they were 1112 mM and 0.033 mM s^{-1}. It was indicated that the rate of β-hydrogen elimination was drastically facilitated in the bimetallic AuPd-PVP/HT catalyst than that in the monometallic Au_{100}/HT catalyst. To further investigate the reaction mechanism, the results of Lineweaver-Burk plot and Michaelis-Menten kinetics of the aerobic oxidation of 1-phenylethanol over the Au_{100}Pd_{40}-PVP/HT were compared in the presence and absence of TEMPO as a radical scavenger (Figure 8). In the presence of TEMPO, the both K_{M} and k_{2} were decreased to be 475 mM and 0.023 mM s^{-1}, respectively, whereas the slopes in the Lineweaver-Burk plot (K_{M}/V_{max}) were similar irrespective of TEMPO. Therefore, TEMPO affected onto the reaction pathway by the uncompetitive inhibition mechanism; i.e., TEMPO is not combined with the active site but intermediate species. Since TEMPO cannot combine the alkoxide intermediate, the prospective radical-like peroxy-species were protected by TEMPO and which makes the reaction slower. These results suggested that the remarkable activity of Au_{100}Pd_{40}-PVP/HT catalysts for aerobic oxidation of alcohols might be originated from the negatively charged Au (5d states) generating the peroxy- and/or superoxy-species which strongly enhances the reaction rate in the β-hydrogen elimination of the alkoxide intermediates.

Fig. 8 Lineweaver-Burk plot and Michaelis-menten kinetics in the aerobic oxidation of 1-phenylethanol over the Au_{100}Pd_{40}-PVP/HT catalyst in the presence (solid line) and absence (dash line) of TEMPO radical scavenger. Reaction conditions : 1-phenylethanol (0.25-3 mM), catalyst (10 mg), TEMPO (0.0032 mM), toluene 5 mL, 313 K, 5 min, O_{2} flow (20 mL·min^{-1}).


The TON and TOF were estimated as > 682,300 and 119,260 h⁻¹, respectively, assuming only Au atoms could act as active sites in 0.2 g of Au₂O₅-Pd₁₈-PVP/HT catalyst.

In the standard condition for comparing the catalytic activities among heterogeneous catalysts (40 mmol scale of 1-phenylethanol), the TON exhibited at up to 207,000 at 423 K for 24 h (> 99 % yield and selectivity).

