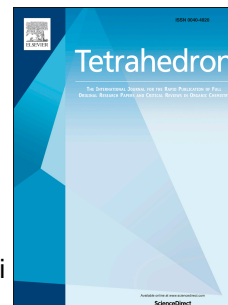


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Bimetallic Co-Pd Alloy Nanoparticles as Magnetically Recoverable Catalysts for the Aerobic Oxidation of Alcohols in Water

Yoshikazu Ito, Hidetoshi Ohta, Yoichi MA. Yamada, Toshiaki Enoki, Yasuhiro Uozumi



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## Graphical Abstract

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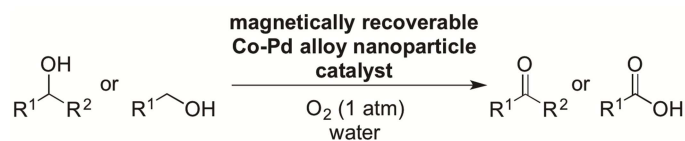
*Yoshikazu Ito,<sup>a,b</sup> Hidetoshi Ohta,<sup>a</sup> Yoichi M. A. Yamada,<sup>a\*</sup> Toshiaki Enoki,<sup>b</sup> and Yasuhiro Uozumi<sup>a,c\*</sup>*

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# Bimetallic Co-Pd Alloy Nanoparticles as Magnetically Recoverable Catalysts for the Aerobic Oxidation of Alcohols in Water

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## ABSTRACT

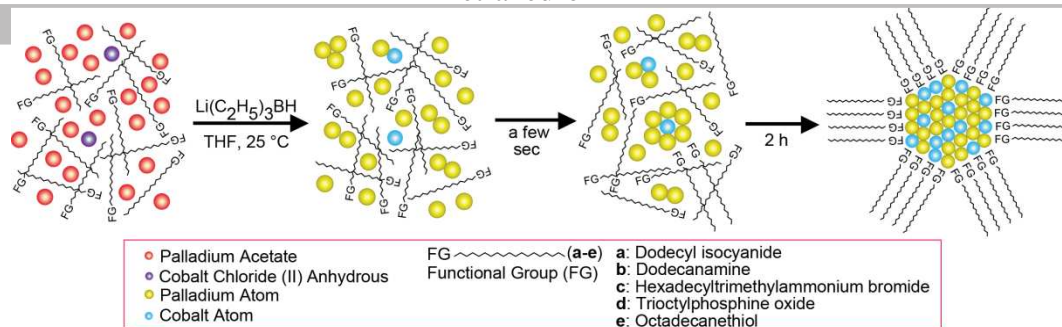
Co-Pd bimetallic alloy nanoparticle catalysts were prepared from  $\text{CoCl}_2$ ,  $\text{Pd}(\text{OAc})_2$  and several capping agents with  $\text{Li}(\text{C}_2\text{H}_5)_3\text{BH}$ . The nanoparticle catalysts were applied to the aerobic oxidation of a variety of alcohols in water to give the corresponding carbonyl products. The catalyst was magnetically recovered and reused for further oxidation. The nanoparticle catalysts were characterized with TEM, ICP, and XPS analyses.

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## 1. Introduction

The development of heterogeneous catalysts for the aerobic oxidation of alcohols in water is an important topic for pure and industrial chemistry.<sup>1</sup> For example, we<sup>2</sup>, Kaneda et al.<sup>3</sup>, Sheldon et al.<sup>4</sup>, Corma et al.<sup>5</sup>, and Sakurai et al.<sup>6</sup> developed non-magnetic heterogeneous nanoparticle catalysts for the aerobic oxidation of various alcohols in water as recoverable catalysts. Recent attention has focused on magnetically recoverable heterogeneous catalysts that can be readily collected by magnetic attraction: metal species supported on magnetic solids have been prepared for the aerobic oxidation of alcohols as magnetically recoverable catalysts.<sup>7-12</sup>  $\text{Fe}_2\text{O}_3$ -immobilized Pd nanoparticles,<sup>7</sup> mesoporous silica-immobilized  $\text{Fe}_2\text{O}_3$ ,<sup>8</sup>  $\text{Fe}_3\text{O}_4$ -immobilized Ru nanoparticles,<sup>9</sup>  $\text{Fe}_3\text{O}_4$ -immobilized Au nanoparticles,<sup>10</sup>  $\text{Fe}_3\text{O}_4$ -immobilized  $\text{Ru}(\text{OH})_x$ <sup>11</sup> and  $\text{NiFe}_2\text{O}_4$ -immobilized Ru nanoparticles<sup>7, 12</sup> are typical examples with which the oxidation was carried out in  $\text{H}_2\text{O}_2$  in  $\text{H}_2\text{O}$ ,<sup>7, 8</sup> polyglycol,<sup>8</sup> toluene<sup>9-11</sup> and isopropanol<sup>12</sup> at 70-130 °C. In these materials, non-magnetic catalytic species are supported on non-catalytic magnetic nanoparticles.

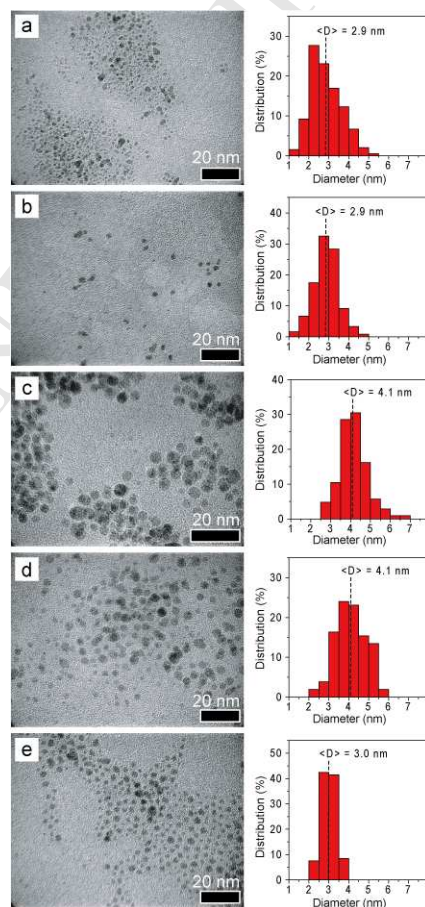
Although these pioneering works are valuable, it is important to develop bifunctional bimetallic alloy nanoparticles in which multiple functions of both catalytic and magnetic properties are simultaneously provided by utilizing surface and ligand modification.<sup>13</sup> Therefore, we decided to develop fine bimetallic alloy magnetic nanoparticles having a strong magnetic moment and high catalytic activity for the aerobic oxidation of alcohols in water. Since Pd nanoparticle catalysts are paramagnetic,<sup>14</sup> ferromagnetic sources should be combined for magnetizing Pd nanoparticles. Recently, we reported ferromagnetic Pd alloy nanoparticles of Co-Pd<sup>15</sup>, Fe-Pd<sup>16</sup> and Ni-Pd<sup>17</sup> with giant magnetic moment. According to our previous reports, Co-Pd alloy nanoparticles have the strongest giant magnetic moment enhanced by Co atoms that attract a neodymium (Nd) magnet. We envisioned that bifunctional and bimetallic Co-Pd alloy nanoparticles having a high surface area and strong magnetic moment could be used as magnetically recoverable nanoparticle catalysts. Here we report the development of bimetallic Co-Pd nanoparticles with surface modification by using five capping agents. The nanoparticles were applied to the aerobic oxidation of various alcohols in water as magnetically recoverable and reusable catalysts.



**Scheme 1.** Preparation of Co-Pd alloy nanoparticles **1a–e** with their surface modified by different capping agents **a–e**.

## 2. Results and Discussion

Bimetallic Co-Pd alloy nanoparticles were prepared by the reduction of  $\text{CoCl}_2$  and  $\text{Pd}(\text{OAc})_2$  in the molar ratio of 1:1, with lithium triethylborohydride in THF solution in the presence of the capping agents **1a–e** (dodecyl isocyanide (**a**), dodecanamine (**b**), hexadecyltrimethylammonium bromide (**c**), trioctylphosphine oxide (**d**), octadecanethiol (**e**)) as shown in Scheme 1. The nanoparticles **1a–e** were characterized by transmission electron microscope (TEM), and inductively coupled plasma (ICP) and X-ray photoelectron spectroscopy (XPS) to reveal their structures. Figure 1 shows representative TEM images and the distribution of the nanoparticles. All the nanoparticles **1a–e** have a small average diameter with narrow distribution (**1a**:  $2.9 \pm 0.8$  nm, **1b**:  $2.9 \pm 0.6$  nm, **1c**:  $4.1 \pm 0.7$  nm, **1d**:  $4.1 \pm 0.7$  nm, **1e**:  $3.0 \pm 0.4$  nm) (Table 1). The ratio of Co and Pd was determined by ICP analysis to be 1:1 (Table 1). Table 2 shows XPS analysis data of the nanoparticles **1a–d** for Pd and Co surface state where the binding energy of Pd  $3d_{5/2}$  was **1a**: 335.1 eV, **1b**: 335.3 eV, **1c**: 335.5 eV and **1d**: 335.2 eV, respectively. These values were close to that of bulk Pd (334.9 eV).<sup>18</sup> In these nanoparticles **1a–d**, the binding energy of the nanoparticles modified with dodecyl isocyanide **a** was the lowest and that of the nanoparticles modified with hexadecyltrimethylammonium bromide **c** was the highest. These differences are thought to be caused by surface modification of the capping agents that changed the surface state. On the other hand, the binding energy of Co  $2p_{3/2}$  was **1a**: 781.0 eV, **1b**: 779.9 eV, **1c**: 780.3 eV and **1d**: 780.7 eV, which were close to that of bulk CoO (780.0 eV).<sup>18</sup> The results suggest that Co atoms on the surface were air-oxidized.



**Figure 1** TEM images and the distribution of Co-Pd alloy nanoparticles **1a–e** with their surface modified by different capping agents **a–e**. The black scale bars are 20 nm.

**Table 1.** Structural information of Co-Pd alloy nanoparticles **1a–e**

Co-Pd alloy nanoparticle	Diameter $\pm$ SD (nm)	Co atomic %	Pd atomic %
<b>1a</b>	$2.9 \pm 0.8$	44	56
<b>1b</b>	$2.9 \pm 0.6$	50	50
<b>1c</b>	$4.1 \pm 0.7$	49	51
<b>1d</b>	$4.1 \pm 0.7$	49	51
<b>1e</b>	$3.0 \pm 0.4$	50	50

**Table 2** Binding energies of Co-Pd alloy nanoparticles **1a–d** in the Pd 3d<sub>5/2</sub> and Co 2p<sub>3/2</sub> obtained from XPS spectra regions<sup>[a]</sup>

Co-Pd alloy nanoparticle	Pd 3d <sub>5/2</sub> (eV)	Co 2p <sub>3/2</sub> (eV)
<b>1a</b>	335.1	781.0
<b>1b</b>	335.3	779.9
<b>1c</b>	335.5	780.3
<b>1d</b>	335.2	780.7

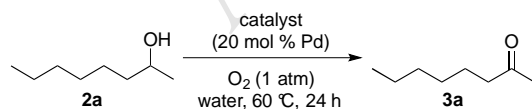
<sup>[a]</sup>The spectra are normalized with C 1s 284.6 eV.<sup>18</sup>



**Figure 2.** The aerobic oxidation of 2-octanol (**2a**) in water with Co-Pd alloy nanoparticles **1a**. Left: the mixture after the reaction. Right: separation of the Co-Pd alloy nanoparticles from the reaction mixture with a Nd magnet. The recovery of magnetic catalysts took 10–15 min.

For the Co-Pd alloy nanoparticles **1a–e** having different capping agents, the aerobic oxidation of 2-octanol (**2a**) was investigated in water (Table 3). Thus, the oxidation of **2a** was carried out with the nanoparticles **1a–d** (20 mol% Pd) in water at 60 °C for 24 h under oxygen atmospheric conditions (1 atm). The nanoparticles **1a** (modified with dodecyl isocyanide **a**) showed the highest catalytic activity, giving 2-octanone (**3a**) with 88% yield (entry 1). The reaction with **1b–d** under similar conditions gave **3a** with 78–64% yield (entries 2–5). The catalytic activity was different regardless of similar diameter [**1a** vs. **1b** (**1a**: 2.9 ± 0.8 nm (**3a**: 88% yield), **1b**: 2.9 ± 0.6 nm (**3a**: 78% yield)), and **1c** vs. **1d** (**1c**: 4.1 ± 0.7 nm (**3a**: 71% yield), **1d**: 4.1 ± 0.7 nm (**3a**: 64% yield))]. The difference is thought to be caused by differences of capping agents: considering the surface state of the nanoparticles **1a**, the back donation of Pd to the isocyanide group could serve to enhance catalytic activity.<sup>19</sup> The nanoparticles **1d**, modified with trioctylphosphine oxide, should have strong affinity to Pd nanoparticles, thus degrading the catalytic activity.<sup>20</sup> The nanoparticles **1e** modified with octadecanethiol showed no catalytic activity because the thiol group capped their surface too strongly (entry 9).

**Table 3.** The aerobic oxidation of 2-octanol (**2a**) in water with Co-Pd alloy nanoparticles **1a–e**<sup>[a]</sup>

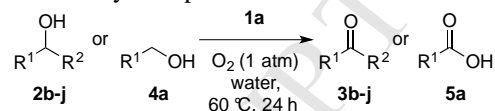


Entry	Catalyst	Yield (%)
1	<b>1a</b>	88
2	<b>1a</b> <sup>[b]</sup>	91
3	<b>1a</b> <sup>[c]</sup>	80
4	<b>1a</b> <sup>[d]</sup>	18
5	<b>1a</b> <sup>[e]</sup>	38

6	<b>1b</b>	78
7	<b>1c</b>	71
8	<b>1d</b>	64
9	<b>1e</b>	<1

<sup>[a]</sup> conditions: catalyst (20 mol% Pd), **2a** (0.2 mmol), water (2 mL), O<sub>2</sub> (1 atm), 60 °C, 24 h; <sup>[b]</sup>2nd use of **1a**; <sup>[c]</sup>3rd use of **1a**; <sup>[d]</sup>4th use of **1a**; <sup>[e]</sup>5th use of **1a**.

**Table 4.** The aerobic oxidation of alcohols **2b–j** or **4** in water with the Co-Pd alloy nanoparticles **1a**<sup>[a]</sup>



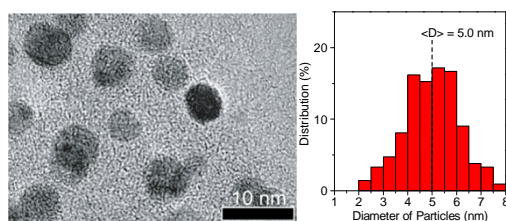
Entry	<b>2</b> or <b>4</b>	Mol% Pd of <b>1a</b>	<b>3</b> or <b>5</b>	Yield (%)
1	<b>2b</b>	4	<b>3b</b>	85
2 <sup>[b]</sup>	<b>2c</b>	5	<b>3c</b>	76
3	<b>2d</b>	4	<b>3d</b>	65
4	<b>2e</b>	15	<b>3e</b>	71
5	<b>2f</b>	21	<b>3f</b>	59
6	<b>2g</b>	14	<b>3g</b>	93
7	<b>2h</b>	13	<b>3h</b>	51
8	<b>2i</b>	13	<b>3i</b>	89
9	<b>2j</b>	14	<b>3j</b>	88
10 <sup>[c]</sup>	<b>4a</b>	20	<b>5a</b>	56

<sup>[a]</sup> All reactions were carried out with **1a**, alcohols (0.2 mmol) in water (2 mL) at 60 °C for 24 h under atmospheric oxygen; <sup>[b]</sup> 20 mmol scale; <sup>[c]</sup> K<sub>2</sub>CO<sub>3</sub> (1 mol equiv) was added.

The nanoparticle catalyst **1a** showing the highest catalytic activity was applied to the aerobic oxidation of various secondary alcohols **2b–j** and a primary alcohol **4a** in water (Table 4). The oxidation of reactive benzylic alcohols **2b–d** gave **3b–d** with 65–75% yield by use of 4–5 mol% Pd of the catalyst **1a** (entries 1–3). The selective oxidation of an alcohol **2d** which consists of benzylic and aliphatic alcohol moieties was achieved to give the benzylic ketone **3d** with 65% yield (entry 3). Sterically hindered benzylic alcohols **2e** and **2f** required a larger amount of the catalyst (entries 4 and 5). The nanoparticle catalyst **1a** promoted the aerobic oxidation of less reactive alicyclic alcohols, cyclopentanol (**2g**), cycloheptanol (**2i**) and cyclooctanol (**2j**) to give **3g**, **3i**, and **3j** with 93%, 89% and 88% yield, respectively (entries 6, 8, and 9), while cyclohexanol (**2h**) was converted to **3h** with 51% yield (entry 7). The reaction of a primary aliphatic alcohol 1-octanol (**4a**) gave octanoic acid (**5a**) with 56% yield

(entry 10) in which the resulting carboxylate could act as a capping agent of nanoparticles to decrease the catalytic activity.<sup>20</sup>

The nanoparticle catalyst **1a** for the oxidation of 2-octanol (**2a**) was employed for magnetic recovery and reuse experiments (Table 1, entries 1–5). After completion of the first reaction, the catalyst **1a** was magnetically recovered with a Nd magnet (Figure 2), and then the 2nd, 3rd, 4th, and 5th reactions were carried out with the recovered catalyst under similar conditions to give 91%, 80%, 18% and 38% yield of 2-octanone (**3a**), respectively. Figure 3 shows a representative TEM image after the 4th reaction. The diameter of the nanoparticle catalyst **1a** increased from  $2.9 \pm 0.8$  nm (before use) to  $5.0 \pm 1.1$  nm (after the 4th reaction). Leaching of Co and Pd species after the 1st reaction was checked with ICP analysis. Leaching of Co and Pd was only  $9 \times 10^{-3}$  mol% and  $8 \times 10^{-6}$  mol%, respectively, whose ratio of Co to Pd is  $>99.9 : <0.1$ . This result can be explained with an oxidizing ability of  $E_{ox}$ : 0.951 V of Pd(0)/Pd(II) and  $E_{ox}$ :  $-0.28$  V of Co(0)/Co(II) with reference to the standard hydrogen electrode. Co(0) should be readily oxidized by Pd(II) to give ionic Co(II) that could be leached out. The resulting Pd(0) could aggregate with initial nanoparticles to provide larger nanoparticles with wider distribution (2–8 nm).



**Figure 3.** Representative TEM image of Co-Pd alloy nanoparticles **1a** after the 4th run in the aerobic oxidation in water. The black scale bar is 10 nm.

### 3. Conclusion

In conclusion, we prepared and characterized bimetallic Co-Pd alloy nanoparticles modified with various capping agents whose atomic concentrations were finely controlled. We bifunctionalized Co-Pd alloy nanoparticles with catalytic activity by Pd as well as magnetic recoverability by Co simultaneously. The Co-Pd alloy nanoparticle catalyst showed catalytic activity for the aerobic oxidation of various alcohols in water with recyclability under mild conditions.

## 4. Experimental Section

### 4.1. General Methods

The aerobic oxidation of alcohols was performed in a glass tube under oxygen gas at atmospheric pressure in a balloon. THF was distilled from Na/benzophenone. Water was deionized with a Millipore system.  $^1\text{H}$  NMR (500 MHz) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (126 MHz) spectra were measured with a JNM ECA-500 spectrometer.  $^1\text{H}$  NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm) as an internal standard. The  $^{13}\text{C}\{^1\text{H}\}$  NMR chemical shifts are reported relative to  $\text{CDCl}_3$  (77.0 ppm). The GC-MS was measured by an Agilent 7890A GC/MS detector that was used with *o*-xylene or mesitylene as an internal standard for determining the GC yield. TEM images were obtained by using a transmission electron microscope (JEOL JEM-2100F) operated at 200 kV. TEM samples were

prepared by placing a hexane suspension of nanoparticles on carbon-coated Cu grids, and allowed to dry at room temperature. XPS spectra were measured by ESCALAB 250 (Thermo Scientific). Elemental analyses of Co and Pd were carried out by inductively coupled plasma spectroscopy using Shimadzu ICPS-8100 equipment by the chemical analysis team in RIKEN. Magnet recovery of catalysts was performed with a Nd magnet (ca 0.34 T). Capping agents, dodecanamine (**b**), hexadecyltrimethylammonium bromide (**c**) and trioctyl phosphine oxide (**d**) were purchased from Aldrich and Wako. Dodecyl isocyanide (**a**) was prepared according to the literature<sup>21</sup>. The alcohols, 2-octanol (**2a**), 1-phenylethanol (**2b**), diphenylmethanol (**2c**), 1-phenyl-1-hexanol (**2d**), 1,2,3,4-tetrahydro-1-naphthol (**2e**), 1-phenyl-1,2-ethanediol (**2f**), cyclopentanol (**2g**), cyclohexanol (**2h**), cycloheptanol (**2i**), cyclooctanol (**2j**), 1-octanol (**4a**), palladium acetate, anhydrous cobalt chloride (II) and lithium triethylborohydride were purchased from Aldrich, TCI, Wako and ACROS Organics.

All oxidation products are known compounds whose CA registry numbers are provided as below:

**3a**: 111-13-7, **3b**: 98-86-2, **3c**: 942-92-7, **3d**: 582-24-1, **3e**: 119-61-9, **3f**: 529-34-0, **3g**: 120-92-3, **3h**: 108-94-1, **3i**: 502-42-1, **3j**: 502-49-8, **5a**: 124-07-2.

### 4.2. General Procedure for Co-Pd Alloy Nanoparticles

The nanoparticles of Co-Pd alloy modified with capping agents **a–e** were prepared similarly to Co-Pd alloy nanoparticles.<sup>14</sup> A mixture of  $\text{Pd}(\text{OAc})_2$  (0.25 mmol), anhydrous  $\text{CoCl}_2$  (0.25 mmol), and capping agents **a–e** (0.5 mmol (**a–d**) or 0.35 mmol (**e**)) was dissolved in 10 mL of freshly distilled dry THF under nitrogen. To this solution lithium triethylborohydride solution in THF (1 M, 5 mL) was rapidly added in one portion at 24 °C. The resulting suspension was stirred at 24 °C for 2 h under nitrogen. The resulting nanoparticles were collected by centrifugation and purified with ethanol to give the corresponding nanoparticles **1a–e** as a suspension in ethanol (the concentrations of Co and Pd in ethanol were determined by ICP analysis) (CAUTION! Dried nanoparticles are ignitable.).

### 4.3. General Procedure for Catalytic Aerobic Oxidation of Primary Alcohols in Water

A mixture of magnetic nanoparticles **1a–e** (suspension in ethanol;  $\sim 0.16$  M Co-Pd), primary alcohol (0.2 mmol), and potassium carbonate (0.2 mmol) in water (2 mL) was stirred at 60 °C under oxygen gas at atmospheric pressure. After being cooled, the mixture was washed with ether, and acidified with 5% hydrochloric acid. The mixture was extracted with ethyl acetate ( $5 \times 1$  mL). The extract was dried over magnesium sulfate. The resulting solution was analyzed by GC and GC-MS (with Mass Spectral Reference Database). The yield of the product was determined by GC with an internal standard (*o*-xylene).

### 4.4. General Procedure for Catalytic Aerobic Oxidation of Secondary Alcohols in Water

A mixture of magnetic nanoparticles **1a** (suspension in ethanol) and secondary alcohol (0.2 mmol) in water (2 mL) was stirred at 60 °C under oxygen gas at atmospheric pressure. After it was cooled, the mixture was extracted with ethyl acetate ( $5 \times 1$  mL). The extract was analyzed by GC and GC-MS (with Mass Spectral Reference Database). The yield of the product was

determined by GC with an internal standard (*o*-xylene or mesitylene).

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