Highly selective oxidation of allylic alcohols catalysed by monodispersed 8-shell Pd nanoclusters in the presence of molecular oxygen

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Treatment of $Pd_4phen_2(CO)_2(OAc)_4$ with metal nitrates such as $Cu(NO_3)_2$ produced monodispersed Pd nanoclusters with a mean diameter and standard deviation ($d \pm \sigma$) of 38 ± 2.1 Å ($\sigma/d = 6\%$). The Pd nanoclusters act as heterogeneous catalysts for the selective oxidation of primary aromatic allylic alcohols using molecular oxygen as an oxidant. This unique catalysis can be ascribed to multiple interactions between the alcohol and specific ensemble sites consisting of Pd^0, Pd^+, and Pd^{2+} on the cluster surface.

Transition metals, especially Pd, are among the most important catalysts in organic synthesis.[1] Adjusting the steric and electronic properties of metal centers using organic ligands generally affords high-performance Pd complex catalysts with respect to the target organic transformations.[1b] On the other hand, the heterogeneous catalysis properties of Pd particles depend upon their size, because of alterations in the geometric and electronic properties of the surface Pd atoms. Recently, synthesis of giant Pd clusters containing more than 100 Pd atoms has opened up an exciting field,[2–6] offering the possibility of unprecedented catalytic reactions based on specific surface ensemble Pd sites within a regular arrangement of multiple Pd species.[6]

Previously, we reported the synthesis of anion ligand-preserved giant Pd clusters by a novel method using treatment of $Pd_4(CO)_4(OAc)_4{\cdot}2AcOH$ (PCA) with metal nitrates [*e.g.* $Cu(NO_3)_2$ and $Fe(NO_3)_3$] in the presence of 1,10-phenanthroline (phen) under an atmospheric O_2.[7] This method yielded mixed-valence states on the surface with Pd^0, Pd^+, and Pd^{2+} species to form specific ensemble Pd sites. The giant Pd clusters with the highest percentage of Pd^+ species showed high catalytic activity for the oxidative acetoxylation of toluene to benzyl acetates under an atmospheric pressure of O_2, compared with conventional Pd catalysts such as Pd/carbon, Pd/Al_2O_3, and $Pd(OAc)_2$. The unique catalytic ability of these Pd nanoclusters was attributed to the ensemble Pd sites on the cluster surface.

Attention has focused on Pd-catalysed oxidation of alcohols into the corresponding carbonyl compounds using molecular oxygen as an environmentally friendly oxidant.[8–11] In this report, we explore the catalytic potential of Pd nanoclusters for the aerobic oxidation of alcohols. The Pd nanoclusters show high catalytic activity for the oxidation of primary allylic alcohols, which may be due to the unique surface ensemble Pd sites of the monodispersed Pd nanoclusters. We also demonstrate that each surface Pd species (*i.e.* Pd^0, Pd^+, and Pd^{2+}) does not act individually as a catalytic site, but together work cooperatively as a "trio" on the same cluster surface to provide unique selectivity. The Pd cluster provides a new strategy to design highly selective Pd catalysts for many organic syntheses.

Experimental

Materials and characterization

$Pd(OAc)_2$ was purchased from N. E. Chemcat Co. Ltd. and used without further purification. 1,10-Phenanthroline (phen) and $Cu(NO_3)_2{\cdot}3H_2O$ were obtained from Nacalai Tesque Co. Ltd. Acetic acid and all commercially obtained alcohols were purified by standard procedures. Noncommercial alcohols, 4-methoxycinnamyl alcohol, 4-chlorocinnamyl alcohol, 4-phenyl-3-buten-2-ol and 4-methyl-3-penten-2-ol, were synthesized according to literature procedures.[12] TiO_2 was supplied by the Catalysis Society of Japan as a reference catalyst of JRC-TIO-2.[7] X-Ray diffraction (XRD) was performed on an X'pert diffractometer (Phillips Co., Ltd.). The procedure for determining the number of surface Pd_2O species using CO consumption has been described in a previous paper.[7] The amount of O_2 absorption was measured volumetrically using a gas buret directly connected to the rotary vacuum pump. The O_2 uptake during preparation of the Pd nanoclusters was determined by trapping the evolved CO_2 in a cold trap at −120 °C. Field emission scanning electron microscopy (FE-SEM) was done on a Hitachi S-5000 L microscope (18.0 kV). The high-resolution transmission electron microscopy (HR-TEM) measurement of the single Pd nanocluster was performed on a JEOL JEM-3000F (300 kV).

Synthesis of monodispersed Pd nanoclusters. A solution of $Pd(OAc)_2$ (0.20 g; 0.89 mmol) in AcOH (20 mL) was stirred at 50 °C for 2 h under continuous CO flow, yielding 0.12 g of $Pd_4(CO)_4(OAc)_4{\cdot}2AcOH$ (PCA) as a yellow precipitate.[13] The obtained PCA (0.155 mmol; Pd 0.62 mmol) and phen (0.31 mmol) were stirred in AcOH (2.5 mL) at room temperature for 30 min in air to give a dark brown solution of $Pd_4phen_2(CO)_2(OAc)_4$.[14] Anal. calcd for $Pd_4C_{34}H_{28}N_4O_{10}$: C,

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37.9; H, 2.6; N, 5.2; found: C, 34.1; H, 2.7; N, 5.2%. Then, 0.0155 mmol of $Cu(NO_3)_2{\cdot}3H_2O$ was added to the mixture and heated at 90 °C under an atmosphere of O_2. After 15 min, a black solid precipitated with the consumption of 0.067 mmol O_2 ($O_2/Pd = 0.108$ mol/mol). The precipitate was washed with AcOH several times and dried *in vacuo* to yield the Pd nanoclusters (0.032 g, *ca.* 30% yield based on Pd). Anal. calcd for $Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$: Pd, 83.02; C, 3.28; H, 0.41; N, 1.91; found: Pd, 86.50; C, 3.21; H, 0.23; N, 1.34%. No appreciable copper signals were detected by elemental analysis and XPS measurement of the precipitate. The XRD pattern of the precipitate exhibited three peaks, at 40°, 46°, and 68°, which correspond to the {111}, {200}, and {220} planes of a face-centerd cubic (fcc) lattice, respectively.[7]

The following eqn. (1) represents the formation of the Pd clusters:

$$\begin{aligned}&90[Pd_4phen_2(CO)_2(OAc)_4] + 9[Cu(NO_3)_2\cdot 3H_2O] + 172AcOH\\ &\quad + 137\mathbf{O_2} \rightarrow 0.05[Pd_{\sim 2060}(NO_3)_{\sim 360}(OAc)_{\sim 360}\mathbf{O}_{\sim 80}]\\ &\quad + 180[Pdphen(OAc)_2] + 77[Pd(OAc)_2] + 9[Cu(OAc)_2]\\ &\quad + 113\mathbf{H_2O} + 180\mathbf{CO_2} \qquad (1)\end{aligned}$$

During preparation of the Pd clusters, molecular oxygen was consumed to form CO_2, H_2O, and the oxygen species (Pd_2O) on the cluster surface.

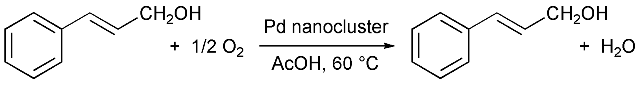
A typical procedure for the immobilization of the Pd clusters on TiO_2 was described in a previous paper.[7]

Alcohol oxidation

A typical procedure for the alcohol oxidation is as follows. Acetic acid (4 mL) and cinnamyl alcohol (2 mmol) were added to a reaction vessel containing the Pd nanoclusters (0.05 mmol of Pd atoms). The heterogeneous mixture was stirred at 60 °C for 2 h under an atmospheric pressure of O_2. The yield of products was determined by GC analysis using an internal standard technique. Filtration of the heterogeneous mixture gave a solution devoid of any oxidizing ability. The amount of Pd species in the filtrate was less than 0.01% by ICP analysis.

Results and discussion

Treatment of $Pd_4phen_2(CO)_2(OAc)_4$ with $Cu(NO_3)_2{\cdot}3H_2O$ at 90 °C under an O_2 atmosphere produces Pd nanoclusters. The Pd nanoclusters act as efficient heterogeneous catalysts for the selective oxidation of cinnamyl alcohol to cinnamaldehyde in the presence of molecular oxygen. In monitoring O_2 uptake during the oxidation of cinnamyl alcohol, the ratio of O_2 consumed to cinnamaldehyde was 1:2, indicating molecular oxygen was quantitatively used for the dehydrogenation as an oxidant.



Results of the aerobic oxidation of various alcohols catalysed by the Pd nanoclusters are displayed in Table 1 together with those using the $Pd_{561}phen_{60}(OAc)_{180}$ cluster[6] and $Pd(OAc)_2$–pyridine[10e] catalytic systems. Interestingly, the giant Pd clusters efficiently catalysed the oxidation of primary aromatic allylic alcohols using molecular oxygen. For example, cinnamyl alcohol and its para-substituted derivatives having electron-donating groups were smoothly transformed into the corresponding α,β-unsaturated aldehydes in high yields (entries 1 and 4), while electron-withdrawing groups such as chloro and nitro markedly retarded the reaction rates (entries 5 and 6). Introduction of a methyl group onto the olefinic bond resulted in a longer reaction time to obtain a high yield of the aldehyde (entry 7). It should be noted that these Pd nanoclusters show lower reactivity for primary aliphatic allylic alcohols [*e.g.* 3-methyl-2-buten-1-ol and 2-hexen-1-ol (entries 8 and 10, respectively)] than for aromatic alcohols. Furthermore, oxidation of secondary aromatic allylic alcohols proceeded slowly; prolonged reaction times afforded a high yield of the corresponding ketone (entry 14). Interestingly, benzylic alcohols were oxidized more slowly than allylic alcohols (entries 18 and 21). This high reactivity for allylic alcohols was also exemplified in a competitive reaction of an equimolar mixture of cinnamyl alcohol and benzyl alcohol, in which cinnamaldehyde was selectively obtained in 92% yield with only 1% of benzaldehyde after 2 h. Oxidation of saturated alcohols such as 2-octanol and 1-octanol hardly occurred using Pd nanoclusters.

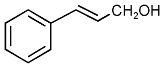
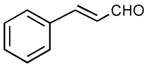
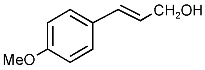
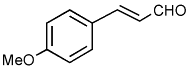
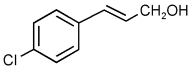
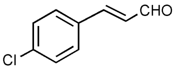
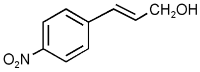
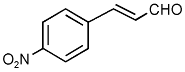
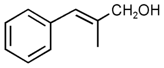
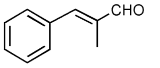
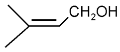
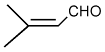
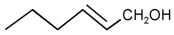
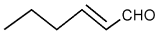
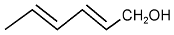
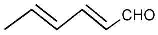
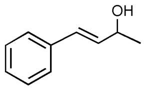
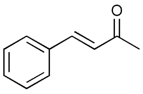
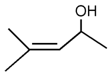
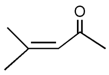
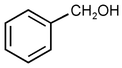
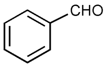
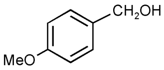
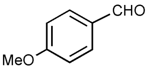
Generally, divalent Pd catalysts are prone to facilely oxidize benzyl alcohols, but are not suitable for the oxidation of allylic alcohols because of irreversible coordination of allylic alcohols to the Pd species.[10] Indeed, the $Pd(OAc)_2$–pyridine catalyst system does not efficiently oxidize cinnamyl alcohol (entry 3). The difference between the giant Pd clusters described here and conventional Pd^{2+} complexes lies in the high reactivity of allylic alcohols over benzylic alcohols. As compared with the $Pd_{561}phen_{60}(OAc)_{180}$ cluster, which has Pd^+ cation species over all its surface,[6] the present Pd nanoclusters prefer aromatic allylic alcohols to aliphatic ones. Cinnamyl alcohol was completely oxidized after only 1 h, while oxidation of 3-methyl-2-buten-1-ol required 5 h (entry 1 *vs.* 8). In contrast, $Pd_{561}phen_{60}(OAc)_{180}$ catalysed the oxidation of both allylic alcohols at similar rates (entry 2 *vs.* 9).

In order to consider the origin of the unique Pd nanocluster catalysis of aerobic alcohol oxidation, the particle size distribution and ordering of Pd atoms of the Pd clusters were estimated by FE-SEM and HR-TEM. The Pd clusters were immobilized on a TiO_2 surface because this does not change their original cluster size or the local ordering of the Pd atoms on the cluster surface.[6] As shown in Fig. 1, the FE-SEM image of the Pd clusters on the TiO_2 surface revealed that the Pd nanoclusters were well dispersed with a quite narrow size distribution over the TiO_2 surface. The mean diameter and standard deviation ($d \pm \sigma$) of the Pd clusters were 38 ± 2.1 Å ($\sigma/d = 6\%$). The use of $Fe(NO_3)_3$ instead of $Cu(NO_3)_2$ also afforded Pd nanoclusters having a narrow size distribution with a mean diameter and standard deviation ($d \pm \sigma$) of 38 ± 4.4 Å ($\sigma/d = 11\%$).

Concerning the size distribution of Pd clusters, Teranishi and Miyake also reported a narrow size distribution for giant Pd clusters prepared by reduction of aqueous H_2PdCl_4 in the presence of poly(*N*-vinyl-2-pyrrolidone), which had a standard deviation of the mean diameter of ~14% ($\sigma = 3.6$ Å, $d = 24.4$ Å).[15a] To the best of our knowledge, the Pd nanoclusters prepared by our method using metal nitrates have the narrowest size distribution of Pd nanoparticles obtained by chemical and electrochemical methods.[15–19] One reason for the narrow size distribution of these Pd nanoclusters could be the strong ability of the metal nitrate for the disproportionation of monovalent Pd ions. This leads to the formation of a relatively small Pd assembly through fast nucleation of Pd^0 species.[7] Furthermore, partial oxidation of surface Pd^0 species by the metal nitrate retards further growth of the nanoclusters.

Fig. 2 represents the HR-TEM image of the Pd nanocluster immobilized on the TiO_2 surface. A regular arrangement of Pd atoms on the Pd nanocluster surface can be clearly observed, with 17 Pd atoms along the {111} planes. A possible arrangement of the Pd atoms of the eight-shell Pd cluster is illustrated in Fig. 3, where the Pd^0 and Pd^+ species are situated on the face of the cluster.[7] These observations indicate that the present giant Pd clusters have an fcc cuboctahedral shape with an eight-shell structure composed of 2060 Pd atoms as the

Table 1 Oxidation of alcohols catalysed by Pd nanoclusters under an oxygen atmosphere[a]

Entry	Substrate	Product	Catalyst	Time/h	% Conv	% Yield[b]
1			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	2	93	91
2			$Pd_{561}phen_{60}(OAc)_{180}$	1	100	94
3			$Pd(OAc)_2$–pyridine[c]	2	46	35
4			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	2	100	91
5[d]			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	10	43	35
6[d]			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	10	46	37
7			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	4	91	87
8			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	5	90	83
9			$Pd_{561}phen_{60}(OAc)_{180}$	1	100	89
10			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	5	66	49[e]
11			$Pd_{561}phen_{60}(OAc)_{180}$	1	100	79
12			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	5	77	50[f]
13			$Pd_{561}phen_{60}(OAc)_{180}$	2	100	100
14			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	14	94	80
15			$Pd_{561}phen_{60}(OAc)_{180}$	4	47	36
16			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	24	< 1	Trace
17			$Pd_{561}phen_{60}(OAc)_{180}$	24	8	1
18			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	14	95	92
				4	45	44
19			$Pd_{561}phen_{60}(OAc)_{180}$	24	78	24
20			$Pd(OAC)_2$–pyridine[c]	2	100	100
21			$Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$	14	95	91
				4	53	50
22			$Pd(OAC)_2$–pyridine[c]	2	97	95

[a] Reaction conditions: substrate (2 mmol), Pd (0.05 mmol), AcOH (4 mL), 60 °C, O_2 atmosphere. [b] Yields of aldehydes and ketones were determined by GC analysis using an internal standard technique. [c] Substrate (2 mmol), $Pd(OAc)_2$ (0.05 mmol), pyridine (0.2 mmol), MS3A (0.5 g), toluene (4 mL), 80 °C, O_2 atmosphere. [d] Substrate (1.5 mmol). [e] 15% of 2-hexenyl acetate was formed. [f] 22% of 2,4-hexadienyl acetate was formed.

magic number. $Pd^+(Pd_2O)$ species comprised 23% of the surface Pd atoms; the percentages of Pd^{2+} and Pd^0 species were 56% and 20%, respectively.[7] This agrees with the composition of the Pd nanocluters, $Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$; the surface divalent Pd cations were preserved at corner/edge sites by NO_3^- and OAc^- anions, where oxygen species were bound to the two monovalent Pd ions on the face of the cluster.

Selection of the $Cu(NO_3)_2$/PCA molar ratio can control the fraction of surface Pd^+ species in the Pd nanocusters.[7] To determine the effect of surface Pd^+ fraction on alcohol oxidation, the catalytic activity of the Pd clusters was examined in the aerobic oxidation of cinnamyl alcohol as a function of $Cu(NO_3)_2$/PCA molar ratio. As depicted in Fig. 4, the highest catalytic activity was obtained for the Pd_{2060} cluster prepared with a 0.10 $Cu(NO_3)_2$/PCA molar ratio. The most active Pd_{2060} cluster had the highest fraction (23%) of Pd^+ among the surface Pd atoms.

The ensemble Pd sites of the Pd nanocluster catalyst described here play a pivotal role in the oxidative acetoxylation of toluene using molecular oxygen, where the reaction is initiated by a π-bond interaction between toluene and the cationic Pd^{2+} species, followed by rupture of the methyl C–H bond of adsorbed toluene by a neighboring Pd^0 to form a π-benzyl Pd adduct together with formation of a Pd–H species.[7] Then, the oxygen from Pd_2O reacts with the hydride to give Pd^0. In a similar fashion, the highly selective oxidation of aromatic alcohols by the Pd nanoclusters can be explained by a π-bond interaction between the aromatic allylic alcohols and the cationic Pd^{2+} species.

The initial step is a π-bond interaction between the phenyl group of the primary aromatic allylic alcohol and the Pd^{2+} species, followed by oxidative addition of the O–H bond of a coordinated alcohol to a neighboring Pd^0 species. A Pd^{2+}–alcoholate species subsequently undergoes β-hydride elimination to produce an α,β-unsaturated aldehyde and a Pd–H species.[8e,20] Then, the hydride readily reacts with oxygen from a neighboring Pd_2O to give H_2O, regenerating the Pd^0. Finally, the Pd_2O species is restored by the dissociative adsorption of molecular oxygen on the surface of Pd^0. As shown in Fig. 4, the Pd nanocluster having the maximum fraction of Pd^+ species effectively catalysed the oxidation. This behavior is responsible for the high concentration of the ensemble sites consisting of three components (*i.e.* Pd^0, Pd_2O, and Pd^{2+}) on the cluster surface (Fig. 3), where an interconversion between $Pd^+(Pd_2O)$ and Pd^0 facilely occurs in the presence of molecular oxygen.[7] The above mechanism involving electron donation from an aromatic ring to the Pd cation to form the π-arene Pd complex accounts for the para-substitution effect of cinnamyl alcohols;

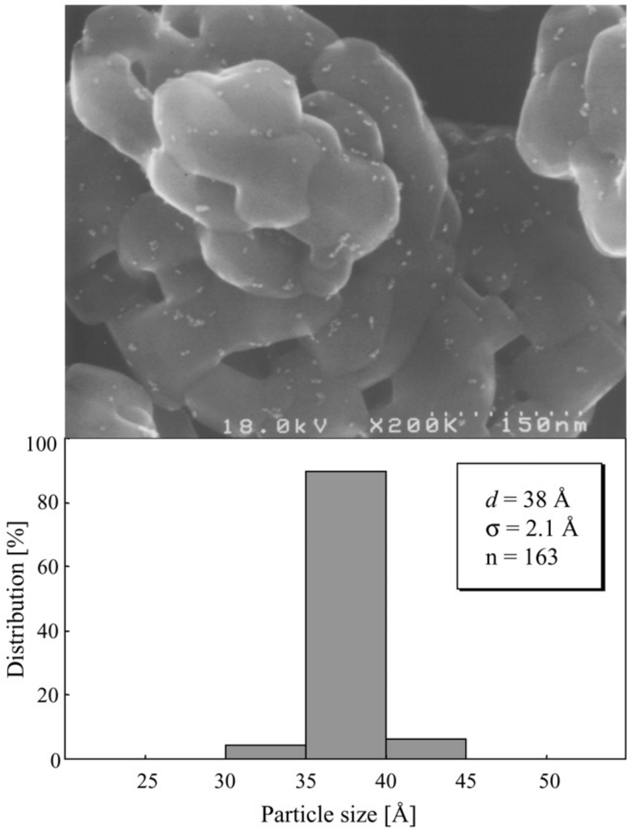


Fig. 1 FE-SEM photograph of the Pd nanoclusters dispersed on TiO_2 and their particle size distribution.

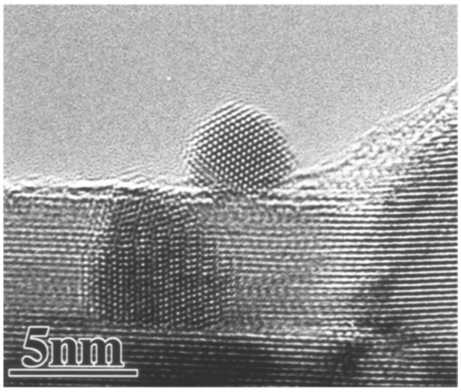


Fig. 2 HR-TEM image of the single Pd nanocluster prepared with a 0.10 $Cu(NO_3)_2$/PCA molar ratio.

4-methoxycinnamyl alcohol showed higher reactivity than the corresponding chloro and nitro derivatives. The high selectivity for the oxidation of allylic alcohols when compared with benzyl alcohol might be related to a coordination of the C=C bond with a Pd cation, for example Pd^{2+}. Correspondingly, the distance between the Pd cation and Pd^0 fits with that found for the distance between a terminal β-carbon of a C=C bond and an oxygen atom of the OH of allylic alcohols.[21]

Conclusions

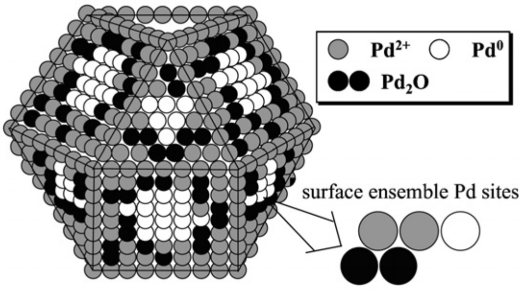


Fig. 3 Proposed structural model of the 8-shell Pd cluster, $Pd_{2060}(NO_3)_{360}(OAc)_{360}O_{80}$, with surface ensemble Pd sites. The anionic ligands in the outer sphere are omitted.

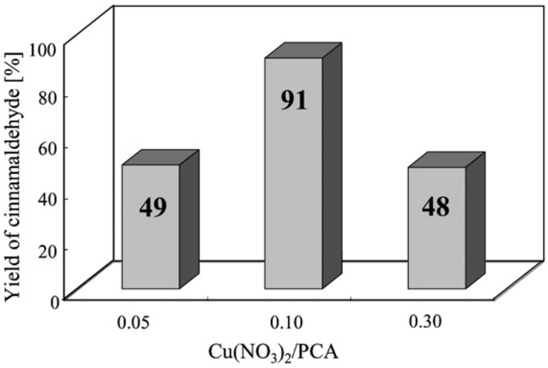


Fig. 4 Aerobic oxidation of cinnamyl alcohol as a function of $Cu(NO_3)_2$/PCA molar ratio. Reaction conditions: Pd (0.05 mmol), cinnamyl alcohol (2 mmol), AcOH (4 mL), 60 °C, 2 h, O_2 atmosphere.

In summary, the present study reveals the monodispersion of eight-shell Pd clusters having surface ensemble Pd sites composed of Pd^0, Pd^+, and Pd^{2+}, which exhibit unique catalysis of the oxidation of alcohols using molecular oxygen as the oxidant. Research continues into the synthesis of monodispersed polynuclear metal clusters (*e.g.* 5, 6, and 7-shell nanoclusters) as heterogeneous catalysts for the selective oxidation of organic compounds[22] in relation to the preparation chemistry of nanocluster materials.

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