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Remarkable Effect of Bimetallic Nanocluster Catalysts for Aerobic Oxidation of Alcohols: Combining Metals Changes the Activities and the Reaction Pathways to Aldehydes/Carboxylic Acids or Esters

Kosuke Kaizuka, Hiroyuki Miyamura, and Shū Kobayashi*

Department of Chemistry, School of Science and Graduate School of Pharmaceutical Sciences, the University of Tokyo, HFRE Division, ERATO, JST, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Received April 25, 2010; E-mail: shu_kobayashi@chem.s.u-tokyo.ac.jp

Abstract: Selective oxidation of alcohols catalyzed by novel carbon-stabilized polymer-incarcerated bimetallic nanocluster catalysts using molecular oxygen has been developed. The reactivity and the selectivity were strongly dependent on the combination of metals and solvent systems; aldehydes and ketones were obtained by the gold/platinum catalyst in benzotrifluoride, and esters were formed by the gold/palladium catalyst in methanol. To the best of our knowledge, this is the first example that the reaction pathway has been changed dramatically in gold catalysis by combining with a second metal. The differences in the activity and the selectivity are considered to be derived from the difference in the structure of the bimetallic clusters.

Since Haruta's discovery, aerobic oxidation reactions catalyzed by gold nanoclusters have been widely investigated.[1,2] In particular, the selective oxidation of alcohols to the corresponding carbonyl compounds such as aldehydes, carboxylic acids, and esters catalyzed by gold nanoclusters is attractive both for industry and in the laboratory.[3,4] In those investigations, bimetallic nanoclusters, such as gold/platinum, gold/silver, gold/palladium, etc., sometimes show higher activity than the gold nanocluster itself.[5] In these cases, the activity of gold can be tuned by combining with other metals. This seems to be due to the "ligand effect" and the "ensemble effect" of bimetallic nanoclusters.[6] The "ligand effect" is derived from the change of properties of the nanocluster surface by the donating and accepting of electrons between a core metal and a surface metal, and the "ensemble effect" is derived from the independent activation of substrates on each metal on the nanocluster surface. However, to the best of our knowledge, there have been no reports that reaction pathways in gold catalysis are changed dramatically by combining with a second metal.

Selective oxidation of alcohols is one of the most important transformations in organic synthesis, because the resulting carbonyl compounds possess higher energy and reactivity to allow many kinds of carbon−carbon bond-forming and other transforming reactions. While several metal-based oxidizing reagents have been developed,[7] these protocols usually require stoichiometric amounts of metal oxidants, and thus a large amount of waste is formed in many cases. In this context, alcohol oxidation using molecular oxygen catalyzed by reusable heterogeneous catalysts under mild conditions is desired from the viewpoints of atom economy and energy efficiency.[3,8,9] Although several excellent catalysts for aerobic oxidation of alcohols to the corresponding carbonyl compounds have been developed, primary alcohols suffer from overoxidation to form carboxylic acids, and selective oxidation to form aldehydes, which are more valuable compounds, is difficult. In particular, selective oxidation to aliphatic aldehydes is one of the most difficult missions, and heterogeneous catalysts that are effective for aerobic oxidation of aliphatic alcohols to aldehydes under ambient conditions are limited.[10] Ester formation is also an important transformation in organic synthesis; however, it usually requires synthesis of carboxylic acids or activated carboxylic acid derivatives such as acid chlorides or acid anhydrides.[8b] In this respect, direct oxidative ester formation from alcohols using molecular oxygen is attractive and challenging for organic synthesis and green chemistry. Although oxidation of aldehydes to esters proceeds under mild conditions,[11] examples starting from alcohols under mild conditions (atmospheric pressure and ambient temperature) are rare.[4,12] In particular, transformation of primary aliphatic alcohols to the corresponding esters is another difficult mission.

Recently, we reported that gold and/or platinum nanocluster catalysts immobilized on polystyrene-based polymers with cross-linked moieties, polymer-incarcerated catalysts (PI catalysts), were highly effective for aerobic oxidation of alcohols to carbonyl compounds[5c,13] and hydroquinones to quinones[14] and direct oxidative ester formation of primary benzyl alcohols.[15] In these investigations, bimetallic nanocluster catalysts showed distinctive activity compared with monometallic nanoclusters. For example, PI Au/Pt could oxidize alcohols under neutral conditions, although PI-Au required a certain amount of base.

Here, we describe the selective aerobic oxidation of alcohols to the corresponding carbonyl compounds, aldehydes, carboxylic acids, and esters under very mild conditions, namely, ambient temperature and atmospheric pressure, catalyzed by novel carbon-stabilized polymer-incarcerated bimetallic nanocluster catalysts (PI-CB catalysts). Interestingly, the reactivity and selectivity are strongly dependent on the combination of metals and solvent systems.

The preparation of PI-CB monometallic, bimetallic, and trimetallic catalysts followed the preparation of PI-CB/**Au** we have already reported.[13b,16] The catalytic activities of the prepared catalysts in the aerobic oxidation of alcohols were assessed using 1-octanol as a model substrate. Under neutral conditions in a benzotrifluoride (BTF)/water solvent system,[17] monometallic nanocluster catalysts (PI-CB/**Au**, **Pt**, **Pd**) did not show any catalytic activities (Table 1, entries 1−3). In contrast, a bimetallic catalyst, PI-CB/**Au**−**Pt**, oxidized 1-octanol to octanal in excellent yield and 1-octanoic acid in low yield (entries 4,5). In the presence of K_2CO_3, the major product was 1-octanoic acid (entry 6). It is noted that overoxidation of 1-octanal to 1-octanoic acid was suppressed under neutral conditions. In a methanol/water solvent system, oxidation of 1-octanol was suppressed significantly, and a small amount of methyl 1-octanoate was obtained (entries 7−9). In contrast, PI-CB/**Au**−**Pd** showed completely different activity and selectivity compared with PI-CB/**Au**−**Pt**. In the BTF/water solvent system, the activity was much lower than that of PI-CB/**Au**−**Pt** despite the presence of K_2CO_3 and/or heating (entries 10−13). Surprisingly, direct oxidative methyl ester formation catalyzed by PI-CB/**Au**−**Pd** pro-

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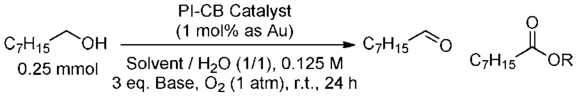
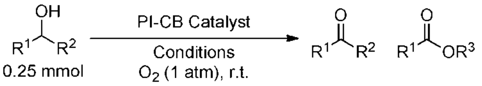
Table 1. Aerobic Oxidation of 1-Octanol Catalyzed by PI-CB Catalysts



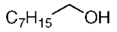
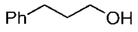
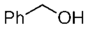
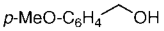
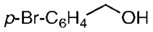
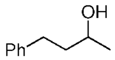
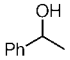
entry	catalyst	solvent	base	yield[a] (%) ester	acid	aldehyde	alcohol
1	PI-CB/Au	BTF	none	–	trace	trace	99
2	PI-CB/Pt	BTF	none	–	n.d.	1	99
3	PI-CB/Pd	BTF	none	–	trace	trace	99
4	PI-CB/**Au−Pt**	BTF	none	–	22	**63**	9
5[b]	PI-CB/**Au−Pt**	BTF	none	–	6	**92**	trace
6	PI-CB/**Au−Pt**	BTF	K_2CO_3	–	**94**	2	n.d.
7	PI-CB/Au−Pt	MeOH	none	<1	n.d.	2	94
8[c]	PI-CB/Au−Pt	MeOH	none	4	1	6	86
9	PI-CB/Au−Pt	MeOH	K_2CO_3	9	7	4	78
10	PI-CB/Au−Pd	BTF	none	–	1	3	90
11[c]	PI-CB/Au−Pd	BTF	none	–	2	8	87
12	PI-CB/Au−Pd	BTF	K_2CO_3	–	17	2	79
13[c]	PI-CB/Au−Pd	BTF	K_2CO_3	–	16	30	53
14	PI-CB/Au−Pd	MeOH	none	<1	n.d.	2	90
15	PI-CB/Au−Pd	MeOH	K_2CO_3	47	32	n.d.	18
16[d]	PI-CB/**Au−Pd**	MeOH	K_2CO_3	**78**	7	n.d.	13
17[d]	PI-CB/Au−Pt PI-CB/Au−Pd	MeOH	K_2CO_3	43	27	1	29
18[d]	PI-CB/Au−Pt−Pd	MeOH	K_2CO_3	19	22	1	56
19	PI-CB/Pt−Pd	BTF	none	–	1	10	88

[a] Determined by GC. n.d.: not detected. [b] PI-CB/Au−Pt (2 mol %), 0.25 M, 9 h. [c] Reaction was conducted at 60 °C. [d] MeOH/H_2O = 1/2.

Table 2. Aerobic Oxidation of Various Alcohols Catalyzed by the PI-CB Catalysts



Condition A: PI-CB/Au-Pt (2 mol%), BTF / H_2O (1/1), 0.25 M, 9 h
Condition B: PI-CB/Au-Pt (1 mol%), BTF / H_2O (1/1), 0.125 M, 24 h
Condition C: PI-CB/Au-Pd (1 mol%), MeOH / H_2O (1/2), 0.125 M, 3 eq. K_2CO_3, 24 h
Condition D: PI-CB/Au-Pd (1 mol%), MeOH / H_2O (2/1), 0.125 M, 1 eq. K_2CO_3, 24 h

entry	substrate	conditions	yield[a] (%) ester	acid	aldehyde ketone	alcohol
1		A	-	6	**92**	trace
2		C	**78**	7	n.d.	13
3		A	-	8	**90**	1
4		C	**81**	5	3	10
5		A	-	n.d.	**quant.**	n.d.
6		D	**98**	2	n.d.	n.d.
7		A	-	n.d.	**quant. (96)**	n.d.
8		D	**96 (89)**	3	n.d.	n.d.
9		A	-	n.d.	**94**	4
10		D	**97**	3	n.d.	n.d.
11		B	-	-	**94**	n.d.
12	c-C_5H_9−OH	B	-	-	**quant.**	n.d.
13		B	-	-	**96**	n.d.

[a] Determined by GC. Isolated yields of 1 mmol scale reactions were shown in parentheses. n.d.: not detected.

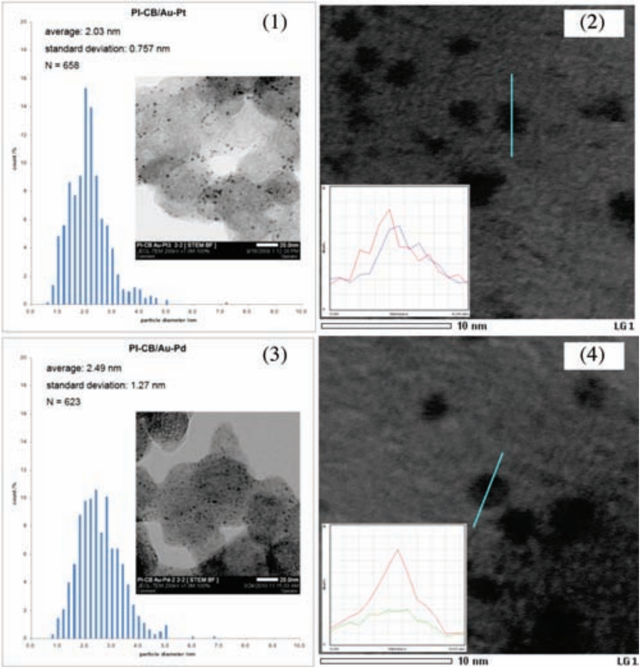


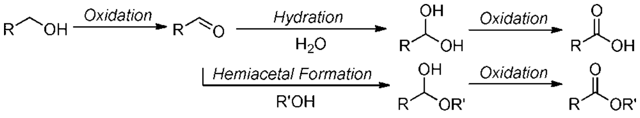
Figure 1. STEM and EDS analyses of PI-CB catalysts: (1) Typical STEM image and size distribution of PI-CB/**Au−Pt**; (2) EDS analysis of a cluster of PI-CB/**Au−Pt** (red: Au, blue: Pt); (3) Typical STEM image and size distribution of PI-CB/**Au−Pd** (Au/Pd = 1:1 by ICP); (4) EDS analysis of a cluster of PI-CB/**Au−Pd** (Au/Pd = 1:1 by ICP) (red, Au; green, Pd).

ceeded smoothly in methanol/water under basic conditions (entries 14,15). After optimizing the reaction conditions, the yield of the ester improved to 78% (entry 16). A PI-CB/**Au−Pt** and PI-CB/**Au−Pd** mixture (entry 17) and trimetallic nanocluster catalyst, PI-CB/**Au−Pt−Pd** (entry 18), were also examined, but the yields of the ester were lower. PI-CB/**Pt−Pd** did not show any catalytic activity for oxidation (entry 19). According to these results, it was found that gold-based bimetallic nanocluster catalysts were suitable for the aerobic oxidation of primary aliphatic alcohols and that the reaction pathways were changed significantly by PI-CB/**Au−Pt** and PI-CB/**Au−Pd** catalysts under these conditions.

Aerobic oxidation by the PI-CB catalysts could be applied to various alcohols. Primary aliphatic alcohols (Table 2, entries 1−4) and primary benzyl alcohols (entries 5−10) were smoothly converted to the corresponding aldehydes (condition A) and esters (condition C or D) in high yields. Substituents on the aromatic ring did not affect the reactivity. Secondary alcohols (entries 11−13) were also oxidized to the corresponding ketones under condition B in excellent yields.

We then conducted scanning transmission electron microscopy (STEM) and energy-dispersive spectroscopy (EDS) analyses of PI-CB/**Au−Pt** and PI-CB/**Au−Pd** (Figure 1), and the following features of the bimetallic catalysts have been discovered. (1) The size of the clusters is almost the same in PI-CB/**Au−Pt** and PI-CB/**Au−Pd** (around 2−2.5 nm). (2) The size distribution is a bit narrower for PI-CB/**Au−Pt** compared with PI-CB/**Au−Pd**. (3) The **Au−Pt** clusters contain an ∼1:1 ratio of gold to platinum in alloy clusters; the ratio is consistent with the metal loading determined by inductively coupled plasma-atomic emission spectrometry (ICP). (4) The **Au−Pd** clusters contain an ∼4:1−3:1 ratio of gold to palladium in alloy clusters although the metal loading determined by ICP is almost 1:1. The difference in the activity and the selectivity between PI-CB/**Au−Pt** and PI-CB/**Au−Pd** catalysts could be explained by the difference in the structure of the clusters. Because of their electronegativities,[18−20] palladium is more positive than gold in the bimetallic clusters. We assume that the oxidation reaction pathways shown in Scheme 1 to carboxylic acids or esters are dependent on hydration or hemiacetal formation from aldehydes. It is likely that in the presence of the **Au−Pd** clusters containing the acidic palladium, hemiacetal formation occurred preferentially.

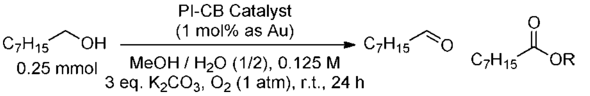
Scheme 1. Two Reaction Pathways for Oxidation of Alcohols



At this stage, it is not clear why the **Au−Pt** clusters contain an ∼1:1 ratio of gold to platinum and the **Au−Pd** clusters contain an ∼4:1−3:1 ratio of gold to palladium in alloy clusters that were formed by our standard preparation method (in both cases 1:1 Au/Pd or 1:1 Au/Pd was combined).

We further prepared PI-CB/**Au−Pd** catalysts with different Au/Pd ratios (Table 3). It was found that in all cases the ratios of gold to palladium in clusters determined by EDS were larger than those determined by ICP. This means that palladium exists not only in clusters but also in the polymer backbone.[16] For catalyst activity, PI-CB/**Au** showed almost no selectivity for the ester or carboxylic acid (entry 1). The PI-CB/**Au−Pd** catalyst with a high Au ratio gave a similar result (entry 2). When a PI-CB/**Au−Pd** catalyst with a 2:1 or 1:1 ratio of Au/Pd was used, the desired ester was obtained in high selectivity (entries 3, 4). On the other hand, when the ratio of palladium was larger (Au/Pd = 1:2 or 1:3), the ester selectivity was significantly decreased (entries 5, 6). PI-CB/**Pd** showed much lower reactivity and gave the carboxylic acid and the aldehyde (entry 7). It should be noted that the PI-CB/**Au−Pd** catalyst with a 1:1 ratio of Au/Pd gave the best ester selectivity.

Table 3. Effect of Ratio of Gold and Palladium for Direct Oxidative Ester Formation



entry	catalyst	Au[a] (mmol/g)	Pd[a] (mmol/g)	ratio in clusters[b]	yield[c] (%) ester	acid	aldehyde	alcohol
1	Au	0.2178	−	−	43	55	n.d.	n.d.
2	Au−Pd(3:1)	0.1522	0.06655	7:1	41	53	4	n.d.
3	Au−Pd(2:1)	0.1802	0.1137	6:1−5:1	62	29	trace	8
4	Au−Pd(1:1)	0.1933	0.2167	4:1−3:1	**78**	7	n.d.	13
5	Au−Pd(1:2)	0.1400	0.2856	2:1−1:1	45	47	5	2
6	Au−Pd(1:3)	0.1070	0.3265	2:1−1:2	46	51	2	n.d.
7	Pd	−	0.2534	−	7	42	50	n.d.

[a] Determined by ICP. [b] Au−Pd ratio in clusters determined by EDS. [c] Detemined by GC. n.d.: not detected.

In summary, we have developed novel carbon-stabilized polymer-incarcerated gold-based bimetallic nanocluster catalysts (PI-CB/**Au−Pt**, PI-CB/**Au−Pd**). The catalysts can be applied for the aerobic oxidation of alcohols and direct oxidative ester formation under very mild conditions, such as atmospheric oxygen and ambient temperatures. While PI-CB/**Au−Pt** catalysts provided aldehydes/carboxylic acids, PI-CB/**Au−Pd** catalysts gave esters. The STEM and EDS analyses suggested formation of **Au−Pt** clusters containing an ∼1:1 ratio of gold to platinum, and the **Au−Pd** clusters contain an ∼4:1−3:1 ratio of gold to palladium in the alloys, respectively. This structure difference is considered to be a key for selective formation of aldehydes/carboxylic acids and esters. Further investigation to clarify the role of carbon, the effect of bimetallic clusters, and the reaction mechanisms is ongoing.

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Supporting Information Available: Experimental details, STEM images, and EDS analyses. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Details are shown in the Supporting Information.
(17) Reactivity depended on the solvent system. See Supporting Information.
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