Gold–platinum bimetallic clusters for aerobic oxidation of alcohols under ambient conditions†

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We have developed gold/platinum alloyed bimetallic cluster catalysts supported on a cross-linked polystyrene derivative, which present much higher activity and selectivity than single metal gold or platinum clusters for aerobic oxidation of alcohols under ambient conditions.

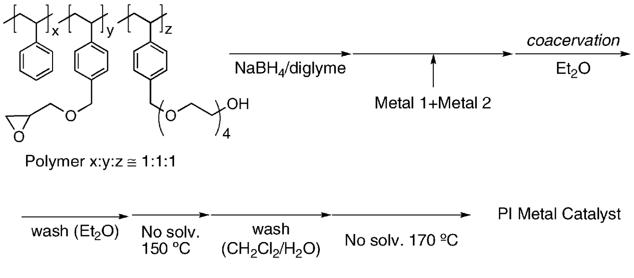
Selective oxidation of alcohols is one of the most important transformations in organic synthesis, the resulting carbonyl compounds possess higher energy and reactivity to allow many kinds of carbon–carbon bond forming and other transforming reactions.[1] Whilst several metal-based oxidizing reagents have been developed, these protocols usually require stoichiometric amounts of metal oxidants, and thus a large amount of waste is formed in many cases.[2,3] In this context, alcohol oxidation using molecular oxygen catalyzed by reusable heterogeneous catalysts under mild conditions is desired.[4] Although several excellent catalysts for aerobic oxidation of alcohols to the corresponding aldehydes or ketones have been disclosed, most of them required heating and addition of bases, which is undesirable from the view point of energy efficiency, minimization of waste and selectivity of products,[5] and to the best of our knowledge, no example of truly efficient aerobic oxidation of alcohols that proceeds *at room temperature without base* using heterogeneous catalysts has been reported.

Recently, we have developed novel gold cluster catalysts, polymer incarcerated gold catalysts (PI Au), for oxidation of a wide range of alcohols at room temperature, that can be recovered by simple procedures without loss of activity.[6] The gold clusters in those catalysts are stabilized by weak interactions between gold clusters and benzene rings of the cross-linking moieties.[7] While they have high activity for oxidation at room temperature, a drawback is that basic conditions were needed, which for example made the selective oxidation of primary alcohols to aldehydes difficult. In light of recent reports where several groups have demonstrated that doping a secondary metal component into metal catalysts is advantageous for the activity and selectivity of various reactions, we decided to combine gold with a second metal.[4,5e,8]

Our catalysts were prepared by adding a solution of gold and a secondary metal salt dropwise to a solution of a polymer and sodium borohydride (Scheme 1). Diethyl ether was added to the mixture to form microcapsules.[9] Cross-linking was conducted by heating the resultant mixture under solvent-free conditions. The solid thus prepared was washed with water and an organic solvent, powdered and heated again to afford PI Au/metal catalysts.

The PI bimetallic clusters were then tested for catalytic activity in the aerobic oxidation of alcohols. When palladium and platinum were used as dopants, the desired ketone was obtained quantitatively (Table 1, entries 1 and 2). It is noted that the oxidation proceeded smoothly *at room temperature in the absence of base*. Nickel and iridium were also promising dopants, while the catalyst prepared with silver showed no activity (entries 3–7). Remarkably, the catalysts prepared from pure gold metal required addition of a base for high productivity (entries 8 and 9), whilst the catalysts prepared from either Pd or Pt metal showed little or no activity regardless of the presence of the base (entries 10–13). The ratio of gold to platinum was varied (entries 14–16) which revealed that a 1 : 1 mixture provided the most active catalyst.

With the optimized conditions in hand, several alcohols were then oxidized under atmospheric oxygen in the presence of 1–3 mol% of the PI Pt/Au catalyst. Aromatic secondary alcohols were oxidized smoothly to afford the corresponding ketones quantitatively (Table 2, entries 1 and 7). Although aliphatic ketones had relatively low reactivity, the desired ketones were also obtained in high yields by prolonging the reaction time (entries 10–12). It has been well documented that the oxidation of primary alcohols to carboxylic acids readily occurs under traditional methodologies. However, to our delight aromatic and allylic primary alcohols, which had both electron-donating and electron-withdrawing groups, were oxidized smoothly under the same conditions as those of secondary alcohols to afford the corresponding aldehydes in excellent



Scheme 1 Preparation of PI metal catalysts.

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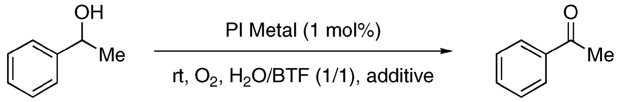
Table 1 Activity of PI metal catalysts



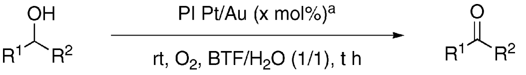
Entry	Metal 1	Metal 2	Metal 1/Metal 2	Additive	Yield for 12 h (%)	Yield for 3 h (%)
1	$AuClPPh_3$[a]	$Pd(OAc)_2$	1/1	—	>99	72
2	$AuClPPh_3$[a]	Na_2PtCl_6	1/1	—	>99	95
3	$AuClPPh_3$[a]	$Ni(OAc)_2$	1/1	—	72[b]	—
4	$AuClPPh_3$[a]	$NiCl_2(PPh_3)_2$	1/1	—	72[b]	—
5	$AuClPPh_3$[a]	$Ni(PPh_3)_4$	1/1	—	57[b]	—
6	$AuClPPh_3$[a]	AgOCOPh	1/1	—	0[b]	—
7	$AuClPPh_3$[a]	$HIr(PPh_3)_3$	1/1	—	51[b]	—
8	$AuClPPh_3$[a]	None	—	K_2CO_3 (3 eq.)	>99	95
9	$AuClPPh_3$[a]	None	—	—	49	18
10	$Pd(OAc)_2$	None	—	K_2CO_3 (3 eq.)	0	—
11	$Pd(OAc)_2$	None	—	—	0	—
12	$Pd(OAc)_2$	None	—	K_2CO_3 (3 eq.)	11	—
13	Na_2PtCl_6	None	—	—	5	1
14	$AuClPPh_3$[a]	Na_2PtCl_6	1/0.25	—	—	74
15	$AuClPPh_3$[a]	Na_2PtCl_6	1/0.5	—	—	82
16	$AuClPPh_3$[a]	Na_2PtCl_6	0.5/1	—	—	88

[a] Catalyst loading based on Au. [b] Reaction time was 24 h.

yields without formation of carboxylic acids (entries 2–6, 8 and 9). These results are remarkable owing to the fact that the previously reported PI Au catalyst required basic conditions for obtaining high activity, resulting in the formation of carboxylic acids and esters by over-oxidation. Alcohols including heteroatoms such as sulfur and nitrogen, which are known to strongly coordinate to gold nanoparticles, could also be oxidized smoothly to give the desired ketones in high yields (entries 13 and 14).

Furthermore, it was found that the aerobic oxidations also proceeded smoothly in water without organic solvents under exposed to air (Scheme 1). Notably, this is the first example of aerobic oxidation of alcohols at room temperature under base-free conditions in water using heterogeneous catalysts.

Table 2 Substrate scope of PI Pt/Au catalyzed aerobic oxidation of alcohols[a]



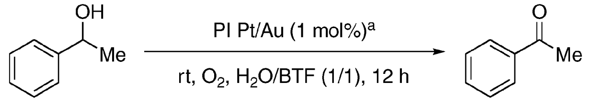
Entry	Product	x	Time/h	Yield[b] (%)
1	Acetophenone	1	5	>99
2	Benzaldehyde	1	5	93
3	*p*-Tolualdehyde	1	5	88
4	*o*-Tolualdehyde	1	5	84
5	*p*-Anisaldehyde	1	5	90
6	*p*-Chlorobenzaldehyde	2	5	86
7	2-Acetonaphthone	1	18	>99
8	1-Naphthalaldehyde	1	18	93
9	Cinnamaldehyde	1	36	94
10	4-Phenyl-2-butanone	3	72	>99
11	2-Butanone	1	8	67
12	Cyclopentanone	2	115	90
13	2-Acetylthiophene	2	96	94
14	2-Acetylpyridine	1.5	48	80

[a] Catalyst loading based on Au. Ratio of Pt to Au is 1 : 1. [b] Determined by GC analysis.

The recovery and reuse of the developed PI Pt/Au catalyst was examined (Table 3). It was found that the activity of the catalyst was maintained by treatment of the recovered catalyst with hydrogen under heating conditions. It should be noted that this recovery method enabled us to reuse the catalyst at least 6 times without loss of activity.

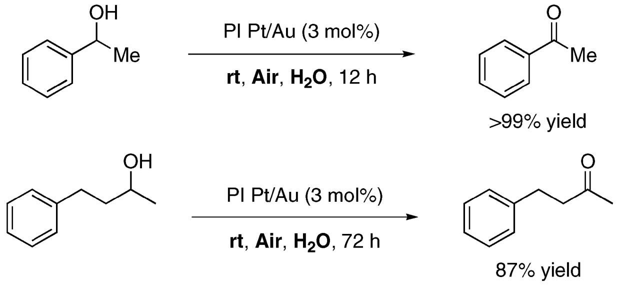
The catalysts were analyzed by scanning transmission electron microscopy (STEM) and energy-dispersive X-ray spectroscopy (EDS) to confirm size and composition of clusters.[10] PI Pd/Au and PI Pt/Au contained clusters of 1.5–5 nm, each cluster consisted of both metals. This may suggest that the alloyed clusters were formed by the simultaneous reduction of the metal salts and that they are the active catalysts in this system. Although extensive mechanistic study has not yet been conducted, the α-hydrogen abstraction of an alcohol may be involved in the rate determining step based on the isotope kinetic study ($k_H/k_D = 3.0$).[10,11] In addition, water was found to be indispensable for the reaction progress,[10] which prompted us to suppose that water helped the abstraction of the α-hydrogen as a hydrogen transporter under hydrophobic polystyrene surroundings.[12] Indeed, the oxidation proceeded smoothly in water without organic solvents (Scheme 2).

Table 3 Recovery and reuse of PI Pt/Au catalyst[a]



1st (%)	2nd (%)	3rd (%)	4th (%)	5th (%)	6th (%)
>99	>99	>99	>99	>99	>99

[a] Catalyst loading based on Au. Ratio of Pt to Au is 1 : 1. Collected catalyst was heated at 170 °C for 5 h under hydrogen atmosphere without solvent before next use.



Scheme 2 Aerobic oxidation of alcohols in water open to air at room temperature.

In conclusion, we have developed novel gold–platinum bimetallic cluster catalysts, which show high activity with good substrate generality *at room temperature without base* in aqueous media. Although catalytic turnover number and turnover frequency are not the best compared to those of previously reported catalysts, it should be noted that this is the first example of oxidation of alcohols *at room temperature without base* using heterogeneous catalysts.[13] Significantly the selective oxidation of primary alcohols to the corresponding aldehydes, which is difficult using pure gold catalysts, has been realized.[5f,6] The catalyst was recovered and reused several times without loss of activity by simple operations. Further investigations to apply these catalysts to other oxidation as well as to clarify the precise mechanism of this oxidation process are now in progress.

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12 In course of oxidation reactions, both hydrogens are transferred as protons mediated by a solvent, but to maintain neutrality two electrons are transferred through metal clusters. This type of mechanism was proposed for aerobic oxidations catalyzed by metalloenzymes which also work at body temperature open to atmosphere under neutral conditions in aqueous solutions. See: G. A. Hamilton, *Adv. Enzymol.*, 1969, **32**, 55.

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