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Aerobic Oxidation of Alcohols under Mild Conditions Catalyzed by Novel Polymer-Incarcerated, Carbon-Stabilized Gold Nanoclusters

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Dedicated to Professor Ryoji Noyori on the occasion of his 70th birthday.

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Abstract: Polymer-incarcerated, carbon-stabilized gold nanoclusters were found to be highly active in heterogeneous catalysis for the oxidation of secondary alcohols using molecular oxygen in aqueous medium. After optimization of catalyst preparation methods, highly loaded and highly effective catalysts were obtained, and a broad range of secondary alcohols could be oxidized by using these catalysts under mild conditions. The catalysts could be recovered and reused several times without significant loss of activity. Moreover, kinetics of the oxidation reaction with (\pm) -1-phenylethanol was investigated.

Keywords: gold; nanoparticles; oxidation; water

The selective oxidation of alcohols is an important transformation in synthetic organic chemistry.^[1] While conventional oxidation methods often require stoichiometric amounts of metallic oxidants which induce a large quantity of by-products, a current challenge is the use of molecular oxygen with a heterogeneous reusable catalyst related to green sustainable chemistry. Recently, we reported the effective oxidation of a wide range of alcohols using polymer-incarcerated gold(0) catalysts (PI-Au).^[2,3] In these catalysts, gold nanoclusters are stabilized by weak interactions with a polystyrene-based matrix, and cross-linking of the polymer matrix prevents the metal from leaching to the reaction medium (incarceration).^[4] In addition, this structure allows simple and efficient recovery and reuse of the catalyst without significant loss of activity. However, an increase of gold loading amounts was hampered by aggregation during the incarceration step, which is well-known to decrease the catalytic activity of gold-based catalysts significantly.^[5] In order to circumvent this drawback, we incorporated carbon black (CB),^[6] whose partially graphitic structure^[7] was expected to enhance the stability of gold nanoclusters during the preparation step. In addition, its high specific surface area might allow a high dispersion of the gold nanoclusters on the support. We describe here preparation and characterization of new gold nanocluster catalysts stabilized by both a polymer and carbon black (PI/CB-Au). The oxidation of various alcohols by molecular oxygen catalyzed by PI/CB-Au is also reported.

Two synthetic procedures for the preparation of PI/ CB-Au were evaluated. The first procedure leading to PI/CB-Au **1a** (Scheme 1) involves preliminary loading of gold onto carbon black (CB), isolation, and finally combination with polymer **2**. The second procedure is a one-pot synthesis of PI/CB-Au **1b** (Scheme 2). It involves *in situ* reduction of the gold precursor, Au-(PPh₃)Cl, by NaBH₄ in the presence of both polymer **2** and CB. In both cases, the final step is the crosslinking of the polymer upon heating without solvent. For comparison, carbon black-supported gold nanocluster (CB-Au) was also synthesized (Scheme 3).

The catalytic activities of the prepared catalysts in the aerobic oxidation of alcohols were assessed using (\pm) -1-phenylethanol as a model substrate (Scheme 4). The yields and the characteristics of each catalyst are summarized in Table 1. Despite the relatively small mean diameters of gold nanoclusters, CB-Au was inactive (Table 1, entry 1). This is presumably due to

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Scheme 3. Synthesis of CB-Au.

$$\begin{array}{c} OH \\ Ph \\ \hline Me \\ Me \end{array} \xrightarrow[O_2 (1 \text{ atm}), 30 \ ^\circ\text{C}, 3 \text{ h} \end{array} \xrightarrow[O_2 (1 \text{ atm}), 30 \ ^\circ\text{C}, 3 \text{ h} \end{array} \xrightarrow[O_2 (1 \text{ atm}), 30 \ ^\circ\text{C}, 3 \text{ h} \end{array} \xrightarrow[O_2 (1 \text{ atm}), 30 \ ^\circ\text{C}, 3 \text{ h} } O$$

Scheme 4. Standard procedure for assessment of the catalytic activity of CB-Au and PI/CB-Au.

the highly hydrophobic nature of carbon black (CB), which may not be suitable for the oxidation. The procedure involving the isolation leading to PI/CB-Au **1a** resulted in aggregation of gold nanoclusters upon heating, which led to low catalytic activity (Scheme 1 and Table 1, entry 2). On the other hand, the one-pot procedure leading to PI/CB-Au **1b** proved to be successful (Scheme 2 and Table 2, entry 3). The diameter of the gold nanoclusters was small and remained constant even after heating. The final loading amount was 0.25 mmol g^{-1} , which implied that the entire gold precursor was reduced and loaded onto the final material without any leaching. Moreover, PI/CB-Au **1b** was shown to be highly efficient in the oxidation of (\pm) -1-phenylethanol, affording acetophenone quantitatively.^[8,9] Using the standard procedure illustrated in Scheme 4, an increase of the gold loading amount

Table 1. Characterization of catalysts CB-Au and PI/CB-Au 1a and 1b.

Entry	Catalyst	MC/CB-Au	PI	Oxidation	
	,	Diameter [nm]	Diameter [nm]	Loading $[mmolg]^{-1}$	Yield [%]
1 ^[a]	CB-Au	1–2	_[b]	0.43	0
2 ^[c]	PI/CB-Au 1a	3.8	10.9	0.17	9
3 ^[c]	PI/CB-Au 1b	2.7	2.9	0.25	>99

^[a] Targeted Au loading amount is 0.51 mmol g^{-1} .

^[b] CB-Au was not heated at 150 °C.

^[c] Targeted Au loading amount is 0.25 mmol g^{-1} .

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Entry	Catalyst	Targeted loading [mmolg] ⁻¹	MC/CB-Au Diameter [nm]	PI/0 Diameter [nm]	CB-Au ^[a] Loading [mmolg] ⁻¹	Oxidation Yield [%]
1	1b	0.25	2.7	2.9	0.25	>99
2	1c	0.50	2.7	5.1	0.40	90
3	1d	0.75	2.2	3.8	0.52	91
4	1e	1.00	1.8	3.8	0.60	86

Table 2. Increase of the loading amount for PI/CB-Au.^[a]

from 0.25 mmol g^{-1} (5 wt%) to 1.00 mmol g^{-1} (20 wt%) was investigated (Table 2). Although the incorporation ratio decreased when the loading amounts were increased, the loading amount of 0.60 mmolg⁻¹could be reached and successfully employed in the aerobic oxidation of (\pm) -1-phenylethanol with a slight loss of catalytic activity.

Several secondary alcohols were then oxidized in the presence of 1 mol% of 1b (Table 3). Aromatic and allylic alcohols were oxidized smoothly to afford the corresponding ketones in quantitative yields (Table 4, entries 1-7). Secondary aliphatic alcohols proved to be less reactive, thus needing longer reaction times (entries 8-12). Finally, as for secondary alcohols bearing heteroatoms, 2-thiophenylethanol reacted smoothly to afford the corresponding ketone (entry 13), although 2-pyridylethanol proved to be less reactive (entry 14). It should be noted that no leaching of the metal was observed in all entries.

The PI/CB-Au catalyst could be recovered by simple filtration and reused without significant loss of catalytic activity (Table 4). No gold leaching was detected during the investigation.

Time [h]

Yield^[a] [%]

Table 3. [a] General synthetic procedure is depicted in Scheme 2. Table 3Oxidation of various secondary alcohols catalvzed by PI/CB-Au 1b

OH	PI/CB-Au 1	b (1 mol%)	0		он		
	R ² K ₂ CO ₃ (3 equiv.), O ₂ (1 atm),	C ₆ H ₅ CF ₃ /H ₂ O 1:1, 30 °C, time	$R^1 R^2$	7		24	>99
Entry	Substrate	Time [h]	Yield ^[a] [%]	0		10	00
1	OH Me	3	> 99	8	MeO,	48	99
2	СТ ОН	3	>99	9	OMe	48	86
3	OH	6	>99	10		48	82
	MeO' ~ OH			11	—он	48	57
4	MeO	24	>99	12	ОН	48	62
5	OH	48	> 99	13	S OH	48	99
6	CI OH	48	95	14	() OH	48	58
				^[a] Det	termined by GC analysis.		

Table 3. (Continued)

Substrate

Entry

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Table 4. Recovery and reuse of PI/CB-Au 1b.

ОН	PI/		0 II		
Ph Me K ₂ CO ₃ (3 equiv.), C ₆ H ₅ CF ₃ /H ₂ O 1:1, Ph O ₂ (1 atm), 30 °C, 15 h					
	Run 1	Run 2	Run 3	Run 4	Run 5
Yield [%] Au leaching	>99 no	>99 no	>99 no	>99 no	>99 no

For obtaining a mechanistic insight, the kinetic study of the oxidation of (\pm) -1-phenylethanol was performed using PI/CB-Au **1b** (0.25 mmol g⁻¹). The observed straight curve (Figure 1) is characteristic of a zero-order kinetics, which suggests either that the uptake of O₂ into the reaction medium is a rate-limiting step, or that the reaction mainly occurs in a spatially limited hydrophobic environment, where the concentration of the substrate is almost constant throughout the reaction.

In summary, we have developed the aerobic oxidation of alcohols catalyzed by novel polymer-incarcerated, carbon-stabilized gold nanoclusters. The inclusion of carbon black (CB) to the composition of the catalyst, together with an amphiphilic copolymer, enhances the stability of gold nanoclusters probably *via* synergistic π - π interactions between the three components, which enables us to increase the metal loading amount up to 0.60 mmol g⁻¹. Secondary alcohols could be oxidized smoothly to afford analytically pure products in excellent yields after simple phase separation without further purification. The catalyst could be recovered and reused several times without significant loss of activity or metal leaching in the reaction medium. Further investigations to clarify the precise



Figure 1. Kinetics of the oxidation reaction of (\pm) -1-phenylethanol with PI/CB-Au 1b.

mechanism of this reaction and the exact role of CB are in progress.

Experimental Section

Preparation of PI/CB-Au 1b

To a solution of copolymer 2 (2.1 g) in diglyme (32 mL) at 0°C were successively added carbon black (CB, 499.6 mg), NaBH₄ (43.1 mg in 8 mL diglyme, 1.14 mmol) and AuPPh₃Cl (139 mg in 20 mL diglyme, 0.28 mmol). After stirring for 3 h from 0°C to room temperature, diethyl ether (120 mL) was added dropwise while stirring. The resulting MC/CB-Au was filtered, washed several times with diethyl ether and dried under vacuum for 24 h. The cross-linking step was performed at 150°C for 3 h without solvent to afford PI/CB-Au **1b**.

Typical Procedure for the Oxidation of Alcohols

(±)-1-Phenylethanol (30.5 mg, 0.25 mmol), K_2CO_3 (103.7 mg, 0.75 mmol), PI/CB-Au **1b** (10 mg, 0.0025 mmol), water (1.5 mL) and benzotrifluoride (1.5 mL) were combined in a round-bottomed flask. The mixture was stirred for 3 h under an O_2 atmosphere at 30 °C. After the reaction, the catalyst was filtered and washed with diethyl ether and water. The aqueous layer was extracted with diethyl ether. The yield was determined by GC analysis using anisole as an internal standard. The leaching of gold in both aqueous and organic layers was checked by ICP analysis.

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- [9] A preliminary kinetic study has shown that the initial reaction rate using PI/CB Au **1b** was 1.38 times faster than that using PI Au^[2] in the oxidation of (\pm) -1-phenylethanol.