Tetrahedron 65 (2009) 1461–1466

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Recyclable gold nanoparticle catalyst for the aerobic alcohol oxidation and C–C bond forming reaction between primary alcohols and ketones under ambient conditions

Sungjin Kim [a], Sang Won Bae [b], Jae Sung Lee [b], Jaiwook Park [a,*]

[a] Department of Chemistry, Pohang University of Science and Technology (POSTECH), San 31 Hyojadong, Pohang, Kyungbuk 790-784, Republic of Korea
[b] Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), San 31 Hyojadong, Pohang, Kyungbuk 790-784, Republic of Korea

ARTICLE INFO

Article history:
Received 2 October 2008
Received in revised form 3 December 2008
Accepted 3 December 2008
Available online 9 December 2008

Keywords:
Heterogeneous catalyst
Gold nanoparticle
Aerobic alcohol oxidation
Room temperature
C–C bond formation

ABSTRACT

A recyclable gold catalyst is synthesized from readily available reagents by immobilizing gold nanoparticles in aluminum oxyhydroxide support through a simple sol–gel method. The catalyst showed the high activity even at room temperature in the aerobic oxidation of various alcohols and in the coupling reaction between primary alcohols and ketones.

1. Introduction

The selective oxidation of alcohols is one of the most important reactions in the organic synthesis.[1] Generally, several metal-based oxidants and halooxoacids have been used for alcohol oxidation.[2] Although these reagents are quite general in scope, they cannot be appropriate in green chemistry point of view, because the oxidation requires them in stoichiometric amount and produces problematic byproducts. Hence, the development of efficient and environment-friendly catalysts for alcohol oxidation, particularly that of aerobic oxidation catalysts, is ongoing research interest.[3] For aerobic oxidation of alcohols, there are noticeable heterogeneous catalysts such as the hydroxyapatite (HAP) bound RuHAP and PdHAP,[4,5] as well as Ru/Al_2O_3.[6] However, they often require high reaction temperatures, which are not applicable to thermally unstable compounds. Since Haruta et al. reported CO oxidation at low temperature,[7] several heterogeneous Au-based catalysts such as Au/CeO_2,[8] $Au\text{-}Pd/TiO_2$,[9] and $Au/Ga_3Al_3O_9$[10] have been developed. However, they also needed high reaction temperatures for alcohol oxidation. Furthermore, in general, synthetic procedures for these gold catalysts are not easy, which require pH adjustment, concentration control, strong reductant, and/or calcination at high temperature.[8–11] Recently, Kobayashi et al. have developed a polymer incarcerated gold catalyst (PI Au),[12] which shows very high activity and selectivity in the aerobic oxidation of alcohols even at room temperature. However, multistep procedure and strong reductant are still required for preparing the gold catalyst. We herein report a recyclable gold catalyst that can be made from readily available reagents by a one-pot procedure without pre- and post-treatments and strong reductant. The catalyst is highly active for the aerobic oxidation of a wide range of alcohols at room temperature. Furthermore, the catalyst can be used for C–C bond forming reaction between primary alcohols and ketones under ambient conditions.

2. Results and discussion

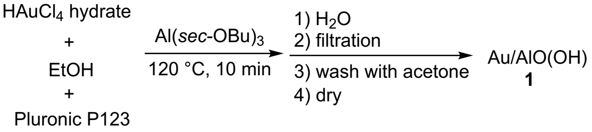
2.1. Synthesis of gold nanoparticle catalyst

The catalyst was made from a solution of hydrogen tetrachloroaurate hydrate, aluminum tri-*sec*-butoxide, Pluronic P123 in ethanol through a procedure similar to those reported previously by us for other metal nanoparticle catalysts (Scheme 1).[13,14] The solution was heated at 120 °C for 10 min to give greenish-brown suspension containing gold nanoparticles.[15] Here the ethanol served as both solvent and reductant. Water was added into the suspension to form a red gel of aluminum oxyhydroxide. The resulting gel was washed with acetone, filtered, and dried at 120 °C

---

[*] Corresponding author. Tel.: +82 54 279 2117; fax: +82 54 279 3399.
E-mail address: pjw@postech.ac.kr (J. Park).

0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.12.005



Scheme 1. Preparation of Au/AlO(OH) (**1**).

for 2 h to give reddish powder (Au/AlO(OH), (**1**)). The reddish powder was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photo-electron spectroscopy (XPS), inductively coupled plasma (ICP), and nitrogen isotherm experiment. Gold nanoparticles of 5–13 nm size and aluminum oxyhydroxide fibers were observed in the TEM images (Fig. 1). By the XRD and XPS data, we confirmed that the nanoparticles are metallic gold.[16] ICP results implicated that almost all of the gold source is entrapped in the support.

Table 1
Oxidation of 1-phenylethanol using gold catalysts

Entry	Catalyst (mol %)	Base	Solvent	Oxidant	T (°C)	Time (h)	Yield[a] (%)
1	1 (0.30)	Cs_2CO_3	Toluene	O_2	25	3	>99
2	1 (0.30)	Cs_2CO_3	Toluene	Air	25	6	>99
3	1 (0.30)	K_3PO_4	Toluene	O_2	25	3	32
4	1 (0.30)	K_2CO_3	Toluene	O_2	25	3	2
5	1 (0.30)	Et_3N	Toluene	O_2	25	3	3
6	1 (0.30)	Cs_2CO_3	Toluene	O_2	25	2	84
7	1 (0.30)	Cs_2CO_3	CH_2Cl_2	O_2	25	2	70
8	1 (0.30)	Cs_2CO_3	Hexane	O_2	25	2	60
9	1 (0.30)	Cs_2CO_3	EtOAc	O_2	25	2	40
10[b]	Au/CeO_2 (0.66)	Na_2CO_3	H_2O	O_2	50	5	51
11[c]	PI Au (1.0)	K_2CO_3	TFT/H_2O	O_2	25	5	>99
12[d]	$Au/Ga_3Al_3O_9$ (3.0)	—	Toluene	Air	25	40	>99

[a] Determined by GC.
[b] Ref. 8.
[c] Ref. 12.
[d] Ref. 10.

2.2. Aerobic oxidation of alcohols at room temperature

We tested the catalytic activity of **1** in the aerobic oxidation of 1-phenylethanol. Acetophenone was obtained in quantitative yield in 3 h at room temperature under O_2 balloon by using only 0.30 mol % of Au in the presence of 3 equiv of cesium carbonate (Table 1). Even in the air, the oxidation was completed in 6 h. Cesium carbonate was clearly more efficient than potassium phosphate, potassium carbonate, or triethylamine (entries 1–5).[17] The oxidation in toluene was faster than that in dichloromethane, hexane, or ethyl acetate (entries 6–9). Notably, our catalyst **1** shows an activity higher than those of reported heterogeneous Au catalysts in the aerobic oxidation, possibly due to its highly porous structure of the support (630 m^2/g) and good dispersion of the gold nanoparticles.[18] In the case of Au/CeO_2, acetophenone is obtained from 1-phenylethanol only in 51% even at 50 °C after 5 h by using 0.66 mol % of Au.[8] PI Au reported by Kobayashi et al. can oxidize alcohols at room temperature, but the oxidation of 1-phenylethanol takes 5 h even with 1 mol % of Au under oxygen atmosphere in a mixed solvent of trifluorotoluene and water.[12] Although $Au/Ga_3Al_3O_9$ is a noticeable catalyst for the aerobic oxidation of alcohols at room temperature without base,[10] the activity is far lower than that of our catalyst system under the ambient conditions.

The scope of our catalyst system was investigated for the oxidation of other benzylic alcohols and aliphatic alcohols under oxygen balloon at room temperature (Table 2). Secondary benzylic alcohols were oxidized with 0.30 mol % of Au successfully (entries 1–7). The electronic effect of the substituent of phenyl ring was not significant (entries 1–3). Cyclopropyl group survived during

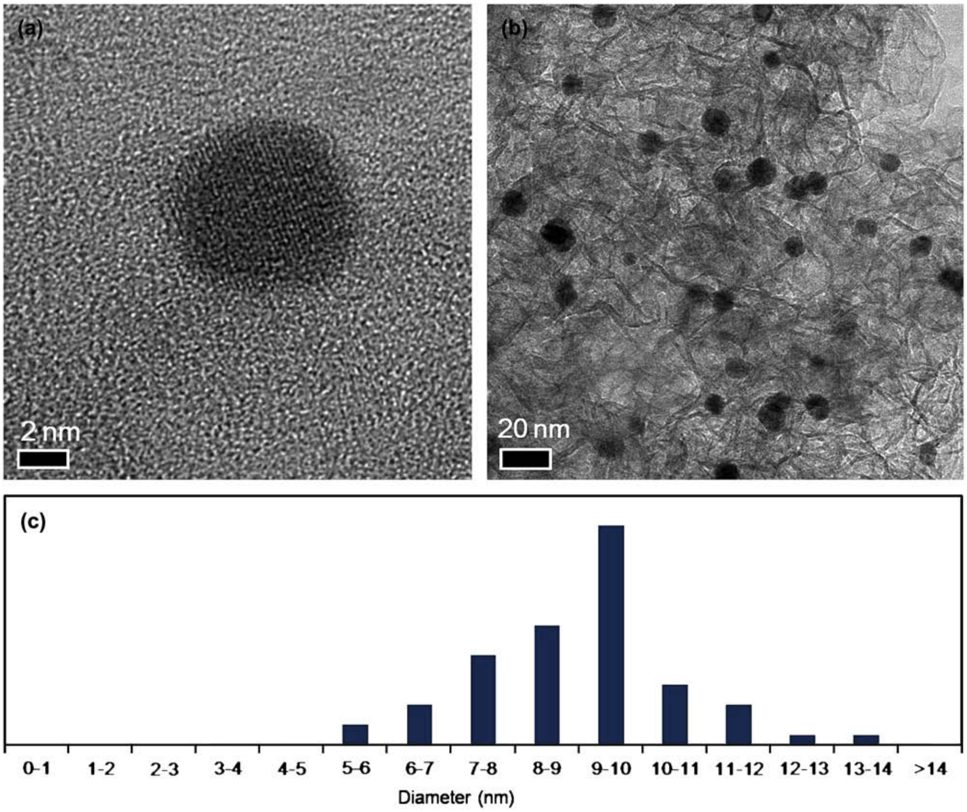
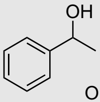
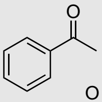
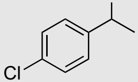
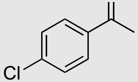
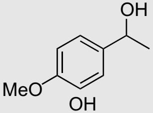
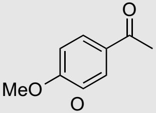
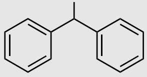
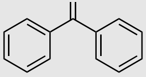
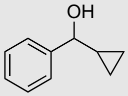
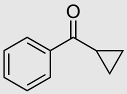
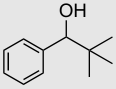
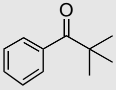
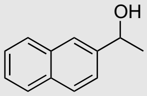
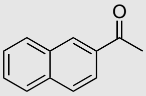
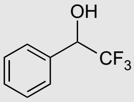
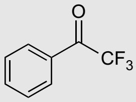
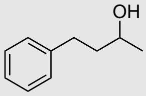
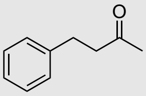
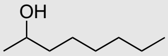
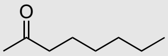
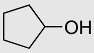
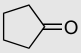
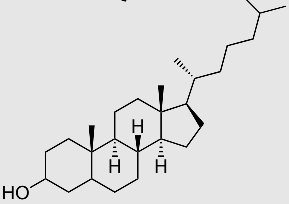
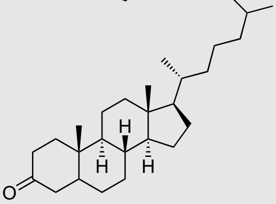
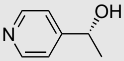
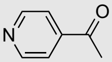
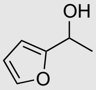
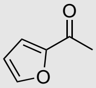
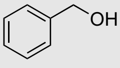
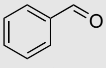
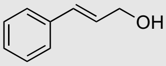
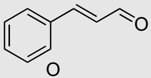
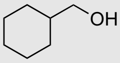
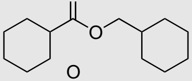
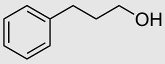
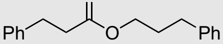


Figure 1. TEM images of **1**: (a) high resolution (2 nm bar scale), (b) low resolution (20 nm bar scale), (c) size distribution of Au nanoparticles.

Table 2

Oxidation of various alcohols using **1** at room temperature[a]

Entry	Substrate	Product	Time (h)	Yield (%)
1			3	>99[b]
2			4	>99[b] 99[c]
3			5	>99[b] 93[c]
4			4	>99[b] 99[c]
5			7	>99[b] 96[c]
6			25	>99[b] 92[c]
7			6	>99[b] 96[c]
8			24	Trace[g]
9			8	>99[b,d] 95[c,d]
10			19	>99[b,d]
11			7	99[b,d]
12			72	83[c,g]
13			24	25[b,g]
14			24	50[b,g]
15			9	86[b,e]
16			6	77[c,f]
17			24	77[c,g]
18			24	72[c,h]

[a] The reaction was performed on 0.50 mmol of substrate dissolved in 2.0 mL of toluene with 0.30 mol % Au and Cs_2CO_3 (1.5 mmol) at 25 °C under O_2 balloon.

[b] Determined by GC.

[c] Isolation yield.

[d] % of Au (1.0 mol %) was used.

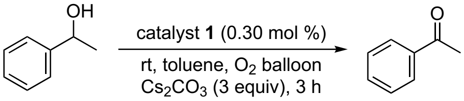
[e] Benzyl benzoate was formed in 14%.

[f] Cinnamyl cinnamate was formed in 23%.

[g] Au (3 mol %) was used.

[h] Au (5 mol %) was used.

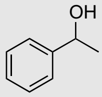
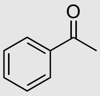
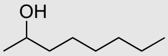
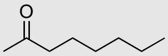
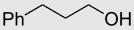
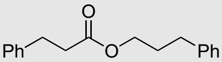
Table 3
Recycling test for **1**[a]



Reuse	First	Second	Third	Fourth	Fifth
Yield[b] (%)	>99	>99	>99	>99	>99

[a] After washing the catalyst with toluene (3 mL) three times, 1.5 equiv of Cs_2CO_3 was added for each run.
[b] Determined by GC.

Table 4
Scale-up experiments[a]

Entry	Substrate	Product	Time (h)	Yield (%)
1			5	>99[b]
2[d]			24	97[b]
3[e]			30	75[c]

[a] The reaction was performed on 10 mmol of substrate dissolved in 30 mL of toluene with 0.30 mol % Au and Cs_2CO_3 (3 equiv) at 25 °C under O_2 balloon.
[b] Determined by GC.
[c] Isolation yield.
[d] Au (1.0 mol %) was used.
[e] Au (5.0 mol %) was used.

oxidation (entry 5). *tert*-Butyl group slowed down the oxidation rate significantly (entry 6). Trifluoromethyl group inhibited the oxidation (entry 8). The oxidation of aliphatic alcohols was much slower than that of benzylic alcohols (entries 9–12). However, the oxidation can be accelerated by increasing the amount of **1**. Cholestanone was obtained in 83% yield from cholestanol in 72 h using 3 mol % of Au (entry 12). Alcohols containing heteroaromatic rings were not successful substrates of our catalyst system (entries 13 and 14). The oxidation of primary alcohols did not stop at the stage of aldehyde. Benzaldehyde was produced in 86% yield with forming benzyl benzoate in 14% yield (entry 15). The ester formation was also the side reaction in the oxidation of cinnamyl alcohol (entry 16). Meanwhile, ester formation was the major reaction in the oxidation of primary aliphatic alcohols (entries 17–18). The corresponding esters were formed in 77% and 72% in the oxidation of cyclohexylmethanol and in that of 3-phenylpropan-1-ol, respectively. The ester formation from the oxidation of primary alcohols by gold catalysts can be explained by the following mechanism.[19] Aldehyde formed initially is reacted with alcohol to produce hemiacetal, which is further oxidized into ester.

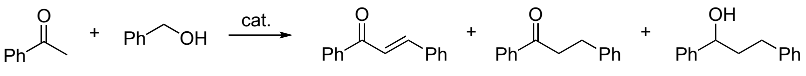
2.3. Recycling test and scale-up experiments

We tested the recyclability of **1** in the oxidation 1-phenylethanol under the conditions described in Table 2. After each run, the resulting solution was separated by decantation, and 1.5 equiv of Cs_2CO_3 was added for next run. Even in the fifth use loss of the catalytic activity was not observed (Table 3). Leached metal species was not detected by inductively coupled plasma analysis for the solution phase in the recycling test, whereas the TEM images of the recovered catalyst showed that the average size of gold nanoparticles slightly increases during the test.[16] Scale-up experiments were carried out for 1-phenylethanol, 2-octanol, and 3-phenylpropan-1-ol in 10 mmol scale (Table 4). The reaction efficiencies were almost same as those observed in 0.5 mmol scale reactions.

2.4. Coupling of acetophenone with benzyl alcohol under ambient conditions

We tested the potency of our catalyst system for the coupling of ketones with primary alcohols (Table 5). Indeed, chalcone was produced as the major product in 54% yield from the reaction of acetophenone with benzyl alcohol under the conditions for the oxidation of benzyl alcohol in Table 2 (entry 1). Chalcone was obtained in 94% when 1 mol % of Au was used (entry 2). Cesium carbonate was a more effective base than potassium phosphate or potassium carbonate (entries 3 and 4). Our palladium catalyst, which is composed of palladium nanoparticles embedded in aluminum oxyhydroxide, also has been used in the coupling of ketones with primary alcohols to produce α,β-unsaturated ketones, but the reaction temperature should be higher than 80 °C to complete the reaction within 20 h (entry 5).[20] An homogeneous iridium complex, $[IrCl(cod)]_2$, can be used for the catalytic α-alkylation of ketones in the presence of phosphine ligands at 100 °C. However, the major product is ketone formed by the hydrogenation of the intermediate α,β-unsaturated ketone under the conditions using excess primary alcohol (entry 6).[21a] As heterogeneous catalysts for the α-alkylation of ketones, a polymeric palladium catalyst and a ruthenium catalyst have been reported. The palladium catalyst is active under

Table 5
Coupling with acetophenone and benzyl alcohol using **1**

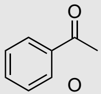
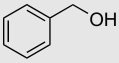
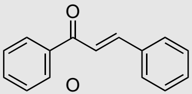
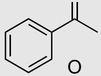
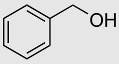
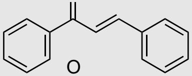
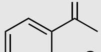
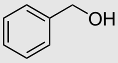
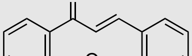
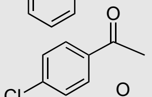
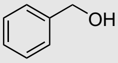
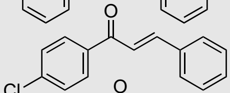
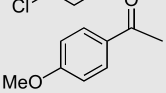
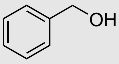
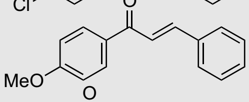
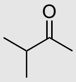
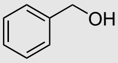
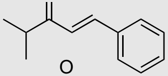
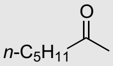
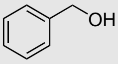
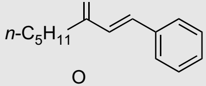
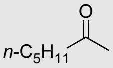
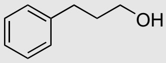
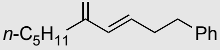
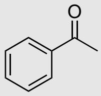
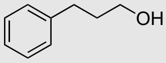
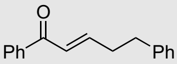


2 **3** **4**

Entry	Catalyst (mol %)	Base (equiv)	*T* (°C)	Time (h)	Conv.[a] (%)	Product yield[b] (%)		
						2	**3**	**4**
1	**1** (0.3)	Cs_2CO_3 (3)	25	24	54	54	—	—
2	**1** (1.0)	Cs_2CO_3 (3)	25	24	94	94	—	—
3	**1** (1.0)	K_3PO_4 (3)	25	24	88	88	—	—
4	**1** (1.0)	K_2CO_3 (3)	25	24	20	20	—	—
5	Pd/AlO(OH) (0.20)	K_3PO_4 (3)	80	20	95	95	—	—
6	$[IrCl(cod)]_2$ (1.0)	KOH (0.1)	100	4	—	—	86	10
7	Pd/viologen polymer (5.0)	$Ba(OH)_2$ (1)	100	24	—	—	91	—
8	Ru/HT (0.75)	None	180	20	85	—	85	—

[a] Conversion of acetophenone.
[b] Determined by GC.

Table 6
Coupling with various ketones and alcohols using of 1[a]

Entry	Ketone	Alcohol	Time (h)	Product	Yield[b] (%)
1			24		90
2[c]			24		85
3[d]			24		82
4			24		86
5			24		70
6[e]			30		79
7[e]			30		78
8[e–g]			30		Trace
9[e–g]			30		Trace

[a] The reaction was performed on 1.0 mmol of ketone and 3.0 mmol of alcohol dissolved in 3.0 mL of toluene with 1.0 mol % Au and Cs_2CO_3 (3 equiv) at 25 °C under O_2 balloon.
[b] Isolation yield.
[c] Second reuse.
[d] Third reuse.
[e] Alcohol (4.0 mmol) was used.
[f] Au (3.0 mol %) was used.
[g] In GC the ratio of 3-phenylpropanol and 3-phenylpropyl 3-phenylpropanoate was about 3:1.

atmospheric conditions without organic solvent although the activity is lower than the iridium catalyst (entry 7).[21b] The heterogeneous ruthenium catalyst dose not require base, but the reaction temperature should be high (180 °C) (entry 8).[21c]

2.5. Coupling with various ketones and alcohols under ambient conditions

On the basis of the results obtained from the coupling of acetophenone and benzyl alcohol, we tested the reaction with various ketones and alcohols (Table 6). Under the conditions similar to the entry 2 of Table 5, α,β-unsaturated ketones were obtained as the major products in 70–90% yields. Our gold catalyst was reusable although additional cesium carbonate was required in reuse (entries 1–3). Acetophenone derivatives such as 4′-chloroacetophenone and 4′-methoxyacetophenone were also coupled with benzyl alcohol successfully (entries 4 and 5). The coupling reaction of aliphatic ketone with benzyl alcohol was slower than those of aromatic ketones (entries 6 and 7). Increasing the amount of benzyl alcohol to 4 equiv produced the corresponding α,β-unsaturated ketones in about 80% after 30 h. Meanwhile, the reaction of aliphatic ketone (or aromatic ketone) with aliphatic primary alcohol did not afford the corresponding coupling product in significant yield (entries 8 and 9).

3. Conclusion

We have developed a new recyclable gold catalyst that can be made from readily available reagents through simple procedures. The catalyst is highly active for the aerobic oxidation of a wide range of alcohols at room temperature in the presence of base. In addition, the catalyst system is effective for the coupling of primary alcohol with ketone to produce α,β-unsaturated ketone selectively under ambient conditions.

4. Experimental section

4.1. Synthesis of Au/AlO(OH) (1)

Hydrogen tetrachloroaurate hydrate (49% Au) (120 mg, 0.23 mmol), Pluronic P123 (1.5 g) ($EO_{20}PO_{80}EO_{20}$ (EO=ethylene oxide, PO=propylene oxide)), and absolute ethanol (7.0 g) were placed in a 100 mL flask equipped with condenser. The reaction mixture was heated at 120 °C for 10 min. The yellow solution turned into greenish-brown suspension. To the resulting suspension, water (8 mL) was added slowly to form red gel. After cooling to room temperature, the red gel was filtered, washed with acetone, and dried at 120 °C for 2 h to give **1** as red powder (2.0 g; 2.8 wt % of Au). The gold content was estimated by ICP analysis.

4.2. Aerobic oxidation of 1-phenylethanol at room temperature

Cs_2CO_3 (490 mg, 1.5 mmol, 3 equiv) and **1** (12 mg, 0.30 mol % of Au) were added to a solution of 1-phenylethanol (61 mg, 0.50 mmol) in toluene (2 mL) and the reaction mixture was stirred at room temperature for 3 h under O_2 balloon.

4.3. Recycling test of 1

After the oxidation reaction for 1-phenylethanol (61 mg, 0.50 mmol) with **1** (12 mg, 0.30 mol % of Au) and Cs_2CO_3 (490 mg, 1.5 mmol, 3 equiv) in toluene (2 mL), solid containing the catalyst was recovered by decanting the solution. For next run 1.5 equiv of Cs_2CO_3 was added.

4.4. Reactions of benzyl alcohol with ketones

The reaction of benzyl alcohol with acetophenone is typical. Cs_2CO_3 (980 mg, 3.00 mmol) and **1** (69 mg, 1.0 mol % of Au) were added to a solution of acetophenone (120 mg, 1.00 mmol) and benzyl alcohol (324 mg, 3.00 mmol) in toluene (3 mL) in a 10 mL tube. The tube with a rubber stopper was connected with an oxygen balloon through a needle, and the mixture was stirred at room temperature for 24 h.

Acknowledgements

We are grateful for the financial supports from Korea Research Foundation (KRF-2008-314-C00203) and the Korean Ministry of Education through the BK21 project for our graduate program.

Supplementary data

Characterization data for **1**, and GC data and NMR spectra for the products. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.12.005.

References and notes

1. (a) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, NY, 1984; (b) Hudlicky, M. *Oxidation in Organic Chemistry*; American Chemical Society: Washington, DC, 1990.
2. (a) Sheldon, R. A. *Catal. Today* **1987**, *1*, 351–355; (b) Menger, F. M.; Lee, C. *Tetrahedron Lett.* **1981**, *22*, 1655–1656; (c) Lee, D. G.; Spitzer, U. A. *J. Org. Chem.* **1970**, *35*, 3589–3590.
3. Mallet, T.; Baiker, A. *Chem. Rev.* **2004**, *104*, 3037–3058.
4. Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2000**, *122*, 7144–7145.
5. Mori, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2004**, *126*, 10657–10666.
6. Yamaguchi, K.; Mizuno, N. *Angew. Chem., Int. Ed.* **2002**, *41*, 4538–4542.
7. (a) Haruta, M.; Yamada, N.; Kobayashi, T.; Iijima, S. *J. Catal.* **1989**, *115*, 301–309; (b) Chen, M. S.; Goodman, D. W. *Science* **2004**, *306*, 252–255.
8. Abad, A.; Concepcion, P.; Corma, A.; Garcia, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 4066–4069.
9. Enache, D. I.; Edwards, J. K.; Landon, P.; Solsona-Espriu, B.; Carley, A. F.; Herzing, A. A.; Watanabe, M.; Kiely, C. J.; Knight, D. W.; Hutchings, G. J. *Science* **2006**, *311*, 362–365.
10. Su, F.-Z.; Liu, Y.-M.; Wang, L.-C.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Angew. Chem., Int. Ed.* **2008**, *47*, 334–337.
11. (a) Hu, J.; Chen, L.; Zhu, K.; Suchopar, A.; Richards, R. *Catal. Today* **2007**, *122*, 277–283; (b) Haider, P.; Baiker, A. *J. Catal.* **2007**, *248*, 175–187; (c) Deng, J.-P.; Shih, W. C.; Mou, C.-Y. *ChemPhysChem* **2005**, *6*, 2021–2025; (d) Porta, F.; Prati, L.; Rossi, M.; Coluccia, S.; Martra, G. *Catal. Today* **2000**, *61*, 165–172; (e) Biella, S.; Prati, L.; Rossi, M. *J. Catal.* **2002**, *206*, 242–247; (f) Porta, F.; Prati, L. *J. Catal.* **2004**, *224*, 397–403; (g) Choudhary, V. R.; Dhar, A.; Jana, P.; Jha, R.; Uphade, B. S. *Green Chem.* **2005**, *7*, 768–770.
12. Miyamura, H.; Matsubara, R.; Miyazaki, Y.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2007**, *46*, 4151–4154.
13. Pluronic P123 was essential for the preparation of **1**, but more than 95% of the employed amount was recovered from the filtration step.
14. (a) Kwon, M.-S.; Kim, N.; Park, C.-M.; Lee, J.-S.; Kang, K.-Y.; Park, J. *Org. Lett.* **2005**, *7*, 1077–1079; (b) Kim, W.-H.; Park, I.-S.; Park, J. *Org. Lett.* **2006**, *8*, 2543–2545; (c) Park, I.-S.; Kwon, M.-S.; Kim, N.; Lee, J.-S.; Kang, K.-Y.; Park, J. *Chem. Commun.* **2005**, 5667–5669; (d) Park, I.-S.; Kwon, M.-S.; Kang, K.-Y.; Lee, J.-S.; Park, J. *Adv. Synth. Catal.* **2007**, *349*, 2039–2047; (e) Park, I.-S.; Kwon, M.-S.; Kim, Y.; Lee, J.-S.; Park, J. *Org. Lett.* **2008**, *10*, 497–500.
15. Schulz-Dobrick, M.; Sarathy, K. V.; Jansen, M. *J. Am. Chem. Soc.* **2005**, *127*, 12816–12817.
16. See, Supplementary data.
17. Without base, the oxidation was too slow to observe the production of acetophenone under the standard conditions in Table 1.
18. There are many factors for the aerobic catalytic oxidation of alcohols with heterogeneous gold nanoparticles. See the recent paper for the catalyst parameters of supported gold nanopaticles: Abad, A.; Corma, A.; García, H. *Chem.—Eur. J.* **2008**, *14*, 22–222.
19. (a) Hayashi, T.; Inagaki, T.; Itayama, N.; Baba, H. *Catal. Today* **2006**, *117*, 210–213; (b) Marsden, C.; Taarning, E.; Hansen, D.; Johansen, L.; Klitgaard, S. K.; Egeblad, K.; Christensen, C. H. *Green Chem.* **2008**, *10*, 168–170; (c) Su, F.-Z.; Ni, J.; Sun, H.; Cao, Y.; He, H.-Y.; Fan, K.-N. *Chem.—Eur. J.* **2008**, *14*, 7131–7134.
20. Kwon, M.-S.; Kim, N.; Seo, S.-H.; Park, I.-S.; Cheedrala, R. K.; Park, J. *Angew. Chem., Int. Ed.* **2005**, *44*, 6913–6915.
21. (a) Taguchi, K.; Nakagawa, H.; Hirabayashi, T.; Sakaguchi, S.; Ishii, Y. *J. Am. Chem. Soc.* **2004**, *126*, 72–73; (b) Yamada, Y. M. A.; Uozumi, Y. *Org. lett.* **2006**, *8*, 1375–1378; (c) Motokura, K.; Nishimura, D.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2004**, *126*, 5662–5663.