Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

Volume 11 | Number 6 | June 2009 | Pages 741–896

ISSN 1463-9262

Saito *et al.*
Efficient synthesis of glyceryl ethers

Kaneda *et al.*
Gold nanoparticles as reusable catalyst for synthesis of lactones

Sato *et al.*
Highly-selective Claisen rearrangement

Fan *et al.*
Enantioselective hydrogenation of quinolines

RSC Publishing

Supported gold nanoparticles as a reusable catalyst for synthesis of lactones from diols using molecular oxygen as an oxidant under mild conditions†

Takato Mitsudome,[a] Akifumi Noujima,[a] Tomoo Mizugaki,[a] Koichiro Jitsukawa[a] and Kiyotomi Kaneda*[a,b]

Received 12th January 2009, Accepted 3rd March 2009
First published as an Advance Article on the web 23rd March 2009
DOI: 10.1039/b900576e

The oxidative lactonization of various diols using molecular oxygen as a primary oxidant can be efficiently catalyzed by hydrotalcite-supported Au nanoparticles (Au/HT). For instance, lactonization of 1,4-butanediol gave γ-butyrolactone with an excellent turnover number of 1400. After lactonization, the Au/HT can be recovered by simple filtration and reused without any loss of its activity and selectivity.

Introduction

The selective synthesis of lactones is of considerable interest to both academic and industrial chemists because lactones are ubiquitous among natural and synthetic organic compounds.[1] Among the various methods of synthesizing lactones, oxidative lactonization of α,ω-diols is one of the most promising methodologies for industrially acceptable process.

Traditionally, stoichiometric lactonization of α,ω-diols has been carried out using large amounts of metal reagents such as silver carbonate[2] and chromium compounds.[3] However, these reagents are expensive and/or toxic. To date, several homogeneous catalytic lactonizations have appeared utilizing Ru,[4] Rh,[5] Pd,[6] and Ir[7] as catalysts combined with organic co-oxidants such as ketones and alkenes. In light of ever-increasing environmental concerns, much interest has been directed toward the development of promising catalytic protocols employing molecular oxygen (O_2) as a primary oxidant, which is readily available, and producing water as the sole byproduct. A more environmentally benign and practical method of oxidative lactonization would utilize O_2 as an oxidant in combination with highly active and reusable catalysts under mild reaction conditions.[8]

Hydrotalcite (HT, $Mg_6Al_2(OH)_{16}CO_3{\cdot}nH_2O$) is a layered anionic clay consisting of a positively charged two-dimensional brucite layer with anionic species such as hydroxide and carbonate located in the interlayer.[9] HT has attracted attention not only for adsorption[10] and drug delivery[11] applications, but also for catalysis[12] due to the following characteristics: (i) the cation-exchange ability of the brucite layer; (ii) the anion-exchange ability of the interlayer; (iii) the tunable basicity of the surface; and (iv) the adsorption capacity. We have previously reported on the benefit of utilizing HT as an inorganic support for various organic syntheses involving the oxidation of various alcohols, where the synergistic effect between the metal and the base sites of the HT can lead to high-performance heterogeneous catalysts.[13] Recently, the use of gold nanoparticles on organic and inorganic supports for the aerobic oxidation of alcohols has attracted considerable interest because of the high catalytic activities.[14] In these systems, the choice of supports is one of the most important factors for achieving high catalytic activities.[15]

Herein, we report on the formation of small Au nanoparticles on the surface of HT to give HT-supported Au nanoparticles (Au/HT), which operated as a highly efficient solid catalyst for lactonization of α,ω-diols under mild reaction conditions. The Au/HT catalyst can overcome the problems such as the requirements for high temperatures, additives, and high catalyst loading that have plagued the previously reported lactonization catalyst systems. Moreover, Au/HT shows wide applicability for various substrates and good reusability without any loss of its activity and selectivity.

Results and discussion

The synthesis of the Au/HT catalyst was as follows. First, hydrotalcite (HT) was prepared according to a procedure in the literature.[9] The obtained HT (1.0 g) was then added to 50 mL of an aqueous solution of $HAuCl_4$ (2 mM). After stirring for 2 min, 0.09 mL of aqueous NH_3 (10%) was added and the resulting mixture was stirred at room temperature for 12 h. The obtained slurry was filtered, washed with deionized water, and dried at room temperature in vacuo. Subsequent treatment with KBH_4 at room temperature for 1 h yielded Au/HT as a purplish red powder. The XRD peak positions of Au/HT were similar to those of the parent HT, and the Au loading on Au/HT was estimated to be 0.89 wt% by elemental analysis. k^3-Weighted Au L-edge extended X-ray absorption fine structure (EXAFS) of Au/HT revealed a peak at around 2.6 Å in the Fourier transform, which was assignable to the Au–Au shell. From transmission electron microscopy, Au nanoparticles were identified on the surface of the HT support with a mean diameter of 2.7 nm and a narrow size distribution with a standard deviation of 0.7 nm.[16]

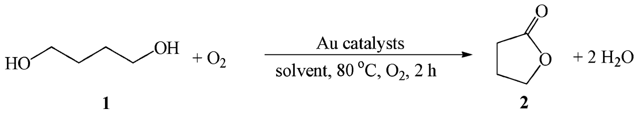
For the catalysis, a mixture of 1,4-butanediol (**1**) and Au/HT in toluene was heated at 80 °C under atmospheric O_2 pressure. The substrate **1** was smoothly oxidized to afford the

---

[a] *Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan. E-mail: kaneda@cheng.es.osaka-u.ac.jp; Fax: +81 6-6850-6260; Tel: +81 6-6850-6260*
[b] *Research Center for Solar Energy Chemistry, Osaka University, 1-3Machikaneyama, Toyonaka, Osaka 560-8531, Japan*

† Electronic supplementary information (ESI) available: EXAFS and TEM of Au/HT. See DOI: 10.1039/b900576e

Table 1 Oxidation of 1,4-butanediol using supported gold catalysts[a]



Entry	Catalyst	Solvent	Conv. (%)[b]	Yield (%)[b]	Particle size (nm)
1	Au/HT	Toluene	99	99	2.7
2	Au/HT[c]	Toluene	99	99	2.7
3	Au/HT[d]	Toluene	83	82	4.6
4[e]	Au/HT	Toluene	99	99	
5[f]	Au/HT	Toluene	96	96	
6[g]	Au/HT	Toluene	99	96	
7[h]	Au/HT	Toluene	99	99	
8	Au/HT	TFT	93	93	
9	Au/HT	Ethyl acetate	91	91	
10	Au/HT	Heptane	80	76	
11	Au/HT	*tert*-Butanol	70	66	
12	Au/HT	DMA	63	63	
13	Au/HT	Acetonitrile	45	36	
14	Au/MgO	Toluene	72	70	3.1
15	Au/MgO[c]	Toluene	28	24	3.4
16	Au/Al_2O_3	Toluene	51	51	3.6
17	Au/Al_2O_3[c]	Toluene	24	20	4.2
18	Au/TiO_2	Toluene	18	16	3.7
19[i]	Au/TiO_2	Toluene	64	64	
20	Au/SiO_2	Toluene	1<	1<	14
21[j]	Pd/HT	Toluene	42	19	
22[j]	Ru/HT	Toluene	1	1<	
23[j]	Ag/HT	Toluene	1<	1<	

[a] Reaction conditions: Supported Au catalysts (Au: 0.45 mol%), 1,4-butanediol (1 mmol), solvent (5 mL). [b] Determined by GC using internal standard technique. [c] H_2 was used as a reductant in place of KBH_4. [d] Hydrazine was used as a reductant in place of KBH_4. [e] Reuse 1. [f] Reuse 2. [g] Substrate (0.5 mmol), 40 °C, 2 h. [h] Under air atmosphere, 10 h. [i] Na_2CO_3 (3 mmol) was added. [j] M/HT (M: 0.45 mol%) was employed in place of the use of Au catalyst.

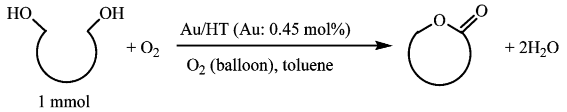
corresponding lactone γ-butyrolactone (**2**) in 99% yield after 2 h (Table 1, entry 1). Among the solvents examined, less polar solvents such as toluene, TFT, and ethyl acetate were superior to polar solvents (entries 1, and 8–10 *vs*. entries 11–13). The choice of solid supports was found to influence the catalytic efficiency; using the other basic supports, Au/MgO and Au/Al_2O_3 also functioned as catalysts (entries 14, and 16), while Au/TiO_2 and Au/SiO_2 gave low yields of **2** (entries 18 and 20). Interestingly, adding Na_2CO_3 as a base to the reaction mixture for the Au/TiO_2 system significantly improved the yield of **2** (entry 18 *vs*. 19). Among the basic supports of HT (entries 1–3), MgO (entries 14 and 15), and Al_2O_3 (entries 16 and 17), the yield of **2** increased with decreasing the particle size, respectively. From these results, it can be said that the basicity of the supports and the size of the Au particles are key factors in promoting the above oxidative lactonization. In addition, we also attached other metal particles with catalytic potential such as Pd, Ru, and Ag to the HT support and employed them in lactonization under similar reaction conditions. The use of Pd/HT gave a moderate yield of **2** (entry 21), while only trace amounts of **2** were obtained using Ru/HT and Ag/HT (entries 22 and 23). The Au/HT catalyst clearly gave the best activity for lactonization of **1**.

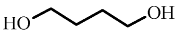
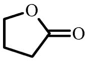
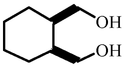
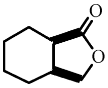
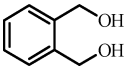
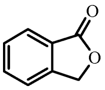
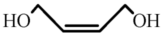
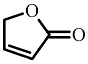
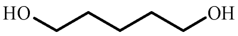
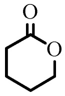
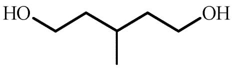
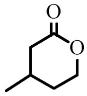
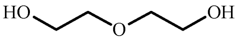
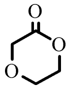
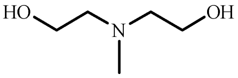
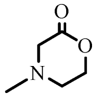
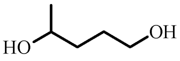
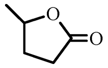
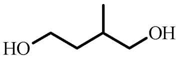
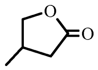
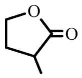
Au/HT was filtered from the reaction mixture at 50% conversion of **1**. Continued stirring of the filtrate under similar conditions did not give any products. Inductively coupled plasma (ICP) analysis of the filtrate showed that no Au was present (detection limit: 0.10 ppm). These results indicate that lactonization occurred on the Au nanoparticles immobilized on HT. Notably, using Au/HT promoted lactonization successfully even at 40 °C (entry 6). Moreover, the Au/HT catalyst was effective when pure O_2 was replaced with ambient air; a quantitative yield of **2** was obtained within 10 h (entry 7).

The scope of this Au/HT catalyst system was investigated for the lactonizations of other diols (Table 2). A wide range of α,ω-diols was oxidized to afford the corresponding lactones in high yields. The diol bearing an olefinic group, *cis*-2-butene-1,4-diol, was chemoselectively converted to an unsaturated lactone 2(5*H*)-furanone with suppression of hydrogenation of the olefinic group (entries 8 and 9). The catalyst system was also applicable to the syntheses of heterocyclic lactones that included oxygen and nitrogen atoms. For example, diethyleneglycol and *N*-methyldiethanolamine gave the corresponding lactones in high yields (entries 14 and 15).

In scale-up conditions, **1** (70 mmol; 6.3 g) successfully gave **2** (91% isolated yield; 5.5 g) with a TON of up to 1400 (entry 3). This value is considerably greater than those reported for the aerobic lactonization of **1** by other catalysts: (PVP-stabilized Au:Pd nanoparticles with K_2CO_3 (TON: 428),[8a] Au/FeOx (TON: 322),[8b] Au/TiO_2 (TON: 102),[8c] Pd/AlO(OH) (TON: 50),[8d] and Ru-Co$(OH)_2$-CeO_2 (TON: 4)[8e]). Although some catalytic lactonizations required the addition of a base such as *t*-BuOK,[4a] NEt_3,[4d,4e] or K_2CO_3,[6a,8a] our Au/HT catalyst did not require any additives to facilitate the catalytic cycle even under an air atmosphere. Furthermore, Au/HT was durable and recyclable for the lactonization. After the Au/HT catalyzed reaction of **1**, Au/HT was recovered by a simple filtration and

Table 2 Oxidation of various α,ω-diols using Au/HT[a]

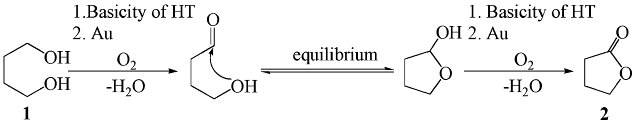


Entry	Diol	Product	Temp. (°C)	Time (h)	Conv. (%)[b]	Yield (%)[b]
1 2[c] 3[d]			80 40 100	2 2 48	99 99 92	99 (96) 96 92 (91)
4 5[c]			80 40	1 2	99 99	99 (96) 97
6 7[c]			80 40	1 2	99 99	99 (95) 98
8 9[c]			80 40	2.5 2	96 98	96 (91) 98
10 11[e]			110 40	1 8	98 99	96 (96) 98
12 13[c]			110 40	1 14	98 99	98 (96) 98
14			110	1	93	92 (87)
15			110	2	90	89 (86)
16[f]			80	4	88	44 (44)
17			80	2	99	95 (89)
						β:α = 1:1

[a] Reaction conditions: Au/HT (0.1 g, Au: 0.45 mol%), diol (1 mmol), toluene (5 mL). [b] Determined by GC and LC using an internal standard technique; values in parentheses are the yield of the isolated products. [c] Substrate (0.5 mmol). [d] Substrate (70 mmol), Au/HT (1.0 g, Au: 0.06 mol%), toluene (180 mL), DMA (5 mL). [e] Substrate (0.3 mmol). [f] 5-Hydroxy-2-pentanone and 4-oxo-pentanal were formed as byproducts.

showed good reusability without any loss of its activity and selectivity in several reuse experiments (Table 1, entries 4 and 5).

A possible reaction mechanism of the lactonization is proposed based on cooperative action between Au and HT. We have found that basic supports and an additive base have a strongly positive effect on the oxidative lactonization (Table 1, entries 1, 14, 16, and 19) (*vide supra*). In this mechanism, a basic site on the HT could promote the formation of an Au–alcoholate species, allowing smooth oxidation of one of the hydroxyl groups of the diol to hydroxyaldehyde, which is equilibrium with a lactol.[17] Subsequent further oxidation of the lactol would furnish the corresponding lactone (Scheme 1).



Scheme 1 Reaction path of lactonization.

Conclusions

We have prepared a Au/HT catalyst which can facilitate aerobic lactonization of various diols without additives under mild reaction conditions. Unlike previous catalyst systems, this Au/HT catalyst is able to achieve lactonization without the need for high temperatures, additives, and high catalytic loading. In addition, Au/HT could be reused without any loss of its activity and selectivity.

Experimental

General

All organic reagents were purified before use. $HAuCl_4 \cdot xH_2O$ was obtained from N. E. Chemcat. Co. Ltd. MgO (GR for analysis) was purchased from Merck Chemical Industries Co. Ltd. Al_2O_3 (JRC-ALO-3), SiO_2 (JRC-SIO-6) and TiO_2 (JRC-TIO-4) were obtained from the Catalysis Society of Japan as reference catalysts. Powder X-ray diffraction (XRD) was measured using an X'pert diffractometer (Philips Co. Ltd.). Inductively coupled plasma (ICP) spectroscopy was performed using a Nippon Jarrell-Ash ICAP-575 Mark II. ^1H and ^{13}C Nuclear magnetic resonance (NMR) spectra were recorded on Jeol JNM-AL400 and 270 MHz. Gas chromatography (GC-FID) was performed on a Shimadzu GC-2014 equipped with a KOCL-3000T column (2 m). High-performance liquid chromatography (HPLC) was performed on a Shimadzu LC-10ADvp: STR ODS-II (150 × 4 mm). Au L-edge X-ray absorption spectra were recorded at room temperature using a fluorescence-yield collection technique at the beam line 01B1 station attached with a Si(111) monochromator at SPring-8, Japan Atomic Energy Research Institute (JASRI), Harima, Japan. Data analysis was performed using the REX 2000 program, ver. 2.0.4 (Rigaku). Fourier transformation (FT) of k^3-weighted extended X-ray absorption fine structure (EXAFS) data was performed to obtain the radial structural function.

Characterization of Au/HT

Elemental analysis showed that the Au loading was 0.89 wt% Au L-edge X-ray absorption spectra and transmission electron microscopy (TEM) showed that Au nanoparticles were formed on the surface of the HT support with a mean diameter of 2.7 nm and a narrow size distribution with a standard deviation of 0.7 nm. The mean diameters, d, and standard deviations (σ) of the Au particles for the Au/MgO, Au/Al_2O_3, Au/TiO_2, and Au/SiO_2 systems were $d = 31$ Å ($\sigma = 10.8$ Å), 36 Å ($\sigma = 7.7$ Å), 37 Å ($\sigma = 7.9$ Å), and 140 Å ($\sigma = 66.5$ Å), respectively.

General reaction procedures

A typical procedure for the lactonization of **1** using the Au/HT catalyst was as follows. Au/HT (0.10 g, 0.0045 mmol Au) was placed in a reaction vessel, followed by the addition of toluene (5 mL) and **1** (1 mmol), and the reaction mixture was vigorously stirred at 80 °C for 2 h under O_2 balloon (500 mL). After the lactonization reaction, the Au/HT was removed by filtration, and the resulting solution was evaporated. The resulting residue was purified by column chromatography using silica gel (Wakogel C-200, 75–150 μm) to give γ-butyrolactone **2** (82.7 mg, 96% as a colorless oil).

Product identification

γ-Butyrolactone, phthalide, 2(5*H*)-furanone, δ-valerolactone, γ-valerolactone were commercially available. The yields of products were determined by GC and HPLC [STR ODS-II (150 × 4 mm); detection at 254 nm, flow rate 1.0 mL/min, eluent: a mixture of acetonitrile and water (3 : 7)]. Gas chromatography (GC) and/or LC retention times and ^1H and ^{13}C NMR chemical shifts of products were in agreement with those of authentic samples and also with the reported data.

NMR data

***γ*-Butyrolactone.** ^1H NMR (400 MHz, $CDCl_3$) δ 2.23–2.31 (m, 2H), 2.49 (t, $J = 8.3$ Hz, 2H), 4.35 (t, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.10, 27.69, 68.40, 177.45. See ref. 18, SDBS No. 1325.

***cis*-Hexahydrophthalide.** ^1H NMR (270 MHz, $CDCl_3$) δ 1.16–1.31 (m, 3H), 1.56–1.69 (m, 3H), 1.74–1.87 (m, 1H), 2.08–2.13 (m, 1H), 2.43–2.53 (m, 1H), 2.62–2.68 (m, 1H), 3.93 (dd, $J = 8.8$, 1.4 Hz, 1H), 4.19 (dd, $J = 8.8$, 5.0 Hz, 1H); ^{13}C NMR (70 MHz, $CDCl_3$) δ 20.79, 22.44, 22.85, 23.34, 35.29, 39.33, 71.55, 178.08. See ref. 7.

Phthalide. ^1H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 2H), 7.50 (d, $J = 7.6$ Hz, 1H), 7.55 (dd, $J = 7.6$, 7.4 Hz, 1H) 7.70 (dd, $J = 7.6$, 7.4 Hz, 1H), 7.94 (d, $J = 7.6$ Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 69.60, 121.99, 125.62, 125.75, 128.96, 133.89, 146.42, 171.06.

See ref. 18, SDBS No. 1158.

2(5*H*)-Furanone. ^1H NMR (400 MHz, $CDCl_3$) δ 4.92 (dd, $J = 2.2$, 1.7 Hz, 2H), 6.15 (dt, $J = 5.8$, 2.2 Hz, 1H), 7.60 (dt, $J = 5.8$, 1.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 72.08, 121.51, 152.62, 173.49. See ref. 19.

***δ*-Valerolactone.** ^1H NMR (400 MHz, $CDCl_3$) δ 1.83–1.95 (m, 4H), 2.55 (t, $J = 7.0$ Hz, 2H), 4.34 (t, $J = 6.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.02, 22.25, 29.74, 69.28, 171.07. See ref. 7.

4-Methyltetrahydropyran-2-one. ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (d, $J = 7.0$ Hz, 3H), 1.48–1.57 (m, 1H), 1.90–1.96 (m, 1H), 2.04–2.17 (m, 2H), 2.63–2.71 (m, 1H), 4.23–4.30 (m, 1H), 4.39–4.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.40, 26.50, 30.60, 38.17, 68.39, 170.93. See ref. 4(*h*).

4-Methylmorpholine-2-one. ^1H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 2.64 (t, $J = 5.5$ Hz, 2H), 3.26 (s, 2H), 4.40 (t, $J = 5.5$ Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 44.89, 51.00, 57.41, 68.64, 167.08. See ref. 4(*f*).

***γ*-Valerolactone.** ^1H NMR (400 MHz, $CDCl_3$) δ 1.41 (d, $J = 6.3$ Hz, 3H), 1.78–1.88 (m, 1H), 2.32–2.56 (m, 1H), 2.52–2.59 (m, 2H), 4.60–4.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.00, 29.00, 29.63, 77.09, 176.90. See ref. 7.

Acknowledgements

The investigation was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. This work was also supported by Grant-in-Aid for Scientific Research on Priority Areas (No.18065016, "Chemistry of Concerto Catalysis") from Ministry of Education, Culture, Sports, Science and Technology, Japan. A part of the present experiments were carried out by using a facility in the Research Center for Ultrahigh Voltage Electron Microscopy, Osaka University.

References

1 A. Parenty, X. Moreau and J.-M. Campagne, *Chem. Rev.*, 2006, **106**, 911.

2 (*a*) M. Fetizon, M. Golfier and J.-M. Louis, *Chem. Commun.*, 1969, 1118; (*b*) M. Fetizon, M. Golfier and J.-M. Louis, *Tetrahedron*, 1975, **31**, 171.

3 (*a*) V. I. Stenberg and R. J. Perkins, *J. Org. Chem.*, 1963, **28**, 323; (*b*) P. Johnton, R. C. Sheppard, C. E. Stehr and S. Turner, *J. Chem. Soc. (C)*, 1966, 1847.

4 (*a*) M. Ito, A. Osaku, A. Shiibashi and T. Ikariya, *Org. Lett.*, 2007, **9**, 1821; (*b*) K. Nozaki, M. Yoshida and H. Takaya, *J. Organomet. Chem.*, 1994, **473**, 253; (*c*) Y. Shvo, Y. Blum, D. Reshef and M. Menzin, *J. Organomet. Chem.*, 1982, **226**, C21; (*d*) Y. Ishii, K. Osakada, T. Ikariya, M. Saburi and S. Yoshikawa, *J. Org. Chem.*, 1986, **51**, 2034; (*e*) Y. Ishii, K. Osakada, T. Ikariya, M. Saburi and S. Yoshikawa, *Chem. Lett.*, 1982, 1179; (*f*) S.-I. Murahashi, T. Naota, K. Ito, Y. Maeda and H. Taki, *J. Org. Chem.*, 1987, **52**, 4319; (*g*) S.-I. Murahashi, K. Ito, T. Naota and Y. Maeda, *Tetrahedron Lett.*, 1981, **22**, 5327; (*h*) Metal polyhydrides: Y. Lin, X. Zhu and Y. Zhou, *J. Organomet. Chem.*, 1992, **429**, 269; (*i*) H. C. Maytum, B. Tavassoli and J. M. J. Williams, *Org. Lett.*, 2007, **9**, 4387; (*j*) Acceptor-free: J. Zhao and F. Hartwig, *Organometallics*, 2005, **24**, 2441.

5 Y. Ishii, K. Suzuki, T. Ikariya, M. Saburi and S. Yoshikawa, *J. Org. Chem.*, 1986, **51**, 2822.

6 (*a*) Y. Tamaru, Y. Yamada, K. Inoue, Y. Yamamoto and Z. Yoshida, *J. Org. Chem.*, 1983, **48**, 1286; (*b*) I. Minami and J. Tsuji, *Tetrahedron*, 1987, **43**, 3903.

7 T. Suzuki, K. Morita, M. Tsuchida and K. Hiroi, *Org. Lett.*, 2002, **4**, 2361.

8 (*a*) W. Hou, N. A. Dehm and R. W. J. Scott, *J. Catal.*, 2008, **253**, 22; (*b*) J. Huang, W.-L. Dai, H. Li and K. Fan, *J. Phys. Chem. C*, 2008, **112**, 16110; (*c*) J. Huang, W.-L. Dai, H. Li and K. Fan, *J. Catal.*, 2007, **252**, 69; (*d*) M. S. Kwon, N. Kim, C. M. Park, J. S. Lee, K. Y. Kang and J. Park, *Org. Lett.*, 2005, **7**, 1077; (*e*) H. Ji, T. Mizugaki, K. Ebitani and K. Kaneda, *Tetrahedron Lett.*, 2002, **43**, 7179.

9 F. Cavani, A. Trifiró and A. Vaccari, *Catal. Today*, 1991, **11**, 173.

10 P. S. Braterman, Z. P. Xu, F. Yarberry, in *Handbook of Layered Materials*, ed. S. M. Auerbach, K. A. Carrado and P. K. Dutta, Marcel Dekker, New York, 2004, p. 373.

11 (*a*) J. H. Choy, S. Y. Kwak, J. S. Park and Y. J. Jeong, *J. Mater. Chem.*, 2001, **11**, 1671; (*b*) J. H. Choy, S. Y. Kwak, Y. J. Jeong and J. S. Park, *Angew. Chem. Int. Ed.*, 2000, **39**, 4042.

12 (*a*) K. Ebitani, K. Motokura, K. Mori, T. Mizugaki and K. Kaneda, *J. Org. Chem.*, 2006, **71**, 5440; (*b*) K. Motokura, D. Nishimura, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2004, **126**, 5662; (*c*) M. J. Climent, A. Corma, S. Iborra and A. Velty, *J. Catal.*, 2004, **221**, 474; (*d*) B. M. Choudary, M. L. Kantam, A. Rahman, C. V. Reddy and K. K. Rao, *Angew. Chem. Int. Ed.*, 2001, **40**, 763; (*e*) K. Yamaguchi, K. Mori, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Org. Chem.*, 2000, **65**, 6897; (*f*) K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida and K. Kaneda, *J. Am. Chem. Soc.*, 1999, **121**, 4526; (*g*) B. Sels, D. De Vos, M. Buntinx, F. Pierard, A. K.-D. Mensmaeker and P. A. Jacobs, *Nature*, 1999, **400**, 855.

13 (*a*) T. Mitsudome, Y. Mikami, H. Funai, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Angew. Chem. Int. Ed.*, 2008, **47**, 138; (*b*) T. Mitsudome, Y. Mikami, K. Ebata, T. Mizugaki, K. Jitsukawa and K. Kaneda, *Chem. Commun.*, 2008, 4804; (*c*) K. Ebitani, K. Motokura, T. Mizugaki and K. Kaneda, *Angew. Chem. Int. Ed.*, 2005, **44**, 3423.

14 (*a*) A. Abad, P. Concepción, A. Corma and H. García, *Angew. Chem. Int. Ed.*, 2005, **44**, 4069; (*b*) D. I. Enache, J. K. Edward, P. Landon, B. S. Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362.

15 A. Abad, A. Corma and H. García, *Chem. Eur, J.*, 2008, **14**, 212.

16 See ESI†.

17 The Au/HT also showed high catalytic activity for the oxidation of various mono-alcohols to carbonyl compounds. For example, the Au/HT catalyst could oxidize 1-phenylethanol and benzyl alcohol efficiently, affording acetophenone and benzaldehyde in 99% yields after 20 min and 4 h, respectively, under similar reaction conditions to Table 1 entry 1.

18 SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 2008.11.30).

19 R. Garzelli, S. Samaritani and C. Malanga, *Tetrahedron*, 2008, **64**, 4183.