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## Efficient Aerobic Oxidation of Alcohols using a Hydrotalcite-Supported Gold Nanoparticle Catalyst

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**Abstract:** Hydrotalcite-supported gold nanoparticles (Au/HT) were found to be a highly efficient heterogeneous catalyst for the aerobic oxidation of alcohols under mild reaction conditions (40 °C, in air). This catalyst system does not require any additives and is applicable to a wide range of alcohols, including less reactive cyclohexanol derivatives. This Au/HT catalyst could also function in the oxidation of 1-phenylethanol under neat conditions; the turnover number (TON) and turnover frequency (TOF) reached

200,000 and 8,300 h<sup>-1</sup>, respectively. These values are among the highest values compared to those of other reported catalyst systems at high conversion. Moreover, the Au/HT can be recovered by simple filtration and reused without any loss of its activity and selectivity.

**Keywords:** aerobic oxidation; alcohols; clays; gold nanoparticles; green chemistry; heterogeneous catalysis

### Introduction

Selective oxidation of alcohols is a widely recognized key and fundamental transformation in both laboratory and industrial synthetic chemistry, as the resulting carbonyl compounds serve as important and versatile intermediates in the synthesis of fine chemicals.<sup>[1–3]</sup> Such oxidations have traditionally required oxidizing reagents such as permanganate and dichromate,<sup>[4–6]</sup> which are expensive and/or toxic, and result in the production of large amounts of waste. Therefore, much attention has been directed towards the development of reusable solid catalysts that employ widely available molecular oxygen (O<sub>2</sub>) as the primary oxidant and produce water as the sole by-product.<sup>[7–23]</sup> Examination of highly active solid catalysts has identified Au nanoparticles as a potential catalyst. Various types of catalytic systems, including organic- and inorganic-supported Au nanoparticles in combination with additives such as NaOH and Cs<sub>2</sub>CO<sub>3</sub> have been developed.<sup>[24–30]</sup>

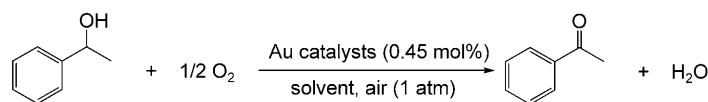
Recently, we reported on the use of uniformly small Au nanoparticles (*ca.* 2.7 nm) supported on hydrotalcite (Au/HT) as a highly active solid catalyst for

the oxidative lactonization of  $\alpha,\omega$ -diols under atmospheric pressure of O<sub>2</sub> without additives.<sup>[31]</sup> Oxidation of the diols was shown to be strongly affected by the basic surfaces of HT *via* formation of an Au-alcoholate species.

In this paper, the Au/HT catalyst was further employed in the oxidation of various alcohols under the following mild reaction conditions: 1) without additives other than the Au catalyst, 2) under atmospheric O<sub>2</sub>, and 3) at ambient temperature. The catalyst was also effective towards less reactive cyclohexanol derivatives to produce the corresponding cyclohexanones with excellent yields. Moreover, the Au/HT catalyst could be reused without any loss of activity or selectivity.

### Results and Discussion

Initially, the oxidation of 1-phenylethanol (**1**) was carried out in the presence of the Au/HT catalyst in toluene under atmospheric O<sub>2</sub> at room temperature to quantitatively yield acetophenone (**2**) after 6 h (Table 1, entry 1). To determine whether Au/HT

**Table 1.** Oxidation of 1-phenylethanol using supported gold catalysts.<sup>[a]</sup>

Entry	Catalyst	Solvent	Temp. [°C]	Time [h]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>
1	Au/HT	toluene	27	6	99	99
2	Au/HT	toluene	40	3	99	99
3	Au/HT	toluene	80	0.33	99	99
4 <sup>[c]</sup>	Au/HT	toluene	0	50	94	94
5 <sup>[d]</sup>	Au/HT	toluene	40	3	99	99
6 <sup>[e]</sup>	Au/HT	toluene	40	3	98	98
7 <sup>[f]</sup>	Au/HT	toluene	40	3	98	98
8	Au/HT	heptane	40	3	86	83
9	Au/HT	TFT	40	3	66	66
10	Au/HT	ethyl acetate	40	3	47	47
11	Au/HT	<i>tert</i> -butanol	40	3	36	35
12	Au/HT	acetonitrile	40	3	18	18
13	Au/HT	DMA	40	3	8	8
14	Au/HT	water	40	10	99	95
15	Au/MgO	toluene	40	3	71	71
16	Au/Al <sub>2</sub> O <sub>3</sub>	toluene	40	3	71	71
17	Au/TiO <sub>2</sub>	toluene	40	3	16	14
18 <sup>[g]</sup>	Au/TiO <sub>2</sub> + Na <sub>2</sub> CO <sub>3</sub>	toluene	40	3	65	65
19	Au/SiO <sub>2</sub>	toluene	40	3	<1	<1

<sup>[a]</sup> Reaction conditions: Au/HT (0.1 g, Au: 0.0045 mmol), 1-phenylethanol (1 mmol), solvent (5 mL).

<sup>[b]</sup> Determined by GC using internal standard technique.

<sup>[c]</sup> Au/HT (0.2 g, Au: 1.8 mol%), 1-phenylethanol (0.5 mmol).

<sup>[d]</sup> Reuse 1.

<sup>[e]</sup> Reuse 2.

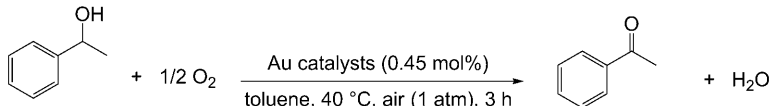
<sup>[f]</sup> Reuse 3.

<sup>[g]</sup> Na<sub>2</sub>CO<sub>3</sub> (3 mmol) was added.

worked as a heterogeneous catalyst, Au/HT was removed from the reaction mixture by simple filtration at 50% conversion of **1**. Continued stirring of the filtrate under similar conditions did not give any products. The absence of Au ions in the filtrate was verified using inductively coupled plasma analysis (detection limit: 0.10 ppm). These results clearly demonstrate that oxidation took place only on the Au nanoparticles immobilized on HT. As shown in Table 1 (entries 2 and 3), the turnover frequency (TOF) of the catalyst was dramatically improved by increasing the reaction temperature. An excellent yield was also obtained even at 0 °C although a longer reaction time

was required (Table 1, entry 4). Among the solvents tested, high yields of **2** were obtained using less polar solvents, especially toluene (Table 1, entries 2, 8 and 9). In contrast, low yields were obtained using ethyl acetate, *tert*-butyl alcohol, acetonitrile, and DMA as solvents (Table 1, entries 10–13). Interestingly, the Au/HT-catalyzed alcohol oxidation can also be carried out in water (Table 1, entry 14).

The effect of inorganic supports on the oxidative activity was investigated for Au nanoparticles. As shown in Table 1, Au/MgO (entry 15) and Au/Al<sub>2</sub>O<sub>3</sub> (entry 16) provided moderate yields of **2**, whereas Au/TiO<sub>2</sub> (entry 17) and Au/SiO<sub>2</sub> (entry 19) were inef-

**Table 2.** Size-effect of gold nanoparticles.<sup>[a]</sup>


Entry	Catalyst	Reducing reagent	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>	Particle size [nm]
1	Au/HT	KBH <sub>4</sub>	99	99	2.7
2	Au/HT	H <sub>2</sub>	99	99	2.7
3	Au/HT	hydrazine	71	69	4.6
4	Au/MgO	KBH <sub>4</sub>	71	71	3.1
5	Au/MgO	H <sub>2</sub>	37	37	4.4
6	Au/MgO	hydrazine	18	18	5.7
7	Au/Al <sub>2</sub> O <sub>3</sub>	KBH <sub>4</sub>	71	71	3.6
8	Au/Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub>	32	32	4.2
9	Au/Al <sub>2</sub> O <sub>3</sub>	hydrazine	22	22	5.8
10 <sup>[c]</sup>	Ru/HT <sup>[d]</sup>		3	2	
11 <sup>[c]</sup>	Ag/HT	KBH <sub>4</sub>	2	2	
12 <sup>[c]</sup>	Pd/HT	KBH <sub>4</sub>	2	2	

<sup>[a]</sup> Reaction conditions: Au catalyst (0.45 mol%), 1-phenylethanol (1 mmol), toluene (5 mL).

<sup>[b]</sup> Determined by GC using internal standard technique.

<sup>[c]</sup> M/HT (M: 0.45 mol%) was used.

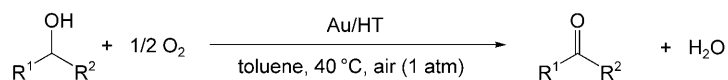
<sup>[d]</sup> Ru/HT was obtained from N. E. Chemcat.









































fective as catalysts. However, for Au/TiO<sub>2</sub>, the addition of Na<sub>2</sub>CO<sub>3</sub> as a base to the reaction mixture significantly improved the yield of **2** (entry 17 vs. 18). These results indicate that a concerted catalysis occurring between the base sites of the inorganic support and the Au nanoparticles is essential for achieving high catalytic activity in the oxidation of **1**.

Next, we investigated the relationship between the size of the Au nanoparticles and the catalytic activity for the above oxidation (Table 2). In our previous work, we found that the particle size of the Au nanoparticles could be controlled by the reducing reagents used during preparation of the catalyst; specifically, the size of the Au nanoparticles decreased in order for the following reducing reagents: hydrazine > molecular hydrogen > potassium borohydride. For all three basic supports (HT, entries 1–3; MgO, entries 4–6; Al<sub>2</sub>O<sub>3</sub>, entries 7–9), the yields of **2** increased with decreasing particle sizes of the Au nanoparticles – in other words, a small particle size is essential for the successful oxidation of alcohols. The use of other metal particles with catalytic potential, such as Pd, Ru, and Ag, resulted in significantly lower yields of **2** for the oxidation of **1** under similar reaction conditions (entries 10–12). Our results clearly show that the

Au/HT catalyst has the optimal activity for oxidation of **1** (entry 1).

Subsequent investigations exhibited that the Au/HT catalyst could oxidize a wide range of alcohols to the corresponding carbonyl compounds with high yields under mild reaction conditions (Table 3). Among the alcohols examined, benzylic secondary alcohols having both electron-donating and electron-withdrawing groups proved to be good substrates (entries 2 and 3). Dehydrogenative oxidation of benzylic primary alcohols (entries 13 and 14) proceeded, but with slightly lower yields. An aliphatic secondary alcohol was oxidized to give the corresponding ketone with an excellent yield (entry 6), while an aliphatic primary alcohol, 1-octanol (entry 15), was not reactive. The Au/HT catalyst was also effective for the oxidation of various allylic alcohols (entries 7, 16 and 17) to the corresponding  $\alpha,\beta$ -unsaturated carbonyl compounds. For heteroaromatic alcohols (entries 18–20), the catalytic activity may be hampered by strong coordination between the active metal atom and the oxygen (entry 19) or sulfur (entry 20) atoms of the heteroaromatic ring. Surprisingly, the catalyst was tolerant of nitrogen atoms in the heteroaromatic ring (entry 18), giving a high yield of the corresponding ketone.

**Table 3.** Oxidation of various alcohols by using Au/HT.<sup>[a]</sup>

Entry	Alcohol	Product	Time [h]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>
1			3	99	99 (97)
2			3	99	99 (97)
3			6	98	98
4			1.5	99	94 (94)
5			4	99	96 (95)
6			15	91	90
7			12	83	83
8 <sup>[c]</sup>			36	93	93
9			24	90	88
10			7	92	91
11 <sup>[c]</sup>			36	93	93
12			8	95	94
13 <sup>[d]</sup>			24	85	78
14 <sup>[d]</sup>			8	99	81
15			12	<1	trace
16 <sup>[d]</sup>			6	95	85
17			24	60	60
18			24	81	81
19 <sup>[d]</sup>			72	60	41
20 <sup>[d]</sup>			24	36	17

<sup>[a]</sup> Reaction conditions: Au/HT (0.1 g, Au: 0.45 mol%), alcohol (1 mmol), toluene (5 mL).

<sup>[b]</sup> Determined by GC or HPLC using internal standard technique. Isolated yields were shown in parentheses.

<sup>[c]</sup> Alcohol (0.5 mmol).

<sup>[d]</sup> Ester was formed as a by-product.

Au/HT also could oxidize alicyclic alcohols including bulky alcohols into ketones in high yields when the reaction times were prolonged (entries 8–12). Cyclohexanol, which is not readily oxidized by previously reported catalysts,<sup>[32]</sup> was effectively converted to cyclohexanone in the presence of the Au/HT catalyst under mild conditions (entry 9). Based on this encouraging result, the Au/HT catalyst was consequently extended to the oxidation of 9 representative cyclohexanol derivatives to yield the corresponding cyclohexanones with excellent yields (Table 4).

Furthermore, for oxidation of **1**, the Au/HT catalyst was effective under neat conditions. Specifically, **1** (30 mmol, 3.7 g) was oxidized in the absence of solvents to give a 93% yield of **2** (3.4 g) with 99% selec-

tivity after 24 h. The reaction exhibited high turnover number (TON) and turnover frequency (TOF) reaching 200,000 and 8,300 h<sup>-1</sup>, respectively,<sup>[33]</sup> which were comparable to those of other catalyst systems showing high conversion of **1**, i.e., Au/CeO<sub>2</sub> (TON, 250,000; TOF, 12,500 h<sup>-1</sup>),<sup>[17]</sup> Au-Pd/TiO<sub>2</sub> (TON, 134,500; TOF, 269,000 h<sup>-1</sup>),<sup>[16]</sup> PdHAP (TON, 236,000; TOF, 9800 h<sup>-1</sup>),<sup>[19]</sup> and Au(0)-Pd(0)/PI (TON, 117,200; TOF, 117,200 h<sup>-1</sup>).<sup>[12]</sup>

The reusability of the Au/HT catalyst was investigated using a recycling experiment involving three consecutive runs of the oxidation of **1**, in which the Au/HT catalyst was filtered and reused under identical conditions. As shown in Table 1 (entries 5–7), the recovered Au/HT exhibited consistent catalytic activi-

**Table 4.** Oxidation of various cyclohexanols.<sup>[a]</sup>

Entry	Alcohol	Product	Time [h]	Conv. [%] <sup>[b]</sup>	Yield [%] <sup>[b]</sup>
1			4	93	91
2			2	96	96
3			2	99	99 (98)
4			2	96	96
5			2	99	99 (97)
6			2	98	98
7			12	99	99 (96)
8			6	92	89
9 <sup>[c]</sup>			10	99	99 (98)

<sup>[a]</sup> Reaction conditions: Au/HT (0.1 g, Au: 0.45 mol%), alcohol (1 mmol), toluene (5 mL).

<sup>[b]</sup> Determined by GC using internal standard technique. Isolated yields were shown in parenthesis.

<sup>[c]</sup> Alcohol (0.5 mmol).

ty and selectivity.<sup>[34]</sup> Subsequently, the catalyst was examined using TEM and Au L-edge EXAFS analyses<sup>[34]</sup>. TEM images of the Au nanoparticles showed that the average size and distribution of the Au nanoparticles were not significantly altered and that Au aggregates were not formed. Atomic scale analysis using Au L-edge EXAFS showed that the intensity of the FT peak derived from the Au-Au shell at 2.7 Å was not varied, supporting that the size of the Au nanoparticles in the reused Au/HT catalyst was unchanged. Results of these structural analyses are consistent with the retention of the catalytic activity of Au/HT in the recycling experiment.

## Conclusions

An Au/HT heterogeneous catalyst involving a hydrotalcite support with Au nanoparticles with an average size of 2.7 nm and a very narrow size distribution was shown to be highly effective in the oxidation of alcohols, including cyclohexanols. The Au/HT catalysis system offers significant benefits in achieving “green” organic synthesis due to: (1) high catalytic efficiency, (2) wide applicability, (3) no requirement for additives, (4) mild reaction conditions (40 °C, atmospheric O<sub>2</sub>), and (5) reusability of the catalyst. It is also found that (i) the catalytic activity of Au nanoparticles on basic supports increased with decreasing size of Au nanoparticles, (ii) basic supports or an additive base showed concerted catalysis with Au nanoparticles to achieve high performance in the aerobic oxidation.

## Experimental Section

### General

All organic reagents were purified before use. HAuCl<sub>4</sub>·xH<sub>2</sub>O was obtained from N. E. Chemcat. Co., Ltd. MgO (GR for analysis) was purchased from Merck Chemical Industries Co., Ltd. Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-3), SiO<sub>2</sub> (JRC-SIO-6), and TiO<sub>2</sub> (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. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-AL spectrometer at 400 and 270 MHz, respectively. 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 equipped with a STR ODS-II column (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 an Si (111) monochromator at the SPring-8, Japan Atomic Energy Research Institute (JASRI), Harima,

Japan. Data analysis was performed using the REX 2000 program, ver. 2.0.4 (Rigaku). A Fourier transformation (FT) of *k*<sup>3</sup>-weighted extended X-ray absorption fine structure (EXAFS) data was performed to obtain the radial structural function.

### Product Identification

The yields of products were determined by GC and HPLC (detection at 254 nm, 1.0 mL min<sup>-1</sup>, acetonitrile/water 3:7). Retention times (GC and/or LC) and chemical shifts (<sup>1</sup>H and <sup>13</sup>C NMR) of the products were in agreement with those of authentic samples (commercially available) and/or reported data.

### Preparation of Supported Au Nanoparticles

Samples (1.0 g) of inorganic supports such as HT, Al<sub>2</sub>O<sub>3</sub>, MgO, TiO<sub>2</sub>, and SiO<sub>2</sub> were added to 50 mL of a 2 mM HAuCl<sub>4</sub> aqueous solution. After stirring for 2 min, 0.09 mL of aqueous NH<sub>3</sub> (10%) was added, and the resulting mixture was stirred at room temperature for 12 h. The resulting slurry was filtered, washed with deionized water, dried at room temperature under vacuum, and treated with KBH<sub>4</sub> at room temperature for 1 h to produce the supported Au nanoparticles.

### 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 (*d*) of 2.7 nm and a narrow size distribution with a standard deviation ( $\sigma$ ) of 0.7 nm. Values of *d* and  $\sigma$  for the Au particles in Au/MgO, Au/Al<sub>2</sub>O<sub>3</sub>, Au/TiO<sub>2</sub>, and Au/SiO<sub>2</sub> were *d*=3.1 nm ( $\sigma$ =1.1 nm), 3.6 nm ( $\sigma$ =0.8 nm), 3.7 nm ( $\sigma$ =0.8 nm), and 14.0 nm ( $\sigma$ =6.7 nm), respectively.

### Oxidation of Alcohols using the Au/HT Catalyst

Au/HT was placed in the flask, and then a toluene solution of alcohol was added. The reaction mixture was heated at 40 or 80 °C for appropriate times under air conditions. After filtering the solid catalyst, biphenyl was added as an internal standard to the filtrate for quantitative GC analysis. For isolation of the products, the filtrate was subjected to short column of silica gel to give a pure product. Typically, Au/HT (1.0 g, Au: 0.045 mmol) was placed in a reaction vessel, followed by the addition of toluene (30 mL) and **1** (10 mmol: 1.22 g), and then the reaction mixture was vigorously stirred at 40 °C for 3 h under air flow. After the reaction, the Au/HT was removed by filtration, and toluene was evaporated. The residue was purified on a short column of silica gel (Wakogel C-200) using ethyl acetate and *n*-hexane (1:9) as an eluent to give **2** as a colorless oil; yield: 1.19 g (99% isolated yield).

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- [32] For example, low yields of cyclohexanone were obtained using our Pd<sup>[19]</sup> and Ru<sup>[23]</sup> supported on hydroxyapatite which showed extremely high activities for a wide range of alcohols and only two reported catalysts with high efficiency for the oxidation have appeared to date (see refs.<sup>[11,25]</sup>). 30% and 19% yields of cyclohexanone were obtained using 1 mol% of RuHAP and PdHAP, respectively, under an atmospheric pressure of O<sub>2</sub> at 80 °C for 24 h.
- [33] There are other previously reported catalysts with high TOF at low conversion of **1** such as ref.<sup>[10]</sup> [Au/Ga<sub>3</sub>Al<sub>3</sub>O<sub>9</sub> (conversion: 5%, TOF: 25,000 h<sup>-1</sup>), ref.<sup>[28]</sup> [PI Au (conversion: 6%, TOF: 20,000 h<sup>-1</sup>), and ref.<sup>[8]</sup> [Au/MnO<sub>2</sub> (conversion: 20%, TOF: 15,760 h<sup>-1</sup>)]. Our Au/HT catalyst gave a higher TOF: 37,000 h<sup>-1</sup> at 16% conversion of **1**.
- [34] See Supporting Information for details.