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Genesis of Catalytically Active Gold Nanoparticles Supported on Hydrotalcite for Base-free Selective Oxidation of Glycerol in Water with Molecular Oxygen

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Hydrotalcite-supported gold nanoparticles (Au/HT) were synthesized by deposition–precipitation using NH_3 and successive calcination at various temperatures. Gold nanoparticles of less than 5 nm with narrow size distribution were deposited onto hydrotalcite surfaces, which were determined by TEM measurements. Au L_{III}-edge XANES spectra clearly indicated that calcination at temperatures higher than 373 K leads to the generation of metallic Au which is the catalytically active site for selective glycerol oxidation to glycolic acid in water with molecular oxygen under mild reaction conditions.

Gold nanoparticles have been widely studied as highly active oxidation catalysts including CO oxidation, alcohol oxidation, epoxidation, and hydrogen peroxide synthesis, which afford environmentally benign reaction using molecular oxygen as an oxidant.[1,2] Mg–Al hydrotalcite, an anionic clay composed of $Mg_6Al_2(OH)_{16}CO_3$ is a superior basic support for a variety of metals such as platinum, ruthenium, and palladium.[3]

Recently, Kaneda et al. demonstrated oxidation of various monoalcohols and diols to the corresponding carbonyl compounds and lactones using hydrotalcite-supported gold (Au/HT) catalyst in the presence of molecular oxygen.[4] They prepared Au/HT by addition of reducing agents such as KBH_4 to form metal gold nanoparticles of 2.7 nm with narrow size distribution. The reaction mechanism for alcohol oxidation was proposed to be initiated by the proton abstraction from alcohol by a basic site of HT, formation of gold metal–alcolate intermediate and successive β-hydride elimination affording gold–hydride species. They also showed that particle size of Au plays key roles in the reaction, which means small gold particles exhibited high catalytic activity. A similar study was reported by Wang et al. for oxidant-free dehydrogenation of alcohols using Au/HT.[5] They used supported gold nanoparticles of 2.7 nm which were obtained by deposition–precipitation (DP) and successive calcination at 393 K. The oxidation state of gold of this active catalyst, which is expected to be an important factor for gold catalysis is however, unclear.

Oxidation of glycerol, a simple triol, has received much attention because of utilization of glycerol as a by-product from biodiesel manufacture.[6] Supported Au metal catalysts, e.g., Au/C are known to exhibit high catalytic activity for the reaction.[7–9] However, high oxygen pressure and addition of strong base (NaOH) are necessary to promote the reaction. The latter results in the formation of products as Na-salts, which requires excess energy consumption for purification of products in free form. In these regards, glycerol oxidation in water without addition of homogeneous base under ambient oxygen pressure would be desirable.

Here we synthesized hydrotalcite-supported gold nanoparticles by DP and successive heat treatment at various temperatures from room temperature to 473 K. Effect of calcination temperature on both particle size and oxidation state of gold were investigated. In addition, their oxidation activity was evaluated by base-free glycerol oxidation in pure water with molecular oxygen.

Au/HT was synthesized as follows.[10] Hydrotalcite (Mg/Al = 5, 1.0 g) was added to aqueous solution (100 mL) containing $HAuCl_4 \cdot 4H_2O$ (0.25 mmol). After stirring for 2 min, 1 mL of 25% NH_3 (aq) was added followed by 2 h stirring at room temperature. The resulting solid was collected by filtration and washed with deionized water. Finally, the solid catalyst was obtained after drying in air at various temperatures from room temperature to 473 K for 12 h. The amount of loaded Au was determined to be 4.56 wt% by ICP.

The X-ray diffraction measurement confirmed that crystal structure of Au/HT is identical to that of parent HT. Figure 1 shows TEM images of Au/HT calcined at various temperatures, indicating that small Au particles were well dispersed on HT for all samples (see also Supporting Information (SI), Figure S1[10]). The size distributions of Au species are also shown in Figure 1. The uncalcined sample (room temperature) has the smallest Au particles of 2.0 nm among samples prepared. The average particle size increased from 2.2 to 4.8 nm by calcination from 323 to 473 K. The size distributions of Au were also influenced

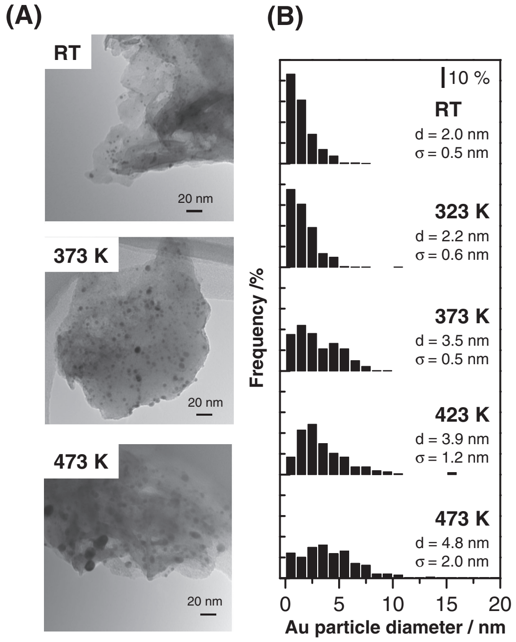


Figure 1. TEM images (A) and Au particle size distributions (B) of hydrotalcite-supported gold catalysts (Au/HT) prepared at various calcination temperature.

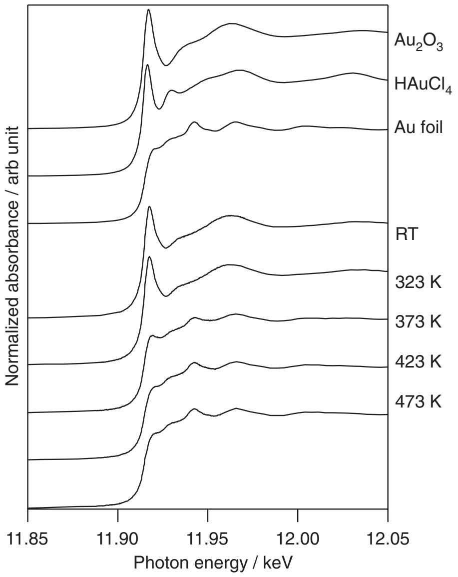


Figure 2. Au L_{III}-edge XANES spectra for Au/HT catalysts.

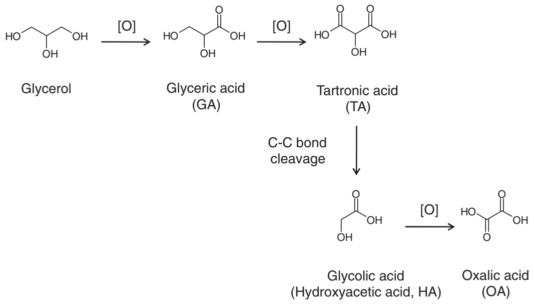
Table 1. Average particle size and metal concentration of hydrotalcite-supported gold prepared by calcination at various temperatures

Calcination temp/K	Au average particle size/nm[a]	Au oxidation state/%[b]	
		Au^0	Au^{3+}
RT	2.0	0	100
323	2.2	0	100
373	3.5	80	20
423	3.9	100	0
473	4.8	100	0

[a]Estimated from TEM measurements. [b]Estimated from the intensity of white line at Au L_{III}-edge XANES.

with increase of average particle size on calcination. Above 423 K, large particles over 10 nm could be observed, resulting in wide size distribution.

The oxidation state of Au on HT was determined by using XAFS. XANES provides powerful information of the oxidation state of gold species.[11] In particular, for the case of HT, this analysis is very powerful compared with XPS spectroscopy. XPS spectra for Au/HT have the peaks of Au^{3+} at 86.0 (Au $4f_{7/2}$) and 89.7 eV (Au $4f_{5/2}$), which should be overlapped with the big peak of Mg 2s at ca. 90 eV, resulting in difficulty in deconvolution.[12] Figure 2 shows Au L_{III}-edge XANES spectra for Au/HTs prepared at various calcination temperatures. Au metal foil, Au_2O_3, and $HAuCl_4$ were used as references with known oxidation state. For samples uncalcined (dried in vacuo at room temperature) and calcined at 323 K, Au species remained completely oxidized Au^{3+}. A significant change of the spectra was clearly observed for samples calcined at temperatures higher than 373 K. The portion of each Au species and particle sizes were described in Table 1. Sample calcined at 373 K have high concentration of Au^0 (80%) along with cationic Au^{3+} species. Increase of calcination temperature increased the portion of Au^0, resulting in up to 100% Au^0 for samples calcined at 423 and 473 K.



Scheme 1. A possible reaction pathway of glycerol oxidation.

Table 2. Glycerol oxidation using hydrotalcite-supported gold catalysts in water in the presence of oxygen[a]

Entry	Catalyst	Calcination temp/K	Conv./%	Selectivity/%			
				GA[b]	TA[c]	HA[d]	OA[e]
1	Au/HT	RT	0	0	0	0	0
2	Au/HT	323	0	0	0	0	0
3	Au/HT	373	70	1	4	18	0
4[f]	Au/HT	373	78	0	0	53	15
5	Au/HT	423	71	0	3	22	0
6	Au/HT	473	76	0	3	24	0
7	Au/C[g]	—	0	0	0	0	0
8	HT[g]	—	0	0	0	0	0

[a]*Reaction conditions*: Glycerol (0.5 mmol), H_2O (5 mL), Au/HT (0.1 g), under O_2 flow (10 mL min^{-1}), 333 K, 6 h. [b]Glyceric acid. [c]Tartronic acid. [d]Hydroxyacetic acid (or Glycolic acid). [e]Oxalic acid. [f]293 K, 72 h. O_2 atmosphere. [g]0.1 g.

The addition of NH_3 to $HAuCl_4$ aqueous solution during the catalyst preparation could form amino–hydroxo or amino–hydroxo–aquo cationic complex $[Au(NH_3)_2(H_2O)_{2-x}(OH)_x]^{(3-x)+}$.[13,14] This complex with Au^{3+} species is thought to be stable on HT until calcination below 323 K, and decompose above 373 K, resulting in formation of gold metal Au^0.[13]

The catalytic activity of Au/HTs was evaluated for glycerol oxidation in water with molecular oxygen.[10] The reaction was performed using 0.5 mmol of glycerol, 5 mL of water, and 0.1 g of Au/HT at 333 K for 6 h. All experiments were carried out in a Schlenk tube attached to a reflux condenser under O_2 flow (10 mL min^{-1}). After the reaction, the vessel was cooled to room temperature, and the catalyst was separated by filtration. The conversions and yields were estimated using high-performance liquid chromatography (HPLC). Oxidation of glycerol afforded a variety of products including glyceric acid (GA), tartronic acid (TA), glycolic acid (another name; hydroxyacetic acid (HA)), and oxalic acid (OA) as shown in Scheme 1. Glycolic acid is a useful chemical for skin care products, intermediates for organic synthesis, monomer for biocompatible copolymers, and food additives,[6] which is formed by C–C bond cleavage of tartronic acid.

Table 2 lists the results of glycerol oxidation using Au/HT under mild reaction conditions. Au/C showed no activity under the same conditions due to lack of base. Hydrotalcite itself also did not transform glycerol (Entry 8). The samples prepared by calcination below 323 K showed no activity for the reaction

(Entries 1 and 2). In contrast, the samples prepared by calcination at temperatures higher than 373 K exhibited high glycerol conversion over 70% (Entries 3–6). Increase of calcination temperature improved gold metal concentration and glycerol conversion. The main product was glycolic acid (hydroxyacetic acid, HA) with approximately 20% selectivity. C_3 products (sum of glyceric acid and tartronic acid) were slightly obtained after the reaction. Davis et al. examined glycerol oxidation using Au/C under high O_2 pressures in the presence of NaOH and revealed that hydrogen peroxide was produced during the reaction under highly basic conditions, leading to the formation of glycolic acid via C–C bond cleavage.[15] Furthermore, Hutchings et al. demonstrated glycerol oxidation using Au/C in the presence of NaOH with hydrogen peroxide as an oxidant. They also obtained glycolic acid selectively and proposed a reaction mechanism for glycolic acid formation by the decarboxylation of tartronic acid.[16] Actually, we have detected CO_2 formation by trapping in $Ba(OH)_2$ aqueous solution. They also showed high reaction temperature leads to decomposition of hydrogen peroxide, resulting in low yield of glycolic acid. Accordingly, we tested glycerol oxidation at low temperature, affording high selectivity toward glycolic acid (53%) at high glycerol conversion (78%) at 293 K (Entry 4). This suggests that the basicity of hydrotalcite functioned as not only promoter by proton abstraction of the alcohol but also as in situ generator of hydrogen peroxide.[17] We should consider other products for the glycerol oxidation. Formic acid, acetic acid, and lactic acid were not detected, indicating that base-catalyzed degradation of glycelaldehyde did not occur.[15] One possible explanation is adsorption of tartronic acid on HT.[10] Tartronic acid well adsorbed on HT whereas glyceric acid and glycolid acid partly adsorbed because of these acidities ($pK_a = 2.37$ (pK_{a1}), 3.52, and 3.83 for tartronic acid, glyceric acid, and glycolic acid, respectively). Therefore, rapid decarboxylation of tartronic acid should be necessary to improve glycolic acid selectivity.

In summary, hydrotalcite-supported gold nanoparticle catalysts were synthesized by simple deposition–precipitation and successive calcination. Without calcination, 2.0 nm average gold particles were deposited on hydrotalcite. It was found that average particle size and size distribution of gold on hydrotalcite gradually increased with increase of calcination temperature. XANES revealed that uncalcined Au/HT has totally cationic Au species and calcination at temperatures higher than 373 K afforded reduction of Au cation to metal, which is catalytically active for oxidation of glycerol. Au/HT was found to transform glycerol to glycolic acid in water with molecular oxygen through C–C bond cleavage. Low-temperature reaction afforded high selectivity of glycolic acid at high glycerol conversion. Hydrotalcite as basic support for nanosized gold catalyst may play important roles in promotion of alcohol oxidation and formation of Au–alcolate intermediate.

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17 Glycerol oxidation using Au/HT calcined at 473 K with hydrogen peroxide was performed (*Reaction conditions*: glycerol (0.5 mmol), H_2O_2 (0.5 mmol), H_2O (5 mL), Au/HT (0.1 g), 333 K, 6 h)). Low glycerol conversion (14%) with 19% selectivity of glyceric acid, 6% of tartronic acid and trace amount of glycolic acid were obtained due to rapid decomposition of H_2O_2. In situ generation of H_2O_2 with aldehyde formation by alcohol oxidation would be beneficial to high activity.