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Selective Oxidation of Glycerol by Using a Hydrotalcite-Supported Platinum Catalyst under Atmospheric Oxygen Pressure in Water

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A hydrotalcite-supported platinum (Pt/HT) catalyst was found to be a highly active and selective heterogeneous catalyst for glycerol oxidation in pure water under atmospheric oxygen pressure in a high glycerol/metal molar ratio up to 3125. High selectivity toward glyceric acid (78 %) was obtained even at room temperature under air atmosphere. The Pt/HT catalyst selectively oxidized the primary hydroxyl group of 1,2-propandiol to give the corresponding carboxylic acid (lactic acid) as well as glycerol. The activity of the catalyst was greatly influenced by the Mg/Al ratio of hydrotalcite. Glycerol conversion increased with increasing the Mg/Al ratio of hydrotalcite (from trace to 56 %). X-ray absorption fine structure (XAFS) measurements indicated that the catalytic oxidation activity was proportional to the metallic platinum concentration, and more than 35 % of metallic platinum was necessary for this reaction. TEM measurements and titration analysis by using benzoic acid suggested that the solid basicity of hydrotalcite plays important roles in the precise control of platinum size and metal concentration as well as the initial promotion of alcohol oxidation.

Introduction

Alternative energy resources are becoming important because of decreasing petroleum reserves and increasing environmental concerns. In this regard, biomass is an intriguing candidate as a renewable and carbon neutral resource.[1] As a biomass-derivative, glycerol is currently produced in a large amount as a byproduct in manufacturing biodiesel by transesterification of vegetable oils. Biodiesel producers will soon look to new applications to convert the byproduct glycerol into value-added products to make the biodiesel industry economically more attractive.[2] Furthermore, glycerol is a highly functionalized molecule and a large number of valuable compounds can be obtained by oxidation, hydrogenolysis, dehydration, esterification, transesterification, polymerization, and so forth.[3]

Oxidation reactions are important for the synthesis of fine chemicals. In particular, the oxidation of alcohols and polyols to chemical intermediates represents a challenging target. Oxidation of glycerol leads to a large number of compounds, including glyceraldehyde, glyceric acid, glycolic acid, tartronic acid, and oxalic acid (Scheme 1) and a key problem is concerned with the selectivity of desired compound. Therefore, control of the reaction selectivity by careful design of the catalyst is required. In this regard, supported platinum, palladium, gold, and bimetallic (Au–Pd) catalysts have been extensively studied for the oxidation of glycerol in the presence of oxygen.[4–8] Most of these catalysts are highly efficient, but are limited the use of high oxygen pressures and homogeneous bases. Oxidations of glycerol over gold-based catalysts were totally inactive in the absence of the base NaOH. Furthermore, glyceric acid is the main product in the oxidation of glycerol obtained in the form of sodium salt, which requires additional neutralization and acidification to get the free glyceric acid. From the environmental and green chemistry point of view, homogeneous bases should not be used. Very recently, the oxidation of glycerol in water without the addition of base was examined.[9, 10] Zheng et al. used Pt/multiwall carbon nanotubes for base-free glycerol oxidation under O_2 flow in water.[9] In contrast, Prati et al. performed glycerol oxidation in water by using an acidic zeolite as a support for Au–Pt nanoparticle catalysts.[10] In both cases, high glycerol conversion (70 %) and high glyceric acid selectivity (70–80 %) were achieved, but glycerol/metal molar ratios were low (below 500) and the zeolite reaction was carried out under 3 atm O_2 pressure.

Hydrotalcites, a family of anionic clays, present positively charged brucite-like layers ($Mg(OH)_2$) in which some of Mg^{2+} is replaced by Al^{3+} in the octahedral sites of the hydroxide sheets. Mg–Al hydrotalcite itself was used as the catalyst for base-catalyzed reactions, in particular, aldol condensations, the Knoevenagel reaction, epoxidations, and transesterifications.[11, 12] Metal-supported hydrotalcite catalysts have immense importance in the field of catalysis, especially for the oxidation of alcohols in the presence of oxygen under more

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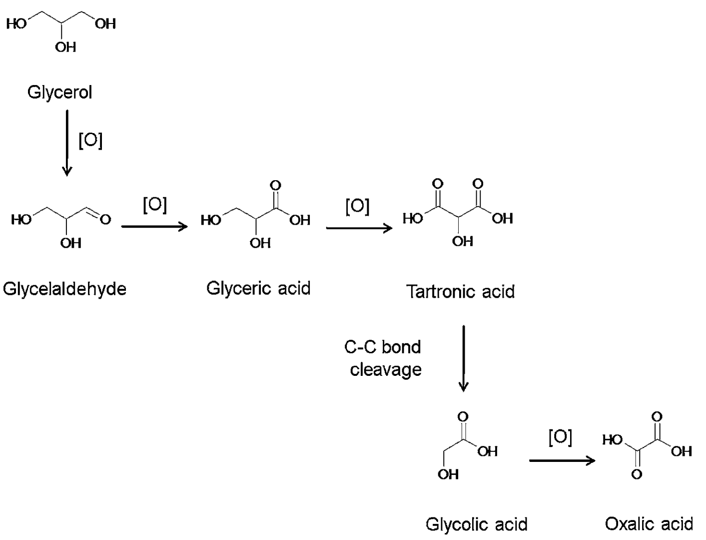

Scheme 1. A possible reaction pathway of glycerol oxidation.

environmentally friendly conditions.[13] Herein, a simple approach to replace homogeneous bases with heterogeneous bases has been demonstrated. We reveal that basic hydrotalcite-supported platinum nanoparticles (Pt/HT) are highly active and selective heterogeneous catalysts for glycerol oxidation at high glycerol/metal molar ratios (800–3125) in water without the addition of any homogeneous base under atmospheric oxygen pressure.

Results and Discussion

Glycerol oxidation by using gold and platinum catalysts supported on carbon and HT

Pt/HT catalyst was prepared by adsorbing $H_2PtCl_6{\cdot}6H_2O$ on HT in water and subsequent metal reduction by using formaldehyde under reflux conditions. An X-ray diffraction measurement confirmed that the crystal structure of Pt/HT was identical to that of unsupported HT. The amount of loaded Pt was estimated to be 0.64 wt %, as determined by inductively coupled plasma atomic emission spectroscopy.

Glycerol oxidation was performed by using gold and platinum catalysts supported on commercial carbon and hydrotalcite. The reaction was carried out in water at 363 K with a very low glycerol/metal molar ratio of 20. The results are shown in Figure 1. Although no activity was found for Au/C, the addition of NaOH (NaOH/glycerol = 2) led to glycerol conversion.[14] The addition of base is essential for selective oxidation of glycerol because of initial dehydrogenation through proton abstraction from primary hydroxyl groups.[5] In contrast, an HT-supported gold catalyst (Au/HT) could oxidize glycerol without NaOH addition and reached 100 % glycerol conversion. A significant difference was clearly observed between Au/C and Au/HT, which suggested that HT, an efficient solid base support, had enough basicity for glycerol oxidation.

Comparison of glycerol oxidation activity for Pt/HT, Au/HT, Ru/HT, and Pd/HT catalysts

The catalytic activity of a variety of metal supported on HT, including Pt/HT, Au/HT, Pd/HT, and Ru/HT was compared at 333 K. The results indicated that the Pt/HT catalyst exhibited the highest catalytic activity among those tested: Pt > Au > Pd > Ru (Figure 2).

Selective glycerol oxidation in water under ambient oxygen pressure by using Pt/HT

Table 1 shows the catalytic performance of Pt/HT for selective glycerol oxidation. A variety of supports, including carbon, HT, $Mg(OH)_2$, Al_2O_3, and SiO_2, were compared (Table 1, entries 1, 6–9) under the same reaction conditions with a glycerol/metal molar ratio of 800. Among them, Pt/HT exhibited highest conversion (55 %) with remarkable selectivity of glyceric acid (75 %) (Table 1, entry 1). The activity was much higher than that of Pt/$Mg(OH)_2$, Pt/Al_2O_3, Pt/SiO_2, and Pt/C (Table 1, entries 6–9). For Pt/Al_2O_3, Pt/C, and Pt/SiO_2, glycerlaldehyde formation was observed to-

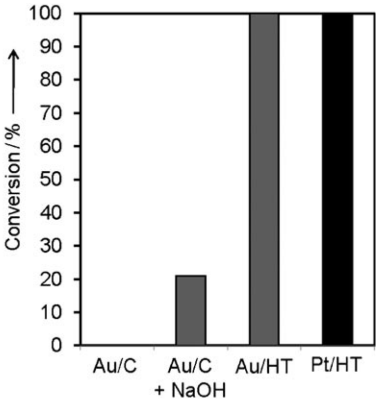

Figure 1. Glycerol oxidation in water by using supported metal catalysts with molecular oxygen. Reaction conditions: glycerol (0.5 mmol), H_2O (5 mL), glycerol/metal = 20 (mol/mol), under O_2 flow (100 mL min^{-1}), 393 K, 6 h.

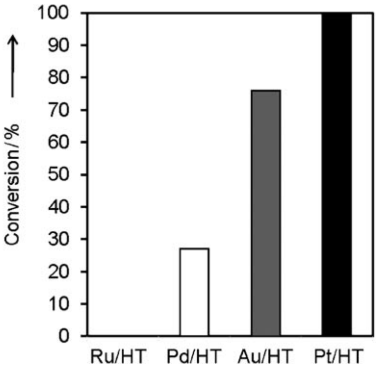

Figure 2. Glycerol oxidation in water by using HT-supported metal catalysts with molecular oxygen. Reaction conditions: glycerol (0.5 mmol), H_2O (5 mL), glycerol/metal = 20 (mol/mol), under O_2 flow (100 mL min^{-1}), 333 K, 6 h, HT (Mg/Al = 5).

Table 1. Base-free glycerol oxidation with molecular oxygen in water by using supported platinum catalysts.[a]

Entry	Catalysts	Conversion [%]	Selectivity [%]		
			GA	GLA	TA
1	Pt/HT[b]	55	75	0	5
2[c]	Pt/HT[b]	54	74	0	3
3[d]	Pt/HT[b]	40	74	0	12
4[e]	Pt/HT[b]	16,[f] 47	96,[f] 78	0,[f] 0	0,[f] 3
5	Pt/HT[b,g]	0	0	0	0
6	Pt/$Mg(OH)_2$	18	85	0	0
7	Pt/Al_2O_3[h]	9	28	58	trace
8	Pt/C[h]	5	51	49	0
9	Pt/SiO_2[h]	8	21	76	trace
10	Au/HT	0	0	0	0
11	Pd/HT	0	0	0	0
12	Ru/HT	0	0	0	0
13	blank	0	0	0	0

[a] Reaction conditions: glycerol (0.5 mmol), H_2O (5 mL), glycerol/metal = 800 (mol/mol), under O_2 flow (10 mL min^{-1}), 333 K, 6 h. GA = glyceric acid. GLA = glycelaldehyde. TA = tartronic acid. [b] 0.64 wt% Pt. Mg/Al = 5. [c] Glycerol/metal = 2500, 363 K, 24 h. [d] Glycerol/metal = 3125, 363 K, 24 h. [e] Glycerol/metal = 625, 303 K, 6 h, air atmosphere. [f] 1 h. [g] Unreduced. Without the use of formaldehyde during catalyst preparation. [h] 1 wt% Pt. Purchased from Sigma–Aldrich.

gether with glyceric acid (Table 1, entries 7–9). Under our HPLC measurement conditions, the peak of glycelaldehyde was detected as a shoulder of the peak of glyceric acid at low glycerol conversions. At the initial stages of the oxidation reaction, glycerlaldehyde could be formed for all cases. These results were obtained by slow oxidation at low conversions. Pt/HT could catalyze this reaction at high glycerol/metal ratios of 2500 and 3125 (Table 1, entries 2 and 3). High glycerol conversion with high glyceric acid selectivity was achieved even at high glycerol/metal ratios at 363 K for 24 h with high turnover numbers of at least 1350. It should be noted that Pt/HT selectively gave glyceric acid even at 303 K under air atmosphere as shown in Figure 3 (Table 1, entry 4). At the initial stages of the reaction (1 h), a considerably high selectivity of glyceric acid (96%) was obtained. With an increased reaction time, the glycerol conversion increased and the selectivity of glyceric acid gradually decreased. Unreduced Pt/HT obtained without the use of formaldehyde, however, showed no activity (Table 1, entry 5). Again, Pt metal was found to be best catalyst for glycerol oxidation. When the glycerol/metal ratio was 800, Au/HT, Pd/HT, and Ru/HT showed no activity (Table 1, entries 10–12). These results clearly indicate that a platinum catalyst affords much higher activity than gold. In addition, HT is a desirable support for selective oxidation of glycerol towards glyceric acid under such moderate reaction conditions, including base-free and atmospheric O_2 pressure. For the elucidation of the reaction mechanism, the addition of a radical scavenger, 4-*tert*-butylpyrocatechol, to the reaction medium hardly influenced the oxidation of glycerol, which indicated that oxidation of glycerol did not proceed by a radical mechanism. The Pt/HT catalyst selectively oxidized the primary alcohol group of the diol (1,2-propanediol) as well as the triol (glycerol). Lactic acid was obtained from 1,2-propanediol with a high selectivity (over 70%; see Figure S1 in the Supporting Information).

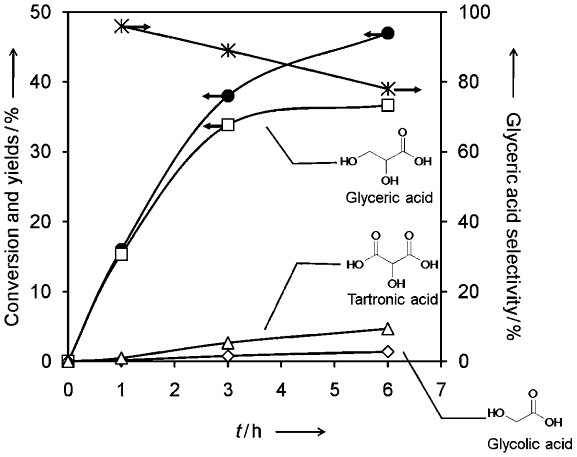

Figure 3. Time course of glycerol oxidation over Pt/HT in water at 303 K under an air atmosphere. Reaction conditions: glycerol (0.5 mmol), H_2O (5 mL), Pt/HT (0.64 wt%; Mg/Al = 5), glycerol/metal = 625 (mol/mol), air atmosphere, 303 K. ●: glycerol conversion, □: glyceric acid yield, △: tartronic acid yield, ◇: glycolic acid yield, and *: glyceric acid selectivity.

Recyclability of the HT-supported platinum catalyst for glycerol oxidation

The catalysts could be reused at least four times without the loss of activity. The same glycerol conversion and glyceric acid selectivity were obtained after the third reuse (55% glycerol conversion and 75% glyceric acid selectivity). TEM images of the reused catalyst showed no significant changes to the Pt particle size or the morphology of support (see below). We simply used uncalcined HT as the support. This type of HT could be reused as the base catalyst for several reactions, including transesterification,[12a] isomerization,[12b] and epoxidation with aqueous hydrogen peroxide,[11a] without the loss of activity. XRD measurements revealed that the crystal structure of HT remained unchanged after the reaction (Figure 4).

The possibility of platinum leaching was confirmed by successive reactions after removal of solid catalyst from the solution. The reactions were performed under the following conditions: 0.1 M aqueous solution of glycerol (5 mL) and Pt/HT catalyst (0.64 wt%; glycerol/Pt molar ratio = 800) at 333 K under an

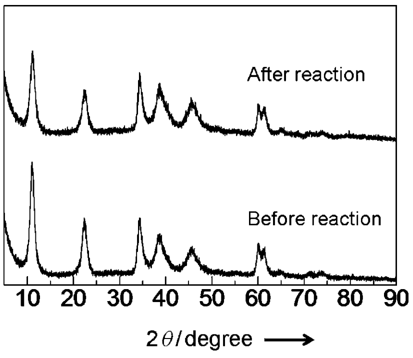

Figure 4. XRD patterns for the Pt/HT catalyst before and after the reaction.

oxygen flow (10 mL min^{-1}). A glycerol conversion of 21.5 % of with >99 % selectivity for glyceric acid was obtained after reaction for 3 h in the presence of Pt/HT. After the quick removal of the Pt/HT catalyst by filtration, the aqueous solution remained at 333 K with stirring under an oxygen flow for a further 3 h, resulting in same glycerol conversion (21.6 %) and glyceric acid selectivity (>99 %). This result indicates that this oxidation is performed over heterogeneous Pt catalyst.

Effect of the initial glycerol concentration on catalytic activity

In addition, experiments at higher glycerol concentrations (0.2 and 0.3 M) were carried out by using Pt/HT (0.64 wt %; Mg/Al = 5) at 343 K for 3 h under an oxygen flow (10 mL min^{-1}) in which the glycerol/Pt molar ratio was fixed at 2380 (Table 2).

Table 2. Effect of initial glycerol concentration on glycerol oxidation by using HT-supported platinum catalysts with molecular oxygen.[a]

Initial glycerol concn [M]	Conversion [%] (glycerol consumed [mmol])	Yield [mmol] GA (selectivity [%])[b]	TA[c]	HA[d]	OA[e]	Sum [%][f]
0.1	34.0 (0.17)	0.13 (76)	trace	0.02	0.01	94
0.2	52.3 (0.52)	0.24 (46)	0.01	0.06	0.02	63
0.3	46.1 (0.69)	0.25 (36)	0.01	0.08	0	50

[a] Reaction conditions: Pt/HT (0.64 wt %), glycerol/metal = 2380 (mol/mol), H_2O (5 mL), under O_2 flow (10 mL min^{-1}), 343 K, 3 h. [b] GA = glyceric acid. [c] TA = tartronic acid. [d] HA = glycolic acid (hydroxyacetic acid). [e] OA = oxalic acid. [f] (Sum of the products, including glyceric acid, tartronic acid, glycolic acid, and oxalic acid)/amount of glycerol consumed × 100.

The amount of glycerol consumed increased with increasing the initial glycerol concentration. The amount of glyceric acid produced increased from 0.13 to 0.24 mmol on going from 0.1 to 0.2 M solutions, and then reached a plateau (0.24 to 0.25 mmol from 0.2 to 0.3 M solutions). The selectivity towards glyceric acid decreased with increasing the glycerol concentration (76, 46, and 36 % for 0.1, 0.2, and 0.3 M initial glycerol concentrations, respectively). In contrast, glycolic acid formation gradually increased with increasing the initial glycerol concentration. The sum of the products, including glyceric acid, tartronic acid, glycolic acid, and oxalic acid, was nearly equal (94 %) to the glycerol conversion for the case of 0.1 M glycerol oxidation. However, at higher glycerol concentration, the sum of the four products was lower than the glycerol conversion (63 and 50 % for 0.2 and 0.3 M glycerol oxidation, respectively). These results indicated that overoxidation (e.g., CO_2 formation) occurred at higher glycerol concentrations.

Effect of HT as a support on glycerol oxidation

We further examined the effect of HT as a support on glycerol oxidation by varying the Mg/Al ratio (Mg/Al = 3–6) of HTs that were prepared by a conventional coprecipitation method. Table 3 lists the glycerol oxidation activity obtained when using Pt/HTs with various Mg/Al ratios. Interestingly, the activity of the catalyst was greatly influenced by the HT Mg/Al ratio.

Table 3. Glycerol oxidation in water by using HT-supported platinum catalysts with molecular oxygen.[a]

Catalyst	Conversion [%]	Selectivity [%] GA	GLA	TA
Pt/HT (Mg/Al = 3)	trace	N. D.	N. D.	N. D.
Pt/HT (Mg/Al = 4)	8	94	0	trace
Pt/HT (Mg/Al = 5)	55	75	0	5
Pt/HT (Mg/Al = 6)	56	70	0	9

[a] Reaction conditions: glycerol (0.5 mmol), H_2O (5 mL), 0.64 wt % Pt/HT, glycerol/metal = 1250 (mol/mol), under O_2 flow (10 mL min^{-1}), 333 K, 6 h. N. D. = not detected. GA = glyceric acid. GLA = glycelaldehyde. TA = tartronic acid.

Glycerol conversion increased with increasing the HT Mg/Al ratio (from trace to 56 %). The Pt/HTs with Mg/Al ratios of 5 and 6 showed high glycerol conversions with high selectivity towards glyceric acid. We have further examined glycerol oxidation under different reaction conditions (at a higher glycerol/Pt ratio of 2380 and 343 K) to compare the catalytic activity of Mg/Al = 5 and Mg/Al = 6. The time course of product distribution is shown in Figure 5. Although higher glycerol conversion was observed for the catalyst with Mg/Al = 6 at the initial stages of the reaction, the glyceric acid yield and selectivity were almost the same between the two catalysts over the reaction time monitored.

Oxidation state and particle size of Pt nanoparticles supported on HT

Pt nanoparticles on HT were characterized by using X-ray absorption fine structure (XAFS) and transmission electron microscopy (TEM) measurements to examine the oxidation state and particle size distribution. The intensity of the white line at the Pt L_{III}-edge XANES spectra gives us valuable information for the oxidation state of platinum.[15] Figure 6 shows Pt L_{III}-edge XANES spectra for Pt/HTs and the results are listed in Table 4; these results indicate that the concentration of Pt^0 increased with increasing the Pt/HT Mg/Al ratio. It was found that glycerol conversion was proportional to the Pt^0 concentration of the Pt/HT catalysts, and more than 35 % of Pt^0 was necessary for this reaction. TEM measurements revealed that the average size of supported Pt was approximately 2 nm for all samples (Table 4 and Figure 7). The size distribution of Pt was, however, very different for the Pt/HTs (Figure 8). Pt particle size distribution gradually increased with increasing the Mg/Al ratio of HT. Table 4 also includes the basicity of HT estimated by ti-

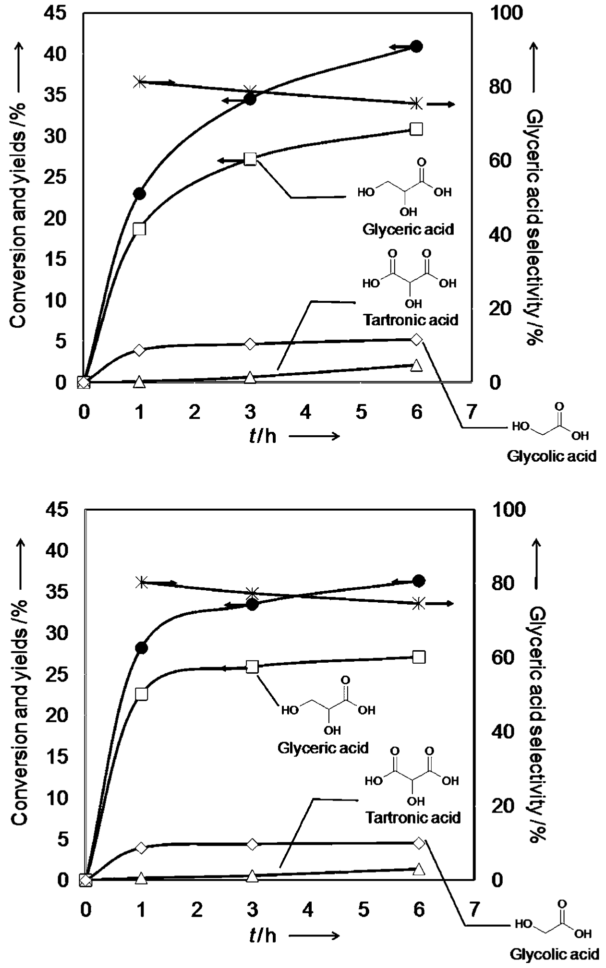

Figure 5. Time course of glycerol oxidation over Pt/HT with Mg/Al = 5 (top) and 6 (bottom) in water under air atmosphere. Reaction conditions: Pt/HT (0.64 wt%; Mg/Al = 5 and 6), glycerol/Pt = 2380 (mol/mol), H_2O (5 mL), under an oxygen flow (10 mL min^{-1}), 343 K. ●: glycerol conversion, □: glyceric acid yield, △: tartronic acid yield, ◇: glycolic acid yield, *: and glyceric acid selectivity.

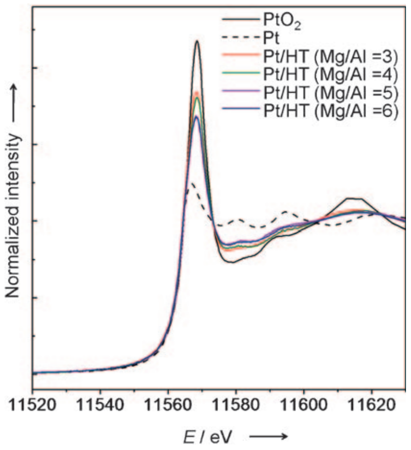

Figure 6. Pt L_{III}-edge XANES spectra for Pt/HT catalysts.

Table 4. Oxidation state and particle size of Pt nanoparticles supported on Pt/HT catalysts and their solid basicity.

Catalysts	Pt^0 [%][a]	Pt average size[b] [nm]	Base amount[c] [mmol]
Pt/HT (Mg/Al = 3)	35	2.1	0.11
Pt/HT (Mg/Al = 4)	39	2.1	0.11
Pt/HT (Mg/Al = 5)	52	2.1	0.16
Pt/HT (Mg/Al = 6)	54	2.5	0.18

[a] Estimated from the intensity of the white line at the Pt L_{III}-edge XANES spectra. [b] Determined by TEM. [c] Determined by titration with benzoic acid.

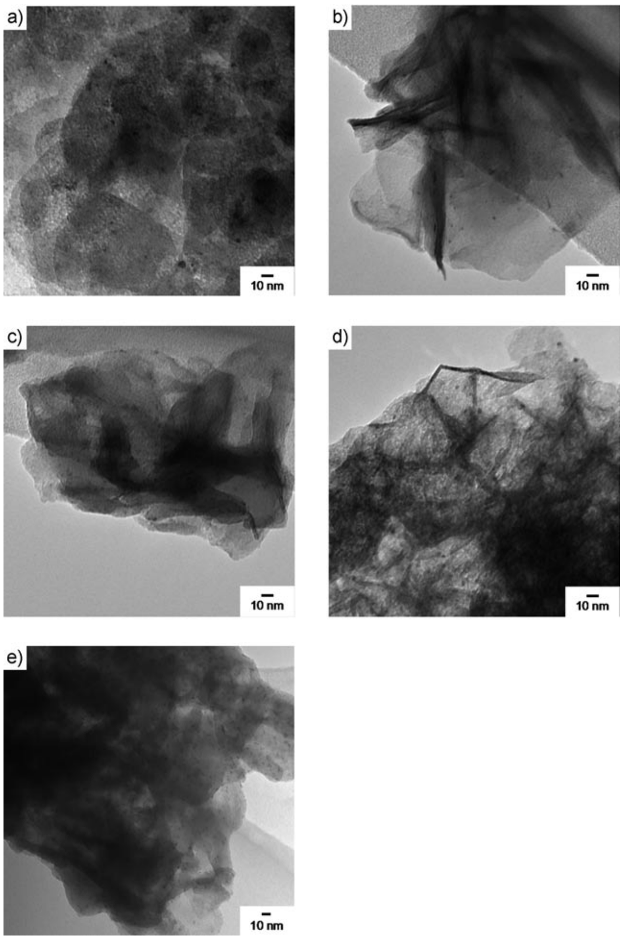

Figure 7. TEM images of HT-supported platinum catalysts. a) Pt/HT (Mg/Al = 3), b) Pt/HT (Mg/Al = 4), c) Pt/HT (Mg/Al = 5), d) Pt/HT (Mg/Al = 6), and e) Pt/HT (Mg/Al = 5) after the reaction.

tration with benzoic acid,[11] indicating that the basicity of Pt/HTs increased with increasing the Mg/Al ratio.

By considering the Pt size distributions and the basicity of the Pt/HTs, clear differences in Pt^0 concentration among the Pt/HTs could be explained as follows: First, H_2PtCl_6 was adsorbed on basic HT to form $Pt(OH)_xCl_{6-x}$ as Pt hydroxide.[16] The size of this Pt hydroxide should be influenced by the basicity of the HTs. Small Pt hydroxide particles could be formed on

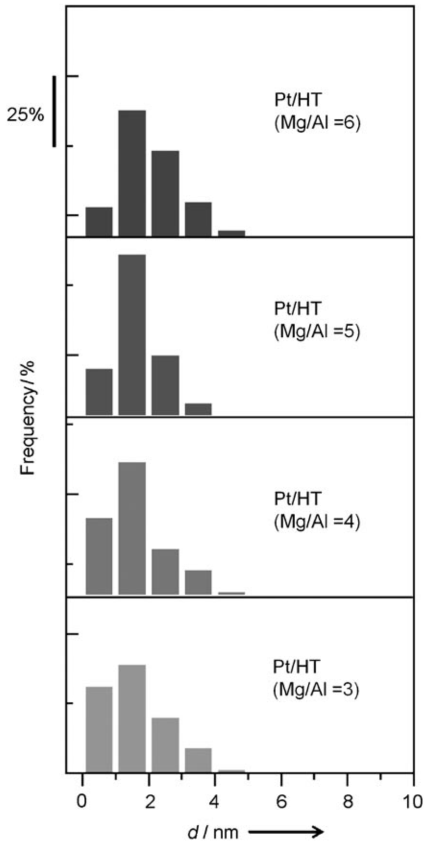

Figure 8. Pt particle size distribution of the Pt/HT catalysts estimated from TEM measurements.

HTs with low Mg/Al ratios, and large ones on HTs with high Mg/Al ratios. Reflux in aqueous formaldehyde resulted in the formation of Pt^0 from Pt hydroxide species for all cases. However, the surface of Pt^0 could be immediately oxidized when exposed to air,[17] which greatly affects small Pt particles. Therefore, Pt/HTs with low Mg/Al ratios (3 and 4) have small Pt particles with low Pt^0 concentrations, resulting in poor activity. In contrast, Pt/HTs with high Mg/Al ratios (5 and 6) have relatively large Pt particles with high Pt^0 concentrations and enough basicity to give good activity. These two characteristics of Pt^0 concentration and HT basicity are advantageous to produce good Pt/HT catalysts for the oxidation of glycerol.

Conclusion

Base-free selective glycerol oxidation in water with molecular oxygen was successfully demonstrated by using Pt/HT catalysts under mild conditions. Pt/HT catalysts selectively afforded glyceric acid with high activity, even at high glycerol/metal molar ratios of up to 3125 under atmospheric oxygen pressure. This remarkable catalytic activity was attributable for the precise control of Pt^0 concentration and solid basicity of the support.

Experimental Section

Materials: $H_2PtCl_6{\cdot}6H_2O$ (99.9%), $HAuCl_4{\cdot}4H_2O$ (99.9%), $PdCl_2$, aqueous formaldehyde solution (36%), $Mg(NO_3)_2{\cdot}6H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, $Na_2CO_3{\cdot}10H_2O$, KCl, and activated carbon (Norit SX Plus) were purchased from Wako Pure Chemicals. Pt/Al_2O_3 (platinum, 1 wt% on alumina, dry), Pt/C (platinum, 1 wt% on activated carbon), Pt/SiO_2 (platinum, 1 wt% silica granules, dry), and $RuCl_3{\cdot}nH_2O$ (99.98%) were supplied from Sigma–Aldrich. NaOH and $NaBH_4$ (90.0%) were obtained from Kanto Chemicals.

Preparation of HT: Mg/Al HTs (Mg/Al = 3–6) were prepared as follows: $Mg(NO_3)_2{\cdot}6H_2O$ (30–60 mmol) and $Al(NO_3){\cdot}6H_2O$ (10 mmol) were dissolved in water (100 mL). The aqueous solution containing Mg and Al ions was added to an alkaline solution composed of $Na_2CO_3{\cdot}10H_2O$ (30 mmol) and water (100 mL) by using peristaltic pump at speed of 1 mL min^{-1} at room temperature. During the addition of Mg and Al ions, the pH value of the solution was maintained at 10 by adding a 1 M aqueous solution of NaOH. After aging for 1 h at 338 K, the white solid was filtered off and washed with excess water (2 L) to remove sodium ions. The obtained solid was dried at 373 K in an oven overnight.

Preparation of Pt/HT: HT (Mg/Al = 5, 0.54 g) was added to an aqueous solution containing $H_2PtCl_6{\cdot}6H_2O$ (2.5 mM, 11 mL). After stirring overnight at room temperature, aqueous formaldehyde (36%, 1 mL) was added as a reducing agent and the solution was vigorously stirred for 30 min. Then, the temperature increased to 373 K and the solution was stirred for 30 min to reduce Pt species. The resulting solid was recovered by filtration and washed with deionized water. Finally, the gray-colored solid catalyst was obtained after drying in oven at 373 K overnight.

Preparation of Au/HT and Ru/HT catalysts: Au/HT and Ru/HT were prepared by same method as that used for the synthesis of Pt/HT. $HAuCl_4{\cdot}4H_2O$ and $RuCl_3{\cdot}nH_2O$ were used as starting reagents for Au/HT and Ru/HT, respectively.

Preparation of Au/C: Au/C was prepared according to the literature.[5] $HAuCl_4{\cdot}4H_2O$ (50 mM $HAuCl_4$, 10 mL) was dropped into water (90 mL) containing activated carbon (1.0 g, Norit SX Plus) at a speed of 1 mL min^{-1} with vigorous stirring. After stirring 30 min, aqueous formaldehyde (10 mL) was added and the solution was further stirred for 30 min. Then, the temperature was increased to 373 K and kept for 30 min with stirring to reduce the Au species. The resultant solid was filtered off, washed with water, and dried at 373 K overnight.

Preparation of Pd/HT: Pd/HT was prepared according to the literature with a minor modification.[18] $PdCl_2$ (0.25 mmol) and KCl (2.5 mmol) were dissolved into water (500 mL), resulting in yellowish brown aqueous solution. HT (1.0 g) was added to the aqueous solution with stirring overnight. The resultant solid was filtered off, washed with water (300 mL), and dried at 373 K overnight. After the solid was redispersed into water, $NaBH_4$ (50 mM, 10 mL) was added to the solution at room temperature with vigorous stirring for 30 min. Then, the solid was again filtered off, washed with water, and dried overnight.

Characterization: Samples were characterized by XRD (RINT-2000, Rigaku), TEM (H-7100, Hitachi), and XAFS. Pt L_{III}-edge XAFS spectra were recorded at room temperature by the fluorescence method using a Si(111) monochromator at the BL01B1 station in the SPring-8 synchrotron radiation facility, Japan. The oxidation state of platinum was estimated from the height intensity of the white line at the Pt L_{III}-edge XANES by using a linear relationship in which the intensities of PtO_2 and Pt foil were assigned to be 0 and 100% Pt^0, respectively.

Selective oxidation of glycerol: The reaction was typically performed by using glycerol (0.5 mmol), water (5 mL), and adequate amount of supported metal catalyst at 333 K for 6 h. All experiments were carried out in a Schlenk tube with a reflux condenser attached under O_2 flow (typically 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 by using HPLC (Waters) with an Aminex HPX-87H column from Bio-Rad Laboratories. Samples were diluted with water before each HPLC measurement. The products were analyzed by using a refractive index (RI) detector. 20 μL of each sample was injected to HPLC for analysis. The concentrations of the products were determined from calibration curves obtained with reference samples. The analysis conditions were set as follows: eluent, 10 mM H_2SO_4; flow rate, 0.5 mL min^{-1}; column temperature, 323 K. We have calculated the selectivity of each product as follows. Selectivity (%) = amount of product (mmol)/amount of glycerol consumed (mmol) × 100 = product yield (%)/glycerol conversion (%) × 100.

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