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FULL PAPER

Oxidant-free Dehydrogenation of Glycerol to Lactic Acid by Heterogeneous Platinum Catalysts

S. M. A. H. Siddiki, [a] Abeda S. Touchy, [a] Kenichi Kon, [a] Takashi Toyao,[a,b] Ken-ichi Shimizu*[a,b]

Abstract: Among various supported metal nanoparticle catalysts, Pt-loaded carbon (Pt/C) catalysts, including a commercial one, showed the highest yield for selective dehydrogenation of glycerol to lactic acid (LA) under oxidant-free, solvent-free, and alkaline conditions. For the reaction with Pt/C, the effects of conditions (type of basic additives, the amount of water, atmosphere, reactor) on the catalytic activity and selectivity were studied. Combined with a reaction pathway in the literature and our result of control reactions, we proposed a strategy for decreasing the selectivity of byproducts. The optimized conditions gave a high turnover number (TON) of 69000. To clarify the structural factors affecting the catalytic activity, we show the effect of electronic states of various transition metals on the activity as well as the effect of Pt particle size on the turnover frequency (TOF) per surface Pt atom.

Introduction

Biodiesel fuel is manufactured by transesterification of renewable resources, triglycerides. Rapid increase in the production of biodiesel resulted in increasing production of glycerol as the byproduct. For upgrading of this waste material, a number of catalytic methods for glycerol conversion to chemicals (propanediols, lactic acid, etc.) have been developed.[1] Most of the known methods use O_2 or H_2 as reagents, which promote over-reduction or over-oxidation of the target product, resulting in low selectivity. The low selectivity is one of the most critical issue in the glycerol conversion.

Among the glycerol-derived products, lactic acid (LA) is important as it is a monomer of a commercial bioplastic, poly LA, with growing demand.[2] Industrially, LA is produced by fermentation of glucose, which has problems of low space-time yield, complicated purification and co-production of large amount of wastes. Recent studies [3-5] reported the synthesis of LA via oxidation of glycerol by O_2 with heterogeneous catalysts. Various transition-metal-based solid catalysts can promote the reaction. However, the methods[3-5] have a general drawback of low chemo-selectivity caused by oxidation of intermediates to side products (glyceric, tartronic, and glycolic acids) which are more thermodynamically stable than LA. [5a] To prevent the unselective oxidation reactions, recent efforts have been focused on oxidant-free[6,7] or O_2-free[8] dehydrogenation of glycerol to LA in alkaline conditions. Most of these studies used homogeneous catalysts,[6] such as Ir,[6a-c] Ru,[6d] Fe[6e] complexes, and the methods generally showed high selectivity to LA and high TON. Considering industrial application of the catalytic system, it is important to develop the oxidant-free method with heterogeneous catalysts, especially a commercially available heterogeneous catalyst. However, a few heterogeneous catalysts[7] reported so far have serious problem of low selectivity to LA due to the formation of 1,2-propanediol and C1-C3 alcohols as side products as well as lower TON than the homogeneous catalysts.[6] For example, Chaudhari et al. [7a] reported that oxidant-free dehydrogenation of glycerol in alkaline aqueous solution by a commercial Pt/C catalyst under 1.4 MPa N_2 at 160 °C for 6 h resulted in 36.5% selectivity to LA, 25.6% selectivity to 1,2-propanediols, and 21.6% selectivity to C1-C3 alcohols at 78.7% conversion. The yield of LA (28.7%) corresponds to TON of 184, which is lower than the homogeneous catalysts for the same reaction.[6]

We have previously found that heterogeneous Pt catalysts are effective for the oxidant-free dehydrogenation of alcohols.[9] In this report, we show a detailed optimization study of catalyst and reaction conditions for the dehydrogenation of glycerol to LA. Under the optimized conditions, a commercial Pt/C catalyst shows 93% yield of LA and two orders of magnitude higher TON than previously reported heterogeneous catalysts. On the basis of control experiments and catalyst structure-activity relationship study, we show a strategy for increasing the activity and selectivity of the present catalytic system.

Results and Discussion

Catalyst characterization

A Pt-loaded carbon purchased from Sigma-Aldrich (Pt/C_{SA}, Pt = 5 wt%) was used as a catalyst precursor. Table 1 lists the mean size (*D*) of Pt metal particles on as-purchased Pt/C_{SA} and Pt/C_{SA} reduced by H_2 at different temperatures (T_{H2}). The mean Pt size (*D*) was estimated by a conventional CO adsorption method. The as purchased Pt/C_{SA} sample showed the smallest Pt particle size of 2.4 nm. The Pt particle size in Pt/C_{SA} increased with increases in the reduction temperature. Thus, the Pt/C_{SA} catalysts with the same Pt content (5 wt%) and different Pt particle size (2.4-7.0 nm) were prepared. To confirm the accuracy of the Pt particle size, TEM analysis of the samples was carried out. Figure 1 shows typical TEM pictures and Pt size distributions of the Pt/C_{SA} samples. The volume-area mean diameter[10] of Pt particles estimated by TEM analysis (Figure 1, right) is listed in Table 1. The volume-area mean diameter is consistent with the mean size estimated by the CO adsorption experiment within the experimental error of TEM analysis. This confirms the accuracy of the mean Pt size estimated by the CO adsorption method.

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Optimization of Catalysts and Conditions

A catalyst screening study was carried out for dehydrogenation of neat glycerol (6.84 mmol) in the presence of 1.1 equiv. of KOH and various supported transition metal catalysts pre-reduced at 300 °C containing 0.0021 mmol of the metal (0.03 mol % with respect to glycerol). The reaction was initially carried out under 1 atm N_2 in a closed reactor. Soon after heating the mixture at 160 °C, a needle-shaped pipe was put on the septum rubber on the reactor in order to release H_2 gas produced during the reaction. Table 2 compares the conversion of glycerol and the yield of LA. The reaction under the catalyst-free conditions (in the presence of KOH, entry 1) gave no conversion of glycerol to LA. This indicates that KOH itself does not promote the reaction at 160 °C. The Pt/C_{SA} catalyst reduced at 300 °C (entry 2) showed higher yield (93%) than as-purchased Pt/C_{SA} (73%, entry 4). Exposure of the reduced Pt/C_{SA} catalyst to air for 0.5 h resulted in low yield of 61% (entry 3). This could be due to oxidation of the surface Pt^0 species by air to Pt oxides. On the basis of these results, hereafter the catalysts reduced at 300 °C were tested for the reaction without exposure of the reduced catalyst to air. Various metal oxide-supported Pt catalysts (entries 5-12) were tested, but these catalysts showed lower yields (17-64%) than Pt/C_{SA} (93%, entry 2). The metal oxides have basic or acidic nature, whereas carbon is basically neutral. Hence, the result suggests that the acidity or basicity of the support material has negative impact on the Pt-catalyzed dehydrogenation of glycerol in the presence of KOH. Then, various transition metal-loaded carbon catalysts were prepared using an active carbon support and tested for the reaction (entries 13-21). The platinum-group metal (Pt, Rh, Ir, Ru, Pd) catalysts and Ni/C showed higher yields than the other catalysts. Among the metals-loaded carbon catalysts, the home-made Pt/C (entry 13) showed the highest yield. Summarizing the screening results, and considering wide availability of the commercial Pt/C_{SA} catalyst, we have selected the Pt/C_{SA} catalyst reduced at 300 °C (entry 2) as the standard catalyst.

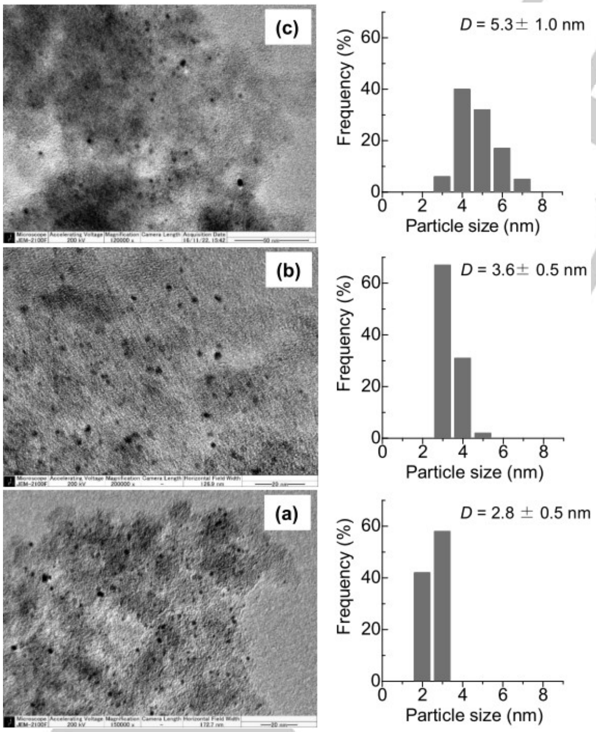


Figure 1. Typical TEM images (left) and Pt particle size distributions (right) of Pt/C_{SA}: (a) as-purchased Pt/C_{SA}, Pt/C_{SA} reduced in H_2 at 300°C (b) and 500°C (c). The volume-area mean diameter of Pt particles is shown in the right figures.

Table 1. Preparation conditions, Pt particle size and catalytic activity of 5 wt% Pt/C catalysts.

T_{H2} [a] [°C]	D [b] [nm]	D [c] [nm]	Rate [d] [mol mol_{Pt} h^{-1}]	TOF [e] [h^{-1}]
-	2.4	2.8 ± 0.5	554	1119
300	3.9	3.6 ± 0.5	651	2086
500	7.0	5.3 ± 1.0	684	3967

[a] Temperatures of reduction under H_2.

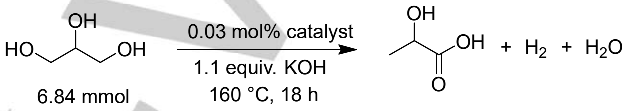
[b] Mean particle diameter of the supported Pt particles estimated by CO adsorption experiments.

[c] Volume-area mean diameter of Pt particles estimated by TEM.

[d] Initial rate defined as moles of LA h^{-1} per mole of Pt.

[e] TOF defined as moles of LA h^{-1} per mole of surface Pt.

Table 2. Catalyst screening for LA synthesis form glycerol. [a]



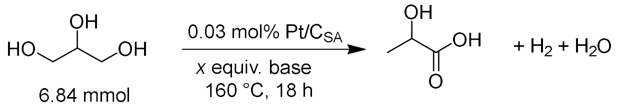
Entry	Catalysts	Conv. [%]	Yield [%]
1	blank	0	0
2	Pt/C_{SA}	95	93
3[b]	Pt/C_{SA}-air	67	61
4[c]	Pt/C_{SA}	80	73
5	Pt/Al_2O_3	37	35
6	Pt/CeO_2	66	64
7	Pt/MgO	58	56
8	Pt/CaO	55	53
9	Pt/Nb_2O_5	38	36
10	Pt/TiO_2	25	23
11	Pt/SiO_2	21	17
12	Pt/Hβ	21	20
13	Pt/C	98	96
14	Rh/C	68	63
15	Ir/C	38	33
16	Ru/C	49	42
17	Pd/C	64	61
18	Ag/C	3	1
19	Cu/C	3	0
20	Ni/C	45	39
21	Co/C	4	0

[a] Conversion and yield of LA were determined by ^{1}H-NMR.

[b] Pt/C_{SA} reduced at 300°C was exposed to air at 25°C for 0.5 h.

[c] As-purchased Pt/C_{SA} without reduction.

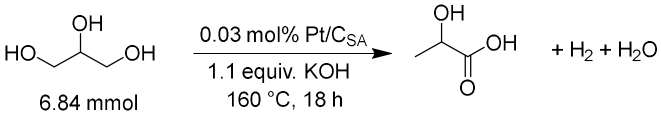
Table 3. Dehydrogenation of glycerol to LA by Pt/C_{SA} with various base.



Entry	Base (*x*)	*T* [°C]	Conv. [%]	Yield [%]
1	-	160	<1	0
2	Na_2CO_3 (1.1)	160	19	12
3	K_2CO_3 (1.1)	160	22	16
4	NaOH (1.1)	160	71	63
5	KO*t*Bu (1.1)	160	82	78
6	KOH (1.1)	160	95	93 (81) [a]
7	KOH (1.0)	160	86	81
8	KOH (0.5)	160	50	42
9	KOH (1.1)	140	88	82
10	KOH (1.1)	120	57	51

[a] Isolated yield.

Table 4. Dehydrogenation of glycerol to LA by Pt/C_{SA} with KOH.[a]



Entry	Atmosphere	Conv. [%]	Yield [%]				
			LA	PD	EG	ROH	FA
1	O_2 flow[b]	82	75	4	2	0	1
2	N_2 flow[b]	95	93	1	<1	0	<1
3	1 atm N_2 [c]	95	93	1	<1	0	<1
4	1 atm N_2[d]	90	59	11	2	8	4
5	1 atm O_2[d]	88	56	10	2	8	7
6	0.8 MPa H_2[d]	82	36	31	4	11	0
7[e]	1 atm N_2[d]	73	40	16	4	7	2

[a] LA (lactic acid), PD (1,2-propanediol), EG (ethylene glycol), ROH (methanol, ethanol, propanols), FA (formic acid).
[b] 20 cm^3 min^{-1}.
[c] a needle-shaped pipe was put on the upper side of the reactor to release H_2 gas from the system.
[d] In a closed system (stainless autoclave).
[e] Water (275 mmol) was added to the mixture.

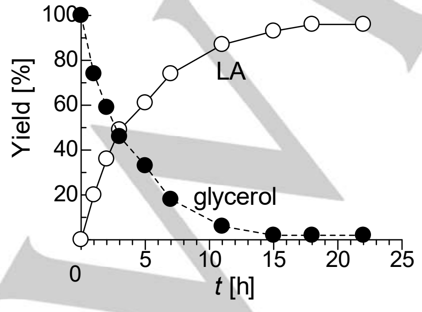
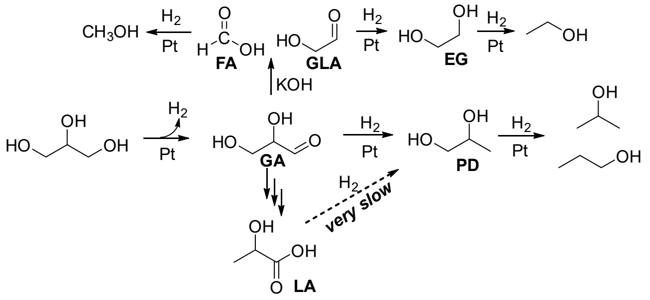


Figure 2. Time course of the yields of glycerol (●) and LA (○) for the reaction of entry 13 in Table 3.

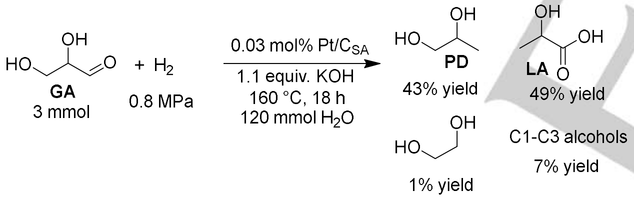
Figure 2 shows the time course of the yields of LA and unconverted glycerol for the reaction by Pt/C (entry 13 in Table 2). After 18 h, the conversion of glycerol to LA leached the highest value. So, the reaction time of 18 h is adopted in the standard conditions. Then, we carried out optimization of the reaction conditions for the reaction of glycerol by Pt/C_{SA} (Table 3). The Pt/C_{SA}-catalyzed reaction in the absence of base (entry 1) gave no yield of LA. Addition of basic additives (entries 2-6) increased the yield. Among the various bases (1.1 equiv. with respect to glycerol), KOH (entry 6) gave the highest yield (93%). The yield decreased with the decreasing amount of KOH (entries 6-8). In the presence of 1.1 equiv. of KOH, the yield decreased with decrease of the reaction temperature (entries 6,9,10). Under the best conditions (entry 6), the yield of LA, estimated by H^1 NMR, was 93%, and the yield of pure LA isolated from the mixture was 81%.

Table 4 shows the effect of atmosphere and reactor on the yields of LA and byproducts: PD (1,2-propanediol), EG (ethylene glycol), C1-C3 alcohols (methanol, ethanol, propanols), FA (formic acid) under the optimized conditions (1.1 equiv. KOH, 160 °C). The yield of LA under a flow of 1 atm O_2 (entry 1, 75 %) was lower than that under N_2 flow (entry 2, 93%). This indicates that O_2 is not an effective hydrogen-acceptor for the dehydrogenation of glycerol under the present conditions. High yield of LA (93%) was obtained by the standard reactor (entry 3) used in the experiments in Tables 1-3, where a needle-shaped pipe was put on the upper side of the reactor to release H_2 gas from the system. The reaction under 1 atm N_2 in a closed reactor, stainless autoclave, (entry 4) gave the lower LA yield (59%) and higher PD yield (11%) than those under N_2 flow conditions (93% LA and 1% PD in entry 2). The reaction under 1 atm O_2 in the closed autoclave (entry 5) also showed a relatively low LA yield (56%) and a high PD yield (10%). Taking into account that PD can be produced by hydrogenation of glycerol, these results suggest that PD is produced by hydrogenation of glycerol by the H_2 produced by the dehydrogenation of glycerol and removal of H_2 by N_2 flow suppress the hydrogenation of glycerol to PD. To verify this hypothesis, we carried out the reaction under 0.8 MPa H_2 in the closed autoclave (entry 6). As expected, the reaction under H_2 gave lower yield of LA (36%) and higher yields of PD (31%) and C1-C3 alcohols (11%) than the standard conditions (entry 3) and the N_2 flow conditions (entry 2). In the literature, water has been generally used as solvent for the oxidation (or dehydrogenation) of glycerol to LA by heterogeneous catalysts.[4,7] We have also carried out the reaction in the presence of excess water (275 mmol) in the closed autoclave (entry 7), which results in lower conversion (73%), lower LA yield (40%) and higher PD yield (16%) than those in the absence of excess water with the same reactor (entry 4): 90% conversion, 59% LA yield, and 11% PD yield. The result demonstrates that water has negative impact on the reaction; water inhibits the dehydrogenation of glycerol to LA, while it promotes formation of PD via hydrogenation of glycerol by the H_2 produced by the dehydrogenation of glycerol.

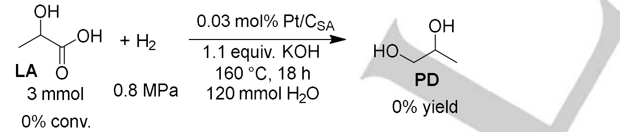


Scheme 1. Possible pathways for the conversion of glycerol to LA and byproducts.

Considering the proposed reaction mechanism in the literature,[3-8] presumable pathways from glycerol to LA and byproducts are proposed in Scheme 1. Glycerol can be dehydrogenated by Pt sites to from H_2 and glyceraldehyde (GA), which can be converted to LA via dehydration and subsequent benzylic acid rearrangement of GA. If H_2 is present in the system, GA can be hydrogenated by Pt sites to yield PD, which can be further hydrogenated to propanol. Also, GA can undergo a retro-aldol reaction to give formic acid (FA) and glycolaldehyde (GLA), and these can be hydrogenated to methanol and ethylene glycol (EG), respectively. To verify the reaction of GA to PD, we tested a control reaction of GA with Pt/C_{SA} and KOH under 0.8 MPa H_2 as shown in eqn. (1). The result shows 43% yield of PD, which is consistent with the proposed pathway of PD formation. As shown in eqn. (2), hydrogenation of LA under the same conditions gave no conversion of LA and no yield of PD. This indicates that LA is stable under H_2 and is not hydrogenated to PD.



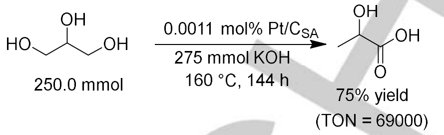
(1)



(2)

By adopting the pathways in Scheme 1, combined with the results in Table 4, we discuss a strategy for suppression of the undesirable side reactions. First, removal of H_2, produced by the dehydrogenation of glycerol, from the gas phase is effective to inhibit the hydrogenation of GA to PD. For the removal of H_2, oxidation of H_2 by O_2 (a H_2-acceptor) is not effective, but spontaneous release of H_2 from the needle pipe on the reactor or purging by flowing N_2 is effective. So, a closed reactor such as a stainless autoclave should not be used. Second, water should not be used as solvent, because it promotes hydrogenation of the intermediate to PD and C1-C3 alcohols.

The present catalytic method was applicable for a gram-scale reaction with small amount of the catalyst. As shown in eqn. (3), the reaction of 250 mmol of glycerol with 275 mmol KOH and 0.0027 mmol of Pt/C_{SA} (0.0011 mol%) gave 75% yield of LA. The yield corresponds to TON of 69000 with respect to the total number of Pt atoms in the catalyst, which is larger than those of the previously reported heterogeneous catalysts[7] for the oxidant-free dehydrogenation of glycerol to LA.



(3)

Structural factors affecting the catalytic activity

The effect of Pt particle size of Pt/C_{SA} was tested using the catalysts in a Pt size range of 2.4-7.0 nm. The initial rates of LA formation, shown in Table 1, were measured under the conditions where conversions were below 25%. Using the number of the surface Pt atoms estimated by the CO adsorption experiment, TOF with respect to the surface Pt atoms were calculated as listed in Table 1. The TOF increased with the size of Pt particles (Figure 3). Taking into account the well-established fact that the larger the size of a metal particle the lower the fraction of under-coordinated sites and the larger the fraction of the plane sites, the result suggests that the Pt atoms at flat surfaces have higher activity than the Pt atoms at under-coordinated sites.

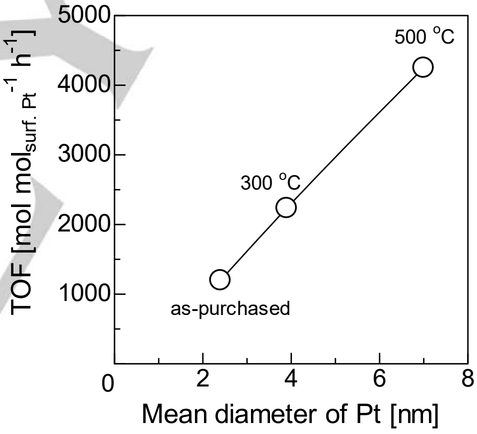


Figure 3. TOF for conversion of glycerol to LA vs Pt particle size by Pt/C_{SA} H_2-reduced at various temperature.

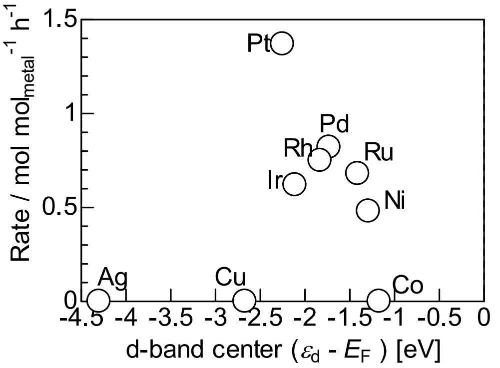


Figure 4. Effect of the d-band center [11] of the metals relative to the Fermi energy on the reaction rates by metal-loaded carbon.

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To discuss the effect of the electronic properties of metals on the catalytic activity of the carbon-supported transition metals (entries 13-21 in Table 2), the initial rates of LA formation by metal-loaded carbon catalysts is plotted as a function of the d-band center (ε_d) relative to the Fermi energy (E_F), ε_d - E_F, calculated by Hammer and Nørskov (Figure 4).[11] The plot shows a volcano-type dependence of the catalytic activity on the d-band center, except for the Ir/C catalyst. Generally, there is a tendency that the interaction between metal surfaces and adsorbed species is weaker for a metal with deeper the d-band center. [11] Hence, our result suggests that platinum, having an intermediate d-band center level, shows higher catalytic activity than the other metals, because the interaction between surface intermediates and the metal surface is moderately strong, which can be suitable to the metal-catalyzed dehydrogenation step.

Conclusions

Carbon-supported Pt metal nanoparticles, including a commercial Pt/C_{SA} catalyst, was found to be effective for oxidant-free dehydrogenation of glycerol to lactic acid under oxidant-free, solvent-free, and alkaline conditions. The effects of conditions on the catalytic activity and selectivity were studied. Considering the mechanism in the literature, we proposed the following strategy for suppression of the undesirable side reactions. Removal of H_2, produced by the dehydrogenation of glycerol, from the gas phase is effective to lower the yields of hydrogenation products (1,2-propanediol and C1-C3 alcohols). For the removal of H_2, oxidation of H_2 by O_2 is not effective, but spontaneous release of H_2 from the needle pipe on the reactor or purging by flowing N_2 is effective. So, a closed reactor (a stainless autoclave) should not be used. Water should not be used as solvent, because it promotes the hydrogenation of glycerol to 1,2-propanediol and C1-C3 alcohols. The structure-activity relationship study showed the following trends. The TOF increased with the size of Pt particles, which suggests that the Pt atoms at flat surfaces have higher activity than the Pt atoms at under-coordinated sites. Among various metals, platinum, having an intermediate d-band center level, showed higher catalytic activity than the other metals.

Experimental Section

Catalyst Preparation

The standard catalyst, Pt-loaded carbon catalyst (Pt/C_{SA}, Pt = 5 wt%), was purchased from Sigma-Aldrich. The Pt/C_{SA} powder was reduced in a flow of H_2 for 0.5 h at different temperatures (300, 500, 700 °C). Thus, Pt/C_{SA} catalysts with different Pt particle size were prepared as listed in Table 1.
Active carbon (296 m^2 g^{-1}) was purchased from Kishida Chemical. γ-Al_2O_3 (124 m^2 g^{-1}) was prepared by calcination of γ-AlOOH (Catapal B Alumina from Sasol) at 900 °C for 3 h. SiO_2 (Q-10, 300 m^2 g^{-1}) was supplied from Fuji Silysia Chemical Ltd. TiO_2 (JRC-TIO-4, 50 m^2 g^{-1}), MgO (JRC-MGO-3, 19 m^2 g^{-1}), and HBEA zeolite (SiO_2/Al_2O_3 = 25±5, JRC-Z-HB25) were supplied from Catalysis Society of Japan. Nb_2O_5 (54 m^2 g^{-1}) was prepared by calcination of $Nb_2O_5 \cdot nH_2O$ (CBMM) at 500 °C for 3 h.

Metal (5 wt%)-loaded active carbon (C) catalysts, M/C (M = Pt, Pd, Rh, Ir, Ru, Ni, Cu, Co, Ag), were prepared by impregnation method using aqueous HNO_3 solution of $Pt(NH_3)_2(NO_3)_2$ (Furuya Metal Co., Ltd.), $Pd(NH_3)_2(NO_3)_2$ (Kojima Chemicals Co., Ltd.), HNO_3 solution of $Rh(NO_3)_3$ (Furuya Metal Co., Ltd.) or aqueous solution of metal nitrates (for Ni, Cu, Co, Ag) or $RuCl_3$ or $IrCl_3 \cdot nH_2O$. A mixture of the carbon (Kishida Chemical) and the metal solution was evaporated at 50 °C, followed by drying at 90 °C for 12 h. Before the reaction and characterization experiments, the precursor was reduced under H_2 flow (20 cm^3 min^{-1}, 300 °C, 0.5 h) in a pyrex tube. The Pt catalysts loaded on various metal oxides were prepared by the same method as Pt/C.

Catalyst Characterization

The number of surface Pt^0 atoms on Pt/C_{SA}, pre-reduced by H_2 at a temperature in Table 1, was estimated by the CO uptake of the samples at room temperature using the pulse-adsorption of CO in a flow of He by BELCAT (MicrotracBEL). The mean size of Pt particles is estimated from the CO uptake based on the assumption that CO is adsorbed on the surface of spherical Pt particles with a stoichiometry of CO/(surface Pt atom) = 1/1. Transmission electron microscopy (TEM) experiment was carried out by a JEOL JEM-2100F TEM operated at 200 kV.

Catalytic tests

Organic compounds were purchased from Tokyo Chemical Industry and were used without further purification. Typically, 5 wt% Pt/C_{SA} reduced at 300 °C was used as a standard catalyst. Catalytic tests were carried out using a batch-type reactor without exposing the reduced catalyst to air as follows. Glycerol (6.84 mmol) was injected to the pre-reduced catalyst inside the reactor (cylindrical glass tube, 17 mL) through a septum inlet, followed by adding KOH (7.52 mmol) and filling with N_2. The tube was heated at 160 °C for 18 h and magnetically stirred (500 rpm). For the standard conditions for Tables 1-3 and entry 3 of Table 4, a needle-shaped pipe was put into the septum on the upper side of the reactor to release H_2 gas from the system. For the reactions in a closed system (entries 4-7 in Table 4), glycerol was injected through the septum inlet to a glass tube with the reduced Pt/C_{SA} catalyst, and then, the septum was removed under air, and a magnetic stirrer was put in the tube, followed by inserting the tube inside stainless autoclave (28 cm^3), followed by charging with various gas (N_2, O_2 or H_2). After 18 h of the reaction, D_2O (2 mL) and an aqueous solution of sodium acetate (internal standard) were added to the products, and ^1H NMR analysis (JEOL-ECX 600 operating at 600.17 MHz) of the crude mixture was carried out to determine to conversion of glycerol and yield of LA and byproducts. To estimate the yield of isolated LA (entry 6, Table 3), pure LA was obtained as follows. After the reaction, 1 M HCl solution was added to the reaction mixture, followed by extraction of the products with diethylether (10 mL, 3 times), evaporation of the ether solution reduced pressure, and by removal of the byproducts by a column (silica gel 60, spherical, 63-210 μm, Kanto Chemical Co. Ltd.) using hexane/ethylacetate (80/20) as the eluting solvent. The purity of the obtained LA was confirmed by ^1H NMR.

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Keywords: dehydrogenation • glycerol • lactic acid • biomass • platinum

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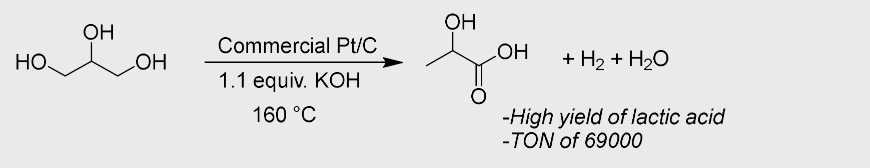

Pt-loaded carbon catalysts showed high yield and high turnover number for selective dehydrogenation of glycerol to lactic acid under oxidant-free, solvent-free, and alkaline conditions. Catalytic and structural studies are shown to discuss a strategy to improve activity and selectivity of the reaction.

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Oxidant-free Dehydrogenation of Glycerol to Lactic Acid by Heterogeneous Platinum Catalysts