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A Combined Catalyst of Pt Nanoparticles and TiO_2 with Water-Tolerant Lewis Acid Sites for One-Pot Conversion of Glycerol to Lactic Acid

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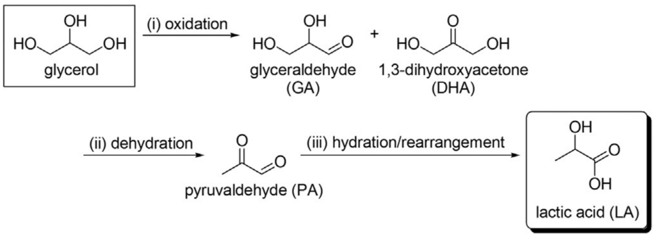
Catalytic conversion of glycerol to valuable chemicals has been recognized as an attractive and challenging reaction in biorefinery. In this paper, we demonstrated that a combined catalyst of Pt nanoparticles and TiO_2 worked as a highly active catalyst for the one-pot conversion of glycerol to lactic acid in water. The yield of lactic acid reached 63 % under oxygen atmosphere without the use of any additives such as strong bases, and the catalyst could be reused without significant loss of the catalytic performance. The mechanistic studies revealed that Pt nanoparticles on TiO_2 selectively oxidized glycerol to C3 aldehyde/ketone, and Lewis acid sites on TiO_2 smoothly promoted the dehydration and rehydration/rearrangement reactions of the intermediates to produce lactic acid efficiently.

Introduction

Glycerol (1,2,3-propanetriol) is an abundant and sustainable biomass resource because it is obtained as a main coproduct of biodiesel formation through the transesterification of seed oils with alcohols.[1] Along with the market growth in biodiesel production, the selective conversion of glycerol into useful chemicals (e.g., esters, ethers, acetals/ketals, diols, epoxides, oxidation products) has also received significant attention in recent years.[2] Among these, lactic acid (LA) is a promising target chemical owing to its wide application to food additives, biodegradable polymers, and as a platform chemical in biorefinery.[3] LA is mainly produced by the fermentation of carbohydrates via the corresponding lactate, however, the production efficiency is still low and large amounts of salts are formed as byproduct wastes. In this context, there is a strong demand for the development of novel chemical processes for the one-pot synthesis of LA from glycerol including a better method to directly separate LA.

As shown in Scheme 1, LA can be chemically obtained from glycerol according to the following three sequential reactions: (i) the oxidative dehydrogenation of glycerol to trioses (glyceraldehyde (GA) and 1,3-dihydroxyacetone (DHA)), (ii) dehydration of trioses to pyruvaldehyde (PA), and (iii) hydration/rearrangement of PA to LA. The DFT-calculated free energy diagram for the one-pot conversion of glycerol to LA is shown in Figure 1 (see also Table S1 in the Supporting Information). The formation of C3 acids, such as glyceric acid and tartronic acid, by the overoxidation of trioses was calculated to be more thermodynamically favorable than LA formation, which indicates that fine control of the catalyst properties for oxidation and rearrangement is an important factor for the selective synthesis of LA from glycerol. Brønsted bases or Lewis acids accelerate



Scheme 1. One-pot conversion of glycerol to LA through (i) oxidation, (ii) dehydration, and (iii) hydration/rearrangement.

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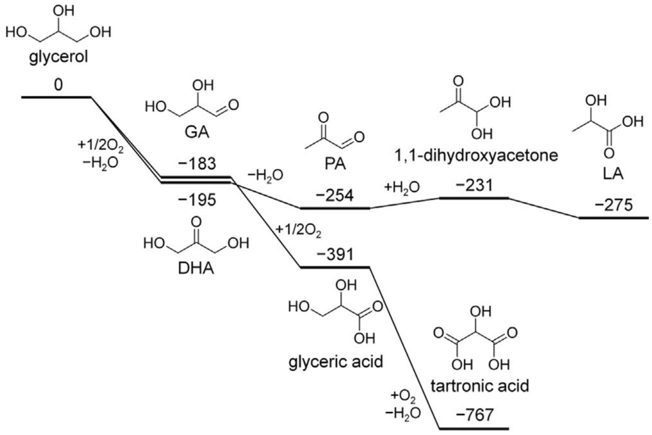

Figure 1. Computational free energy diagrams of the transformation of glycerol into LA (top) and tartronic acid (bottom). Energies are shown in $kJ\,mol^{-1}$.

the important step (iii) by benzilic acid rearrangement or an intramolecular 1,2-hydride shift, respectively,[4] so that various effective combined systems of Ir-, Cu-, Pt-, and Au-based oxidation catalysts and homogeneous Brønsted bases (NaOH and KOH) or Lewis acids ($AlCl_3$) have been reported (Table S2).[5] However, these systems share common drawbacks in the complicated procedure for catalyst/product(s) separation, difficulty of reuse for expensive catalysts, and the additional neutralization of lactate to obtain LA. Recently, a bifunctional Pt/Sn–MFI zeolite catalyst has been reported to efficiently catalyze the base-free one-pot conversion of glycerol to LA in water.[6] In this case, Sn–MFI acts as a heterogeneous Lewis acid catalyst, however, a gradual decrease in the catalytic activity is observed for the recycled catalyst, which is likely the result of significant leaching of the Sn species in water in the presence of LA.[7] Therefore, the development of active and durable combined catalytic systems of oxidation and heterogeneous Lewis acid catalysts is still a challenging issue to achieve efficient one-pot conversion of glycerol to LA in aqueous media.

We have recently reported that early transition metal oxides such as TiO_2 and Nb_2O_5 can act as highly active and durable heterogeneous Lewis acid catalysts for various types of reactions, such as the direct conversion of glucose to 5-(hydroxymethyl)furfural, allylation of benzaldehyde with tetraallyltin, and the rearrangement reaction of PA to LA in aqueous media.[8] Coordinatively unsaturated metal species such as NbO_4 and TiO_4 tetrahedra formed on the oxide surface can function as water-tolerant Lewis acid sites, which results in high catalytic activity comparable to that of the active homogeneous $Sc(OTf)_3$ catalyst.[9] From these results, we envisaged that a combined catalyst consisting of noble-metal nanoparticles and an early transition metal oxide with water-tolerant Lewis acid sites would be feasible for the one-pot conversion of glycerol into LA in water; the former efficiently catalyzes the selective oxidation of alcohols to carbonyl compounds with molecular oxygen as the sole oxidant,[10] and the latter exhibits high catalytic performance for conversion of the resulting GA or DHA into LA. Herein, a catalyst of Pt nanoparticles immobilized on TiO_2 is demonstrated to function as a recyclable solid catalyst for the one-pot additive-free conversion of glycerol into LA without significant loss of the catalytic activity.

Results and Discussion

The most suitable combination of noble-metal nanoparticles (as oxidation catalysts) and metal oxides (as Lewis acid catalysts) for the one-pot conversion of glycerol to LA was explored under additive-free conditions (Table 1). Initially, the effect of noble-metal nanoparticles stabilized with polyvinylpyrrolidone (PVP) or polyethylenimine (PEI) (metal: 0.1 wt% with respect to TiO_2; Pt–PVP, Ru–PVP, Pd–PVP, Au–PEI, Ir–PVP, Rh–PVP, Ag–PEI, Cu–PVP) on the one-pot reaction in the presence of TiO_2 (50 mg) with O_2 (0.5 MPa) at 423 K for 18 h was investigated. Apart from LA, the dehydrogenated/dehydrated chemicals (DHA, GA, and PA) and some further oxidized products such as acetic acid (AA) were also formed, and the details are summarized in Table S3. Among the nanoparticles tested, the combined catalyst of Pt–PVP and TiO_2 (denoted as Pt–PVP + TiO_2) gave the highest yield of LA at 49%, with 70% selectivity (Table 1, entry 1). If prolonging the reaction time from 18 h to 48 h, the LA yield increased up to 63% (entry 2). Notably, the Pt–PVP + TiO_2 combined catalyst gave smaller amounts of energetically stable C3 acids (2% selectivity) such as glyceric

Table 1. Effect of catalysts on one-pot conversion of glycerol into LA.[a]

Entry	Catalyst	Conversion of glycerol [%]	Yield of LA [%]	Selectivity to LA [%]
1	Pt–PVP + TiO_2	70	49	70
2[b]	Pt–PVP + TiO_2	> 99	63	63
3	Ir–PVP + TiO_2	19	14	72
4	Pd–PVP + TiO_2	20	6	30
5	Ru–PVP + TiO_2	11	2	15
6	Rh–PVP + TiO_2	3	1	40
7	Ag–PEI + TiO_2	4	1	31
8	Au–PEI + TiO_2	7	< 1	–
9	Cu–PVP + TiO_2	< 1	< 1	–
10	Pt–PVP + Nb_2O_5	82	39	48
11	Pt–PVP + ZrO_2	79	36	45
12	Pt–PVP + Al_2O_3	68	28	42
13	Pt–PVP + MgO	75	15	20
14	Pt–PVP + SnO_2	79	7	9
15	Pt–PVP + SiO_2	70	3	4
16	Pt–PVP + AC	70	< 1	–
17	TiO_2	9	1	12
18	Pt–PVP	62	2	3
19	blank	< 1	< 1	–
20	Pt/TiO_2[c]	78	55	70

[a] Reaction conditions: glycerol (1 mmol), metal oxide or AC (50 mg), noble metal nanoparticles (metal: 0.1 wt% with respect to meal oxide or AC), water (5 mL), 423 K, 18 h, O_2 (0.5 MPa). Conversion (%) = converted glycerol (mol)/initial glycerol (mol) × 100. Yield (%) = carbon in product (mol)/carbon in initial glycerol (mol) × 100. Selectivity (%) = LA (mol)/converted glycerol (mol) × 100. Yields of other products are summarized in Table S3. [b] 48 h. [c] Pt nanoparticles loaded TiO_2 was prepared by the reaction of Pt–PVP and TiO_2 in water at 423 K for 1 h under 0.5 MPa O_2.

acid and tartronic acid by the overoxidation of trioses than those reported for Pt or Au catalysts (10–19% selectivity).[5,6] There is no significant difference in reaction between entry 17 for TiO_2 without metal nanoparticles and entry 19 as a blank test without any catalysts. Although the conversion of glycerol reaches 62% using Pt–PVP without TiO_2 (entry 18), the LA selectivity is only 3%, which suggests that the high catalytic activity and selectivity for the present reaction require both TiO_2 and Pt–PVP. The one-pot reaction in the presence of Pt–PVP and various metal oxides (TiO_2, Nb_2O_5, ZrO_2, Al_2O_3, SnO_2, SiO_2, and MgO) or activated carbon (AC) was also examined. Nb_2O_5 and ZrO_2, early transition metal oxides with Lewis acid sites, gave smaller LA yields and lower LA selectivity than TiO_2 (entries 10 and 11). The high density of water-tolerant Lewis acid sites with poor basicity on TiO_2 could be suitable for this reaction.[8,11] Al_2O_3 and MgO are inferior to Nb_2O_5 and ZrO_2 in catalytic performance, and SnO_2, SiO_2 and AC resulted in considerably smaller LA yields, although glycerol conversion using these materials exceeded 70%. This can be attributed to the absence of Lewis acid sites which accelerate the selective conversion of the trioses to LA (entries 12–16).

To investigate the correlation of Pt–PVP with TiO_2, a time course of the reaction was measured (Figure 2). The product distribution is summarized in Figure S1 (Supporting Information). The reaction was completely stopped by removal of Pt–PVP + TiO_2. Pt–PVP itself can oxidize glycerol in the absence of TiO_2 and the glycerol conversion exceeds 60% at 18 h, as shown in entry 18 in Table 1. It was confirmed by inductively coupled plasma atomic emission spectroscopy (ICP–AES) analysis that negligible amounts of Pt (<2%) and Ti (<0.01%) species were present in the filtrate. Therefore, it is considered that almost all Pt species are immobilized on TiO_2 during reaction.

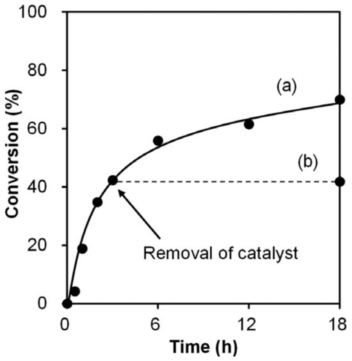

Figure 2. Time course of glycerol conversion for Pt–PVP + TiO_2. (a) The reaction was performed for 18 h in the presence of Pt–PVP + TiO_2 at 423 K. (b) The reaction solution was filtrated after reaction for 3 h in the presence of Pt–PVP + TiO_2 at 423 K, and then the filtrated liquid was heated at 423 K (total heating time; 18 h). Reaction conditions are the same as those reported in Table 1. Yields of other products are presented in Figure S1.

In Figure 3, the high-angle annular dark-field scanning transmission electron microscopy (HAADF–STEM) images of Pt–PVP and the solid sample filtered out of the reaction solution after 1 h are presented. The images reveal that Pt nanoparticles are dispersed on the TiO_2 surface and their particle size is close to that of Pt–PVP, which suggests that Pt–PVP nanoparticles are immobilized on TiO_2. Such immobilization can be expected to occur during the early stages of the reaction. A Pt-nanoparticles-loaded TiO_2 sample (denoted as Pt/TiO_2) was prepared by stirring Pt–PVP and TiO_2 in water for 1 h at 423 K under 0.5 MPa O_2 followed by filtration.[12] The resulting Pt/TiO_2 exhibited high catalytic performance comparable to that of the Pt–PVP + TiO_2 system (Table 1, entry 20).

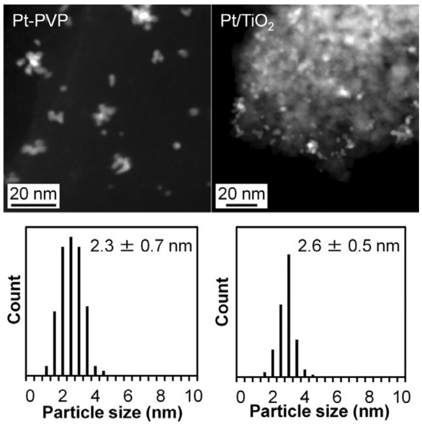

Figure 3. HAADF–STEM images (top) and particle size distributions (bottom) of Pt–PVP and Pt/TiO_2 after the reaction for 1 h, respectively.

The electronic state of Pt nanoparticles for Pt/TiO_2 was evaluated by using X-ray photoelectron spectroscopy (XPS) and the results are shown in Figure 4. Two peaks are observed at 70.6 eV and 73.7 eV in Figure 4, assignable to $Pt\,4f_{7/2}$ and $Pt\,4f_{5/2}$ of Pt^0, respectively.[13] It was also confirmed by XRD, N_2 adsorption–desorption isotherm, and FTIR measurements using pyridine as a basic probe molecule that there is no significant difference in the structure (Figure S2), surface area (Figure S3), and amount of Lewis acid sites between bare TiO_2 and Pt/TiO_2 formed in the Pt–PVP + TiO_2 system (Figure 5). These results demonstrate that Pt^0 nanoparticles are immobilized on the TiO_2 surface but do not prevent the Lewis acid catalytic activity of TiO_2. Furthermore, the FTIR experiments revealed that the bands attributed to C–H and C–N stretching of PVP

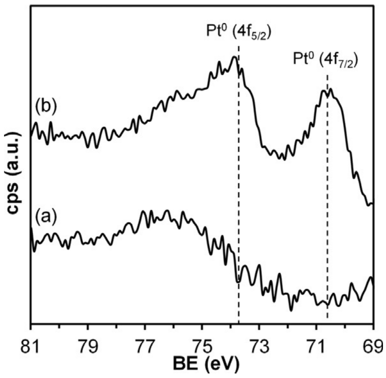

Figure 4. Pt 4f X-ray photoelectron spectra of (a) TiO_2 and (b) Pt/TiO_2.

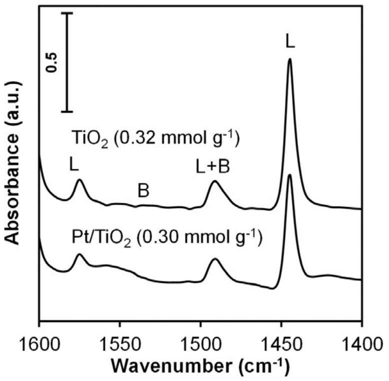

Figure 5. Difference FTIR spectra of pyridine-adsorbed catalysts TiO_2 and Pt/TiO_2. L = coordinated pyridine on Lewis acid site, B = pyridinium ion formed on Brønsted acid site.

(2970 cm^{-1} and 1280 cm^{-1}) for Pt/TiO_2 are much smaller than those of a simple mixture of Pt–PVP and TiO_2 (not shown), suggesting the decrease in PVP covering Pt during reaction. It has been generally accepted that Pt-nanoparticle-deposited TiO_2 are inactive for the one-pot reaction of glycerol to LA[6] because the density of effective Lewis acid sites on TiO_2 is typically not so high.[14] However, the TiO_2 used in this study has a much higher density of effective water-tolerant Lewis acid sites.[8] In addition, the Lewis acid properties of TiO_2 were not much changed by the immobilization of Pt nanoparticles on TiO_2, which resulted in high catalytic performance for the conversion of glycerol to LA.

Recycle experiments of Pt–PVP + TiO_2 catalyst were conducted to examine the durability of the catalyst. After the reaction was carried out for 18 h, the catalyst was retrieved from the reaction mixture by centrifugation. It was confirmed by ICP–AES that the leaching of Pt species reached 7 % after the catalytic reaction for 18 h. Such leaching of Pt species was not observed at the early stage of the reaction (1 and 3 h), suggesting that small leaching of Pt species is caused by the increase in lactic acid formation. As shown in Figure 6 and Table S4, the retrieved catalyst could be reused without significant loss of the catalytic performance, even after three reuses. The total turnover numbers for LA production based on bulk Pt metal and Lewis acid sites on TiO_2 were 7520 and 154, respectively. In addition, the XRD pattern, BET surface area, and STEM image of the retrieved catalyst after three reuses did not much change from those of the fresh Pt/TiO_2 catalyst (Figure S2, S3, and S4). As a result, Pt/TiO_2, which is smoothly formed from Pt–PVP + TiO_2 catalyst under the reaction conditions, functions as a recyclable and efficient catalyst for the one-pot synthesis of LA from glycerol.

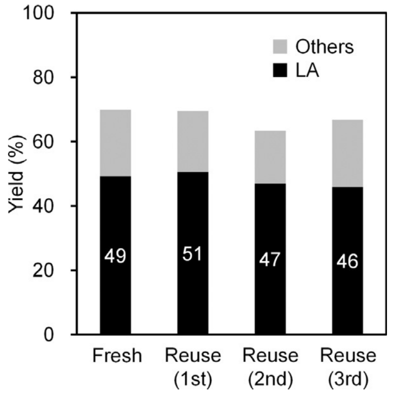

Figure 6. Recycle experiments of Pt–PVP + TiO_2 for the one-pot reaction of glycerol into lactic acid. The reaction was performed under the same conditions as those of entry 1 in Table 1.

Reactions of GA, DHA, and PA as starting substrates instead of glycerol were also examined under the same reaction conditions as those in Table 1 to clarify the possible reaction pathway and mechanism for the present system. The results are summarized in Table 2. In the case of Pt–PVP + TiO_2, the conversion of each substrate and LA yields reached 95–99 % and 40–58 %, respectively, within 1 h (Table 2 entries 3–5, 8, and 12). These conversions and LA yields are comparable to those for the reaction of glycerol with Pt–PVP + TiO_2 after 18 h. In addition, bare TiO_2 had almost the same catalytic performance as that of Pt–PVP + TiO_2 (entries 2 vs. 3, 7 vs. 8, and 11 vs. 12), although the LA yield was negligibly small in the absence of the catalysts (entries 1, 6, and 10). Lower LA yield for GA conversion over Nb_2O_5[15] (entry 9) also represents the high efficiency of water-tolerant Lewis acid sites on TiO_2[8] as well as glycerol conversion (Table 1, entry 1 vs. 10). These results indicate that the formation of LA from GA, DHA, and PA intermediates is catalyzed by TiO_2 and that oxidation of glycerol into GA/DHA could be the rate-determining step for the present reaction.[16] Notably, LA was not selectively obtained with only Pt–PVP, even at a relatively high conversion of glycerol (Table 1, entry 18). Therefore, glycerol oxidation into GA/DHA is catalyzed by Pt nanoparticles loaded on TiO_2 and the GA/DHA intermediates are thus easily converted into LA by TiO_2, and side reactions such as the overoxidation and intermolecular condensation of GA/DHA are suppressed. The yield of LA in-

Table 2. Conversion of intermediates into LA by Pt–PVP + TiO_2 catalyst.[a]

Entry	Substrate [mmol]	Catalyst	Conversion [%]	Yield of LA [%]
1	DHA (1)	without	22	<1
2	DHA (1)	TiO_2	97	39
3	DHA (1)	Pt–PVP + TiO_2	95	40
4	DHA (0.5)	Pt–PVP + TiO_2	98	50
5	DHA (0.25)	Pt–PVP + TiO_2	>99	58
6	GA (1)	without	50	2
7	GA (1)	TiO_2	99	40
8	GA (1)	Pt–PVP + TiO_2	>99	42
9	GA (1)	Nb_2O_5	>99	29
10	PA (1)	without	34	<1
11	PA (1)	TiO_2	95	53
12	PA (1)	Pt–PVP + TiO_2	97	54

[a] TiO_2 or Nb_2O_5 (50 mg), Pt–PVP (0.1 wt % with respect to TiO_2), water (5 mL), 423 K, 1 h, O_2 (0.5 MPa). Conversion (%) = converted substrate (mol)/initial substrate (mol) × 100. Yield (%) = carbon in LA (mol)/carbon in initial substrate (mol) × 100. Yields of other products are summarized in Table S5.

creased with a decrease in the initial DHA concentrations, which supports this pathway (Table 2, entries 3–5).

Conclusions

The catalytic one-pot conversion of glycerol to LA was investigated in water media under an oxygen atmosphere in the absence of any additives. Among the catalysts tested, the combination of Pt nanoparticles and TiO_2 exhibited high catalytic activity and durability for the reaction. Pt nanoparticles oxidized glycerol into GA/DHA, and Lewis acid sites on TiO_2 readily accelerated the dehydration and 1,2-hydride shift reaction into LA.

Experimental Section

Catalyst preparation

Anatase TiO_2 was prepared by the hydrolysis of Ti(O*i*Pr)$_4$ (40 g, Kanto Chemical) in distilled water (160 mL) at 313 K for 5 h with stirring, followed by filtration and washing with distilled water.[8b] The resulting material was dried overnight at 353 K, and then was calcined at 473 K for 5 h. ZrO_2 was obtained by the calcination of $Zr(OH)_4$ (Aldrich) at 473 K for 5 h. Nb_2O_5 (Companhia Brasileira de Metalurgia e Mineração), Al_2O_3 (Japan Reference Catalyst, JRC–ALO–6), MgO (Ube Material Industries), SiO_2 (Fuji Silysia Chemical, CARiACT Q-10), and AC (Aldrich, Activated Charcoal Norit) were purchased and pretreated at 473 K for 5 h under air except for AC. Metal-nanoparticles-dispersed solutions (Aldrich) were utilized as the oxidation catalyst without any pretreatment.

Glycerol conversion

The conversion of glycerol was operated in 18 mL Teflon high-pressure reactor covered by SUS external cylinder with one gas injection port. The metal oxide or activated carbon (50 mg), metal nanoparticle (0.1 wt% metals with respect to metal oxide or activated carbon), and aqueous glycerol solution (5 mL, 0.2 м, glycerol: Kanto Chemical) were loaded into the reactor, and then introduced at 0.5 MPa O_2. The reaction mixture was stirred at 423 K. After the removal of the catalyst by filtration, the products in the liquid phase were analyzed by HPLC (JASCO, LC-2000 plus) equipped with Aminex HPX-87 H column (diameter: 300 mm × 7.8 mm, eluent: 0.005 м H_2SO_4 0.5 mL min^{-1}, temperature: 308 K), refractive index (RI) and photodiode array (PDA). The spent catalyst was recovered by centrifugation. After washing with water (30 mL), the recovered catalyst was dried at 353 K, and was utilized for reuse experiment and/or characterizations. The reactions of DHA (Merck), GA (Wako Pure Chemical Industries), PA (40 wt% solution, Aldrich), 1-butanol (Tokyo Chemical Industry), and 2-butanol (Tokyo Chemical Industry) were also performed in the same procedure above.

Catalyst characterization

XPS analysis was performed with JEOL JPC-9010MC for Pt 4f using $Mg_{K\alpha}$ radiation (1253.6 eV) at 10 kV and 25 mA. Samples were pressed into pellet and fixed on a double-stick carbon tape. The binding energies were calibrated using sputtered Au ($4f_{7/2}$ peak at 83.8 eV). HAADF–STEM measurement were performed by using ESCA-3400 (Shimadzu) at an acceleration voltage of 200 kV. Samples were dispersed on a copper grid with ethanol, and dried overnight under vacuum. XRD patterns were measured with Ultima IV (Rigaku) using $Cu_{K\alpha}$ radiation (40 kV, 40 mA). N_2 adsorption–desorption isotherms were recorded at 77 K ($0.050 \leq p/p_0 \leq 0.995$) with Nova-4200e (Quantachrome). The catalysts were pretreated under vacuum at 423 K for 1 h to remove adsorbed water and gasses. The isotherms were analyzed by the BET method to calculate the specific surface area in the range of $0.050 \leq p/p_0 \leq 0.300$.

FTIR spectroscopy measurement for acid site characterization

The Lewis acid site density on TiO_2 was estimated for pyridine-adsorbed samples at 298 K. Pt/TiO_2 sample for the IR measurement was prepared in water solution for 1 h at 423 K under Ar. The sample was pressed into a self-supporting disk (20 mm diameter, ca. 20 mg) and placed in an IR cell attached to a closed glass-circulation system (0.38 dm^{-3}). The disk was dehydrated by heating at 473 K for 1 h under vacuum to remove physisorbed water and was then exposed to pyridine vapor (>4 kPa) at RT. The intensities of the IR bands measured at 1445 cm^{-1} (pyridine coordinatively bonded to Lewis acid sites, molecular absorption coefficient: 4.86 μmol cm^{-1}) were plotted against the amounts of pyridine adsorbed on the Lewis acid sites of the samples.

Quantum chemical calculations

The DFT calculations were conducted at the B3LYP level theory (6-31++G* basis sets for H, C, and O) by using conductor-like polarizable continuum model (CPCM) with parameters of the Universal Force Field (UFF).[17] The geometries of glycerol, lactic acid, and all intermediates were optimized, and the vibrational analysis was performed to confirm that they have no imaginary frequency. The Gibbs free energies (at 1 atm and 298.15 K) were compared. All calculations were performed with the Gaussian09 program package.[18]

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Keywords: biomass · Lewis acids · oxidation · platinum · titanates

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