

Efficient Synthesis of Lactic Acid by Aerobic Oxidation of Glycerol on Au–Pt/TiO₂ Catalysts

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Biomass and its derivatives provide renewable alternatives to fossil fuel resources for sustainable production of chemicals and liquid fuels.^[1–3] One such example is glycerol, which is currently available in surplus as an inevitable by-product from biodiesel production by transesterification of vegetable oils, and can also be potentially obtained from more sustainable microalgae or cellulose and its derivatives in the near future.^[1,3–6] Glycerol is polyfunctional and it is reported to convert to a variety of valuable chemicals or intermediates by different catalytic reactions, such as selective hydrogenolysis, oxidation, and dehydration.^[1–3,5,6] These features render glycerol viable as a versatile biobuilding block,^[1–3,5,6] and thus its new chemistry has been largely exploring to expand its outlets, which can also in turn optimize the economy of biodiesel production. Herein, we report a new oxidation reaction of glycerol to lactic acid.

Lactic acid (2-hydroxypropanoic acid) is an important platform chemical and widely applied in the food, pharmaceutical, and chemical industries.^[7–9] Its market demand grows rapidly, in particular, because of its application in the synthesis of polylactic acids useful as biodegradable plastics and biocompatible medical materials.^[7–9] Lactic acid can be produced by chemical and fermentation routes.^[7–9] The chemical routes involve the reactions of petroleum-based feedstocks, such as acetaldehyde with HCN in the presence of H₂SO₄, which are clearly not green and sustainable. Therefore, lactic acid is currently manufactured mainly by fermentation of carbohydrates (e.g., starch-derived glucose). However, the efficiency and productivity of the fermentative

method are low and need to be improved substantially. It is thus imperative to develop more efficient methods, including the use of new reactants for the large-scale production of lactic acid.

Recently, Kishida, et al.^[10] reported that a hydrothermal reaction of glycerol with NaOH at 573 K forms lactic acid in high yields. Davis et al.^[11] also detected the formation of lactic acid in glycerol hydrogenolysis to propylene glycol in alkaline solutions at 473 K and 4.0 MPa H₂. These previous studies have shown the potential of glycerol as an alternative reactant for the synthesis of lactic acid, irrespective of their low efficiencies or harsh reaction conditions, which may present significant hurdles to their industrial practice. Moreover, these studies proposed the formation of lactic acid in the presence of bases via a glyceraldehyde intermediate formed from glycerol dehydrogenation,^[10,11] which appears to be thermodynamically more favorable under oxidation conditions. This proposition is in accordance with the known isomerization of glyceraldehyde and its isomer dihydroxyacetone to lactic acid.^[8,12] However, extensive studies on glycerol oxidation have shown that glyceric acid is generally the dominant product in the presence of bases, without the formation of lactic acid in any significant amount,^[13–17] apparently reflecting the susceptibility of glyceraldehyde or dihydroxyacetone to oxidation. For instance, Hutchings, et al.^[13] reported glycerol oxidation to glyceric acid with 100 % selectivity at 56 % conversion on Au/C in the presence of NaOH (at 333 K and 0.3 MPa O₂). Herein, we report a one-pot approach to the efficient conversion of glycerol into lactic acid at atmospheric pressure by a combination of glycerol oxidation with O₂ on Au–Pt/TiO₂ to glyceraldehyde and dihydroxyacetone intermediates and their instantaneous reactions with NaOH in water.

Table 1 shows the activities (normalized to total metal atoms) and selectivities for the aerobic glycerol oxidation at atmospheric pressure of O₂ and 363 K in the presence of NaOH at similar glycerol conversions (ca. 30 %) on TiO₂-supported bimetallic Au–Pt with various Au/Pt atomic ratios (3:1–1:3) and, for comparison, monometallic Au, Pt, and Pd catalysts. Characterization of these catalysts by TEM

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Table 1. Glycerol conversion activities and selectivities on different catalysts.^[a]

Entry	Catalyst	Activity ^[b] [h ⁻¹]	Selectivity [%]				
			Lactic acid	Glyceric acid	Tatronic acid	Oxalic acid	Glycolic acid
1	Au/TiO ₂	374.4	73.8	21.0	3.5	0.3	0.5
2	Pt/TiO ₂	405.2	84.8	9.5	0.7	0.2	3.2
3	Pd/TiO ₂ ^[c]	9.1	10.3	63.9	6.2	0.0	14.4
4	Au–Pt/TiO ₂ (1:1) ^[d]	517.1	85.6	10.6	0.5	0.2	1.7
5	Au–Pt/TiO ₂ (3:1) ^[d]	507.4	84.3	11.5	0.6	0.2	1.7
6	Au–Pt/TiO ₂ (1:3) ^[d]	501.3	85.3	11.5	0.7	0.2	3.2
7	Au/TiO ₂ + Pt/TiO ₂ (1:1) ^[e]	386.7 (389.8) ^[f]	81.5 (79.3) ^[f]	11.7 (15.3) ^[f]	1.4 (1.8) ^[f]	0.2 (0.2) ^[f]	3.1 (2.7) ^[f]

[a] 363 K, 1 atm O₂, 2.5 × 10⁻³ mmol metal, 0.22 mol L⁻¹ glycerol in H₂O, NaOH/glycerol = 4:1 (mole ratio), ≈ 30 % glycerol conversion. [b] Glycerol conversion activities normalized per metal atom. [c] 9.4 × 10⁻³ mmol metal was used because of its low activity. [d] Data in parentheses represent Au/Pt molar ratios. [e] Physical mixture of Au/TiO₂ and Pt/TiO₂ with equal amounts. [f] Data in parentheses correspond to the theoretical values calculated by the assumption that Au/TiO₂ and Pt/TiO₂ behave independently.

showed that they possessed similar metal particle sizes (2.7–3.8 nm, Figure 1 and Figures S1–S4 in the Supporting Information). Au, Pt, and Pd were studied because of their wide applications as active catalyst components for glycerol oxidation.^[13–17] The choice of TiO₂ support was based on our experiments showing that Au dispersed on TiO₂, Al₂O₃, CeO₂, ZrO₂ and Fe₂O₃ actively produced lactic acid (Table S1 in the Supporting Information) in good selectivities (67.5–73.8 %) at atmospheric pressure of O₂ and TiO₂ was superior to the other supports in term of both the cata-

lytic activity and lactic acid selectivity. As shown in Table 1, entry 1, Au/TiO₂ catalyzed glycerol oxidation to lactic acid with an activity of 374.4 h⁻¹ and 73.8 % selectivity; other products included glyceric acid (21 %), tatronic acid (3.5 %), and insignificant glycolic acid, oxalic acid, and formic acid (in total ≈ 1.6 %). Pt/TiO₂ was also active for glycerol oxidation, showing an activity of 405.2 h⁻¹ and lactic acid selectivity of as high as 84.8 % (Table 1, entry 2). In contrast, Pd/TiO₂ was much less active (9.1 h⁻¹) with only 10.3 % selectivity for the synthesis of lactic acid under identical conditions (Table 1, entry 3), which is in agreement with the low activity of Pd catalysts previously reported in glycerol oxidation.^[15] Notably, combination of Au and Pt (Au/Pt = 1:1) on TiO₂ led to an enhanced activity (517.1 h⁻¹) with a high lactic acid selectivity (85.6 %; Table 1, entry 4), which remained essentially constant over a relatively broad range of Au/Pt ratios (1:3–3:1) (Table 1, entries 4–6). Moreover, the Au–Pt/TiO₂ catalysts retained such high selectivity to lactic acid (ca. 86 %) even at 100 % glycerol conversion (Figure S5 in the Supporting Information), corresponding to approximately 86 % yield of lactic acid. To the best of our knowledge, this is the highest lactic acid yield directly from glycerol conversion reported to date in the literature under such mild conditions.

For comparison, a physical mixture of Au/TiO₂ and Pt/TiO₂ (Au/Pt = 1:1) was examined in glycerol oxidation. Its activity and product selectivity (Table 1, entry 7) were essentially equal to the average of the activity and of the selectivity for the two individual components tested separately. Therefore, the improved performance of the bimetallic Au–Pt catalysts, compared to the monometallic Au and Pt catalysts, is not due to the coexistence of Au and Pt, but can be tentatively ascribed to the interaction and synergism between the two metals, as evidenced from previously reported IR spectra for CO adsorption.^[18,19] The interaction leads to electron transfer from Au to Pt on Au–Pt/TiO₂, in agreement with the finding by X-ray photoelectron spectroscopy.^[20] Such an interaction between Au and Pt may originate from their alloying on Au–Pt/TiO₂, which can be seen from the high-resolution TEM images, showing uniform lattice spacings of 2.29 Å (Figure 1a) between the values of 2.35 and 2.23 Å (Figures S1a and S2a in the Supporting Information), characteristic for Au (111) and Pt (111) planes,^[21] as reported previously.^[19b,22]

Such interaction and synergism also led to excellent reusability of the Au–Pt catalysts, which is an important feature of solid catalysts in liquid-phase reactions. As shown in Figure 2, no essential decline in lactic acid yields was observed on Au–Pt/TiO₂ (Au/Pt = 1:1) after five successive

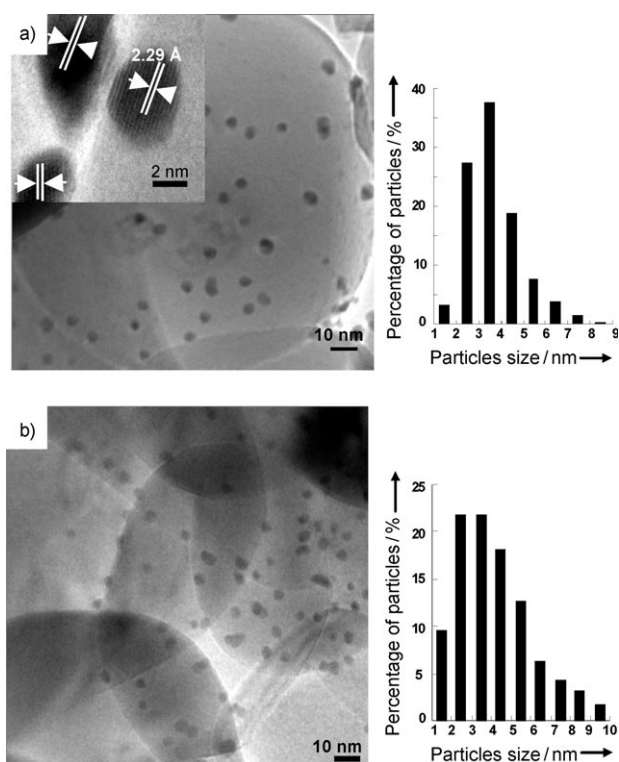


Figure 1. TEM images and histograms of Au–Pt particle size distribution of Au–Pt/TiO₂ (Au/Pt = 1:1) before (a) and after (b) five reaction cycles at 363 K. Inset in (a) represents HRTEM image of Au–Pt/TiO₂ (Au/Pt = 1:1) before the reaction.

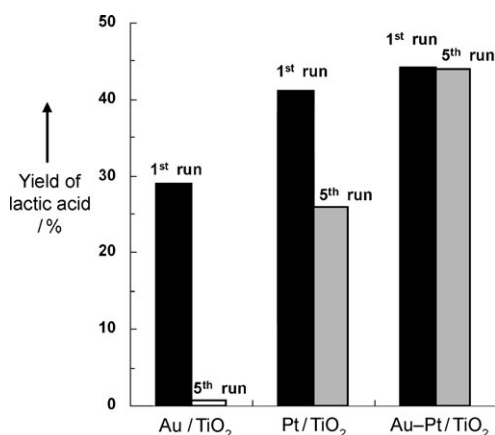
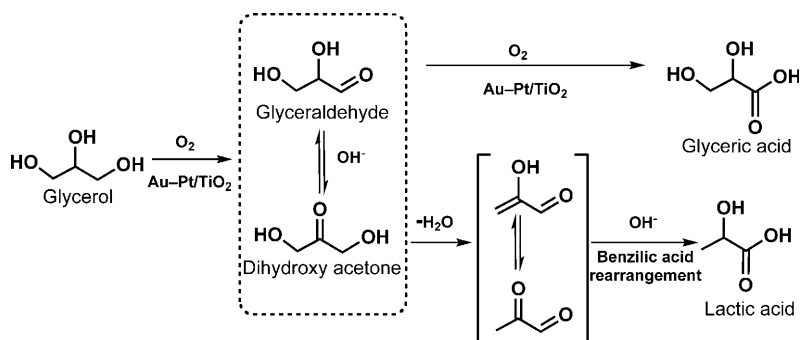


Figure 2. Yields of lactic acid after five reaction cycles at 363 K on Au/TiO₂, Pt/TiO₂, and Au-Pt/TiO₂ (Au/Pt=1:1, 2.5×10^{-3} mmol metal, 0.22 mol L^{-1} glycerol in H₂O, NaOH/glycerol=4:1 (mole ratio), 1 atm O₂)

cycles. This is consistent with the characterization results for this catalyst. Analysis of the aqueous reaction solutions by inductive coupled plasma emission spectroscopy (ICP) after each cycle showed no detectable leaching of Au and Pt into the reaction mixture. The mean diameters of the Au-Pt nanoparticles and their size distributions were essentially unaltered after the five cycles (Figure 1b). These results demonstrate that the bimetallic Au-Pt/TiO₂ catalysts are stable and recyclable under the reaction conditions used in this work, which are in sharp contrast to the monometallic Au and Pt catalysts that showed dramatic decrease in their activities (Figure 2). No leaching of Au or Pt was detected by ICP for these two catalysts. Together with the TEM characterization results (Figure S1 in the Supporting Information), Au/TiO₂ deactivation can be ascribed to the large aggregation of the Au nanoparticles (3.8 vs. 7.6 nm). No significant growth of Pt nanoparticles for Pt/TiO₂ after the recycling was observed (Figure S2 in the Supporting Information), and thus oxygen covering or oxidation of the Pt surfaces may account for the deactivation of Pt/TiO₂, as generally found for Pt catalysts in the literature.^[15c,23] Taken together, it is clear that the interaction between Au and Pt can efficiently prevent the agglomeration of Au particles and the poisoning of Pt sites by O₂, leading to the observed superior stability of the Au-Pt/TiO₂ catalysts.

To understand the reaction pathways and mechanism for the glycerol reaction to lactic acid, several experiments were performed with no Au-Pt/TiO₂ catalyst, NaOH, or O₂ (other conditions were the same as those given in Table 1). It was found that glycerol reaction did not occur at all in the absence of either Au-Pt/TiO₂ (Au/Pt=1:1) or O₂ at 363 K, even when

NaOH was present. In the absence of NaOH, glycerol was oxidized on Au-Pt/TiO₂ (Au/Pt=1:1) predominantly to glyceraldehyde, dihydroxyacetone, and glyceric acid with selectivities of 61.3, 22.5, and 11.8%, respectively (at $\approx 10\%$ conversion), reflecting the preference of this catalyst for oxidizing the primary hydroxyl groups over the secondary ones in glycerol. The activity was 411.6 h^{-1} (normalized by the total Au and Pt atoms), which is comparable to that in the presence of NaOH and indicates that there is no involvement of NaOH in the rate-determining step of glycerol oxidation. With increasing the glycerol conversion, the glyceraldehyde selectivity decreased concurrently with an increase in the selectivity to glyceric acid, while the selectivity to dihydroxyacetone and also the sum of the selectivities to glyceraldehyde and glyceric acid remained essentially constant. Further, we confirmed that no tautomerization occurred between glyceraldehyde and dihydroxyacetone in such neutral aqueous solutions, although it is known to occur under basic or acidic conditions, showing that these two products are all primarily formed from glycerol. Taken together, these results demonstrate that glycerol oxidation requires the presence of both Au-Pt catalysts and an O₂ atmosphere; NaOH itself does not catalyze glycerol conversion under our reaction conditions (especially at temperatures as low as 363 K), consistent with the results reported by Kishida et al.^[10] Glyceraldehyde and dihydroxyacetone are formed primarily from glycerol, while glyceric acid is a secondary product from the oxidation of glyceraldehyde. Our separate reactions of glyceraldehydes and dihydroxyacetone with NaOH showed that these intermediates readily converted to lactic acid and other products in the absence or presence of Au-Pt/TiO₂, at rates much faster than that of the glycerol oxidation. Taken together, we propose that glycerol oxidation proceeds, as shown in Scheme 1, by kinetically relevant oxidative dehydrogenation of glycerol to glyceraldehyde and dihydroxyacetone intermediates on Au-Pt nanoparticle surfaces, followed by base-catalyzed dehydration and benzilic acid rearrangement of these intermediates to lactic acid, or their further oxidation to glyceric acid by Au-Pt/TiO₂. The two secondary reaction steps are competitive, and accordingly, dictate the final selectivities to lactic acid and glyceric acid. Such reaction pathways offer directions to optimize the reaction conditions and thus the catalytic activities and



Scheme 1. Proposed glycerol reaction pathways on Au-Pt/TiO₂.

lactic acid selectivities, as our preliminary results confirmed that higher reaction temperatures and lower O₂ concentrations favor the formation of lactic acid (not shown here).

In conclusion, we have developed an efficient approach to the synthesis of lactic acid from glycerol aerobic oxidation in high yields on the bimetallic Au–Pt catalysts in alkaline aqueous solutions, which proceeds through glyceraldehyde and dihydroxyacetone intermediates formed from glycerol oxidative dehydrogenation as rate-determining step. Further optimization of the two competitive reactions of the dehydrogenated intermediates, for example, by design of the catalysts and tuning of the reaction parameters will improve the yield and productivity in this work and lead to potential industrial practice of this approach.

Experimental Section

TiO₂-supported monometallic Au, Pt, and Pd and bimetallic Au–Pt catalysts were prepared by a single-step borohydride reduction method.^[24] Upon treatment in air at 673 K for 4 h, TiO₂ was dispersed in deionized water at 298 K, into which aqueous solutions of HAuCl₄, H₂PtCl₆, and PdCl₂, and of HAuCl₄ and H₂PtCl₆ (Beijing Chemicals, AR grade) with varying Au/Pt atomic ratios were added with vigorous stirring, followed by adding an aqueous solution of excess NaBH₄ (Beijing Chemicals, AR grade) dropwise. The total metal loadings were kept around 1 wt%. After agitation for 2–4 h, the mixtures were filtered and washed with H₂O until no Cl[–] was detected in the filtrate by using AgNO₃. All catalysts were dried in an oven under vacuum at 298 K overnight, and then treated in flowing air at 573 K for 2 h.

Oxidation reactions of glycerol (Beijing Chemicals, AR grade) were typically carried out in a three-necked flask (100 mL) at 363 K with atmospheric pressure O₂ flowing through the reaction solutions under vigorous stirring. Liquid-phase products were analyzed by HPLC and ESIMS, and gas-phase products were analyzed by GC. Glycerol reaction activities were reported as molar glycerol conversion rates per mole of metal per hour, and selectivities on a carbon basis; carbon mass balance was better than (99 ± 3) % in this work.

TEM and high-resolution TEM images for supported Au, Pt, Pd, and Au–Pt catalysts were taken on a Philips Tecnai F30 FEG-TEM and a Hitachi H-9000NAR microscope, respectively, operated at 300 kV. Samples were prepared by uniform dispersion in ethanol and were then placed onto carbon-coated copper grids. The average size of metal particles and their size distributions were calculated by averaging of not less than 300 particles randomly distributed in TEM images.

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