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Bimetallic AuPt/TiO₂ Catalysts for Direct Oxidation of Glucose and Gluconic Acid to Tartaric Acid in the Presence of Molecular O₂

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Abstract

Tartaric acid is an important industrial building block in food and polymer industry. However, green manufacture of tartaric acid remains a grand challenge in this area. Up to date, chemical synthesis from nitric acid-facilitated glucose oxidation leads to only < 10% yield with significant toxics as by-products. We reported a one-pot aqueous phase oxidation of glucose and gluconic acid using bimetallic AuPt/TiO₂ catalysts in the presence of molecular O₂, with ~50% yield toward tartaric acid at 110 °C and 2 MPa. Structural characterization and DFT calculation reveal that, the lattice mismatch between fcc Pt and bcc Au induces the formation of twinned boundaries in nanoclusters, and Jahn-Teller distortion in electronic field. Such structural and electronic reconfiguration leads to enhanced σ -activation of C-H bond competing with π - π electronic sharing of C=O bond on catalyst surface. As a result, both C-H (oxidation) and C-C (decarboxylation) bond cleavage reactions synergistically occur on the surface of bimetallic AuPt/TiO₂ catalysts. Therefore, glucose and gluconic acid can be efficiently transformed into tartaric acid in base-free medium. Lattice distortion enhanced reconfiguration of electronic field in Pt-based bimetallic nanocatalysts can be utilized in many other energy and environmental fields for catalyzing synergistic oxidation reactions.

Key words: oxidation; bimetallic catalysts; glucose; tartaric acid; lattice distortion; electronic reconfiguration

 Replacing petroleum and coal feedstocks with renewable carbon resources is considered to be critical for existing energy and environmental issues.^{1, 2} Biomass feedstocks represent promising alternative sources owing to their great abundance on earth. Up to date, the catalytic conversion of bio-derived molecules to valuable chemicals has been the subject of extensive research efforts in both academia and industry.³ In this context, aqueous phase oxidation (APO) of carbohydrates provides emerging alternative routes for the sustainable production of renewable carboxylic acids and derivatives.^{4, 5} This effort is largely driven by the increasing demands from bio-based plastic industry. Sugar-derived carboxylic derivatives are major building blocks for a variety of commodity products such as BPA-free plastics, bio-degradable polymers and environment friendly detergents for human society.⁶ Obviously, clean synthesis of renewable carboxylic acids is essential for reduced reliance on fossil-based resources, shaping the future sustainability of chemical industry.

Tartaric acid (TA), a C₄ hydroxyl dicarboxylic acid, is an important additive and monomer with broad applications in food and polymer industry.^{5, 7} For example, TA is used as an antioxidant and acidification agent. It can also be utilized as a performance enhancer of cement.⁸ TA is also an essential component for manufacturing pharmaceuticals as well as electronic devices.⁹ To our best knowledge, very limited work has been reported on catalytic synthesis of TA from either bio- or fossil-derived feedstocks (see left part of Figure 1). In particular, (a) TA is traditionally obtained *via* biological route using enzyme catalysts (Figure 1a, hydrolase). However, it suffers from poor production rate thus hindered for further industrial applications.^{10, 11} As an alternative route, Scheel and colleagues first (in 1769) found that, (b) TA could be recovered from tartar, a less-valued residue formed during wine production (Figure 1b).^{12, 13} After century development, TA manufacturing still heavily relies on the wine-making industry. Poor extraction efficiency, distributed but small scaled batch production technique, prevents its mass production for chemical industry. (c) In 1951,

Church and co-workers demonstrated that TA could be synthesized from maleic acid, in H₂O₂ solution over tungstic acid as the catalyst (Figure 1c).¹⁴ This process generates significant amounts of corrosives and hazards. (d) Similar issues have also bottlenecked Mo/W catalyzed oxidation of gluruconic acid (Figure 1d).¹⁵ Energy intensive separation and poor recyclability of homogeneous catalysts have posed a grand challenge, making the process less sustainable and environmentally benign. Therefore, it is urgently demanded greener approaches for making TA economically and efficiently from biomass.



Figure 1. Different conversion routes for synthesis of tartaric acid from fossil- and biofeedstocks, (a) biological route, (b) extraction from tartar, (c) H₂O₂ oxidation of maleic anhydride, (d) homogeneous gluruconic acid oxidation, (e) proposed direct oxidation of glucose using O₂ as oxidant.

Direct synthesis of TA from glucose provides a promising route for the production of various downstream polymers and pharmaceutical products (Figure 1e). However, initial attempts in both academia and industry remains unsuccessful. Numerous reports have proposed Pt-based mono and bimetallic catalysts for glucose oxidation to glucaric, tartronic and oxalic acids as valuable hydroxyl dicarboxylic acids.¹⁶⁻¹⁸ Overall TA yields are, however, very low (Y < 10%).¹⁸⁻²³ In addition, the detailed mechanism for glucose oxidation to TA is still under debate, as rational control of C-C and C-H cleavage of glucose molecule remains to be addressed in this field.

In this work, we reported a series of synergistic AuPt/TiO₂ catalysts (TOF: 959 h⁻¹ at 110 °C) for direct glucose oxidation to TA using molecular O₂. A record high yield of 50% TA was achieved in one-pot glucose conversion. The key finding in this work is that, the twinned bimetallic AuPt clusters and Jahn-Teller distortion of d orbital at Au-Pt interface synergistically contribute to enhanced production rate of TA (2.3 mol/molmetal/h) from glucose at 110 °C and 2.0 MPa (literature results: ~0.52 mol/molmetal/h).^{19, 20, 22} It is confirmed that, gluconic acid is the key intermediate for the generation of TA. Experimental studies further demonstrated that, gluconic acid display significantly high substrate inhibition effect on bimetallic AuPt/TiO2, compared with glucose in aqueous medium. Based on surface characterization using UV-Vis and structure-dependency studies obtained from kinetic analysis, it is highly possible that simultaneous C-H and C=O bond activation competitively proceed on the surface of AuPt/TiO₂ catalysts. Furthermore, the influence of catalyst composition, reaction temperature, pressure as well as compositional dependent kinetics on oxidation of glucose and gluconic acid was studied systematically, with the aim to elucidate plausible reaction mechanism for direct oxidation of glucose to TA. The outcome of this work offers new insights into atom efficient oxidation of sugars to renewable chemical products.

2. Experimental

2.1 Materials

TiO₂ (rutile & anatase), glucaric acid potassium salts, D-xylonic acid provided by Sigma-Aldrich. Glyoxylic acid (50% in water), DL-glyceraldehyde (90%) and DLtartaric acid (AR) were purchased by Macklin Biochemical Co., Ltd. D-glucose, $H_2PtCl_6 \cdot 6H_2O$, HAuCl₄·4H₂O, Co(NO₃)₂·6H₂O, Mn(NO₃)₂, NaOH, Na₂CO₃, glycolic acid, NaBH₄ were supplied by Sinopharm Chemical Reagent Co., Ltd. Gluconic acid was supplied by Hubei Wande Chemical Co., Ltd.

2.2 Catalyst preparation

2.2.1 Synthesis of TiO₂ supported monometallic Pt and Au catalysts

We used NaBH₄ as the reducing agent to prepare monometallic Pt and Au nanocatalysts, which is similar to previous reports.²⁴ Specifically, certain amounts of the metal precursor H₂PtCl₆ or HAuCl₄ were added to a 150 mL aqueous slurry containing approximately 1.5 g of TiO₂ powders. The whole mixture was vigorously stirred at room temperature for 1 h, after which freshly prepared NaBH₄ aqueous solution (0.07 g in 100 mL) was added slowly to the slurry. The catalyst sample was then aged for 10 h under stirring. The solid catalyst samples were filtrated and washed with deionized (DI) water at least four times to remove the residual species during catalyst synthesis. The as-prepared catalysts were dried in a vacuum oven at 70 °C for another 10 h before using in oxidation tests. Metal loading for Pt and Au on TiO₂ support is 2 wt%, respectively.

2.2.2 Synthesis of bimetallic catalysts supported on TiO₂

Bimetallic AuPt/TiO₂ catalysts were also synthesized using NaBH₄ as the reducing agent, the preparation procedure of which is similar with that for monometallic catalysts. The loading of Pt/Au was varied from 0.5/0.5, 1.0/1.0, 2.0/2.0, 4.0/4.0 wt%/wt%. The average particle size of these bimetallic AuPt/TiO₂ catalysts is 4.2±0.1 nm, 4.8±0.1 nm, 7.5±0.2 nm and 8.4±0.3 nm, respectively. These samples were denoted as AuPt/TiO₂-4.2, AuPt/TiO₂-4.8, AuPt/TiO₂-7.5 and AuPt/TiO₂-8.4, respectively. Similar procedures were also followed to prepare the AuCo/TiO₂, AuMn/TiO₂, PtCo/TiO₂ PtMn/TiO₂ catalysts. The metal loading of these samples is same as 2.0/2.0 wt%/wt%.

2.3 Catalyst characterization

Inductively coupled plasma-optical emission spectrometry (ICP-OES) using an Agilent 730 spectrometer was used to determine Pt and Au content. The N_2 adsorptiondesorption isotherms were measured on a Micromeritics ASAP 2020 instrument. Transmission electron microscope (TEM) images were obtained with a Tecnai G2 F20 S-Twin instrument equipped with a digital imaging system. X-ray photoelectron spectroscopy (XPS) as performed using a Perkin-Elmer PHI ESCA system. The binding energy of the C1s peak, i.e., 284.6 eV, was used was the standard for calibration.

The dispersion of metals was checked by CO adsorption using static volumetric methods (Micromeritics AutoChem 2920 analyzer). Sample (about 0.05 g) was firstly pretreated in hydrogen (50 cm³/min) at 150 °C for 1 h and purged with helium (50 cm³/min) for 1 h at the same temperature. And then, the catalyst was cooled to 50 °C and CO pulses were injected from a calibrated on-line sampling valve. CO adsorption equilibrium criterion is 1.2. Stoichiometry of 2 was used for calculations.

UV-Vis absorption spectra and diffuse reflectance (DR) spectra were recorded with a UV-Vis-NIR Cary 5 (Varian) spectrophotometer. DR spectra were plotted in Kubelka-Munk (KM) arbitrary unit *vs* wavelength. UV-vis spectra of liquid phase were recorded using a spectrophotometer (TU-1901), for which the solutions were left in a cell for the measurement.

2.4 Oxidation test

The catalytic performances of solid catalysts were evaluated in a 50 mL autoclave. In a typical experiment, a certain amount of the catalyst and 15 mL of glucose or gluconic acid aqueous solution (0.3 mol/L) were transferred into the reactor, respectively. The autoclave was then purged twice with pure O₂ at room temperature and then filled with O₂ before heating. The reaction mixture was heated under 200 rpm till target reaction temperature (e.g., 110 °C), when stirring rate was switched and maintained at 1000 rpm for pre-determined time (e.g., 4 h). Following each batch reaction, the reactor was cooled down and the mixture was analyzed by high-performance liquid chromatography (HPLC) using a Shimadzu LC-20AT equipped with both refractive index (RID-10A) and ultraviolet-visible (SPD-20A) detectors. A 5 mmol/L aqueous H₂SO₄ solution flowing at 0.8 mL/min was used as the mobile phase in conjunction with an ion-exclusion column (Rezex ROA-Organic Acid H⁺ (8%), 300×7.8 mm) at 60 °C. The definitions of turnover frequency (TOF), conversion, selectivity, carbon balance (%) and reaction rate used herein are similar to those previously described in literature.²⁵ In particular, TOF is defined as the amounts of reactant being converted over certain amounts of surface metals during a period of time. Conversion (X) is defined as the ratio of amounts of reactant transformed to that initially charged.

Selectivity (S) is defined as the ratio of total moles of carbon in particular product to the carbon mole in the converted reactant. Carbon balance (C%) is defined as the ratio of total amounts of carbon in the product formed to that existing in converted reactants.

TOF = $\frac{\Delta N_{reactant}}{N_{surface metal} \times Reaction time}$ (calculation of surface metal: refer to Supporting

Information)

$$\text{Conversion} = \frac{\frac{C_{moles, reactant}^{initial} - C_{moles, reactant}^{initial}}{C_{moles, reactant}^{initial}} \times 100\%$$

Selectivity =
$$\frac{C_{moles, products}^{final}}{C_{moles, reactant}^{initial} - C_{moles, reactant}^{final} \times 100\%$$

$$C\% = \frac{C_{moles, products}^{final}}{C_{moles, reactant}^{competted}} \times 100\%$$

Reaction rate = $\frac{\Delta N_{reactant}}{Mass_{catalyst(total)} \cdot Time_{reaction}}$

2.5 Density functional theory (DFT) calculations

DFT calculation was carried out to estimate change of bond length and electronic reconfiguration in nanoclusters. The procedure has been discussed in our previously thus stated briefly. Pt (111) surface were modeled using a triple-layer p (4×4) slab comprising 3 metal layers with 16 atoms per layer and each slab was separated by a vacuum of 17 Å to ensure the interaction between neighboring cells was negligible, which is similar to our previously reported method.^{26, 27} All DFT calculations were performed using CASTEP code.^{28, 29} Using the PBE functional, the exchange-correlation effects were described with the generalized gradient approximation (GGA). The electron wave functional was expanded by a plane-wave basis set with a cutoff energy of 400 eV. A $3 \times 3 \times 2$ Monkhorst-Pack k-point grid was used for the integrations of the Brillouin zone. The performance of the three-layer slab model and the calculation parameters, including the p (3×4) supercell, $3 \times 3 \times 2$ k-point, 15 A vacuum zone, and the energy cutoff of 400 eV, have been tested extensively in previous studies.

3. Result and discussion

3.1 Catalyst screening

We selected several mono and bimetallic catalyst candidates and tested their performances in direct oxidation of glucose base-free medium. These catalysts include Au/TiO₂, Pt/TiO₂, AuPt/TiO₂*, PtCo/TiO₂, PtMn/TiO₂, AuCo/TiO₂ and AuMn/TiO₂ materials. Conversion and selectivity of glucose over these catalysts are studied at 110 °C and 1 MPa O₂, the results of which are presented in Table 1. Before we compared the conversion and selectivity data, calculation on mass transfer significance was performed to exclude possible contribution of external and internal mass transfer limitation (refer to Supporting Information).

Selectivity (%) Conversion # Catalyst С% (%) GA ΤA XA Others Au/TiO₂ 48.1 67.6 2.7 0.0 11.2 81.5 1 2 Pt/TiO₂ 38.2 63.2 12.4 0.0 11.7 87.3 3 AuPt/TiO₂* 20.0 100.0 57.1 3.8 13.9 94.8 4 PtCo/TiO₂ 38.8 48.9 11.7 6.2 13.9 80.8 5 PtMn/TiO₂ 37.2 49.8 12.1 5.5 11.5 78.9 6 AuCo/TiO₂ 62.2 0.0 5.6 12.2 80.1 78.1 7 AuMn/TiO₂ 72.2 5.3 7.3 67.2 41.6 13.1

Table 1. Oxidation of glucose over various mono and bimetallic catalysts

Reaction conditions: C_{glucose,0}: 0.3 M, catalyst amount: 0.05 g, Pt loading: 2wt%, Pt/M (Au, Co, Mn) mass ratio: 1/1, Au loading: 2 wt%, Au/M (Co, Mn) mass ratio: 1/1, T: 110 °C, 1 MPa O₂, 4 h. AuPt/TiO₂* is the AuPt/TiO₂-7.5 sample mentioned later.

We found from entries#1 and #2 in Table 1 that, monometallic Au/TiO₂ and Pt/TiO₂ catalysts exhibit 48.1% and 38.2% conversion of glucose, respectively, after 4 h batch time. It is found that the major products include gluconic acid (GA), tartaric acid (TA), xylonic acid (XA), with xylaric acid (XYLA), glucaric acid, tartronic acid and glyceric acid formed as well. The selectivity towards TA over Pt/TiO₂ (12.4%) is slightly higher than that on Au/TiO₂ catalyst (2.7%). We further observed in entry#3 that, bimetallic AuPt/TiO₂* catalyst shows a complete conversion of glucose within 4 h. Selectivity of TA over bimetallic AuPt/TiO₂* catalyst is approximately 20%, which is higher than

monometallic Au/TiO₂ and Pt/TiO₂ catalysts. This value is also higher compared with previously reported data in literature (<10%).^{18, 20}

The conversion and product distribution over other bimetallic catalysts were also analyzed quantitatively (entries#4-#7). We confirmed that the major oxidation products over PtCo/TiO₂ and PtMn/TiO₂ catalysts (entries#4, #5) also include GA, TA and XA, but the conversion levels are much lower compared to AuPt/TiO₂* catalyst. In addition, we found that the overall conversion of glucose on AuCo/TiO₂ and AuMn/TiO₂ (entries#6 and #7) is higher than PtMn/TiO₂ and PtCo/TiO₂ catalysts. However, TA selectivity is low (< 5%). Based on our preliminary studies, it is possible that, while Au content shows good activity for glucose oxidation, Pt seems to be more selective towards TA formation. Therefore, the bimetallic AuPt/TiO₂* catalyst show synergism during glucose conversion.

Since bimetallic AuPt/TiO₂* catalyst showed enhanced performances for both activity and selectivity toward TA, we were also interested in evaluating its performance in oxidation of gluconic acid, as it is known to be a key primary product from glucose conversion. Results in Figure 2 show that, for oxidation of gluconic acid, Pt/TiO₂ (15.5%) outperforms Au/TiO₂ catalyst (8.4%) in term of conversion at 110 °C after 4 h. It is clear that Au/TiO₂ gives XA (a C₅ product) as the major product, while Pt/TiO₂ material leads to the formation of both TA and XA (combined selectivity > 70%). Therefore, it is plausible that, gluconic acid tends to follow C₁-C₅ cleavage reaction via decarboxylation reaction (orange route in Figure 2) over Au/TiO₂ catalyst, thus XYLA is formed as the major product.³⁰ But for Pt/TiO₂ catalyst, gluconic acid (GA in Figure 2) seems to undergo subsequent C-C cleavage and oxidation, which eventually gives XYLA and TA as major products (orange and green routes).²² Again, bimetallic AuPt/TiO₂* catalyst shows improved conversion compared with Au/TiO₂ and Pt/TiO₂ catalysts, promoting consecutive C-C cleavage of gluconic acid (via orange and green routes), thus TA is formed as the main product with almost 40% selectivity. Therefore, it is clear that, selective formation of TA requires two types of active sites for effective catalytic materials, one catalyzing oxidation reactions while the other facilitating C-C



Figure 2. Conversion and selectivity of gluconic acid (GA) oxidation over Au/TiO₂, Pt/TiO₂ and AuPt/TiO₂* catalysts and possible formation route for tartaric acid (TA). Reaction conditions: C_{GA0}=0.3 M, catalyst amount=0.05 g, T=110 °C, 1 MPa O₂, 4 h.

3.2 Catalyst characterization

3.2.1 Physical properties

Structural properties of Pt/TiO₂ and various AuPt/TiO₂ catalysts were measured for surface areas and pore volume. As shown in Table 2, all catalyst samples display very low surface areas in the range of $8.5 - 9.1 \text{ m}^2/\text{g}$. The pore volume varies insignificantly for different catalysts ($2.5 - 3.7 \ 10^{-2}\text{m}^3/\text{g}$). Metal dispersion for Pt and Au content was measured by both chemisorption and TEM images. In fact, Au possesses very weak

chemisorption properties due to the absence of vacancies in its d-bands .³¹ Since the AuPt alloy will reduce the amount of CO adsorbed, the measured dispersion data will be lower than the actual value. Due to unusual adsorption behaviors of CO on Pt and Au sites, chemisorption data cannot precisely reflect actual metal dispersion state.^{32, 33} Therefore, we used particle size distribution obtained from TEM characterization to determine metal dispersion, which is an extensively accepted protocol.³⁴

Catalyst	S _{BET} (m²/g)	V _{pore} (10 ⁻² m ³ /g)	Metal content by ICP (wt%)		Metal dispersion (%)	
			Au	Pt	Chemisorption	TEM
Pt/TiO ₂	8.7	2.5	-	1.8	24.2	-
AuPt/TiO ₂ -8.4	9.1	3.7	3.4	3.2	0.3	13.5
AuPt/TiO ₂ -7.5	8.9	2.6	1.6	1.7	0.2	15.1
AuPt/TiO ₂ -4.8	9.0	2.5	0.9	0.9	14.1	23.3
AuPt/TiO ₂ -4.2	8.5	2.7	0.7	0.6	12.3	26.9

Table 2. Physical properties of solid catalyst samples

3.2.2 Surface morphologies

TEM images for various AuPt/TiO₂ provide important information on particle size distribution and surface morphology. Figures 3 and S1 present low resolution TEM images for AuPt/TiO₂-8.4 (Figure 3a), AuPt/TiO₂-7.5 (Figure 3b), AuPt/TiO₂-4.8 (Figure 3c) and AuPt/TiO₂-4.2 (Figure 3d), respectively. The particle size distribution is 4.2 ± 0.1 nm, 4.8 ± 0.1 nm, 7.5 ± 0.2 nm and 8.4 ± 0.3 nm, respectively for the four samples. The TEM images of monometallic Pt/TiO₂ are shown in Figure S3a. It can clearly see that the average size of Pt is 6.9 ± 0.7 nm in Pt/TiO₂. From the deviation, there is a wide range of particle size. TEM images in Figure 3 and Figure S3a also confirm the poor porosity of TiO₂ support, as majority of metallic particles exist at outer surface of TiO₂ materials. Therefore, there is no doubt that catalytic reactions of glucose mostly occur at outer surface of TiO₂ with negligible contribution from AuPt and Pt

nanoparticles embedded in pore channels. There are no diffraction peaks of metal components except for the peaks of TiO_2 in XRD patterns of AuPt/TiO₂ catalysts (Figure S4). It also indicates that the bimetallic AuPt nanoparticles have a small size, which cannot be detected using XRD technique (see supporting information for more discussion on XRD results).



Figure 3. TEM images of various AuPt/TiO₂ catalysts



Figure 4. HR-TEM images for (a, b) AuPt/TiO₂-8.4 and (c, d) AuPt/TiO₂-7.5 catalysts. (e) is elemental mappings of AuPt/TiO₂-8.4.

HR-TEM images in Figures 4 (a-d) and S2 further show that, there exist large quantities twinned grains with clear boundaries at Au-Pt interfaces. We selected AuPt/TiO₂-8.4 and AuPt/TiO₂-7.5 samples for detailed characterization of their lattice structures. As shown in Figure 4a, we observed variously oriented lattice planes within selected nanoparticles for AuPt/TiO₂-8.4 sample. The orientation of facets highlighted by yellow dash lines suggest that, the lattice mismatch between Au (100) and Pt (111) induces formation of new interfaces, thus twinned grains are formed in this system.^{35,36-} ³⁸ While similar observation was found in Figure 4b for the same sample, measurement of lattice spacing of AuPt/TiO₂-7.5 sample in Figures 4c and 4d also implies typical Pt (111) and Au (100) facet co-existing in bimetallic AuPt nanoparticles. However, HR-TEM images in Figure S3b shows that, there are the regular lattice planes in Pt/TiO_2 , which is consist with Pt (111) plane. Since Pt and Au show fcc and bcc crystallinity in monometallic clusters, respectively, incorporation of Au in Pt facets undoubtedly creates large surface strain during the growth of clusters. As a result, the tensile strain at Pt and Au interface often leads to anisotropic growth of bimetallic nanoclusters.³⁹ EDS-mapping was conducted to examine the elemental distribution in AuPt/TiO₂-8.4 (Figure 4e). Figure 4e shows the representative STEM images and corresponding colorcoded EDS spectral maps of catalysts AuPt/TiO₂-8.4. Obviously, Au (green) and Pt (red) are uniformly distributed on the same particle in the AuPt/TiO₂-8.4 sample without obvious segregation, which confirming the formation of AuPt alloy.

In this work, at the very early stage, the precursors of Pt and Au were quickly reduced to form metallic atoms upon the addition of NaBH₄, owing to the strong reducing property of NaBH₄. Instantaneous formation of large amounts of Pt and Au nuclei contributes as perfect template to homogeneous crystal growth for both monometallic clusters. From the view of the kinetics, TiO_2 provides the electron transfer channel from Au³⁺ to Pt⁴⁺ which will help in the co-reduction of Au and Pt ions. It should be pointed out that the Au-Pt interaction exists in the solution, which provides the possible nucleation of AuPt alloys when the core is induced to mix at the atomic level.⁴⁰ Thus the newly formed Au and Pt atoms quickly fuse together to form small AuPt nuclei.⁴¹

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However, co-existence of structurally distinguished clusters and strong tendency for agglomeration under polymer-free condition, leads to interfacial tension-determined anisotropic growth, as we already described in previous cases with PtFe and PtMn clusters.^{25, 42} In general, such strong interface strain without surface mediating agents could possibly induce formulation of random Janus structures. As seen from Figure 4, it is noted that the low energy AuPt crystal (100) and (111) planes as the directing agent. Therefore, different metal loadings could determine the final alloy particle size. Such growth underwent approximately 10 h aging in aqueous phase. Therefore, the anisotropic growth of small AuPt clusters overcomes strong interfacial force and eventually formulated twinned boundaries within bimetallic particles. The strong metal-metal interaction will lead to changes in the structure of the catalyst interface, and the stabilization of transition states on alloy catalysts is an additional benefit. Prolonged aging time results in structural reconstruction with several defected sites on catalyst surface. In addition, the slight difference in electronegativity between Pt and Au could also intrinsically affect the final morphology. Slightly higher electron affinity of Au element might lead to faster reduction rates in aqueous solution. As a result, bond length and electronic configuration of Pt-Pt sites might be altered on Au-Au template (confirmed in later sections), which contributes to enhanced catalytic performances during oxidation of glucose and gluconic acid.

3.2.3 Electronic reconfiguration

(1) Electronic binding properties. XPS analysis was conducted to evaluate the variation in the chemical states of Au and Pt elements and possible changes of binding energies (BE). Two chemical states of Ti were separated in the Ti 2p spectrum at the BE of Ti $2p_{3/2}$ peak close to 458.6 eV and 458.1 eV, which can be identified as Ti⁴⁺ and Ti³⁺, respectively (Figure 5c). The Au 4f spectra were fitted successfully with Au^{δ+} and Au⁰ components (Figure 5a), which were separated at the BE of Au 4f_{7/2} peak at around 83.5 eV and 82.8eV. The Au⁰ species are oxidized to Au^{δ+} on the surface of TiO₂ facets, which could be ascribed to the strong interaction between metallic Au clusters and the surface Ti³⁺ centers at defects in the TiO₂ ^[43, 44]. Pt XPS spectra (Figure 5b) can be

divided into two pairs of peaks. The binding energy bands centered at 70.4 eV can be assigned to the Pt metal state (Pt $4f_{7/2}$ energy levels). The other peaks are in good agreement with Pt^{2+} , indicating the presence of oxidized Pt species ^[45, 46]. In the spectra of Au 4f and Pt 4f(as shown in Figure 5a and 5b), the variation of BE for $Au^{\delta+}$ and Pt^{2+} contents show quite a distinct tendency in mono and bimetallic samples. Therefore, it is indicate the formation of Au/Pt alloy compounds.^[47] Compared with monometallic samples, the Pt²⁺ content ascends, while the Au^{δ +} content slightly reduces in AuPt/TiO₂ samples. It is clear that the strain at Au-Pt interface also induces electronic redistribution. The positively charged Pt sites are more conducive to the formation of π - π bonds with -C=O groups. As a result, the bimetallic AuPt/TiO₂ catalyst promotes the C-C cracking (decarboxylation reaction) caused by this interaction, which ultimately leads to the formation of smaller products. The varied size for AuPt nanoparticles shows the trend on BE values that the positively charged Pt increases as the size of the AuPt alloy particles increases. In the following two sections, therefore, we conducted detailed ex-situ and in-situ characterization of AuPt/TiO₂ catalysts to further reveal the plausible mechanism of C-H and C=O groups on the modified catalyst surface. The surface Au-Pt ratio (Table S2) measured by XPS is consist with the bulk Au-Pt ratio, which confirms that the AuPt alloy is uniformly distributed on the surface.



Figure 5. XPS spectra of mono and bimetallic catalysts

(2) Electronic coupling at Au-Pt and AuPt-TiO₂ interfaces. UV-Vis DR spectra for monometallic Pt/TiO₂, Au/TiO₂, bimetallic AuPt/TiO₂-7.5 and blank TiO₂ samples confirm the Au-Pt electronic coupled effect and strong AuPt-TiO₂ interaction (Figure 6). We also showed that activation of gluconic acid follows alternative mechanism on the surface of mono and bimetallic catalysts (Figure 7). Specifically, as shown in Figure 6a, the blank TiO₂ sample (black curve) displays no signal in visible area (> 400 nm). Signals for monometallic Pt/TiO₂, Au/TiO₂ and bimetallic AuPt/TiO₂ catalysts are different from the blank TiO₂ support. In particular, Au/TiO₂ sample (yellow curve in Figure 6a) displays a typical peak around 554 nm, which is a characteristic response for surface plasmonic resonance of Au element,³⁵ while no such peak is not found for AuPt/TiO₂-7.5 catalyst. This observation suggests that electronic transfer at Au-Pt interface alters the configuration of *d* orbital at Au sites in bimetallic AuPt/TiO₂-7.5 catalyst.



Figure 6. (a) UV-Vis absorption spectra and (b) band gap energy estimation of TiO₂ supported mono Pt, Au and bimetallic AuPt catalyst samples

Band gap energy estimation for TiO_2 support is shown in Figure 6b. As it is observed, the value of band gap energy for blank TiO_2 sample is approximately 3.2 eV, while AuPt immobilized TiO_2 sample has a higher band gap. Increased band gap induces oxidation Ti^{3+} to Ti^{4+} species in TiO_2 framework, and subsequent electronic transfer from oxide structure to metallic sites.^{48, 49} The result is also consistent with our benchmark data over anatase and rutile TiO_2 supports (Table S1), where the both supports show similar promotional effect for oxidation of glucose to TA. Therefore, it is clear that Au-Pt and AuPt-TiO₂ interaction leads to reconfiguration of electronic orbitals at metallic sites.

(3) Activation of -C-OH and -C=O groups on catalyst surface. According to the possible reaction pathways shown in Figure 2, conversion of glucose to TA is achieved by forming gluconic acid as the primary product, followed by decarboxylation (C-C cleavage) and deep oxidation reactions. Hence, we conducted UV-Vis spectra measurement for solid catalysts in aqueous gluconic acid solution, to reveal possible mechanism for C-OH and C=O bond activation on catalyst surface. Three key findings are presented and discussed as below.



Figure 7. UV-Vis spectra for gluconic acid solution in the presence/absence of solid catalysts

(i) n to σ^* Excitation. As shown in Figure 7a, the blank gluconic acid solution sample displays typical peaks for n to σ^* excitation of hydroxyl (-C-OH) and aldehyde (-C=O) groups. However, the original conformation is interrupted by adding TiO₂ support in the aqueous gluconic acid solution (Figure 7b). It displays detectable signals for n to σ^* excitation of -C=O and -C-OH groups.⁵⁰ This observation is well agreed with previous findings that, surface -OH groups of TiO₂ could interact with -C-OH groups and form H bond.^{51, 52}

Further control measurements were conducted in the presence of Pt/TiO₂ (Figure 7c), Au/TiO₂ (Figure 7d) and AuPt/TiO₂-7.5 (Figure 7e) catalysts. Distinguished from other four samples, UV-Vis spectra for Pt/TiO₂ catalyst in gluconic acid solution (Figure 7c) display a stronger peak for n to σ^* excitation of -C-OH group than that of -C=O group, suggesting that Pt sites play a determining role in activating gluconic acid molecules to aqueous oxidation.⁵³ Compared with Pt/TiO₂ catalyst, n to σ^* excitation of -C-OH group is relatively weaker in the presence of Au/TiO₂ catalyst (see Figure 7d). However, the peak for n to σ^* excitation of -C=O group has been intensified to a higher level. Taking into account the poor catalytic activity of Au/TiO₂ catalyst (Figure 2), weakened

activation of -C-OH group leads to poor conversion of gluconic acid to dicarboxylic acids, while strong -C=O interaction favors formation of active per-acid species with strong oxidative properties.^{54, 55}

(ii) **n** to π^* Excitation. For bimetallic AuPt/TiO₂-7.5 catalyst, the presence of Au species induces the generation an adjacent active sites closing to Pt, leading a more strong signal of n to π^* excitation (see Figures 7c, 7e).⁵⁶ It tends to interact strongly with unpaired electrons in gluconic acid molecule. Therefore, activation of gluconic acid on bimetallic AuPt/TiO₂ catalysts is highly possibly following n to π^* mechanism.

(iii) π to π^* Excitation. We also detected signals for π to π^* excitation in Pt/TiO₂ (Figure 7c), Au/TiO₂ (Figure 7d) and bimetallic AuPt/TiO₂-7.5 (Figure 7e) catalyst samples. Such signal is absent for blank gluconic acid solution. Compared with TiO₂ and Au/TiO₂ samples, π to π^* excitation for -C=O group on Pt/TiO₂ catalyst display a red shift, suggesting facile π - π interaction on the surface of Pt/TiO₂ catalyst.

Based on the above-mentioned findings, it is possible that, the existing two competing activation mechanism for gluconic acid, (a) one predominately initiated by the activation of terminal -C-OH group, (b) the other involving π - π excitation of -C=O group. The former one results in the formulation of dicarboxylic acids by oxidative C-H bond cleavage (σ bond activation), while the latter case facilitates C-C bond cleavage, due to the fact that decarboxylation reactions starts with strong π - π excitation of carboxylic groups.^{57, 58} Simultaneous occurrence of the two competing reactions eventually contribute to the formation of C₅, C₄ and C₃ dicarboxylic acids, such as XLYA (C₅), TA (C₄) and tartronic acid (C₃) acids.

3.3 Structure-sensitivity

(1) Size-dependency of AuPt particle on oxidation reactions. It is demonstrated in this part that, both glucose and gluconic acid conversion over bimetallic AuPt/TiO₂ catalysts display a typical dual-site mechanism involving π - π interaction on catalyst surface. As shown in Figure 8a, as cluster size of AuPt increases from 4.2 nm to 8.4 nm, TOF values measured on glucose conversion show significant enhancement from

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434 h⁻¹ to approximately 982 h⁻¹ at 110 °C and 1 MPa O₂ (purple line in Figure 8a). Although the overall reaction rates for gluconic acid (blue line) over bimetallic AuPt/TiO₂ catalysts are much lower than those for glucose oxidation, it is clear that a similar size-dependent trend was also observed. Although σ - σ interaction for C-H bond on AuPt sites is critical for oxidation reactions, the overall conversion rate of glucose and gluconic acid is determined by π - π bond activation of C=O group (a dual-site mechanism). Clearly, the size-dependency found on these AuPt/TiO₂ catalysts with different sizes in Figure 8a is agreed very well with the results obtained from UV-Vis spectra (Figure 7).

(2) Substrate inhibition. We conducted additional sets of control experiments to understand the significance of σ - σ and π - π bond interaction under different concentration of glucose and gluconic acid. As seen in Figures 8b and 8c, control experiments were carried out over two selected catalysts, Pt/TiO₂ and AuPt/TiO₂-7.5. It is found that, as glucose concentration increases, initial reaction rates measured on both Pt/TiO₂ and AuPt/TiO₂-7.5 catalysts are enhanced (blue zone in Figure 8b), although AuPt/TiO₂-7.5 catalyst displays much higher reaction rates.

However, when glucose concentration is higher than 1.5 mol/L, we observed a typical Langmuir-type adsorption behavior, with almost unchanged initial reaction rates (see 2.4 for definition) over both catalysts (orange zone in Figure 8b). This observation implies that for glucose conversion, σ -activation for C-H bond is important for oxidation step to form gluconic acid. The π - π interaction is also important, but the fact that decarbonylation of glucose is almost negligible in the presence of Pt/TiO₂ or AuPt/TiO₂-7.5 catalysts, indicates C=O induced C-C bond cleavage is negligible under the reaction condition. Therefore, initial reaction rates of glucose display such profiles over both mono and bimetallic catalysts.



Figure 8. Conversion profiles on mono and bimetallic catalysts for glucose and gluconic acid conversion at 110 °C and 1 MPa O₂. (a) TOF vs size of AuPt clusters for both glucose and gluconic acid conversion (Reaction conditions: C_{GA,0} (C_{glucose,0}): 0.3 M, catalyst amount:
AuPt/TiO₂-4.2(0.2g), AuPt/TiO₂-4.8(0.1g), AuPt/TiO₂-7.5(0.05 g), AuPt/TiO₂-8.4 (0.025g)) , (b) influence of glucose and (c) gluconic acid concentration on initial reaction rate over monometallic Pt/TiO₂ and bimetallic AuPt/TiO₂-7.5 catalysts (refer Figure 2 for other experimental details; refer 2.4 for definition of reaction rate)

Interesting results were observed for oxidation of gluconic acid (Figure 8c). We were surprised to find that concentration-dependence on initial reaction rate of gluconic acid is completely different from that of glucose. It is clear that overall conversion rate of gluconic acid is much lower than that of glucose over both catalysts. More critically, the apparent conversion rates for gluconic acid decrease dramatically when its concentration is higher than 0.3 mol/L. Therefore, the substrate inhibition effect of gluconic acid is significantly stronger compared with glucose molecule. The big orange

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area in Figure 8c obviously illustrates that this is a typical substrate inhibitory effect caused by a strong π - π interaction. This observation implies that for gluconic acid conversion, π -activation for C=O bond is important for oxidation step.

In particularly, initial reaction rate measured on Pt/TiO_2 catalyst reaches maximum value at 340 mmol/g/h, which is surprisingly higher than AuPt/TiO₂-7.5 catalyst. But the curve drops much more rapidly when concentration of gluconic acid is higher than 0.3 mol/L. Therefore, the substrate inhibition effect of gluconic acid on Pt/TiO_2 is stronger than on AuPt/TiO₂-7.5 surface.

3.4 Plausible reaction mechanism

(1) Role of Au on σ - σ and π - π bond interaction. As already confirmed (Table 1, Figures 2, 4 and 7), the presence of Au in Pt clusters creates more active sites for both σ - σ and π - π bond activation. HR-TEM images in Figures 4 (a-d) and S2 show the lattice distortion at Au-Pt interfaces. In addition, the devolution of the XPS spectra of the mono and bimetallic samples in Figure 5 have confirmed that, there exists the electronic reconfiguration at AuPt/TiO₂ samples. However, the detailed picture for them are still not clear at this stage. Therefore, we performed DFT calculation on metal-metal bonding and Mulliken charge distribution to understand plausible electronic and structural reconfiguration in bimetallic AuPt clusters. Therefore, reaction mechanism on catalyst surface can be established accordingly. As shown in Figure 9a, it is found that Pt-Pt bond displays a dramatic distortion when Au is introduced to Pt clusters. Specifically, the average Pt-Pt bond length increases from 0.27 nm to approximately 0.28 nm, with a wider distribution from < 0.27 nm to 0.3 nm. The widened distribution of Pt-Pt bond confirms the lattice distortion induced by Pt-Au interfacial strain. Such distortion is found in both random alloy (AuPt-1 and AuPt-2 in Figure 9) and ordered alloyed structures (AuPt-3 and AuPt-4 in Figure 9). The main difference in random and ordered alloy is that, Pt-Pt lattice tends to undergo both lattice compression and expansion due to the introduction of Au in the former case (phase segregation), while Pt-Pt preferably tends to expand in ordered alloy case. Such lattice distortion contributes to the formation of twinned structures (TEM images in Figure 4) and more





Figure 9. Metal-metal bond and surface charge distribution of Pt and AuPt clusters. (a) Pt-Pt and Pt-Au length, (b) surface electronic charge for Pt and Au sites

The strain at Au-Pt interface also induces electronic redistribution. It is not surprising to find that Au atoms display more negative charges while overall charge for Pt sites are more positive (Figures 9b). Detailed inspection on charge distribution on Pt sites further show that both positively and negatively charged Pt sites co-exist in bimetallic AuPt clusters, while Au sites are shifting towards more negatively charged characteristics. Therefore, it can be seen there is electron transfer from Pt to Au in the AuPt alloy system. Such electronic redistribution contributes that the positively charged Pt²⁺ content increases, while the Au^{$\delta+$} content slightly reduces in AuPt/TiO₂ samples

(XPS spectra in Figure 5). This observation indicates that, there actually exists distortion induced phase segregation for Pt phase in bimetallic AuPt clusters. In other words, two categories of catalytically active Pt sites are available. The more positively charged Pt sites is more favorable for π - π bond formation with -C=O group. As a result, C-C cleavage (decarboxylation reaction) induced by such interaction is facilitated on bimetallic AuPt/TiO₂ catalysts, which eventually leads to the formation of smaller products.

In contrast, the relatively negatively charged Pt site are capable for nucleophilic attack on C-H bond (σ - σ activation), therefore oxidation of aldehyde (-CHO) and terminal hydroxyl (-CH₂-OH) groups to carboxylic groups can be achieved under mild conditions. The synergism of the above-mentioned features on bimetallic AuPt/TiO₂ catalysts leads to σ - σ and π - π bond activation, selectivity for TA can thus be enhanced eventually. Results from DFT calculation is consistent with the observation from UV-Vis spectra shown in Figure 7 and size-dependency trend presented in Figure 8.



Figure 10. Orbital hybridization for Pt atom induced lattice and electronic reconfiguration in bimetallic AuPt cluster (orbital hybridization refer to ref ⁵⁹)

(2) Reaction mechanism. We also analyzed orbital hybridization of Pt atom in bimetallic AuPt clusters, to further understand the underlying mechanism for the

synergism of bimetallic AuPt/TiO₂ catalysts during glucose conversion. It is known that Pt active center tends to formulate tetrahedral coordination with d_{xy} , d_{xz} and d_{yz} orbitals elevated to relatively higher energy levels.⁵⁹ This is the reason that Pt catalysts easily interact with -C=O groups *via* π - π bonding. The presence of Au atom leads to strong lattice strain at Pt-Au interface. Such structural uniqueness lead to altered binding energies (BE, see Figure 5). As DFT results shown in Figure 9, lattice mismatch between Pt and Au results in structural distortion with elongated Pt-Pt bond at equatorial orientation at Pt-Au interface. Such structural evolution induces distortion of electronic orbitals.⁵⁹ Based on the schematic description of ball-model in Figure 10, the elongated Pt-Pt bond at near equatorial of tetrahedral coordination induces further orbital split of d_{x2-y2} and d_{z2} for σ -bonding. Such orbital reconfiguration leads to following two key outcomes.

(i) Enhanced C-H bond activation. Such upshift (orbital split of d_{x2-y2} and d_{z2}) minimizes the energetic difference for crystal field splitting (Δ ' in Figure 10). Considering the fact that Au atoms have relatively higher electronegativity than Pt elements, the unpaired electron at d_{xy} , d_{xz} and d_{yz} levels has a strong tendency for electron transfer (coupling) to adjacent Au site. As a result, the paired electrons at d_{z2} orbital can be relatively easier to excite to d_{xy} , d_{xz} and d_{yz} levels. Such facile electron excitation undoubtedly induces Jahn-Teller distortion in Pt orbitals.⁶⁰⁻⁶³ The lone electron at d_{z2} orbital is very active for σ -bonding formation *via* perpendicular orientation to the surface of Pt facet. This is the underlying mechanism for enhanced catalytic activity for oxidation of C-H bond (Figure 11).







Figure 12. Schematic description for C-C cleavage of gluconic acid over monometallic Pt and bimetallic AuPt catalysts

(ii) Facile C-C cleavage. Strong π - π electron sharing with C=O bonds on the surface of noble metals, leads to either inhibited surface for consecutive reactions,^{22, 64} or C-C cleavage at terminal position of carbon chain to CO₂.^{65, 66} But π - π interaction is weakened on AuPt/TiO₂ catalysts to some extent. This is because that the unpaired electrons are excited from d_{z2} prior to π - π bond formation (Figures 10 and 12), such electronic reconfiguration induced π - π electron sharing results in C-C cleavage, rather than substrate inhibition effect. This is the underlying reason that, conversion of both glucose and gluconic acid over bimetallic AuPt/TiO₂-7.5 catalyst displays a less π - π bonding-determined trend compared with monometallic Pt/TiO₂ catalyst (Figures 8b and 8c).

3.5 Kinetic modeling on Pt/TiO₂ and AuPt/TiO₂-7.5 catalysts

Since the electronic reconfiguration effect on C-H and C-C bond cleavage has been clarified by both experimental and computational studies, we were interested in obtaining the activation energies for conversion of glucose and gluconic acid on both Pt/TiO₂ and AuPt/TiO₂-7.5 catalysts. Kinetic data on the initial reaction rates of glucose and gluconic acid is presented in Figures 13a and 13b. Data fitting and regression suggest that conversion of both substrates over Pt/TiO₂ and AuPt/TiO₂-7.5 catalysts follows a 1nd order kinetics (Figures 13a and 13b), which agrees well with previous findings.^{16, 25} It is found from inset table of Figure 13 that, activation of glucose molecule over AuPt/TiO₂-7.5 catalyst needs to overcome much higher energy barrier

(90.6 kJ/mol) than Pt/TiO₂ catalyst (36.3 kJ/mol). This result appears to be inconsistent with reaction results shown in Table 1 and Figure 2. Detailed inspection on kinetic data (Figure 13a) actually reveals that, the pre-exponential factor (A) of rate constant of glucose oxidation on AuPt/TiO₂-7.5 catalyst is 10⁸ times that of Pt/TiO₂, suggesting that the presence of Au on Pt surface creates additional active sites for effective glucose conversion to primary and secondary products. This result is consistent with Figures 4 and 8. As already confirmed (Table 1, Figures 2, 4 and 7), the presence of Au in Pt clusters creates more active sites for both σ - σ and π - π bond activation. On the one hand, Au is the active sites for σ - σ activation. On the other hand, the addition of Au causes lattice distortion at Au-Pt interfaces, leading to the electronic reconfiguration at AuPt/TiO₂ samples. Just as the XPS and DFT discussions, such electronic redistribution contributes that the positively charged Pt2⁺ content increases. The positively charged Pt sites are more conducive to the formation of π - π bonds with -C=O groups. For oxidation of glucose, σ-activation for C-H bond is important for oxidation step to form gluconic acid (as seen in Figure 8b). However, π -activation for C=O bond is important for oxidation of gluconic acid (as seen in Figure 8c). Obviously, the addition of Au provides more σ - σ active sites than π - π . So the number of pre-exponential factor for oxidation of glucose is higher than gluconic acid oxidation. Similar observation has also been made for conversion of gluconic acid over the two catalysts (inset table of Figure 13).





Figure 13. Kinetic data on the initial reaction rates of (a) glucose and (b) gluconic acid conversion on Pt/TiO₂ and AuPt/TiO₂-7.5 catalysts at three temperatures (100, 110, 120 °C), A: pre-exponential factor.

Clearly, the addition of Au changes the reaction behaviors. We further studied the kinetics for C-C & C-H bond cleavage reactions based on the reaction rates and product distribution of gluconic acid conversion (Figure 14 and Table S3, the calculation method described in supporting information). It is found in Figure 14a that, activation of C-C cleavage over AuPt/TiO₂-7.5 catalyst needs to overcome a relatively higher energy barrier (64.2 kJ/mol) than Pt/TiO₂ catalyst (35.9 kJ/mol). This is because the interaction of -C=O with Pt is weakened due to adjacent Au sites.⁶⁷ This observation reveals that the introduction of Au to Pt surface can efficiently prevent irreversible

inhibition by "C=O"-containing intermediates, and thus leading to enhanced activities of bimetallic AuPt/TiO₂ catalysts (see Figure 8c).

Furthermore, the activation of C-H bond over AuPt/TiO₂-7.5 catalyst also shows a higher energy barrier (see Figure 14b). This is because activation of C-H bond over Au has a very high barrier without the assistance of adsorbed OH⁻ species on Au surface (~204 kJ/mol).⁵⁵ The ensuing alkoxide intermediate to form the aldehyde over Au show poor activity (also see experimental results over Au/TiO₂ catalyst in Figure 2a). Therefore, elevated activation energy of AuPt/TiO₂-7.5 catalyst is possibly ascribed to the relatively high activation barrier of C-H due to existence of Au site. Therefore, the fact that AuPt/TiO₂-7.5 catalyst shows enhanced activity for conversion of glucose and gluconic acid originates from strong electronic effects and more defected sites induced by Au doping to Pt system.

One may also notice that on bimetallic AuPt/TiO₂-7.5 catalyst, the apparent activation energy for conversion of gluconic acid (90.2 kJ/mol) is higher compared with total activation energy of C-C cleavage and C-H cleavage reaction (almost 64-65 kJ/mol). This is because that conversion of gluconic acid to small molecule acids consists of a series of tandem reactions without desorbing intermediates. This observation proves the reaction process consists of C-C bond cleavage to form smaller intermediates on catalyst surface, followed by C-H bond activation of as-formed smaller intermediates to generate carboxylic acids as final products. Therefore, smaller carboxylic acids such as TA can be formed in the presence of AuPt/TiO₂ catalysts. Based on the kinetic analysis of initial reaction rates for both glucose and gluconic acid, it is clear that more detailed derivation of mechanistic models should be conducted with rigorous parameter estimation and model discrimination, considering simultaneous π - π and σ activation on catalyst surface, in order to reveal the intrinsic kinetics of formation of TA during conversion of glucose and gluconic acid.



Figure 14. Kinetic data on the initial reaction rates of (a) C-C cleavage and (b) C-H cleavage of gluconic acid on Pt/TiO₂ and AuPt/TiO₂-7.5 catalysts at three temperatures (100, 110, 120 °C), A: pre-exponential factor.

Additional experiments were conducted to understand the influence of reaction temperature and O₂ pressure on conversion of glucose and gluconic acid. The major

temperature and O₂ pressure on conversion of glucose and gluconic acid. The major products include TA, XA, XYLA and GLA. Entries#1 - #4 in Table 3 show that higher O₂ pressure slightly increase conversion of gluconic acid and with decreasing selectivity of TA. Oxidation of gluconic acid at 100 °C and 1 MPa O₂ (entry#5) pressure marginally increase the selectivity towards TA, while higher temperature (entry#6), although favoring higher conversion (76.8%), leads to poor TA selectivity. Higher temperatures, higher O₂ pressure cause C-C cleavage of C₄ species to short chain carboxylic acids, resulting in lower TA selectivity. Based optimization of reaction parameters, a maximum of 50.1% TA selectivity at quantitative conversion of glucose is achieved at 110 °C, 2 MPa O₂ (entry#7). As shown in Figure 15, after three recycles,

the AuPt/TiO₂-8.4 catalyst still displays complete glucose conversion. However the selectivity toward tartaric acid decreasing from 42% to 21%. In fact, after the first reaction, the selectivity of tartaric acid has been maintained at about 20%. Therefore, it is plausible that he catalyst overflows in the dissolution of water at 110 °C, causing the catalyst structure to change.

Table 3. Effect of reaction parameters on conversion and product distribution during oxidation of gluconic acid in the presence of AuPt/TiO₂ catalysts

Entry	T (°C)	O ₂ (MPa)	Substrate	conversion _ (%)	Selectivity (%)				
					TA	XYLA	XA	GLA	Others
1 ^a	110	0.5	Gluconic	50.4	48.9	15.6	8.7	6.7	8.4
2 ^a	110	1.0	Gluconic	47.1	45.8	14.7	8.4	7.1	8.0
3ª	110	2.0	Gluconic	59.4	43.4	14.4	8.3	9.9	8.5
4 ^a	110	3.0	Gluconic	40.7	44.4	16.0	10.9	9.1	9.2
5ª	100	1.0	Gluconic	40.7	52.4	12.6	9.9	7.5	4.2
6 ^a	120	1.0	Gluconic	76.8	32.5	9.9	3.5	13.3	9.4
7 ^b	110	2.0	Glucose	100.0	50.1	10.2	3.2	0.0	15.7

a: AuPt/TiO₂-7.5 catalyst; b: AuPt/TiO₂-8.4 catalyst; TA: tartaric acid, XYLA: xylaric acid, XA: xylonic acid, GLA: glucaric acid, GA: gluconic acid. Reaction conditions: $C_{GA,0}$ ($C_{glucose,0}$): 0.3 M, catalyst amount: 0.05 g



Figure 15 Recycling studies on AuPt/TiO₂-8.4 catalyst for glucose oxidation.

It is important to mention that, theoretical yield for TA from glucose is 66.7% as one glucose molecule produces one TA. The reported yield of TA is significantly higher compared with results obtained from nitric acid oxidation of glucose (<10%). In addition, the reported formation rate of TA over bimetallic AuPt/TiO₂ catalysts (production rate: 2.3 mol/mol-metal/h) is also much higher compared with literature reports on glucose oxidation (literature results: < 0.52 mol/mol-metal/h). Further studies need to be conducted to improve the catalyst stability and production rates of TA, with respect to optimization of catalyst structures and reaction parameters. Obviously, catalytic synthesis of TA from glucose exhibit both environmental and technological advantages over traditional synthetic routes. Structural manipulation of bimetallic AuPt/TiO₂ catalysts for various other energy and environmental applications.

4. Conclusions

In this work, direct oxidation of glucose to TA (yield: 50%) using a bimetallic AuPt/TiO₂ catalyst is reported here for the first time. In particular, the structureactivity/selectivity relationship of bimetallic AuPt-based nanocatalysts has been studied for oxidation of glucose and gluconic acid. Surface characterization using TEM, XPS, and UV-vis of bimetallic AuPt nanoparticles confirmed that, TiO₂ supported AuPt catalysts exhibited synergistic activity compared with monometallic Au and Pt ones for oxidation of glucose and gluconic acid. Concentration-time profiles on monometallic and bimetallic AuPt/TiO₂ catalysts showed the strong substrate inhibition effect for conversion of gluconic acid, suggesting two mechanisms: σ - σ and π - π interaction on the surface of bimetallic AuPt/TiO₂ catalysts for enhanced C-H and C-C cleavage reactions. DFT calculation and kinetic data over Pt/TiO₂ and AuPt/TiO₂ catalysts also confirmed that, the presence of Au on Pt cluster created additional defected sites and altered kinetics for both oxidation and decarboxylation reactions. The results presented here on the structural uniqueness of bimetallic catalysts and the observed inhibition effect of sugars derivatives provide guidelines for the rational design of metal catalysts and process optimization for manufacture of renewable chemicals for energy industry.

Author contribution

M. L. conducted most experiments and drafted the manuscript. G. Z., H. Y., W. Z., J.

W., Q. X. assisted data analysis. L. L., Y. S., J. D. carried out additional experiments.

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