Simultaneously Converting Carbonate/Bicarbonate and Biomass to Value-added Carboxylic Acid Salts by Aqueous-phase Hydrogen Transfer

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Ⓢ *Supporting Information*

ABSTRACT: A novel approach to coproduce value-added carboxylic acids has been developed via a "one-pot" aqueous-phase hydrogen transfer (APHT) process, in which hydrogen in biomass molecules is transferred to carbonate/bicarbonate ions over supported noble metal nanocatalysts. In mild hydrothermal media, a variety of biomass derived alcohols or polyols have been efficiently converted to carboxylic acids, while simultaneously, formates have been obtained from the reduction of carbonates/bicarbonate salts without using external H_2. In an APHT process at the optimized reaction conditions, a high yield of lactate, ~55%, was achieved using glycerol as the hydrogen donor, and simultaneously, ~30% of formate was produced by the reduction of sodium bicarbonates over the Pd on a carbon catalyst. The catalyst was stable after three-time consecutive reuse without regeneration, and the possible APHT reaction mechanism was proposed.

KEYWORDS: *Aqueous-phase hydrogen transfer, bicarbonate hydrogenation, biomass dehydrogenation, palladium catalyst, carboxylic acids*
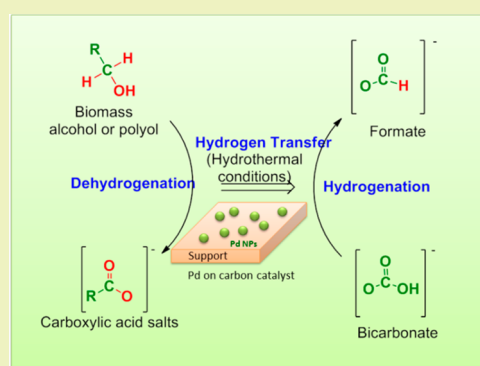
■ INTRODUCTION

Catalytic reduction of carbon dioxide (CO_2) to fuels or value-added chemicals is a "Holy Grail" paradigm that may ease two major concerns, "Climate Change" and "Energy Crisis", caused by the anthropic release of an overwhelming amount of CO_2 into the atmosphere by combusting fossil fuels.[1−3] Hydrogenation of CO_2 to formic acid (FA) is considered to be one of the feasible processes of utilizing abundant CO_2. However, CO_2 is the lowest in energy of all carbon-containing binary neutral species, and thus direct activation of CO_2 often implies high external energy inputs. Additionally, dihydrogen gas (H_2), the most commonly used chemical reductant, is produced mainly by steam reforming of natural gas, which is neither inexpensive nor sustainable. Therefore, CO_2 hydrogenation faces two techno-economic challenges: how to activate CO_2 with a low external energy and how to maintain a sustainable, inexpensive hydrogen supply.[4,5] Unlike thermodynamically unfavorable gas-phase processes ($\Delta G°_{298\ K} = 33$ kJ·mol^{-1}), hydrogenation of CO_2, in the form of bicarbonates in water, is exergonic ($\Delta G°_{298\ K} = -4$ kJ·mol^{-1}).[6,7] In aqueous media, CO_2 (in the form of bicarbonate/carbonate ions, HCO_3^-/CO_3^{2-}) can be readily reduced with H_2 to CO, formic acid (FA), methanol, methane, or acetic acid with homogeneous or heterogeneous catalysts.[8−11]

On the other hand, using renewable biomass feedstock for hydrogen production can be realized through gasification and reforming processes. However, gasification is an energy intensive process of converting biomass to syngas, usually operating at very high temperatures (800−900 °C). Thus far, the cost of hydrogen production through gasifying biomass is still much higher than reforming natural gas. A less explored approach is to directly transfer hydrogen from biomass molecules to reduce CO_2 at mild temperatures in aqueous media, which could potentially solve the above-mentioned CO_2 hydrogenation challenges, i.e., thermodynamic limitation and hydrogen supply. Hydrogen abundant biomass derived molecules such as alcohols or polyols are one of the major byproducts in the biofuels industry. To improve biofuel economics, it is desirable to upgrade such biomass wastes into value-added chemicals, e.g., to oxidize alcohols to aldehydes, ketones, or carboxylic acids.

Several research groups studied transfer hydrogenation of CO_2 with alcohols, e.g., 2-propanol, by transition metals, such as Fe, Zn, and Ni, in high-temperature (300−400 °C) hydrothermal media.[12−16] The transition metals acted as reducing agents instead of catalysts that reduce CO_2, while metals were simultaneously oxidized. The H_2 gas evolved from alcohols might reduce the metal oxides back to the metals. In such reactions, repeated phase transformations between metal

Table 1. Comparison of the Reduction of Bicarbonates/Carbonates/CO$_2$ with Glycerol at Different Hydrothermal Conditions

		reaction conditions			results					
entry	reactants	catalyst[e]	time (h)	initial pH	glycerol conversion (%)	lactate yield (%)	pyruvate yield (%)	PG[f] yield (%)	formate yield (%)	TON[g]
1[a]	NaHCO$_3$	Pd/AC	1	8.0					0	0
2[b]		Pd/AC	1	8.0	14.5	6.1	0.5	0.6	0	0
3[c]	NaHCO$_3$		1	8.0	5.1	3.9	0.0	0.0	1.4	
4	NaHCO$_3$	Pd/AC	1	8.0	31.2	20.7	1.3	1.5	14.6	265.6
5	NaHCO$_3$	Ru/AC	1	8.0	38.6	29.7	1.2	0.9	8.7	128.7
6	NaHCO$_3$	Pt/AC	1	8.0	23.4	15.3	0.6	0.3	10.1	187.6
7	NaHCO$_3$	Rh/AC	1	8.0	28.6	17.9	1.7	1.3	11.4	191.4
8	NaHCO$_3$	Ni/AC	1	8.0	9.2	4.2	0.1	0.0	1.6	22.9
9	NaHCO$_3$	Pd/AC	12	8.0	80.7	55.0	5.0	6.3	29.4	535.0
10	Na$_2$CO$_3$	Pd/AC	12	11.6	82.7	42.4	6.3	4.5	30.3	551.3
11	KHCO$_3$	Pd/AC	12	8.3	78.2	49.3	5.6	6.9	29.9	544.0
12	K$_2$CO$_3$	Pd/AC	12	12.1	84.6	33.2	7.6	5.8	39.8	742.2
13[d]	CO$_2$ gas	Pd/AC	12	8.0	23.9	9.0	0.7	0.5	1.2	21.7

[a]Bicarbonates reduction without an alcohol reactant. [b]Glycerol dehydrogenation in the presence of NaOH (without bicarbonate). [c]Reduction of bicarbonates with glycerol without the Pd/AC catalyst. [d]Directly use CO$_2$ gas to replace bicarbonate (equal moles) and use NaOH to adjust pH value to 8.0. [e]The metal loading of all the catalysts is 5 wt %. [f]PG stands for propylene glycol. [g]TON is turnover number per active metal atom, e.g., TON of Pd was calculated by the formula: (total moles of formate formed)/(total mol/of Pd atom × 23.2%), in which the dispersion of Pd atom on the surface of the Pd/AC catalyst was 23.2%. Metal dispersion was calculated based on the carbon monoxide chemisorption results (Table S1, Supporting Information). Reaction conditions: 240 °C, 400 psi (N$_2$), 1 M glycerol and 1 M NaHCO$_3$ in 20 mL H$_2$O, 0.1 g catalyst loading.

and metal oxide with appreciable volume expansion/contraction may destroy the material's integrity and thus lead to leaching and deactivation. Jin and co-workers reported the reduction of NaHCO$_3$ with base catalyst using isopropyl alcohol or glycerol as the hydrogen donor in alkaline hydrothermal media.[14,15] In their studies, excess NaOH and NaHCO$_3$, e.g., the molar ratio of NaHCO$_3$ to glycerol is >16, were used, which were highly corrosive. Moreover, the bicarbonate reduction efficiencies of these alkaline hydrothermal reactions were very low. The formate "yield" in these studies was described as the amount of formate formed over the amount of reductant, i.e., 2-propanol or glycerol. The true formate yields, in terms of the amount of formate formed over the initial amount of bicarbonate, were only less than 10%.

In this study, we have developed a green, noncorrosive "one-pot" process in which aqueous-phase hydrogen transfer (APHT) bridges the dehydrogenation of biomass derived alcohols or polyols with the hydrogenation of CO$_2$ in hydrothermal water at milder temperatures. Unlike the previous studies, both dehydrogenation and hydrogenation are catalyzed by the same supported noble metal nanocatalysts without volume changes and much higher yields of formates have been obtained without adding strong bases.

EXPERIMENTAL SECTION

Materials. The catalyst samples Pd/AC (5 and 10 wt %), Pd/CaCO$_3$, Pd/BaSO$_4$, Pd/Al$_2$O$_3$, Ru/AC, Pt/AC, and Rh/AC (5 wt %) were purchased from Sigma-Aldrich. Pd/ZrO$_2$ (5 wt %) and Ni/AC (5 wt %) were prepared by an impregnation method. Glycerol (≥99.5%), 1-propanol (≥99.5%), 2-propanol (≥99.5), 1-butanol (≥99.5%), tert-butanol (≥99.5), phenol (≥99.5), xylitol (≥99%), ethylene glycol (99%), and propylene glycol (99%) were purchased from Sigma-Aldrich.

APHT Activity Tests. The APHT reaction experiments were carried out in the 50 mL stirred Parr microreactor. The appropriate amounts of alcohol, bicarbonate, and catalyst were added into 20 mL of water in the reactor. The reactor was then sealed, purged with high purity nitrogen three times, and then charged with N$_2$ to the set initial pressure. During the reaction, mixing was achieved through an internal propeller operating at 800 rpm. Once the set temperature was attained,

the reactor was held at the set temperature for a certain period of time and then quenched in an ice bath. The reactor was quickly cooled to approximately 25 °C, and then the gas pressure was recorded. The reactor was vented and then immediately broken down and the liquid was collected for analysis. The typical reaction conditions were: the concentrations of hydrogen donor (alcohol or polyol) and sodium bicarbonate are both 1 mol/L (initial pH 8.0), the reaction temperature is 240 °C, the initial pressure is 400 psi (N$_2$), the fresh or spent catalyst loading is 0.1 g, and the reaction time is 1 h. The catalyst stability testing was carried out in the same Parr microreactor. The catalyst after a batch reaction was separated by centrifugation and washed with water and ethanol for five times, then the catalyst was dried at 50 °C in flowing N$_2$. At last, the spent catalyst was reused in the next repeated APHT reaction.

The conversion and yield were calculated on the carbon basis and defined as follows

$$\text{conversion (\%)} = \frac{\text{weight of reactant charged} - \text{weight of reactant after reaction}}{\text{weight of reactant charged}} \times 100$$

$$\text{yield of detected products (\% } - \text{C)} = \frac{\text{mol}_{\text{product}} \times \text{C atoms in product}}{\text{mol}_{\text{reactant charged}} \times \text{C atoms in reactant}} \times 100$$

Note: the yield of formate was based on the reactant of bicarbonate.

Product Analysis. Aqueous samples collected were filtered through a 0.22 μm pore-size filter for total organic and inorganic carbon distribution, high performance liquid chromatography (HPLC) and electrospray ionization mass spectrometer (ESI-MS) analysis. The total carbon, total organic carbon, and total inorganic carbon were measured by a Shimadzu total organic carbon analyzer (model TOC-V). HPLC analysis was performed using a Shimadzu HPLC system equipped with a dual UV−vis detector (Shimadzu SPD 10-AV) at 208 and 290 nm and a refractive index detector (Shimadzu RID-10A). For analysis of organic acids and reaction intermediates, the samples were separated in an Aminex 87-H column from Bio-Rad, using 5 mM H$_2$SO$_4$ as the mobile phase at 0.7 mL/min flow and a column temperature of 55 °C. All samples for ESI-MS analysis were diluted with a base solution containing 0.1 wt % triethylamine and the analysis was performed using a Waters Micromass ZQ quadrupole mass

spectrometer. After the reaction, the reactor was cooled until approximately 25 °C, and the off gas was collected by a gas bag then analyzed by the SRI 8610C gas chromatograph equipped with a 3′ Haysep D column and a 6′ MS13X column, as well as a thermal conductivity detector (TCD). The gas chromatography (GC) oven temperature is 200 °C.

Catalyst Characterization. Transmission electron microscopy (TEM) was done on a Hitachi S-4700 II scanning electron microscope operated at 200 kV. The crystalline structure and the size of nanocatalysts was characterized by a PANalytical X'Pert PRO diffractometer (Cu Kα radiation, λ = 0.154 18 nm) at 45 kV and 40 mA. The X-ray photoelectron spectroscopy (XPS) measurements were performed on an SSX-100 system (Surface Science Laboratories, Inc.), equipped with a monochromated Al Kα X-ray source, a hemispherical sector analyzer (HSA), and a resistive anode detector. The base pressure was 6.0×10^{-10} Torr. During the data collection, the pressure was ca. 1.0×10^{-8} Torr. Each sample was mounted on a piece of Al sticking tape on a separate sample holder. The X-ray spot size was 1 × 1 mm, which corresponded to an X-ray power of 200 W. A slight differential charging was found for all samples and a low-energy electron beam (10 eV) was used for charge neutralization. The survey spectra were collected using 10 scans at 150 eV pass energy and 1 eV/ step. The high resolution spectra were recorded at 20 scans for the C 1s peak and 80 scans for the Pd 3d peaks using 50 eV pass energy and 0.1 eV/step. For high resolution data, the lowest binding-energy C 1s peak was set at 285.0 eV and used as the reference for the Pd 3d peaks. The curve fitting used a combination of Gaussian/Lorenzian function with the Gaussian percentages being at 80% or higher. Asymmetric factors were used in fitting some of the Pd 3d data.

■ RESULTS AND DISCUSSION

Glycerol is the byproduct of biodiesel refining processes with an annual production rate of over 1.5 M metric tons,[17] and thus an ideal hydrogen donor feedstock in our APHT process. Table 1 shows that the simultaneous production of lactate, pyruvate, propylene glycol (PG), and formate are realized by combining glycerol conversion and bicarbonate reduction in hydrothermal media. The yields of lactate, pyruvate, propylene glycol (PG), and formate were 55.0%, 5%, 6.3%, and 29.4%, respectively, in the presence of the activated carbon supported palladium catalyst (5% Pd/AC) after reacting for 12 h in subcritical water at 240 °C (Table 1 entry 9). Because glyceraldehyde or dihydroxyketone, instead of lactic acid, are the common dehydrogenation products of glycerol at low temperatures,[18] it is reasonable to hypothesize that the dehydrogenation of glycerol is the initial key step in the APHT process, followed by consecutive dehydration, keto–enol tautomerization, intra- molecular Cannizzaro reactions, which can be catalyzed by the hydronium and hydroxyl ion pairs from the autodissocia- tion of subcritical water, to generate lactate (Scheme 1). On the
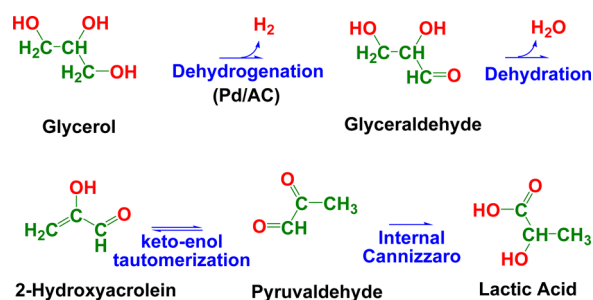
other hand, the formation of pyruvate and PG may due to the further dehydrogenation and hydrogenolysis of the intermedi- ate of pyruvaldehyde, respectively.[19] The initial step starting from the dehydrogenation of glycerol in the APHT system is further verified by the fact that in the presence of bicarbonate salts, which are readily hydrogenated to formate in water and therefore a suitable hydrogen acceptor,[7] the conversion of glycerol to lactate was significantly promoted: while keeping other conditions the same, the lactate yield increased from 6.1% to 20.7% with only adding the 1 M sodium bicarbonate (Table 1, entries 2 and 4).

A general concern of the AHPT is whether or not formic acid is a product from the biomass degradation in such a complex hydrothermal reaction system. To confirm that the formate salts are from the reduction of sodium bicarbonate instead of the degradation of glycerol derived compounds in the APHT process, the control reactions were carried out. First, without adding glycerol, HCO_3^- could not be reduced with the Pd/AC catalyst and no formate was formed (Table 1 entry 1); and second, using NaOH to replace $NaHCO_3$ and regulating the initial pH to 8.0, we only observed the formation of lactate through the dehydrogenation of glycerol and there were still no formic acid salts (Table 1 entry 2). Therefore, it is verified that the formate was formed from reducing $NaHCO_3$ with the hydrogen donated from glycerol, instead of decomposing lactate at operating temperatures similar to the typical APHT process. Synthesis of lactate salts by alkaline hydrothermal conversion of glycerol has been considered as an alternative to the commercial fermentative process.[20,21] However, the APHT process using the heterogeneous catalyst is viewed as a more environmentally friendly process since highly corrosive strong base catalysts are avoided.

The catalytic effect of the Pd/AC was obvious in the APHT reaction since only a trace amount of lactic and formic acid salts was produced without adding the Pd/AC catalyst (Table 1 entry 3). In our study, approximately 5% glycerol was converted and 1.4% formate was yielded at 240 °C in a weakly alkaline hydrothermal solution (initial pH is 8.0) without adding the Pd/AC catalyst, which is in agreement with the previous studies by Jin and co-workers (with adding NaOH, ~1.0% and ~4.5% formate were yielded from reducing bicarbonate for 2.5 h at 260 and 300 °C, respectively, using isopropyl alcohol as the reactant,[15] and while with glycerol as the reductant, the formate yield after a 1 h reaction was ~2.0% at 260 °C.[14]). However, after adding the Pd/AC catalyst, the formate yield has increased 1 order of magnitude to 14.6% (Table 1 entry 4) when the other reaction conditions were kept the same. The Pd catalyst thus exhibits catalytic performance on both the dehydrogenation of glycerol and the hydrogenation of bicarbonate; we herein propose a possible APHT reaction mechanism, as shown in Scheme 2. Using Pd catalysts in the APHT process lowers the hydrothermal reaction temperature (in the range of 240 to 300 °C) and thus significantly reduces the reaction pressure. In contrast, higher temperatures and pressures are necessary for the high-yield production of formates in previous studies[14,15] but, unfortunately, much more costly.

We have screened different noble metal catalysts for the APHT process (Table 1 entries 4–8). Other carbon supported noble metal catalysts, Pt, Ru, and Rh, seem to be active as well; while not as active as Pd/AC toward hydrogenating sodium bicarbonate. However, under the conditions that the Pd/AC catalyst is active, Ni/AC failed to yield a significant amount of

Scheme 1. Proposed Reaction Pathway of the Conversion of Glycerol to Lactic Acid That Starts from the Dehydrogenation of Glycerol over the Pd/AC Catalyst
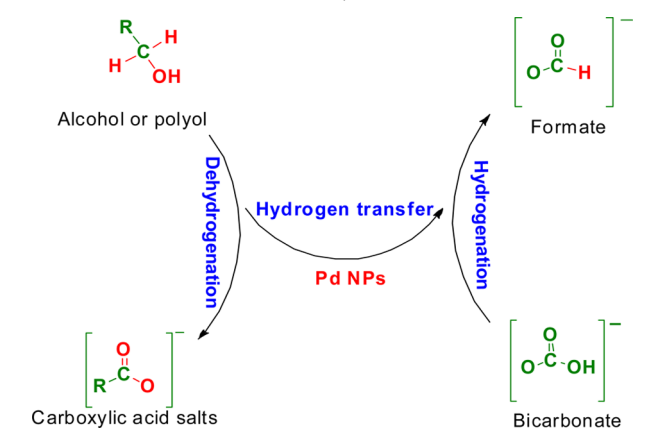
Scheme 2. Proposed Reaction Pathway of Reducing Bicarbonate over Pd/AC Catalyst with Alcohol as H Donor

formic acid salts product. The Ru/AC appears to be the most active toward the dehydrogenation of glycerol, which reached the highest lactate yield of 29.7% after a 1 h reaction at 240 °C. We also tested different catalyst supports and found that the activated carbon support shows the superior performance over the metal oxide/sulfate supports (Table 2). The properties of

**Table 2. Effects of Different Supports and Pd Loading Amounts on the Reduction of NaHCO$_3$ with Glycerol**

entry	catalyst (wt %)	glycerol conversion (%)	lactate yield (%)	pyruvate yield (%)	PG yield (%)	formate yield (%)
1	Pd/AC (5%)	31.2	20.7	1.3	1.5	14.6
2	Pd/AC (10%)	37.5	25.1	2.2	1.9	11.7
3	Pd/CaCO$_3$ (5%)	20.6	16.1	0.9	1.3	13.8
4	Pd/BaSO$_4$ (5%)	30.3	23.9	2.0	1.2	10.8
5	Pd/ZrO$_2$ (5%)	27.6	23.5	1.9	0.4	10.7
6	Pd/Al$_2$O$_3$ (5%)	18.1	13.7	1.1	0.2	8.9

Reaction conditions: 240 °C, 400 psi (N$_2$), 1 h, initial pH 8.0, 20 mL H$_2$O, 1 M glycerol and 1 M NaHCO$_3$, 0.1 g catalyst loading.

support materials, such as specific surface area, pore size distribution, hydrophilicity/hydrophobicity, or structure stability, may have great effects on the morphology of Pd NPs and diffusion of reactants in aqueous phase, and thus influence the catalytic performance of the catalyst. Our future research will focus on the development of catalytic materials for the APHT process.

It is very interesting that we found that both carbonates (CO$_3^{2-}$) and bicarbonates (HCO$_3^-$) were efficiently reduced to formate in similar yields. The highest formate yield, ~40%, was actually obtained using K$_2$CO$_3$ as the hydrogen acceptor (Table 1 entry 12). Our findings are different from the literature reports on electrochemical reduction of CO$_2$, which have showed that HCO$_3^-$ was much easier to be reduced than aqueous dissolved CO$_2$ or CO$_3^{2-}$ because protonation of CO$_2$ in ambient liquid water could significantly diminish the redox potential by 1 order of magnitude.[22,23] We think that the unique properties of subcritical water may overcome the barrier of the protonation of CO$_3^{2-}$ to HCO$_3^-$. With a less extensive hydrogen-bond network, subcritical water is less capable of accepting the ejected proton than ambient liquid water. The free proton thus can quickly recombine with its conjugate base, i.e., CO$_3^{2-}$. These results are in agreement with thermodynamic studies showing dramatic decreases in the acid dissociation constant for a wide variety of weak acids in hydrothermal media. However, when directly using CO$_2$ gas as the feedstock, only a very low yield of formic acid, 1.2%, was obtained. We ascribe the low formate yields to the low solubility of CO$_2$ gas, and thus low concentrations of HCO$_3^-$/CO$_3^{2-}$ ions, in weakly alkaline subcritical water.

To optimize the yields of formic and lactic acid salts, the effects of the process conditions on the dehydrogenation of glycerol, as well as simultaneously the NaHCO$_3$ hydrogenation, were studied. As shown in Figure 1, below 180 °C, neither dehydrogenation nor hydrogenation reactions occurred. The yields of lactic and formic acid salts increased with increasing temperature from 180 °C and appeared to reach the maximum values at 240 °C. However, further increasing temperature to 270 °C decreased both acid yields, probably due to the decomposition of the acid salts at higher temperatures. At 240 °C, the yields of lactic and formic acid salts both increased rapidly with extending reaction time but reached the plateaus
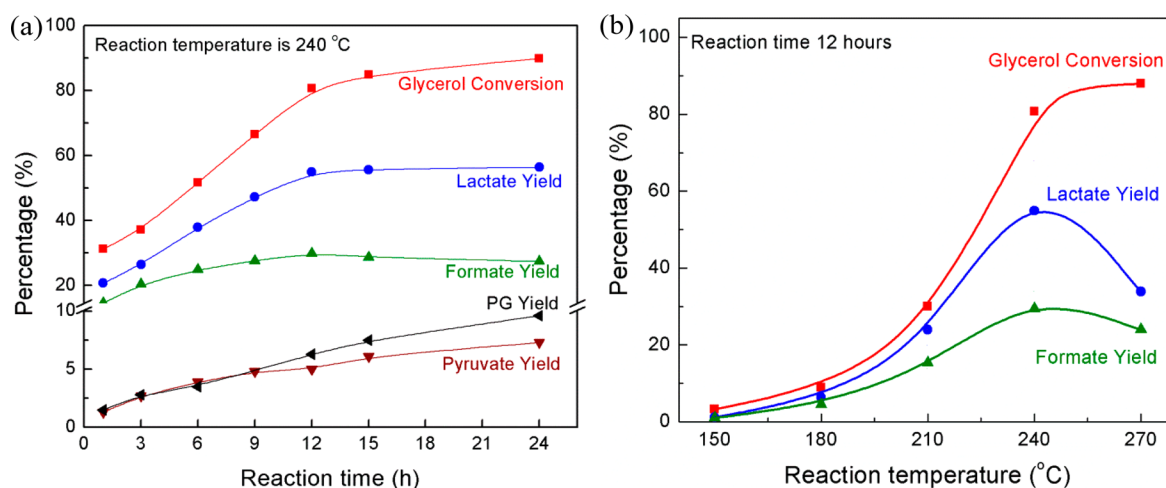
Figure 1. Effect of reaction time (a) and reaction temperature (b) on the reduction of NaHCO$_3$ with glycerol. Other reaction conditions: 400 psi (N$_2$), initial pH 8.0, 20 mL H$_2$O, 1 M glycerol or NaHCO$_3$, 0.1 g Pd/AC (5 wt %).

after 12 h. The reduction of $NaHCO_3$ by glycerol was rapid; an initial rate of reduction from the data available at 1 h reaction time gave a turnover rate of >256 formate ions produced per active Pd catalyst site per hour. The total turnover number (TON) has been shown to be 535 for 12 h (Table 1 entry 9). This is a lower limit of the TON since the reused Pd/AC catalysts have been demonstrated to be active. Figure 2 shows
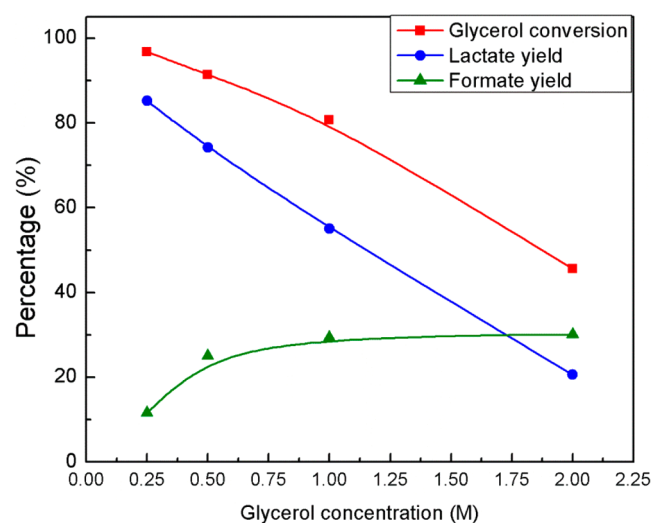

Figure 2. Effect of glycerol concentration on the hydrogenation of $NaHCO_3$. Reaction conditions: 240 °C, 400 psi (N_2), 12 h, initial pH 8.0, 20 mL H_2O, 1 M $NaHCO_3$, 0.1 g Pd/AC (5 wt %).

that the effect of concentration of glycerol on the yields of formic and lactic acid salts. When the concentration of glycerol was decreased from 2.0 to 0.25 M but that of $NaHCO_3$ was kept unchanged at 1.0 M, the glycerol conversions increased from ~50% to ~95% with the corresponding lactate yields increased from ~20% to ~85%, while at the same time, the formate yields decreased from ~30% to ~10%. At low glycerol concentrations, the excess CO_3^{2-}/HCO_3^- ion pairs, as the hydrogen acceptor, promoted the dehydrogenation of glycerol. The OH^- ions generated from the equilibrium reaction of between aqueous HCO_3^- and CO_3^{2-} in hydrothermal media[24] might also act as a catalyst to promote the conversion of

glycerol into lactate.[20,21] On the other hand, the decrease of formate yields was due to insufficient hydrogen released in the first dehydrogenation step of the AHPT process since glycerol, the source of H_2, is in substoichiometric quantity.

It is anticipated that the yield of the dehydrogenation product on the molar basis should be equal to that of the hydrogenation product in a stoichiometric transfer hydrogenation reaction. However, in the APHT process, the ideal stoichiometry does not apply because the formate yields are lower than the corresponding lactate yields when the feed concentrations of glycerol and $NaHCO_3$ are the same. For example, ~30% yield of formate, together with ~55% yield of lactate, was obtained in a 12 h APHT reaction at 240 °C when the initial concentrations of glycerol and $NaHCO_3$ are both 1 M. Further prolonging the reaction time to 24 h did not increase the formate yield, as shown in Figure 1a. Because the decomposition of formate and the hydrogenation of bicarbonate are two reversible reactions, and thus at a certain temperature and pressure, it is possible that the formate yield in the APHT is limited by the reaction equilibrium of the formate decomposition and production. Using H_2 gas as the reductant, we carried out the hydrogenation of $NaHCO_3$ at the same conditions as that of the typical APHT reaction. It is found that the presence of higher H_2 pressure shifted the equilibrium toward formate production. As shown in Figure 3a, when the molar ratio of H_2 to bicarbonate was 1:1, the formate yield became 35% after 12 h, but further increasing the ratio to 2:1, the formate yield increased to 42.5% and then reached the plateau, ~50%, as the ratio was >3:1. Unlike the hydrogenation with H_2, using glycerol as the hydrogen donor, the formate yields almost kept the same at ~30%; even the molar ratio of glycerol to bicarbonate increased from 1:1 to 2:1, as shown in Figure 2. The dehydrogenation of glycerol may be the rate-limiting step under the AHPT conditions since even the initial concentration of glycerol was twice than that of sodium bicarbonate, the hydrogen supplied by glycerol was not enough and thus caused the reduction of bicarbonate being hydrogen starved. Also, it is known that formic acid or formate can be readily decomposed to H_2 and CO_2 with the Pd/AC catalyst, especially when the reaction is carried out under low pressures and high temperatures.[25−27] As shown in Figure 3b, under the typical APHT reaction conditions, the conversion of formic
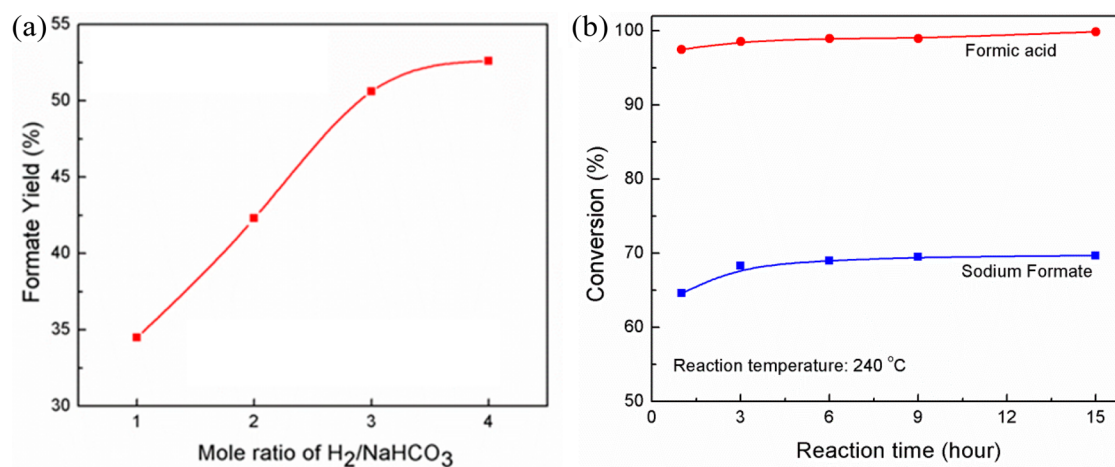

Figure 3. (a) Hydrogenation of sodium bicarbonate with H_2 gas directly. Hydrogenation reaction conditions: 240 °C, 20 mL H_2O, 1 M $NaHCO_3$, initial pH 8.0, 0.1 g Pd/AC (5 wt %), and 12 h. (b) Decomposition of formic acid and sodium formate. Decomposition reaction conditions: 240 °C, 400 psi (N_2), 20 mL H_2O, 1 M HCOOH or HCOONa, 0.1 g Pd/AC (5 wt %).
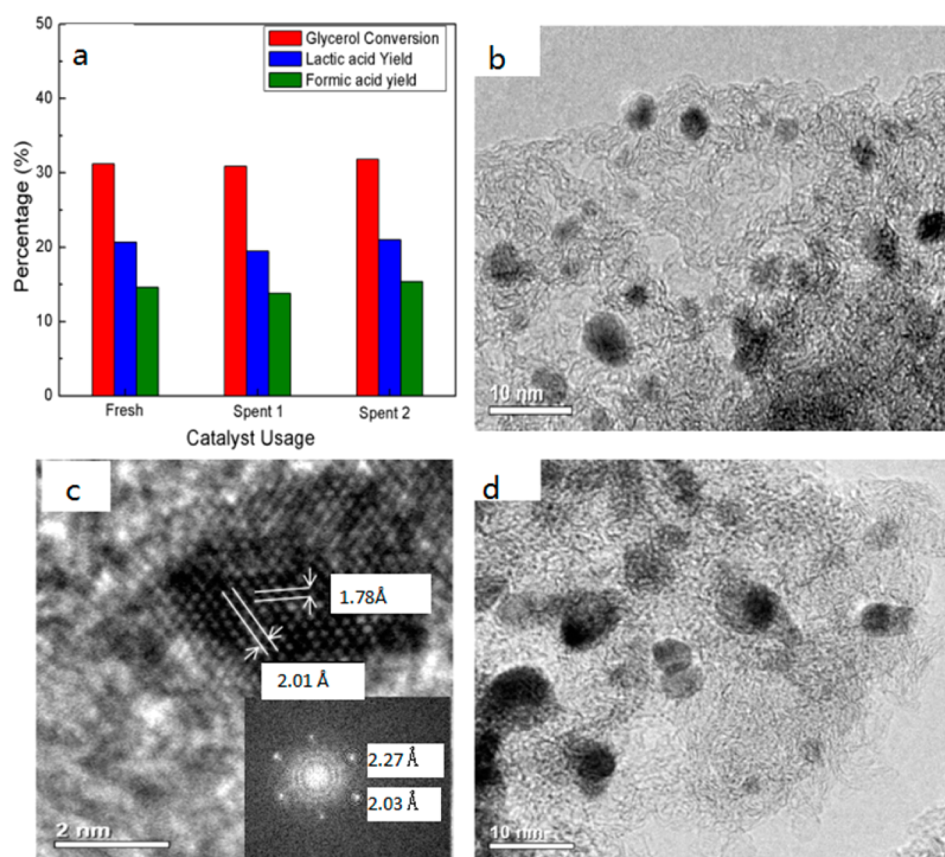
Figure 4. Pd/AC (5 wt %) catalyst stability testing (A) and TEM images (B, C, and D). Images B and C are the fresh 5 wt % Pd/AC catalyst, and image D is the spent Pd/AC catalyst after 1 time use (24 h).

acid over the Pd/AC catalyst was almost 100%. However, the conversion of sodium formate was ~70% under the identical conditions, indicating that sodium formate is more stable than formic acid in the APHT process, which may explain why the maximum formate yield at 240 °C was kept at ~30% regardless the higher concentrations of glycerol.

There are two possible hydrogen transfer routes in an APHT reaction: first, glycerol is dehydrogenated to form H_2 gas, which then hydrogenates HCO_3^-; or second, hydrogen in glycerol is directly transferred to reduce HCO_3^-. In the former case, glycerol would be just simply supplying H_2 gas in the APHT system and thus the effect of glycerol to bicarbonate ratio on the formate yield should be as same as that of H_2 to bicarbonate ratio. The discrepancy of the results using glycerol and H_2 as the reducing agents suggested that the AHPT more likely follows the second route, i.e., hydrogen in glycerol is directly transferred to reduce bicarbonate and would be limited by the active sites of the Pd NPs. However, the first route of dehydrogenating glycerol to produce H_2 cannot be ruled out because H_2 is the major gaseous product in the APHT process, as shown in Figure S10 (Supporting Information). If the second route is dominant, we expect that the advantage of the APHT is that the gas−liquid mass transfer resistance commonly existed in the large-scale hydrogenation process with H_2 gas can be circumvented by transferring hydrogen from highly water-soluble alcohols/polyols to aqueous dissolved CO_2.

Moreover, catalyst stability is critical for hydrothermal reactions. Previous studies show that in the hydrothermal conditions, transition metal such as Zn, Fe, and Ni NPs show

obvious leaching or agglomeration.[10,14−16] However, to reduce sodium bicarbonate with glycerol in the APHT process, the Pd/AC catalyst was reused for three times without regeneration and yielded almost the same yields of lactic and formic acid salts (Figure 4a). The sintering of the Pd NPs on carbon support was insignificant, even in hydrothermal media at 240 °C. The TEM images (Figure 4b,d) indicate that the size of Pd NPs of the fresh catalyst is ca. 3.0 nm, while the size increases to ca. 3.4 nm after three times of reuse. A particle size calculated based on the X-ray diffraction (XRD) spectra (Figure 5) is ca. 4.7 nm after three times reuse and 5.05 nm after reacting for 24 h. The HRTEM image shows that the interplanar spacing is 0.23 and 0.20 nm, indicating the lattice planes [111] and [200] of the Pd^0 metal, respectively, which is in accordance with the calculated interplanar spacing according to the electron diffraction spectra (inset of Figure 4c). These two main facets of Pd are also identified by the XRD characterization.

To validate the generalization of alcohols and polyols derived from biomass as the hydrogen donor in the APHT process, a variety of alcohols and polyols were used as the feedstocks. An appreciable amount of bicarbonates was converted to formates with all tested biomass derived alcohols or polyols, as shown in Table 3. It is widely accepted that, during a typical alcohol dehydrogenation reaction, two hydrogen atoms abstracted from the hydroxyl group and the hydrogen on the α-carbon of the alcohol form the dihydrogen.[28−30] Therefore, primary alcohols were usually dehydrogenated to form aldehydes and/or acids, while ketones were obtained from secondary alcohols. Interestingly, in the APHT reaction system, only a few
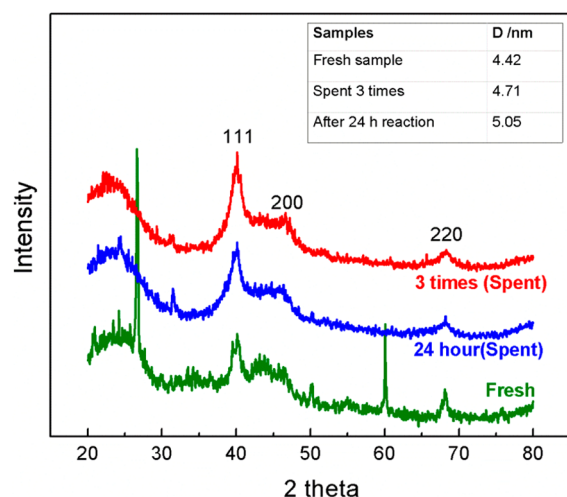
Figure 5. XRD pattern and the size of the Pd nanoparticles of the 5 wt % Pd/AC catalysts before and after the reactions. The size of the Pd nanoparticles was calculated by Scherrer equation: $D = K\lambda/B\cos\theta$; K, Scherrer constant 0.89; D, particle size (nm); B, half-width (rad); θ, angle of diffraction (rad); λ, X-ray wavelength, 0.154 nm.

Table 3. Reduction of NaHCO$_3$ with Various Alcohols or Polyols over the Pd/AC (5 wt %) Catalyst

| entry | alcohols or polyols | conversion (%) | products yields (%) | |
			main dehydrogenation products	formate
1	ethanol	35.6	acetate 5.8	20.4
2	1-propanol	20.9	propionate 6.9	16.3
3	2-propanol	34.6	acetone 18.6	16.9
4	1-butanol	21.6	butyrate 4.6	17.7
5	*tert*-butanol	0.9		0.0
6	phenol	1.5		0.0
7	glycerol	80.7	lactate 55.0	29.4
8	xylitol	99.9	lactate 25.6	19.0
9	ethylene glycol	85.6	lactate 10.5	44.1
10	propylene glycol	43.9	lactate 27.9	23.9

Reaction conditions: 240 °C, 400 psi (N$_2$), 12 h, initial pH 8.0, 20 mL H$_2$O, 1 M alcohols or polyols and 1 M NaHCO$_3$, 0.1 g catalyst loading.

aldehyde products were detected. Compared to alcohols, C3 polyols were converted to a more complicated product mixture among which lactic acid was dominant but other byproducts were not negligible (Table 1 and Figures S2−9, Supporting Information). For example, glycerol was converted to 55% lactate, 5% pyruvate, 6.3% PG, and 50.4% H$_2$ (Table 1 entry 9 and Figure S10, Supporting Information), as well as 14.4% unidentified aqueous phase products (Figure S7, Supporting Information), in a slightly basic aqueous solution (initial pH value is 8.0). As shown in (Figure S10 and Table S11, Supporting Information), the proportion of the CO$_2$ gaseous product to the total carbon is approximately 5.4%, which was probably produced from the decomposition of bicarbonates or formates. The highest yield of formic acid reached 44.1% (Table 3 entry 9) when using ethylene glycol (EG) as the hydrogen donor in the APHT, which is near the same formate yield of hydrogenating NaHCO$_3$ with H$_2$ at the same reaction conditions (Figure 3a). It is interesting to find that the yields of carboxylic acids from the corresponding biomass derived alcohols/polyols were in the order of glycerol > propylene glycol (PG) > ethylene glycol (EG) ≫ 1-butanol > 1-propanol > ethanol. When EG was used as the hydrogen donor, lactic acid was still one of the main products. Jin's group also observed the formation of lactic acid from the hydrothermal oxidation of glycolaldehyde in alkaline hydrothermal solutions.[31] The formation of C3 hydroxyacid from C2 diol may be realized through the aldol condensation and then consecutive reverse aldol condensation reactions (Scheme 3).

The XPS spectra of the fresh and spent Pd/AC samples a and b show that the Pd^{2+} in the fresh catalyst was completely reduced to Pd^0 after the APHT reaction (Figure 6). The reduction of partially oxidized fresh Pd/AC catalyst by glycerol is very similar to that by H$_2$, referring to the XPS spectra of the samples b and c, which were reduced in the APHT reaction and in H$_2$ flow, respectively. Therefore, even without adding external H$_2$, the APHT process is under a reductive atmosphere. To better understand the underlying reaction mechanism of the APHT, the role of the Pd/AC catalyst needs to be elucidated. Two hydrogen transfer schemes[32] are widely accepted: first, the dehydrogenation of the hydrogen donor forms a palladium hydride followed by transfer of hydride to the hydrogen acceptor; second, both hydrogen donor and acceptor are coadsorbed onto the Pd surface followed by the direct transfer of hydrogen on the catalyst surface without forming hydrides. The differences of XPS spectra between Pd and PdH$_x$ are that the core levels show three distinct changes from the metal to the hydride: the asymmetry of the line profile

Scheme 3. Proposed Reaction Pathway of the Conversion of Ethylene Glycol to Lactic Acid That Starts from the Dehydrogenation of Ethylene Glycol over Pd/AC Catalyst
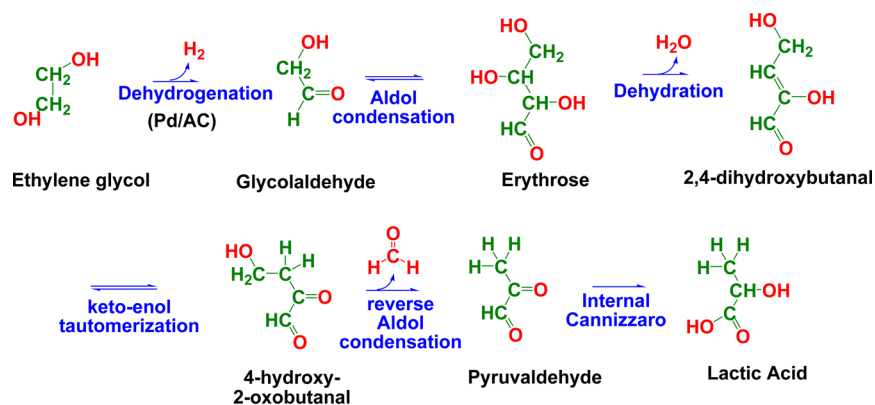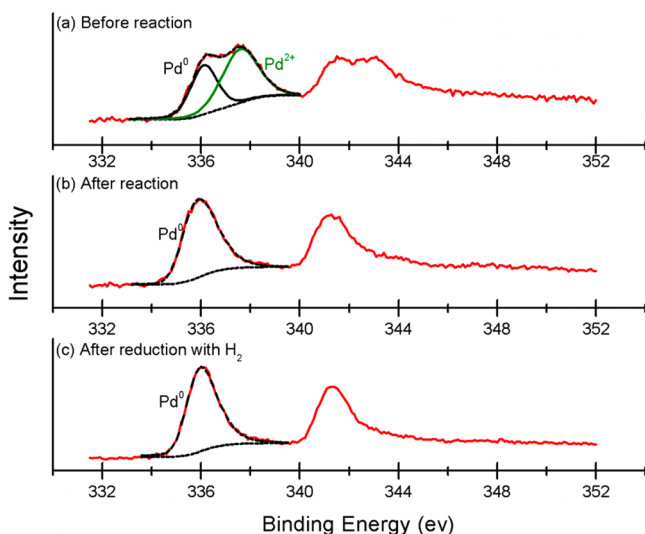
Figure 6. Pd 3d XPS spectra of the different Pd/AC catalyst samples: (a) fresh Pd on activated charcoal purchased from Sigma-Aldrich (Storage in air atmosphere before use.); (b) after reaction. (Reaction conditions: 240 °C, 1 h, 1 M glycerol and 1 M sodium bicarbonate are in 20 mL H_2O.) After the reaction, the catalyst was centrifuged with water and ethanol for three times, respectively, and then the sample was dried at 40 °C in N_2 atmosphere for 2 h and was sealed inside a vial in N_2. (c) After the reduction with H_2. The sample was reduced in a tube furnace with dry H_2 flow at 60 °C in tube furnace for 3 h, then purge with N_2 for 1 h at 100 °C (for eliminating the Pd hydride) and for 1 h at room temperature. Then the sample was sealed inside a vial in N_2.

is significantly reduced, the shakeup satellite ∼6 eV from the $3d_{3/2}$ line has almost completely disappeared, and the high energy leading edge of the $3d_{5/2}$ emission is shifted (0.2 ± 0.1) eV to lower energy.[33] We do not see any of the above differences from the side-by-side comparison of the sample b with sample c in Figure 6. The $3d_{5/2}$ binding energies for both samples are identical (336.0 eV). There is no obvious difference in the peak shapes. Unexpectedly, the satellite peak at 348 eV is more clearly seen in sample b. The satellite peak of Pd and a slightly narrower $3d_{5/2}$ peak for PdH_x were also observed by other groups.[34] However, this peak width difference was not observed in another study.[35] In our spectra, the $3d_{5/2}$ peak widths are very close. It is very likely that both samples b and c are metallic Pd and there is no XPS evidence showing that sample b contains a significant amount of PdH_x. We thus tentatively propose the direct hydrogen transfer mechanism for the APHT reduction of CO_2, which would be strongly catalyst structure-sensitive since the coadsorption of biomass molecules and bicarbonate ions could be rate-limiting. Our future research will examine the structure/activity relationship of the Pd/AC catalysts with the shape-control or alloying synthesis. However, the hydride transfer mechanism cannot be ruled out without in situ dynamic characterizations. Recently, Lercher's group explored the structure and chemical state of Pd/C in contact with H_2 in hydrothermal water by X-ray absorption spectroscopy. They concluded that Pd hydrides are presented and such PdH_x NPs are hardly influenced by the presence of hydrothermal water.[36] Thus, Pd hydrides might be present in the APHT due to the analogy between the APHT reaction system and Lercher's system.

CONCLUSIONS

In summary, we have demonstrated that the aqueous-phase hydrogen transfer (APHT) process is feasible toward coupling the dehydrogenation of biomass derived alcohols and polyols and the hydrogenation of bicarbonates and carbonates at mild hydrothermal conditions. At the certain reaction conditions and using glycerol as a hydrogen donor, up to ∼40% of formate was produced by the reduction of bicarbonates or carbonates over the Pd/AC catalyst, while in the same "one-pot" reaction system, up to ∼85% of lactate was coproduced from glycerol. A variety of biomass derived alcohols or polyols including ethanol, butanol, xylitol, etc. have been proven to be hydrogen donors in the APHT process. A possible APHT reaction mechanism is that both alcohol/polyol and bicarbonate/carbonate are coadsorbed onto the Pd surface followed by the direct transfer of hydrogen on the catalyst surface without forming hydrides. This novel APHT process may open a door to integrate biorefineries with CO_2 capture and storage facilities to coproduce value-added carboxylic acid products from biomass waste and redundant CO_2 resources. Such an integrated process can not only improve the overall process economics but also have significant environmental benefits.

ASSOCIATED CONTENT

Ⓢ Supporting Information
Pulse chemisorption analysis of Pd/AC sample, HPLC and LC-MS analysis of aqueous phase products, GC analysis of gas products and the carbon balance calculation. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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