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Atom Economical Aqueous-Phase Conversion (APC) of Biopolyols to Lactic Acid, Glycols, and Linear Alcohols Using Supported Metal Catalysts

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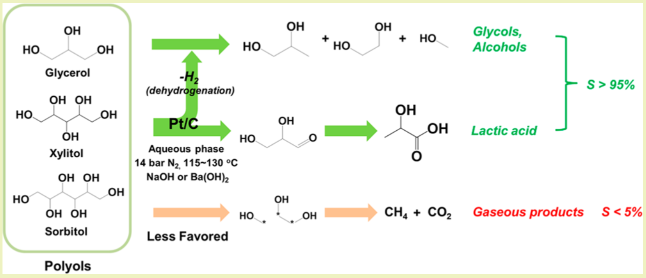
Supporting Information



ABSTRACT: Conversion of renewable biopolyols to value-added chemicals such as lactic acid and glycols usually demands excess hydrogen/oxygen or harsh reaction conditions in strong alkaline medium (220−350 °C). This unfortunately promotes significant side reactions resulting in low carbon selectivity to liquid products, posing significant challenges for the development of sustainable technologies. We report here a new atom economical catalytic conversion of various biopolyols (glycerol, xylitol, mannitol, and sorbitol) to lactic acid with glycols and linear alcohols as co-products at much lower temperatures (115−160 °C) without external addition of either hydrogen or oxygen. Among various metal-based catalysts (Pt, Pd, Rh, Ru, Raney Ni, Raney Co, and Cu) evaluated, Pt/C catalyst gives the highest chemoselectivity (S > 95%) for lactic acid, glycols, and linear alcohols at 115−160 °C. An important finding is that approximately two-thirds of the hydrogen generated in situ via dehydrogenation of polyols over Pt/C catalyst is efficiently utilized for the conversion of the remaining polyols and intermediates to useful products (e.g., glycols and linear alcohols instead of gaseous products) with the remaining available hydrogen for use elsewhere in a biorefinery. The Pt/C catalyst is thus multifunctional facilitating tandem dehydrogenation/hydrogenolysis of polyols. Furthermore, it is observed that Ba^{2+} alkali ion promotes the activity of the Pt/C catalyst by almost 12-fold compared to other alkali promoters such as NaOH, KOH, and $Ca(OH)_2$. In addition to being the first reported study on the conversion of C_5~C_6 polyols (e.g., xylitol and sorbitol) to lactic acid at relatively low temperatures, the results also provide new insights into the mechanism of tandem catalysis of biopolyols conversion to value-added commodity chemicals.

KEYWORDS: *Lactic acid, Biopolyols, Tandem catalysis, Dehydrogenation/Hydrogenolysis*

INTRODUCTION

During the past decade, there has been much interest in the catalytic conversion of renewable bioderived feedstocks to transportation fuels[1,2] and value-added chemicals,[3,4] aimed at alleviating dependence on fossil fuels. Biopolyols, including glycerol, xylitol, sorbitol, and mannitol, are regarded as promising raw materials due to their relatively abundant availability from biomass.[2,5] They represent renewable alternatives to petroleum-based feedstocks for making industrial chemicals such as propanediol (PDO), ethylene glycol (EG), and lactic acid (LA), which are important intermediates for the manufacture of antifreeze, detergents, and other biodegradable materials.[6−11]

The conversion of polyols to LA is very important because LA can be further converted to commodities such as acrylic acid and esters or polylactic acid.[12] LA is conventionally produced from renewable sugars by a fermentation route; however, this process suffers from low liquid products selectivity (*S* = 54−78%) and complex separation steps.[13] The hydrothermal route for direct conversion of glycerol to lactic acid in strong alkaline medium is another approach; however, this route requires significantly high temperatures (>300 °C) and suffers from severe corrosion problems due to the presence of alkali at such high temperatures.[14,15] Catalytic oxidation of glycerol to LA using supported PtAu catalysts has been reported under a high NaOH:glycerol ratio (4:1 molar ratio).[16] Hydrogenolysis of glycerol using Ru-based catalysts also gives LA as a coproduct (*S* < 35%) besides PDO.[17] A study combining density functional theory (DFT) and experimental work using Rh and Ir catalysts shows that glycerol dehydrogenation and dehydration might both contribute to LA formation (*S* ~ 50%); however the role of a base in the proposed routes as well as the deoxygenation pathway are unclear because approximately 18−26% carbon was not accounted for in the

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Table 1. Comparison of Different Metal Catalysts in Aqueous-Phase Glycerol Conversion

			selectivity (%)						
entry #	catalysts	X[a] (%)	LA	PDO	GLA+PAD[d]	EG	alcohols[e]	CH_4	C_{2+} alkanes
1	R-Ni[b]	99.3	7.4	0.3	0.3	–	0.6	64.6	3.0
2	R-Co[b]	99.0	37.6	1.1	0.3	–	1.8	34.3	2.2
3	Ru/C[c]	97.7	39.6	4.8	0.5	–	13.2	15.8	8.7
4	Pt/C[c]	97.1	37.2	9.6	0.4	0.9	15.9	1.9	1.3
5	Pd/C[c]	91.1	40.1	6.9	0.5	1.4	14.5	3.7	0.5
6	Rh/C[c]	87.0	37.9	10.9	0.5	1.0	15.0	7.9	2.9

[a] Conversion at 220 °C. Reaction time: 6 h. P_{N2}: 1.4 MPa. Glycerol: 1.1 kmol/m^3. Solvent: H_2O. NaOH/glycerol molar ratio: 1.1. [b] Raney Ni and Raney Co catalysts: charge, 100.0 kg/m^3. [c] Noble metal catalyst supported on carbon: charge, 6.7 kg/m^3. [d] Glyceraldehyde (GLA) and pyruvaldehyde (PAD). [e] Alcohols including methanol, ethanol, and traces of propanols.

final products.[18,19] Recently, we reported Cu-catalyzed conversion of glycerol to LA (S = 74−84%) with PDO as a co-product at 200 °C without external addition of either hydrogen or oxygen.[8,20] This Cu-catalyzed synthesis is a significant advance over the conventional hydrothermal[14,21,22] as well as hydrogenolysis/oxidation processes that require high temperatures and alkali/substrate ratios. However, the mechanisms of the competing reactions including dehydrogenation, hydrogenolysis, methanation, and water gas shift (WGS) reactions on metal catalysts are still not well understood. Further, the lower intrinsic activity of Cu catalysts and their high tendency for promoting side reactions (combined selectivity of methane and CO_2 approximately 12−24%) are major drawbacks.

The aforementioned challenges motivated us to further investigate alternative catalysts that are active for atom economical transformation of bioderived C_3~C_6 polyols to useful industrial chemicals at relatively low temperatures. We report here for the first time the conversion of cellulosic polyols such as xylitol (C_5), mannitol (C_6), and sorbitol (C_6) to LA with glycols as co-products without external addition of either hydrogen or oxygen. Specifically, experimental data on the activity, selectivity, and stability of supported Pt, Cu, Rh, Ru, Pd, Raney Ni, and Co catalysts for glycerol, xylitol, sorbitol, and mannitol conversion are reported. We demonstrate that the Pt/C catalyst is the most active among these catalysts, facilitating tandem dehydrogenation and hydrogenolysis (DH/HDO) of polyols. We also show that with Pt/C catalyst, high carbon efficiency (>95%) is achievable at significantly lower temperature (T = 115−130 °C). For the Pt/C catalyst, the effect of reaction conditions such as substrate concentration, temperature, and different types of alkali promoters on activity and selectivity were also investigated. On the basis of these studies, possible reaction pathways and the reaction mechanism for tandem DH/HDO are discussed.

■ EXPERIMENTAL SECTION

Chemicals including glycerol (>99.5%), D-sorbitol (99+ %), D-glucose (99.5%), D-fructose (99+ %), glyceraldehyde (95%), pyruvaldehyde (40 wt % in H_2O), 1, 2-propanediol (99.5+ %), ethylene glycol (99.8+ %), ethanol (99.5%), methanol (99.8%), $Ca(OH)_2$, $Ba(OH)_2$, KOH, NaOH, and sulfuric acid (95−98%) were purchased from Sigma-Aldrich. Lactic acid and formic acid were purchased from Fluka and glycolic acid from Acros. Precious metal catalysts such as Pt, Pd, Ru, Rh, all supported on activated carbon with 5 wt % metal loading (particle size range: 0.07−0.09 mm), and unsupported Cu_2O catalysts (particle size <0.075 mm) were purchased in powder form from Sigma-Aldrich. Base metal catalysts such as Raney Ni and Raney Co were purchased from Grace Davison and Sigma-Aldrich, respectively. Raney Ni and Raney Co catalysts were reduced at 240 °C and 10 MPa hydrogen pressure for 6 h prior to batch reaction tests. Hydrogen (>99.5%) and nitrogen (>99%) were procured from Air Gas, Inc. and Linweld, respectively, and used without further purification.

Transmission Electron Microscopy (TEM). Samples were prepared by suspending solid catalysts in ethanol and agitating in an ultrasonic bath for 15 min. Ten microliters of catalyst sample was placed onto a copper mesh grid with lacey carbon film (purchased from Ted Pella, Inc.). The wet grids were allowed to air-dry for several minutes prior to being examined under TEM. The catalyst particle size and morphology were examined by bright-field and dark-field transmission electron microscopy (TEM) using an FEI Technai G_2 transmission electron microscope at an electron acceleration voltage of 200 kV. High resolution images were captured using a standardized normative electron dose and a constant defocus value from the carbon-coated surfaces. Energy dispersive X-ray spectroscopy (EDS) was carried out using an EDAX detector.

Catalytic Tests. Catalytic tests were carried out in a high temperature, high pressure, magnetically stirred, multiple batch, slurry reactor setup.[8] PTFE liners were used in each reactor to avoid the catalytic effect of reactor wall materials at elevated temperatures (115−220 °C) in the presence of alkali. For a typical test, known amounts of polyols and alkali were dissolved in 30 mL water. This solution was charged to the reactor along with a known amount of solid catalyst and purged three times with N_2 at 2 MPa. The reactor was first heated to the desired temperature. Following temperature equilibration, the N_2 pressure was increased to 1.5 MPa, and the agitation speed was set at 800 rpm signaling the start of a batch run. The external and intraparticle mass transfer limitations were estimated to be negligible under our reaction conditions.[23] Following a fixed-time batch reaction, the reactor contents were cooled to room temperature, and the gas phase was sampled directly into a GC (Shimadzu, Model GC-2014) for quantitative analysis of gas-phase composition. Then the reactor was opened, and the pH value of the liquid samples was measured (pH > 11). Twenty milliliters of sulfuric acid solution in water was added to acidify the liquid products (pH 2−4) to match the pH of the HPLC mobile phase (0.005 N H_2SO_4 with a pH of 2.3). The final volume of the liquid sample was measured before HPLC analysis [Rezex ROA-Organic Acid H^+ (8%) column, 0.005 N aqueous H_2SO_4 as mobile phase and RI detector]. The final pH value of the acidified liquid phase is largely dependent on the conversion of substrate (e.g., glycerol, xylitol, and sorbitol), concentration of alkali [e.g., NaOH, KOH, $Ca(OH)_2$, and $Ba(OH)_2$] remaining in the liquid product, and concentration of lactate formed. The analytical results from the GC and HPLC were combined to get a quantitative assessment of each product in the gas and liquid phases and for calculation of conversion/selectivity values.

Conversion (X) is defined as the ratio of moles of substrate converted to the moles of substrate charged initially. *Carbon Selectivity* (S, also referred to as selectivity) is defined as the moles of carbon in a specific product to the moles of carbon equivalent in the substrate. *Yield* (Y) of a specific product is defined as conversion multiplied by the selectivity to the specific product. *Turnover frequency* (TOF) is defined in terms of the substrate converted per metal content per reaction time (mol/g/h at conversion values of typically 20%). The

Table 2. Aqueous-Phase Glycerol Conversion over Metal Catalysts at Low Temperatures (150−160 °C)

				selectivity (%)					
entry #	catalysts	time (h)	X^a (%)	LA	PDO	GLA+PAD[d]	EG	alcohols[e]	gas[f]
1	R-Ni[b]	6	87.0	20.3	41.0	5.0	3.8	3.9	5.2
2	R-Co[b]	6	94.4	44.5	37.5	5.1	1.0	0.7	2.7
3	Pt/C[c]	2	44.9	54.1	20.9	1.0	1.6	17.7	0.4
4		6	78.7	36.5	25.8	0.6	1.9	21.6	2.0
5	Ru/C[c]	2	51.8	30.4	35.9	0.9	2.8	10.5	4.0
6		6	83.9	32.5	35.9	0.5	2.1	18.0	4.4
7	Rh/C[c]	2	33.0	46.3	27.3	0.5	0.9	16.9	4.7
8		6	57.1	46.9	31.2	0.2	1.2	14.8	4.4

[a] Conversion at P_{N2}: 1.4 MPa. Glycerol: 1.1 kmol/m^3. Solvent: H_2O. NaOH/glycerol molar ratio: 1.1. [b] Raney Ni and Raney Co catalysts: T, 150 °C; charge, 33.3 kg/m^3. [c] Noble metal catalyst supported on carbon: T, 160 °C; charge, 6.7 kg/m^3. [d] Glyceraldehyde (GLA) and pyruvaldehyde (PAD). [e] Alcohols including methanol, ethanol, and traces of propanols. [f] Mainly methane, traces of C_{2+} alkanes.

formation rate of a certain product (e.g., LA, EG) is defined as the amount of product formed at a finite conversion value (<100%) normalized with respect to both the metal content in the catalyst as well as the batch time.

RESULTS AND DISCUSSION

Conversion of Glycerol to Lactic Acid. *Catalyst Screening.* Conversion and selectivity of carbon-supported Pt, Pd, Ru, Rh, Raney Ni, and Raney Co catalysts were evaluated for glycerol conversion in aqueous phase under alkaline conditions without adding external hydrogen. The experimental details and results at 220 °C are shown in Table 1. Almost complete glycerol conversion was achieved in 6 h over the various catalysts. However, the LA selectivity was different in each case. It is clearly seen that Raney Ni displays a poor selectivity toward LA (S = 7%, entry #1 in Table 1) with significant methane formation. Raney Co and Ru catalysts (entries #2 and #3 in Table 1) show relatively higher LA selectivity and lower methane selectivity (S = 65%) compared to Raney Ni. Supported Pt, Pd, and Rh catalysts on carbon (entries #4−6 in Table 1) also show high glycerol conversion with LA selectivity between 37−40% and significantly lower methane formation. It is obvious that a carbon balance deficiency (15−24%) in the final products was observed on these metal catalysts (Table 1) at 220 °C. Most notably, GC analysis of the gas phase does not reveal any detectable CO_2 in the gas phase. This does not seem possible given the preponderance of evidence that CO_2 is formed from aqueous phase reforming on such systems at the temperatures under investigation.[8,17,29] Hence, this C deficit is partly attributed to the absorption of gas-phase CO_2 at 220 °C in the alkaline reaction medium to form carbonates (which could not be reliably measured). In previous work[8] and this work, we observed release of gas bubbles from the liquid phase when dilute H_2SO_4 was added during liquid product workup for analysis. This might indicate that the CO_2 formed in the gas phase during the reaction might react with the base in the liquid phase to form carbonate or bicarbonate and is released upon H_2SO_4 addition. The fact that the pH of the product mixture remained >11 (prior to product workup) confirms that the conditions are favorable for the CO_2 to react directly with the hydroxide to form bicarbonate but that the CO_2 amount was not significant enough to lower the pH value. Under similar conditions, the Cu_2O catalyst gives high LA selectivity (S = 74%) at 70% conversion of glycerol.[8] The intermediate products such as glyceraldehyde (GLA) and pyruvaldehyde (PAD) observed with Cu_2O catalysts were also observed with the other catalysts, albeit in small quantities, indicating that the reaction pathway for LA formation is similar on different catalysts. It must be noted that a reaction with NaOH but without the metal component gave negligible conversion of glycerol (<1%) in a PTFE-lined reactor in a temperature range of 130−220 °C. A similar result was also obtained previously when the reaction was performed with a Cu catalyst but without a base.[8] Further, a comparison of the foregoing results with previous studies with Ru/C and Pt/C catalysts under neutral conditions (i.e., without adding bases or acids)[24] indicates that the selectivity for methane on noble metals is significantly reduced in the presence of alkali (Table 1, entries #3, #4, and #6) while increasing the total yield of liquid products.

In order to understand the temperature effects, additional tests were carried out using the various catalysts at milder conditions (T = 150−160 °C) with varied batch times, the results of which are shown in Table 2. To our surprise, significant glycerol conversion was observed with all catalysts even at lower temperatures. Compared with the results at 220 °C, combined LA and PDO selectivity increases on Raney Ni and Co catalysts at 160 °C with significantly lower formation of gaseous products (S < 10%). The initial LA selectivity is higher on Pt/C than Raney Ni, Raney Ni, Ru/C, and Rh/C but decreases with reaction time (compare entries #3, #5, and #7 with #4, #6, and #8). The selectivities to LA and PDO remain almost unchanged with time on Ru/C and Rh/C catalysts. For Pt and Ru catalysts, the combined selectivity to LA and PDO is approximately 70−78% initially and declines with batch time while the formation of linear alcohols increases at longer reaction times.

The activities of the noble metal catalysts were also compared with the Cu catalyst reported previously.[8,20] As shown in Figure 1, Pt/C, Pd/C, Ru/C, and Rh/C catalysts exhibit TOFs of 1.32, 1.60, 1.60, and 1.17 mol/g/h, respectively, at 160 °C. In contrast, the TOF observed on Cu catalyst (0.004−0.51 mol/g Cu/h) is significantly lower. The formation rates (also in terms of TOF) for LA and linear alcohols on Pt/C are 0.92 and 0.31 mol/g Pt/h, respectively, while Ru/C and Rh/C show slightly higher formation rates for glycols compared to other products. In addition, Ru/C and Rh/C also display higher TOFs for linear alcohols (mainly methanol). From these results, it is clear that the Pt/C catalyst outperformed other noble metal catalysts during low-temperature conversion of glycerol to LA and glycols and was investigated further.

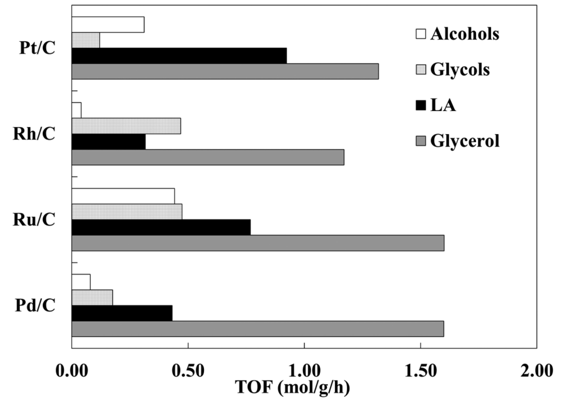


Figure 1. Activity of supported metal catalysts for aqueous-phase glycerol conversion (T: 160 °C. P_{N2}: 1.4 MPa. Glycerol: 1.1 kmol/m^3. Solvent: H_2O. NaOH/glycerol molar ratio: 1.1. Catalyst charge: 6.7 kg/m^3. Glycols: PDO and EG. Alcohols: methanol, ethanol, and propanols.). Note: TOF values were calculated based on polyol conversion of ~20%)[25].

TEM Characterization of Pt/C Catalyst. Figure 2 shows the TEM data of fresh [(2a) and (2b)] and used [(2c) and (2d)] Pt/C catalysts. The fresh Pt/C catalyst displays a size distribution of approximately 5−10 nm. The dominant plane manifested in fresh C-supported Pt nanoparticles is the [111] surface planes. The size of the Pt particles in the used catalysts remains in the 5−10 nm range. Further, the lattice structure of Pt nanoparticles appears to remain stable after the experimental runs.

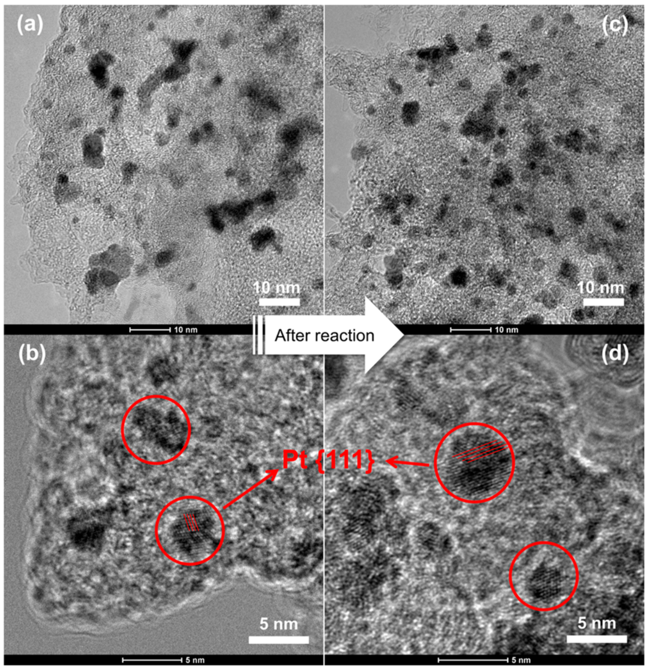


Figure 2. TEM data for fresh [(a), (b)] and used [(c), (d)] Pt/C catalysts.

Temporal Reaction Profiles on Pt/C Catalyst. Figure 3 shows the temporal concentration profiles of each reactant/product as a function of batch time during glycerol conversion at 160 °C on Pt/C under N_2 pressure and *without* external H_2 addition. Clearly, LA is the major product, and its concentration increases with time and saturates after 4 h. The concentration of the alkali species decreases continuously (due to their consumption for LA formation). The concentrations of the other liquid products, PDO and linear alcohols, increase continuously even after 4 h, resulting in not only high glycerol conversion (almost 80% in only 6 h) but remarkably high selectivity to liquid products (95%) in alkaline medium at 160 °C.[25]

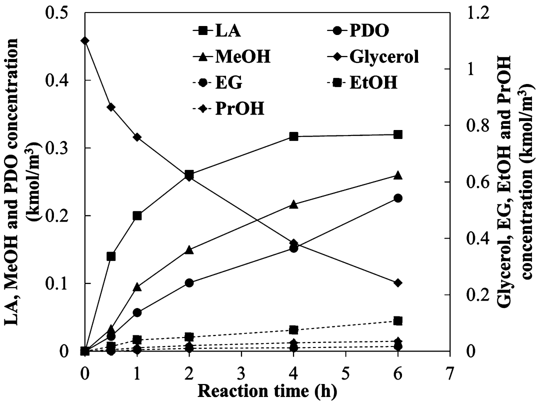


Figure 3. Concentration−time profiles during aqueous-phase glycerol conversion over Pt/C catalyst (T: 160 °C. P_{N2}: 1.4 MPa. Glycerol: 1.1 kmol/m^3. Solvent: H_2O. NaOH/glycerol molar ratio: 1.1. Pt/C catalyst charge: 6.7 kg/m^3)[25].

Table 3 shows the reaction results at even lower temperature (130 °C). It is found that glycerol conversion to LA and PDO is also observed at even lower temperature than previously reported.[17,26] Initial selectivity to LA is almost identical at 130 and 160 °C (compare entries #1 and #4). As conversion increases (entries #3 and #6), selectivity to LA remains almost constant at 130 °C, while that at 160 °C declines. The selectivity to linear alcohols at 130 °C is <6% at 45% conversion (compared to 18% at the same conversion at 160 °C). It is tempting to hypothesize that at 160 °C, the PDO undergoes progressive reaction through C−C cleavage to form alcohols (methanol and ethanol). However, diagnostic experiments with PDO as a starting material clearly show that PDO is not reactive in the 130−160 °C range (<5% conversion after 3 h). Experiments with various initial alkali concentrations (Table 4 and Figure S1, Supporting Information) reveal that the TOF increases several-fold with increasing initial NaOH concentration and reaches a plateau. The optimal alkali/glycerol ratio is approximately 0.9. This ratio is significantly lower compared with literature reports (2.0−10.0 molar ratio).[14,15,17,18,27]

Table 3. Aqueous-Phase Glycerol Conversion on Pt/C Catalyst at 130°C and 160°C[a]

				selectivity (%)		
entry #	temperature (°C)	time (h)	conversion (%)	LA	glycols	alcohols
1	130	2.5	20.1	63.6	27.9	−
2	130	4.5	30.0	64.0	24.3	6.2
3	130	8.0	45.6	62.8	26.7	5.7
4	160	0.5	21.6	69.8	9.1	11.2
5	160	1.0	30.2	62.0	16.5	19.9
6	160	2.0	44.9	54.1	22.4	17.7

[a] P_{N2}: 1.4 MPa. Glycerol: 1.1 kmol/m^3. Solvent: H_2O. NaOH/glycerol molar ratio: 1.1. Pt/C catalyst charge: 6.7 kg/m^3.

Table 4. Influence of NaOH Concentration on Observed TOF on Pt/C Catalyst

		reaction/formation rates[b] (mol/g Pt/h)			
entry #	alkali ratio[a]	glycerol	LA	glycols	alcohols
1	0.15	0.13	0.06	0.003	0.004
2	0.44	0.27	0.16	0.03	0.05
3	0.90	0.53	0.27	0.08	0.22
4	1.10	0.53	0.23	0.11	0.24

[a]NaOH/glycerol molar ratio. Reaction time: 4 h. T: 160 °C. P_{N2}: 1.4 MPa. Glycerol: 1.1 kmol/m^3. Solvent: H_2O. Pt/C catalyst charge: 6.7 kg/m^3. [b]Global TOF of glycerol or formation rates of specific products.

These results clearly demonstrate that tandem DH/HDO of glycerol occurs on Pt/C catalysts at relatively low temperatures (130−160 °C) without external H_2 addition with much higher selectivity to liquid products compared with conventional reforming[28,29] and conventional hydrogenolysis with external H_2 addition.[6,7,9,26,30]

Comparison of Pt/C Performance with and without External Hydrogen Addition. At 160 °C, glycerol conversion on the Pt/C catalyst with externally added H_2 (H_2, 2 h and H_2, 6 h in Figure 4) is lower than that observed when H_2 was replaced with N_2 at similar total pressure. Without the external H_2 addition (i.e., with N_2 only), the glycerol conversion increases from 45% in 2 h to 79% in 6 h. In contrast, the glycerol conversion is approximately 15% lower when external H_2 was added, which is attributed to the fact that in the presence of excess hydrogen (comprised of externally added H_2 and H_2 formed in situ), the GLA formation by the dehydrogenation step is likely to be hindered by equilibrium limitation.[26] It is to be noted in Figure 4 that after 2 h, LA selectivity is higher with *no* external H_2 addition compared to that with external H_2 addition. In contrast, PDO selectivity is higher under conditions with external H_2 addition. After 6 h, even without external hydrogen addition, PDO selectivity increased significantly, while the LA selectivity decreased from 54% in 2 h to 36% in 6 h. These trends indicate that under limited H_2 availability (i.e., with in situ generated H_2 alone), LA is favored, while in the presence of excess H_2 (i.e., includes in situ H_2 and externally added H_2), PDO is more easily formed. Furthermore, the selectivity of linear alcohols is much higher without external H_2 addition than with external H_2 addition. The significant hydrogenolysis activity without external H_2 addition suggests that H_2 formed in situ via dehydrogenation is a highly active form of adsorbed H_2 that reacts rapidly on the catalyst surface.

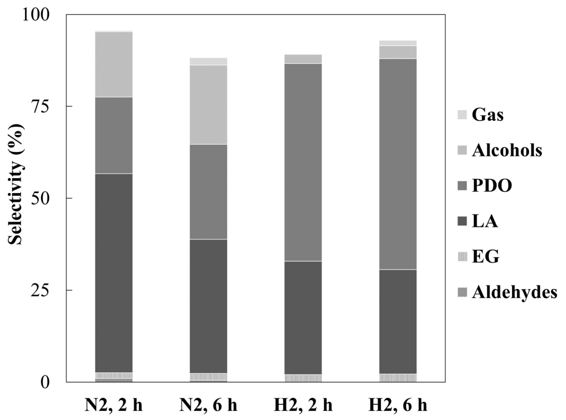
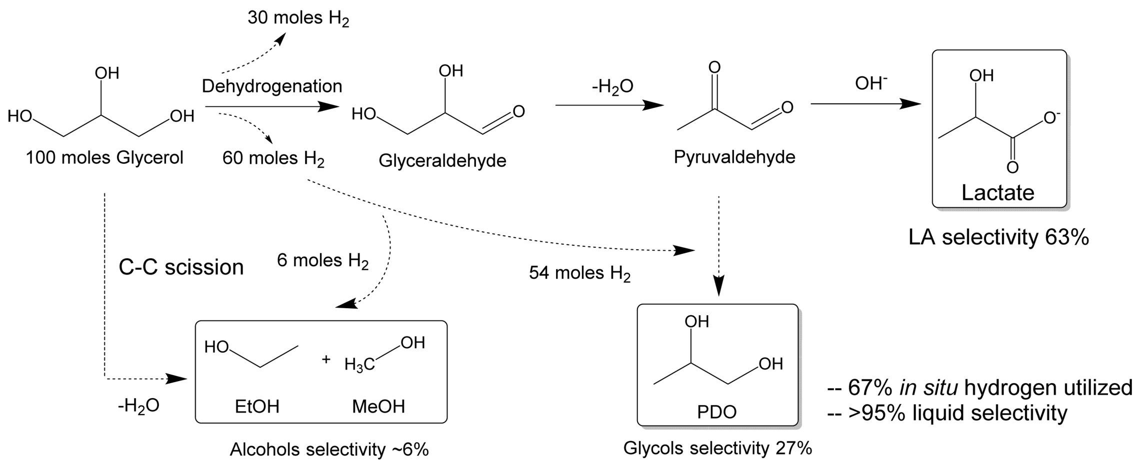


Figure 4. Product distribution over Pt/C catalyst at 160 °C under P_{N2}: 1.4 MPa and P_{H2}: 4.1 MPa. Conversion under P_{N2}: 44.9% in 2 h, 78.7% in 6 h. Conversion under P_{H2}: 37.3% in 2 h and 64.8% in 6 h. Other conditions are same as in Table 2.

Plausible Reaction Pathways and C Selectivity toward Desired Products. On the basis of the conversion/selectivity data on the Pt/C catalyst, a detailed reaction scheme for tandem DH/HDO of glycerol to LA and glycols at low temperatures is proposed. As depicted in Scheme 1, glycerol generates H_2 via dehydrogenation. Following dehydrogenation, glycerol can form lactate in the alkaline medium via multiple sequential steps.[21] Thus, LA selectivity at low temperatures is high (S = 64−69%, Table 3). The high PDO selectivity (S = 20−30%, Table 3 and Figure 4) without addition of external H_2 implies that the H_2 formed (via dehydrogenation) is very active resulting in facile glycerol hydrogenolysis to form PDO (rather than gaseous products) on Pt/C. The tandem DH/HDO pathways explain why the yields of liquid products including LA and PDO are enhanced even at lower temperatures compared with previous reports.[26,31]

Further, methanol is produced possibly from metal-adsorbed C−O* species formed via C−C scission and followed by in situ hydrogenolysis.[32] With regard to ethanol formation, previous

Scheme 1. Atom Economical Aqueous-Phase Conversion of Glycerol to LA, PDO, and Alcohols with H_2 Formed in situ via Dehydrogenation (no CO_2 formation)



reports[17,30] had proposed that ethylene glycol (EG) is the main source. It has been postulated that ethanol could form at elevated temperature (>220 °C) by either C−O cleavage of *O−C−C-O* species or dehydration and subsequent hydrodeoxygenation of EG molecules.[32] However, we find that this finding is not supported by control experiments with EG as the starting substrate (without external H_2 addition) that showed no conversion at 130−160 °C. Therefore, it is likely that the ethanol detected in our reaction system results from the direct C−O cleavage of the C_2 intermediate (Scheme 1) from C−C scission before being hydrogenated to EG on catalyst surface.

A distinct and desirable characteristic for tandem DH/HDO of glycerol to LA and PDO using H_2 generated in situ on the Pt/C catalyst is the atom economical nature of the conversion process toward valuable liquid products. As known previously, the conversion of polyolic alcohols (like glycerol) to acids (e.g., LA) can be also realized via the oxidation of hydroxyl groups by externally added molecular oxygen.[33] Our experimental results show that similar products can form on Pt/C via dehydrogenation of glycerol to GLA and benzilic rearrangement[21] in the presence of OH^- species to finally form the relevant carboxylic acid. Clearly, oxidation converts two hydrogen atoms in the substrate to one water molecule (not a useful product) and might also promote undesired side reactions.[27] In contrast, the glycerol dehydrogenation pathway on Pt/C produces very active H_2 that can be efficiently utilized for in situ hydrogenolysis of the substrate itself. Entries #1−3 in Table 3 support this hypothesis quantitatively. The estimated carbon selectivity based on glycerol conversion to these liquid products is approximately 96%. Thus, there is almost no carbon loss (through WGS to form CO_2) to gaseous products and humic substances[27] during reactions. On the basis of these observations, the proposed pathways in Scheme 1 may be justified as follows. Approximately 90 out of 100 mols of starting glycerol undergoes dehydrogenation to from glyceraldehyde, which upon dehydration forms pyruvaldehyde. Thus, 90 mols of H_2 are formed in situ on the Pt/C catalyst. On the basis of our experimental results, 63 mols of the intermediates react with OH^- to form LA (based on 63% selectivity to LA), while the remaining 27 mols are hydrogenated to glycols (based on 27% selectivity to PDO and EG) by 54 out of the 90 mols of H_2 formed in situ. Approximately, 6 mols of H_2 (out of the 90 mols of in situ H_2) react with intermediates from C−C scission of glycerol to produce the C_1 and C_2 alcohols (based on the combined 6% selectivity toward C_1 and C_2 alcohols). Thus, approximately 67% of the H_2 formed in situ (via dehydrogenation) is utilized for hydrogenolysis while the remaining hydrogen may be used in other processes within the biorefinery. Clearly, the product selectivity in our proposed tandem aqueous-phase conversion (APC) process provides higher carbon utilization in the substrate towards liquid products compared to conventional oxidation and hydrogenolysis processes.

Conversion of Other Sugar-Derived Polyols to Lactic Acid. *Performance of Pt Catalyst.* The activity and selectivity of the Pt/C catalyst was also investigated for conversion of C_5 and C_6 polyols (sorbitol, xylitol, and mannitol) at 160 °C and 1.5 MPa N_2 (without H_2 addition), and the results are presented in Table 5. To the best of our knowledge, this is the first published report on the low-temperature conversion of C_5 and C_6 polyols to LA, glycols, and linear alcohols without external H_2 addition. We find that like glycerol, the higher polyols can also be quantitatively converted to LA and useful hydrodeoxygenated products with hydrogen produced in situ. As shown in Table 5, the TOFs over Pt/C catalyst are 1.32, 1.33, 1.58, and 1.85 mol/g Pt/h for glycerol, xylitol, sorbitol, and mannitol substrates, respectively, increasing with the carbon number of the polyols. This trend indicates that sugar-derived polyols are converted to LA more efficiently compared to glycerol. Interestingly, we observed that the formation of linear alcohols (methanol, ethanol, and propanols) on the Pt/C catalyst is significantly higher from C_5 and C_6 polyols than with glycerol.

Table 5. Reactivity of Different Polyols during Aqueous-Phase Conversion on Pt/C Catalyst

			formation rate (mol/g Pt/h)			
entry #	substrate[a]	TOF_{subs}[b]	LA[c]	glycols[d]	alcohols[e]	other acids[f]
1	glycerol	1.32	0.92	0.12	0.31	–
2	xylitol	1.33	1.51	0.28	1.07	0.53
3	sorbitol	1.58	1.65	0.17	0.81	1.03
4	mannitol	1.85	2.55	0.30	1.06	1.26

[a] *T*: 160 °C. P_{N2}: 1.4 MPa. Substrate: 1.1 kmol/m^3. Solvent: H_2O. NaOH/substrate molar ratio:1.1. Pt/C catalyst charge: 6.7 kg/m^3. Note: TOF values were calculated based on polyol conversion of ~20%. [b] Reaction rate of substrates: mol/g Pt/h. [c] Formation rate of LA: mol/g Pt/h. [d] Formation rate of PDO and EG: mol/g Pt/h. [e] Formation rate of methanol, ethanol, and propanols: mol/g Pt/h. [f] Formation rate of formic acid, acetic acid, and glycolic acid: mol/g Pt/h.

Temporal Reaction Profiles of Xylitol and Sorbitol with Pt/C Catalyst. We find that high conversions of xylitol and sorbitol to LA and alcoholic chemicals can be achieved even at as low as 115 °C. The reaction profiles for xylitol and sorbitol conversion in the presence of Pt/C and NaOH are presented in Figures 5 and 6, respectively. It is found that xylitol conversion increases almost linearly with reaction time and the LA selectivity decreases slightly (from 60% to 55%, Figure 5), while the combined selectivity toward glycols and alcohols is found to increase (from 15% to 22%) with conversion. Similar product distribution is also observed during sorbitol conversion (Figure 6). The combined selectivity to formic and glycolic acid is about 13% in both cases. These results demonstrate that tandem DH/HDO of sugar polyols can occur under significantly milder reaction conditions (P_{N2} = 1.4 MPa, *T* = 115 °C) with much higher yields to liquid products compared

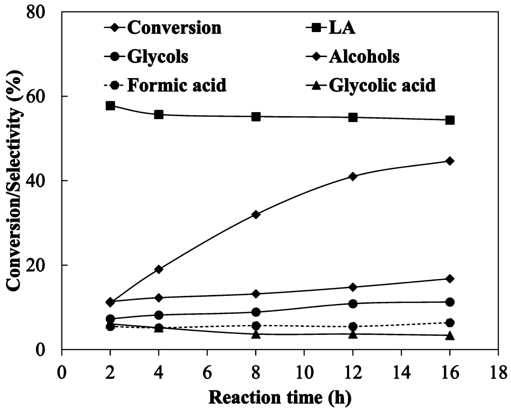


Figure 5. Reaction profiles for aqueous phase xylitol conversion on Pt/C catalyst (*T*: 115 °C. P_{N2}: 1.4 MPa. Xylitol: 100 kg/m^3. Solvent: H_2O. NaOH: 1.20 kmol/m^3. Pt/C catalyst charge: 6.7 kg/m^3.).

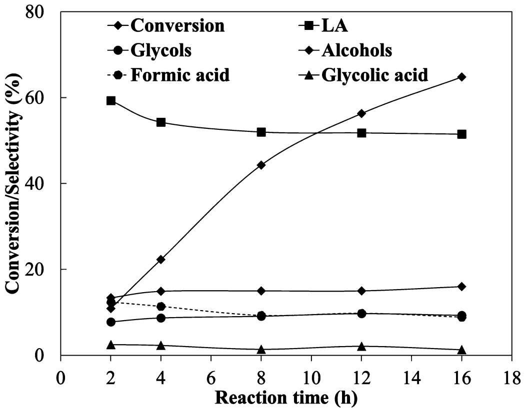


Figure 6. Reaction profiles of aqueous phase sorbitol conversion on Pt/C catalyst (T: 115 °C. P_{N2}: 1.4 MPa. Sorbitol: 100 kg/m^3. Solvent: H_2O. NaOH: 1.20 kmol/m^3. Pt/C catalyst charge: 6.7 kg/m^3.).

with catalytic hydrogenolysis processes (P_{H2} = 2−8 MPa, T > 180−220 °C).[6,7,9,11]

Similar to glycerol, the selectivity towards glycols is not high for xylitol and sorbitol. However, the selectivities to linear alcohols (methanol, ethanol, and propanol) and acids (glycolic acid and formic acid) in xylitol and sorbitol conversion are markedly different. As shown in Table 5, formic acid and glycolic acid are observed in significant amounts during xylitol and sorbitol conversion. Further, while the selectivity towards C_3 products (LA, PDO and propanol) from xylitol is close to the theoretical value (60%), we find that the selectivity toward C_2 products (EG, ethanol, and glycolic acid) is much lower (<15%) than the theoretical value (40%). This suggests facile C_1−C_1−C_3 retro-aldol cleavage, while C_2−C_3 cleavage is not favored on Pt/C catalyst.

Role of Metal Ions on Conversion of Polyols. Because it is known that alkali promotes C−C cleavage of aldehydes and ketones via retro-aldol condensation,[34] a direct comparison of the promotional effects of different liquid bases was performed to further understand the role of alkali during polyols conversion. As shown in Table 6, the promotional effect of various cations including Na^+, K^+, Ba^{2+}, and Ca^{2+} for sorbitol conversion is summarized in terms of TOF and selectivity to various liquid products in the presence of Pt/C at 115 °C. The Pt/C+NaOH system (entry #1) displays a TOF of 0.09 mol/g Pt/h and approximately 95% selectivity to liquid products. The Pt/C+KOH system (entry #2) shows a higher TOF than Pt/C$^+$ NaOH but a slightly lower formation of liquid products. Compared with K^+ and Na^+, a lower TOF of 0.05 mol/g Pt/h is observed in the Ca^{2+} system (entry #3) although selectivity towards LA is much higher. The lower TOF with Ca^{2+} could be attributed to the lower $Ca(OH)_2$ solubility under reaction conditions (only 0.165 g/100g water at 25 °C and 0.077 g/100g water at 100 °C).[35]

Table 6. Activity of Pt/C Catalyst for Aqueous-Phase Sorbitol Conversion

			selectivity (%)			
entry #	alkali[a]	TOF[b]	LA	glycols[c]	alcohols[d]	acids[e]
1	NaOH	0.09	54.5	8.6	15.0	17.2
2	KOH	0.22	35.1	5.8	5.0	2.3
3	$Ca(OH)_2$	0.05	78.1	1.2	0.9	4.3
4	$Ba(OH)_2$	1.10	57.0	11.7	9.7	14.7

[a] T: 115 °C. P_{N2}: 1.4 MPa. Sorbitol: 100 kg/m^3. Solvent: H_2O. OH^-/sorbitol molar ratio: 2.2. Pt/C catalyst charge: 6.7 kg/m^3. Conversion: ∼20%. Note: TOF values were calculated based on polyol conversion of ∼20%. [b] Reaction rate of sorbitol: mol/g Pt/h. [c] Selectivity of PDO and EG. [d] Selectivity of methanol, ethanol, and propanols. [e] Selectivity of formic acid, acetic acid, and glycolic acid.

In the presence of $Ba(OH)_2$ (entry #4), a 12-fold higher activity is observed although the selectivity toward LA and glycols is similar to NaOH. Zhao and co-workers[6] also found distinct differences in the performances of different alkali promoters during sorbitol hydrogenolysis with external H_2 addition. At similar OH^- concentrations, a metal catalyst (supported Ru on carbon nanofiber) showed high sorbitol conversion but lower selectivity towards glycols (PDO and EG) with Na^+ compared to Ca^{2+} promoter. King and co-workers[29] proposed that cations (e.g., K^+) might influence the electron density of Pt catalyst and thus alter its catalytic activity and reaction pathways. Yan and co-workers[22] observed that Ca^{2+} as a bication works more efficiently than Na^+ at the same concentration as it affects the position where C−C cleavage (preferentially C_3−C_3 cleavage) occurs. However, this conclusion is not consistent with our observation. Unlike $Ca(OH)_2$ that has limited solubility in the aqueous phase, $Ba(OH)_2$ is completely dissolved in the aqueous phase under our reaction conditions and provides higher overall yields of LA, glycols and other liquid products than $Ca(OH)_2$.

The presence of Ba^{2+} was found to not only facilitate pyruvate formation via cationic effect and OH^- attack at electron deficient parts[36] in the carbon chain but also convert the pyruvate and LA to formic, acetic acid, and CO_2 at higher temperatures (T ≥ 250 °C).[37] However, the byproducts (aliphatic acids and CO_2) are not significant under our mild reaction conditions (115−160 °C). This result also reveals that $Ba(OH)_2$ facilitates glyceraldehyde dehydration (to form pyruvate) at higher rates than alkali metal hydroxides, possibly due to the extra positive charge of the bications.[15,22] Additional tests conducted for glycerol and xylitol conversion to LA, glycols, and alcohols (Figure 7) confirm that $Ba(OH)_2$ is an effective promoter for conversion of various polyols to LA with other alcoholic compounds as co-products. After only 1.5 h, the overall yields of LA, glycols, alcohols, and other products from

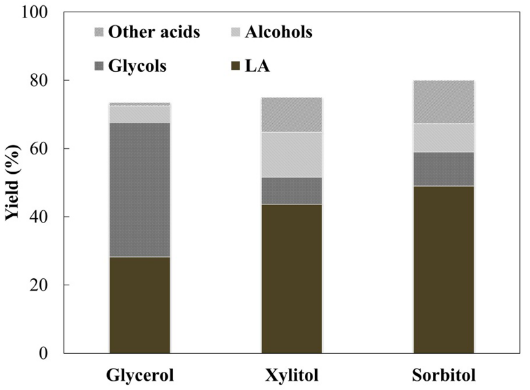
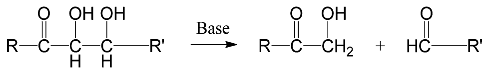


Figure 7. Product yields from aqueous phase conversion of various polyols on Pt/C in the presence of $Ba(OH)_2$ (P_{N2}: 1.4 MPa. Substrates: 100 kg/m^3. Solvent: H_2O. OH^-: 1.2 kmol/m^3. Pt/C catalyst charge: 6.7 kg/m^3. For glycerol: T, 160 °C; reaction time, 1.5 h. For sorbito: T, 115 °C; reaction time, 1.5 h).

Scheme 2. Retro-Aldol Reaction (C−C cleavage) of Dehydrogenated Polyols in Alkaline Medium



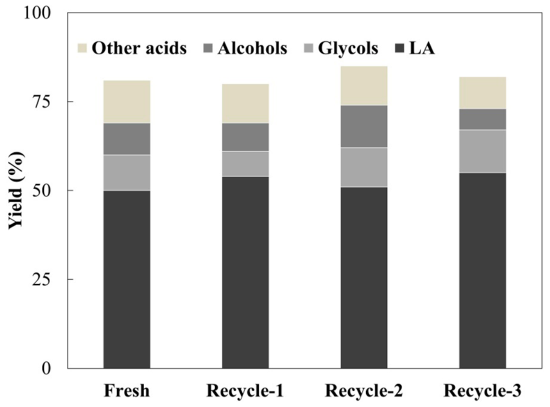


Figure 8. Recycle of Pt/C+$Ba(OH)_2$ catalyst for aqueous-phase conversion of sorbitol (T: 115 °C. P_{N2}: 1.4 MPa. Sorbitol: 100 kg/m^3. Solvent: H_2O. OH^-: 1.20 kmol/m^3. Reaction time: 1.5 h. Pt/C catalyst charge: 6.7 kg/m^3.).

xylitol and sorbitol are observed to be approximately 80% at 115 °C in the presence of Pt/C+$Ba(OH)_2$.

Similar to the observations with NaOH, the polyols with higher carbon number display higher activity than lower polyols in the presence of $Ba(OH)_2$ as well (Figure 7). With regard to the nature of C−C cleavage of polyols, Aguilera and co-workers[38] observed that the rate of (retro-)aldol condensation increases with higher electron density in the R and R′ groups (Scheme 2) because they more easily form carbanion with base promoters. Our results are consistent with this explanation because xylitol and sorbitol have more −OH groups (compared to glycerol) that share electrons with a carbanion structure.

As shown in Figure 8, recycle studies of the Pt/C catalyst for sorbitol conversion in the presence of $Ba(OH)_2$ show excellent recyclability for conversion of sorbitol to LA, glycols, linear alcohols, and other renewable acids. Further, elemental analysis for Pt via inductively coupled plasma/atomic emission spectroscopy (ICP-AES) revealed that there was negligible Pt leaching during our experimental studies (Supporting Information). This confirms that Pt/C is an active, selective, and stable catalytic system that can convert various polyols to value-added products at significantly lower temperatures (130−160 °C). These observations confirm that the conversion of polyols to LA and other liquid-phase products is strongly dependent on the types of promoter cations in the hydroxides as well as their concentrations in the aqueous phase.

Reaction Pathways and Mechanism for Higher Polyol Conversions. The first step in the transformation of sorbitol and xylitol to various liquid products involves sorbitol dehydrogenation over metal catalysts to produce hex-aldose (Scheme 3). Given that acids often result from the reaction between aldehydes/ketones and OH^- species, it seems plausible that the intermediate hex-aldose species undergoes retro-aldol reaction to form aldehydes and ketones of small molecules (formaldehyde, glycolic aldehyde and dihydroxyacetone/GLA) that react rapidly to form acids in alkaline medium. Because of these complex parallel reactions, the LA selectivity in sorbitol conversion is lower compared to glycerol substrate.

Previous results have shown that the hex-aldose species undergoes reorganization to form hex-2-ketose, which further dehydrates in the presence of lewis acids (Sn^{2+} ion[39] and Cr^{3+} ion[40]). In contrast, alkaline earth metal ions (such as Ca^{2+} in Scheme 4) promote C_3−C_3 breakage (based on product distribution of entry #3 in Table 6) with the product distribution depending on the cations. Consequently, two C_3 intermediates are likely to be formed. Furthermore, the formation of PDO and EG indicates that C_3 intermediates can undergo consecutive hydrogenolysis on Pt catalyst surface with the H_2 generated in situ.

As discussed in Scheme 3, C−C cleavage leads to the formation of GLA, which further converts to PAD in alkaline media. In order to understand the behavior of these intermediates as well as the mechanism involved in the formation of LA and other acids, additional experiments were carried out at milder conditions (T = 65 °C) in the absence of a

Scheme 3. Reaction Pathway of Sorbitol at Low Temperatures (120−160 °C) on Pt Catalyst

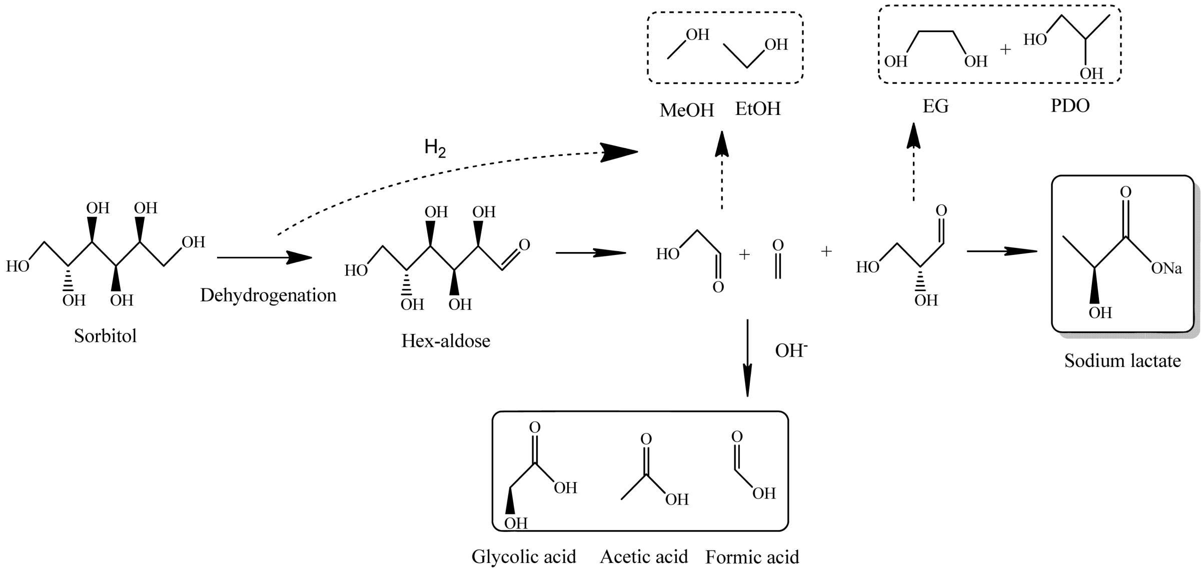
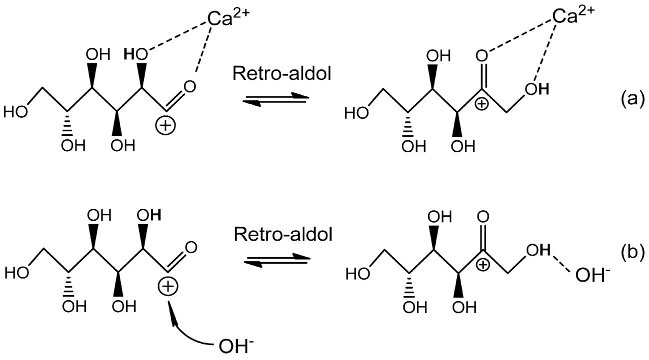


Table 7. Conversion of Various C_3 Intermediates under Milder Conditions

entry #	substrate[a]	promoter	X^b (%)	selectivity (%) LA	glucose	fructose	C_{1-2}-acid	unknown
1	GLA	NaOH	77.5	76.5	7.1	10.1	3.4	2.9
2	PAD	NaOH	100	99.6	–	–	–	0.4
3	GLA	$NaNO_3$	–	–	–	–	–	–

[a] Substrates: 1.1 kmol/m^3. NaOH/substrate: 2.2 molar ratio. Solvent: H_2O. [b] Conversion at T, 65 °C; P, 0.1 MPa; time, 30 min.

Scheme 4. Cation (a) and Base-Catalyzed (b) Hydride Transfer in Sugar Molecules[41,42]



metal catalyst. Entries #1 and #2 in Table 7 support our proposed mechanism that GLA and PAD are important intermediates[8] during LA formation. GLA undergoes dehydration to form PAD before forming LA via benzilic acid rearrangement.[14] Presumably, this step occurs instantaneously at 65 °C because we only detect PAD in our experiments in small amounts. At this temperature, aldolization of GLA also occurs because we observe the formation of small amounts of hex-aldose and hex-2-ketose, while no reaction (entry #3) is detected in the absence of OH^-. PAD was previously found in equilibrium with GLA at room temperature,[21] while it is observed here at 65 °C that PAD reacts easily and forms LA with a significant selectivity. The presence of Ba^{2+} enhances the conversion of polyols significantly possibly via facilitating dehydration of GLA to form PAD under our reaction conditions. However, we do not observe an increase in the reaction rate of GLA in the presence of $Ba(OH)_2$ (GLA conversion = 70.1% under the same reaction conditions as Table 7). It is possible that the solubility of $Ba(OH)_2$ becomes a limiting factor at 65 °C.

CONCLUSIONS

APC of polyols (glycerol, xylitol, and sorbitol) is found to proceed remarkably well on a Pt/C catalyst without external H_2 addition at relatively low temperatures (115−160 °C). Our results show that tandem DH/HDO of biopolyols results in higher yields of LA and alcoholic co-products compared to conventional aqueous-phase processes with external H_2 addition. High selectivity for LA formation with glycols and alcohols as useful co-products is achieved from polyols in the presence of Pt/C catalyst (and other noble metal catalysts). Factors that influence the product distribution include temperature, types of alkali promoters, and the OH^- concentration in the reaction phase. The low-temperature conversion of polyols (via dehydrogenation, retro-aldolization, and hydrogenolysis of polyols) promoted by alkali is a significant advance over previously proposed high-temperature hydrogenolysis or hydrothermal strategies. It is shown that the Pt/C catalyst facilitates hydrogenolysis with H_2 formed in situ (via dehydrogenation) to form useful liquid chemicals with high carbon utilization. The proposed low-temperature conversion of various polyols in the absence of external redox agents displays significant potential as a sustainable alternative to conventional processes.

ASSOCIATED CONTENT

Supporting Information

Additional experimental results, catalyst particle sizes, ICP and XRD characterization data. 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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ABBREVIATIONS

APC: Aqueous phase conversion
PDO: Propanediol
EG: Ethylene glycol
LA: Lactic acid
DH/HDO: Dehydrogenation/hydrogenolysis
GLA: Glyceraldehyde
PAD: Pyruvaldehyde

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