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# Hydrogenolysis of glycerol over carbon-supported Ru and Pt catalysts

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### Abstract

Commercial carbon-supported Ru and Pt catalysts were evaluated in the batchwise hydrogenolysis of glycerol in aqueous solution at 473 K and 40 bar H<sub>2</sub>, with and without added base. At neutral pH, Ru was more active than Pt at converting glycerol to glycols. However, Ru favored the production of ethylene glycol over propylene glycol and also catalyzed methane formation. Although less active, Pt catalyzed propylene glycol formation with high selectivity. Addition of base enhanced the reactivity of Pt to a greater extent than Ru, but lactate formation was significant at high pH in the presence of either Pt or Ru. The cleavage of C–C bonds leading to the formation of ethylene glycol from glycerol is proposed to occur primarily through a metal-catalyzed reaction on Ru, whereas this cleavage is thought to occur through a base-catalyzed reaction in the presence of Pt. An overall reaction network for glycerol hydrogenolysis is presented.

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Keywords: Glycerol hydrogenolysis; Ruthenium; Platinum; Retro-aldol; Hydrogenation; Ethylene glycol; Propylene glycol; Lactic acid

# 1. Introduction

It is generally accepted that the primary source of renewable organic fuels, chemicals, and materials will be from plantderived biomass [1–4]. In 2004, only 3% of all chemicals produced in the U.S. were derived from biomass [5]. The U.S. Department of Energy has set the goal to increase this percentage to 10% by the year 2020 and 50% by the year 2050 [5]. Glycerol has been identified by the DOE as one of the top-12 building block chemicals that can be derived from sugar and converted to high-value bio-based chemicals or materials [6]. Additionally, glycerol is the major by-product of biodiesel production by transesterification of vegetable oil [7]. Therefore, using the growing supply of glycerol is a logical step in moving toward a more sustainable economy. One route for the conversion of glycerol to oxygenated chemicals involves hydrogenolysis to ethylene glycol, propylene glycol, and lactic acid (Scheme 1).

Ethylene and propylene glycol are industrially important chemicals used in the production of polymers, resins, functional fluids (antifreeze, deicing), foods, and cosmetics. Lactic acid and lactate salts are also important for the food and beverage

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industry; however, the greatest opportunity for the utilization of lactic acid is the production of polylactic acid (PLA). With global demands of over 1, 3, and 5 billion pounds for lactic acid [8], propylene glycol [9], and ethylene glycol [10], respectively, the production of these chemicals from biorenewable glycerol can be both environmentally and economically attractive. In fact, the industrial scale utilization of glycerol to produce these smaller chemicals will occur in the near future. Both Archer Daniels Midland (ADM) and Cargill have announced plans to commercialize a glycerol-to-glycols process [11,12].

Previous studies have demonstrated the effectiveness of heterogeneous catalysts in the hydrogenolysis of polyols to lower molecular weight glycols and acids [13–15]. Furthermore, the addition of base has been reported to enhance the conversion of polyols [16–18]. For example, Montassier et al. [14] investigated the use of silica-supported Co, Pt, Ru, Rh, and Ir as catalysts for the hydrogenolysis of glycerol. However, due to the high oxygen functionality and low thermal stability of polyol feedstocks, reaction typically occurs in the aqueous phase at moderate temperatures and pressures. Previous research in our laboratory has shown that silica supports are not suitable for aqueous-phase processing because the silica is hydrolyzed under reaction conditions leading to coalescence and sintering of metal particles on the support [19]. In addition, silica com-

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Scheme 2. Mechanism suggested by Montassier et al. for cleavage of C-C and C-O bonds during polyol hydrogenolysis [14,15,22].

pletely dissolves in high pH solutions that may be of interest in the aqueous-phase hydrogenolysis of polyol feedstocks. More recent studies on the hydrogenolysis of glycerol have focused on the use of Raney metals [14,20,21] and carbon-supported catalysts [17,21–27].

Ruthenium is well known to be active in the hydrogenolysis of glycerol [14,17,22,23,25]. Unfortunately, Ru often promotes excessive C–C cleavage resulting in a high selectivity to hydrocarbons (mainly methane) [14,17,22]. Platinum has also been recognized as a catalyst for glycerol hydrogenolysis [14,21,26,27]. Whereas Pt is typically found to be less active than Ru, previous studies of Pt-based catalysts were only conducted under neutral conditions.

Because both a transition metal catalyst and the solution pH influence the rate of glycerol hydrogenolysis, it is quite likely that the reaction network is composed of steps occurring on the catalyst surface as well as in the solution. Whereas several mechanisms have been suggested for the hydrogenolysis of polyols, a widely accepted one was proposed by Montassier et al. [14,15,22], shown in Scheme 2. In this mechanism, the cleavage of C–C bonds is proposed to occur through a base-catalyzed retro-aldol reaction, whereas C–O cleavage occurs through a base-catalyzed dehydration reaction. The initial dehydrogenation step is thought to occur on the transition metal catalyst.

Whereas the mechanism proposed by Montassier et al. provides a good foundation to begin a study on glycerol hydrogenolysis, the role of the transition metal component relative to the solution phase still needs to be elucidated. Therefore, this work aims to compare the differences in activity and selectivity of Ru/C and Pt/C catalysts during glycerol hydrogenolysis, with the intent of elucidating a relationship between metal type and the mechanism of hydrogenolysis. The importance of solution pH will also be investigated through the addition of basic promoters such as NaOH and CaO.

# 2. Experimental

Activated carbon-supported Ru and Pt catalysts were obtained from Acros Organics and Sigma-Aldrich, respectively. The Ru/C (5 wt% Ru, 50% w/w water) catalyst was dried in air at 493 K overnight before use; Pt/C (3 wt% Pt) was used as received. The metal dispersion of the Ru/C and Pt/C catalysts was determined by H<sub>2</sub> adsorption using a Micromeritics ASAP 2020 chemisorption analyzer at 303 K in the pressure range of 10-450 Torr. Before chemisorption, the catalysts were heated from ambient conditions to 523 K at 4 K min<sup>-1</sup> in flowing H<sub>2</sub> (GT&S 99.999%). The catalysts were reduced in H<sub>2</sub> at 523 K for 90 min followed by evacuation at 523 K for 4 h. After cooling to 308 K, the catalysts were evacuated again for 2 h followed by analysis at 308 K. Surface Ru and Pt were evaluated by the total amount of H<sub>2</sub> adsorbed at 303 K extrapolated to zero pressure, assuming a stoichiometry  $(H/M_{surf}, M = Ru,$ Pt) equal to unity.

Glycerol hydrogenolysis reactions were conducted semibatchwise in a 300 mL stainless steel reactor (Parr Instruments) equipped with an electronic temperature controller, a mechanical stirrer, a catalyst addition device, and a dip tube for periodic sampling of the liquid phase. In a typical reaction, glycerol (Acros Organics, 99%) was diluted with distilled, deionized water to form a 1 wt% solution. One hundred fifty milliliters of this solution was loaded into the reactor along with the appropriate amount of NaOH (Mallinckrodt) or CaO (Fisher) when necessary. The appropriate amount of Ru/C and Pt/C was loaded into the catalyst addition device to maintain a substrate/surface metal (S/M<sub>surf</sub>) ratio of approximately 700. The reactor was sealed and flushed with flowing N<sub>2</sub> (GT&S, 99.998%) at 1 bar for 10 min to remove air in the headspace. To remove the  $N_2$ , the reactor was subsequently flushed with flowing H<sub>2</sub> (GT&S, 99.995%) at 2 bar for 20 min. The reactor was then pressurized to 5 bar with H<sub>2</sub> and heated under moderate agitation (100 rpm) to a final reaction temperature of 473 K. Once this temperature was reached, an initial liquid sample was removed to mark the start of the reaction. Catalyst was subsequently introduced into the reaction medium through the catalyst addition device, the pressure was increased to 40 bar with H<sub>2</sub>, and the rate of agitation was increased to 475 rpm. The reaction was allowed to proceed under these conditions for 5 h whereas liquid samples were periodically removed. The liquid samples were allowed to cool to room temperature before the pH was measured. The reactor was back filled with H<sub>2</sub> after each sample to maintain constant pressure. Liquid samples were analyzed by high performance liquid chromatography (HPLC) using a ThermoSeparations Products (TSP) AS1000 autosampler equipped with a TSP P2000 pump, an Aminex HPX-87H (Bio Rad) column, a Waters R-401 refractive index detector, and Millenium data acquisition software. The HPLC column was maintained at 333 K, with a mobile phase of 5 mM H<sub>2</sub>SO<sub>4</sub> flowing at  $0.7 \text{ mLmin}^{-1}$ . The major liquid-phase products observed were ethylene glycol, propylene glycol, lactic acid, and formic acid; other by-products detected in trace amounts by HPLC include glyceraldehyde, methanol, and ethanol.

At the conclusion of the 5 h reaction, the reactor was allowed to cool to room temperature. Gas samples in the headspace were removed by gas-tight syringe and analyzed for  $CO_2$  and  $CH_4$  by gas chromatography. The HP 5890 GC was equipped with an Alltech CTR1 column and TCD detector.

To aid our understanding of the mechanism of glycerol hydrogenolysis, the batchwise reactions of lactic acid and propylene glycol with dihydrogen over the commercial Ru/C (Acros, 5 wt%) and Pt/C (Aldrich, 3 wt%) catalysts were also performed. The hydrogenation of a 10 wt% aqueous solution of lactic acid (ICN Biomedicals Inc., 85–90%) to propylene glycol was conducted at 473 K and 40 bar H<sub>2</sub> using a substrate:catalyst ratio of 345:1 (mol lactic acid:mol total metal). The hydrogenolysis of a 1 wt% aqueous solution of propylene glycol was conducted at 473 K and 40 bar H<sub>2</sub> using a substrate:catalyst ratio of 700:1 (mol propylene glycol:mol surface metal). Products were analyzed by HPLC as described above.

## 3. Results and discussion

The results of the  $H_2$  adsorption studies are reported in Table 1. Characterization of the Ru/C and Pt/C revealed that both

Table 1	
Results from H <sub>2</sub> chemisorption	

Catalyst	Metal loading (wt%)	Metal dispersion <sup>a</sup> (H/M <sub>surf</sub> )	Metal particle size <sup>b</sup> (nm)
Ru/C	5.0 <sup>c</sup>	0.43	2.3
Pt/C	3.0 <sup>d</sup>	0.43	2.3

<sup>a</sup> Determined by H<sub>2</sub> chemisorption.

<sup>b</sup> Estimated as the inverse of metal dispersion.

<sup>c</sup> Determined by elemental analysis performed by Galbraith Laboratories (Knoxville, TN).

<sup>d</sup> Provided by manufacturer.

catalysts have a similar metal dispersion (43%) and presumably a similar metal particle size (2.3 nm).

Fig. 1 illustrates the effects of transition metal and base addition on the glycerol hydrogenolysis reaction. Under neutral conditions, Ru/C was more active than Pt/C. The addition of base (both NaOH and CaO) enhanced the rate of reaction over both catalysts. These results are consistent with the previous studies mentioned earlier.

Table 2 summarizes the reaction studies of Ru/C and Pt/C catalysts for glycerol hydrogenolysis in the presence and absence of base. The overall turnover frequency (TOF<sub>overall</sub>) is reported as the rate of glycerol reacted at 20% conversion per surface metal atom counted by H2 chemisorption. The turnover frequency for glycol production (TOF<sub>glycol</sub>) is based on the ethylene glycol and propylene glycol formation rates at 20% conversion of glycerol, normalized by the number of surface metal atoms. The carbon balance is reported as the percentage of carbon accounted for in the system (both liquid and gas phase) at the end of 5 h. The amount of missing carbon in the system can be explained by loss of gas phase products during sampling of the reaction mixture. Because the reactor system was not equipped to separate and analyze the gas and liquid phase products simultaneously, a small amount of gas phase products were inevitably lost during liquid sampling. Thus, larger errors in the material balance are expected for runs with larger gas phase product inventories. The product selectivities of the reactions are summarized in Table 3. The selectivities are reported both at 20% conversion of glycerol and after the reaction was stopped at 5 h. The selectivity of each product is determined as a carbon selectivity, where

selectivity = 
$$\frac{\text{moles of carbon in specific product}}{\text{moles of carbon in all observed products}}$$

As shown by run #1 in Table 2, the presence of catalyst was required for hydrogenolysis to proceed. Inspection of the product distributions reported in Table 3 when Ru/C was used as the catalyst reveals significant methane formation. Methane formation could be the result of methanation of the carbon support as suggested by Rodriguez-Reinoso [28]. However, a blank reaction run in the absence of glycerol (run #2 of Tables 2 and 3) failed to produce methane, indicating all methane formed during the reactions can be attributed to the hydrogenolysis of glycerol and not methanation of the carbon support.

Runs #3 and 4 of Table 2 revealed that in the absence of base (pH  $\sim$ 6), Ru/C was more active than Pt/C for the hydrogenolysis of glycerol. This result is consistent with other studies that



Fig. 1. Conversion of glycerol over (a) Ru/C and (b) Pt/C in the absence and presence of base. Reaction conditions: 1 wt% glycerol,  $S/M_{surf} = 700$ , 0.8 M base (when present), 473 K, 40 bar H<sub>2</sub>. Error bars represent 95% confidence limits.

Table 2 Summary of catalyst activity for glycerol hydrogenolysis<sup>a</sup>

Run #	Catalyst	Base	Base conc. (M)	Conversion (%) <sup>b</sup>	Carbon balance <sup>c</sup>	${{{\rm TOF}_{{\rm overall}}} \over {({{\rm s}^{-1}})^{\rm d}}}$	$TOF_{glycol}$ $(s^{-1})^e$
1	None	None	_	<0.7	100	_	_
2	Ru/C <sup>f</sup>	None	_	0	100	-	_
3	Ru/C	None	-	40	84	$0.02 \pm 0.003$	$0.02\pm0.003$
4	Pt/C	None	_	13	97	$0.006 \pm 0.002^{\mathrm{g}}$	$0.004 \pm 0.0006^{\text{g}}$
5	None	NaOH	0.8	4	97	-	_
6	Ru/C	NaOH	0.01	48	93	$0.04 \pm 0.01$	$0.01\pm0.002$
7	Pt/C	NaOH	0.01	25	95	$0.01\pm0.006$	$0.005\pm0.001$
8	Ru/C	NaOH	0.8	100	85	$0.2 \pm 0.03$	$0.07\pm0.003$
9	Pt/C	NaOH	0.8	92	83	$0.3 \pm 0.05$	$0.09\pm0.01$
10	Ru/C	CaO	0.01	50	87	$0.07\pm0.03$	$0.02\pm0.01$
11	Pt/C	CaO	0.01	40	93	$0.04 \pm 0.04$	$0.02 \pm 0.01$
12	Ru/C	CaO	0.8	85	75	$0.1 \pm 0.03$	$0.04\pm0.006$
13	Pt/C	CaO	0.8	100	80	$0.4\pm0.07^{\rm h}$	$0.2\pm0.03^{\text{h}}$

<sup>a</sup> Reaction conditions: 1 wt% glycerol solution,  $S/M_{surf} = 700$ , 5 wt% Ru/C or 3 wt% Pt/C, T = 473 K,  $P_{H_2} = 40$  bar.

<sup>b</sup> Conversion determined after 5 h of reaction.

<sup>c</sup> Percentage of carbon accounted for after 5 h of reaction.

<sup>d</sup> Determined at 20% conversion of glycerol. Error represents 95% confidence limits.

e Calculated using the sum of ethylene and propylene glycol formation determined at 20% conversion of glycerol. Error represents 95% confidence limits.

<sup>f</sup> Reaction run without glycerol to check for possible methanation of carbon support.

<sup>g</sup> Determined after 5 h of reaction as glycerol conversion never reaches 20%.

<sup>h</sup> Determined at first time sample of reaction (30% conversion).

compare the activity of Ru- and Pt-based catalysts for the hydrogenolysis of glycerol [14,21,26,27]. Although no lactate was observed in the absence of base, regardless of metal, close examination of the product selectivities given in Table 3 shows an interesting dependence on the nature of the metal regarding glycol formation. At 20% conversion of glycerol and in the absence of base, Ru/C promoted 68% selectivity to ethylene glycol with only 32% selectivity to propylene glycol. Even after 5 h of reaction, the selectivity to ethylene glycol (47%) was still greater than that to propylene glycol or methane (26% each). Platinum, on the other hand, favored formation of propylene glycol (79% selectivity) over ethylene glycol (17% selectivity), even after 5 h of reaction. These results suggest that a favorable C–C cleavage pathway exists on Ru that is not available on Pt.

The proposed mechanism of Montassier et al. shown in Scheme 2 suggests that the first step in the reaction sequence is the dehydrogenation of glycerol over the transition metal catalyst to form a glyceraldehyde intermediate. Although C–C

Table 3
Summary of product selectivities during glycerol hydrogenolysis <sup>a</sup>

Run # <sup>b</sup>	Catalyst	Base	Base conc. (M)	Conversion (%) <sup>c</sup>	Carbon selectivity				
					EG	PG	LA	CH4 <sup>d</sup>	CO <sub>2</sub> <sup>d</sup>
2	Ru/C <sup>e</sup>	None	_	0	0	0	0	0	0
3	Ru/C	None	-	20	0.68	0.32	0	_	_
				40	0.47	0.26	0	0.26	0.01
4	Pt/C	None	-	_	_	-	_	_	-
				13	0.17	0.79	0	0	0
5	None	NaOH	0.8	-	-	-	-	_	-
				4	0	0	Trace	0	0
6	Ru/C	Ru/C NaOH	0.01	20	0.21	0.14	0.65	-	-
				48	0.19	0.27	0.21	0.31	Trace
7	Pt/C	C NaOH	0.01	20	0.04	0.51	0.43	-	-
				25	0.05	0.55	0.39	0	0
8	Ru/C	NaOH	0.8	20	0.12	0.37	0.47	-	-
				100 <sup>f</sup>	0.01	0.19	0.34	0.01	0.01 <sup>g</sup>
9	Pt/C	C NaOH	0.8	20	0.02	0.30	0.62	_	-
				92	0.02	0.46	0.48	0	0
10	Ru/C	CaO	0.01	20	0.14	0.32	0.54	_	_
				50	0.16	0.46	0.32	0.06	0
11	Pt/C	CaO	0.01	20	0.08	0.55	0.37	_	_
				40	0.09	0.71	0.19	0	0.007
12	Ru/C	Ru/C CaO	0.8	20	0.09	0.35	0.54	_	_
				85	0.11	0.36	0.48	0.06	0
13	Pt/C	CaO	0.8	30 <sup>h</sup>	0.05	0.36	0.58	_	_
				100	0.04	0.36	0.58	0	0

<sup>a</sup> Reaction conditions: 1 wt% glycerol solution, substrate/surface metal = 700, 5 wt% Ru/C or 3 wt% Pt/C, T = 473 K,  $P_{H_2} = 40$  bar. EG: ethylene glycol; PG: propylene glycol; LA: lactic acid (in the form of lactate).

<sup>b</sup> Run numbers are the same as those listed in Table 2.

<sup>c</sup> Carbon selectivities were determined both at 20% conversion of glycerol and at the final conversion attained after 5 h of reaction.

<sup>d</sup> The gas phase was only sampled after the completion of the reaction. Therefore gas phase compositions at 20% conversion of glycerol are not available.

<sup>e</sup> Reaction run in the absence of glycerol to investigate possible methanation of carbon support.

<sup>f</sup> Balance in the carbon selectivity is to formic acid.

<sup>g</sup> In the form of carbonate.

<sup>h</sup> Selectivities determined at first timed-sample during reaction.

cleavage is speculated to occur through a base-catalyzed retroaldol reaction, whereas C–O cleavage is thought to proceed through a base-catalyzed dehydration, the authors suggest that both reactions occur in the adsorbed state [14,22]. The resulting intermediates are then re-hydrogenated on the metal catalyst to form ethylene glycol, propylene glycol, and methanol, with the latter being easily converted to methane [22]. Wang et al. [29] supported this mechanism through studying the hydrogenolysis of 1,3-diol model compounds.

Our results seem to be in agreement with the idea that a metal catalyst is necessary for the initial dehydrogenation of glycerol to glyceraldehyde, because essentially no reaction was observed in the absence of catalyst (runs #1 and 5 of Table 2). However, the mechanism described in Scheme 2 suggests that addition of base should increase the conversion of glycerol to both ethylene glycol and propylene glycol because the retro-aldol and dehydration reactions are both thought to be catalyzed by adsorbed hydroxyls. As reported in Table 2 and illustrated in Fig. 1, the addition of 0.8 M base to maintain a constant pH (pH<sub>NaOH</sub> ~14; pH<sub>CaO</sub> ~12) increased the overall rate of glycerol hydrogenolysis over both catalysts. Comparison of runs #3, 8, and 12 in Table 2 show that the addition of base increased the TOF<sub>overall</sub> on Ru/C by an order of magnitude. Runs #4, 9, and 13, however, show that the TOF<sub>overall</sub> on Pt/C is enhanced by

over a factor of 50 in the presence of base. Evidently the observed activity on Ru and Pt depends strongly on the solution pH. A study performed by Ukisu and Miyadera explored the enhancement in activity of 2-propanol dehydrogenation over Ru/C and Pt/C in the presence of basic compounds such as NaOH and Ca(OH)<sub>2</sub> [30]. They found that the addition of NaOH had relatively little effect on the rate of dehydrogenation over Ru/C resulting in an enhancement factor of only 1.06. Interestingly, the dehydrogenation activity of Pt/C was enhanced by a factor of 18.1 in the presence of NaOH. Thus, they suggested the rate-determining step for alcohol dehydrogenation is different over Ru than over Pt, i.e., the dissociation of the methine C-H bond may be limiting over Pt, whereas formation of molecular hydrogen may be limiting over Ru. Ukisu and Miyadera concluded that the addition of alkaline compounds assisted in the dissociation of the methine hydrogen on Pt, thereby increasing the rate of dehydrogenation. These findings are consistent with our results showing that the addition of base has a greater effect on the rate of glycerol hydrogenolysis on Pt/C than on Ru/C. Ukisu and Miyadera also explored the promotional effect of Ca(OH)<sub>2</sub>. However, due to the limited solubility of Ca(OH)<sub>2</sub> in 2-propanol, an enhancement factor of only 1.47 for dehydrogenation was obtained over Pt/C. As CaO readily forms Ca(OH)<sub>2</sub> in an aqueous environment and a pH of  $\sim 12$ 



Fig. 2. Reaction profile for the hydrogenolysis of glycerol on Ru/C in the presence of 0.8 M NaOH. Reaction conditions: 1 wt% glycerol, S/M<sub>surf</sub> = 700, 473 K, 40 bar H<sub>2</sub>. ( $\blacklozenge$ ) Glycerol; ( $\circledast$ ) formic acid; ( $\bigcirc$ ) lactic acid; ( $\triangle$ ) propylene glycol; ( $\Box$ ) ethylene glycol; (+) methanol; ( $\times$ ) carbon dioxide trapped as carbonate.

is maintained during reaction, our system does not appear to be limited by solubility to the same extent as the 2-propanol system. In fact, Cameron and Patten have shown that the solubility of  $Ca(OH)_2$  is actually greater in aqueous solutions of glycerol than in water itself [31]. Therefore, it appears that Pt/C is actually more active than Ru/C for the hydrogenolysis of glycerol in the presence of base, and this increased activity may be attributed to the base promoting the initial dehydrogenation of glycerol to glyceraldehyde.

Inspection of Table 3 indicates that the activity of Pt/C was enhanced to a greater extent by the presence of CaO than NaOH. Because a constant pH was maintained in the runs performed with 0.8 M base, this behavior is not attributed to buffering of the solution by CaO. Instead, previous authors have proposed that the cation may have a role in the complexation of aldehydes leading to saccharinic acid formation [32,33], however, our work provides no evidence to further support or dispute these claims.

It is also interesting to note that, in the presence of 0.8 M NaOH, Ru/C promoted significant formation of formic acid (run #8 in Table 3), which did not appear under other reaction conditions. Shown in Fig. 2 is the reaction profile for glycerol hydrogenolysis on Ru/C in the presence of 0.8 M NaOH. It appears that as the conversion of glycerol neared completion, degradation of propylene glycol and ethylene glycol began. The degradation product was primarily formic acid, with small amounts of methanol and CO<sub>2</sub> produced as well. In the basic environment, CO<sub>2</sub> was trapped in the form of carbonate. These findings are consistent with those of Montassier et al. [14] who reported that degradation of glycerol.

The product selectivities reported in Table 3 reveal that the large increase in overall rate of hydrogenolysis in the presence of base can be attributed to the formation of lactate. Although this observation is important, it will be addressed later in the discussion. To better understand the routes to C–C and C–O cleavage over Ru and Pt, the product selectivities for ethylene and propylene glycol as reported in Table 3 are discussed next.

Inspection of runs #3, 8, and 12 in Table 3 shows that the addition of base to a reaction over Ru/C switched the glycol selectivity to favor propylene glycol over ethylene glycol. The actual rate of ethylene glycol formation did not change significantly with the addition of base. Similar comparisons of runs #4, 9, and 13, however, show that over Pt/C, the addition of base enhanced the initial rate of ethylene glycol formation by an order of magnitude or more. In accordance with Scheme 2, Montassier et al. [14] proposed that C-C cleavage of glycerol to ethylene glycol occurred by a retro-aldol step in the adsorbed state catalyzed by surface hydroxyl groups. This speculation implies that addition of base should increase the rate of ethylene glycol formation on both catalysts compared with that without base. Instead, we observed that on Ru/C, the rate of ethylene glycol formation changed by less than a factor of 2 with the addition of base, but on Pt/C, the change was more than an order of magnitude. Therefore, we propose that over Ru, the C-C cleavage involved in the conversion of glycerol to ethylene glycol is primarily metal-catalyzed instead of base-catalyzed. Studies on the ability of supported Ru and Pt to catalyze the hydrogenolysis of ethane to methane indicate Ru is more effective for the cleavage of C-C hydrocarbon bonds than Pt. Under similar reaction conditions, a Pt/SiO<sub>2</sub> catalyst was found to be approximately three orders of magnitude less active than Ru/SiO<sub>2</sub> for ethane hydrogenolysis [34,35]. Because Pt is less effective for the cleavage of C-C bonds, the yield and selectivity to ethylene glycol are low in neutral solution. However, increasing the pH increased the rate of ethylene glycol formation over Pt/C, indicating a base-catalyzed retro-aldol reaction may be an important route to form ethylene glycol from glycerol over Pt. Additional experiments in our laboratory have confirmed that at 473 K and 40 bar H<sub>2</sub>, the hydrogenolysis of a 1 wt% propylene glycol solution yielded no ethylene glycol over Ru/C or Pt/C in the presence or absence of base. Therefore, the formation of ethylene glycol does not result from the subsequent hydrogenolysis of propylene glycol.

Addition of base to the glycerol hydrogenolysis reaction increased the formation rate of propylene glycol over both Ru/C and Pt/C. Comparison of the selectivities reported at 20% conversion of glycerol with the TOF<sub>glycol</sub>'s reported in Table 2 shows that the rate of propylene glycol formation was enhanced by a factor of 5–10 over Ru/C and 27–67 over Pt/C in the presence of 0.8 M base. There are two possible routes of C–O cleavage leading to the formation of propylene glycol from glycerol: (1) metal-catalyzed and (2) base-catalyzed. The metal-catalyzed reaction is analogous to the route proposed by Suppes et al. shown in Scheme 3 [21,36]. In this path, the glycerol is directly dehydrated over the metal catalyst to form an acetol intermediate, which can then be hydrogenated over the metal to form propylene glycol. However, in the work of Sup-



Scheme 4. Alkali induced formation of lactic acid from glyceraldehyde [32,37,38].



Fig. 3. Product formation during glycerol hydrogenolysis over Pt/C with 0.01 M CaO. The pH of the reaction mixture was monitored as a function of the reaction time. PG: propylene glycol; LA: lactic acid (in the form of lactate); EG: ethylene glycol; GA: glyceraldehyde.

pes et al., glycerol hydrogenolysis was carried out using an 80% glycerol solution. In our studies, a 1% glycerol solution was used, and therefore the equilibrium for direct dehydration is less favorable in our system. In addition, the acetol intermediate that was detected by Suppes et al. was never detected in our studies. Furthermore, this direct dehydration route does not account for the enhanced formation of propylene glycol with the addition of base. Therefore, it is likely in our studies that propylene glycol is formed by a mechanism other than metal-catalyzed C–O cleavage.

The second proposed route accounts for the enhanced rate of propylene glycol formation at high pH. Although the overall rate of glycerol hydrogenolysis (TOF<sub>overall</sub>) increased with the addition of base, the rate of glycol formation (TOF<sub>glycol</sub>) did not increase as significantly. Inspection of the product selectivities reported in Table 3 reveals that the increase in the TOF<sub>overall</sub>

can be attributed mainly to the formation of lactate. Moreover, it is worth noting that lactate was only detected in the presence of base. In runs #6, 7, 10, and 11, only 0.01 M base was used so that the transient behavior of the product yields and solution pH could be monitored throughout the reaction. For each of these runs, the lactate yield remained constant once the pH dropped to neutral. A representation of this behavior is shown in Fig. 3 for the case of Pt/C in the presence of 0.01 M CaO. The formation of lactic acid is known to occur in solution by the base-catalyzed isomerization of glyceraldehyde [32,37,38]. A schematic of this process is shown in Scheme 4. Therefore, if the metal catalyst were necessary for the initial dehydrogenation of glycerol to glyceraldehyde, as indicated by Scheme 2 and runs #1 and 5 of Table 2, then the conversion of glyceraldehyde to lactic acid (in the form of lactate) may be catalyzed by hydroxyl groups. With the intent of better understanding the role of lactate formation in the mechanism of glycerol hydrogenolysis, we have conducted studies on the hydrogenation of lactic acid under the standard hydrogenolysis conditions of 473 K and 40 bar H<sub>2</sub>.

The Miller group reported that lactic acid can be easily hydrogenated to propylene glycol over a Ru/C catalyst [39,40]. As shown in Fig. 4a, Ru/C was more active than Pt/C for the hydrogenation of aqueous lactic acid, which is consistent with the well-recognized fact that Ru is superior to other Pt metal catalysts for the hydrogenation of carboxylic acids [41]. However, the reaction profiles shown in Fig. 3 indicate that lactic acid is not a reactive intermediate to propylene glycol, but instead remains bound as a lactate salt in the presence of base. The Miller group has also studied the hydrogenation of potassium and calcium lactate salts, and found that these salts are unable to undergo direct hydrogenation to propylene glycol until addition of sulfuric acid converted the lactate salt to free acid [39]. To confirm that the lactate salts formed during glycerol hydrogenolysis in the presence of NaOH and CaO are not being further reacted, we have also investigated the hydrogenation of sodium and calcium lactate salts over Ru/C under typical hydrogenolysis conditions of 473 K and 40 bar H<sub>2</sub>. In agreement with the work from the Miller group, sodium and calcium lac-



Fig. 4. (a) Hydrogenation of lactic acid to propylene glycol over Ru/C and Pt/C. (b) Hydrogenation of calcium and sodium lactate over Ru/C. Reactions were carried out at 473 K and 40 bar H<sub>2</sub>. Error bars represent 95% confidence limits.

tate salts do not readily hydrogenate to propylene glycol over Ru/C (Fig. 4b). Furthermore, hydrogenation of free lactic acid to propylene glycol over Ru/C was also inhibited by NaCl, suggesting that merely the presence of the alkali cation is enough to bind lactic acid into a nonreactive salt.

It is possible that, in the absence of base, free lactic acid is formed during glycerol hydrogenolysis and is subsequently hydrogenated to propylene glycol. In the presence of an alkali metal or alkaline earth cation, however, the lactic acid might be bound as lactate salt and therefore does not react further to propylene glycol. To investigate this hypothesis, the hydrogenolysis of glycerol was conducted over Ru/C in the presence of 0.8 M NaCl to determine if the Na<sup>+</sup> cation would bind intermediate lactic acid. The solution pH remained constant (pH  $\sim$ 6) throughout the course of the reaction. The resulting TOF<sub>overall</sub> on Ru/C was  $0.01 \pm 0.008 \text{ s}^{-1}$ , whereas the TOF<sub>glycol</sub> was  $0.008 \pm 0.001$  s<sup>-1</sup> at 20% conversion of glycerol, which were significantly lower than the rates on Ru/C in neutral solution (run #3, Table 2). No formation of lactate was observed. As an interesting aside, glycerol hydrogenolysis over Ru/C in the presence of NaCl resulted in greater selectivity to propylene glycol than ethylene glycol (69% PG vs 31% EG at 20% conversion of glycerol). This contrasted what was observed when glycerol hydrogenolysis was conducted over Ru/C in the absence of base (run #3 in Table 3). Apparently, the presence of Cl inhibited the C-C bond cleavage that lead to ethylene glycol formation. Whereas the exact Cl content of the fresh Ru/C was not evaluated, washing Ru/C with distilled deionized water failed to produce any Cl in the filtrate as measured by a 0.1 M AgNO<sub>3</sub> test. Because Cl is a known catalyst poison for transition metals, the lower productivity of ethylene glycol in NaCl solution further supports the idea that ethylene glycol is formed through a metal-catalyzed C-C cleavage route on Ru. The fact



Fig. 5. Turnover frequency for the production of propylene glycol on Ru/C and Pt/C at 20% conversion of glycerol under various conditions. Reaction conditions: 1 wt% glycerol,  $S/M_{surf} = 700$ , 0.8 M base (when present), 473 K, 40 bar H<sub>2</sub>. Error bars represent 95% confidence limits.

that lactate was not observed during the hydrogenolysis of glycerol in the presence of NaCl indicates that the presence of base is required for the formation of lactic acid. Therefore, under neutral conditions, formation of propylene glycol may be attributed to the hydrogenolysis of glyceraldehyde (as shown in Scheme 2) and not the hydrogenation of intermediate lactic acid. Further support for this idea is obtained by comparing the rates of propylene glycol formation over Ru/C and Pt/C. As shown in Fig. 5, the turnover frequency for the formation of propylene glycol at 20% conversion of glycerol is actually higher on Pt/C than Ru/C in the presence of base. Because Pt/C is ineffective for the hydrogenation of lactic acid to propylene



Scheme 5. Adjusted scheme for glycerol hydrogenolysis on Ru- and Pt-based catalysts. M denotes either Ru or Pt.

glycol, and in the presence of base, lactate salts are nonreactive, propylene glycol formation likely occurs through C–O cleavage without passing through a lactate intermediate.

Scheme 5 shows a proposed mechanism for glycerol hydrogenolysis that is based loosely on that of Montassier et al., but has been adjusted to account for the results of our study. In this mechanism, the first step is the dehydrogenation of glycerol to glyceraldehyde on the transition metal catalyst as suggested by others. Although this step may be enhanced by the presence of a base, the base promotion is greater over Pt than over Ru. Formation of ethylene glycol occurs by two routes. Because Ru is an effective C–C bond cleavage catalyst, glyceraldehyde can be directly converted and hydrogenated to ethylene glycol and methanol on Ru. Because Pt is not effective for the cleavage of C-C bonds, formation of ethylene glycol likely proceeds through a base-catalyzed retro-aldol route. The intermediate formaldehyde and glycol aldehyde is then hydrogenated over the metal to form ethylene glycol and methanol. Although methanol is sometimes detected as a product, it also can be converted to methane, as proposed by Montassier et al. [22]. The cleavage of C-O bonds has not been altered from the mechanism in Scheme 2 where glyceraldehyde undergoes basecatalyzed dehydration. This route has only been adjusted to account for the formation of lactate in the presence of base according to Scheme 4. The base-catalyzed dehydration of glyceraldehyde yields pyruvaldehyde, which in the presence of base forms lactate. The subsequent hydrogenation of the dehydration intermediates on the metal catalyst gives propylene glycol.

For verification, the hydrogenation of a 4 wt% aqueous solution of pyruvaldehyde on Ru/C (S/M<sub>surf</sub> = 350) under standard hydrogenolysis conditions of 473 K and 40 bar H<sub>2</sub> yielded propylene glycol. However, a large percentage ( $\sim$ 50%) of the carbon was unaccounted for during this experiment due to the thermal degradation of pyruvaldehyde under the hydrogenolysis reaction conditions. Nevertheless, the formation of propylene glycol is consistent with the mechanism proposed in Scheme 5. Propylene glycol formation does not appear to occur via hydrogenation of lactate. The formation of CO<sub>2</sub> reported in Table 3 can be attributed to a Cannizzaro reaction of the intermediate aldehydes, as proposed by Wang et al. [29].

# 4. Conclusion

In this work, the activity and selectivity of Ru/C and Pt/C catalysts were compared for the hydrogenolysis of glycerol. The effects of NaOH and CaO addition on the reaction rates were used to help elucidate metal-catalyzed versus base-catalyzed routes in the mechanism of glycerol hydrogenolysis.

The presence of both 0.8 M NaOH and CaO enhanced the rate of glycerol hydrogenolysis over both catalysts, however the extent of enhancement is greater over Pt/C than Ru/C. This trend is consistent with the observation by others that the rate of alcohol dehydrogenation over Pt is enhanced by base to a greater extent than over Ru. Because the dehydrogenation of glycerol to glyceraldehyde is proposed to be the first step in the mechanism of glycerol hydrogenolysis, the activity of Pt/C is

therefore enhanced more than Ru/C with the addition of NaOH and CaO.

In the absence of base, Ru/C was more active than Pt/C for the hydrogenolysis of glycerol. Under neutral conditions, Ru favors the formation of ethylene glycol over propylene glycol. Because the rate of ethylene glycol formation was not enhanced significantly in the presence of base, C–C cleavage is thought to occur over Ru primarily via a metal-catalyzed reaction. The addition of Cl<sup>-</sup> to the system resulted in decreased selectivity to ethylene glycol, further supporting the idea that ethylene glycol is formed via a metal-catalyzed route. Because Pt is a less effective C–C cleavage catalyst, ethylene glycol is proposed to form through base-catalyzed retro-aldol reaction.

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