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Aqueous phase hydrogenolysis of glycerol to 1,2-propanediol without external hydrogen addition

Debdut Roy [a], Bala Subramaniam [a,b], Raghunath V. Chaudhari [a,b,*]

[a] Center for Environmentally Beneficial Catalysis, University of Kansas, 1501 Wakarusa Dr., Lawrence, KS 66047, USA
[b] Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence, KS 66045, USA

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ABSTRACT

Facile aqueous phase hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO), catalyzed by an admixture of 5 wt.% Ru/Al_2O_3 and 5 wt.% Pt/Al_2O_3 catalysts in varying amounts, without externally added hydrogen is reported with comprehensive characterization of liquid and gas phase products. The hydrogen generated *in situ* by aqueous phase reforming of glycerol was used for the conversion of glycerol to 1,2-PDO and other products. The hydrogenolysis reaction may thus be carried out at moderate inert gas pressure and without a need for external hydrogen addition. During 6 h batch runs, it was observed that the 1:1 admixture (w/w) of the Ru and Pt catalysts showed better performance at 493 K [glycerol conversion (X) = 50.1%, 1,2-PDO selectivity (S) = 47.2%] compared to the individual catalysts [X = 19.3%, S = 50% with 5% Ru/Al_2O_3; X = 18.1%, S = 37% with 5% Pt/Al_2O_3]. A run for glycerol hydrogenolysis with the admixture catalyst in the presence of added hydrogen (41 bar), at otherwise identical operating conditions, showed lower selectivity to 1,2-PDO (31.9%) compared to the run without added hydrogen (47.2%). With external hydrogen addition, the availability of excess hydrogen (in addition to the *in situ* hydrogen generation) promotes the transformation of CO and CO_2 to methane and other alkanes, adversely affecting the 1,2-PDO selectivity. Finally, the admixture catalyst showed excellent stability as evidenced by several repeatable runs with the recycled catalyst.

1. Introduction

The dwindling supply and exponential growth in the demand of fossil fuels have motivated researchers to explore alternative resources and technologies for fuels and chemicals. In this context, biomass materials are receiving increased attention as these are renewable, and the conversion processes have the potential to be carbon-neutral and environmentally friendly. To date, major advances have been made in the transesterification of vegetable oil-based fatty acids to bio-diesel, which is already at an advanced stage of commercialization. The utilization of the relatively large amounts of glycerol side product (10wt.%) formed in bio-diesel manufacture is a major factor in the overall cost effectiveness of the process [1]. Therefore, use of this glycerol as a renewable feedstock to produce value added chemicals is crucial to biorefinery economics [2]. Several review papers [1,3–6] have appeared in recent literature focusing on the possible utilization of glycerol for chemicals and chemical building blocks. In this context, glycerol conversion to 1,2-propanediol (1,2-PDO) by catalytic hydrogenolysis [7–14] has emerged as one of the important processes because of the huge market of 1,2-PDO as an industrial solvent, antifreeze, deicing agent and approved additive in food, cosmetic and pharmaceutical industries [15].

Hydrogenolysis of glycerol to 1,2-PDO has been reported previously using several supported transition metal catalysts such as Ru [7,11,16,17], Pt [12,18], Cu [8,9,14,19], Ni [20] including some bimetallic catalysts consisting of Pt–Ru, Au–Ru [10] and Ru–Re [13]. The effects of acidic [11,17,21–24] and basic promoters [18,25] on activity and selectivity, along with a comparison of different catalysts under neutral [8,9], acidic [23] and basic conditions [18], have also been reported in the literature. The activity of different supported metal catalysts for glycerol hydrogenolysis follows the order $Ru \approx Cu \approx Ni > Pt > Pd$ [26]. Supported Ru is the most reported catalyst in the literature, providing very good conversion (X) and selectivity to 1,2-PDO (S) under neutral (X = 40–90%, S = 50–20%), acidic (X = 40–50%, S = 40–70%) and basic (X = 65–90%, S = 50–90%) conditions.

Given that the aqueous phase reforming of glycerol for hydrogen production using supported Pt catalysts is already known (70% hydrogen selectivity with 77% conversion of glycerol in a tubular reactor with 10 wt. % glycerol feed at 498–538 K) [27], it seems worthwhile to evaluate the possibility of conducting

* Corresponding author at: Center for Environmentally Beneficial Catalysis, University of Kansas, 1501 Wakarusa Dr., 117B, Lawrence, KS, USA.
Tel.: +1 785 864 1634; fax: +1 785 864 6051.
E-mail address: rvc1948@ku.edu (R.V. Chaudhari).

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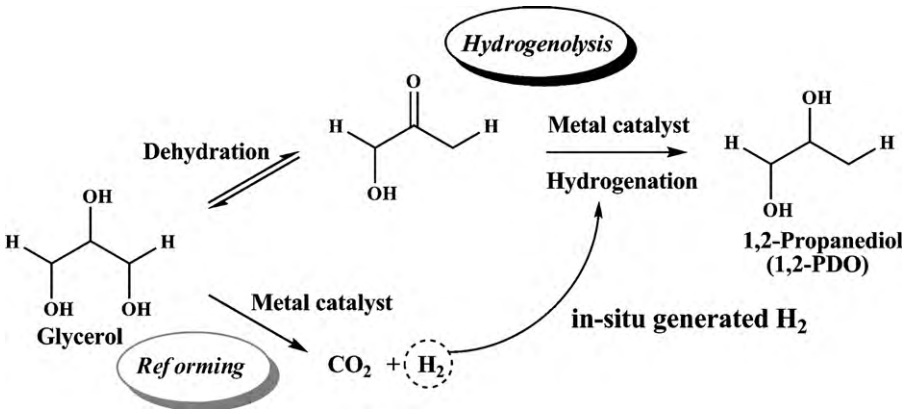

Fig. 1. Schematic representation of *in situ* generated hydrogen utilization for glycerol hydrogenolysis to 1,2-propanediol.

hydrogenolysis of polyols using such *in situ* generated hydrogen. The concept is presented in Fig. 1.

The *in situ* hydrogen production–hydrogenolysis combo reaction has several advantages over the conventional hydrogenolysis reactions using externally added hydrogen. This concept obviates the need for external hydrogen produced from either a feedstock or power derived from fossil sources and can lead to processes with improved economics. Further, the hydrogenolysis reaction in the absence of added hydrogen can run even at mild pressure with an inert gas leading to improved operational safety. Recently D'Hondt et al. [12] reported a Pt/NaY catalyst for 1,2-PDO formation (41.5% selectivity) from glycerol (58.8% conversion) in the absence of added hydrogen at 503 K. However, detailed parametric studies including a comparison of this approach with that involving externally added hydrogen and the stability of the catalyst were not reported. To systematically explore the concept and demonstrate its potential advantages for glycerol hydrogenolysis to 1,2-propanediol, we report here results of detailed parametric studies performed with an admixture of 5 wt.% Pt/Al_2O_3 and 5 wt.% Ru/Al_2O_3 catalysts. The Pt/Al_2O_3 was chosen to promote the aqueous phase reforming of glycerol to hydrogen [27,28], whereas Ru/Al_2O_3 was chosen to facilitate the hydrogenolysis of glycerol. We demonstrate that the admixture catalyst outperformed the individual catalysts with respect to 1,2-PDO selectivity and yield under without added hydrogen condition. The yield of 1,2-PDO was also higher with the admixture catalyst when compared to the externally added hydrogen condition.

2. Experimental

2.1. Materials

Glycerol (≥99.5%, spectrophotometric grade) was purchased from Sigma–Aldrich and used without further purification. The 5% Ru/Al_2O_3 and 5% Pt/Al_2O_3 catalysts were purchased from Sigma–Aldrich and used as received. The 5% Ru/Al_2O_3 and 5% Pt/Al_2O_3 catalysts were in powder form with particle size ranging 75–150 μm and 100–125 μm respectively (measured in our laboratory using Tyler standard sieves). Hydrogen (purity >99.5%) and nitrogen (purity >99%) were procured from Air Gas Inc. and Linweld, respectively, and used as received.

2.2. Reaction experiments

The catalytic reactions of glycerol were carried out in a high pressure, high temperature multiple slurry reactor system supplied by Parr Instrument Co., Moline, AL. The reactor system consists of a parallel array of six autoclave reactors that can be operated simultaneously at different temperatures and pressures (Fig. 2). Each autoclave reactor is equipped with a thermowell, pressure transducer, gas inlet, gas outlet and a rupture disc. A magnetic stirrer with maximum agitation speed of 30 Hz provides mixing in each reactor. The temperatures and pressures in the individual reactors are independently controlled and monitored with a computer interfaced with the control module of the reactor system. The common agitation speeds of the reactors can be controlled from the computer interface or with the manual controller in the reactor setup itself. The temperature and pressure of the reactors as well as the H_2 reservoir are logged every 5 s through SpecView data acquisition software.

In a typical hydrogenolysis experiment, a known amount of glycerol dissolved in water was charged into a reactor. An initial sample was collected at that condition. Predetermined amounts of the 5% Pt/Al_2O_3 and 5% Ru/Al_2O_3 catalysts, either alone or a mixture of the two, were then charged into the reactor and the vessel was sealed. The other reactors were charged in a similar manner. The reactors were placed into the heating slots of the multiple reactor assembly (Fig. 2) and then purged 2–3 times with N_2 at room temperature. The reactor bombs were heated to a desired temperature under low agitation speed (3–4 Hz). After attaining the desired temperature, N_2 was introduced into the reactor to make up the pressure to 14 bar; the agitator speed was increased to 25 Hz and the reactions were allowed to proceed. The N_2 pressurization allows easy and adequate sampling of the gas phase for GC analysis at the end of the run. Following a predetermined batch reaction time, the reactors were allowed to cool down to

Fig. 2. Multiple slurry reactor setup.

Table 1
Effect of N_2 pressure on glycerol hydrogenolysis without external H_2 addition.

	P_{N_2}		
	0 bar	14 bar	41 bar
Glycerol conversion, %	43.2	50.2	42.8
Liquid phase product selectivity, %			
EG	7.2	6.3	7.5
1,2-PDO	48.7	47.2	45.8
Glyceraldehyde	0	0	0.01
Lactic acid	1.9	1.6	1.3
MeOH	0	0.3	0.0
EtOH	3.9	1.1	3.8
Gas phase product selectivity, %			
Methane	17.4	18.3	12.9
Ethane	1.6	0.9	0.9
Propane	0.6	0.4	0.5
n-Butane	0.1	1.2	0.1
n-Pentane	0.6	0.6	0.5
CO	0.4	1.3	0.8
CO_2	9.8	14.3	15.1
C deficit, %	5.3	3.8	4.5

Reaction conditions: glycerol: 3 g; 5% Ru/Al_2O_3: 0.125 g; 5% Pt/Al_2O_3: 0.125 g; temp: 493 K; solvent: H_2O; initial liquid volume: 30 mL; batch reaction time: 6 h.

room temperature. The gas phase samples were analyzed by GC (Shimadzu GC 2014). In one sampling loop, H_2, CO, CO_2, methane and methanol were analyzed using a 60/80 Carboxen 1000 column (packing material: carbon molecular sieve; 4.5 m × 2.1 mm × 0.50 μm film thickness) connected to a thermal conductivity detector (TCD). In another loop, C_1–C_5 alkanes were analyzed using a Hayesep DB (packing material: divinylbenzene; 2.5 m × 3.1 mm × 0.25 μm film thickness) column and a flame ionization detector (FID). The liquid samples were analyzed by HPLC (Shimadzu) using a Rezex ROA-Organic Acid H+ (8%) column (300 mm × 7.8 mm), 0.005 N aqueous H_2SO_4 as mobile phase and a refractive index detector (RID). The analytical results from the HPLC and GC were combined to get a quantitative assessment of each product (in the gas and liquid phases) and to calculate the glycerol conversion and product selectivities. In all the runs, the analytical procedure is able to account for >90% of the starting glycerol.

The influence of N_2 pressure on activity and product selectivity was studied (Table 1). The results indicate that the H_2 generated *in situ* from aqueous phase reforming of glycerol (which subsequently reacts with the remaining glycerol to produce 1,2-PDO and other products) is unaffected by the N_2 pressure. We employed 14 bar of N_2 in all the experiments to provide adequate gas phase samples for analysis.

As mentioned in Section 1, admixture catalysts consisting of various weight ratios of 5% Ru/Al_2O_3 and 5% Pt/Al_2O_3 were used in this work. For clarity, the quantities of supported Ru and Pt catalysts used in each admixture catalyst are shown in Table 2.

For catalyst recycling studies, the reactor content following a run was transferred into a centrifugation tube using a pipette. The solid phase, containing the Ru/Al_2O_3 and Pt/Al_2O_3 admixture, was separated from the liquid phase by centrifugation. The liquid phase at the top was pipetted out carefully. The wet solid was then washed with water and separated from the catalyst. This washing and filtering procedure was repeated 3–4 times to remove any remaining adsorbed organic species from the catalyst surface. A fresh charge of the required amount of glycerol dissolved in water was used to transfer the solid from the centrifuge tube to the reactor bomb for a recycle run. After three such recycle runs, the catalyst was separated from the liquid phase, washed with water as described above and then centrifuged a few times with added acetone to remove traces of water adsorbed on the catalyst. The catalyst was then dried under flowing nitrogen first and then in a furnace at 373 K under nitrogen flow. The surface areas of the fresh and recovered catalysts were measured using a Gemini 2360 surface area analyzer (Micromeritics).

Table 2
Composition of admixture Ru:Pt catalysts.

Ru:Pt catalyst wt. ratio	5% Ru/Al_2O_3 (g)	5% Pt/Al_2O_3 (g)
0.5:1	0.0625	0.125
1:1	0.125	0.125
2:1	0.250	0.125
4:1	0.500	0.125
1:2	0.125	0.250

The glycerol conversion is defined as the percentage ratio of the moles of glycerol consumed during the reaction to the moles of glycerol charged initially expressed. Selectivity to a particular product is defined as the percentage ratio of carbon in a particular product to the total carbon in all products. The usefulness of this selectivity definition in a reaction where degradation products (glycerol to lower carbon molecules such as ethylene glycol and methane) are also expected, had been discussed earlier by Miyazawa et al. [24]. In other words, the carbon-based selectivity defined above considered the products in the liquid phase as well as in the gas phase. There are several reports on glycerol hydrogenolysis where selectivity was calculated based on liquid phase products only [13,19,29]. However, it is well known that CO, CO_2 and methane can form with this class of catalytic reaction, as confirmed in our present study. Clearly therefore, the selectivities based on considering liquid phase products alone are not the intrinsic values and are always overestimated. The analytical protocol described above was developed to provide complete analysis of liquid as well as gas phase products in order to quantify them and the extent of material balance closure. The percentage difference in the measured molar carbon content in the feed and product streams, relative to the feed stream, is termed as the 'carbon deficit'.

$$\text{Carbon deficit} = \frac{100 \times (C_{\text{feed}} - C_{\text{unreacted glycerol+products}})}{C_{\text{feed}}}\%$$

A typical material balance analysis showing quantities of the detected liquid phase and gas phase products is shown in Table 3.

3. Results and discussion

3.1. Possible reactions in glycerol hydrogenolysis

From the literature reports, it is evident that glycerol hydrogenolysis involves several consecutive as well as parallel reactions [23] and the product profile strongly depends upon the catalyst, promoters and reaction conditions. To understand the reaction network involved in glycerol hydrogenolysis, published literature information [18,30] was used as guidance. In addition, we conducted several diagnostic experiments to test the significance of side reactions under different conditions to confirm and better discern plausible reaction pathways. For example, glyceraldehyde at lower concentrations was identified in a few of our hydrogenolysis reactions. Glyceraldehyde can form by dehydrogenation of glycerol on the metal surface as proposed earlier by Maris et al. [18]. Montassier et al. [30] and Maris et al. [18] also suggested the mechanism for formation of ethylene glycol (EG) and 1,2-PDO from glyceraldehyde. Maris et al. proved that the retro-aldol reaction and the dehydration step may occur on a catalyst surface in absence of either an acidic or a basic promoter as speculated earlier by Montassier et al. Maris et al. reported that lactic acid forms during glycerol hydrogenolysis reaction via glyceraldehyde and pyruvaldehyde intermediates in the presence

Table 3
Typical material balance sheet for glycerol hydrogenolysis.

	Conc. (kmol/m^3)	C moles ($\times 10^3$)	%
Initial			
Glycerol	1.084	97.56	
Final sample			
Liquid phase components			
Glycerol	0.541	48.69	50.09[a]
Ethylene glycol (EG)	0.051	3.06	6.26[b]
1,2-propanediol (1,2-PDO)	0.257	23.13	47.33[b]
1,3-propanediol (1,3-PDO)	0	0	0.00[b]
Glyceraldehyde	0	0	0.00[b]
Lactic acid	0.009	0.81	1.66[b]
Oxalic acid	0	0	0.00[b]
Ethanol	0.009	0.54	1.10[b]
2-Propanol	0	0	0.00[b]
1-Propanol	0	0	0.00[b]
Methanol	0.002	0.07	0.14[b]
Gas phase components			
Methane	0.129	9.02	18.46[b]
Ethane	0.003	0.43	0.87[b]
Propane	9.4×10^{-4}	0.19	0.41[b]
Methanol	9.6×10^{-4}	0.01	0.14[b]
CO	0.009	0.66	1.35[b]
CO_2	0.101	7.04	14.40[b]
n-Butane	0.002	0.62	1.26[b]
n-Pentane	9.3×10^{-4}	0.33	0.67[b]
Totals		94.65	94.05[b]
C deficit	2.98%		

Hydrogenolysis reaction conditions: glycerol: 2.992 g; 5% Ru/Al_2O_3: 0.125 g; 5% Pt/Al_2O_3: 0.125 g; temp: 493 K; P_{N_2}: 14 bar; solvent: H_2O; initial liquid volume: 30 mL; batch time: 6 h.
[a] Conversion.
[b] Selectivity.

of either an acidic or a basic promoter. We found lactic acid formation (selectivity: 1–4%) in all the experiments involving *in situ* hydrogen generation. A possible explanation is that CO_2 formed during the aqueous phase reforming of glycerol dissolves in the aqueous phase to generate carbonic acid (H_2CO_3), which upon dissociation can produce a free proton that promotes the transformation of pyruvaldehyde to lactic acid [12].

Our diagnostic experiments with the individual liquid phase products of glycerol hydrogenolysis revealed that all the products (including methanol) undergo reforming at the experimental conditions (473–523 K; 14 bar N_2 initial pressure). Methanol reforming to methane was observed with and without externally added hydrogen. Though methane was the major product from methanol when hydrogen was added from external sources, CO_2 was the major product (60% with 20% CH_4) in experiments without added hydrogen. Formation of methane from methanol was also reported earlier by Montassier et al. [31]. In another experiment with CO and added hydrogen in the presence of a Ru/Al_2O_3 catalyst, we found alkanes such as methane and ethane as products. However, a similar experiment with CO_2 and hydrogen produced only methane. Based on the literature data and our diagnostic experiments, possible reaction pathways involved in glycerol hydrogenolysis are shown in Fig. 3.

3.2. Hydrogenolysis of glycerol with in situ hydrogen generation

A major objective of this work is to demonstrate the proof of concept of using a Ru–Pt catalyst combination to generate hydrogen *in situ* from aqueous phase reforming of glycerol and utilization of this hydrogen for hydrogenolysis of the remaining glycerol. Specifically, the following investigations were performed: (a) comparison of individual catalysts with the admixture catalyst under conditions of no external hydrogen addition; (b) effect of catalyst (Ru/Al_2O_3 and Pt/Al_2O_3) weight ratio on activity and selectivity of products in glycerol hydrogenolysis in absence of added hydrogen; (c) temperature effect; (d) catalyst performance comparison of the admixture with and without added hydrogen for glycerol hydrogenolysis; and (e) stability of the admixture catalyst during recycle runs.

The results with 5% Ru/Al_2O_3 and 5% Pt/Al_2O_3 admixture combinations and the monometallic catalysts on glycerol hydrogenolysis in absence of externally added hydrogen at 493 K are compared in Fig. 4.

It is evident from Fig. 4 that 1:1 (w/w) Ru–Pt admixture catalyst combination displays a positive synergy in improving the yield of 1,2-PDO compared to the monometallic catalysts. Though the glycerol conversion was similar (~20%), the 5% Ru/Al_2O_3 catalyst gave higher selectivity to 1,2-PDO (50.1%) compared to the 5% Pt/Al_2O_3 catalyst (37.2%). The lower 1,2-PDO selectivity with Pt/Al_2O_3 catalyst is attributed to the higher reforming activity of Pt catalysts over hydrogenolysis reaction compared to Ru catalysts. For the same overall loading of the admixture catalyst with equal weights of the Pt and Ru catalysts, significant improvement in glycerol conversion (50.2%) is noted while retaining high 1,2-PDO selectivity (47.1%). The fact that the glycerol conversion with the admixture catalyst is more than twice the value achieved with an identical amount of either the Pt or the Ru catalyst confirms a beneficial synergistic effect between Pt and Ru in the admixture catalyst.

The effect of the relative amounts of Ru and Pt content in the admixture was studied and the results are shown in Fig. 5. The amounts of the individual catalysts (5% Ru/Al_2O_3 and 5% Pt/Al_2O_3) used in various Ru:Pt admixtures studies are shown in Table 2. Glycerol conversion improved as the Ru:Pt ratio in the admixture is increased from 0.5:1 to 4:1 (30.2–65.8%). While the increase is due to increasing amounts of Ru/Al_2O_3 catalyst used in these runs, it must be noted that the conversion does not increase linearly with increase in Ru content. This may be due to the fact that Ru/Al_2O_3 is not a very good catalyst for reforming and as such there was insufficient hydrogen generated *in situ* to convert the remaining glycerol to 1,2-PDO. Interestingly, the liquid phase concentration of 1,2-PDO in runs with 1:1 and 4:1 Ru:Pt admixture catalysts was very similar (0.253 and 0.245 kmol/m^3 respectively) although the glycerol conversion was higher in the latter case (65.8% for 4:1 Ru:Pt compared to 50.2% for 1:1 admixture). This indicates that the hydrogen available for hydrogenolysis reactions was similar in the two cases. Given that the amount of Pt/Al_2O_3 catalyst was identical (0.125 g) in these two cases, this further suggests that the hydrogen generated *in situ* is mainly due to the Pt catalyst. This is supported by the data obtained from the run with a 1:2 Ru–Pt catalyst admixture (containing 0.125 g of 5% Ru/Al_2O_3 and 0.250 g of 5% Pt/Al_2O_3), where 1,2-PDO selectivity improved with respect to 2:1 Ru–Pt catalyst admixture (containing 0.250 g of 5% Ru/Al_2O_3 and 0.125 g of 5% Pt/Al_2O_3) for nearly the same glycerol conversion. Further, the marginally lower 1,2-PDO selectivity with the 1:2 Ru:Pt admixture compared to 1:1 Ru:Pt admixture at nearly identical conversions indicates the absence of hydrogen starvation for hydrogenolysis even with the lower amount of Pt/Al_2O_3 in the 1:1 Ru:Pt admixture. This is in sharp contrast with the results obtained with 2:1 and 4:1 Ru:Pt admixture catalysts, wherein increasing amounts of Ru/Al_2O_3 at a fixed loading of Pt/Al_2O_3 (0.125 g) resulted in hydrogen starvation as inferred from the lower 1,2-PDO selectivity.

It is important to note that Ru is known to convert CO_2 to methane [32]. Therefore, with increasing Ru content in the admixture catalysts, more CO, CO_2 and hydrogen are consumed to form methane and other alkanes (methane selectivity: 18.3%, 22.9% and 22.0% with 1:1, 2:1 and 4:1 Ru–Pt admixture catalysts,

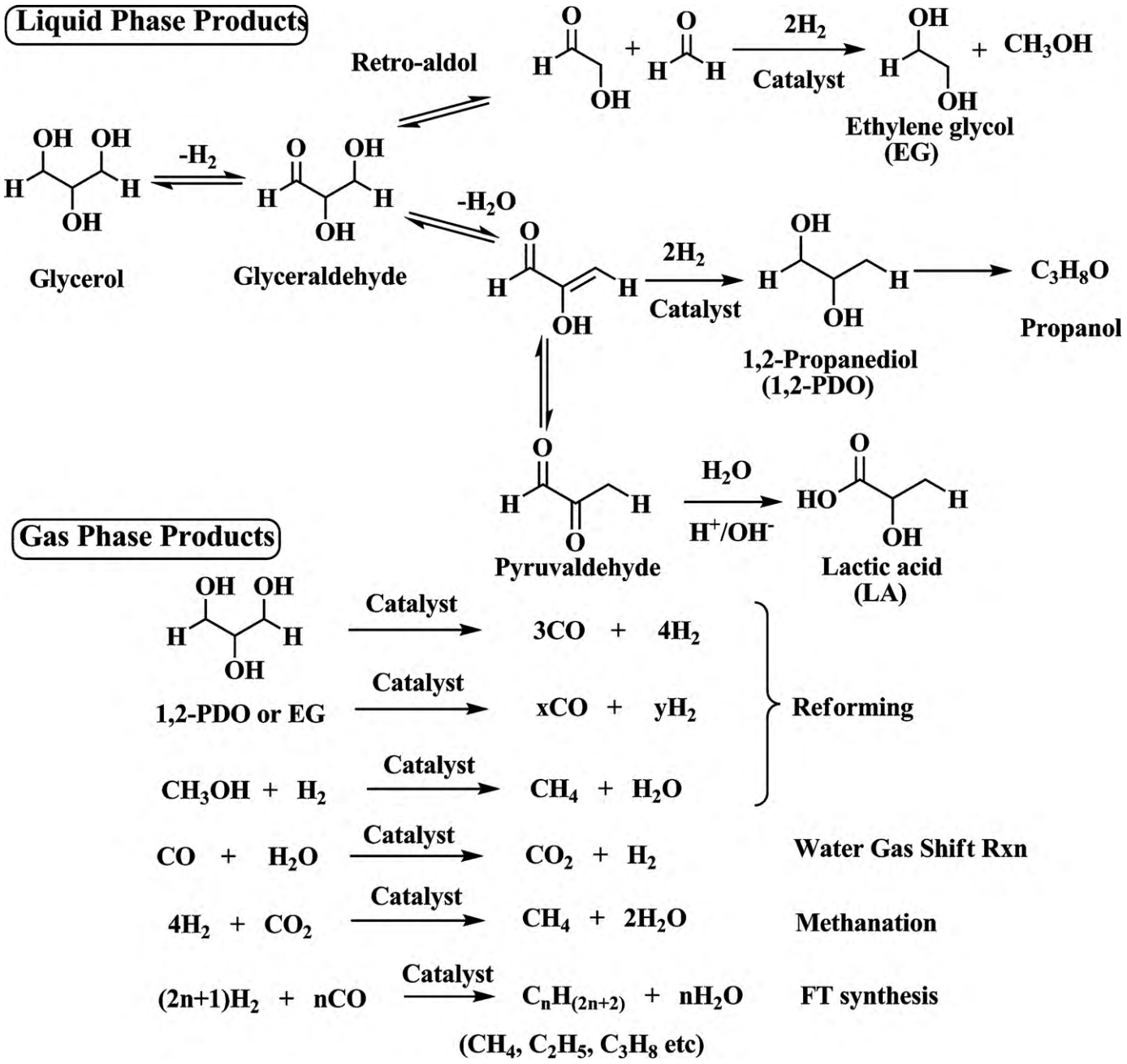

Fig. 3. Possible reactions in glycerol hydrogenolysis.

respectively). These results indicate that reactions involving CO and CO_2 with H_2 occur simultaneously with the hydrogenolysis reaction. As noted by Cortright et al. [27], it is quite difficult to stop the methane (and alkanes too) formation due to the high equilibrium constant for the conversion of CO_2 and H_2 to methane (on the order of 10^{10} per mole of CO_2 at 500 K).

From the foregoing results and discussion, we conclude that an increase in Ru content with respect to Pt, with no external hydrogen addition, has no beneficial effect on the overall productivity of 1,2-PDO and that the 1:1 Ru/Al_2O_3:Pt/Al_2O_3 admixture catalyst provides the optimum glycerol conversion and 1,2-PDO selectivity. Therefore, further experiments were carried out with 1:1 Ru:Pt admixture catalyst.

Effects of temperature on glycerol conversion and 1,2-PDO selectivity in the 473–523 K range are summarized in Table 4. Glycerol conversion increased from 20.6% at 473 K to 82.6% at 523 K; however, 1,2-PDO selectivity decreased steadily from 53.1% to 26.5%. The decrease in 1,2-PDO selectivity with temperature is attributed to the higher reforming rate of hydrogenolysis products (for example 1,2-PDO) at higher reaction temperature. The increased methane yield in the gas phase at higher temperatures indicates enhanced methanation activity that further reduces hydrogen availability for the hydrogenolysis reaction. As expected, the total yield of liquid phase products decreased at higher temperatures.

To evaluate the advantage of *in situ* hydrogen generation for glycerol hydrogenolysis to 1,2-PDO, experiments were performed with 1:1 Ru:Pt admixture catalyst with and without external H_2 addition under otherwise identical conditions. The results at 493 K are compared in Table 5.

The results in Table 5 clearly demonstrate the advantage of *in situ* hydrogen generation for glycerol hydrogenolysis (1,2-PDO

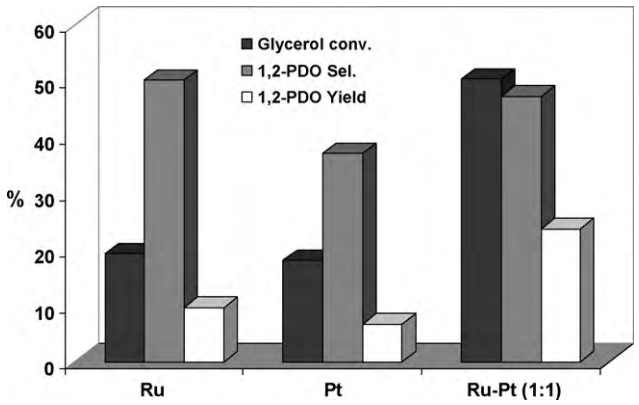

Fig. 4. Effect of Ru, Pt and Ru–Pt admixture catalysts on glycerol hydrogenolysis in the absence of added hydrogen. Reaction conditions: glycerol: 3 g, total catalyst (wt.): 0.25 g, temp: 493 K, P_{N_2}: 14 bar, solvent: H_2O; initial liquid volume: 30 mL; batch reaction time: 6 h.

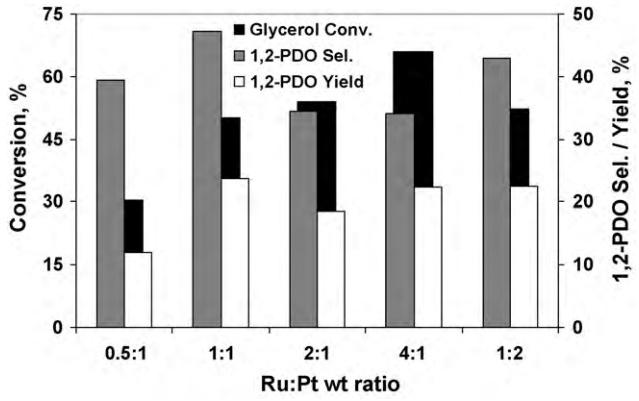

Fig. 5. Effect of Ru and Pt weight ratio on glycerol hydrogenolysis with no externally added hydrogen. Reaction conditions: glycerol: 3 g, catalyst: as shown in Table 2, temp: 493 K, P_{N_2}: 14 bar, solvent: H_2O, initial liquid volume: 30 mL, batch reaction time: 6 h.

selectivity: 47.2%) over the externally added hydrogen condition (1,2-PDO selectivity: 31.9%). It is important to note that alkane selectivity increased and CO_2 selectivity decreased sharply with external hydrogen addition. In this case, more hydrogen (in addition to the *in situ* generated hydrogen) is available to convert the CO and CO_2 to methane and other alkanes. This would favorably shift the equilibrium for further glycerol reforming to CO and therefore to more undesired gaseous products. The increased ethylene glycol (EG) selectivity with externally added hydrogen also suggests enhanced glycerol reforming (via C–C cleavage) activity.

Table 4
Effect of temperature on glycerol hydrogenolysis without external H_2 addition.

Temperature (K)	473	493	513	523
Glycerol conversion, %	20.6	50.2	65.8	82.6
Liquid phase product selectivity, %				
EG	8.9	6.26	2.7	2.6
1,2-PDO	53.1	47.2	30.4	26.5
Glyceraldehyde	0.1	0.0	0.0	0.0
Lactic acid	2.6	1.6	3.3	3.6
MeOH	0.3	0.3	0.4	0.3
EtOH	2.1	1.1	1.4	7.3
Gas phase product selectivity, %				
Methane	17.1	18.3	18.3	21.2
Ethane	1.1	0.9	8.2	7.2
Propane	0.6	0.4	2.6	4.2
n-Butane	0.2	1.2	6.4	3.6
n-Pentane	1.2	0.6	2.1	0.2
CO	3.6	1.3	0.03	0.16
CO_2	20.9	14.3	15.5	17.3
C deficit, %	−1.82	3.84	1.85	6.6

Reaction conditions: glycerol: 3 g; 5% Ru/Al_2O_3: 0.125 g; 5% Pt/Al_2O_3: 0.125 g; P_{N_2}: 14 bar; solvent: H_2O; initial liquid volume: 30 mL; batch reaction time: 6 h.

Table 5
Glycerol hydrogenolysis with and without external H_2 addition.

	Without external H_2 addition (P_{N_2}: 14 bar)	With externally added H_2 (P_{N_2}: 41 bar)
Glycerol conversion, %	50.2	62.8
Liquid phase product selectivity, %		
EG	6.26	11.1
1,2-PDO	47.2	31.9
Glyceraldehyde	0.0	0.01
Lactic acid	1.6	1.01
MeOH	0.3	0.0
EtOH	1.1	1.0
2-Propanol	0.0	0.1
Gas phase product selectivity, %		
CH_4	18.3	34.6
C_2H_6	0.9	9.3
C_3H_8	0.4	5.5
n-C_4H_{10}	1.2	0.4
n-C_5H_{12}	0.6	0.2
CO	1.3	1.0
CO_2	14.3	2.4
C deficit, %	3.84	3.07

Reaction conditions: glycerol: 3 g; 5% Ru/Al_2O_3: 0.125 g; 5% Pt/Al_2O_3: 0.125 g; temp: 493 K; solvent: H_2O; initial liquid volume: 30 mL; batch reaction time: 6 h.

In order to check the stability and reusability of the Ru:Pt admixture catalyst system under the glycerol hydrogenolysis conditions, the catalyst was recycled three times. It was observed that the glycerol conversion as well the total yields of liquid and gas phase products and their compositions remained identical during all the recycle runs within experimental error (Fig. 6) indicating very good catalyst stability and recyclability. It is important to note that using the catalyst recovery protocol described in Section 2.2, we were able to recover ~97% of the catalyst used in the first run. The BET surface areas of the admixture catalyst before and after the recycle studies were nearly identical (170 and 167 m^2/g) indicating that there was no catalyst

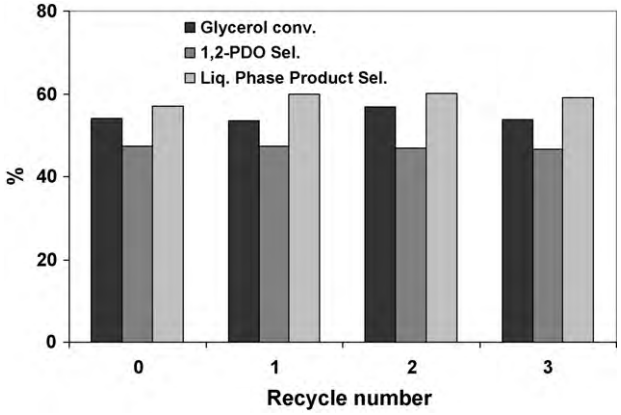

Fig. 6. Catalyst recycling studies with 1:1 (w/w) 5% Ru/Al_2O_3–5% Pt/Al_2O_3 admixture catalysts on glycerol hydrogenolysis without externally added hydrogen. Reaction conditions: glycerol: 3 g, 5% Ru/Al_2O_3: 0.125 g, 5% Pt/Al_2O_3: 0.125 g, Temp: 493 K, P_{N_2}: 14 bar, solvent: H_2O, initial liquid volume: 30 mL, batch reaction time: 6 h.

fouling during the recycle runs. Tanksale et al. [28] employed by X-ray diffraction (XRD) and thermo-gravimetric analysis (TGA) to study deactivation of Pt catalyst during aqueous phase reforming of fructose at 493 K and reported carbon deposition. However, the authors did not report any carbon deposition when studying similar reactions with glucose or sucrose. The results indicate that catalyst deactivation by fouling may be substrate specific. In summary, the 1:1 (w/w) 5% Ru/Al_2O_3 and 5% Pt/Al_2O_3 admixture catalyst is very stable and this combo catalyst approach shows much promise for performing hydrogenolysis with no externally added hydrogen.

4. Conclusions

Based on detailed characterization of both liquid phase and gas phase products, we have demonstrated that aqueous phase hydrogenolysis of abundantly available and renewable glycerol feedstock with a admixture catalyst system comprised of a reforming (Pt) and a hydrogenolysis catalyst (Ru) and without external hydrogen addition is a promising approach for producing 1,2-propanediol. The hydrogen generated from aqueous phase reforming of glycerol is used for simultaneous hydrogenolysis of remaining glycerol to 1,2-PDO. The fact that the hydrogen is derived from part of the feedstock obviates the need for external hydrogen addition. Most significantly, the admixture catalyst showed synergistic effect over individual metal components providing better selectivity to the hydrogenolysis product (1,2-PDO) without than with external hydrogen addition. The admixture catalyst showed very good stability during several recycle runs. The proposed strategy can also be applied for hydrogenolysis of other polyols to value added chemicals and indicates a potential to design bimetallic catalysts for the combo reforming-hydrogenolysis reactions.

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