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RESEARCH ARTICLE

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Abstract

In recent years, much attention has been focused on the hydrogenolysis of biodiesel derived glycerol to other high value products for the sustainable development and efficient valorization strategies. In the present work, alumina-supported Ir catalyst was prepared by the incipient wetness impregnation method and tested in the glycerol hydrogenolysis reaction. The synthesized catalyst was characterized by neutron activation analysis, N₂ physisorption, and H₂ chemisorption techniques. The experiments standard conditions were 150 mL feed volume, 0.3 g catalyst, 1500 rpm stirring speed, and 5 wt% glycerol aqueous solution for 4 h. The effects of catalyst amount, temperature, hydrogen pressure, stirring speed, and solution pH on glycerol conversion and selectivity of the principal products obtained were also investigated. The glycerol conversion and the 1,2-propanediol selectivity varied from 4.9% to 22% and from 23.8% to 70.3%, respectively. It was found that the selectivity of 1,2-propanediol increased significantly with the increased alkalinity of the reaction medium.

Keywords

hydrogenolysis, glycerol valorization, iridium, catalysis, alumina, biodiesel

1 Introduction

The fluctuating increasing oil prices and the increased world-wide environmental concerns towards minimizing CO₂ emissions tend to highlight the necessity of renewable resources. Biodiesel derived from renewable resources comprising, for instance, vegetable oils and animal fats has attracted great attention recently. Glycerol is considered to be the main byproduct that results during biodiesel production. Nevertheless, increases in the production of glycerol from biodiesel refining accompanied with the tight markets of glycerol supply and demand created a glut in the glycerol market. This resulted in a significant fall in the glycerol price and limited options for glycerol byproduct management are hence available to biodiesel refiners [1]. Thus, finding solutions for the effective utilization of glycerol waste is crucial to achieve both economic and environmental benefits. Consequently, this will turn the biofuel producers to view the byproduct as a valuable resource for their own production processes instead of viewing glycerol as a waste [2, 3].

Over the past decades, the hydrogenolysis of higher polyols like sorbitol, xylitol, and glycerol has been investigated in literature [4, 5]. Recently, the hydrogenolysis of glycerol into value-added chemicals emerged as an attractive process for glycerol valorization [6, 7]. Going forward, aqueous phase hydrogenolysis of glycerol was performed on different catalysts/support combinations. Previous examples can include Ru/Al₂O₃ [7–9], Ru/TiO₂ [10, 11], Ru/ZrO₂ [9, 12], Ru/Al₂O₃-AlF₃ [13], Pt/SiO₂ [7], Pt/Al₂O₃ [7], Pt/ZnO [14], Pd/SiO₂ [7], Pd/Al₂O₃ [7], Rh/C [7, 15], Rh/SiO₂ [7], Rh/Al₂O₃ [7, 15], Cu/SiO₂ [16], Cu/MgO [17], Cu/Al₂O₃ [18], Raney Ni [8], Ni/Al₂O₃ [18], and Ni-Cu/Al₂O₃ [18].

Iridium catalysts have been tested for hydrogenolysis of glycerol towards producing high value chemicals, like 1,2-propanediol and 1,3-propanediol, under hydrogen atmosphere [19, 20]. However, few researchers used the iridium-based catalysts in the glycerol hydrogenolysis reaction. Examples comprise Ir/C [21], Ir-ReOx/SiO₂ [22, 23], Ru-added Ir-ReOx/SiO₂ [24], Re-modified Ir/ZrO₂ [25], Ir-ReOx/SiO₂ with HZSM-5 zeolite as a solid acid co-catalyst [26], and Ir-Ni bimetallic

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catalysts [27]. It is worth noting that the reactivity of glycerol and reaction intermediates on iridium catalysts are extensively affected by the nature of the adopted support [28].

In this paper, alumina-supported Ir catalyst was prepared using the aqueous incipient wetness technique and examined for glycerol hydrogenolysis, towards the objective of producing value-added chemicals and subsequently achieving efficient glycerol valorization option. The effects of catalyst amount, temperature, hydrogen pressure, stirring speed, and solution pH on conversion of glycerol and selectivity of main products obtained were also investigated so as to assess the catalytic performance of the prepared catalyst.

2 Materials and methods

Iridium-supported catalyst on γ -Al₂O₃ (Saint-Gobain NorPro, supplied as 1/16 in extrudates) was prepared by the aqueous incipient wetness technique. Prior to catalyst impregnation, the extrudates were grinded down to particle size less than 75 μ m in a synthetic sapphire mortar. The resulted powder was dried overnight at 135 °C before the impregnation with hexachloroiridic acid (H₂IrCl₆) (Sigma-Aldrich) solution. After impregnation, the powder was dried at room temperature for an hour before being dried at 110 °C for 24 h. The powder was reduced with H₂ at 400 °C for 3 hours (ramp rate = 10 °C/min; H₂ flow = 550 scc/min) and cooled down under a flow of Helium. Finally, the cooled down powder was kept in ammonia solution (10% w/v) overnight to remove the residual chlorine from the catalyst [29] then washed at least three times with deionized water.

BET surface area, pore volume, and pore diameter were measured by nitrogen physisorption at its boiling point using a Tristar 3000 analyzer (Micromeritics, Inc.). Iridium loading of the catalyst was determined by NAA (Elemental Analysis, Inc.). Finally, hydrogen chemisorption was performed on Quantachrome Autosorb 1 analyzer (Micromeritics, Inc.).

The hydrogenolysis experiments were carried out in a 300 mL stainless steel autoclave (Autoclave Engineers) equipped with a magnetically-driven agitator (Autoclave Engineers). A Dispersimax turbine-type impeller was mounted on the shaft of the agitator. The reactor is equipped with a dip tube, a purge valve, rupture disc, pressure transducer, and a thermocouple placed in a thermo-well. The experiments were conducted at constant total pressure since H₂ was fed continuously to the reactor to makeup for the H₂ consumption in the reactions. Unless otherwise is mentioned, the experiments standard conditions were 5 wt% initial aqueous solution of the feed material, 150 mL feed volume, 0.3 g catalyst, 1500 rpm stirring speed, and 4 h reaction time.

In a typical experiment, the catalyst powder is placed in the reactor then the reactor is sealed and purged with H₂ (99.999%; Airgas) five times. The catalyst is reduced another time in-situ

with hydrogen at 260 °C for one hour and then the reactor is cooled down to 150 °C. The hydrogen pressure is adjusted to about 10 bar and the feed solution is injected using an HPLC pump (Alltech 301 HPLC pump). Afterwards, the reactor is heated up to the desired temperature and the total pressure is adjusted. At the end of the reaction time, the hydrogen feed is stopped and the vessel is quenched down quickly to 21 °C using water/ice bath. The gas is collected in a 250 mL gas bulb and the liquid is collected using the dip tube of the reactor. Finally, the liquid is filtered and diluted down with deionized water to 5X dilution.

The analysis of the liquid sample was carried out using a GC equipped with a flame ionization detector and a thermal conductivity detector using Restek MTX-Wax column (0.53 mm internal diameter, 60 m length, and 1 μ m phase thickness). As for the gas samples, the analysis was carried out using another GC equipped with a helium ionization detector and a thermal conductivity detector using a Restek ShinCarbon ST 80/100 packed column (1/8 in outside diameter, 2 m length). Products were identified by Edison Analytical Laboratories, Inc using an HP5890 GC connected to an HP5972 mass selective detector. Liquid products identified were: 1,2-propanediol (1,2-PD), ethylene glycol (EG), methanol (MeOH), ethanol (EtOH), n-propanol (n-PrOH), i-propanol (i-PrOH), and traces of acetone (AC) and hydroxyacetone (acetol) (H-AC). Gas products identified were methane, ethane, propane, and carbon dioxide.

3 Results and discussion

3.1 Catalyst characterization

Iridium-supported catalyst on γ -Al₂O₃ was prepared to be tested in the glycerol hydrogenolysis experiments. The Ir content for the catalyst was about 2.6 \pm 0.1 wt%. Table 1 summarizes the catalyst characteristics.

Table 1 Catalyst characterization

Catalyst	BET SA, m ² /g	Pore vol, cm ³ /g	Average pore diam, Å	Wt% Ir by NAA	Metal dispersion using H ₂ , %
Cat Ir	227	0.67	103.1	2.6 \pm 0.1	36.3

3.2 Hydrogenolysis of glycerol

In order to test the catalytic quality and performance of the prepared catalyst for glycerol hydrogenolysis, the effect of catalyst weight, temperature, pressure, stirring speed, and solution pH were investigated. The values obtained in the experimental results are the average of two experiments. The repeatability of the results is within \pm 5-10%. Carbon material balance at end of the reaction time, conversion, and selectivity were estimated using Eqs. (1), (2), and (3), respectively.

$$C - \text{Material Balance}(\%) = \frac{C\text{-based moles of (products + unreacted feed)}}{C\text{-based moles of initial feed}} \times 100 \quad (1)$$

$$\text{Conversion}(\%) = \frac{C\text{-based moles of initial feed} - C\text{-based moles of unreacted feed}}{C\text{-based moles of initial feed}} \times 100 \quad (2)$$

$$\text{Selectivity of product } i(\%) = \frac{C\text{-based moles of product } i}{C\text{-based moles of all products}} \times 100 \quad (3)$$

3.3 Effect of catalyst amount

The influence of weight of catalyst was investigated with 0.3, 0.57, and 0.97 g catalyst loadings, respectively. Table 2 and Fig. 1 show the experimental results of glycerol hydrogenolysis using the three different loadings of Cat Ir. The conversion showed a slight decrease or rather a constant behaviour (from 5.2 to 5.1%) with increasing the catalyst loading from 0.3 to 0.57g. However, with more increasing in the catalyst loading (0.97 g), there was a pronounced decrease in the conversion from 5.1 to 3.2%. This suggests some hindrance behaviour. As for the selectivity of different products, the 1,2-PD and H-AC selectivity interestingly increased from 38.3% to 53.2% and from 9.8 to 19.2%, respectively with increasing the catalyst loading from 0.3 to 0.97 g. On the other hand, EG selectivity decreased from 20.6 to 9.3%.

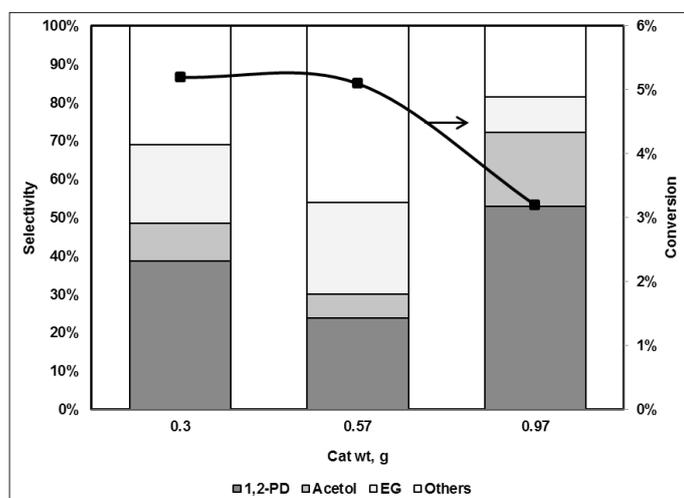


Fig. 1 Effect of amount of catalyst on the conversion of glycerol and the selectivity of main products. Reaction conditions: 40 bar total pressure, 200 °C, 5 wt% initial solution, 150 mL feed volume, 1500 rpm stirring speed, and 4 h reaction time

3.4 Effect of temperature

The temperature effect was investigated at 200, 220, and 240 °C, respectively. Table 3 and Fig. 2 summarize the experimental results of the effect of temperature on glycerol hydrogenolysis on Cat Ir. The conversion of glycerol increased from 5.2% to 13.3%, the 1,2-PD selectivity gradually increased from 38.8% to 49.4% passing through a maximum value of 53.9%

at 220 °C, and the EG selectivity decreased from 20.6% to 5.1% with increasing the temperature from 200 to 240 °C. As expected, the hydrogenolysis of glycerol has accelerated with the temperature increase. Moreover, there was an appreciable increase in the H-AC selectivity from 9.8% to 30.9% with the temperature rise. In the meanwhile, EG selectivity showed a systematic decrease with temperature.

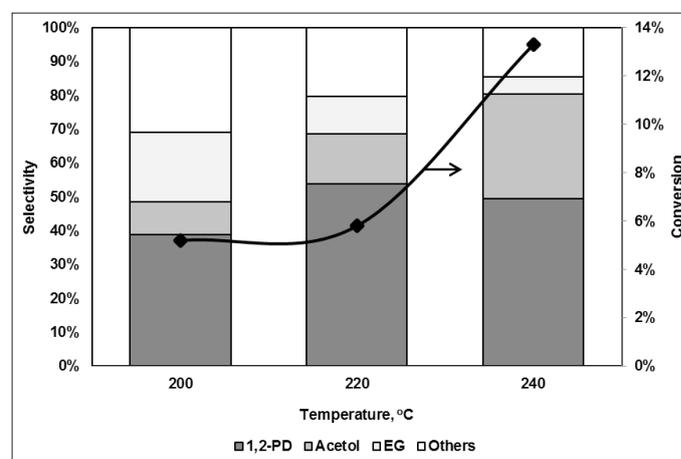


Fig. 2 Effect of temperature on the conversion of glycerol and the selectivity of main products. Reaction conditions: 40 bar total pressure, 0.3 g catalyst, 5 wt% initial solution, 150 mL feed volume, 1500 rpm stirring speed, and 4 h reaction time

3.5 Effect of hydrogen pressure

The glycerol hydrogenolysis reaction generally occurs at elevated hydrogen pressures, indicating that it is an important parameter in the reaction. The pressure effect was investigated at 20, 40, and 80 bar total hydrogen pressures, respectively. Table 4 presents the experimental results of the influence of hydrogen pressure on glycerol hydrogenolysis on Cat Ir. Fig. 3 depicts the influence of changing hydrogen pressure on the glycerol conversion and the selectivity of the main products (1,2-PD, Acetol, EG, and other products) in the range of 20-80 bar total hydrogen pressure. As can be seen, with increasing total pressure, the conversion level of glycerol increased slightly from 4.9% to 5.3%. Though, there was no systematic trend in the change of the selectivity of the hydrogenolysis products. However, there was a notable reduction in the total selectivity towards gaseous hydrogenolysis products with increasing the pressure up to 80 bar.

Table 2 Glycerol hydrogenolysis experiments on Ir/Al₂O₃ catalyst. Reaction conditions: 40 bar total pressure, 200 °C, 5 wt% initial solution, 150 mL feed volume, 1500 rpm stirring speed, and 4 h reaction time

Cat weight, g	C-Material balance, 100%	Conversion, 100%	Selectivity, 100%											
			AC	MeOH	i-PrOH	EtOH	n-PrOH	H-AC	1,2-PD	EG	CH ₄	CO ₂	C ₂ H ₆	C ₃ H ₈
0.3	96.8	5.2	0.7	7.0	4.4	10.9	5.5	9.8	38.8	20.5	2.2	0.0	0.1	0.1
0.57	97.2	5.1	0.7	11.3	8.5	12.5	9.9	6.4	23.8	23.8	2.9	0.0	0.2	0.0
0.97	98.1	3.2	0.6	2.4	0.9	8.0	3.8	19.2	53.1	9.3	2.4	0.0	0.2	0.1

Table 3 Glycerol hydrogenolysis experiments on Ir/Al₂O₃ catalyst (Temperature effect) (0.3 g catalyst, 40 bar, 1500 rpm, 5 wt% Glyc in H₂O, 150 mL)

T, °C	C-Material balance, 100%	Conversion, 100%	Selectivity, 100%											
			AC	MeOH	i-PrOH	EtOH	n-PrOH	H-AC	1,2-PD	EG	CH ₄	CO ₂	C ₂ H ₆	C ₃ H ₈
200	96.8	5.2	0.7	7.0	4.4	10.9	5.5	9.8	38.8	20.5	2.2	0.0	0.1	0.1
220	98.2	5.8	0.8	5.4	3.1	5.4	3.8	14.6	53.9	11.1	1.5	0.1	0.2	0.1
240	96.3	13.3	1.0	1.8	0.5	2.8	6.8	30.9	49.4	5.1	1.3	0.2	0.1	0.1

Table 4 Glycerol hydrogenolysis experiments on Ir/Al₂O₃ catalyst (Pressure effect) (0.3 g catalyst, 200 °C, 1500 rpm, 5 wt% Glyc in H₂O, 150 mL)

P, bar	C-Material balance, 100%	Conversion, 100%	Selectivity, 100%											
			AC	MeOH	i-PrOH	EtOH	n-PrOH	H-AC	1,2-PD	EG	CH ₄	CO ₂	C ₂ H ₆	C ₃ H ₈
20	96.7	4.9	0.5	1.6	0.4	3.9	1.5	36.6	45.2	8.2	1.6	0.2	0.2	0.1
40	96.8	5.2	0.7	7.0	4.4	10.9	5.5	9.8	38.8	20.5	2.2	0.0	0.1	0.1
80	95.7	5.3	0.5	2.8	1.0	9.7	7.0	14.9	46.4	16.8	0.9	0.0	0.0	0.0

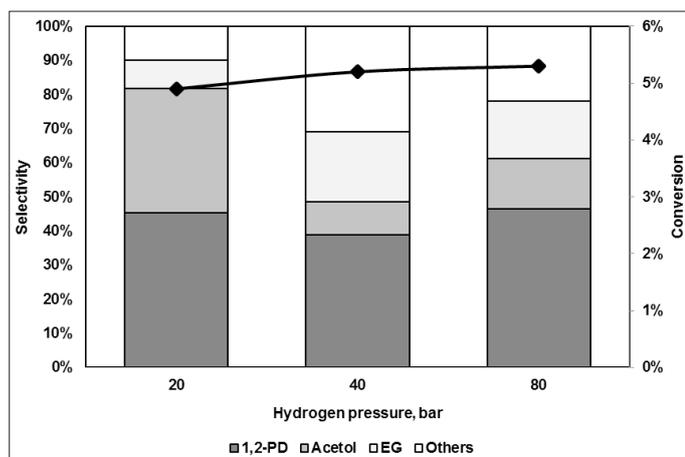


Fig. 3 Effect of hydrogen pressure on the conversion of glycerol and the selectivity of main products. Reaction conditions: 0.3 g catalyst, 200 °C, 5 wt% initial solution, 150 mL feed volume, 1500 rpm stirring speed, and 4 h reaction time

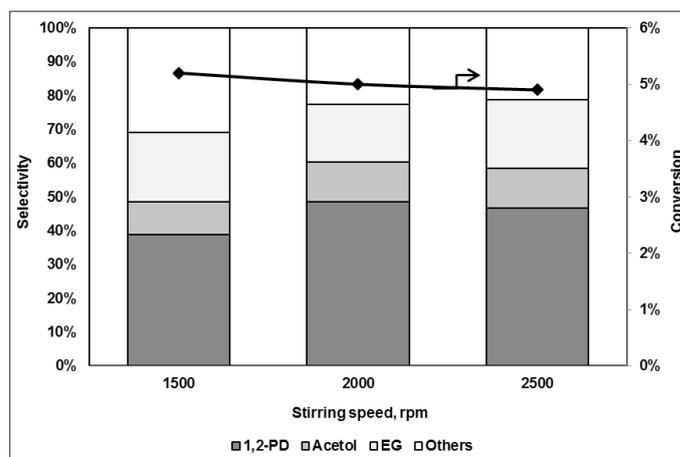


Fig. 4 Effect of stirring speed on the conversion of glycerol and the selectivity of main products. Reaction conditions: 0.3 g catalyst, 200 °C, 40 bar total pressure, 5 wt% initial solution, 150 mL feed volume, and 4 h reaction time

3.6 Effect of stirring speed

The effect of changing stirring speed was investigated at three different speeds of values: 1500, 2000, and 2500 rpm, respectively. This can potentially provide a basis for further kinetic studies. Table 5 and Fig. 4 summarize the experimental results of the effect of varying stirring speed on crude glycerol hydrogenolysis over Cat Ir. No external mass transfer limitation was detected, as the conversion values acquired at the three different stirring speeds were nearly the same. In addition, all the selectivity values attained were essentially unchanged at the three stirring speeds.

3.7 Effect of pH

Table 6 reports the effect of varying alkalinity on the hydrogenolysis of crude glycerol over Cat Ir employing 0.1M NaOH solution as a reaction medium, under the previous stated experimental standard conditions. The presence of NaOH resulted in a significant increase in the glycerol conversion from 5.2% to 22%, suggesting that the base can serve as a co-catalyst in the hydrogenolysis of glycerol. This agrees well with results obtained in literature by different catalysts under basic conditions, as an increase in the catalyst activity was expected in the

Table 5 Glycerol hydrogenolysis experiments on Ir/Al₂O₃ catalyst (Stirring speed effect) (0.3 g catalyst 200 °C, 40 bar, 5 wt% Glyc in H₂O, 150 mL)

Speed, rpm	C-Material balance, 100%	Conversion, 100%	Selectivity, 100%											
			AC	MeOH	i-PrOH	EtOH	n-PrOH	H-AC	1,2-PD	EG	CH ₄	CO ₂	C ₂ H ₆	C ₃ H ₈
1500	96.8	5.2	0.7	7.0	4.4	10.9	5.5	9.8	38.8	20.5	2.2	0.0	0.1	0.1
2000	96.3	5.0	1.3	3.7	1.9	7.8	4.8	11.7	48.5	17.2	2.5	0.1	0.3	0.2
2500	96.3	4.9	1.2	3.6	1.5	7.4	4.5	11.7	46.8	20.2	2.7	0.1	0.2	0.1

Table 6 Glycerol hydrogenolysis experiments on Ir/Al₂O₃ catalyst (pH effect) (0.3 g catalyst 200 °C, 40 bar, 1500 rpm, 5 wt% Glyc in H₂O, 150 mL)

Medium	C-Material balance, 100%	Conversion, 100%	Selectivity, 100%											
			Acetone	MeOH	i-PrOH	EtOH	n-PrOH	H-AC	1,2-PD	EG	CH ₄	CO ₂	C ₂ H ₆	C ₃ H ₈
Neutral	96.8	5.2	0.7	7.0	4.4	10.9	5.5	9.8	38.8	20.5	2.2	0.0	0.1	0.1
In 0.1 M NaOH	82.8	22.0	8.4	5.0	1.1	2.8	4.1	0.0	70.3	7.9	0.3	0.0	0.0	0.1

basic environment [6, 30]. In addition, a remarkable change in the selectivity of 1,2-PD, H-AC, AC, and EG was observed. The 1,2-PD selectivity increased from 38.8% to 70.3%, the H-AC selectivity decreased from 9.8% to 0%, the AC selectivity increased from 0.7% to about 8.4%, and the EG selectivity decreased from 20.6% to 7.9% with increasing the alkalinity of the reaction medium. Interestingly, the increase in the 1,2-PD selectivity value attributed to the increased hydroxide concentration was found to be a significant boost over the prepared catalyst, highlighting that the base addition can aid the initial dehydrogenation of glycerol to glyceraldehyde. On the other hand, the decrease in the selectivity of EG, in particular, can be due to conversion of a reactive intermediate between EG and glyceraldehyde that subsequently eliminates some substance from the glycol route to a degradation product pathway. Also, it can be referred to the fact that the retro-aldol reaction of glyceraldehyde is very difficult under basic conditions [31].

4 Conclusions

Iridium-supported catalyst on γ -Al₂O₃ were prepared for hydrogenolysis of crude glycerol derived from biodiesel industry for the sake of producing value-added chemicals from this biowaste. The effects of key reaction parameters like catalyst amount, temperature, hydrogen pressure, stirring speed, and solution pH on the conversion of glycerol and the selectivity of the main products obtained were investigated. The glycerol conversion and the 1,2-PD selectivity were dependent on the reaction parameters. It was remarked that the highest glycerol conversion and the highest 1,2-PD selectivity were obtained through increasing the alkalinity of the reaction medium. The effect of pH will be thoroughly considered in future studies to determine the optimal reaction conditions that achieve higher glycerol conversion and 1,2-PD selectivity.

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Dedication

This paper is dedicated to the memory of George W. Roberts, Professor Emeritus and Former Department Head of Chemical & Biomolecular Engineering at North Carolina State University.

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