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Catalytic hydrogenolysis of glycerol into propyl acetate with

ruthenium complexes

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Abstract: Ru complexes have been utilized as catalyst precursors for glycerol hydrogenolysis under mild conditions, which gave propyl acetate (PA) as a major product. Notably, the esterification reaction of acetic acid with glycerol can prevent glycerol from polymerization. $In(OTf)_3$ played a critical role in facilitating esterification of glycerol and sequential dehydration, while the Ru complexes' function was hydrogenation. The promoter (FeCl₃) can suppress the reduction of Ru complex to Ru particles, improving the catalytic performance. The present catalytic system can give full glycerol conversion and 57% yield of PA. Finally, the reaction pathway was proposed accordingly.

Keywords: Glycerol hydrogenolysis; Propyl acetate; Ruthenium complexes; Homogeneous catalysis.

1. Introduction

The dependence of human well-being on fossil fuels will have to be reduced in the future, mainly owing to geopolitical, natural resource scarcity and environmental factors [1]. The use of renewable biomass resources as a partial replacements for petroleum-derived chemicals and fossil fuels is essential for the sustainable development of our society [2, 3]. The transesterification of vegetable oils with alcohols gives bio-diesel, a fuel that can be used directly in diesel engines. However, the transesterification process co-generates glycerol at a rate of 1 mol for every 3 mol of alkyl-fatty esters synthesized [4, 5], decreasing the atom efficiency and economic feasibility of the process. It is therefore essential to find effective approaches to use this oversupply of glycerol, which would enhance the biodiesel economy [6].

Based on the current research, glycerol can be catalytically converted into value-added chemicals by hydrogenolysis, oxidation, dehydration, etherification, esterification and polymerization, etc [7-10]. One of the most important approach is the hydrogenolysis of glycerol to propanediols (PDOs), which have found considerable application in the manufacture of fine chemicals and polymers [11, 12]. Supported heterogeneous metal (Rh, Ir, Ru, Pd, Co, Ni, etc.) catalysts have been widely applied for the hydrogenolysis of glycerol under a temperature condition of 250-350 °C [13-15]. Vapor phase hydrogenolysis of glycerol to PDOs has also been studied recently. Zeolites or metal oxide supported Ru catalysts exhibited good catalytic activity at 230-280 °C [16,17].

However, much less efforts were constructed to convert glycerol into 1-propanol (1-PO) up to date, although 1-PO is a valuable chemical used as solvent, organic intermediate and raw materials. 1-PO is industrially produced via hydroformylation of ethylene and subsequent hydrogenation [18]. The synthesis of 1-PO from biomass is a potential alternative to petroleum-derived processes, which has attracted great interest recently. It has been reported that Pd/C catalyst gave a promising selectivity to 1-PO (87.7%) under batch-reaction conditions, but the conversion of glycerol was poor (4.5%) [19]. Furthermore, the sequential two-layer catalysts containing H β zeolite and Ni/Al₂O₃ catalyst can provide good 1-PO selectivity (69%) at full glycerol conversion [20]. In our previous studies, we found that the two sequential zirconium phosphate

and Ru/SiO₂ layer catalyst system also showed a good selectivity (77%) to 1-PO at full of glycerol conversion [21]. Nevertheless, the reactions above were normally conducted under fairly harsh conditions (>200 °C).

Comparatively, although the easily available RuCl₂(PPh₃)₃, RuHCl(PPh₃)₃ and $RuCl_2(dppp)_2$ complexes were highly active for the hydrogenation reaction [22-24] and these Ru complexes have rarely applied to glycerol hydrogenolysis. It was reported that the HI/Ru(CO)₄I₂ catalyst system was active for the conversion of glycerol into 1-PO (25.4% yield) [25]. In addition, the Ru complexes [Cp*Ru(OH₂)(N-N)]⁺OTf { $[Cp*Ru(CO)_2]_2(\mu-H)$ }⁺OTf and $(Cp^*=\eta^5$ -pentamethylcyclopentadieny; N-N=2,2'-ipyridine or phen=1,10-phenanthroline; OTf=trifluoromethanesulfonate) also afforded moderate yield of 1-PO (<20%) in the presence of HOTf [26, 27]. These results demonstrated the homogeneous Ru complexes were indeed capable of catalyzing hydrogenolysis of glycerol under mild conditions, but the catalytic efficiency of this process needs to be substantially improved.

In this work, glycerol was hydrogenolyzed by using Ru(II) complexes in acetic acid (HOAc) under mild conditions. After the reaction, PA was detected as a dominant product, and 1,3-propyleneglycol diacetate (1,3-PGDA), 1,2-propyleneglycol diacetate (1,2-PGDA), triacetin (TA) and monoacetin (MA) as minor products. It is well known that propyl acetate (PA) can be readily hydrolyzed to 1-PO and is also primarily intended as a good solvent and a flavor additive. PGDAs, TA and MA are all important chemicals and applied in the manufacture of dyes, plasticizers and pharmaceuticals etc [28, 29]. Hence, it is highly promising that glycerol can be transformed into PA and other valuable chemicals like PGDAs, TA and MA effectively through an alternative, biomass-derived approach.

2. Results and discussion

2.1 Glycerol hydrogenlysis with Ru(II) complexes

Initially, the Ru(II) complexes (Fig. S1-S6) have been prepared and screened for the glycerol hydrogenlysis in the presence of the acidic additives and HOAc solvent.

For the sake of comparison, commercially supplied RuCl₃·3H₂O and Ru(acac)₃ were also used as catalysts. As shown in Fig. 1, it indicated that although glycerol was consumed completely after 12 h, only a trace of PA and TA were found without Ru catalysts. All products were obtained in the form of acetates due to the presence of excess HOAc. The yield of PA can reach up to 40% with RuCl₂(PPh₃)₃ (Fig. 1). However, if RuCl₂(PPh₃)₃ was replaced by RuCl₂(dppp)₂, RuCl₃·3H₂O, RuHCl(PPh₃)₃ and Ru(acac)₃, the yield of PA was lower (Fig. 1). Thus RuCl₂(PPh₃)₃ was the most efficient catalyst for the glycerol hydrogenolysis.

<Insert Fig. 1>

Next, the influence of dosage of Ru(II) complex on the reaction have been examined. Fig. S7 demonstrated that PA yield increased with the concentration of RuCl₂(PPh₃)₃ catalyst (C_{cat.}) ranged from 2 mmol/L to 7 mmol/L, which can be attributed to more active ruthenium centres accessible to substrate molecules. However, if C_{cat.} raised continuously, the yield of PA leveled off. This demonstrated that C_{cat.} had a great influence on yield of PA, and the optimal yield was achieved at C_{cat.}=5 mmol/L.

Since the acid was shown to be crucial in the hydrogenolysis of glycerol [30], the impact of different types of Lewis acids and Brønsted acids on PA yield was examined thereafter. As shown in Fig. 2, PA yield was improved by adding acids. It can be seen that the addition of Brønsted acids gave rise to an increase of PA yield following the order: HOTs·H2O<HOTf<PW12<HNTf2 (Fig. 2). Interestingly, except for PW12, the catalytic activity order was consistent with the acidity order of different acids, that is, HOTs·H2O(pKa=-1.90)<HOTf(pKa=-3.91)<HNTf₂(pKa=-10.42)<PW₁₂(pKa=-13.16). The effect of Lewis acids on the catalytic activity was also examined. The catalytic activity towards PA formation increased in the order: Bi(OTf)₃< Zn(OTf)₂<Ce(OTf)₃<Y(OTf)₃<Al(OTf)₃<Sc(OTf)₃<In(OTf)₃ (Fig. 2). According to the previous report [31], (ion charge)²/(ion radius) (e^{2}/r) can be used as an approximate measure for the electron-withdrawing ability, or in other word, Lewis

acidity of metal cations. The catalytic activity order was partially consistent with e^2/r order, that is, Zn^{2+} (5.4 Å⁻¹)<Bi³⁺ (8.3 Å⁻¹)<Ce³⁺ (8.7 Å⁻¹)<Y³⁺ (10.0 Å⁻¹)<Sc³⁺ (11.1 Å⁻¹)<Al³⁺ (18.0 Å⁻¹). Moreover, Lewis acidity was expressed by H₀ (Table S1), and the H₀ order of different Lewis acids was consistent with e^2/r order. These results indicated that strong Lewis acids like In(OTf)₃ activate glycerol molecule at the beginning of reaction, with the intermediate product undergoing sequential dehydration and hydrogenation.

<Insert Fig. 2>

Because $In(OTf)_3$ was an effective acidic additive for producing PA (Fig. 2), the effect the concentration of $In(OTf)_3$ was examined and the results were shown in Table S2. It was observed that the yield of PA increased from 15% to 40% as the n_{sub}/n_{acid} ratio increased from 6:1 to 8:1. However, when the n_{sub}/n_{acid} further increased to 16:1, the PA yield decreased continuously from 40% to 12%. This indicated that an excess of acidic additive could result in more side-reactions due to the occurrence of glycerol polymerization and coking [32].

2.2 The role of FeCl₃ in glycerol hydrogenolysis

In the next step, promoters were added to further improve the PA yield. As shown in Fig. S8, the use of $Co(CH_3COO)_2 \cdot 4H_2O$ and $CoCl_2 \cdot 6H_2O$ had an only marginal effect on PA yield, while the addition of $Co_2(CO)_8$, $Cu(CH_3COO)_2 \cdot 4H_2O$, $AlCl_3$, $CuCl_2 \cdot 4H_2O$, $Ni(CH_3COO)_2 \cdot 4H_2O$ and $InCl_3$ produced a negative effect (Fig. S8). To our delight, the use of FeCl_3 led to a significant increase of PA yield. It was worth noticing that MA and TA were main products if $In(OTf)_3$ was replaced by FeCl_3 (Fig. S8), indicating that $In(OTf)_3$ was essential for the formation of PA.

It was visually observed that the homogeneous mixture changed from brick-red to brown after reaction. It was hypothesized that $RuCl_2(PPh_3)_3$ was reduced by H_2 and deactivated in the course of reaction. To further identify the role of FeCl₃, HRTEM was employed to discern the nature of reaction mixture. It can be seen that Ru

nanoparticles (around 5-8 nm) were generated in the absence of FeCl₃ (Fig. 3, left). Nevertheless, the reaction mixture was transparent and no particles can be observed when FeCl₃ was added to the reaction system (Fig. 3, right). It indicated that FeCl₃ can prevent the formation of Ru nanoparticles. ³¹P NMR spectra of RuCl₂(PPh₃)₃ did not change after treatment with FeCl₃ (Fig. S9), indicating that the Ru complex was actually not influenced by the FeCl₃. Additionally, the images of HRTEM showed that Ru nanoparticles indeed disappeared once FeCl₃ was added. Meantime, the color of reaction mixture became almost colorless in the presence of FeCl₃ (Fig. S10). As a result, we proposed that the oxidizing ability of Fe(III) may be involved in impeding the tendency of forming Ru(0) cluster [33].

< Insert Fig. 3>

As shown in Fig. S11, after reaction, the 31 P NMR resonance signal of the Ru complex (around 42 ppm) was still seen although the intensity became weaker. The signal at 24 ppm was assigned to OPPh₃. New peaks around 46-48 ppm could be attributed to the ruthenium dihydride [RuH₂(PPh₃)₄] or its derivatives after hydrogenation reaction. This indicated that a part of Ru(II) complexes underwent a possible structural evolution in the course of hydrogenation reaction [34].

Based on the activity evaluation, the effect of reaction temperature on the catalytic activity was examined. As shown in Table S3, the conversion of glycerol increased from 83% to 100% as the reaction temperature increased from 120 to 180 °C (Table S3, entries 1-3). Actually, PA was generated starting at 150 °C, and the yield increased remarkably with the temperature until 180 °C. This indicated that the production of PA was facilitated at higher reaction temperature. However, the amount of glycerol lost to unidentified products also increased at the elevated temperature condition (Table S3, entries 4 and 5). Also, a large amount of black precipitate was observed at the bottom of liner after the reaction. The glycerol polymerization under high temperature may account for the partially deficient mass balances. Another possibility that would explain the mass balance is that the glycerol is deoxygenated to

the gas phase products, which due to their low solubility in the polar reaction mixture and are lost upon venting the reactor. GC analysis of gas samples collected from the head space indicated that propane, methane (CH₄) and CO₂ were indeed formed. But total yield of the three gases was less than 5%. Hence, the main reason for the loss of mass balance resulted from glycerol polymerization. This demonstrated that an appropriate reaction temperature was crucial for the conversion of glycerol to PA. Thus the optimal yield of PA can reach 57% around 180 °C.

Subsequently, the impact of H₂ pressure on the glycerol hydrogenolysis was studied, and the results are shown in Fig. S12a. The conversion of glycerol was normally close to 100% in the pressure range of 1-7 MPa. However, the yield of PA was increased obviously as the H₂ pressure was increased from 1 MPa to 5 MPa. A reasonable explanation was that more H₂ can be dissolved in HOAc as increasing reaction pressure, which was favorable for the hydrogenation of intermediates into PA. However, the PA yield did not show more obvious changes and propane was found in a small amount under higher pressure of H_2 (>5 MPa). On the other hand, the impact of reaction time on the glycerol hydrogenolysis was also examined. As shown in Fig. S12b, the conversion of glycerol gradually increased from 2 h to 12 h reaching close to 100 % after 12 - 16 h. The yield of PA increased slowly within 8 h, but it raised sharply as the reaction was further prolonged to 12 h. The obvious increase of PA yield (57%) was obtained, accompanying with a decrease of other intermediate products (MA, TA, PGDAs). However, when reaction time was longer than 12 h, the yield of PA declined slightly and the yields of propane, CH₄ and CO₂ increased (Fig. S12b). It indicated that PA was possibly converted into gas-phase products at the prolonged reaction times.

Different organic solvents also produced a significant effect on the product yields. When HOAc was used as solvent, the main product was PA. As shown in Table S4, when HOAc was replaced by acetic anhydride, a large amount of black precipitate was produced after reaction. We believed that the deficient mass balance could result from the formation of the polymer under this condition. A similar tendency was observed when sulfolane and acetonitrile were used as solvents. As a result, HOAc

was advantageous for the glycerol hydrogenolysis due to esterification reaction of glycerol by HOAc, suppressing the polymerization of glycerol to some extent.

Glycerol conversion in the presence of different components was summarized in Table S5. It demonstrated that the absence of FeCl₃, PPh₃ or In(OTf)₃ led to a significant decrease of PA yield (Table S5, entries 4, 6 and 7). The results above indicated that all components are essential for glycerol hydrogenolysis into PA (Table S5, entries 1-10).

2.3 Reaction pathway

In order to explore the reaction pathway, the possible intermediate species in glycerol hydrogenolysis were hydrogenated with RuCl₂(PPh₃)₃ under the same condition. As shown in Table 1, both 1,2-PDO and HA could be converted completely and the main product was PA (Table 1, entries 1 and 3). Nevertheless, 1,3-PDO only gave esterification products without further hydrogenation (Table 1, entry 2). If AE was used as substrate, self-polymerization occurred and only a trace of PA was detected (Table 1, entry 4). Especially, when MA and TA were used as substrates, PA was formed in substantial amounts and even the former was converted into PA with much better yield (Table 1, entries 5 vs 6). Notably, it was observed that when only either acid or Ru catalyst was present, the main products were MA and TA, and no PA was found in the products (Table S5, entries 8-10), demonstrating that both the acid and Ru catalyst are important for the production of PA. In addition, it can be inferred that FeCl₃ played an important role in not only preventing from forming Ru nanoparticles, but also enhancing the esterification reaction of glycerol with HOAc (Table S5, entries 8 vs 9). With respect to the results above, it is highly believable that MA was an important intermediate due to the excess of HOAc as solvent, although TA was not excluded as an intermediate.

< Insert Table 1>

Overall, a conceivable reaction mechanism is proposed in Scheme 1. Glycerol

was initially esterified with HOAc through an acid-catalyzed reaction to form intermediate (MA) and then MA was subsequently dehydrated and hydrogenated to generate 1,3-propyleneglycol monoacetate (1,3-PGMA) and 1,2-propyleneglycol monoacetate (1,2-PGMA). PA was produced by further dehydration and the sequential hydrogenation over Lewis acid and Ru(II) complex. In addition, 1,3-PGDA and 1,2-PGDA were obtained as minor by-products via hydrogenation and esterification (Scheme 1). The preferential dehydration reaction of PGMAs over esterification reaction is the main cause for high selectivity towards PA. Noteworthy is that the esterification reaction of HOAc with glycerol played a key role in inhibiting the polymerization of glycerol to polyether, in comparison with that of the other solvents (Table S4).

< Insert Scheme 1>

3. Conclusion

In summary, an alternative approach has been developed for the catalytic transformation of glycerol to C3 alcohol acetate over Ru(II) complexes. It indicated that the RuCl₂(PPh₃)₃ as a catalyst precursor gave 57% PA yield at full of glycerol conversion under reaction conditions. FeCl₃, In(OTf)₃ and RuCl₂(PPh₃)₃ were indispensable for the glycerol hydrogenolysis involving esterification, dehydration and hydrogenation process. Compared with heterogeneous catalytic system, the present homogeneous catalytic system, due to its easy preparation, high efficiency, and mild conditions, has a great potential for the transformation of glycerol into value-added chemicals.

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Figure and Table captions

Fig. 1 The Ru complex-catalyzed hydrogenolysis of glycerol. Reaction conditions: glycerol 5 mmol, Ru catalysts 0.025 mmol, PPh₃ 0.075 mmol, $In(OTf)_3$ 0.6 mmol, HOAc 5 mL, 180 °C, 12 h, 5 MPa H₂. The glycerol conversion was normally more than 99%.

Fig. 2 Impact of the acidic additives on product yields. Reaction conditions: glycerol 5 mmol, $RuCl_2(PPh_3)_3 0.025$ mmol, PPh₃ 0.075 mmol, acid 0.6 mmol, HOAc 5 mL, 180 °C, 12 h, 5 MPa H₂. The glycerol conversion was normally more than 99%.

Fig. 3 HRTEM images of the reaction mixture without $FeCl_3$ (Left) and with $FeCl_3$ as promoter (Right). Inset (Left): the image with higher magnification.

Table 1 The conversion of the possible intermediates in glycerol hydrogenolysis.

Scheme 1 The proposed mechanism for glycerol hydrogenolysis catalyzed by Ru catalyst in HOAc solvent. In(OTf)₃ was used as acid catalyst (Acid Cat.) and $RuCl_2(PPh_3)_3$ as Ru catalyst (Ru Cat.).



Fig. 1 The Ru complex-catalyzed hydrogenolysis of glycerol. Reaction conditions: glycerol 5 mmol, Ru catalysts 0.025 mmol, PPh₃ 0.075 mmol, $In(OTf)_3$ 0.6 mmol, HOAc 5 mL, 180 °C, 12 h, 5 MPa H₂. The glycerol conversion was normally more than 99%.



Fig. 2 Impact of the acidic additives on product yields. Reaction conditions: glycerol 5 mmol, $RuCl_2(PPh_3)_3 0.025$ mmol, $PPh_3 0.075$ mmol, acid 0.6 mmol, HOAc 5 mL, 180 °C, 12 h, 5 MPa H₂. The glycerol conversion was normally more than 99%.



Fig. 3 HRTEM images of the reaction mixture without $FeCl_3$ (Left) and with $FeCl_3$ as promoter (Right). Inset (Left): the image with higher magnification.

			Yield(%)					
Entry	Substrates	Con (%)	PA	1,2-PGMA	1,2-PGDA	1,3-PGMA	1,3-PGDA	
1	1,2-PDO	100	41	2	1		-	
2	1,3-PDO	100	3	-	-0	6	28	
3	HA	100	30	2	5	-	-	
4	AE	100	3	-		-	-	
5	MA	100	39	- <	1	-	1	
6	TA	95	15	-	3	-	-	

Table 1 The conversion of the possible intermediates in glycerol hydrogenolysis.

Reaction conditions: substrate 5 mmol, RuCl₂(PPh₃)₃ 0.025 mmol, PPh₃ 0.075 mmol, In(OTf)₃ 0.6 mmol, FeCl₃ 0.1 mmol, HOAc 5 mL, 180 °C, 12 h, 5 MPa H₂. (1,2-PDO=1,2-propanediol, 1,3-PDO=1,3-propanediol, HA=hydroxyacetone, AE=acrolein, MA=monoacetin, TA=triacetin, PA=propyl acetate, 1,2-PGMA= 1,2-propyleneglycol monoacetate, 1,3-PGMA=1,3-propyleneglycol monoacetate, 1,2-PGDA=1,2-propyleneglycol diacetate, 1,3-PGDA=1,3-propyleneglycol diacetate.)



Scheme 1 The proposed mechanism for glycerol hydrogenolysis catalyzed by Ru catalyst in HOAc solvent. In(OTf)₃ was used as acid catalyst (Acid Cat.) and $RuCl_2(PPh_3)_3$ as Ru catalyst (Ru Cat.).

Highlight

- Easily available Ru complexes have been utilized for hydrogenolysis of glycerol.
- The reaction can be carried out under relatively mild conditions.
- The hydrogenolysis of glycerol gave propyl acetate (PA) as a major product.
- The In(CF₃SO₃)₃ played a very critical role in the esterification and dehydration.
- The co-catalyst (FeCl₃) can suppress the reduction of Ru complex to Ru particles.

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