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Hydrogenolysis of Glycerol to Propanediol Over Ru: Polyoxometalate Bifunctional Catalyst

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Abstract Ruthenium-doped (5 wt%) acidic heteropoly salt $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (CsPW) is an active bifunctional catalyst for the one-pot hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) in liquid phase, providing 96% selectivity to 1,2-PDO at 21% glycerol conversion at 150 °C and an unprecedented low hydrogen pressure of 5 bar. Rhodium catalyst, 5%Rh/CsPW, although less active, shows considerable selectivity to 1,3-PDO (7.1%), with 1,2-PDO being the main product (65%).

Keywords Glycerol · Propanediol · Hydrogenolysis · Ruthenium · Polyoxometalate

1 Introduction

Production of marketable chemicals via the catalytic transformation of renewable bioresources is a global challenge [1]. Glycerol is one of the top 12 building block chemicals that can be derived from plant sources [1]. In addition, the development of biodiesel production by transesterification of vegetable oils makes large amounts of glycerol available as a reaction by-product, ca. 10 wt% of the biodiesel produced [2]. The availability and low price of glycerol make it a promising feedstock for producing a wide range of value-added chemicals. Synthesis of propanediols, 1,2-PDO and 1,3-PDO, from glycerol has attracted significant interest [3–8]. 1,2-PDO is an important commodity chemical, which finds use as antifreeze, aircraft deicer and lubricant. 1,3-PDO is copolymerised with terephthalic acid to produce polyesters, which are used for manufacturing carpet and textile fibres exhibiting strong chemical and light resistance [3].

1,2-PDO and 1,3-PDO are currently produced from petroleum derivatives by chemical catalytic routes: 1,2-PDO from propylene oxide and 1,3-PDO from ethylene oxide or acrolein [9]. These diols can be produced by an alternative route involving hydrogenolysis of glycerol. A number of patents and papers have disclosed the hydrogenolysis of glycerol in the presence of homogeneous and heterogeneous catalysts ([3–8] and references therein). This reaction has been carried out in liquid-phase batch systems at 110–260 °C and an H_2 pressure up to 300 bar yielding 1,2- and 1,3-PDO together with 1- and 2-propanol, ethylene glycol, ethanol and methane as byproducts. More efficient hydrogenolysis procedures that have been reported recently employ CuO–ZnO (200 °C, 42 bar, 12 h) [3, 7], copper chromite (200 °C, 14 bar, 24 h) [4] and 5%Ru/C + Amberlyst-15 (120 °C, 80 bar, 10 h) [5, 6] as heterogeneous catalysts. These procedures, however, have serious drawbacks such as high temperature and pressure of the process, low selectivity to propanediols, and low catalyst activity hence low glycerol conversion and long reaction times.

The hydrogenolysis of glycerol to 1,2-PDO and 1,3-PDO is suggested to proceed via dehydration of glycerol to acetol and 3-hydroxypropanal by acid catalysis followed by catalytic hydrogenation (Scheme 1), which has been supported by the observation of acetol amongst the reaction products and its selective hydrogenation to 1,2-PDO [4–6]. Alternatively, dehydrogenation of glycerol to glyceraldehyde followed by dehydration to 2-hydroxyacrolein and hydrogenation to yield 1,2-PDO (Scheme 2) has been suggested [8, 10]. These mechanisms imply that bifunctional acid/hydrogenation catalysis should be an effective course to carry out the glycerol hydrogenolysis in one-pot system.

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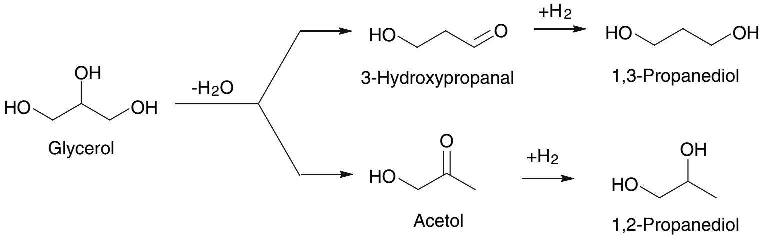
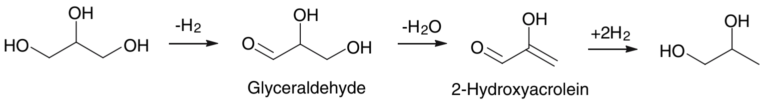
Scheme 1 Hydrogenolysis of glycerol to 1,2-PDO and 1,3-PDO



Scheme 2 Hydrogenolysis of glycerol to 1,2-PDO via glyceraldehyde



Multifunctional catalysis is considered an important future direction of sustainable organic synthesis to effect multi-step reactions in one-pot systems without separating intermediate products [11]. Recently, Miyazawa et al. [5, 6] have used a mixture of 5%Ru/C as a hydrogenation catalyst and Amberlyst-15 acid resin as an acid catalyst for glycerol hydrogenolysis in one-pot system. However, catalyst performance was rather poor: 1,2-POD together with 1,3-POD were obtained with 55 and 5% selectivity, respectively at 13% glycerol conversion. A serious drawback to Amberlyst-15 was its decomposition above 120 °C [5]. In this system, Rh/C also exhibited some catalytic activity, whereas Pd/C and Pt/C were practically inactive.

The aim of this work is to study the hydrogenolysis of glycerol to propanediols using multifunctional catalysis by polyoxometalates modified with ruthenium and rhodium. Polyoxometalates (POMs), especially those of Keggin structure, have found numerous applications as catalysts [12–14]. These are inherently multifunctional compounds [12–14]. Their acid and redox properties can be tuned by varying POM composition. Solid POMs allow for considerable alteration of their texture and can be modified to introduce another chemical function, e.g. metal function [12–14]. Solid Keggin heteropoly acids, e.g. $H_3[PW_{12}O_{40}]$, doped with Pd and Pt have been reported as bifunctional catalysts for alkane isomerisation [15, 16]. Pd-doped heteropoly acid is an active bifunctional catalyst for one-pot hydrogenation of acetone to MIBK [17] and citronellal to menthol [18]. Here we report the Ru-doped acidic heteropoly salt, $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ (CsPW), as an efficient bifunctional catalyst for the one-pot hydrogenolysis of glycerol to propanediol. CsPW is well known as a water-insoluble strong Brønsted acid and a versatile solid acid catalyst possessing considerable thermal stability (≥500 °C) [12–14].

2 Experimental

Glycerol, $RuCl_3 \cdot xH_2O$ and $RhCl_3 \cdot xH_2O$ were purchased from Aldrich. CsPW was prepared as a white nanocrystalline powder as described elsewhere [19]. 5%Ru/CsPW and 5%Rh/CsPW catalysts were prepared by impregnating CsPW with 0.1 M $RuCl_3$ or $RhCl_3$ aqueous solution. The slurry was stirred at room temperature for 24 h, dried in a rotary evaporator at 60 °C, followed by reduction by H_2 at 250 °C for 2 h. The catalyst was stored in a desiccator over P_2O_5.

Surface area and porosity of catalysts were measured by nitrogen physisorption on a Micromeritics ASAP 2000 instrument. Tungsten, ruthenium and rhodium content in the catalysts was measured by inductively coupled plasma (ICP) atomic emission spectroscopy on a Spectro Ciros CCD spectrometer. The dispersion of ruthenium in Ru/CsPW catalyst was measured by hydrogen chemisorption using a modification of Taylor method [20] on a Micromeritics TPD/TPR 2900 instrument. A catalyst sample (100 mg) pre-exposed to air for several days at room temperature was placed in a glass sample tube connected to the instrument and stabilised at 100 °C under nitrogen flow of 70 mL/min. 50 μL pulses of pure H_2 were injected in the flow in 3 min intervals until the catalyst was saturated with hydrogen. It should be noted that H_2 did not adsorb on CsPW under such conditions. The dispersion of ruthenium in the catalyst, D, defined as the fraction of ruthenium at the surface, $D = Ru_s/Ru_{total}$, was calculated assuming the stoichiometry of H_2 adsorption: $Ru_sO + 1.5H_2 \rightarrow Ru_sH + H_2O$ [20]. This stoichiometry has also been found for supported Pt and Pd catalysts [21]. The average size of Ru particles, d, was obtained from the empirical equation d (nm) = $0.9/D$ [20]. The same procedure was used for measuring Rh dispersion in 5%Rh/CsPW.

The hydrogenolysis of glycerol was carried out in a 45-mL Parr 4714 stainless steel autoclave equipped with a magnetic stirrer. The reaction mixture contained 5.0 mL of an aqueous solution of glycerol and 0.20 g catalyst unless stated otherwise. The autoclave was purged with H_2 then pressurised with H_2 (3–14 bar) and placed in the oil bath preheated to the required temperature. After reaction completion, the autoclave was cooled to 0 °C, depressurised and opened. The catalyst was separated by centrifugation.

Products were analysed by GC (Varian CP-3800 gas chromatograph, flame ionisation detector, 30 m × 0.32 mm × 0.5 μm CP-WAX 52 CB capillary column) using *n*-butanol as a standard. This column provided good separation of reaction products. Product selectivities were calculated as the molecular percentage of all organic products obtained.

3 Results and Discussion

Table 1 shows the BET surface area (S_{BET}), pore diameter and pore volume for the catalysts studied, including CsPW, 5%Ru/CsPW and 5%Rh/CsPW. From hydrogen chemisorption, the dispersion of ruthenium in the 5%Ru/CsPW catalyst was $D = 0.11$, corresponding to an average metal particle diameter of 8 nm. For rhodium, these values were 0.88 and 1 nm, respectively, indicating a strong interaction of Rh with CsPW.

Table 2 shows representative results for the hydrogenolysis of glycerol. The CsPW acidic salt itself was not active in the formation of propanediols, providing only a trace of acetol. With water in large excess, the formation of acetol by acid-catalysed dehydration of glycerol is probably limited by unfavourable equilibrium. The Ru/CsPW catalyst showed excellent performance in glycerol hydrogenolysis at an unprecedented low hydrogen pressure of 5 bar, producing selectively 1,2-PDO with only traces of 1,3-PDO under the reaction conditions studied. Acetol, 1- and 2-propanol (1-PO and 2-PO), ethylene glycol (EG) and methane were found amongst byproducts, similar to the previous reports [3–8]. The Ru/CsPW catalyst is much more selective than the Ru/C + Amberlyst-15 [5, 6]. It provides 88% 1,2-PDO selectivity (at 5 bar H_2) compared to 55% (at 80 bar H_2) [5] at similar glycerol conversions, other reaction conditions being the same (120 °C, 10 h, 20 wt% glycerol aqueous solution). As the temperature increases from 120 to 200 °C, the glycerol conversion increases from 9.8 to 27%, with 1,2-PDO selectivity decreasing to 65% mainly due to the formation of ethylene glycol. The latter has been suggested to form by C–C bond cleavage on ruthenium [5, 6, 8]. Our best results were obtained at 150 °C and 5 bar H_2 pressure: 96% 1,2-PDO selectivity at 21% glycerol conversion (20% yield of 1,2-PDO) with 4 wt% catalyst amount and 88% selectivity at 31% conversion (27% yield) with 6 wt% catalyst amount (Table 2). In this reaction, the catalyst turnover frequency (TOF) is 21 h^{-1}, as estimated from the Ru dispersion.

Table 1 Catalyst characterisation

Catalyst	S_{BET} (m^2/g)	Pore diameter (Å)	Pore volume (cm^3/g)	D^a	*d* (nm)
CsPW	123	35	0.107	–	20^b
5.0%Ru/CsPW	100	34	0.063	0.11	8^c
5.0%Rh/CsPW	85	33	0.048	0.88	1^c

[a] Metal dispersion from H_2 chemisorption

[b] CsPW particle size from XRD (the Scherrer equation)

[c] Metal particle size: $d = 0.9/D$

Figure 1 shows the effect of the initial hydrogen pressure on glycerol conversion and product selectivity for the reaction over Ru/CsPW. Unexpectedly, in contrast to other catalysts such as Ru/C + Amberlust-15 [5, 6] and copper chromite [4], the conversion of glycerol over Ru/CsPW instead of a monotonous growth passes a maximum at 5 bar H_2 pressure. The selectivity to ethylene glycol exhibits similar trend, whereas the selectivity to acetol decreases monotonously with increasing the H_2 pressure. The decrease in catalyst activity above 5 bar H_2 pressure may be explained by reduction of tungsten(VI) in CsPW which could lead to a decrease in catalyst acidity [14]. The deactivation due to reduction of W^{VI} may be overcome by using polyoxometalates with a higher negative polyanion charge, such as $SiW_{12}O_{40}^{4-}$ or $BW_{12}O_{40}^{5-}$, which are more difficult to reduce [22].

The conversion of glycerol increases with reaction time, reaching a plateau at about 30% conversion after 14 h (Fig. 2), which may be due to the abovementioned catalyst deactivation. The product selectivity depends weakly on the reaction time. It should be noted that 1,2-PDO and ethylene glycol form in parallel rather than consecutive reactions (Fig. 2), suggesting that the ethylene glycol mainly forms by the cleavage of C–C bond in glycerol or 1,2-PDO precursors rather than in 1,2-PDO itself.

The conversion of glycerol decreases with increasing glycerol concentration in the reaction mixture (Fig. 3). The 1,2-PDO selectivity remains practically constant within the glycerol concentration range from 5 to 50%, slightly decreasing at higher glycerol concentrations, with a simultaneous increase in selectivity to 1-propanol. The selectivity to acetol increases with glycerol concentration reaching 8% at 80% glycerol concentration. This can be explained by more favourable equilibrium for acetol formation at lower water concentration.

Both catalyst functionalities, metal hydrogenation (Ru) and acidity (CsPW), are essential for the efficiency of Ru/CsPW catalyst, acting synergistically in glycerol hydrogenolysis to yield 1,2-PDO. Without ruthenium, CsPW is not active. In the absence of CsPW, ruthenium (e.g. Ru/C) exhibits some activity in 1,2-PDO formation [5, 6]. Supporting ruthenium on the CsPW greatly enhances its activity in this reaction.

As regards the reaction mechanism, the absence of acetol amongst the products when the reaction is carried out with CsPW without Ru present, although it forms in the presence of Ru/CsPW (Table 2), is inconsistent with the

Table 2 Hydrogenolysis of glycerol over 5%Ru/CsPW and 5%Rh/CsPW[a]

Catalyst	Temperature (°C)	Conv. (%)	TOF[b] (h^{-1})	Selectivity (%)					
				1,2-PDO	1,3-PDO	Acetol	1-PO	EG	2-PO
CsPW	120	<1	–	0	0	0	0	0	0
Cs/PW[c]	180	<1	–	0	0	Trace	0	0	0
Ru/CsPW	120	9.8	9.8	88.0	0	0	3.5	0	8.5
Ru/CsPW	150	21	21	95.8	0	0	4.2	0	0
Ru/CsPW[d]	150	31	21	87.6	0	0	4.1	4.6	3.7
Ru/CsPW[e]	150	31	12	82.9	0	1.4	4.8	6.7	4.2
Ru/CsPW	180	23	23	73.6	0	5.7	4.3	11.9	4.5
Ru/CsPW	200	27	27	67.7	0	8.6	5.1	14.0	4.6
Rh/CsPW	180	6.3	0.82	65.4	7.1	0	27.5	0	0

[a] Reaction conditions: 5 bar H_2 pressure, 0.2 g catalyst (4 wt%), 20 wt% glycerol aqueous solution (5 mL), 10 h

[b] TOF as the number of glycerol molecules converted per one surface Ru or Rh atom per 1 h at 10 h reaction time

[c] Reaction in the absence of H_2

[d] 0.3 g catalyst (6 wt%)

[e] 0.5 g catalyst (10 wt%)

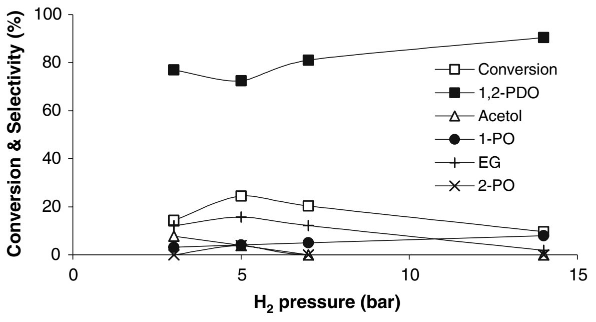


Fig. 1 Effect of H_2 pressure on glycerol hydrogenolysis (Ru/CsPW catalyst, 20 wt% glycerol aqueous solution, 180 °C, 10 h)

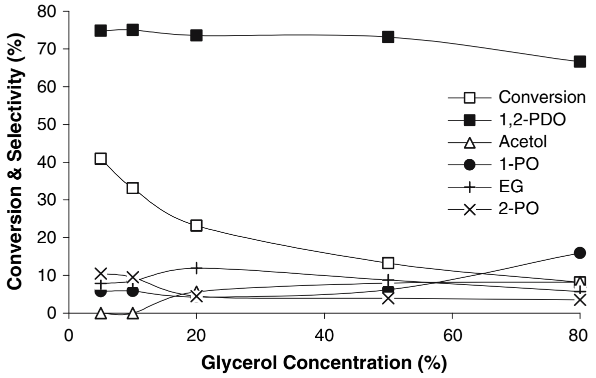


Fig. 2 Effect of reaction time on glycerol hydrogenolysis (Ru/CsPW, 20% glycerol aqueous solution, 180 °C, 5 bar H_2)

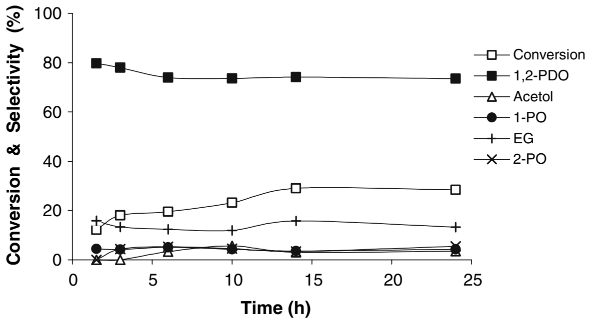
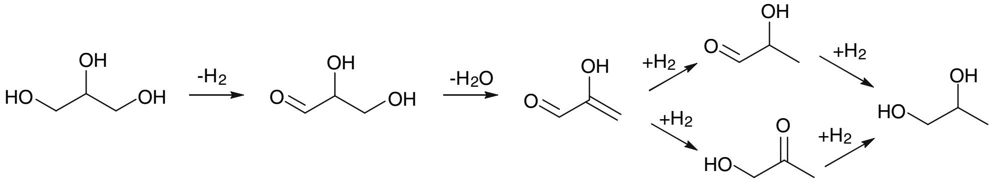


Fig. 3 Effect of glycerol concentration on glycerol hydrogenolysis (Ru/CsPW, 180 °C, 5 bar H_2, 10 h)

mechanism of 1,2-PDO formation presented in Scheme 1. The alternative mechanism shown in Scheme 2 is, therefore, more likely. The question is how does acetol form in the presence of Ru/CsPW? Scheme 3 shows the proposed mechanism of glycerol hydrogenolysis over Ru/CsPW, detailing the formation of 1,2-PDO. In this mechanism, 1,2-PDO forms from 2-hydroxyacrolein by two routes including hydrogenation of either the C=C or C=O bond in 2-hydroxyacrolein over Ru sites. The C=C hydrogenation gives 2-hydroxypropanal. Acetol is formed by the C=O hydrogenation followed by enol–ketone rearrangement. Both the acetol and 3-hydroxypropanal intermediates can be further hydrogenated to yield 1,2-PDO. The hydrogenolysis of glycerol to 1,2-PDO over Ru/C + Amberlyst-15 (120 °C, 80 bar H_2 pressure, 20% glycerol) has been suggested to proceed via the mechanism shown in Scheme 1 [5, 6], although only traces of acetol (<0.01% yield) have been observed. It is conceivable that this reaction also occurs via Scheme 3 like in our case, and the negligible acetol yield may be due to the much higher H_2 pressure in this system. In contrast, with copper chromite catalyst (200 °C, 14 bar H_2, 80% glycerol), 1,2-PDO is likely to form via Scheme 1 because in this case acetol has been obtained with a high yield by interaction of glycerol with



Scheme 3 Proposed mechanism for glycerol hydrogenolysis over Ru/CsPW

copper chromite in the absence of H_2 and further selectively hydrogenated to 1,2-PDO [4].

5%Rh/CsPW catalyst was found considerably less active than the 5%Ru/CsPW catalyst (Table 2). The TOF value for the Rh catalyst is 28 times lower that that for the Ru catalyst at 180 °C. However, the Rh catalyst was more selective to 1,3-PDO and 1-propanol (7.1% and 27.5% selectivity, respectively at 180 °C). The main product with the Rh catalyst was 1,2-PDO (65% selectivity), as with Ru catalyst (Table 2). No ethylene glycol was found, indicating that Rh in contrast to Ru was inactive in C–C bond cleavage. Similar results have been obtained by Miyazawa et al. [5]. In contrast to the Ru and Rh catalysts, 2%Pd/CsPW (prepared as described elsewhere [17]) showed practically no activity in glycerol hydrogenolysis.

4 Conclusion

Ruthenium supported on the strong solid acid $Cs_{2.5}H_{0.5}[PW_{12}O_{40}]$ has been found to be an active bifunctional catalyst for the hydrogenolysis of glycerol providing 1,2-propanediol with 96% selectivity at 21% conversion at 150 °C and an unprecedented low hydrogen pressure of 5 bar. The effect of reaction temperature, glycerol concentration and hydrogen pressure has been established. A more detail mechanistic study is underway.

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References

1. Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick WJ, Hallett JP, Leak DJ, Liotta CL, Mielenz JR, Murphy R, Templer R, Tschaplinski T (2006) Science 311:484
2. Strivastava A, Prasad R (2000) Renewable Sustainable Energy Rev 4:111
3. Chaminand J, Djakovitch L, Gallezot P, Pinel C, Rosier C (2004) Green Chem 6:359
4. Dasari MA, Kiatsimkul PP, Sutterlin WR, Suppes GJ (2005) Appl Catal A 281:225
5. Miyazawa T, Kusunoki Y, Kuminori K, Tomishige K (2006) J Catal 240:213
6. Miyazawa T, Koso S, Kuminori K, Tomishige K (2007) Appl Catal A 318:244
7. Wang S, Liu H (2007) Catal Lett DOI:10.1007/s10562-007-9106-9
8. Maris EP, Davis RJ (2007) J Catal 249:328
9. Weissermel K, Arpe H-J (1997) Industrial organic chemistry, 3rd edn. Wiley
10. Montassier C, Menezo JC, Hoang LC, Renaud C, Barbier J (1991) J Mol Catal 70:99
11. Bruggink A, Schoevart R, Kieboom T (2003) Org Process Res Dev 7:622
12. Okuhara T, Mizuno N, Misono M (1996) Adv Catal 41:113
13. Kozhevnikov IV (1998) Chem Rev 98:171
14. Kozhevnikov IV (2002) Catalysts for fine chemicals, vol. 2. Catalysis by polyoxometalates. Wiley, Chichester, England
15. Baba T, Hasada Y, Nomura M, Ohno Y, Ono Y (1996) J Mol Catal A 114:247
16. Okuhara T (2003) Appl Catal A 256:213
17. Hetterley RD, Kozhevnikova EF, Kozhevnikov IV (2006) Chem Commun 782
18. da Silva Rocha KA, Robles-Dutenhefner PA, Sousa EMB, Kozhevnikova EF, Kozhevnikov IV, Gusevskaya EV (2006) Appl Catal A 317:171
19. Izumi Y, Ono M, Kitagawa M, Yoshida M, Urabe K (1995) Microporous Mater 5:255
20. Taylor KC (1975) J Catal 38:299
21. Benson JE, Hwang HS, Boudart M (1973) J Catal 30:146
22. Pope MT (1983) Heteropoly and isopoly oxometalates. Springer, Berlin, p 105