

# Production of 1,3-propanediol by hydrogenolysis of glycerol catalyzed by Pt/WO<sub>3</sub>/ZrO<sub>2</sub>

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## Abstract

Glycerol hydrogenolysis was catalyzed by Pt/WO<sub>3</sub>/ZrO<sub>2</sub> to give 1,3-propanediol (1,3-PD) in the yields up to 24%. The catalytic activities and the selectivity toward 1,3-PD were remarkably affected by the type of support, loaded noble metal (NM) and the preparation/impregnation procedure. Controlled experiments show that the active site of catalyst for the formation of 1,3-PD may be the Pt over WO<sub>3</sub> supported on ZrO<sub>2</sub>.

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## 1. Introduction

1,3-PD is a valuable chemical used in the synthesis of polymethylene terephthalates and in the manufacture of polyurethanes and cyclic compounds [1,2]. Polymers based on 1,3-PD exhibit many special properties such as good light stability, biodegradability, and improved elasticity. 1,3-PD is currently produced from petroleum derivatives such as ethylene oxide (Shell route) or acrolein (Degussa-DuPont route) by chemical catalytic routes [3]. On the other hand, glycerol is a major byproduct of the biodiesel industry; approximately 1 ton of a crude glycerol is formed for every 10 tons of biodiesel produced [4]. The surging demands for renewable energy sources including biodiesel may offer opportunities for such new applications of glycerol as its conversion to added-value products, and this may contribute to the improvement of the economical viability of the biodiesel production itself [5].

In this context, much attention has been focused on the development of effective methods for the production of 1,3-

PD from glycerol. Relatively well developed is the fermentation method using bacterial strains in which glycerol is converted to 1,3-PD in good yields (>70%), but the reaction proceeds very slowly in water solution and in two steps [6–13]. On the other hand, the direct hydrogenolysis of glycerol to 1,3-PD is particularly interesting because it may be produced in organic solvents and in one step. So far, Bullock et al. reported that the dehydroxylation of glycerol occurred with homogeneous ruthenium catalysts in sulfolan [14]. This reaction proceeds under mild conditions (5.2 MPa, 110 °C), though the yield of 1,3-PD remains very low (<3%). Tomishige et al. reported that the combination of an active carbon-supported Ru catalyst with a cation exchange resin (Amberlyst 15) showed a high level of activity during the hydrogenolysis of glycerol [15,16]. However, 1,2-propanediol (propylene glycol, 1,2-PD) was predominantly formed, while the yield in 1,3-PD remained very low (<0.4%). They also discussed the reaction mechanism over Ru/C + Amberlyst 15 catalysts. The dehydration of glycerol to acetol is catalyzed by the acid catalysts. The subsequent hydrogenation of acetol on the metal catalysts gives 1,2-PD. And the OH group on Ru/C can also catalyze the dehydration of

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glycerol to 3-hydroxypropionaldehyde, which can then be converted to 1,3-PD and the other degradation products through subsequent hydrogenation. Furthermore, Chaminand et al. reported that  $\text{H}_2\text{WO}_4$  was effective in enhancing glycerol conversion and the best result was obtained by using sulfolane as solvent; 1,3-PD was formed in 4% [3].

Therefore, the attempts so far reported show that the reaction conditions favorable for the formation of 1,3-PD involve the presence of solid acids such as tungsten oxide, noble metals, and polar aprotic solvents such as sulfolane. Based on this knowledge, several noble metal types were prepared on tungsten oxide-supported catalysts. The catalytic activity of these noble metal types were examined for the hydrogenolysis of glycerol. DMI (1,3-dimethyl-2-imidazolidinone) was used as solvent, because it was considered more stable than sulfolane under the reaction conditions.

## 2. Experimental

The supported tungsten oxide catalysts ( $\text{WO}_3$ : 20 wt%) were prepared by impregnation method using a  $(\text{NH}_4)_6(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot n\text{H}_2\text{O}$  solution. AlMCM-41,  $\text{SiO}_2\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$  (Anatase type), HY, and  $\text{ZrO}_2$  were used as a support. AlMCM-41,  $\text{SiO}_2\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  were purchased from Sigma–Aldrich and used as received. HY was purchased from Wako Chemicals, Ltd. Zirconium hydroxide,  $\text{Zr}(\text{OH})_4$  was obtained by hydrolyzing  $\text{ZrOCl}_2$  with aqueous ammonia added until the solution reached pH 8.0, followed by washing and then drying at 373 K for 24 h. The catalysts were calcined at 773 K for 3 h in air.

The noble metal (NM) was then loaded on supported tungsten oxide catalysts at 2 wt% based on the NM by the impregnation method using  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ,  $\text{RhCl}$ ,  $\text{PdCl}_2$ ,  $\text{RuCl}$ ,  $\text{ReCl}$ , and  $\text{IrCl}_4$  as their precursors. Pt/ $\text{WO}_3$  catalyst was similarly prepared but using tungsten oxide as support. Pt– $\text{WO}_3/\text{ZrO}_2$  catalyst was prepared by co-impregnation using a  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution and a  $(\text{NH}_4)_6(\text{H}_2\text{W}_{12}\text{O}_{40}) \cdot n\text{H}_2\text{O}$  solution. The resulting solids were dried at 373 K and calcined at 773 K for 3 h in air.

The hydrogenolysis of glycerol was carried out in a 10-mL-stainless steel autoclave. After the autoclave was charged with glycerol (3 mmol), DMI (0.2 mL), and catalyst (0.1 g) and purged with  $\text{H}_2$ , hydrogen was introduced at the initial pressure of 8.0 MPa. Then the autoclave was heated to the reaction temperature (443 K) which was maintained for the entire reaction time of 18 h.

The products were identified by GC–MS (Shimadzu QP-5050 with FFAP capillary column) and analyzed by GC (Shimadzu GC-14B with FFAP capillary column for liquid products, GL sciences GC 353B with RT-QPLOT capillary column for gas products) equipped with FID. The unreacted glycerol and diglycerol were analyzed by HPLC (Jasco LC-2000 with Aminex<sup>®</sup> HPX-87X column). An internal standard method using *n*-butanol was employed to calculate the product yields for both GC and HPLC.

X-ray diffraction (XRD) of the catalysts was recorded on an X-ray diffractometer (Rigaku Co., Cu  $\text{K}\alpha$ , 40 kV, 20 mA).

## 3. Results and discussion

The effect of the supports loaded with tungsten oxide were firstly examined and then with platinum for the hydrogenolysis of glycerol in DMI at 443 K. The results are listed in Table 1.

The predominant products were 1,3-PD, 1,2-PD, and *n*-propanol (*n*-PrOH). The catalytic activity significantly varied with the type of support, but all the catalysts tested outperformed those previously reported in terms of the yield of 1,3-PD. The best result so far was obtained with Pt/ $\text{WO}_3/\text{ZrO}_2$ ; 1,3-PD was formed in the yield of 24.2% and twice the selectivity of 1,2-PD. However, a significant amount of *n*-PrOH was formed with this catalyst, probably because of the severe reaction conditions. *iso*-PrOH, ethanol, diglycerol, propane, ethane and methane were the other minor products analyzed upon which ca. 10% was the total yield.

The results of XRD analyses of these catalysts are shown in Fig. 1a,b. No peak of Pt metal nor tungsten oxide was observed in the case of Pt/ $\text{WO}_3/\text{ZrO}_2$ , Pt/ $\text{WO}_3/\text{Al}_2\text{O}_3$ , and Pt/ $\text{WO}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$ , all of which gave high yields of 1,3-PD (>11%) with high glycerol conversion (>40%). On the other hand, small peak of Pt metal and small peaks of  $\text{WO}_3$  were observed in the XRD analyses of Pt/ $\text{WO}_3/\text{AlMCM-41}$ , Pt/ $\text{WO}_3/\text{HY}$ , and Pt/ $\text{WO}_3/\text{TiO}_2$ , all of which gave the relatively low yields in 1,3-PD (<8%). This trend of result indicates the importance of the high dispersion of  $\text{WO}_3$  and Pt on the supports for the effective hydrogenolysis of glycerol.

The type of NM loaded on the zirconia supported tungsten oxide catalysts also greatly affects the hydrogenolysis of glycerol as shown in Table 2.

Pt and Rh gave much higher glycerol conversions compared with other NMs, but the yield of 1,3-PD remained low with Rh. Since almost similar XRD patterns were observed among the NM/ $\text{WO}_3/\text{ZrO}_2$  catalysts; no peaks

Table 1  
Effect of the supported tungsten oxide catalysts modified by Pt<sup>a</sup>

Catalysts <sup>b</sup>	Yield (%)			
	1,3-PD	1,2-PD	<i>n</i> -PrOH	Glycerol
Pt/ $\text{WO}_3/\text{TiO}_2$	6.5	7.1	5.1	83.1
Pt/ $\text{WO}_3/\text{HY}$	7.2	8.9	5.0	74.1
Pt/ $\text{WO}_3/\text{AlMCM-41}$	7.5	7.0	7.1	72.2
Pt/ $\text{WO}_3/\text{SiO}_2\text{-Al}_2\text{O}_3$	11.0	11.6	9.5	57.8
Pt/ $\text{WO}_3/\text{Al}_2\text{O}_3$	13.2	11.0	11.6	56.1
Pt/ $\text{WO}_3/\text{ZrO}_2$	24.2	12.5	27.5	14.2

<sup>a</sup> Reaction conditions: glycerol: 3 mmol; DMI: 0.2 mL; initial  $\text{H}_2$  pressure: 8.0 MPa; reaction time: 18 h; catalyst: 100 mg (Pt 2 wt%,  $\text{WO}_3$  19.6 wt%); reaction temperature: 443 K.

<sup>b</sup> No product was obtained in the hydrogenolysis of glycerol without any catalyst; 97% of glycerol used was recovered.

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