Effect of Base Additives on the Selective Hydrogenolysis of Glycerol over Ru/TiO$_2$ Catalyst

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Under mild reaction conditions (170 °C, 3 MPa), glycerol is hydrogenolyzed to 1,2-propanediol with very high selectivity at high conversion using Ru/TiO$_2$ as catalyst in basic aqueous solution. The base aids the initial dehydrogenation of glycerol to glyceraldehyde and promotes the dehydration of glyceraldehyde to 2-hydroxyacrolein.

In recent years, the rapid development of biodiesel production formed large quantities of glycerol as a by-product and the conversion of glycerol to other high value-added products has attracted great attention.[1,2] Catalytic hydrogenolysis of glycerol (HG) to glycols represents a feasible, low-cost, and green methodology. Here, the glycols refer to 1,2-propanediol (1,2-PDO) and ethylene glycol (EG). Both of the diols are currently produced from petrochemical resources and are often used in antifreeze, paints, functional fluids, humectants, and polyester resins. Although 1,3-propanediol (1,3-PDO) is also a valuable chemical, it is not recommended to produce it by direct HG because of its low selectivity and yield.[3,4] The HG using supported catalysts has been extensively studied by several groups.[5–13] For example, the Suppes group won the AOCS glycerol innovation award due to their work on selective HG using copper–chromite catalyst.[8] Tomishige and co-workers developed a metal-acid bifunctional catalyst system, which exhibited good performance in the HG.[11] However, most of the works have focused on varying catalyst compositions and operating conditions to optimize both glycol production rates and selectivities. Although it is generally acknowledged that additives can significantly affect the activity and selectivity of this reaction, little research has been done on the effects of the base additives on the HG, and few details are known about how these base additives affect the reaction routes. In this communication, the HG using Ru/TiO$_2$ as catalyst was studied for the first time in basic aqueous solution. We found that glycerol can be hydrogenolyzed to 1,2-propanediol with very high selectivity at high conversion under mild conditions. The effects of the kind and amount of the base additives were discussed in combination with a reaction mechanism.

Ru/TiO$_2$ (5 wt %) was prepared by impregnation technique. TiO$_2$ was added to an aqueous solution of RuCl$_3$ (Johnson–Matthey). The slurry was stirred overnight at room temperature, and then heated at 80 °C for 2 h. The catalyst was reduced by hydrogen at 5 MPa and 200 °C for 8 h, followed by washing repeatedly with deionized water to remove chloride ions, and then dried at 110 °C in vacuum for 10 h. 5 mL of glycerol aqueous solution (20 wt %), 102 mg of Ru/TiO$_2$ and certain amounts of base additives were charged into a 60-mL autoclave. The reactor was pressurized to 3 MPa with hydrogen and heated to 170 °C. After stirring at 1000 rpm for 12 h, samples were analyzed by GC (Agilent 6890N) equipped with a flame ionization detector and a capillary column (Supelco WAX™, 30 m × 0.53 mm × 1

**Table 1.** HG catalyzed by Ru/TiO$_2$ in the presence of different bases[a]

Entry	Base	Conversion/%	Selectivity/%[b]	
			1,2-PDO	EG
1	—	66.3	47.7	26.0
2	LiOH	89.6	86.8	7.5
3	NaOH	83.4	83.5	15.2
4	KOH	62.2	82.7	10.9
5	Li$_2$CO$_3$[c]	80.1	82.3	7.7
6	Na$_2$CO$_3$	78.0	83.6	8.1
7	K$_2$CO$_3$	61.3	78.2	7.8
8	LiOH[d]	<1.0	Trace	—

[a]Reaction conditions: 170 °C, 3 MPa, 12 h, 5-mL glycerol aqueous solution (20 wt %), 102-mg Ru/TiO$_2$, 1 mmol base. [b]C-Based selectivity. [c]10-mL glycerol aqueous solution (10 wt %). [d]Without Ru/TiO$_2$.

µm). 1,2-PDO, 1,3-PDO, EG, 1-propanol, 2-propanol, ethanol, methanol, and methane were analyzed. Only selectivities to 1,2-PDO and EG were discussed in this study in view of their commercial importance and high value.

At first, the HG was performed in the presence of different bases (see Table 1). In general, the addition of lithium or sodium base dramatically increases the conversion of glycerol and the selectivity to 1,2-PDO. The highest conversion of glycerol (89.6%) and the highest selectivity to 1,2-PDO (86.8%) were observed with LiOH (Entry 2, Table 1). Interestingly, the selectivity to 1,2-PDO changed slightly in the case of all added bases, which is due to that the selectivity to 1,2-PDO is independent of base concentration in a certain range.[10] However, the selectivity to EG decreased no matter which base was added. Almost no reaction was observed in the absence of Ru/TiO$_2$ (Entry 8, Table 1), indicating that the metal catalyst is necessary for the taking place of the HG. It should be noted that using potassium base (KOH or K$_2$CO$_3$) as additive resulted in similar conversion of glycerol to the nonadditive reaction (Entries 4 and 7, Table 1). The different influences of alkali bases on the activity indicate that the alkali metal cations have an effect on the HG. The alkali metal cations influenced the activity in the order Li$^+$ > Na$^+$ > K$^+$, which might be associated with the size of the cation. A similar effect was also observed in the hydrogenation reactions of ketones.[14] However, the exact reason is not clear and needs further studies.

The effect of the amount of base on the reaction was investigated using LiOH as additive, and the results are shown in Table 2. As the amount of LiOH increased from 0 to 2.0 mmol, the conversion of glycerol initially exhibited an increase, ultimately reached a maximum at a LiOH dosage of 1.0 mmol (Entry 4, Table 2), after which the conversion began to decrease. The selectivity to 1,2-PDO increased gradually from 47.7 to
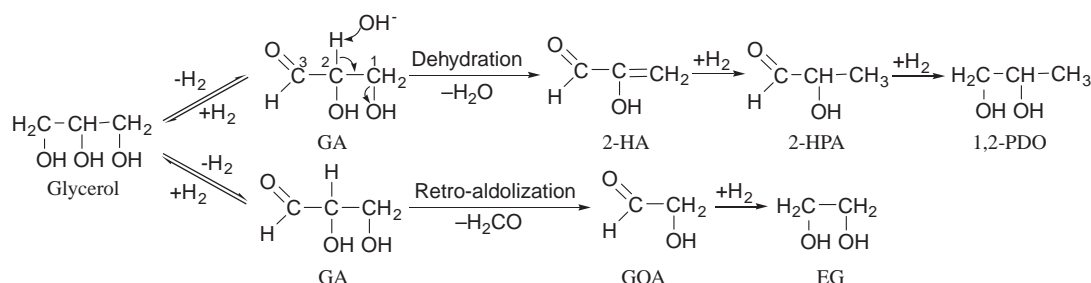
Scheme 1. Reaction pathway for the hydrogenolysis of glycerol to glycols in basic aqueous solution.

Table 2. Effect of the amount of LiOH on the HG over Ru/TiO$_2$ catalyst[a]

Entry	LiOH /mmol	Conversion/%	Selectivity/%[b]	
			1,2-PDO	EG
1	—	66.3	47.7	26.0
2	0.2	63.7	54.2	21.5
3	0.5	74.3	71.2	10.9
4	1.0	89.6	86.8	7.5
5	1.5	82.6	84.1	8.7
6	2.0	75.4	81.3	7.4

[a]Reaction conditions: 170 °C, 3 MPa, 12 h, 5-mL glycerol aqueous solution (20 wt %), 102-mg Ru/TiO$_2$. [b]C-Based selectivity.

86.8% when the amount of LiOH increased from 0 to 1.0 mmol (Entries 1–4, Table 2). However, keeping on increasing the base amount to 2.0 mmol only resulted in slight changes in the selectivity to 1,2-PDO (Entries 4–6, Table 2), which suggests that at a LiOH dosage more than 1.0 mmol, the selectivity to 1,2-PDO is independent of base concentration.[10] In contrast, the selectivity to EG decreased with increasing amount of LiOH.

According to the literature,[12,15,16] a possible mechanism for the HG under basic conditions is shown in Scheme 1. The reaction pathway involves a reversible dehydrogenation of glycerol to glyceraldehyde (GA), followed by dehydration and/or retro-aldolization of GA to 2-hydroxyacrolein (2-HA) and/or glycolaldehyde (GOA), and finally, the two glycol precursors are hydrogenated to 1,2-PDO and EG, respectively. The Ru/TiO$_2$ catalyst serves both hydrogenating and dehydrogenating functions in the whole reaction process.[10]

Notice that the base additives could affect the formation of intermediates in the reaction routes, the role of the base is worthy of further comment. It is proposed that the base aids the initial dehydrogenation of glycerol to form GA. This is the first step in the hydrogenolysis process, and is slow for Ru/TiO$_2$ in the absence of base. As shown in Scheme 1, OH$^-$ attacks the hydrogen at C$_2$ of GA, which makes the primary hydroxy group of GA readily removed by dehydration to form 2-HA. Therefore, the reversible dehydrogenation–hydrogenation equilibrium between glycerol and GA will tend to proceed forward, which is responsible for the increase in the conversion of glycerol and the selectivity to 1,2-PDO. In contrast, the decrease in the selectivity to EG is due to that the conversion of GA to GOA is very difficult in basic conditions.[10] Furthermore, our time followed experiments and previous studies[12] have shown that the obvious

degradation of 1,2-PDO and EG commenced when the glycerol neared completion. This further indicate that the base influenced the selectivities by promoting specific reaction (dehydration of GA to 2-HA), while not only by affecting the conversion. In addition, OH$^-$ is unlikely to attack the hydrogen at C$_1$ of GA because of its much weaker acidity compared with that of the hydrogen at C$_2$ of GA. This can explain that only trace amount of 1,3-PDO formed in the products.

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