

Hydrogenolysis of Glycerol to Propanediols over Multifunctional Catalysts

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Introduction

The production chemicals from catalytic transformation of bio-sustainable resources is a global challenge [1]. Recent development of biodiesel fuel production by transesterification of plant oils and animal fat has made a large amount of glycerol available as a renewable feedstock for the synthesis of value-added chemicals[2].

Hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO), which are important commodity chemicals produced from petroleum derivatives, has attracted significant interest. A number of patents and papers have disclosed the hydrogenolysis of glycerol to propanediols using homogenous and heterogeneous catalysts in liquid-phase at 110-260°C and an H₂ pressure up to 300 bar [3] and recently in gas-phase at 190°C and 6.4 bar of H₂ pressure [4]. The reaction is suggested to proceed via dehydration of glycerol to acetol (hydroxyacetone) and 3-hydroxypropanal by acid catalysis followed by catalytic hydrogenation [2-4]. This mechanism implies that bifunctional acid/hydrogenation catalysis can be an effective course to carry out the glycerol hydrogenolysis in one-pot system.

Our current objective is to study the hydrogenolysis of glycerol to propanediols in the presence of multifunctional catalysis using Ru and Rh modified solid acids, including niobium oxide and polyoxometalates. These solid acids are well known as water-tolerant catalysts as well as possessing considerable thermal stability.

Materials and Methods

The supports Cs_{2.5}H_{0.5}W₁₂O₄₀ (CsPW) and niobium oxide (Nb₂O₅.nH₂O) were prepared as described in literature [5]. 5%Ru and Rh supported metals were obtained by impregnating supports with RhCl₃ and RuCl₃ aqueous solutions followed by reduction of Ru^{III} and Rh^{III} to Ru⁰ and Rh⁰ under flow of hydrogen at 250°C for 2 hr. The catalysts were characterized by BET, FTIR, H₂ chemisorption and XRD. The hydrogenolysis of glycerol was carried out in a stainless steel autoclave (Table 1). Products were analyzed by GC (30m × 0.5 μm CP-WAX 52 CB capillary column).

Results and Discussion

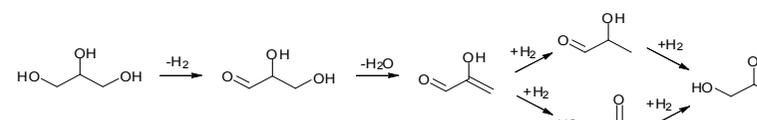
Table 1 shows representative results for the hydrogenolysis of glycerol. The Ru/CsPW catalyst showed excellent performance in glycerol hydrogenolysis at a very low hydrogen pressure of 5 bar, producing selectively 1,2-PDO with only traces of 1,3-PDO under the reaction conditions studied. Rhodium catalyst, 5%Rh/CsPW, although less active, shows considerable selectivity to 1,3-PDO (7.1%) with 1,2-PDO being the main product (65%). Ru/Nb₂O₅ has shown good activity at similar conditions where 20% conversion and 78% selectivity of 1,2-PDO were obtained. Acetol, 1- and 2-propanol (1-PO and 2-PO), ethylene glycol (EG) and methane were found amongst byproducts. CsPW and Nb₂O₅ themselves were not active in the formation of 1,2-PDO, providing only traces of acetol. In the absence of hydrogen, 1,2-PDO was obtained in the presence of Ru on both catalysts; in this system, H₂

could be supplied by the liquid phase reforming of glycerol [6]. These results indicate that the reaction probably occurs via dehydrogenation of glycerol to glyceraldehydes followed by dehydration to 2-hydroxyacrolein and hydrogenation to yield 1,2-PDO (scheme 1).

Table 1. Hydrogenolysis of glycerol over 5%Ru/CsPW and 5%Ru/Nb₂O₅^a

Catalyst	Temp. (°C)	Conv. (%)	TOF ^b (h ⁻¹)	Select. (%)					
				1,2- PDO	1,3- PDO	Acetol	1- PO	EG	2- PO
CsPW ^c	180	<1	-	0	0	Trace	0	0	0
Nb ₂ O ₅ ^c	180	0	-	0	0	0	0	0	0
Ru/CsPW	150	21	21	95.8	0	0	4.2	0	0
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	4.6
Rh/CsPW	180	6.3	0.82	65.4	7.1	0	27.5	0	0
Ru/Nb ₂ O ₅	180	20	-	78.2	0	3.8	8.1	7.9	1.75
Ru/Nb ₂ O ₅ ^d	180	33	-	60.75	0	0	12.6	10.5	12.4

^aReaction conditions: 5 bar H₂ pressure, 0.2 g catalyst (4wt%), 20wt% glycerol aqueous solution, 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 In the absence of hydrogen, ^d 20 bar of H₂ pressure.



Scheme 1. Proposed mechanism for glycerol hydrogenolysis over Ru/CsPW and Ru/Nb₂O₅

Significance

New Bifunctional catalysts for glycerol hydrogenolysis have been found. Evidence supporting reaction mechanism (scheme 1) has been obtained.

References

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