



Solid acid co-catalyst for the hydrogenolysis of glycerol to 1,3-propanediol over Ir-ReO_x/SiO₂

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ARTICLE INFO

Article history:

Received 25 February 2012

Received in revised form 31 March 2012

Accepted 10 May 2012

Available online 17 May 2012

Keywords:

Hydrogenolysis

Glycerol

Iridium

Rhenium

Zeolite

ABSTRACT

Hydrogenolysis of aqueous glycerol was conducted with Ir-ReO_x/SiO₂ catalyst and solid acid co-catalyst. Considering the reusability and activity, H-ZSM-5 is the most suitable solid co-catalyst. The property of Ir-ReO_x/SiO₂ + H-ZSM-5 system including kinetics and selectivity trends in various reaction conditions is similar to the case of Ir-ReO_x/SiO₂ + H₂SO₄. The catalyst stability, activity, and the maximum yield of 1,3-PrD of Ir-ReO_x/SiO₂ + H-ZSM-5 were slightly lower than Ir-ReO_x/SiO₂ + H₂SO₄. The role of added acid may be to protonate the surface of ReO_x cluster to increase the number of hydroxorhenium site, which activates glycerol by the formation of glyceride species.

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1. Introduction

Utilization of biomass is essential in the sustainable development of our society [1–7]. Glycerol is one of the most important compounds in the chemical conversion of biomass, since vast amount of glycerol is co-produced in the manufacture of biodiesel fuel from vegetable oil and lower alcohols [8,9]. Hydrogenolysis of glycerol is an attractive route in the chemical conversion of glycerol because of the large demand of products. The primary products are 1,2-propanediol (1,2-PrD) and 1,3-propanediol (1,3-PrD). Overhydrogenolysis reactions produce 1-propanol (1-PrOH), 2-propanol (2-PrOH) and propane (Scheme 1). Other side-reactions include degradation which produces C2 compounds such as ethylene glycol and C1 compounds such as methane. In these compounds, 1,3-PrD is most valuable and can be used in large scale for polyester production. Despite the recent extensive studies in the developments of catalytic systems for glycerol hydrogenolysis [10], selective formation of 1,3-PrD is very difficult and the reported systems have been limited [11–23]. In the literature, rhodium- or platinum-based catalysts combined with tungsten-based co-catalyst or modifier are relatively effective in the glycerol hydrogenolysis to 1,3-PrD. Our group reported that rhenium is the best modifier for rhodium catalysts in terms of hydrogenolysis activity and selectivity to

1,3-PrD [19]. We have very recently reported that silica-supported rhenium-modified iridium catalyst (Ir-ReO_x/SiO₂) is very effective in the selective hydrogenolysis of glycerol to 1,3-PrD [20,21]. Almost no activity is observed for monometallic Ir/SiO₂ and ReO_x/SiO₂ catalysts, indicating that the synergy between iridium and rhenium enables the hydrogenolysis. The maximum 1,3-PrD yield is 38% [20], which value is still the highest in the literature of the catalytic hydrogenolysis of aqueous glycerol. However, this system requires the addition of sulfuric acid to the reaction mixture. The presence of corrosive sulfuric acid makes it difficult to design the reaction system including reactor and product separation system. Therefore, substituting solid acids for sulfuric acid is advantageous to the practical use of the Ir-ReO_x/SiO₂-based catalytic system. In this study, various solid acids including an ion-exchange resin, silica–alumina and zeolites were applied to the co-catalyst for the glycerol hydrogenolysis over Ir-ReO_x/SiO₂. In terms of the activity and reusability, H-ZSM-5 is the best additive among the solid acids tested. The role of acid in this reaction is also discussed.

2. Experimental

2.1. Catalysts

Ir-ReO_x/SiO₂ catalyst was prepared by sequential impregnation method using Fuji Silysia G-6 silica, H₂IrCl₆ aq and NH₄ReO₄ aq followed by drying and calcination at 773 K, as described in the previous reports [20,21]. Iridium nitrate was also used as a

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