



Priority Communication

Direct hydrogenolysis of glycerol into 1,3-propanediol over rhenium-modified iridium catalyst

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ABSTRACT

Rhenium-oxide-modified supported iridium nanoparticles on silica catalyzes direct hydrogenolysis of glycerol to 1,3-propanediol in an aqueous media. The selectivity to 1,3-propanediol at an initial stage reaches $67 \pm 3\%$. The yield of 1,3-propanediol reaches 38% at 81% conversion of glycerol. The characterization of catalyst and the reactivity of alcohols suggest that 1,3-propanediol is produced by the attack of active hydrogen species on iridium metal to 1-glyceride species formed on the oxidized rhenium cluster.

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1. Introduction

For the sustainable development of our society, much attention has been paid to biorefinery, where renewable biomass-related raw material is converted to valuable chemicals and fuel [1,2]. Glycerol is one of the most important building blocks in the biorefinery feedstock, since enormous amount of glycerol is expected to be produced by the biodiesel production process as well as traditional routes such as soap manufacture [3,4]. Among the chemicals that can be derived from glycerol, 1,3-propanediol is a very promising target because of the high cost of conventional processes of 1,3-propanediol production and the large-scale production of polyester and polyurethane resin from 1,3-propanediol [4,5]. Therefore, the development of an efficient conversion process of glycerol into 1,3-propanediol will make the biodiesel process more profitable. However, selective hydrogenolysis of glycerol into 1,3-propanediol is not easy. Although glycerol hydrogenolysis has been heavily studied in recent years, the main products are less valuable such as 1,2-propanediol and propanols in most cases [4]. Significant amount of 1,3-propanediol is formed only in the cases where oxide of group 6 or 7 metal is added as a co-catalyst [6–12], and the maximum reported yield of 1,3-propanediol is as

low as 26.8% [11]. One example of co-catalyst is ReO_x for Rh/SiO₂. We have very recently reported that the co-catalyst much enhances the glycerol conversion (22 times) and 1,3-propanediol selectivity [12]. However, the selectivity to 1,3-propanediol is still lower than 30% even in the initial stage, and its maximum yield was 11%. Iridium lies just under rhodium in the periodic table. It has been known that iridium complexes, as well as rhodium counterparts, can activate H₂ to give hydride complexes [13]. However, metallic iridium has been received less attention for hydrogenation or hydrogenolysis catalysis because of the lower activity than other noble metals, and little is known of the modification effect of iridium catalyst with metal oxide [14,15]. In this study, we report that the ReO_x -modified iridium nanoparticles catalyzes the selective hydrogenolysis of glycerol into 1,3-propanediol in water. The modification effect of Ir with ReO_x is much more remarkable than the case of Rh in terms of the initial selectivity to 1,3-propanediol (68%) and maximum yield (38%).

2. Experimental

2.1. Preparation of catalyst

An Ir/SiO₂ catalyst was prepared by impregnating SiO₂ with an aqueous solution of H₂IrCl₆ (Furuya Metal Co., Ltd.). The SiO₂ (G-6, BET surface area 535 m²/g, <100 mesh powder) was supplied by Fuji Silysia Chemical Ltd. After impregnation, the catalyst was dried at 383 K for 12 h. The loading amount of Ir was 4 wt.%. Ir– ReO_x /SiO₂ catalysts were prepared by impregnating Ir/SiO₂ after

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the drying procedure with aqueous solution of NH_4ReO_4 (Soekawa Chemical Co., Ltd.). $\text{ReO}_x/\text{SiO}_2$ was prepared by impregnation of SiO_2 with the same precursor as that for $\text{Ir-ReO}_x/\text{SiO}_2$. All catalysts were calcined in air at 773 K for 3 h after drying (at 383 K for 12 h). The ratio of Re to Ir was optimized to maximize the selectivity to 1,3-propanediol in the glycerol hydrogenolysis and was determined to be $\text{Re}/\text{Ir} = 1$ (molar basis).

2.2. Catalytic test

Catalytic tests were performed in a 190-ml stainless steel autoclave with an inserted glass vessel. Water, a spinner and an appropriate amount of catalyst were placed into the autoclave. After sealing the reactor, the air content was purged by flushing thrice with 1 MPa hydrogen. The reactor was then heated to 473 K and pressurized to 8 MPa. After 1 h, the reactor was cooled down and the H_2 inside the reactor was removed. This procedure is needed because the reduction temperature is higher than the reaction temperature. When the pretreatment was conducted at 393 K, the reduction in Ir was incomplete (confirmed by EXAFS) and the catalytic performance was lower. An appropriate amount of glycerol and sulfuric acid was quickly added to the reaction mixture. In this case, it can be possible to avoid direct contact of the reduced catalyst with air because the catalyst is covered with water. After sealing the reactor, the air content was purged by flushing thrice with 1 MPa hydrogen. The reactor was then heated to the reaction temperature (393 K) and pressurized to 8 MPa. After an appropriate reaction time, the reactor was cooled down and the gas inside the reactor was collected in a gas bag. The products in both liquid and gas phases were analyzed using GC (Shimadzu GC-2014) equipped with FID and GC-MS (Shimadzu QP5050). The used catalyst was separated from the reaction mixture by centrifugation, washed with excess water, dried in air and calcined at 773 K for 3 h. A slight loss (<10% in weight) was observed during the recovery process and was compensated with fresh catalyst in each reuse experiment. The yield and selectivity were calculated on the carbon basis and defined as follows:

$$\text{Yield (\%)} = \frac{(\text{mol of the product}) \times (\text{number of carbon atoms in the product})}{(\text{mol of glycerol charged}) \times 3} \times 100$$

$$\text{Selectivity (\%)} = \frac{(\text{mol of the product}) \times (\text{number of carbon atoms in the product})}{(\text{mol of glycerol consumed}) \times 3} \times 100$$

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded by a diffractometer (Philips X'pert). Transmission electron microscope (TEM) images were taken with JEOL JEM 2010. The samples were dispersed in ethanol with supersonic waves and placed on Cu grids under air atmosphere. Average particle size was calculated by $\sum n_i d_i^3 / \sum n_i d_i^2$ (d_i : particle size, n_i : number of particles with d_i). The amount of CO chemisorption was measured in a high-vacuum system using a volumetric method under about 1.1 kPa CO at room temperature after the pretreatment in H_2 at 473 K for 1 h. Temperature-programmed reduction (TPR) was carried out in a fixed bed reactor equipped with a thermal conductivity detector using 5% H_2/Ar in the temperature range from room temperature to 1123 K (heating rate 10 K/min).

The EXAFS spectra were measured at the BL01B1 station at SPring-8 with the approval of the Japan Synchrotron Radiation Re-

search Institute (JASRI; Proposal No. 2008B1235). The storage ring was operated at 8 GeV. A Si (1 1 1) single crystal was used to obtain a monochromatic X-ray beam. Two ion chambers for I_0 and I were filled with 85% $\text{N}_2 + 15\% \text{Ar}$ and 100% Ar, respectively, for Re and Ir $L_{2,3}$ -edge measurement. The data were collected in a transmission mode. The calcined catalyst was reduced with 8 MPa H_2 in water at 473 K for 1 h. After cooling, the wet catalyst powder was transferred to a measurement cell (thickness 2 mm) using a glove box. For curve fitting analysis, the empirical phase shift and amplitude functions for the Re–O, Re–Re and Ir–Ir bonds were extracted from data for NH_4ReO_4 , Re powder and Ir powder, respectively. Theoretical functions for the Re–Ir bond were calculated using the FEFF8.2 program [16], and this bond is denoted as Re–Ir (or -Re) since it is difficult to distinguish between Ir and Re as a scattering atom. Analyses of EXAFS data were performed using a computer program (REX2000, ver. 2.5.9; Rigaku Corp.).

3. Results and discussion

3.1. Catalytic performance

The time course of the glycerol hydrogenolysis catalyzed by $\text{Ir-ReO}_x/\text{SiO}_2$ ($\text{Re}/\text{Ir} = 1$) is shown in Fig. 1. The initial selectivity to 1,3-propanediol was $67 \pm 3\%$. The maximum yield of 1,3-propanediol was 38% at 36 h, which value was much higher than those reported for the other catalytic glycerol hydrogenolysis systems. The ICP analysis of the reaction solution after the filtration of the catalyst showed no appreciable leaching of Ir or Re (<0.3%). The $\text{Ir-ReO}_x/\text{SiO}_2$ catalyst could be reused at least thrice without the change of the reaction rate and selectivities. In contrast, monometallic Ir/SiO_2 showed very low catalytic activity (ca. 2 orders lower than $\text{Ir-ReO}_x/\text{SiO}_2$) and selectivity to 1,3-propanediol (<10% at 0.3% conversion; the main product is 1,2-propanediol). It has been known that the activity of $\text{ReO}_x/\text{SiO}_2$ was very low [12]. Therefore, it is concluded that the synergy between Ir and Re enabled the hydrogenolysis of glycerol to 1,3-propanediol. It should be noted that the additive effect of Re over Ir catalysts on the selectivity to

1,3-propanediol and its maximum yield was much more drastic than that over Rh catalysts.

The present hydrogenolysis system was applied to other alcohols (Table 1). The reactivity decreased in the following order: 1,2-propanediol \geq glycerol \gg 1,3-propanediol \sim 2,3-butanediol \sim propanols. In the hydrogenolysis of 1,2-propanediol, the secondary OH group was selectively removed to give 1-propanol as a main product. These trends show that the OH group adjacent to a primary OH group has much higher reactivity than the other OH groups.

3.2. Characterization and reaction mechanism

In the temperature-programmed reduction (TPR) profile (Fig. S1 in Supplementary Information) of Ir/SiO_2 , H_2 consumption signal with a peak at 510 K was observed between 380 and 600 K. The total amount of H_2 consumption was 2.0 equiv. to Ir, which agreed

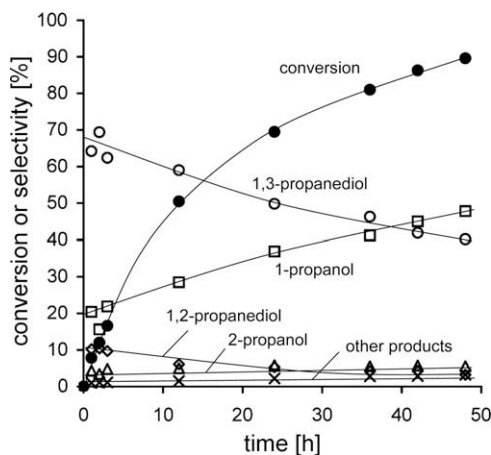


Fig. 1. Time course of the hydrogenolysis of glycerol over Ir–ReO_x/SiO₂ (Re/Ir = 1). Conditions: catalyst (150 mg, 31 μmol Ir), glycerol (4 g), water (1 g), sulfuric acid (H⁺/Ir = 1) and H₂ (8 MPa) at 393 K.

Table 1

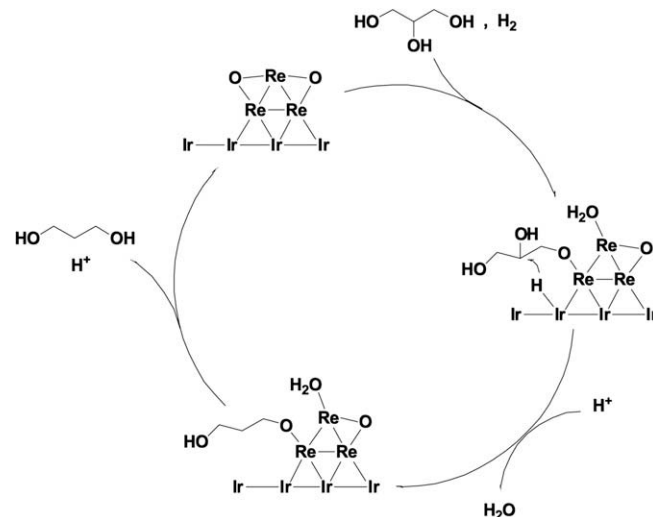
Hydrogenolysis of alcohols over Ir–ReO_x/SiO₂ (Re/Ir = 1).

Entry	Substrate (mmol)	Converted (mmol)	Products (selectivity (%))
1	Glycerol (43)	27	1,3-Propanediol (49), 1,2-propanediol (10), 1-propanol (33), 2-propanol (8)
2	1,2-Propanediol (53)	38	1-Propanol (85), 2-propanol (10), propane (5)
3	1,3-Propanediol (53)	12	1-Propanol (>99)
4	2,3-Butanediol (44)	8	2-Butanol (81), <i>n</i> -butane (19)
5	1-Propanol (67)	10	Propane (>99)
6	2-Propanol (67)	14	Propane (>99)

Reaction conditions: catalyst (150 mg, 31 μmol Ir), alcohol (4 g), water (16 g), sulfuric acid (H⁺/Ir = 1) and H₂ (8 MPa) at 393 K for 24 h.

with the stoichiometry of the reduction of Ir^{IV} to Ir⁰. In the case of ReO_x/SiO₂, where the initial valence of Re was 7, H₂ consumption occurred between 500 and 800 K. The total amount of H₂ consumption was 2.2 equiv. to Re, indicating that low-valent rhenium oxide was formed. In the case of Ir–ReO_x/SiO₂, intense H₂ consumption signal with a peak at 450 K was observed between 380 and 480 K. The consumption amount was 3.8 equiv. to Ir, indicating that Ir and Re were simultaneously reduced. The XRD pattern (2θ range: 10–70°; Fig. S2) of Ir–ReO_x/SiO₂ after the catalytic use showed only one broad peak at 2θ = 41° assignable to Ir metal in addition to the peak of SiO₂ (2θ = 22°). The crystal size of Ir was estimated to be 2.3 nm from the linewidth of the peak. The TEM observation also detected particles of 2.0 ± 0.2 nm size (Fig. S3). The curve fitting of Ir L₃-edge EXAFS of Ir–ReO_x/SiO₂ reduced at 473 K detected Ir–Ir (or –Re) bond with length (*R*) of 2.68 Å and coordination number (CN) of 9.3 (Table S1 and Fig. S4). The Re L₃-edge EXAFS detected Re–O bond (*R* = 2.03 Å, CN = 1.2) as well as Re–Ir (or –Re) bond (*R* = 2.69 Å, CN = 5.5) (Table S1 and Fig. S5). These data showed that iridium and rhenium in the Ir–ReO_x/SiO₂ catalyst were reduced to the metallic state and low-valent metal oxide, respectively. The amount of CO adsorbed on Ir–ReO_x/SiO₂ after the reduction at 473 K was 0.07 equiv. to Ir, while 48% of Ir is calculated to be located on the surface of 2.3-nm Ir crystal [17]. This discrepancy and the single-peak TPR profile suggest that the oxidized Re clusters were attached to the Ir metal particles [12,18].

On the basis of all results, we propose a possible reaction mechanism in Scheme 1. First, glycerol was adsorbed on the surface of ReO_x cluster at the terminal position to form 2,3-dihydroxypropoxide-



Scheme 1. Possible reaction mechanism of glycerol hydrogenolysis catalyzed by Ir–ReO_x/SiO₂.

ide. The larger formation constants of metal alkoxides of primary alcohols than of secondary alcohols have been reported for niobium- or vanadium-containing tungsten oxide clusters and explained by the steric crowding between the cluster framework and the groups bonded with the C–OH carbon of secondary alcohols [19,20]. Next, hydrogen activated on the Ir metal attacks the 2-position of the 2,3-dihydroxypropoxide to produce 3-hydroxypropoxide. The hydrolysis of 3-hydroxypropoxide releases 1,3-propanediol. The growth of oxidized metal cluster large enough to induce steric effect for the preferential terminal alkoxide formation may be the key to high 1,3-propanediol selectivity. In this mechanism, only substrates with OH groups at both 1- and 2-positions such as 1,2-propanediol and glycerol are reactive. The possible mechanisms of the hydrogenolysis of the other positions include the hydrogenolysis of alkoxide, the formation of 1,3-dihydroxyisopropoxide intermediate [12] and the indirect hydrogenolysis composed of acid-catalyzed dehydration and successive hydrogenation [21]. These mechanisms can lead the side-reactions of glycerol hydrogenolysis such as overhydrogenolysis and 1,2-propanediol formation.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jcat.2010.04.009.

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