



C–O bond hydrogenolysis of cyclic ethers with OH groups over rhenium-modified supported iridium catalysts

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ABSTRACT

Hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol and other related substrates such as 3-hydroxytetrahydrofuran and 1,2-cyclohexanediol proceeds over Ir–ReO_x/SiO₂ catalyst. TOF values are higher than those of Rh–ReO_x/SiO₂, which has been reported to be an effective catalyst. The selectivity to the product, where the C–O bond neighboring the C–OH group in the substrate is dissociated, is comparable to or higher than that of Rh–ReO_x/SiO₂. Hydrogenolysis of most substrates except 1,2-cyclohexanediol proceeds via the direct mechanism where hydride species formed from hydrogen molecule attacks the anti-position of C–O bond. In the case of hydrogenolysis of 1,2-cyclohexanediol where attack of anti-position of C–O bond is unfavorable, indirect mechanism involving dehydrogenation to 2-hydroxycyclohexanone is responsible for the formation of cyclohexanol.

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1. Introduction

Biomass becomes more and more important for the realization of sustainable industry, because biomass is the only renewable source of organic carbon. Fuels and chemicals can be produced from biomass-derived raw materials [1,2]. Most biomass-derived raw materials, such as cyclic ethers and polyols, have many C–O bonds [3,4]. Therefore, C–O hydrogenolysis of cyclic ethers and polyols is very important for the production of high-value chemicals from biomass [5–8]. Furfural is manufactured from hemicellulose and can be a building block in a biomass refinery [9–12], like 5-hydroxymethylfurfural that can be derived from hexoses [13–17]. Tetrahydrofurfuryl alcohol (THFA) is derived by the total hydrogenation of furfural and is one of important intermediates because the hydrogenolysis of THFA gives 1,5-pentanediol, which will be used as a monomer for the production of polyesters and polyurethanes [1]. However, the performance of the conventional hydrogenolysis catalysts such as copper chromite has been reported to be low [18–20]. The hydrogenolysis of THFA to 1,5-pentanediol has been developed in a multi-step process including dehydration, isomerization, and hydrogenation reactions [21]. In contrast, the single-step and regioselective hydrogenolysis of THFA

to 1,5-pentanediol over Rh–ReO_x/SiO₂ and Rh–MoO_x/SiO₂ catalysts has been recently reported and higher yield of 1,5-pentanediol than that in the multi-step process has been achieved [22–25]. The Rh–ReO_x/SiO₂ catalyst showed high hydrogenolysis activity and selectivity, and the selectivity of degradation was very low, although in the case of glycerol hydrogenolysis, the selectivity to 1,3-propanediol was not high [26]. In addition, Rh–ReO_x/C was applied to the hydrogenolysis of tetrahydropyran-2-methanol to 1,6-hexanediol as well as the hydrogenolysis of THFA to 1,5-pentanediol [27,28]. Furthermore, hydrogenolysis of 2,5-tetrahydrofuran-dimethanol, which can be produced by the total hydrogenation of 5-hydroxymethylfurfural [11,29–31], to 1,6-hexanediol over Rh–ReO_x/SiO₂ has been also reported [32]. Another effective catalyst is Rh/MCM-41 for the hydrogenolysis of THFA to 1,5-pentanediol in the supercritical CO₂ [33]. Totally, the hydrogenolysis of cyclic ethers with –CH₂OH group has been studied recently.

Regarding the C–O hydrogenolysis reaction, the most typical substrate is glycerol. Glycerol is a by-product in the biodiesel production by the transesterification of vegetable oils and the hydrogenolysis of glycerol gives 1,2-propanediol and 1,3-propanediol, which are useful chemicals. The reaction schemes for glycerol hydrogenolysis proposed in the literature include dehydration + hydrogenation [34–39] and dehydrogenation + dehydration + hydrogenation [40–42], both of which are regarded as indirect hydrogenolysis. On the other hand, the direct reaction

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mechanism of the glycerol hydrogenolysis over Rh–ReO_x/SiO₂ [26] and Ir–ReO_x/SiO₂ [43,44] has been recently reported. It is characteristic that this mechanism promotes the formation of 1,3-propanediol. Considering that Rh–ReO_x catalysts are applicable to the direct hydrogenolysis of THFA to 1,5-pentanediol [24,28], in this study, we investigated the catalytic performance of Ir catalysts modified with Re, Mo, and W in the hydrogenolysis of THFA, other cyclic ethers and related substrates. The performance of Ir–ReO_x/SiO₂ was compared with that of Rh–ReO_x/SiO₂ with Re/Rh = 0.5, which is the best composition [22]. It is found that the performance of Ir–ReO_x/SiO₂ was comparable to that of Rh–ReO_x/SiO₂ in the hydrogenolysis of THFA to 1,5-pentanediol; in contrast, Ir–ReO_x/SiO₂ catalyst exhibited much higher performance in the hydrogenolysis of 3-hydroxytetrahydrofuran (3-HTHF) and 1,2-cyclohexanediols (1,2-CHDs) than Rh–ReO_x/SiO₂ catalyst. In addition, the reaction mechanism of 3-HTHF and 1,2-CHDs was compared to that of THFA.

2. Experimental

2.1. Catalyst preparation

The SiO₂ (G-6, BET surface area 535 m²/g) supplied by Fuji Silysia Chemical Ltd. was used as a support of the catalysts. Ir/SiO₂ catalyst was prepared by impregnating SiO₂ with an aqueous solution of H₂IrCl₆ (Furuya Metals Co., Ltd.). After evaporating the solvent and drying at 383 K for 12 h, it was calcined in air at 773 K for 3 h. The loading amount of Ir was 4 wt%. The Ir–MO_x/SiO₂ (M = Re, Mo, and W) were prepared by impregnating Ir/SiO₂ after the drying procedure with aqueous solutions of NH₄ReO₄ (Soekawa Chemical Co., Ltd.), (NH₄)₆Mo₇O₂₄·4H₂O (Wako Pure Chemical Industries, Ltd.), and (NH₄)₁₀W₁₂O₄₁·5H₂O (Wako Pure Chemical Industries, Ltd.), respectively. These catalysts were calcined in air at 773 K for 3 h after drying at 383 K for 12 h. The loading amount of Ir was 4 wt%, and that of additive was represented by the molar ratio of the additive to Ir. Rh–ReO_x/SiO₂ catalyst was prepared by sequentially impregnating SiO₂ with aqueous solutions of RhCl₃·3H₂O (Soekawa Chemical Co., Ltd.) and NH₄ReO₄ (Soekawa Chemical Co., Ltd.). First, a RhCl₃·3H₂O aqueous solution was impregnated to SiO₂. Second, it was dried at 383 K for 12 h. Then, an NH₄ReO₄ aqueous solution was impregnated to Rh/SiO₂ after the drying procedure. After the impregnation procedure and another drying at 383 K for 12 h, it was calcined in air at 773 K for 3 h. The loading amount of Rh was 4 wt%, and that of Re was 0.5 by the molar ratio of Re to Rh. All the catalysts were used in powdery form with granule size of <100 mesh.

2.2. Activity tests

Activity tests for the hydrogenolysis of THFA were performed in a 190-ml stainless steel autoclave with an inserted glass vessel. Ir/SiO₂ or Ir–MO_x/SiO₂ catalyst was put into an autoclave together with a spinner and an specific amount of water (from 1 g to 19 g) and heated at 473 K with 8 MPa H₂ for 1 h for the reduction pretreatment. After the pretreatment, the autoclave was cooled down, and hydrogen was removed. THFA (Wako Pure Chemical Industries, Ltd., 98%) was put into the autoclave. After sealing the reactor, the air content was purged by flushing three times with 1 MPa hydrogen (99.99%; Takachiho Trading Co., Ltd.). The autoclave was then heated to reaction temperature and pressurized to 1 MPa. The temperature was monitored using a thermocouple inserted in the autoclave. After 1 h, the H₂ pressure was increased to 8 MPa at reaction temperature. During the experiment, the stirring rate was fixed at 250 rpm (magnetic stirring). For Rh–ReO_x/SiO₂, the activity tests were carried out in the same way to

Ir–MO_x/SiO₂, except the absence of the process of reduction pretreatments at 473 K with 8 MPa for 1 h. Reaction conditions are described for each result. After an appropriate reaction time, the reactor was cooled down and the gases were collected in a gas bag. The autoclave contents were transferred to a vial, and the catalyst was separated by centrifugation and filtration. The products were analyzed using three kinds of gas chromatographs (Shimadzu GC-2014, GC-2025, and GC-17A) equipped with FID. A TC-WAX capillary column (diameter 0.25 mm, 30 m) or a Rtx-1-PONA capillary column (diameter 0.25 mm, 100 m) was used for the separation. Products were also identified using GC-MS (QP5050, Shimadzu). The products of the THFA hydrogenolysis were 1,5-pentanediol (1,5-PeD), 1,2-pentanediol (1,2-PeD), and 2-methyltetrahydrofuran (2-MTHF). The overhydrogenolysis reaction of PeDs gave 1-pentanol (1-PeOH), 2-pentanol (2-PeOH), and pentane. The conversion and the selectivity were defined on the carbon basis in the similar way as reported previously [22]. The mass balance was also confirmed in each result, and the difference in mass balance was always in the range of the experimental error. The agreement in terms of the mass balance indicated that polymeric by-products were not formed (±10%). The hydrogenolysis of tetrahydropyran-2-methanol (Sigma Aldrich, Co., 98%), tetrahydro-5-methyl-2-furfuryl alcohol (synthesized by hydrogenation of 5-methyl-2-furfural with Raney Ni [45]), 2-MTHF (Wako Pure Chemical Industries, Ltd., 98%), tetrahydrofuran (Wako Pure Chemical Industries, Ltd., 98%), 3-HTHF (Wako Pure Chemical Industries, Ltd., 98%), 3-hydroxytetrahydropyran (Astatech, Inc., 97%), 4-hydroxytetrahydropyran (Wako Pure Chemical Industries, Ltd., 97%), and tetrahydropyran (Wako Pure Chemical Industries, Ltd., 99.5%) was also tested in the similar way to the case of THFA. The products in the hydrogenolysis of these substrates commercially available as follows: 1,5-PeD, 1,2-PeD, 1-PeOH, 2-PeOH, 1,6-hexanediol (1,6-HxD), 1,2-hexanediol (1,2-HxD), 1-hexanol (1-HxOH), 2-hexanol (2-HxOH), 1,3-butanediol (1,3-BuD), 1,2-butanediol (1,2-BuD), 1-butanol (1-BuOH), and 2-butanol (2-BuOH) were all purchased from Wako Pure Chemical Industries, Ltd. 1,5-hexanediol (1,5-HxD) was purchased from Sigma Aldrich, Co.

The hydrogenolysis of *cis*-1,2-cyclohexanediol (Sigma Aldrich, Co., 99%, *cis*-1,2-CHD) and *trans*-1,2-cyclohexanediol (Wako Pure Chemical Industries, Ltd., 98%, *trans*-1,2-CHD) was carried out in a different way because the different reaction order with respect to H₂ as shown in the chapter of results and discussion. In order to avoid the reaction proceeding during the reduction treatment and temperature increase, the procedure was changed as follows. Ir–ReO_x/SiO₂ (Re/Ir = 2) or Rh–ReO_x/SiO₂ (Re/Rh = 0.5) was put into an autoclave at first together with a spinner and a specific amount of water (from 4 g to 19 g) and heated at 473 K with 8 MPa H₂ or 373 K with 1 MPa for 1 h for the reduction pretreatment, respectively. After the pretreatment, the autoclave was cooled down, and hydrogen was removed. Then, *cis*-1,2-CHD or *trans*-1,2-CHD was put into the autoclave. After sealing the reactor, the air content was purged by flushing four times with 0.3 MPa nitrogen (99.99%) and then pressurized to 0.3 MPa nitrogen; finally, the autoclave was heated to reaction temperature. At the reaction temperature, the nitrogen was removed to be about 0.3 MPa, then the appropriate pressure of hydrogen was introduced and this corresponded to the zero reaction time. The products in the hydrogenolysis of 1,2-CHDs were cyclohexanol (*c*-HxOH) and cyclohexane, whose standard samples were purchased from Wako Pure Chemical Industries, Ltd.

There are two kinds of turnover frequency described in this work. One was calculated on the basis of the number of surface metal atoms (Ir or Rh), which is determined by the CO adsorption measurement as reported in our previous reports [24,44] and it is denoted as TOF (CO). Re in the Ir–ReO_x/SiO₂ and Rh–ReO_x/SiO₂

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