Development of Heterogeneous Rhenium Catalysts for Selective Conversion of 1,4-Anhydroerythritol to 1,4-Butanediol

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Doctoral Thesis

Thesis Title

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Chapter 1

General Introduction

1.1 Fossil fuels and their disadvantages

Fossil fuels, including petroleum, natural gas, and coal, are the worldwide energy resources and feedstocks forming by millions of years and deposit in rock layers. Human life has been greatly changed by using fossil fuels for heating, electricity, transportation, and so on. Because of the have advantages such as easy collection and transportation of fossil fuels, the low cost lets fossil fuels to be main resources for energy consumption in the world. Over 80% of global energy consumption is generated by fossil fuels [1]. Due to the rapid increase of world population, the global energy consumption also increased 18% in last 10 years, and it will increase more than 25% to 2040 [1]-[3]. The global natural gas consumption increased the fastest by 24% in last ten years, meanwhile, the world petroleum consumption and coal consumption increased 11% and 8%, respectively [3]. Other than the use for energy supply, a large proportion of petroleum is used for petrochemical production. Ethylene derivatives, as the main product in the petrochemical industry, is globally demanded with 3.8% growth per year, and the production of ethylene derives would be 177.3 million tons in 2022 [4].

Even though fossil fuels are necessary in our daily life, they still have disadvantages such as their limited supply because they could not be regenerated in short time. The petroleum, natural gas, and coal would deplete by 2040, 2042, and 2112, respectively [5]. Due to the population pressure and the depletion of the fossil fuels, the price of petroleum and natural gas increased dramatically since 2000 and reached the highest price at 2008, and then kept fluctuated in the last ten years [6]. The use of fossil fuel also causes many severe environmental problems such as large amount of carbon dioxide emission in the conversion of fossil fuels into energy. The combustion of fossil fuels releases 82% of total carbon dioxide emission [7]. Green gas emission caused global warming which leads the average global surface temperature increased approximately 1.0°C, and have a trend to rise up to 1.5°C between 2030 and 2052 [8].

Furthermore, burning the fossil fuels also emit other pollutants such as of SO_2, NO_x, PM, and smoke into the air [9],[10]. Collection and production such as oil fields or coal mines cause unrecoverable damages to the surrounding environment including air, water, and soil pollutions.

Therefore, renewable low-carbon energy resources and feedstocks as alternatives for fossil fuels are becoming increasingly significant and attract more attentions in the 21st century.

1.2 Biomass: renewable resources and feedstocks

Renewable energy resources include solar energy, hydropower, wind, wave and tidal, geothermal, as well as biomass. Biomass, includes woody and agricultural plants, has become an important part of the world's chemical feedstock and energy resource. Much of the attention given to biomass has to do with it being more sustainable and renewable than oil and natural gas. Actually, about 55% of biomass was still used in the most traditional way – burning directly for heating with very low combustion efficiency [11]. Therefore, on one hand, biomass can increase the burning efficiency by increasing the bulk density like pelletizition, which can increase the mass density of biomass to 2.6 times [12]. Using electricity for heating is another option because electricity can be produced by other renewable energy such as solar energy and hydroelectric power. On the other hand, the heating value can be improved by thermal pretreatment such as torrefaction, pyrolysis, and gasification, by removing the lignin in biomass to increase the carbon content [13]. Biofuels such as bioethanol, biogas, and biodiesel as renewable low-carbon energy resources are increasingly demanded. In 2018, the world energy consumption by biomass increased 18% from 2017 [1], and 88 Mtoe (152 billion litres) of biofuels was produced globally [14]. Although biofuels are becoming increasingly important energy resources, the higher cost of biofuels production than that of fossil fuels is still the main barrier of the promotion of using biomass instead of fossil fuels. The world energy consumption by biomass was still under 13% nowadays [15].

Due to the worldwide abundance, lignocellulosic biomass is the most inedible carbon storage on the earth, including woody and agricultural feedstocks. Lignocellulosic biomass is composed of cellulose, hemicellulose and lignin (Figure 1-1). Cellulose, as a natural polymer which is the main part of woody biomass (40-60%), has the chain structure composed of D-glucose functioned as the support for cell walls in biomass. Commonly, cellulose is not soluble in water or organic solvents at room temperature. Hemicellulose, as the second largest compound in biomass (20-40%), is composed of polymers of pentoses (xylose, arabinose), hexoses (glucose, mannose, galactose), and sugar acids [16]. Xylans, polysaccharides composed of xyloses, are the main components in hemicellulose (20–30% of hardwood). Lignin functions as the glue in the biomass with the content of 10-25%, which is a class of cross-linked phenolic polymers [16]-[18]. Biomass is composed of 51 wt% of carbon and 42 wt% of oxygen based on the dry weight [17], and the high oxygen content is unwanted. Therefore, decreasing the oxygen content in biomass can increase the value of biomass. Cellulose and hemicellulose as polysaccharides can be degraded into smaller molecules for further production of value-added chemicals with less oxygen content. Comparing with the refinery of petrochemicals, the biorefinery using cellulose and hemicellulose as feedstocks has many advantages such as sustainable, easy accessibility, and large supply.

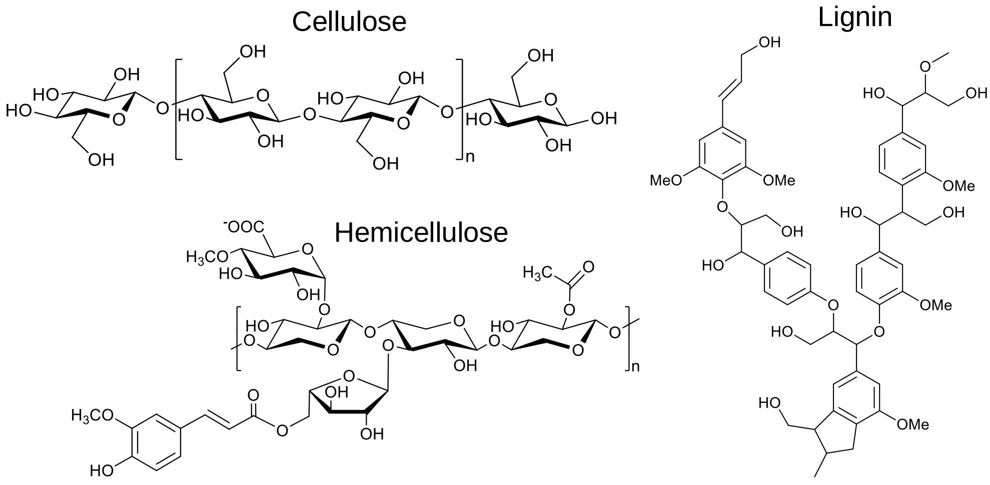


Figure 1-1 Chemical structures of cellulose, hemicellulose, and lignin

1.3 Sugar alcohols and target products of sugar alcohol conversion

The sugar refers to monosaccharides such as fructose, galactose, and glucose, has the ring structure with hydroxyl groups and a carbonyl group. The production of sugar is usually from biomass such as sugarcane or sugar beets. Sugars can also be feedstocks to produce sugar-derived fine chemicals, for example, sugar alcohols.

1.3.1 Sugar alcohol

Sugar alcohols, as thickeners and sweeteners in food industry, comprised of a class of polyols. Sugar alcohols such as glycerol, erythritol, xylitol, and sorbitol (Figure 1-2) have been frequently used as substrates of catalytic conversion because of their large potential supply. Sugar alcohols can be easily obtained from sugars by hydrogenation. Sugar alcohols are more stable than sugars, and they can be versatile intermediate compounds in biomass conversion. Sugar alcohols also contain high oxygen content due to the large amount of OH groups. Therefore, for decreasing the oxygen content, selective removal of OH groups in sugar alcohols by catalytic conversion draws more attention from researchers.

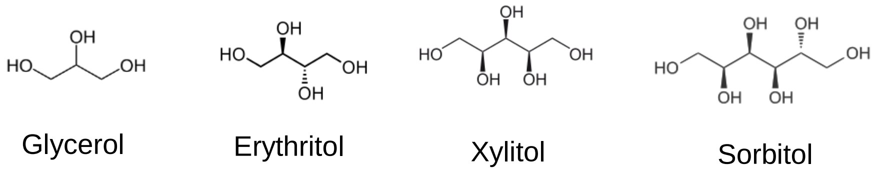


Figure 1-2 Chemical structures of some sugar alcohols

Glycerol is a simple polyol which can be produced as a by-product in the production of biodiesel, soap manufacture, and fatty acid or ester such as triglycerides manufacturing, and so on. Due to the limited consumption of glycerol as a biofuel, a large amount of glycerol cannot be consumed, which can be the feedstocks for chemical conversion to other useful commodity chemicals such as propanediols and allyl alcohol [19]-[21].

Erythritol is a C4 sugar alcohol which is already produced as a sweetener in industrial scale by fermentation [23]-[25]. Production of erythritol by fermentation of glycerol, even non-refined one, is also possible [26]. As chemical platform, erythritol also can be converted to value-added chemicals with less OH groups. Figure 1-3 shows some possible routes of erythritol to derived products such as the dehydration product 1,4-anhydroerythritol, and the deoxydehydration product 1,3-butadiene, as well as the hydrogenolysis products including butanediols and butanetriols, and so on [27],[28].

Xylitol and sorbitol are often used as a sugar substitute in food industry. They can be produced by hydrogenation of xylose and glucose, respectively. Because xylose and glucose are main components of hemicellulose, conversion to xylitol and sorbitol is an important way to consume hemicellulose [29]. As platform chemicals, xylitol and sorbitol can be dehydrated to cyclic products, as well as cleaved to be smaller molecules such as glycerol and ethylene glycol by hydrogenolysis [18].

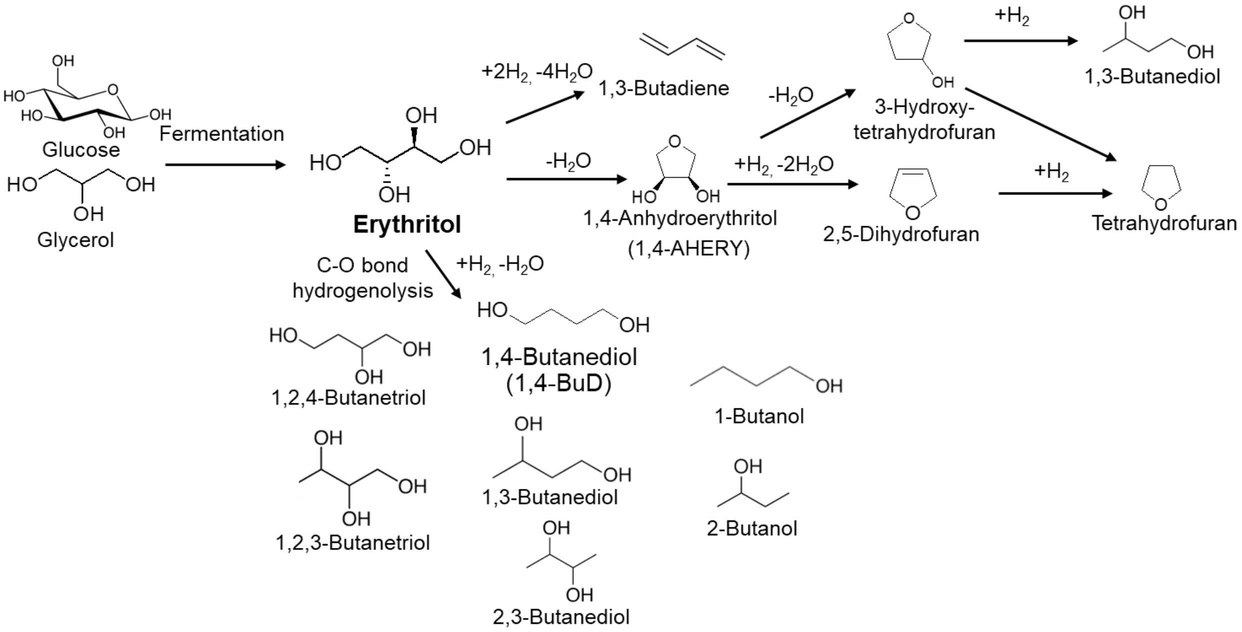
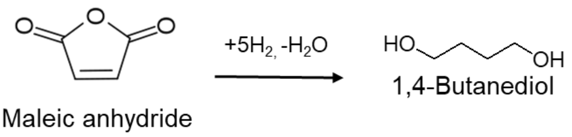


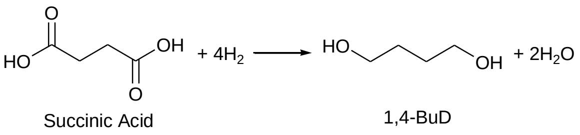
Figure 1-3 Possible routes of erythritol to polyols

1.3.2 *α,ω-Diols: The target products*

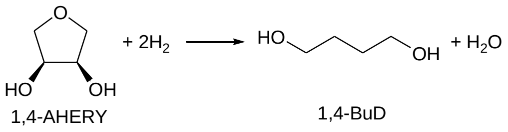
Sugar alcohols are polyols, and therefore alcohols including polyols are the main targets in sugar alcohol conversion. In view of the consumption of H_2, polyols are more attractive targets than mono-alcohols. α,ω-Diols can be generally used as monomers of polyester and polyurethane, and they are very important targets. One attractive target is 1,4-butanediol (1,4-BuD) which is a valuable non-natural chemical as an important solvent or intermediate for polymers and pharmaceuticals. Current production method of 1,4-BuD is hydrogenation of maleic anhydride (eq 1-1) [30]. Biomass-based production method by the fermentation from glucose was reported. Over 70% yield of 1,4-BuD can be produced by the hydrogenation of succinic acid or γ-butyrolactone has been investigated (eq 1-2) [30],[31]. Both erythritol and succinic acid are fermentation products from sugars. However, the production of 1,4-BuD from erythritol and its derived products are limited. Only 25-30% yield of 1,4-BuD could be obtained from erythritol or 1,4-anhydroerythritol (1,4-AHERY) in previous reports [27]-[32]. Therefore, the production cost of 1,4-BuD via erythritol and succinic acid-based routes will largely depend on the amount of H_2 used in the chemical reduction process. Although the reaction route *via* erythritol and 1,4-AHERY requires extra step for dehydration of erythritol, the H_2 consumption in the reduction of 1,4-AHERY to 1,4-BuD (2 equiv., eq 1-3) is just half compared with that in the reduction of succinic acid to 1,4-BuD (4 equiv., eq 1-2). Therefore, the production of 1,4-BuD from erythritol and the dehydrated product, 1,4-AHERY, is worth to be studied.



(1-1)



(1-2)



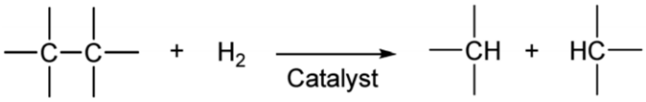
(1-3)

1.4 Techniques for catalytic conversion for sugar alcohols

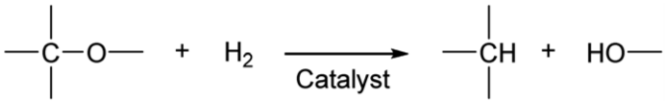
Biomass-derived sugar alcohols are not convenient or economical to be raw materials for chemical use due to their high oxygen content because of the large amount of OH groups. To deal with this problem, catalytic conversions such as selective oxygen removal have been applied to remove the OH groups in the sugar alcohols to decrease the oxygen number and increase their value. Hydrogenolysis, hydrogenation, dehydration, deoxydehydration and other methods have been investigated for the selective oxygen removal methods.

1.4.1 Hydrogenolysis

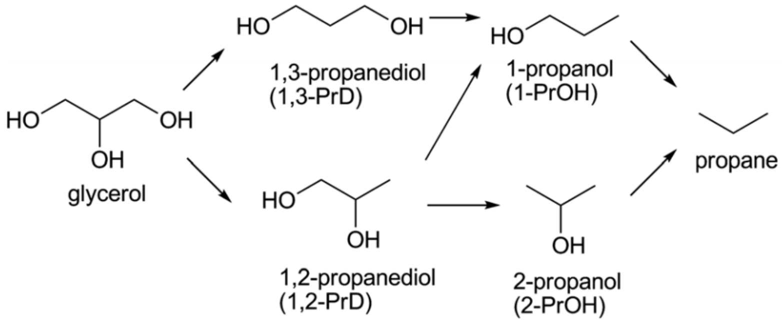
Hydrogenolysis is a chemical reaction that the carbon-carbon or carbon-oxygen single bonds cleave by hydrogen (eq 1-4 and 1-5). Hydrogenolysis is an effective selective oxygen removal method to break the C-O bond in small sugar alcohols like glycerol to produce propanediols as target chemicals with high selectivity. In Tomishige laboratory, silica-supported Re-modified Rh and Ir catalysts were reported can effectively convert glycerol to 1,3-propanediol and 1,2-propanediol by hydrogenolysis (Scheme 1-1) [20],[33]-[42]. However, when the substrates are bigger polyols such as erythritol, xylitol, and sorbitol, the selectivity to target products are difficult to control, and the main products are deeply deoxygenated. Erythritol produced the mixture of butanediols, butanetriols, butanol, and butane with low selectivity by hydrogenolysis, while high selectivity to value-added target products is not achieved [27]. Sorbitol also convert into hexane and smaller (≤ C3) compounds such as propylene glycol by hydrogenolysis [43]-[48].



$$-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}- \quad + \quad H_2 \xrightarrow[\text{Catalyst}]{} -\overset{|}{\underset{|}{C}}H \quad + \quad H\overset{|}{\underset{|}{C}}- \qquad (1\text{-}4)$$



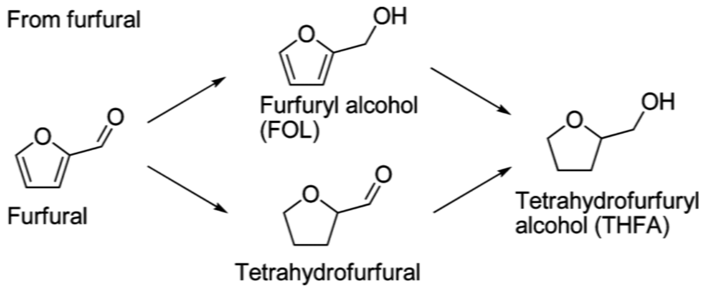
$$-\overset{|}{\underset{|}{C}}-O- \quad + \quad H_2 \xrightarrow[\text{Catalyst}]{} -\overset{|}{\underset{|}{C}}H \quad + \quad HO- \qquad (1\text{-}5)$$



Scheme 1-1 Hydrogenolysis pathways of glycerol

1.4.2 Hydrogenation

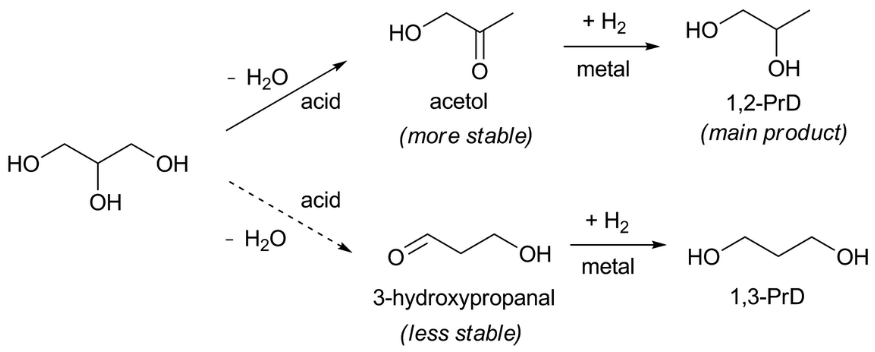
Hydrogenation refer to the addition of hydrogen atoms to a C=C or C=O which makes the unsaturated to become saturated. Selective hydrogenation can be used for the conversion of unsaturated aldehydes including α,β-unsaturated aldehydes to be unsaturated alcohols. Furfural, as a biomass-based product from sugars, can be selectively hydrogenated to furfuryl alcohol without hydrogenation of unsaturated bonds in the ring (Scheme 1-2) [49]-[52].



Scheme 1-2 Selective hydrogenation of furfural to furfuryl alcohol [49]-[52]

1.4.3 Dehydration

Dehydration is commonly carried out in the reaction of sugars and sugar alcohols due to their large amount of OH groups, especially in acid conditions. Biomass-derived chemicals with can form polymers by dehydration of OH groups between molecules, or dehydrate within a molecule to be cyclic structure. In sugar alcohol conversions, dehydration is often combined with hydrogenation to be a dehydration + hydrogenation mechanism. 1,2-Propanediol can be produced from glycerol by dehydration of glycerol to acetol and the hydrogenation of acetol to 1,3-propanediol (Scheme 1-3). Similarly, glycerol can be dehydrated to 3-hydroxypropanl and consecutively hydrogenated to 1,3-propanediol [20].

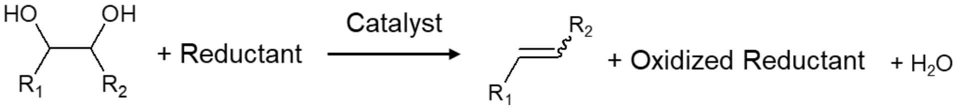


Scheme 1-3 Dehydration + hydrogenation mechanisms for preparing propanediols from glycerol [20]

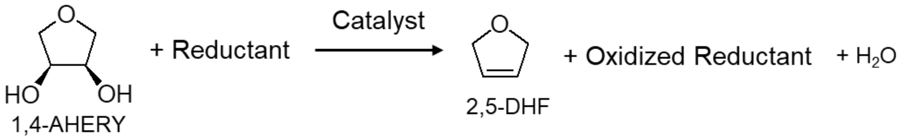
1.5 Deoxydehydration (DODH) process and DODH catalysts

1.5.1 Deoxydehydration (DODH) process

Deoxydehydration (DODH; Scheme 1-4, R1, R2 = alkyl, aryl, or H) is a potential method to effectively decrease the oxygen content in biomass-based products. DODH simultaneously removes vicinal diols which are frequently observed in biomass-based molecules, especially sugars and sugar alcohols, and form corresponding C=C bond. While usually hydrogenolysis systems dissociate C-O bonds step by step and give complex mixture from polyols, DODH system can give much simpler product distribution. 1,4-Anhydroerythritol (1,4-AHERY) as dehydrated product from erythritol is frequently used as substrates for DODH (Scheme 1-5) [53]-[57]. In this research, the DODH of biomass-derived alcohols is discussed.



Scheme 1-4 Deoxydehydration (DODH) reaction



Scheme 1-5 DODH of 1,4-AHERY

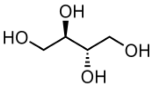
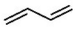
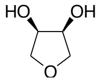
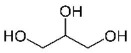
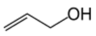
1.5.2 Homogeneous DODH catalysts

Typical DODH systems use homogeneous catalysts, some of them are shown in Table 1-1. In 1996, Cook and Andrews reported that Cp^*ReO_3 (Cp^* = pentamethylcyclopentadienyl) can catalyze the DODH reaction of erythritol to form 1,3-butanediene with the reductant of triphenylphosphine (PPh_3) (Table 1-1, entry 1) [58]. Recently, researchers began to be interested in Re-catalyzed DODH reaction. Since Ziegler reported the DODH system using CH_3ReO_3 (methyltrioxorhenium) as catalyst, CH_3ReO_3 has been the most common homogeneous catalyst in DODH reaction (Table 1-1, entry 2) [59]. Polyols with *syn*-stereoselectivity such as 1,4-AHERY can be converted to the corresponding alkene. H_2 is the cheapest and most environmentally benign reductant in DODH reaction. However, most DODH systems use non-H_2 reductants, because the product yield was low when the H_2 acts as the reductant. Arceo developed a new system for Re-catalyzed DODH reaction by using secondary alcohol as the reducing agent (Table 1-1, entry 3) [60]. By using 3-octanol as reductant, the yield of 2,5-DHF reached 62% over $Re_2(CO)_{10}$ from 1,4-AHERY. Shiramizu and Toste further improved the CH_3ReO_3 activity by using 3-octanol as the reductant, and high yield of 95% of 2,5-DHF was obtained from 1,4-AHERY catalyzed by CH_3ReO_3 (Table 1-1, entry 4) [56]. Under this CH_3ReO_3/3-octanol DODH system, glycerol can be easily converted to allyl alcohol (yield = 90%); moreover, erythritol and *DL*-threitol are converted to 1,3-butanediene with yield of 89% and 81%, respectively. Because the high-valent Re species in Cp^*ReO_3 is easy to degrade to mixed-valent multinuclear species, Raju stabilized high-valent Re species by increasing the complex size from Cp^*ReO_3 to $Cp^{ttt}ReO_3$ (Cp^{ttt} = 1,2,4-tri(*tert*-butyl)cyclopentadienyl) [57]. In the Cp^*ReO_3/PPh_3 DODH system, glycerol was converted to allyl alcohol with the yield of 91%; nevertheless, only 49% yield of 2,5-DHF was converted from 1,4-AHERY (Table 1-1, entry 5), which is much lower than the yield of CH_3ReO_3/3-octanol system.

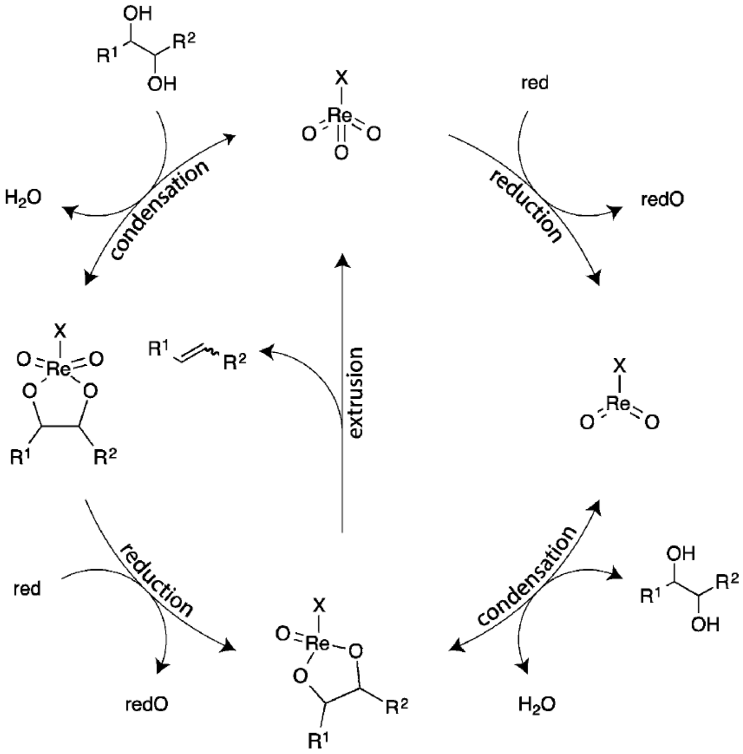
Considering the high price of Re, relatively cheaper elements such as V and Mo have potential to be used in DODH catalysts as oxo-vanadium and oxo-molybdenum complexes (Table 1-1, entries 6 and 7) [54]-[61]. Petersen found that glycerol can be reduced to allyl alcohol by NH_4VO_3 even without external reductant; however, the yield was not high. Dethlefsen reported the $(NH_4)_6Mo_7O_{24}$ have the DODH activity to convert 1,4-AHERY to 2,5-DHF with the reductant of isopropyl alcohol. Erythritol also can be converted to 2,5-DHF with 39% yield under this $(NH_4)_6Mo_7O_{24}$/isopropyl alcohol DODH system because of the formation of 1,4-AHERY as the intermediate.

The mechanism of DODH reaction is widely accepted as shown in Scheme 1-6 [53]. Re species which act as catalytic center condense the two vicinal hydroxyl groups to form diolate oxorhenium complex. The Re^{7+} is proposed to be reduced to Re^{5+} by the external reducing agent, and then reforms to Re^{7+} by extrusion of alkene. The disagreement of researchers is the pathways of the catalytic cycle: reduction first or condensation first. Additionally, Ziegler et. al. proposed Re^{5+} diolate can be further reduced to Re^{3+} diolate [59]. The mechanism of Mo- and V-catalyzed DODH reaction is similar to the reaction using Re catalyst. Mo^{6+}/Mo^{4+} and V^{5+}/V^{3+} can be catalytic center as Re^{7+}/Re^{5+} in the diolate [54]-[61].

Table 1-1 Homogeneous catalysts of DODH systems

Entry	Substrate	Catalyst	Reductant	Reaction conditions	Product	Yield/ %	Ref.
1	Erythritol 	$CpReO_3$ [a]	PPh_3 [b]	408 K 28 h	1,3-Butadiene 	80	[58]
2	1,4-AHERY 	CH_3ReO_3	H_2	423 K, 16 h	2,5-DHF 	25	[59]
3		$Re_2(CO)_{10}$	3-Octanol	433 K 12 h		62	[60]
4		CH_3ReO_3	3-Octanol	443 K 1 h		95	[56]
5		$\text{Cp}^{ttt}ReO_3$ [c]	PPh_3	453 K 37 h		49	[57]
6		$(NH_4)_6Mo_7O_{24}$	Isopropyl alcohol	523 K 18 h		75	[61]
7	Glycerol 	NH_4VO_3	None	548 K 5 h	Allyl alcohol 	22	[54]

[a] Cp = cyclopentadienyl, [b] PPh_3 = triphenylphosphine, [c] Cp^{ttt} = 1,2,4-tri(*tert*-butyl)cyclopentadienyl.



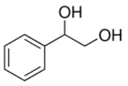
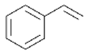
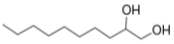
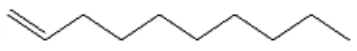
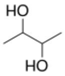
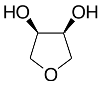
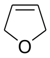
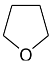
Scheme 1-6 The two fundamentally different pathways for the rhenium-catalyzed DODH of a vicinal diol driven by oxidation of a reductant. Reprinted from Ref. [53] with permission from Wiley.

1.5.3 Heterogeneous DODH catalysts

Compared with homogeneous DODH system, heterogeneous catalysts just start to develop in recent years. Table 1-2 shows examples of DODH reaction using heterogeneous catalysts. Denning reported the ReO_x/C catalyst has the activity for DODH of glycols to their corresponding olefins (Table 1-2, entry 1) [62]. Sharkey stabilized the oxo-rhenium and oxo-molybdenum on solid supports such as Fe_2O_3, TiO_2, Al_2O_3, SiO_2, and ZrO_2 to be DODH catalysts [63]. 1,2-Decanediol can be converted to 1-decene with high yield of 70-78% over ReO_x/SiO_2, ReO_x/Fe_2O_3, and ReO_x/Al_2O_3 catalysts with the reductant of PPh_3; and the yield of 1-decene is much lower over MoO_x/Fe_2O_3, MoO_x/SiO_2, and MoO_x/Al_2O_3 catalysts (< 20%) (Table 1-2, entry 2).

Similarly, Mo and V instead of Re are used in DODH reaction. Sandbrink used the MoO_x/TiO_2 catalyst to convert 1,4-anhydroerythritol to 2,5-dihydrofuran with the reductant of 3-octanol (Table 1-2, entry 3) [64]. This MoO_x/TiO_2 catalyst can be reused for 5 times without significant deactivation. Kwok reported VO_x/SiO_2 as a DODH catalyst in a flow reactor can convert 2,3-butanediol to butenes without external reductant (Table 1-2, entry 4) [64]. Furthermore, the mechanism of VO_x/SiO_2 system is proposed that the hydroxyl groups are not removed simultaneously. The mechanism of heterogeneous Re-catalyzed DODH reaction was also proposed to be Re^{7+}/Re^{5+} redox cycle, which is similar to the that of homogeneous.

Table 1-2 Heterogeneous catalysts of DODH systems

Entry	Substrate	Catalyst	Reductant	Reaction conditions	Product	Yield/ %	Ref.
1	Phenyl-1,2-ethanediol 	ReO_x/C	H_2	423 K 24 h	Styrene 	39	[62]
2	1,2-Decanediol 	ReO_x/Al_2O_3	PPh_3	423 K 24 h	1-Decene 	78	[63]
3	2,3-Butanediol 	VO_x/SiO_2	None	773 K	Butenes	37	[64]
4	1,4-AHERY 	MoO_x/TiO_2	3-Octanol	473 K 18 h	2,5-DHF 	55	[64]
5		ReO_x-Au/CeO_2		413 K 24 h		80	[66]
6		ReO_x-Pd/CeO_2		413 K 24 h	THF 	99	[67]

Recently, in Tomishige laboratory, ReO_x-Au/CeO_2 and ReO_x-Pd/CeO_2 catalysts were reported as effective H_2-driven heterogeneous DODH catalysts (Table 1-2 entries 5 and 6) [66][67]. Both catalyst systems use H_2 as the reductant which is more environmentally benign than other reductants such as alcohols. ReO_x-Au/CeO_2 catalyzed DODH and ReO_x-Pd/CeO_2 catalyzed

DODH + hydrogenation of polyols to be corresponding target alkenes and alkanes with high yield. 1,4-AHERY could be converted to 2,5-DHF over the ReO_x-Au/CeO_2 catalyst with 80% yield (Table 1-2, entry 5). ReO_x-Pd/CeO_2 catalyzed DODH and subsequent hydrogenation of C=C bond. The DODH product of 2,5-DHF from 1,4-AHERY could be further hydrogenated to THF over ReO_x-Pd/CeO_2 catalyst with a very high yield >99% (Table 1-2 entry 6). Recently, ReO_x-Au/CeO_2 and ReO_x-Pd/CeO_2 even could catalyze sugars such as methylglycosides with *cis-* OH groups to corresponding dideoxy products [70],[71]. Au or Pd promoters have the function of activating H_2, and the activated hydrogen moves on CeO_2 surface for the reduction of Re species in the reaction [66]-[71]. While Pd is a more effective promoter for H_2 activation, Pd is also active in C=C hydrogenation and thus the product over ReO_x-Pd/CeO_2 becomes saturated. It has been proposed that CeO_2 support plays an important role in the suppression of deep reduction of Re species to low valent Re species such as Re metal and maintaining high valence ($\geq +4$) of the Re species, which can be an active Re species for the DODH reaction, under the DODH reaction conditions. The studies on the effect of loading amount of Re on CeO_2 and the catalyst characterization suggest that monomeric Re species attached on the surface of CeO_2 support is a catalytically active species and polymeric Re species is inactive species in the DODH reaction. Moreover, the DODH reaction is suggested to proceed by the redox mechanism between Re^{4+} and Re^{6+} (Figure 1-4) [69]. On the other hand, the Au particles have a role on the activation of molecular hydrogen, and the activated hydrogen species are supplied from Au surface to Re species via the CeO_2 surface, to reduce the oxidized Re species (Re^{6+}) to the reduced Re species (Re^{4+}). The preparation method also showed effect on ReO_x-Au/CeO_2 catalysts. The Au particles on CeO_2 were 3 nm and 12 nm on ReO_x-^{dp}Au/CeO_2 (Au loading by deposition-precipitation method) and ReO_x-^{imp}Au/CeO_2 (Au loading by impregnation method), respectively [66]-[69]. The ReO_x-^{dp}Au/CeO_2 showed higher activity than that of ReO_x-^{imp}Au/CeO_2 due to the smaller Au particle size. However, the ReO_x-^{imp}Au/CeO_2 is preferable for the polyol substrates such as glycerol and erythritol (eq 1-6 and 1-7) due to the higher yield of DODH product (allyl alcohol and 1,3-butandiene, respectively), because the low H_2 activation ability of ^{imp}Au slows down the hydrogenation of alkenes. On the other hand, the ReO_x-^{dp}Au/CeO_2 is good

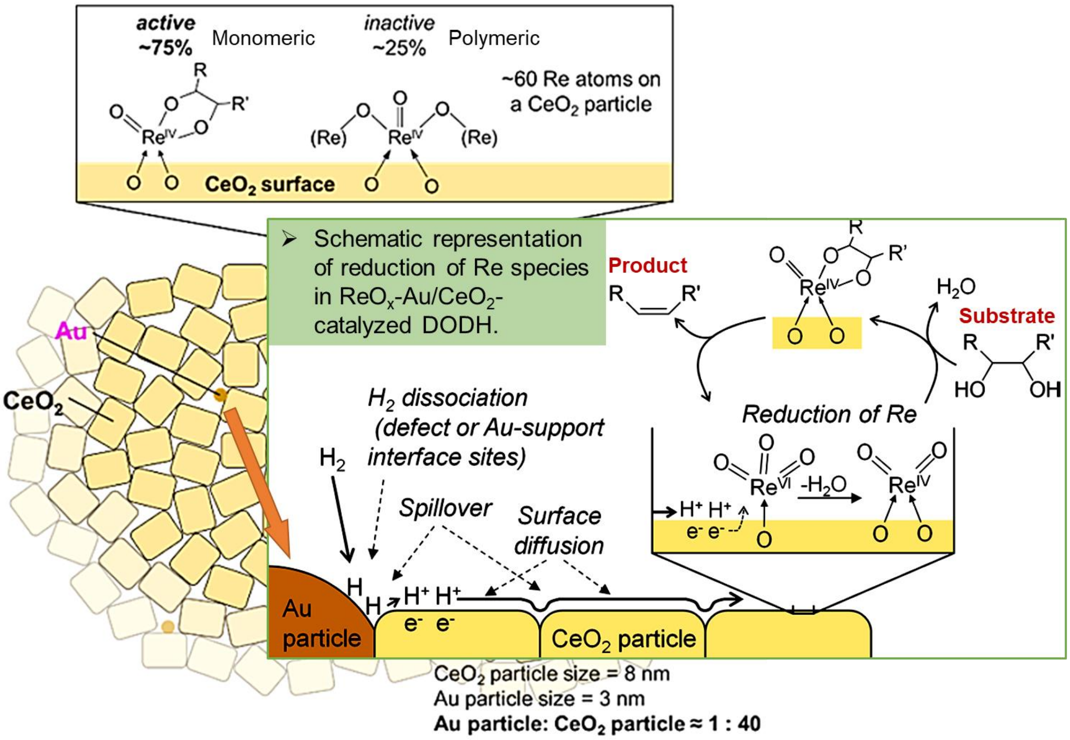
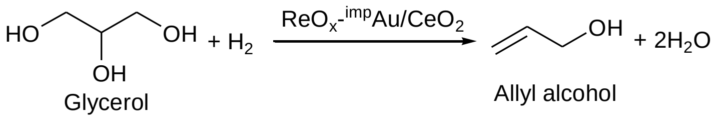
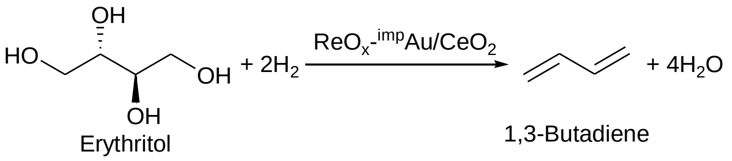


Figure 1-4 Mechanism of DODH over ReO_x-^{dp}Au/CeO_2 catalyst [69]

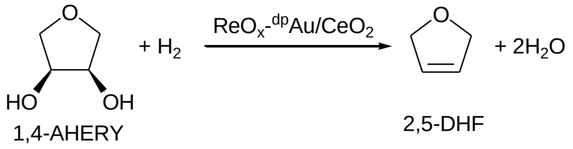
for the DODH reaction of diol substrates such as 1,4-AHERY (eq 1-8), because the selectivity of DHFs of ReO_x-^{dp}Au/CeO_2 (98%) is similar to that of ReO_x-^{imp}Au/CeO_2 (98%), while the reaction rate of ReO_x-^{dp}Au/CeO_2 is 6 times higher than that ReO_x-^{imp}Au/CeO_2. Heterogeneous ReO_x-Pd/CeO_2 catalyst can catalyze the conversion of 1,4-AHERY to tetrahydrofuran (THF) *via* DODH + hydrogenation with high activity and selectivity (99%) [67],[68]. The structure of Re species is the same as that in ReO_x-Au/CeO_2, the high activity of ReO_x-Pd/CeO_2 is derived from the high H_2 activation ability of Pd, and high dispersion of Pd metal particles (<1 nm). While the number of Au (or Pd) promoters were much less than the number of CeO_2 particles (the ratio of Au particle number to CeO_2 particle number was 1: 40 in ReO_x-^{dp}Au/CeO_2 catalyst based on the particle size), the promoters showed high activity of activating H_2. The activated hydrogen species could move from promoters to CeO_2 particle surfaces by spillover, and then reduce of Re species on CeO_2. The active hydrogen species is supposed to move from particle to particle *via* protons and electrons [69].



(1-6)



(1-7)



(1-8)

1.6 One-pot synthesis

One-pot reaction is a sequence of chemical transformations is run in a single reactor, which can improve the efficiency of a chemical reaction. The merits of one-pot reaction are convenient and economical. In one-pot reaction, the separation and purification of intermediate can be avoided between individual reactions, which minimize the chemical waste, as well as save energy, labor, and time. In some cases, the concentration of unstable intermediate can be kept low during the reaction in one-pot system which can suppress side reaction of intermediate and increase the yield of final products. Difficulties for one-pot process include the control of reaction conditions: each step has different optimized conditions and therefore some steps proceed under not-best conditions. [73],[74].

1.7 Research object and strategies

Biomass is becoming a significant sustainable energy resource or chemical feedstock in the 21st century due to the depletion of fossil fuel and the worldwide large potential supply. Even though the fossil fuels are still the main energy resource and refinery feedstock nowadays, the global consumption of biomass-based products is increasing due to the advantages such as less

CO_2 emission which is friendly to the environment, as well as sustainable and renewable properties for the regeneration.

Biomass-derived compounds such as sugar alcohols which can be obtained from cellulose or hemicellulose are important building blocks for chemical synthesis or refinery. As chemical platforms, sugar alcohols such as glycerol, erythritol or sorbitol contain high unwanted oxygen content, therefore, selective oxygen removal of sugar alcohols to target alkenes or alcohols with fewer OH groups is a significant process to decrease oxygen content and increase their value.

1,4-Butanediol (1,4-BuD) which is a value-added non-natural chemical as an important solvent or intermediate for polymers and pharmaceuticals. Current production method of 1,4-BuD is hydrogenation of maleic acid, and biomass-based production method by the hydrogenation of succinic acid or γ-butyrolactone has been investigated. Both erythritol and succinic acid are fermentation products from sugars. However, the production of 1,4-BuD from erythritol via either DODH or stepwise C-O dissociations is lack of investigation because the selective oxygen remove of erythritol is difficult.

DODH as an effective method to remove the OH groups in the presence of vicinal OH groups in sugar alcohols. ReO_x-Au/CeO_2 was found to be an effective DODH catalyst which can catalyze the erythritol to 1,3-butediene, as well as 1,4-AHERY to 2,5-DHF with very high yield. On the other hand, 2,5-DHF, which is the DODH product from 1,4-AHERY, could be converted to 1,4-BuD over ReO_x/TiO_2 in THF and water solvent [72]. Therefore, if the reactions of DODH of 1,4-AHERY and the conversion of 2,5-DHF could carry out in one-pot reaction, it is possible to produce 1,4-BuD from 1.4-AHERY which can be easily dehydrated from erythritol. Because the ReOx-Au/CeO2 catalyst showed very low activity in the water solvent, as well as the reaction temperature in the ReO_x/TiO_2-catalyzed conversion of 2,5-DHF is much higher than the optimized conditions for ReO_x-Au/CeO_2 catalyst, a new co-catalyst system should be developed.

In this study, the author combines the two catalysis within one-pot reaction: the DODH of 1,4-AHERY to 2,5-DHF over ReO_x-Au/CeO_2 and the conversion of 2,5-DHF to 1,4-BuD over another Re catalyst (Figure 1-5). Over the combination of ReO_x-Au/CeO_2 and ReO_x/C catalysts, the yield of 1,4-BuD from 1,4-AHERY obtained ~90% reduced by H_2 at 413 K. This yield is much higher than the literature ones of 1,4-BuD from 1,4-AHERY.

Then the author improved the co-catalyst system and found that the ReO_x/CeO_2 catalyst could catalyze the DODH without Au promoter combined with ReO_x/C catalyst. The yield was as high as the combination with Au promoter. However, the deactivation of the catalyst mixture was still a problem to be solved due to the difficulty of reuse of the contains carbon

The co-catalyst system is improved for the reuse of the catalyst mixture. Instead of carbon support, WO_3-ZrO_2 support could be an alternative combined with ReO_x-Au/CeO_2 catalyst in the production of 1,4-BuD from 1,4-AHERY. However, the yield of 1,4-BuD over the combination of ReO_x-Au/CeO_2 and ReO_x/WO_3-ZrO_2 was not high enough, and the yield might still have potential to be improved.

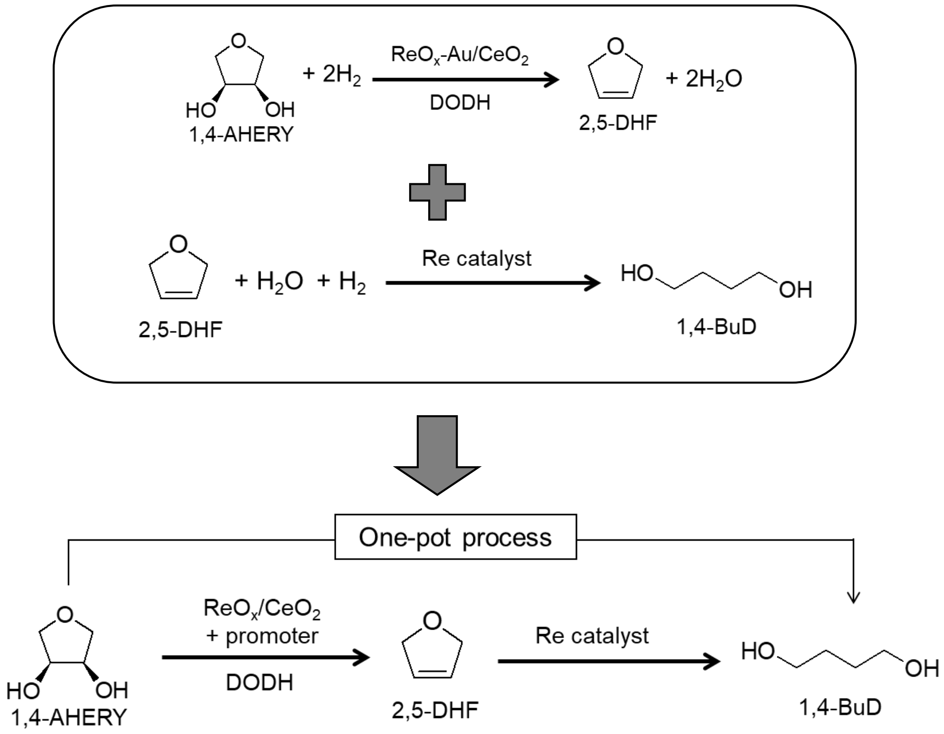


Figure 1-5 Combination of the reaction of 1,4-AHERY to 2,5-DHF and 2,5-DHF to 1,4-BuD in one-pot reaction

1.8 Outline of the thesis

This thesis presents the results of one-pot conversion of 1,4-AHERY to 1,4-BuD over the co-catalyst system of Re catalyst combinations including ReO_x-Au/CeO_2 + ReO_x/C, ReO_x/CeO_2

+ ReO_x/C, as well as ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2.

Chapter 1 is a general introduction of fossil fuels, biomass, biomass-derived products such as sugar alcohols, as well as the techniques for decreasing the high oxygen content in sugar alcohols such as DODH reaction. It also introduces the objects of this study and the strategies for the research.

Chapter 2 presents the study of the one-pot conversion of 1,4-AHERY to 1,4-BuD using the co-catalyst system of ReO_x-Au/CeO_2 + ReO_x/C. 90% yield of 1,4-BuD was obtained from 1,4-AHERY over the physical mixture of ReO_x-Au/CeO_2 + ReO_x/C catalysts in one-pot reaction at H_2 at 413 K with the reductant of H_2. This is the highest yield of 1,4-BuD from erythritol or 1,4-AHERY using heterogenous catalysts. This reaction is composed of ReO_x-Au/CeO_2-catalyzed DODH of 1,4-AHERY to 2,5-DHF and ReO_x/C-catalyzed successive isomerization, hydration and reduction reactions of 2,5-DHF to 1,4-BuD.

Chapter 3 demonstrates the improvement of the co-catalyst system that 1,4-BuD could be produced from 1,4-AHERY in one-pot reaction over the combination of ReO_x/C + ReO_x/CeO_2 without Au promoter. Even simple CeO_2 + ReO_x/CeO_2 could also give 89% yield of 1,4-BuD from 1,4-AHERY. The mechanism of this co-catalyst system was similar the mechanism in Chapter 2, including the DODH of 1,4-AHERY to 2,5-DHF catalyzed by the ReO_x/CeO_2 + ReO_x/C together due to the Re species on C can be reduced to metallic state which act as the promoter like Au in DODH reaction; and the following conversion of 2,5-DHF to 1,4-BuD catalyzed by the ReO_x/C. The activity of ReO_x/CeO_2 + ReO_x/C is higher than that of ReO_x-Au/CeO_2 + ReO_x/C which is probably related to the reducibility of ReO_x/C and the move of Re species between supports. The high-valent Re species such as Re^{7+} on CeO_2 and C supports are mobile in the solvent; however, the low-valent Re species including metal Re species have much lower mobility.

Chapter 4 improved the reusability of the co-catalyst system in Chapter 2 and 3. Because the used mixture with carbon support was difficult to recover the catalytic activity after use, the ReO_x/WO_3-ZrO_2 was found to a potential replacement of carbon support combined with in the reaction of 1,4-AHERY to 1,4-BuD. The yield over 1,4-BuD was 55% over the mixture of

ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2, which was much lower than that obtained in Chapter 2 and 3. However, the catalytic activity of the recycled mixture of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 could be regenerated to the fresh level by calcination at 573 K for 3 h according to the conversion and 1,4-BuD selectivity in the second and third run. The mechanism was similar to that descried in Chapter 2, including the DODH of 1,4-AHERY to 2,5-DHF catalyzed by ReO_x-Au/CeO_2 and the conversion of 2,5-DHF to 1,4-BuD was catalyzed by ReO_x/WO_3-ZrO_2. The low selectivity of 1,4-BuD was due to the formation of hydrogenation of 2,5-DHF to THF catalyzed by ReO_x/WO_3-ZrO_2 in the same time, because the isomerization ability of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 was much slower than that of ReO_x/C.

Chapter 5 summarizes the results in the Chapter 2-4 and make a general conclusion of this thesis.

Reference

[1] BP Statistical Review of World Energy, 2019, Available from: https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf

[2] International Energy Agency (IEA). Statistics, Available from: https://www.iea.org/weo2018/

[3] International Energy Agency (IEA). Statistics, Available from: http://www.iea.org/statistics/

[4] Forecast of Global Supply and Demand Trends for Petrochemical Products (for the period 2009 to 2022), Available from: https://www.meti.go.jp/english/press/2018/1019_003.html

[5] S. Shafiee, E. Topal, Energy Policy, 2009, 37, 181-189.

[6] H. Chen, H. Liao, B. Tang, Y. Wei, Energy Econ., 2016, 57, 42-49.

[7] Global Carbon Budget 2018, Earth Syst. Sci. Data, 10, 2141-2194, Available from: https://doi.org/10.5194/essd-10-2141-2018, 2018.

[8] IPCC - Intergovernmental Panel on Climate Change, Available from: https://report.ipcc.ch/sr15/pdf/sr15_spm_final.pdf

[9] J. E, M. Pham, D. Zhao, Y. Deng, D. Le, W. Zuo, H. Zhu, T. Liu, Q. Peng, Z. Zhang, Renew. Sust. Energ. Rev., 2017, 80, 620-647.

[10] A. Demirbas, Prog. Energy Combust. Sci., 2007, 33, 1-18.

[11] International Energy Agency (IEA). Statistics, Available from: https://www.iea.org/topics/renewables/bioenergy/

[12] H. S. Kambo, A. Dutta, Appl. Energy, 2014, 135, 182-191.

[13] J. J. Chew, V. Doshi, Renew. Sust. Energ. Rev., 2011, 15, 4212-4222.

[14] International Energy Agency (IEA). Statistics, Available from: https://www.iea.org/tcep/transport/biofuels/

[15] J. Popp, Z. Lakner, M. Harangi-Rákos, M. Fári, Renew. Sust. Energ. Rev., 2014 32, 559-578.

[16] F. M. Girio, C. Fonseca, F. Carvalheiro, L. C. Duarte, S. Marques, R. Bogel-Lukasik,

Bioresour. Technol., 2010, 101, 4775-4800.

[17] L. Zhang, C. Xu, P. Champagne, Energ. Convers. Manage., 2010, 51, 969-982.

[18] A. M. Ruppert, K. Weinberg and R. Palkovits, Angew. Chem. Int. Ed., 2012, 51, 2564-2601.

[19] C. Zhou, J. N. Beltramini, Y. Fan, G. Q. Lu, Chem. Soc. Rev., 2008, 37, 527–549.

[20] Y. Nakagawa, M. Tamura, K. Tomishige, J. Mater. Chem. A, 2014, 2, 6688-6702.

[21] D. Sun, Y. Yamada, S. Sato, W. Ueda, Appl. Catal. B, 2016, 193, 75-92.

[22] A. Mirończuk, M. M. Rakicka, A. Biegalska, W. Rymowicz and A. Dobrowolski, Bioresour. Technol., 2015, 198, 445-455.

[23] Y. Kobayashi, H. Iwata, D. Mizushima, J. Ogihara and T. Kasumi, Lett. Appl. Microbiol., 2015, 60, 475-480.

[24] H. J. Moon, M. Jeya, I. W. Kim and J. K. Lee, Appl. Microbiol. Biotechnol., 2010, 86, 1017-1025.

[25] H. Ishizuka, K. Wako, T. Kasumi and T. Sasaki, J. Ferment. Bioeng., 1989, 68, 310-314.

[26] Y. Kobayashi, H. Iwata, D. Mizushima, J. Ogihara and T. Kasumi, Lett. Appl. Microbiol., 2015, 60, 475-480.

[27] Y. Amada, H. Watanabe, Y. Hirai, Y. Kajikawa, Y. Nakagawa and K. Tomishige, ChemSusChem, 2012, 5, 1991-1999.

[28] A. Said, D. D. S. Perez, N. Perret, C. Pinel and M. Besson, ChemCatChem, 2017, 9, 2768-2783.

[29] J. J. Bozell and G. R. Petersen, Green Chem., 2010, 12, 539-554.

[30] Z. Huang, K. J. Barnett, J. P. Chada, Z. J. Brentzel, Z Xu, J. A. Dumesic, G. W. Huber, ACS Catal. 2017, 7, 8429-8440.

[31] K. Kang, U. Hong, Y. Bang, J. Choi, J. Kim, J. Lee, S. Han, I. Song, Appl. Catal. A, 2015, 490, 153-162.

[32] L. E. Manzer (E. I. du Pont de Nemours and Company), US Pat., 6593481B1, 2003.

[33] A. Shimao, S. Koso, N. Ueda, Y. Shinmi, I. Furikado, K. Tomishige, Chem. Lett., 2009, 38, 540-541.

[34] Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, Appl. Catal. B, 2010, 94, 318-326.

[35] Y. Nakagawa, Y. Shinmi, S. Koso, K. Tomishige, J. Catal., 2010, 272, 191-194.

[36] Y. Amada, Y. Shinmi, S. Koso, T. Kubota, Y. Nakagawa, K. Tomishige, Appl. Catal. B, 2011, 105, 117-127.

[37] Y. Nakagawa, X. Ning, Y. Amada, K. Tomishige, Appl. Catal., 2012, 128, 433-434

[38] K. Tomishige, M. Tamura, Y. Nakagawa, Chem. Rec., 2014, 14, 1041-1054.

[39] K. Tomishige, Y. Nakagawa, M. Tamura, Top. Curr. Chem., 2014, 353, 127-162.

[40] M. Tamura, Y. Amada, S. Liu, Z. Yuan, Y. Nakagawa, K. Tomishige, J. Mol. Catal. A: Chemical., 2014, 388-389, 177-187.

[41] S. Liu, M. Tamura, Z. Shen, Y. Zhang, Y. Nakagawa, K. Tomishige, Catal. Today, 2018, 303, 106-116.

[42] L. Liu, S. Kawakami, Y. Nakagawa, M. Tamura, K. Tomishige, Appl. Catal. B Environ., 2019, 256, 117775.

[43] S. Liu, Y. Okuyama, M. Tamura, Y. Nakagawa, A. Imai, K. Tomishige, Catal. Today, 2016, 269, 122-131.

[44] M. Zheng, J. Pang, R. Sun, A. Wang and T. Zhang, ACS Catal., 2017, 7, 1939-1954.

[45] M. Yabushita, H. Kobayashi and A. Fukuoka, Appl. Catal. B: Environ., 2014, 145, 1-9.

[46] X. Liu, X. Wang, S. Yao, Y. Jiang, J. Guan and X. Mu, RSC Adv., 2014, 4, 49501-49520.

[47] Y. Jia and H. Liu, Catal. Sci. Technol., 2016, 6, 7042-7052.

[48] X. Jin, J. Shen, W. Yan, M. Zhao, P. S. Thapa, B. Subramaniam and R. V. Chaudhari, ACS Catal., 2015, 5, 6545-6558.

[49] Y. Nakagawa, K. Tomishige, Catal. Today, 2012, 195, 136-143.

[50] Y. Nakagawa, K. Takada, M. Tamura, K. Tomishige, ACS Catal., 2014, 4, 2718-2726.

[51] Y. Nakagawa, M. Tamura, K. Tomishige, Catal. Surv. Asia, 2015, 19, 249-256.

[52] Y. Nakagawa, M. Tamura, K. Tomishige, J. Jpn. Petrol. Inst., 2017, 60, 1-9.

[53] J. R. Dethlefsen and P. Fristrup, ChemSusChem, 2015, 8, 767-775.

[54] A. R. Petersen and P. Fristrup, Chem. Eur. J., 2017, 23, 10235-10243.

[55] S. Raju, M. Moret and R. J. M. K. Gebbink, ACS Catal., 2015, 5, 281-300.

[56] M. Shiramizu and F. D. Toste, Angew. Chem. Int. Ed., 2012, 51, 8082-8086.

[57] S. Raju, J. T. B. H. Jastrzebski, M. Lutz and R. J. M. K. Gebbink, ChemSusChem., 2013, 6, 1673-1680.

[58] G. K. Cook and M. A. Andrew, J. Am. Chem. Soc., 1996, 118, 9448-9449.

[59] J. E. Ziegler, M. J. Zdilla, A. J. Evans; M. M. Abu-Omar, Inorg. Chem. 2009, 9998-10000.

[60] E. Arceo, Ellman, J. A.; Bergman. R. G. J. Am. Chem. Soc. 2010, 132, 11408–11409.

[61] J. R. Dethlefsen, Lupp, D.; Teshome, A.; Nielsen, L. B.; Fristrup, P. ACS Catal., 2015, 3638-3647.

[62] A. L. Denning, Dang, H.; Liu, Z.; Nicholas, K. M.; Jentoft, F. C. ChemCatChem, 2013, 5, 3567-3570.

[63] B. E. Sharkey, A. L. Denning, F. C. Jentoft, R. Gangadhara, T. V. Gopaladasuc, K. M. Nicholas, Catal. Today, 2017, DOI: 10.1016/j.cattod.2017.05.090.

[64] L. Sandbrink, E. Klindtworth, H. Islam, A. M. Beale, R. Palkovits, ACS Catal., 2016, 6, 677-680.

[65] K. M. Kwok, C. K. S. Choong, D. S. W. Ong, J. C. Q. Ng, C. G. Gwie, L. Chen, A. Borgna, ChemCatChem, 2017, 9, 2443-2447.

[66] S. Tazawa, N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, ACS Catal., 2016, 6, 6393-6397.

[67] N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, Angew. Chem. Int. Ed., 2015, 54, 1897-1900.

[68] N. Ota, M. Tamura, Y. Nakagawa and K. Tomishige, ACS Catal., 2016, 6, 3213-3226.

[69] Y. Nakagawa, S. Tazawa, T. Wang, M. Tamura, N. Hiyoshi, K. Okumura, K. Tomishige, ACS Catal., 2018, 8, 584-595.

[70] J. Cao, M. Tamura, Y. Nakagawa, K. Tomishige, ACS Catal., 2019, 9, 3725-3729.

[71] M. Tamura, N. Yuasa, J. Cao, Y. Nakagawa, K. Tomishige, Angew. Chem. Int. Ed., 2018,

57, 8058-8062.

[72] R. Pinkos, R. H. Fischer, B. Breitscheidel, P. Polanek, CA Pat., 2168458C, 2004.

[73] Y. Hayashi, Chem. Sci., 2016, 7, 866-880.

[74] S. Liu, M. Tamura, Y. Nakagawa, K. Tomishige, ACS Sustainable Chem. Eng., 2014, 2, 1819-1827.

Chapter 2

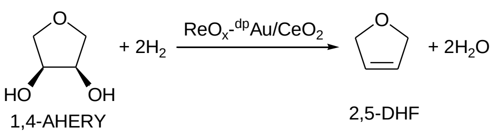
One-pot Catalytic Selective Synthesis of 1,4-Butanediol from 1,4-Anhydroerythritol and Hydrogen

2.1 Introduction

Renewable biomass-based products as energy resources and feedstocks are in increasing demand as replacements of fossil resources [1]-[5]. However, due to the high oxygen content of biomass-derived platform compounds such as sugar alcohols, selective oxygen removal is an important processes to produce value-added chemicals with lower oxygen content [4],[5].

Deoxydehydration (DODH) reaction can simultaneously remove vicinal OH group in sugar alcohols to form corresponding alkenes [9]-[11]. 1,4-Anhydroerythritol (1,4-AHERY) as sugar alcohols from the dehydration of erythritol can product and 2,5-dihydrofuran (2,5-DHF) as main target products by DODH reaction (eq (2-1)) [12],[13]. While typical DODH systems use homogenous Re catalysts such as CH_3ReO_3 and non-H_2 reductants such as secondary alcohol [9], recently, Tomishige laboratory reported ReO_x-Au/CeO_2 and ReO_x-Au/CeO_2 catalysts are effective H_2-driven heterogeneous DODH catalysts [19],[20]. The yield of 2,5-DHF was over 85% over ReO_x-Au/CeO_2-catalyzed DODH reaction of 1,4-AHERY [19]. 1,4-Butanediol (1,4-BuD) as a value-added non-natural product can be produced from the reduction of 2,5-DHF over ReO_x/TiO_2 catalyst (eq (2-2)) with 1,4-dioxane-water or THF-water solvent and H_2 in a flow reactor [24]. Therefore, the 2,5-DHF is possible to be an intermediate from 1,4-AHERY to 1,4-BuD, even though the activity of ReO_x-Au/CeO_2 catalyst was low in water solvent.

In this study, I develop a co-catalyst system combining the ReO_x-Au/CeO_2-catalyzed DODH reaction of 1,4-AHERY to 2,5-DHF, and reduction of 2,5-DHF to 1,4-BuD in one-pot synthesis (eq (2-3)). The yield of 1,4-BuD reached ~90% which was the highest one from 1,4-AHERY and H_2.



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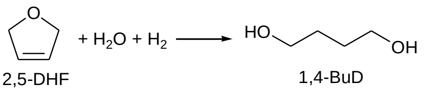

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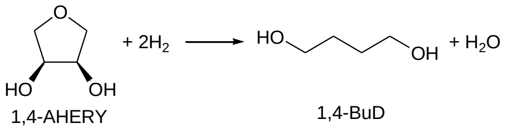

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2.2 Experimental

2.2.1 Catalyst preparation

The ReO_x/Support catalysts were prepared by impregnating support materials with NH_4ReO_4 (Mitsuwa Chemicals Co. Ltd.) aqueous solution at 353 K. Support materials included carbon black “Black Pearl 2000 (BP2000)” (C-BP, Cabot Co., BET surface area: 1282 m^2/g); extruded activated carbon “Norit RX3 extra” (C-NR, Cabot Co., BET surface area: 1159 m^2/g); TiO_2 (Aerosil Co. Ltd., P25, BET surface area: 47 m^2/g); SiO_2 (Fuji Silysia Co. Ltd., G-6, BET surface area: 535 m^2/g); ZrO_2 (Daiichi Kigenso Kagaku Kogyo Co., Ltd., BET surface area: 62 m^2/g), γ-Al_2O_3 (Aerosil Co. Ltd., BET surface area: 82 m^2/g), MgO (Ube Industries, Ltd., 500A, BET surface area: 34 m^2/g). Supports except carbons were calcinated at 773 K for 3 h before impregnation. All the impregnated catalysts were dried in oven at 373 K for 12 h. Then the non-carbon-supported catalysts were calcinated 773 K for 3 h. The loading amount of Re was typically 3wt%.

The Au/CeO_2 catalyst was prepared by deposition–precipitation method [19]. NaOH (Wako Pure Chemical Ind. Ltd.) aqueous solution (0.1 M) was added drop by drop to the stirring suspension of $HAuCl_4 \cdot 4H_2O$ (Wako Pure Chemical Ind. Ltd.) aqueous solution and CeO_2 (HS, Daiichi Kigenso Kagaku Kogyo Co., Ltd., calcinated at 873 K for 3 h, BET surface area: 84 m^2/g) at 353 K until pH = 8. After 4 h stirring, the suspension of Au/CeO_2 was cooled to room temperature, then filtered and washed with 2 L distilled water. The Au/CeO_2 was dried at 373 K for 12 h, and then calcined at 673 K for 4 h. The Re was loaded on Au/CeO_2 by impregnation method using NH_4ReO_4 (Mitsuwa Chemicals Co. Ltd.) aqueous solution for the preparation of ReO_x-Au/CeO_2 catalyst. The ReO_x-Au/CeO_2 was dried at 373 K for 12 h, and then calcinated at

673 K for 4 h again. The loading amount of Re was 1%, and the Au/Re molar ratio was 0.3 (Au 0.3 wt%).

2.2.2 Activity test

Activity tests were carried out in a 190 mL stainless steel autoclave. 1,4-Anhydroerythritol (1,4-AHERY, >98%; Tokyo Chemical Ind. Co., Ltd., substrate), dodecane (>99%; Tokyo Chemical Ind. Co., Ltd., internal standard), 1,4-dioxane (>99%, Wako Pure Chemical Ind., Ltd., solvent), appropriate amount of catalysts, and a spinner were put into an inner glass cylinder placed in the autoclave. The air in the autoclave after sealing was purged by flushing with H_2 (99.99%; Showa Denko K.K.) thrice. Then H_2 pressure was increased to appropriate value. The stirring rate was 250 rpm (magnetic stirring). The autoclave was heated to the reaction temperature monitored via a thermocouple inserted in the autoclave. The reaction time started when the temperature reached the target temperature. The standard reaction conditions were: 0.5 g 1,4-anhydroerythritol, 0.15 g ReO_x-Au/CeO_2, 0.15 g ReO_x/C-BP, 0.1 g dodecane (internal standard), 4 g 1,4-dioxane, 413 K reaction temperature, 8 MPa H_2 pressure (at reaction temperature), and 24 h reaction time. The parameters were changed appropriately for investigating the effects of reaction conditions. Details of the reaction conditions are described in each result. The tests of 2,5-dihydrofuran (2,5-DHF, >98%; Tokyo Chemical Ind. Co., Ltd.) and 2,3-dihydrofuran (2,3-DHF, >98%; Tokyo Chemical Ind. Co., Ltd.) were carried out in the similar method as above. The standard reaction conditions were: 0.15 g substrate, 0.04 g H_2O (substrate: H_2O = 1: 1), 0.15 g ReO_x-Au/CeO_2 or ReO_x/C-BP, 0.1 g dodecane, 4 g 1,4-dioxane, 413 K reaction temperature, 8 MPa hydrogen pressure (at reaction temperature), and 4 h reaction time.

After reaction of all tests, the reactor was cooled down. The gases were collected in a gas bag. The liquid and catalysts in autoclave were transferred to vials, and the catalysts were separated by centrifugation. The products were analyzed by FID-GC (Shimadzu GC-2025) with TC-WAX capillary column (diameter 0.25 mm, 30 m), GC–MS (QP5050, Shimadzu), and nuclear magnetic resonance (NMR, Fourier 300HD, Bruker Co.).

At first, the carbon balance (C.B.) of each analysis result was calculated using eq (2-4). Here, the unidentified products were detected in the GC analysis, the sum of these products are denoted as “others” in each result. The amount of “others” was calculated on the assumption that the sensitivity of “others” are the same as that of 1,4-butanediol (1,4-BuD) unless denoted.

When the C.B. is in the range of 100 ± 10% considering the experimental error, the conversion and selectivity on the carbon basis are calculated by eq (2-5) and (2-6), respectively. The data of C.B. are not shown in each result. In contrast, when the C.B. is clearly lower than 100% (<90%), the conversion and selectivity on carbon basis are calculated by eq (2-7) and (2-8) as below. The selectivity of “others” is the same as the above case. The data of C.B. clearly below 100% are shown in each result. Two possible reasons for low C.B. in the results. One is a substrate with low boiling point, in particular, 2,3-DHF. (boiling point = 328 K). In the experiments of 2,3-DHF substrate (Table 2-3, entries 8-11), and in the results of significant yield of 2,3-DHF product in the reaction of 1,4-anhydroerythritol (Table 2-1, entries 3-5), it is thought that a part of 2,3-DHF can be lost during the purge of H_2 before reaction and the filtration after reaction. The other reason is the side reactions such as polymerization of unsaturated compounds like 2,5-DHF or 2,3-DHF giving undetected products, and this phenomenon seems to be observed remarkably on ReO_x/C-BP in Table 2-3, entries 1 and 4. The yield was calculated by eq (2-9). The TOF based on the conversion and total Re amount of catalyst mixture was calculated by eq (2-10).

$$\text{C. B. (\%)}=\frac{\text{Amount of remaining substrate (C-mol) + Total amount of detected products (C-mol)}}{\text{Amount of initial substrate (C-mol)}}\times 100 \qquad (2\text{-}4)$$

$$\text{Conversion (\%)}=\frac{\text{Total amount of detected products (C-mol)}}{\text{Amount of remaining substrate (C-mol) + Total amount of detected products (C-mol)}}\times 100 \qquad (2\text{-}5)$$

$$\text{Selectivity of product A (\%)}=\frac{\text{Amount of A (C-mol)}}{\text{Total amount of detected products (C-mol)}}\times 100 \qquad (2\text{-}6)$$

$$\text{Conversion (\%; low C. B.)}=100-\frac{\text{Amount of remaining substrate (C-mol)}}{\text{Amount of initial substrate (C-mol)}}\times 100 \qquad (2\text{-}7)$$

$$\text{Selectivity of product A (\%; low C. B.)} = \frac{\text{Amount of A (C-mol)}}{\text{Amount of initial substrate (C-mol) - Amount of remaining substrate (C-mol)}} \times 100 \quad (2\text{-}8)$$

$$\text{Yield (\%)} = \frac{\text{Conversion (\%)} \times \text{Selectivity (\%)}}{100} \quad (2\text{-}9)$$

$$\text{TOF } (\text{h}^{-1}) = \frac{\text{Amount of initial substrate (mol)} \times \Delta\text{Conversion (\%)}}{\text{Amount of Re (mol)} \times \Delta\text{Reaction time (h)}} \quad (2\text{-}10)$$

2.2.3 Catalyst stability test

The reuse procedure of catalysts was as follows: after reaction, the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP was washed by 1,4-dioxane, and centrifuged to remove the liquid, and then dried at 373 K for 12 h. The dried catalyst was treated with various conditions for regeneration. The tested regeneration methods included heating in air at 573 K for 4 h, heating in H_2 at 773 K for 3 h, and heating in N_2 at 773 K for appropriate hours. Due to the weight loss (40%, in four times use) during the recovery process, the weight of substrate and solvent in the next run was adjusted according to the amount of recovered catalyst mixture. The leached Re amount from the catalysts into the reaction solution was analyzed by inductively-coupled plasma atomic emission spectrometry (ICP-AES, ThermoFisher iCAP6500). The catalyst was removed from the liquid phase in glove bag or in air after cooling. The leached amount of Re is represented by its ratio to the total Re amount in Re catalysts.

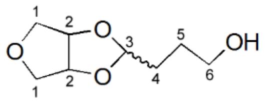
2.2.4 Catalyst characterization

The samples of ReO_x-Au/CeO_2 and ReO_x/C-BP were characterized by X-ray diffraction (XRD), temperature-programmed reduction (H_2-TPR), and thermogravimetric-differential thermal analysis (TG-DTA). XRD patterns were recorded by a diffractometer (Rigaku MiniFlex600). Cu Kα radiation was used as an X-ray source. In the H_2-TPR, 50 mg catalyst in a fixed-bed reactor equipped with a thermal conductivity detector (TCD) was reduced by 5% H_2 diluted with Ar (30 ml/min) from room temperature to 1173 K at a heating rate of 10 K/min. TG-DTA was carried out with Rigaku Thermo plus EVOII under air. Scanning transmission electron microscope (STEM) images were taken by JEOL ARM-200F with Cu grids.

2.2.5 Products determination

Most products were determined by commercially available chemicals include tetrahydrofuran (THF, >98%, Wako Pure Chemical Ind. Ltd.), 2,5-DHF, 2,3-DHF, γ-butyrolactone (GBL, >99%, Wako Pure Chemical Ind. Ltd.), 1-butanol (1-BuOH, >99.7%, Wako Pure Chemical Ind. Ltd.), furan (>98%, Wako Pure Chemical Ind. Ltd.), 3-hydroxytetrahydrofuran (3-HTHF, >95%, Wako Pure Chemical Ind. Ltd.). The acetals which are commercially unavailable were isolated by column chromatography (silica gel; diethyl ether and ethyl acetate mixture) and was qualitatively analyzed by GC-MS and NMR. They include:

(1)



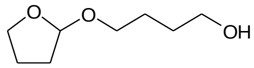
3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran (about 1:1 mixture of stereoisomers), MW = 174.

NMR of about 1:1 mixture of stereoisomers:

^{1}H NMR ($CDCl_3$): 1.153-1.295 (2H, m), 1.551-1.677 (6H, m), 1.700-1.765 (2H, m), 3.323-3.373 (2H, q), 3.416-3.466 (2H, q), 3.538-3.604 (4H, m), 3.974-4.038 (4H, d), 4.577-4.524 (2H, q), 4.664-4.710 (2H, q), 4.840-4.877 (1H, t), 5.101-5.137 (1H, t) ppm.

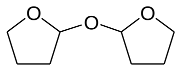
^{13}C NMR ($CDCl_3$): 25.6, 25.7, 28.5, 29.1, 61.3, 61.3, 72.1, 73.4, 79.1, 80.0, 104.7, 105.0 ppm.

(2)



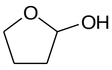
2-(4-hydroxybutyloxy)tetrahydrofuran; MW = 160.

(3)



2,2'-oxybis(tetrahydrofuran); MW = 158.

(4)



2-hydroxytetrahydrofuran (2-HTHF); MW = 88.

2.3 Results and discussion

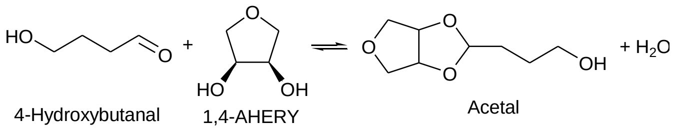
2.3.1 Production of 1,4-butanediol

Various supported Re catalysts were tested for the co-catalysis with ReO_x-Au/CeO_2 (ReO_x-^{dp}Au/CeO_2) in the reaction of 1,4-AHERY (Table 2-1). ReO_x-^{dp}Au/CeO_2 was selected because of the higher activity than ReO_x-$^{imp}Au/CeO_2$ [19],[20]. The combination of carbon-supported rhenium catalysts with ReO_x-Au/CeO_2 (entries 1-2) showed good selectivity of 1,4-BuD. The ReO_x/C-BP (carbon black BP2000) performed higher conversion and better 1,4-BuD selectivity than ReO_x/C-NR (activated carbon Norit RX3 extra). The combinations of ReO_x/SiO_2, ReO_x/TiO_2, ReO_x/ZrO_2, ReO_x/Al_2O_3, and ReO_x/MgO with ReO_x-Au/CeO_2 (entries 3-7) showed very low yield of 1,4-BuD. The main products of these Re catalysts were 2,5-DHF and 2,3-DHF, indicating that they have low activity in the conversion of DHFs. Single ReO_x-Au/CeO_2 had high selectivity of 2,5-DHF by DODH of 1,4-AHERY (entry 8) [19]. Single ReO_x/C-BP showed very low activity in the reaction of 1,4-AHERY (entry 9), and the products include THF and 1,4-BuD. This indicates that ReO_x/C-BP and ReO_x/C-NR have high activity of DHFs ring-opening reaction to 1,4-BuD. Adding ReO_x/C-BP or ReO_x/C-NR to ReO_x-Au/CeO_2 increased the selectivity of 1,4-BuD and effectively decreased the selectivity of other products such as DHFs which were rapidly converted to 1,4-BuD over ReO_x/C-BP and ReO_x/C-NR during the reaction (entries 1 and 2). Meanwhile, the addition also increased the conversion of 1,4-AHERY probably due to the move of some Re species from carbon support to the surface of CeO_2 (entry 12), thereby increasing the number of active site of ReO_x-Au/CeO_2 catalyst (discussed below). Because ReO_x/C-BP co-catalyst showed the best selectivity of 1,4-BuD with ReO_x-Au/CeO_2 catalyst in the reaction of 1,4-AHERY, it was used in the following studies. The reaction over the catalyst mixture under Ar atmosphere (entry 10) gave low conversion and many types of products, probably via dehydrogenation and reduction with hydrogen produced by the dehydrogenation.

The optimizations of Re loading amount of ReO_x/C-BP (Figure 2-1 (a)), weight ratio of ReO_x/C-BP to ReO_x-Au/CeO_2 (Figure 2-1 (b) and (c)), H_2 pressure (Figure 2-1 (d)), and reaction temperature (Figure 2-2) were carried out. The best result was obtained with the conditions in Table 2-1: 3 wt% Re for ReO_x/C-BP, 1:1 catalysts weight ratio, 8 MPa H_2, and 413 K. Addition of Re on carbon dramatically increased the selectivity of 1,4-BuD, as well as the conversion of 1,4-AHERY. In the case of ReO_x-Pd/CeO_2 catalyst for DODH + hydrogenation, the weight-based activity is increased until the Re loading of 2 wt%, and then it is decreased with further Re loading, because the amount of monomeric Re species was maximized at 2 wt% of Re [22]. In the previous study on ReO_x-Au/CeO_2 by Tomishige laboratory [19], the leaching of Re and Au to the liquid phase was negligible in glycerol DODH. On the other hand, metals on carbon support are easier to escape including ReO_x/C, especially at high temperature [26]. The Re loading in ReO_x-Au/CeO_2 is 1 wt%, and thus the move of some Re species from C-BP to CeO_2 can increase the DODH activity and that from CeO_2 to C-BP can decrease the DODH activity. The stability of Re species and the move between supports will be also discussed later. When the Re amount on ReO_x/C-BP was higher than 3%, the THF selectivity slightly increased (Figure 2-1 (a) and (b)). Lower conversion of ReO_x-Au/CeO_2 + C-BP (Figure 2-1 (a)) than that of ReO_x-Au/CeO_2 (Figure 2-1 (b)) can be explained by the move of some Re species from CeO_2 to C-BP. The amount of ReO_x-Au/CeO_2 significantly affected the conversion of the reaction, while the selectivity was not so affected (Figure 2-1 (c)), indicating that the rate of DODH catalyzed by ReO_x-Au/CeO_2 controls the reaction rate of 1,4-AHERY to 1,4-BuD. In the DODH reaction of polyols over single ReO_x-Au/CeO_2, the formation of alkene from the diolate complex is the rate-determining step [20]. Therefore, this step is also the rate-determining step in the conversion of 1,4-AHERY to 1,4-BuD.

At higher temperature of 443 K (Figure 2-2), the selectivity of 1,4-BuD decreased and that to THF increased with the reaction time. The yield of 1,4-BuD at 1 h was 43%, and the yield decreased to be 37% after 4 h reaction time. This behavior suggested that 1,4-BuD is consecutively dehydrated to THF before total conversion of 1,4-AHERY. Thus, lower temperature of 413 K is more suitable for 1,4-BuD formation. This reaction temperature is also lower than those in the patent using ReO_x/C catalyst (473 K), where THF formation decreased the yield of 1,4-BuD [25]. The TOF based on the conversion and total Re amount of the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP at 413 K is calculated to be 5 h^{-1} using the conversion increase during 2 - 4 h reaction time (41% → 49%; Table 2-2, entries 2 and 3), which is comparable to that on ReO_x/C at 473 K (13 h^{-1}). High activity of ReO_x-Au/CeO_2 in DODH can decrease the reaction temperature maintaining the productivity.

Figure 2-3 and Table 2-2 show the time course of the reaction of 1,4-AHERY over the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. The selectivity of 1,4-BuD increased until 1,4-AHERY was totally converted. The selectivity of DHFs was kept low, indicating that DHFs were rapidly converted. At short reaction time, the acetal from 4-hydroxybutanal and 1,4-AHERY (eq (2-11)) (identified by GC-MS and NMR) was detected in significant selectivity. 4-Hydroxybutanal is thought to be in the equilibrium by the intramolecular acetalization with 2-hydroxytetrahydrofuran (2-HTHF) (eq (2-12)). 2-HTHF can be formed by the hydration reaction of 2,3-DHF (eq (2-13)). In fact, 4-hydroxybutanal and 2-HTHF were not detected as products in the reaction of 1,4-AHERY. On the other hand, the selectivity of the acetal at low conversion of 1,4-AHERY was rather high and 4-hydroxybutanal is thought to be trapped by acetalization and this decreases in the reactivity of formyl group. While the formation of the acetal can be rather preferable in the reaction equilibrium, the hydrogenation of 4-hydroxybutanal to 1,4-BuD gradually proceeds and the selectivity of the acetal decreases, and finally the acetal was not detected at longer reaction time. The overreaction of 1,4-BuD to 1-butanol or THF was slow under these reaction conditions. The yield of 1,4-BuD reached 85% at 24 h, and this yield value is much higher than the literature values of erythritol or 1,4-AHERY conversions [6]-[22].



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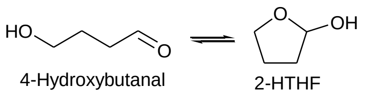

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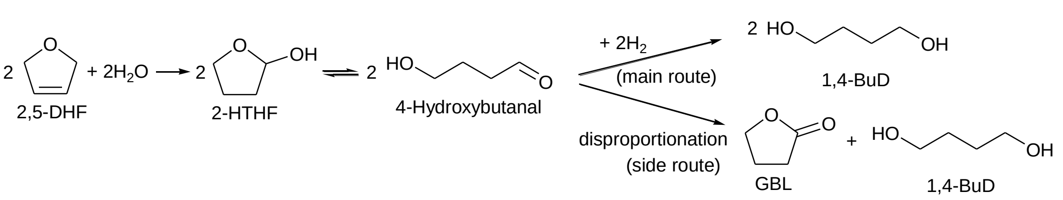


(2-13)

It should be noted that the conversion of 1,4-AHERY to 1,4-BuD involves H_2O release and consumption together with H_2 consumption (eq (1)). In the case of the conversion of 2,5-DHF to 1,4-BuD using ReO_x/TiO_2, THF-water or 1,4-dioxane-water solvents were used, and the water was also a reactant as well as the solvent [24]. In contrast, water is not added at all in this work, and this means that the produced water can react selectively even at the low concentration of H_2O during the reaction of 1,4-AHERY. Therefore, I also tested the effect of water in the solvent in my system (Table 2-3). The addition of water to solvent sharply decreased the conversion, indicating that the DODH activity of ReO_x-Au/CeO_2 is suppressed by the presence of water. The conversion of 1,4-AHERY was very low in water solvent (Table 2-4, entry 4), and similar behavior was observed in the reaction of 1,4-AHERY to THF over ReO_x-Pd/CeO_2 [22]. The conversion of 1,4-AHERY was very low in pure water solvent (Table 2-4, entry 4). The interpretation is that higher concentration of water suppresses the formation of Re diolate which is the very important surface intermediate species in DODH. The use of water solvent in DODH with good yield has been only recently reported with the combination of $KReO_4$, Pd/C, 4-(dimethylamino)pyridine ligand and large amount of activated carbon [27]. In addition, the formation of acetal was suppressed by the presence of water (entries 3 and 4, and Figure 2-3), and the selectivity of 1,4-BuD was slightly higher than the case in the absence of water. This suggests that 4-hydroxybutanal and 2-HTHF intermediates were rapidly hydrogenated to 1,4-BuD in the presence of water. The reaction can be conducted in THF solvent or even without solvent (Table 2-4, entries 1 and 3). The selectivity of 1,4-BuD was almost same although the activity was slightly lower than that in the 1,4-dioxane solvent.

2.3.2 Catalyst characterization

Because the catalysts were well mixed in the reaction, the characterization of used catalyst was rather difficult. In previous reports, the reduction of Re species on CeO_2 is dramatically promoted by addition of promoters such as Au and Pd [19]-[22]. High valence Re species on CeO_2 can be easily reduced to Re^{4+} with H_2 in presence of promoters. In the DODH reaction of 1,4-AHERY to 2,5-DHF, Re species in ReO_x-Au/CeO_2 may have the redox pair of Re^{4+} and Re^{6+}, and Re^{6+} reduced to Re^{4+} with H_2 after the reaction [19]-[22].

The H_2-TPR profiles of ReO_x/C-BP and C-BP support are shown in Figure 2-4. The reduction of C-BP started about 700 K, suggesting that C-BP support was not reduced in the reaction conditions (413 K). The reduction of Re species started around 500 K. Although the temperature was higher than reaction temperature, reduction of supported Re to the mixture of Re^0 and Re^{n+} can take place in the solvent at lower temperature than the TPR peak [23],[28],[29] which can be explained by much higher H_2 pressure under the reaction conditions than that under TPR conditions. When ReO_x/C-BP was pre-reduced at 673 K, the H_2 consumption amount was decreased by 0.41 $mmol \cdot g^{-1}$, which corresponds to the reduction of Re from +7 to average valence +2, suggesting that the part of Re species on C-BP is reduced to metallic state. The formation of Re metal on ReO_x/C-BP is also supported by the data that ReO_x/C-BP alone has some activity in hydrogenation as discussed later.

The XRD patterns (Figure 2-5) only showed CeO_2 peaks in fresh or used catalyst mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. This indicates that Au and ReO_x particles were highly dispersed on both CeO_2 and/or carbon surfaces [19]-[22], and suggesting that the aggregation of particles is not so significant.

The TEM images of used catalyst mixture are shown in Figure 2-6. CeO_2 particles were located on the C-BP support as small aggregates composed of a few CeO_2 crystallites. The aggregate size (10-20 nm) was much smaller than that on the CeO_2 alone or ReO_x-Au/CeO_2 alone (0.2-1 μm) [20], while the primary crystallite size of CeO_2 (8 nm) is similar for CeO_2 alone [20], ReO_x-Au/CeO_2 alone [20], and ReO_x-Au/CeO_2 + ReO_x/C-BP. This suggests that the aggregates of CeO_2 are dispersed by the interaction between CeO_2 crystallite and the carbon surface. Recently, Tomishige group found that the ReO_x species on CeO_2 can be reduced by H_2 even when the promotor Au is absent on the same CeO_2 particle [20]. The active hydrogen species is supposed to move from particle to particle via proton and electron. As well as CeO_2, carbon can carry electrons, and thus the active hydrogen species can move from promotor (Au) to Re in the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. On the C-BP support (Figure 2-6C), Re species existed as highly dispersed state.

2.3.3 Reaction mechanism

To study the possible route of the reaction from 1,4-AHERY to 1,4-BuD and the role of catalyst components, reactions of different substrates (or possible intermediates) were tested over various related catalysts (Table 2-5). In this experiment, small amount of water was added to the system (water: substrate = 1:1) because the DODH step of 1,4-AHERY co-produces water, and formed water is used as a reactant for the subsequent steps. The substrate amount (0.15 g) was set lower than the standard runs (0.5 g, Table 2-1) because the concentration of possible intermediates was low in the standard runs for the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/C-BP, for example Table 2-1, entry 1. The combination of ReO_x-Au/CeO_2 and ReO_x/C-BP (Table 2-5, entry 1) gave high yield of 1,4-BuD (90%), which is similar to the case of standard conditions (Table 2-1, entry 1). It should be noted that this yield is clearly higher than the yield of 1,4-BuD by the reaction of 2,5-DHF over ReO_x/TiO_2 (85%) [24], indicating the superiority of the one-pot system. Single ReO_x-Au/CeO_2 (Table 2-5, entry 2) gave higher yield of THF and 2,3-DHF than the result under the standard conditions in Table 2-1, entry 8, indicating that the successive reactions of 2,5-DHF to THF by hydrogenation and to 2,3-DHF by isomerization are also catalyzed by ReO_x-Au/CeO_2. In spite of this activity of ReO_x-Au/CeO_2 in hydrogenation of 2,5-DHF to THF, very high yield of 1,4-BuD and very low yield of THF over ReO_x-Au/CeO_2 + ReO_x/C-BP were observed, which suggests that the activity of ReO_x/C-BP in the successive reactions of 2,5-DHF can be much higher than that of ReO_x-Au/CeO_2. Single ReO_x/C-BP (Table 2-5, entry 3) showed very low yield of 1,4-BuD, THF and so on, while the conversion was significantly higher than the total yield of detected products. This suggests that polymerized products are formed from 1,4-AHERY or the reduced compounds such as DHFs. The difference between the conversion and the sum of the detected products' yield was also observed over ReO_x/C-BP in the reaction of 2,5-DHF (Table 2-5, entry 6). Medium yield of 1,4-BuD was obtained, indicating that ReO_x/C-BP catalyzes the conversion of 2,5-DHF to 1,4-BuD, although high concentration of 2,5-DHF can promote the polymerization of 2,5-DHF and hydrogenation to THF and can cause the decrease in the yield of 1,4-BuD. The combination of ReO_x/C-BP with ReO_x-Au/CeO_2 enhanced the yield of 1,4-BuD and suppressed the polymerization (Table 2-5, entry 4). The activity of ReO_x-Au/CeO_2 was not so high in the reaction of 2,5-DHF (Table 2-5, entry 5), indicating that the reaction of 2,5-DHF is mainly catalyzed by ReO_x/C-BP (Table 2-5, entry 6). An important point is that single C-BP has almost no activity in the reaction of 2,5-DHF (Table 2-5, entry 7) and Re species supported on C-BP catalyzes the reaction of 2,5-DHF.

Next, the reactions of 2,3-DHF over various catalysts were also tested because 2,3-DHF is a possible intermediate for the formation of 1,4-BuD. It should be noted that the difference between the sum of the detected products' yield and the conversion in the reaction of 2,3-DHF was commonly larger over all the catalysts, and this low carbon balance can be due to the loss of 2,3-DHF during the operation because of the low boiling point of 2,3-DHF (327 K), which is lower than that of 2,5-DHF (340 K). Therefore, the performance should be compared on the basis of the yield of detected products. ReO_x-Au/CeO_2 + ReO_x/C-BP gave relatively high yield of 1,4-BuD in the reaction of 2,3-DHF (Table 2-5, entry 8). Another important product is 2-HTHF formed by the hydration of 2,3-DHF, and 2-HTHF-derived products were also detected such as 2,2'-oxybis(tetrahydrofuran). The yield of 2-HTHF and its derivative was 41% on C-BP (Table 2-5, entry 11, the yield = (46/2+18)%), which was higher than that on ReO_x-Au/CeO_2 (12%, Table 2-5, entry 9). This indicates that the hydration of 2-HTHF is mainly catalyzed by the surface of C-BP, probably the surface carboxylic or phenolic groups formed on the surface of carbons. It should be noted that the formation of 1,4-BuD in the reaction of 2,3-DHF on ReO_x/C-BP (Table 2-5, entry 10) and no formation on C-BP (Table 2-5, entry 11) indicates that Re species on ReO_x/C-BP mainly catalyzes the hydrogenation of 2-HTHF (or 4-hydroxybutanal) to 1,4-BuD.

Scheme 2-1 summarizes the proposed reaction route from 1,4-AHERY to 1,4-BuD. In this co-catalyzed reaction, the ReO_x-Au/CeO_2 catalyst is in charge of the high conversion of 1,4-AHERY to 2,5-DHF (step I). Meanwhile, the ReO_x/C-BP catalyst is responsible for the isomerization of 2,5-DHF to 2,3-DHF (step II), hydration of 2,3-DHF to 4-hydroxybutanal or the hemiacetal/acetal (step III), as well as the hydrogenation to 1,4-BuD (step IV). Although ReO_x-Au/CeO_2 has some activity in the ReO_x/C-BP-catalyzed steps, its role can be limited. The rate-determining step is the reaction of 1,4-AHERY over ReO_x-Au/CeO_2. The main side reaction was the hydrogenation of 2,5-DHF to THF, which was suppressed by rapid conversion of DHFs over ReO_x/C-BP. ReO_x/C-BP has activity in the side reaction of 2,5-DHF and 2,3-DHF to undetectable by-products; however, this activity is suppressed by addition of ReO_x-Au/CeO_2. Overall, the use of both ReO_x-Au/CeO_2 and ReO_x/C-BP at once in one-pot system is effective in suppressing side reaction of reactive intermediates, leading to high yield of 1,4-BuD from 1,4-AHERY. An important point is that the concentration of intermediate with C=C such as 2,5- and 2,3-DHF, which can be polymerized to give by-products and decrease the carbon balance, was maintained to be very low, and this can be connected to high yield of 1,4-BuD.

2.3.4 Catalyst stability

The drawback of this co-catalysis of ReO_x-Au/CeO_2 + ReO_x/C-BP is the decrease of catalytic activity after usage (Table 2-6). The activity of the catalyst mixture dropped from 100% conversion (fresh) to 65% in the 2nd run, and the selectivity of 1,4-BuD also decreased. The carbon balance was about 90%, suggesting that a small amount of products was adsorbed on the catalysts. The carbonaceous deposits on catalyst surface might cover the active sites leading the deactivation of catalysts. The leached amount of Re from the mixture of ReO_x-Au/CeO_2 + ReO_x/C-BP in the absence of air was below 0.01% of total Re amount in the catalysts by ICP analysis (filtration after cooling), indicating that Re in both catalysts was almost not dissolved in the solution during the reaction. However, when the reaction solution was collected in air, the Re leaching amount from the catalyst mixture increased to 0.25%. This is probably due to oxidation of some of Re species and dissolution into the solution. The move of Re species from ReO_x/C-BP in oxidized state was also suggested by the reaction tests with Au/CeO_2 + ReO_x/C-BP (Table 2-1, entry 12). When the ReO_x/C-BP was reduced before mixing, the activity of the mixture was very low (Table 2-1, entry 13). This suggests that the move of Re species is suppressed during the reaction, which agrees with that the leaching of Re from the standard mixture was negligible. Anyway, the leached Re amount was too small to be the reason for the deactivation of catalysts. On the other hand, the Re leaching amount of single ReO_x/C-BP (0.39%) was higher than that of the mixture of ReO_x-Au/CeO_2 + ReO_x/C-BP showing that the Re species on C is more labile than that on CeO_2. The Re species can to move from C surface to CeO_2 surface, which might be a reason for the deactivation of ReO_x/C-BP. In previous paper, used ReO_x-Au/CeO_2 catalyst can perform almost the same activity after regeneration by calcination after each usage [19]. However, the combustibility of carbon support makes such regeneration difficult. Heating pretreatment was tried on the used catalyst mixture at 573 K in air. At this temperature, the combustion of carbon support is minimal based on TG-DTA profile (Figure 2-7). Nevertheless, the activity was further decreased (44% conv.), and the main product was 2,5-DHF, indicating that both ReO_x/C-BP and ReO_x-Au/CeO_2 were deactivated by air treatment. Then I tested the regeneration under N_2 or H_2. H_2 regeneration had little effect on increasing the activity of used catalyst mixture (66% conv.). Regeneration with N_2 at 773 K for 1 h gave better result of 91% conversion and 83% 1,4-BuD selectivity. However, the activity was further decreased by further uses, and it dropped to 54% conversion after 4th run. The decline of selectivity was lower than the decrease of activity, indicating that ReO_x-Au/CeO_2 was more severely deactivated than ReO_x/C-BP. The low carbon balance of entries 9 and 10 might be due to the deactivation of ReO_x/C-BP.

2.4 Conclusions

The physical mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP (C-BP = carbon black 2000) effectively converted 1,4-AHERY to 1,4-BuD with H_2 as reductant. The yield of 1,4-BuD reached ~90% at the reaction temperature of 413 K. This yield is higher than the reported ones from erythritol or 1,4-AHERY over other catalysts such as ReO_x/C single catalyst and Ir-ReO_x/SiO_2 as step-by-step C-O hydrogenolysis catalyst. In this reaction, ReO_x-Au/CeO_2 catalyzed deoxydehydration (DODH) of 1,4-AHERY to 2,5-DHF, and ReO_x/C catalyzed successive isomerization, hydration and reduction reactions of 2,5-DHF. The use of both catalysts at once is effective in suppressing the formation of by-products derived from reactive intermediates such as 2,3- and 2,5-DHFs. Due to the deactivation of the catalyst mixture after reaction, it is important to improve the reusability of ReO_x/C-BP catalyst and develop a regenerable catalyst system in the future study.

References

[1] M. Besson, P. Gallezot and C. Pinel, Chem. Rev., 2014, 114, 1827-1870.

[2] M. Schlaf, Dalton Trans., 2006, 4645-4653.

[3] J. J. Bozell and G. R. Petersen, Green Chem., 2010, 12, 539-554.

[4] A. M. Ruppert, K. Weinberg and R. Palkovits, Angew. Chem. Int. Ed., 2012, 51, 2564-2601.

[5] A. M. Robinson, J. E. Hensley and J. W. Medlin, ACS Catal., 2016, 6, 5026-5043.

[6] Y. Amada, H. Watanabe, Y. Hirai, Y. Kajikawa, Y. Nakagawa and K. Tomishige, ChemSusChem, 2012, 5, 1991-1999.

[7] A. Said, D. D. S. Perez, N. Perret, C. Pinel and M. Besson, ChemCatChem, 2017, 9, 2768-2783.

[8] K. Tomishige, Y. Nakagawa and M. Tamura, Green Chem., 2017, 19, 2876-2924.

[9] J. R. Dethlefsen and P. Fristrup, ChemSusChem, 2015, 8, 767-775.

[10] A. R. Petersen and P. Fristrup, Chem. Eur. J., 2017, 23, 10235-10243.

[11] S. Raju, M. Moret and R. J. M. K. Gebbink, ACS Catal., 2015, 5, 281-300.

[12] M. Shiramizu and F. D. Toste, Angew. Chem. Int. Ed., 2012, 51, 8082-8086.

[13] S. Raju, J. T. B. H. Jastrzebski, M. Lutz and R. J. M. K. Gebbink, ChemSusChem., 2013, 6, 1673-1680.

[14] C. Boucher-Jacobs and K. M. Nicholas, Organometallics, 2015, 34, 1985-1990.

[15] K. Beckerle, A. Sauer, T. P. Spaniol and J. Okuda, Polyhedron, 2016, 116, 105-110.

[16] G. K. Cook and M. A. Andrew, J. Am. Chem. Soc., 1996, 118, 9448-9449.

[17] L. Sandbrink, E. Klindtworth, H. Islam, A. M. Beale and R. Palkovits, ACS Catal., 2016, 6, 677-680.

[18] B. E. Sharkey, A. L. Denning, F. C. Jentoft, R. Gangadhara, T. V. Gopaladasuc and K. M. Nicholas, Catal. Today, 2017, DOI: 10.1016/j.cattod.2017.05.090.

[19] S. Tazawa, N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, ACS Catal. 2016, 6, 6393-6397.

[20] Y. Nakagawa, S. Tazawa, T. Wang, M. Tamura, N. Hiyoshi, K. Okumura and K. Tomishige, ACS Catal., 2018, 8, 584-595.

[21] N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, Angew. Chem. Int. Ed., 2015, 54, 1897-1900.

[22] N. Ota, M. Tamura, Y. Nakagawa and K. Tomishige, ACS Catal., 2016, 6, 3213-3226.

[23] Y. Takeda, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, Catal. Sci. Technol., 2016, 6, 5668-5683.

[24] R. Pinkos, R. H. Fischer, B. Breitscheidel, P. Polanek, CA Pat., 2168458C, 2004.

[25] L. E. Manzer (E. I. du Pont de Nemours and Company), US Pat., 6593481B1, 2003.

[26] A. L. Denning, D. Dang, L. Liu, K. M. Nicholas and F. C. Jentoft, ChemCatChem, 2013, 5, 3567-3570.

[27] R. T. Larson, A. Samant, J. Chen, W. Lee, M. A. Bohn, D. M. Ohlmann, S. J. Zuend and F. D. Toste, J. Am. Chem. Soc., 2017, 139, 14001-14004.

[28] Y. Takeda, Y. Nakagawa and K. Tomishige, Catal. Sci. Technol., 2012, 2, 2221-2223.

[29] Y. Takeda, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, ACS Catal., 2015, 5, 7034-7047.

Table 2-1 Reaction of 1,4-AHERY over various supported Re catalysts combined with ReO_x-Au/CeO_2 [a]

Entry	Catalyst 1	Catalyst 2	Conv. /% (C.B. /%)	Product selectivity /%							
				1,4-BuD	THF	2,5-DHF	2,3-DHF	GBL	1-BuOH	Acetal	Others
1	ReO_x–Au/CeO_2	ReO_x/C-BP	100	86	8	0	0	2	2	0	3
2	ReO_x–Au/CeO_2	ReO_x/C-NR	87	75	9	0	0	3	3	5	4
3	ReO_x–Au/CeO_2	ReO_x/SiO_2	58 (86)	7	8	34	9	1	0	1	16
4	ReO_x–Au/CeO_2	ReO_x/TiO_2	100 (86)	3	3	56	17	2	0	0	5
5	ReO_x–Au/CeO_2	ReO_x/ZrO_2	100 (82)	7	12	29	27	0	1	0	5
6	ReO_x–Au/CeO_2	ReO_x/Al_2O_3	99	1	3	83	11	0	0	0	2
7	ReO_x–Au/CeO_2	ReO_x/MgO	87	2	2	85	9	0	0	0	1
8	ReO_x–Au/CeO_2	—	64	0	1	89	6	0	0	0	4
9	—	ReO_x/C-BP	2	18	10	4	0	0	4	0	65
10[b]	ReO_x–Au/CeO_2	ReO_x/C-BP	8	3	1	23	0	11	1	45	15
11	Au/CeO_2	—	< 1	—	—	—	—	—	—	—	—
12	Au/CeO_2	ReO_x/C-BP	80	90	4	1	1	0	0	1	4
13[c]	Au/CeO_2	ReO_x/C-BP	3	12	2	0	2	0	0	0	82

[a] 1,4-AHERY = 0.5 g, catalyst 1 = 0.15 g (Re = 1 wt%, Au = 0.3 wt%), catalyst 2 = 0.15 g (Re = 3 wt%), 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 24 h. [b] P_{Ar} = 5 MPa. [c] ReO_x/C-BP was reduced by H_2 in 1,4-dioxane at 413 K for 1 h before reaction. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran. C-BP: carbon black BP2000, C-NR: activated carbon Norit RX3 extra.

Table 2-2 Time course of the reaction of 1,4-AHERY over the mixture of ReO_x-Au/CeO_2 + ReO_x/C-BP [a]

Entry	Time /h	Conv. /%	Product selectivity /%							
			1,4-BuD	THF	2,5-DHF	2,3-DHF	GBL	1-BuOH	Acetal	Others
1	1	33	28	3	3	0	2	1	55	10
2	2	41	37	3	3	0	2	1	45	9
3	4	49	55	4	1	0	2	2	28	7
4	12	79	81	6	0	0	2	2	4	4
5	16	89	84	6	0	0	2	2	2	3
6	24	100	86	8	0	0	2	2	0	3
7	48	100	82	13	0	0	0	2	0	2
8	96	100	71	24	0	0	0	2	0	3

[a] 1,4-AHERY = 0.5 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO_x/C-BP (Re = 3 wt%) = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 1 to 96 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran.

Table 2-3 Effect of water addition to the1,4-dioxane solvent in the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 and ReO_x/C-BP catalysts [a]

Entry	Water: 1,4-AHERY molar ratio	Conv. /%	Product selectivity /%							
			1,4-BuD	THF	2,5-DHF	2,3-DHF	GBL	1-BuOH	Acetal	Others
1	0	100	86	8	0	0	2	2	0	3
2	0.25	86	90	5	0	0	1	1	0	2
3	1	77	92	3	0	0	1	1	0	2
4	4	35	91	2	0	0	1	1	0	5

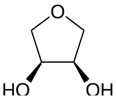
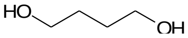
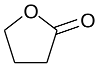
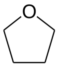
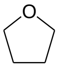
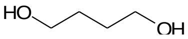
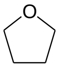
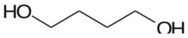
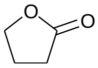
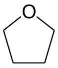
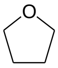
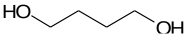
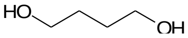
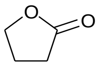
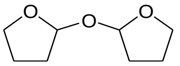
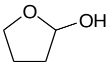
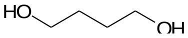
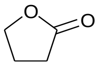
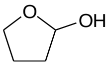
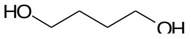
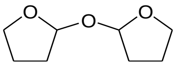
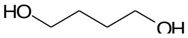
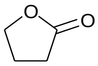
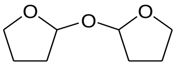
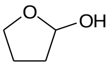
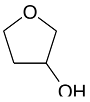
[a] 1,4-AHERY = 0.5 g, water = 0 to 0.3 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO_x/C-BP (Re = 3 wt%) = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran.

Table 2-4 Effect of solvent in the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/C-BP [a]

Entry	Solvent	Conv. /%	Product selectivity /%							
			1,4-BuD	THF	2,5-DHF	2,3-DHF	GBL	1-BuOH	Acetal	Others
1	None	88	88	2	0	0	0	3	4	3
2	1,4-Dioxane	100	86	8	0	0	2	2	0	3
3	THF	79	89	—	0	0	2	3	2	5
4	Water	8	42	1	0	0	0	1	0	55

[a] 1,4-AHERY = 0.5 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO_x/C-BP (Re = 3 wt%) = 0.15 g, solvent = 0 or 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran.

Table 2-5 Reaction of 1,4-AHERY and the intermediates over related catalysts [a]

Entry	Substrate	Catalyst	Catalyst weight /g	Products (yield /%)	Conv. /% (C.B. /%)
1		ReO$_x$-Au/CeO$_2$ + ReO$_x$/C-BP	0.15 + 0.15	 (90),  (4),  (4), others (2)	100
2		ReO$_x$-Au/CeO$_2$	0.15	 (32),  (27),  (25), others (6)	100
3		ReO$_x$/C-BP	0.15	 (1),  (0.3), others (1)	33 (69)
4		ReO$_x$-Au/CeO$_2$ + ReO$_x$/C-BP	0.15 + 0.15	 (80),  (13),  (4), others (3)	98
5		ReO$_x$-Au/CeO$_2$	0.15	 (23),  (13),  (2), others (3)	45
6		ReO$_x$/C-BP	0.15	 (39),  (9),  (8), others (9)	94 (70)
7		C-BP	0.15	 (3),  (1),  (1),  (0.5), others (0.5)	4
8		ReO$_x$-Au/CeO$_2$ + ReO$_x$/C-BP	0.15 + 0.15	 (60),  (12), others (6)	100 (78)
9		ReO$_x$-Au/CeO$_2$	0.15	 (5),  (3),  (2), others (10)	49 (71)
10		ReO$_x$/C-BP	0.15	 (24),  (6),  (2), others (6)	100 (38)
11		C-BP	0.15	 (46),  (18),  (8), others (5)	98 (80)

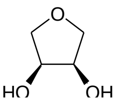
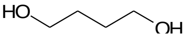
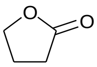
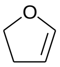
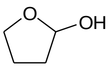
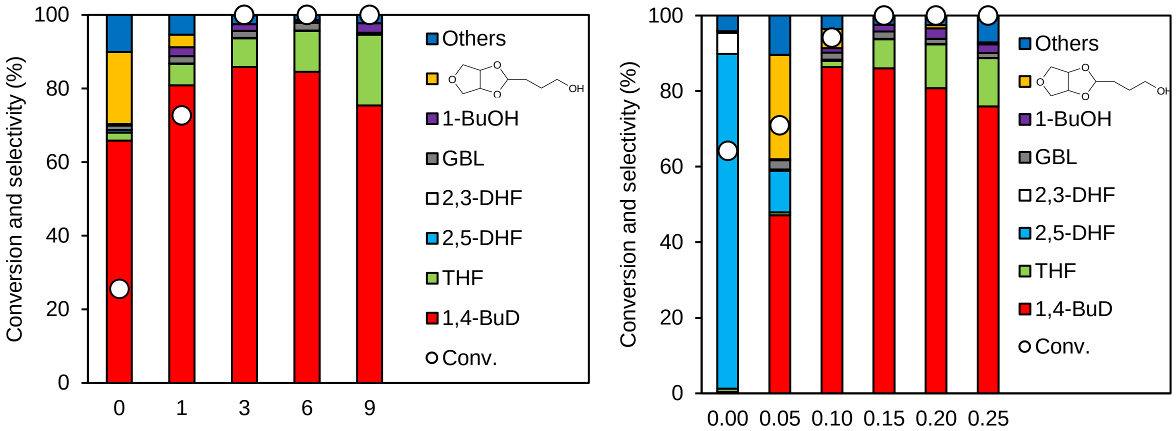
[a] Substrate = 0.15 g, water = 0.03-0.04 g (water : substrate molar ratio = 1 : 1), catalyst = 0.15 g for single, or 0.15 + 0.15 g for mixture (ReO$_x$–Au/CeO$_2$, Re = 1 wt%, Au = 0.3 wt%; or ReO$_x$/C-BP, Re = 3 wt%; or C-BP), 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 4 h.  1,4-AHERY: 1,4-anhydroerythritol;  1,4-BuD: 1,4-butanediol;  GBL: γ-butyrolactone;  THF: tetrahydrofuran;  2,5-DHF: 2,5-dihydrofuran;  2,3-DHF: 2,3-dihydrofuran;  2-HTHF: 2-hydroxytetrahydrofuran.

Table 2-6 Reusability of the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP catalysts [a]

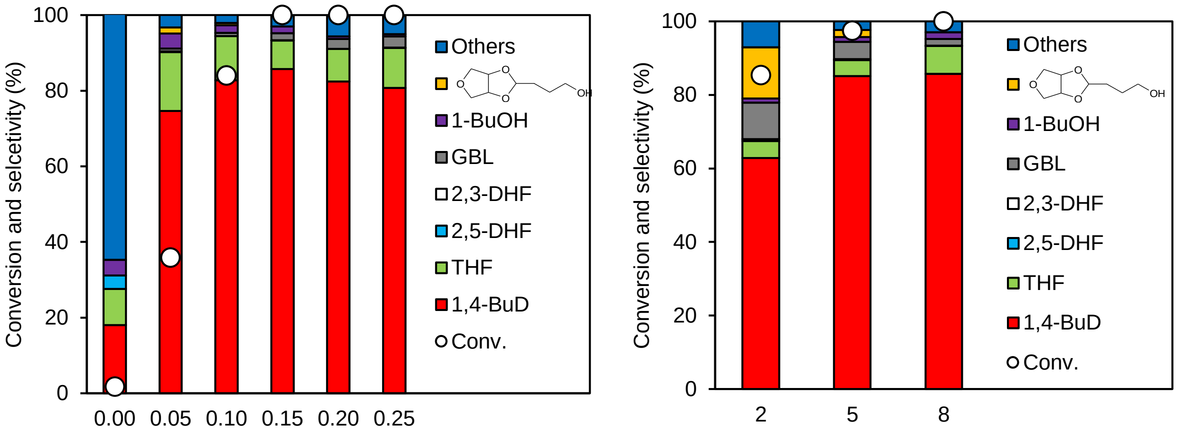
Entry	Pretreatment conditions	Usage time	Conv. /% (C.B. /%)	Product selectivity /%							
				1,4-BuD	THF	2,5-DHF	2,3-DHF	GBL	1-BuOH	Acetal	Others
1	–	1	100	86	8	0	0	2	2	0	3
2	Non-treated	2	65	71	6	2	0	3	1	10	6
3	Air, 573 K, 4 h	2	44	0	1	80	0	1	0	9	9
4	H_2, 773 K, 3 h	2	66	70	8	0	0	4	1	8	9
5	N_2, 773 K, 0.2 h	2	69	68	8	0	0	4	1	9	11
6	N_2, 773 K, 0.5 h	2	79	79	8	0	0	4	1	2	5
7	N_2, 773 K, 1 h	2	91	83	6	0	0	4	1	1	4
8	N_2, 773 K, 3 h	2	65	82	5	0	0	2	1	4	6
9	N_2, 773 K, 1 h	3	76 (84)	58	7	0	0	3	1	1	9
10	N_2, 773 K, 1 h	4	61 (85)	54	6	0	0	2	1	5	7

[a] 1,4-AHERY = 0.5 to 0.3 g (based on the weight of catalysts), catalyst mixture = 0.3 to 0.18 g (ReO_x–Au/CeO_2, Re = 1 wt%, Au = 0.3 wt%; ReO_x/C-BP, Re = 3 wt%), 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran.



(a) Loading amount of Re (wt%) of ReO_x/C-BP

(b) Weight of ReO_x/C-BP (Re = 3 wt%)



(c) Weight of ReO_x-Au/CeO_2
(Re = 1 wt%, Au = 0.3 wt%)

(d) H_2 Pressure (MPa)

Figure 2-1 Effect of (a) Re loading amount of ReO_x/C-BP (0.15 g) in the reaction of 1,4-AHERY with ReO_x-Au/CeO_2 (0.15 g); (b) weight of ReO_x/C-BP (Re = 3 wt%) in the mixture with ReO_x-Au/CeO_2 (0.15 g) in the reaction of 1,4-AHERY; (c) weight of ReO_x-Au/CeO_2 in the mixture with ReO_x/C-BP (Re = 3 wt%, 0.15 g) in the reaction of 1,4-AHERY; (d) hydrogen pressure in the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 (0.15 g) + ReO_x/C-BP (Re = 3 wt%, 0.15 g).
Standard conditions: 1,4-AHERY = 0.5 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO_x/C-BP (Re = 3 wt%) = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol.

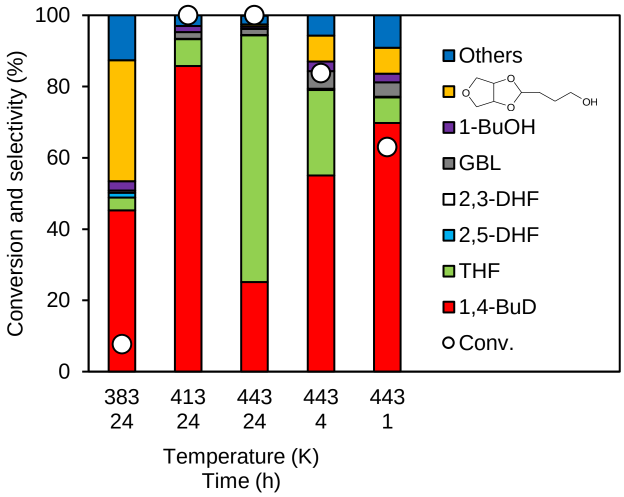


Figure 2-2 Effect of reaction temperature and reaction time in the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/C-BP. 1,4-AHERY = 0.5 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO_x/C-BP (Re = 3 wt%) = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 383 to 443 K, t = 1 to 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol.

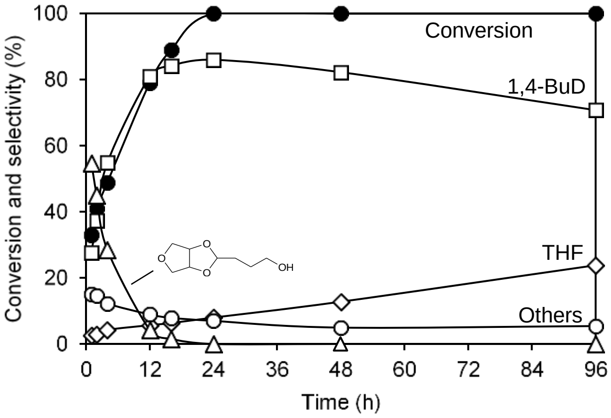


Figure 2-3 Time course of the reaction of 1,4-anhydroerythritol over the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. 1,4-AHERY = 0.5 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO_x/C-BP (Re = 3 wt%) = 0.15 g,1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 1 to 96 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, “others” also include 2,5-DHF (2,5-dihydrofuran), 2,3-DHF (2,3-dihydrofuran), GBL (*γ*-butyrolactone) and BuOH (butanol), as well as by-products shown as “others” in Table 2-2.

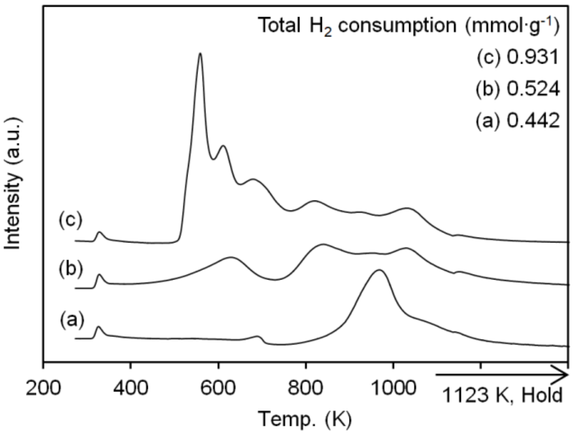


Figure 2-4 H_2-TPR profiles of ReO_x/C-BP (Re = 3 wt%; 0.16 mmol·g^{-1}). (a) C-BP, (b) ReO_x/C-BP after reduction in H_2 flow (30 cc/min) at 673 K for 1 h (at heating rate of 10 K/min), (c) ReO_x/C-BP. Sample weight = 50 mg.

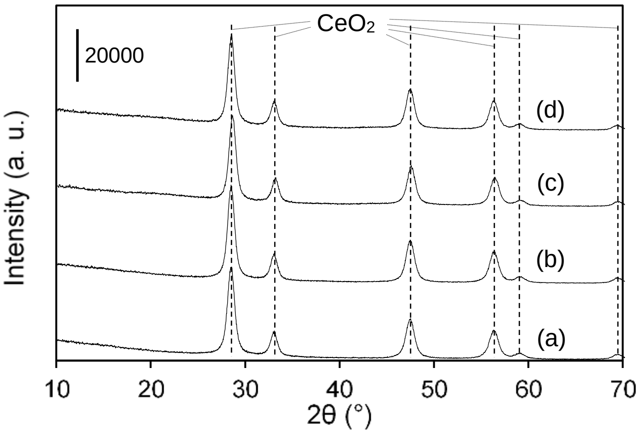


Figure 2-5 XRD patterns of ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) and ReO_x/C-BP (Re = 3 wt%) catalysts. (a) CeO_2, (b) ReO_x-Au/CeO_2, (c) ReO_x-Au/CeO_2 + ReO_x/C-BP, (d) ReO_x-Au/CeO_2 + ReO_x/C-BP after reaction (1,4-AHERY = 0.5 g, ReO_x-Au/CeO_2 = 0.15 g, ReO_x/C-BP = 0.15 g, 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 24 h).

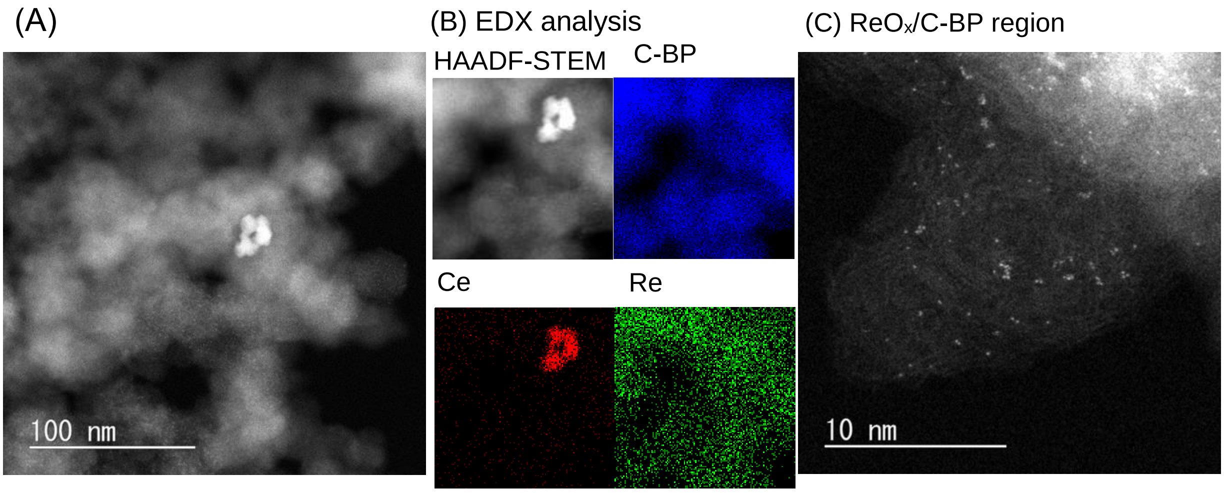


Figure 2-6 HAADF-STEM images of the mixture of ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) and ReO_x/C-BP (Re = 3 wt%) after catalytic use. The conditions for catalytic reaction: 1,4-AHERY = 0.5 g, ReO_x-Au/CeO_2 = 0.15 g, ReO_x/C-BP = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h.

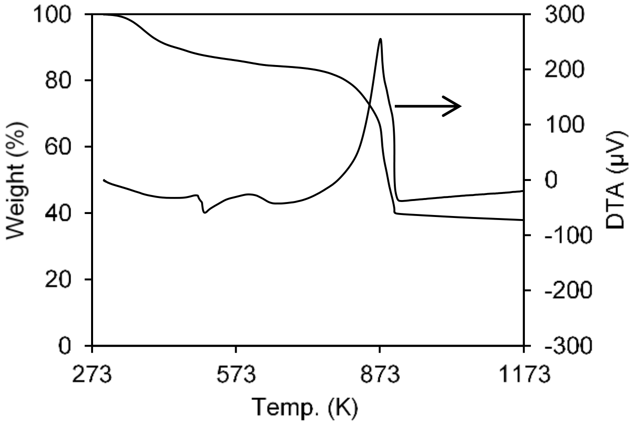
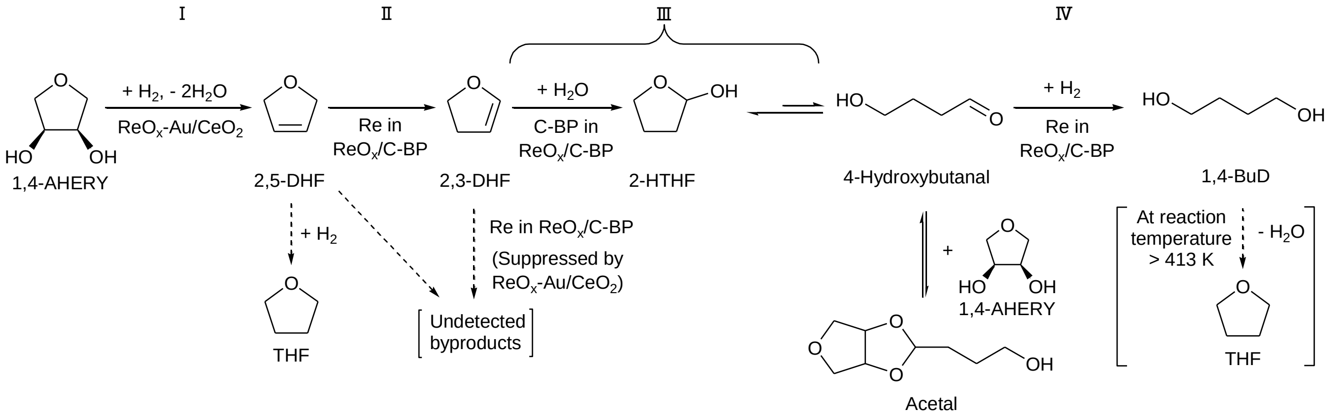


Figure 2-7 TG-DTA graph of the 1:1 mixture of ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) and ReO_x/C-BP (Re = 3 wt%) (after 1st use). Heating rate = 10 K/min, sample weight = 10 mg.



Scheme 2-1 Proposed reaction route from 1,4-AHERY to 1,4-BuD over the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. AHERY: anhydroerythritol, BuD: Butanediol, DHF: dihydrofuran, THF: tetrahydrofuran. HTHF: hydroxytetrahydrofuran.

Chapter 3

Preparation of Highly Active Monometallic Rhenium Catalyst for Selective Synthesis of 1,4-Butanediol from 1,4-Anhydroerythritol

3.1 Introduction

Biomass-derived compounds such as sugar alcohols which can be obtained from cellulose or hemicellulose are important chemical platforms, however, contains unwanted high oxygen content, [1]-[3]. As mentioned in Chapter 1 and 2, deoxydehydration (DODH) is an effective process to reduce the oxygen content in sugar alcohols such as glycerol, erythritol or sorbitol by simultaneously removing the vicinal OH groups to form C=C bond [4]-[7]. Recently, Tomishige laboratory developed heterogenous DODH catalysts use H_2 as the reductant, including ReO_x-Au/CeO_2 and ReO_x-Pd/CeO_2. [9]-[13]. Au or Pd promoters have the function of activating H_2, and the activated hydrogen moves on CeO_2 surface for the reduction of Re species in the reaction [9]-[15]. While Pd is a more effective promoter for H_2 activation, Pd is also active in C=C hydrogenation and thus the product over ReO_x-Pd/CeO_2 becomes saturated.

In Chapter 2, I developed a new co-catalyst system combining ReO_x-Au/CeO_2-catalyzed DODH reaction of 1,4-anhydroerythritol (1,4-AHERY) to 2,5-dihydrofuran (2,5-DHF), and ReO_x/C-catalyzed reduction of 2,5-DHF to 1,4-butanediol (1,4-BuD) for one-pot synthesis of 1,4-BuD from 1,4-AHERY (Scheme 3-1) with very high yield (~90%) [11].

One of the drawbacks of ReO_x-Au/CeO_2 catalyst is the high cost of metal elements, therefore, decreasing the amount of expensive Re and Au is highly desired. The role of Au is activating H_2 to reduce Re species on CeO_2. While the number of Au particles is much fewer than that of CeO_2 support, Au particles effectively activated H_2 which could reduce almost all Re species in the catalyst [10]. Considering that ReO_x/C can catalyze hydrogenation catalyst for 4-hydroxybutanal intermediate to 1,4-BuD (Scheme 3-1), ReO_x/C is possible to be a promoter of ReO_x/CeO_2 similar to Au for the H_2 activation.

In this study, the author further investigate the co-catalyst system and found that the physical mixture of ReO_x/C and ReO_x/CeO_2 without Au promoter can also convert 1,4-AHERY to 1,4-BuD in one-pot reaction under similar reaction conditions to those for ReO_x-Au/CeO_2 + ReO_x/C catalysts system [11]. Even simple CeO_2 can be used instead of ReO_x/CeO_2 or ReO_x-Au/CeO_2, giving 89% yield of 1,4-butanediol. Furthermore, the activity of $(ReO_x/)CeO_2$ + ReO_x/C is higher than that of ReO_x-Au/CeO_2 + ReO_x/C. The high activity will be explained by the investigation of the reducibility of ReO_x/C and move of Re species between supports.

3.2 Experimental

The chemicals used in this chapter were the same as Chapter 2.

3.2.1 Catalyst preparation

The ReO_x/Support catalysts were prepared by impregnating support materials with NH_4ReO_4 aqueous solution at 353 K. Support materials included CeO_2, carbon black "Black Pearl 2000 (BP2000)" (C-BP), extruded activated carbon "Norit RX3 extra" (C-NR), TiO_2, SiO_2, ZrO_2, Al_2O_3, MgO. CeO_2 and non-CeO_2 (except carbons) supports were calcinated at 873 K and 773 K for 3 h, respectively, before impregnation. All the impregnated catalysts were dried in oven at 373 K for 12 h. Then the non-carbon-supported catalysts were calcinated 773 K for 3 h. The Re loading amount of CeO_2 was typically 1 wt%, and 3 wt% of non-CeO_2 supports. For $ReO_x/(CeO_2 + \text{C-BP})_{\text{mixture}}$, the support of CeO_2 and C-BP was physically mixed and stirred in 1,4-dioxane solvent for 2 h at room temperature, and then dried in oven at 373 K for 12 h.

3.2.2 Activity test

Activity tests were carried out as the same method in Chapter 2. The standard reaction conditions were: 0.5 g 1,4-anhydroerythritol, 0.15 g ReO_x/CeO_2, 0.15 g ReO_x/C-BP, 0.1 g dodecane (internal standard), 4 g 1,4-dioxane, 413 K reaction temperature, 8 MPa H_2 pressure (at reaction temperature), and 24 h reaction time. The parameters were changed appropriately for investigating the effects of reaction conditions. Details of the reaction conditions are described in each result. The tests of 2,5-dihydrofuran, 2,3-dihydrofuran, *cis*-1,2-cyclohexanediol (>98%; Tokyo Chemical Ind. Co., Ltd.), *trans*-1,2-cyclohexanediol (>99%; Tokyo Chemical Ind. Co., Ltd.), *cis*-1,2-cyclopentanediol (>97%; Frinton Laboratories, Inc.), 1,2-octanediol (>96%; Tokyo Chemical Ind. Co., Ltd.), glycerol (>98%; Wako Pure Chemical Ind., Ltd.), and 1-octene (>97%; Tokyo Chemical Ind. Co., Ltd.), *trans*-2-octane (>97%; Tokyo Chemical Ind. Co., Ltd.) were carried out in a similar method as above. The products were analyzed by FID-GC (Shimadzu GC-2025) with TC-WAX capillary column (diameter 0.25 mm, 30 m), and GC–MS (QP5050, Shimadzu).

The calculation of products used the same method as Chapter 2. The carbon balance (C.B.) of each analysis result was calculated using eq (3-1). When the C.B. is in the range of 100 ± 10% considering the experimental error, the conversion and selectivity on the carbon basis are calculated by eq (3-2) and (3-3), respectively. When the C.B. is clearly lower than 90%, the conversion and selectivity on carbon basis are calculated by eq (3-4) and (3-5), and shown in results. The yield was calculated by eq (6). The TOF of reaction was calculated by eq (3-7).

$$\text{C. B. (\%)} = \frac{\text{Amount of remaining substrate (C-mol)} + \text{Total amount of detected products (C-mol)}}{\text{Amount of initial substrate (C-mol)}} \times 100 \qquad \text{(3-1)}$$

$$\text{Conversion (\%)} = \frac{\text{Total amount of detected products (C-mol)}}{\text{Amount of remaining substrate (C-mol)} + \text{Total amount of detected products (C-mol)}} \times 100 \qquad \text{(3-2)}$$

$$\text{Selectivity of product A (\%)} = \frac{\text{Amount of A (C-mol)}}{\text{Total amount of detected products (C-mol)}} \times 100 \qquad \text{(3-3)}$$

$$\text{Conversion (\%)} = 100 - \frac{\text{Amount of remaining substrate (C-mol)}}{\text{Amount of initial substrate (C-mol)}} \times 100 \qquad \text{(3-4)}$$

$$\text{Selectivity of product A (\%)} = \frac{\text{Amount of A (C-mol)}}{\text{Amount of initial substrate (C-mol)} - \text{Amount of remaining substrate (C-mol)}} \times 100 \qquad \text{(3-5)}$$

$$\text{Yield (\%)} = \frac{\text{Conversion (\%)} \times \text{Selectivity (\%)}}{100} \qquad \text{(3-6)}$$

$$\text{TOF } (\text{h}^{-1}) = \frac{\text{Amount of initial substrate (mol)} \times \Delta\text{Conversion (\%)}}{\text{Amount of Re (mol)} \times \Delta\text{Reaction time (h)}} \qquad \text{(3-7)}$$

The reuse procedure of catalysts was as the same method mentioned in Chapter 2. The mixture of ReO_x/CeO_2 and ReO_x/C-BP after reaction was washed and dried at 373 K for 12 h, and then treated with various conditions for regeneration. The tested regeneration methods included heating in air at 573 K for 4 h, heating in H_2 at 773 K for 3 h, and heating in N_2 at 773 K for appropriate hours. Due to the weight loss of the catalyst mixture during the recovery process, the lost weight was replenished by fresh catalysts or the catalyst mixture recovered by the same method.

3.2.3 Catalyst characterization

The samples of ReO_x/CeO_2 and ReO_x/C-BP were characterized by X-ray diffraction (XRD), temperature-programmed reduction (H_2-TPR), thermogravimetric-differential thermal analysis (TG-DTA), and scanning transmission electron microscope (STEM), using the same analytical apparatuses and methods as Chapter 2.

3.2.4 Products identification

Most products were identified by commercially available chemicals include tetrahydrofuran, 2,5-DHF, 2,3-DHF, γ-butyrolactone (GBL), 1-butanol (1-BuOH), 3-hydroxytetrahydrofuran (3-HTHF); cyclopentane (>98%; Tokyo Chemical Ind. Co., Ltd.), cyclopentene (>98%; Tokyo Chemical Ind. Co., Ltd.), *trans*-1,2-cyclopentanediol; cyclohexane (>99.5%; Tokyo Chemical Ind. Co., Ltd.), cyclohexene (>99%; Tokyo Chemical Ind. Co., Ltd.), *cis*-1,2-cyclohexanediol, *trans*-1,2-cyclohexanediol; 1-propanol (>99.5%; Tokyo Chemical Ind. Co., Ltd.), 1,2-propanediol (>99%; Tokyo Chemical Ind. Co., Ltd.), allyl alcohol (>99%; Tokyo Chemical Ind. Co., Ltd.); *n*-octane (>99.5%; Tokyo Chemical Ind. Co., Ltd.), 1-octene, *cis*-2-octene (>95%; Tokyo Chemical Ind. Co., Ltd.), *trans*-2-octane, *cis*-3-octene (>98%; Tokyo Chemical Ind. Co., Ltd.), *trans*-3-octene (>98%; Tokyo Chemical Ind. Co., Ltd.) were carried out in a similar method as above. The intermediate acetals which are commercially unavailable were described in Chapter 2.

3.3 Results and discussion

3.3.1 Screening of catalysts

Table 3-1 shows the results of the activity test of the combination of Au-free ReO_x/CeO_2 catalyst and various ReO_x/support co-catalysts for 1,4-AHERY reduction. Carbon-supported ReO_x/C-BP (carbon black BP2000) co-catalyst physically mixed with ReO_x/CeO_2 presented the highest activity and selectivity to 1,4-BuD (entry 1). The yield of 1,4-BuD over the combination of ReO_x/CeO_2 and ReO_x/C-BP reached 83% which is comparable to that over the mixture of ReO_x-Au/CeO_2 + ReO_x/C-BP (entry 2) previously reported as 86% [11]. As reported in previous study [11], single ReO_x/CeO_2 catalyst and ReO_x/C-BP catalyst showed very low activity (entries 3 and 4). Considering that the conversion of 1,4-AHERY to 1,4-BuD starts with the DODH step of 1,4-AHERY, ReO_x/C-BP is an effective co-catalyst of ReO_x/CeO_2-catalyzed DODH. Another Re co-catalyst with carbon support, ReO_x/C-NR (activated carbon Norit RX3 extra, entry 5), showed lower activity and selectivity to 1,4-BuD than ReO_x/C-BP. Other oxides-supported Re co-catalysts such as ReO_x/HZSM5, ReO_x/Al_2O_3, ReO_x/SiO_2, ReO_x/TiO_2, and ReO_x/ZrO_2 (entries 6-10) could not produce 1,4-BuD and the activity in 1,4-AHERY conversion was low. 2,5-DHF was the main product instead, indicating that these oxide-supported Re catalysts have low activity in conversion of 2,5-DHF as well as in co-catalysis for DODH over ReO_x/CeO_2 than ReO_x/C. 1,4-AHERY also can be converted to 1,4-BuD over the catalyst mixture of ReO_x/CeO_2 + C-BP (entry 11) or CeO_2 + ReO_x/C-BP (entry 12) where only one of the catalysts contains Re species. This phenomenon suggests that the Re species can move between CeO_2 and C-BP surface to form ReO_x/C-BP or ReO_x/CeO_2, respectively. The combination of CeO_2 and pre-reduced ReO_x/C-BP showed very low activity in the reaction (entry 13), indicating that the move of low-valent Re species was suppressed [11]. Only oxidized Re species with high valence had mobility on support surfaces. The reaction of 1,4-AHERY over the catalyst mixture was difficult to proceed without reductant of H_2 (entry 14), indicating that alcohols such as substrate itself do not work effectively as the reductant.

According to the report of ReO_x-Pd/CeO_2 catalyst, the optimized Re loading amount is 2 wt%

due to the maximum monomeric Re species which are catalytically active. The effect of Re loading amounts on each support (CeO_2 and C-BP) was investigated (Figure 3-1). Good yield of 1,4-BuD (85%) was obtained over the catalyst combination of ReO_x/C-BP (Re = 3 wt%) with ReO_x/CeO_2 (Re = 1 wt%) (Figure 3-1 (a)). When the Re loading amount of ReO_x/CeO_2 was fixed at 1 wt%, the conversion and selectivity to 1,4-BuD increased with raising the Re loading amount of ReO_x/C-BP up to 3 wt%, then decreased at higher Re loading amount. The activity decrease might be due to the aggregation of the active monomeric Re species on CeO_2 into inactive polymeric species [13] with adding Re loading amount to the whole system.

In the reactions of 1,4-AHERY over the mixture of ReO_x/C-BP (Re = 1 wt%) with different Re loading amount of ReO_x/CeO_2 (Figure 3-1 (b)), ReO_x/CeO_2 (Re = 3 wt%) showed the highest conversion in the co-catalysis with ReO_x/C-BP, while the selectivity to 1,4-BuD dropped when the Re loading amount of ReO_x/CeO_2 over 1 wt%. The conversion dropped more rapidly by raising Re loading amount of ReO_x/CeO_2 over 1 wt% than the case of raising Re amount of ReO_x/C-BP over 3 wt%. The difference in Figure 3-1 (a) and 1 (b) suggests that not all Re species freely move between supports at high Re loading. In the case of high Re loading ReO_x/CeO_2 + ReO_x/C-BP (Re = 1 wt%), more amount of Re species, which formed inactive polymeric species, was still present on CeO_2 during reaction than the case of ReO_x/CeO_2 (Re = 1 wt%) + high Re loading ReO_x/C-BP.

When the reactions of 1,4-AHERY were conducted over the catalyst mixture contains single Re catalyst such as the combination of CeO_2 + ReO_x/C-BP (Figure 3-1 (c)) or ReO_x/CeO_2 + C-BP (Figure 3-1 (d)), the highest yield of 1,4-BuD was obtained at CeO_2 + ReO_x/C-BP (Re = 4 wt%) or ReO_x/CeO_2 (Re = 3 wt%) + C-BP, respectively. The selectivity to THF was increased with the increase of the Re loading amount for both combinations. The formation of THF may be due to acid-catalyzed dehydration of 1,4-BuD and/or Re-metal-catalyzed hydrogenation of 2,5-DHF intermediate. Increasing the amount of CeO_2 in the reaction mixed with ReO_x/C-BP could improve the conversion and selectivity to 1,4-BuD (Figure 3-2), due to the expansion of the support surface for migration of more active Re species c

After all, the total loading amount of Re = 3-4 wt% of the combinations of ReO_x/CeO_2 +

ReO_x/C-BP, in other words, the average loading amount of Re ≈ 2 wt% of both catalysts, was the optimized Re loading amount for the activity in 1,4-BuD production under the standard conditions for 24 h. This average loading amount (Re = 2 wt%) was similar to the Re loading amount of ReO_x-Pd/CeO_2 catalyst with the highest activity in DODH + hydrogenation [12],[13]. The selectivity to 1,4-BuD slightly dropped with increasing the Re loading amount on CeO_2 and decreasing the Re loading amount on C-BP (Table 3-2, entries 1-5). The main by-product was THF which can be produced by dehydration of 1,4-BuD over acid or hydrogenation of dihydrofurans (intermediates) over metal. Considering that ReO_x is more easily reduced on carbon support, the formation of THF was probably due to polymeric ReO_x species on CeO_2 support. When the CeO_2 and C-BP were mixed as one support and then loaded with Re = 2 wt% as ReO_x/(CeO_2 + C-BP)$_{mixture}$ catalyst (Table 3-2, entry 6), its activity and selectivity to 1,4-BuD were lower than those in the reaction of 1,4-AHERY over the physical mixture of ReO_x/CeO_2 (Re = 2 wt%) and ReO_x/C-BP (Re = 2 wt%) catalysts (entry 3). This might be due to the coverage of CeO_2 with C-BP, decreased the surface area of CeO_2 for loading active Re species before loading Re. It also might be due to that the acidic groups on C-BP surface were neutralized by the basic CeO_2, leading to the deactivation of ReO_x/C-BP.

The co-catalyst system of CeO_2 + ReO_x/C-BP is technically simpler than the mixture of ReO_x/CeO_2 + ReO_x/C-BP; and thus, I further investigated the combination of CeO_2 + ReO_x/C-BP. The time course of the reaction of 1,4-AHERY over the combination of CeO_2 + ReO_x/C-BP (Re = 4 wt%) is shown in Figure 3-3 (the detailed data are shown in Table 3-3), which is very similar to the time course over ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) + ReO_x/C-BP (Re = 3 wt%) [11]: the selectivity to 1,4-BuD increased with the conversion of 1,4-AHERY, and slightly decreased at longer reaction time due to the formation of THF from 1,4-BuD as overreaction. The highest yield of 1,4-BuD reached 85% at 24 h. DHF was not detected at all, suggesting that conversion of DHFs was very fast. The acetal of 4-hydroxybutanal and 1,4-AHERY, 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran (identified by NMR in previous research [11]), was formed as an intermediate at the beginning and was finally converted to 1,4-BuD. Therefore, the mechanism of the reaction over CeO_2 + ReO_x/C-BP catalyst might be the same as that over the combination of ReO_x-Au/CeO_2 + ReO_x/C-BP (Scheme 1). The activity of CeO_2 + ReO_x/C-BP (Re = 4 wt%) was higher than that of ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) + ReO_x/C-BP (Re = 3 wt%) (at 12 h, the conversion was 95% and 79% [11], respectively), the possible reason will be discussed later.

Table 3-4 shows the reaction of 1,4-AHERY and the possible intermediates over Re catalysts used in the ReO_x/CeO_2 + ReO_x/C-BP system. The substrate amount was decreased from 0.5 g (standard conditions) to 0.15 g to simulate the low concentration conditions of intermediates during the reaction. The results are similar to those in the previous study about the ReO_x-Au/CeO_2 + ReO_x/C-BP system [11]. The combination of ReO_x/CeO_2 + ReO_x/C-BP gave very high (~90%) yield of 1,4-BuD in the reaction of 1,4-AHERY (entry 1). However, single ReO_x/CeO_2 showed very low activity of 1,4-AHERY conversion (entry 2). Single ReO_x/CeO_2 (entry 5) presented very low activity in the reaction of 2,5-DHF as well, and very little amount of THF and 2,3-DHF were formed, which are the products by hydrogenation and isomerization of 2,5-DHF, respectively. ReO_x/CeO_2 can partially catalyze the hydration of 2,3-DHF to 2-hydroxytetrahydrofuran (2-HTHF) or 2,2’-oxybis(tetrahydrofuran) (entry 10), however, this process mainly proceeded on the C-BP surface (entry 13) [11]. The yield of detected products was much lower than the total yield, which might be due to the polymerization of DHFs during the reaction as well as the low boiling points of DHFs. The Re species on ReO_x/C-BP is responsible for the conversion of DHFs to 1,4-BuD (entries 6-8, 10-12) [11]. Adding ReO_x/CeO_2 to ReO_x/C-BP can suppress the polymerization of 2,5-DHF (entries 4 and 9). Only the significant difference between the presence and absence of Au is that ReO_x/CeO_2 alone has much lower activity in DODH than ReO_x-Au/CeO_2. Based on all the data, the mechanism of 1,4-AHERY reduction to 1,4-BuD over ReO_x/CeO_2 + ReO_x/C-BP can be proposed as: (1) DODH of 1,4-AHERY to 2,5-DHF over ReO_x/CeO_2 promoted by ReO_x/C-BP as catalyst for H_2 activation; (2) ReO_x/C-BP-catalyzed conversion of 2,5-DHF to 1,4-BuD.

3.3.2 Characterization

Figure 3-4 shows the H_2-TPR profiles of the mixture of CeO_2 + ReO_x/C-BP (Re = 4 wt%)

catalysts. The H_2 consumption amount is summarized in Table 3-5. The mixture was stirred in 1,4-dioxane solvent to redistribute the Re species, and dried before TPR measurement. The profiles of CeO_2, ReO_x/CeO_2 (Re = 1 wt%), C-BP and ReO_x/C-BP (Re = 3 wt%) are shown for comparison, which were reported in my previous paper [11]. CeO_2 + ReO_x/C-BP after mixing in 1,4-dioxane showed narrow strong signal with a peak at 510 K. The peak position was almost the same as that of ReO_x/C-BP alone. However, the consumption amount on CeO_2 + ReO_x/C-BP (Re = 4 wt%) (500 – 600 K, 0.028 mmol/(25 mg + 25 mg)) was significantly larger than that of ReO_x/C-BP alone (500 – 600 K, 0.007 mmol /25 mg). Around 740 K, ReO_x/CeO_2 shows reduction signal and the H_2 consumption amount was much larger than that of Re reduction, indicating that the reduction of Ce also largely contributed to this peak at 740 K [13]. In contrast, the peak around 740 K on CeO_2 + ReO_x/C-BP (Re = 4 wt%) was not so significant as that of ReO_x/CeO_2, suggesting that the copresence of ReO_x/C-BP shifts the peak at 740 K to much lower temperature like 500-600 K. The TPR profiles of ReO_x-Au/CeO_2 and ReO_x-Pd/CeO_2 have been already reported [9],[13]. In the cases of ReO_x-Au/CeO_2 and ReO_x-Pd/CeO_2, the H_2 consumption signals for Re reduction were observed around 400 K and 500 K, respectively. ReO_x/C-BP showed the ability of H_2 activation even though it was lower than that of noble metals such as Pd and Au. The Re loading amount can affect the reduction degree of Ce, and the valence of Re species in the catalysts was difficult to be estimated, because the reductions of supported Re species and CeO_2 are overlapped in similar temperature range. Nevertheless, it is expected that the Re species on C-BP can be reduced at relatively low temperature to lower valence or metallic state judging from the H_2 consumption amount of ReO_x/C-BP (Table 3-5, entry 1). In particular, metallic Re can be connected to high activation ability of H_2 molecule to atomic hydrogen. Then the spiltover H atoms migrated from Re metal to C-BP surface, and then to CeO_2 surface. Activated hydrogen species on Au/CeO_2 are possible to move from CeO_2 particle to CeO_2 particle for reducing the high-valent Re species in the reaction [10]. The hydrogen species can move from Re on C-BP to ReO_x species on distant CeO_2 particles. The DODH reaction of 1,4-AHERY proceeded over the mixture of ReO_x on CeO_2 and ReO_x/C-BP to form 2,5-DHF as the intermediate, suggesting that the reduction of Re species on C-BP and

CeO_2 proceeded under the reaction conditions of 413 K and 8 MPa H_2. Although the reduction temperature of ReO_x/C-BP and CeO_2 + ReO_x/C-BP is higher than that of ReO_x-Au/CeO_2 in the TPR profiles [9], the yield of 1,4-BuD over ReO_x/CeO_2 + C-BP was even higher over ReO_x-Au/CeO_2 + ReO_x/C-BP at similar reaction time [11]. This suggests that the activation of H_2 is fast and not the rate-determining step over CeO_2 + ReO_x/C-BP, especially under high pressure in the reaction (8 MPa) like the case of ReO_x-Au/CeO_2 + ReO_x/C-BP. The H_2 consumption of ReO_x-Au/CeO_2 at 500–600 K is larger than that of ReO_x-Pd/CeO_2, indicating that the H_2 was consumed at lower temperature than 500 K. The effect of H_2 pressure on reaction rate is shown later. In fact, the reduction temperature can be influenced by the H_2 pressure, and high hydrogen pressure for the reaction enables the catalyst reduction at much lower temperature than that in the TPR profiles where H_2 pressure was as low as 5% of 0.1 MPa. These behaviors were also verified on Re-Pd/SiO_2 [16],[17]. Another important point is that the hydrogenation activity on metallic Re species on C-BP is so low as the case of Au. When bare Re metal surface is exposed, Re species may catalyze the hydrogenation of C=C bond like the case of ReO_x-Pd/CeO_2. From the similarity between ReO_x-Au/CeO_2 + ReO_x/C-BP and CeO_2 + ReO_x/C-BP, the hydrogenation of C=C bond over ReO_x/C-BP is very slow like that over Au surface. According to the report on the structure of Re/SiO_2 and Re-Pd/SiO_2 [16]-[18], the surface of Re metal particles are interacted and modified with cationic Re species. Moreover, noble metal particles modified with cationic Re species have been reported to be effective catalysts for the selective hydrogenation of unsaturated aldehydes to unsaturated alcohols, indicating that the presence of cationic Re species suppressed the hydrogenation of C=C bond [19]-[21]. In the present case, Re metal surface modified with Re cation can be effective to H_2 activation without the ability to hydrogenate C=C bond.

The XRD patterns of used catalysts only showed the peaks of CeO_2 and/or carbon (Figure 3-5). In previous report of Tomishige group [16], some of Re species in 14 wt% ReO_x/SiO_2 were reduced to metallic state after reaction and showed the broad peaks in the range of 38-45°. No signal of Re species was detected here, indicating that the Re species including metallic ones were highly dispersed and the aggregation of Re species during the reaction of 1,4-AHERY to

1,4-BuD was not significant. Low Re loading amount in this case may be related to the higher dispersion. Because single (ReO_x/)CeO_2 or ReO_x/C-BP was difficult to be separated from the mixture after reaction, the Re species on each support was not further characterized. In previous study, TEM image showed that the CeO_2 granules with > 0.1 μm size were broken into pieces and small aggregates with a few CeO_2 crystallites were dispersed on C-BP after reaction [11].

3.3.3 Kinetic studies

The effect of H_2 pressure on the conversion of 1,4-AHERY over CeO_2 + ReO_x/C-BP is shown in Figure 3-6 (the detailed data are in Figure 3-7 and Table 3-6). The reaction order with respect to H_2 pressure was estimated to be around zero, indicating that the reactions involving hydrogen species were very fast; i.e. activation of H_2 over ReO_x/C-BP, spillover of activated hydrogen species on support surface, and the reduction of Re species on CeO_2 with the hydrogen species. Based on the reaction mechanism of 1,4-AHERY to 1,4-BuD over ReO_x-Au/CeO_2 + ReO_x/C-BP, the step of ReO_x/CeO_2-catalyzed DODH first converts 1,4-AHERY. DODH reaction is generally composed of substrate adsorption to form diolate complex,[7,12-14] reduction of Re, and formation of alkene from the diolate complex. The coordination is generally fast, and considering the fast reduction of Re species on CeO_2, the rate-determining step of the DODH reaction in this system is the formation step of 2,5-DHF from the diolate complex of 1,4-AHERY. Sufficiently high selectivity to 1,4-BuD even at short reaction time indicates that this step is the most important in the total process.

Here, the amount of Re species moved from C-BP to CeO_2 surfaces is estimated by comparison in the reaction rate of 1,4-AHERY between this system and ReO_x-Pd/CeO_2 catalysts. Both ReO_x-Pd/CeO_2 catalyst [12],[13] and CeO_2 + ReO_x/C-BP catalysts showed zero-order conversion rate with respect to H_2 pressure, indicating that the rate-determining step is the formation of 2,5-DHF from the reduced Re species in the DODH reaction. The active Re species is located distant from the promoter (Pd or ReO_x/C-BP) [12],[13], and therefore, the reaction rate simply depends on the number of active Re species on CeO_2. Table 3-7 (the detailed data are in Table 3-8), shows the comparison of the reaction rate between ReO_x-Pd/CeO_2 catalysts and CeO_2

+ ReO_x/C-BP catalyst combinations. As reported in the previous paper [13], the reaction rate over ReO_x-Pd/CeO_2 increased almost linearly up to 2 wt% loading (similar TOF based on total Re amount), and then gradually decreased (TOF also decreased) because of the formation of polymeric Re species. Because the ratio of polymeric Re species to monomeric one depends on the Re surface concentration on CeO_2 surface [13], the reaction rate was also compared based on CeO_2 amount. The reaction rate on the basis of CeO_2 amount over CeO_2 + ReO_x/C-BP (Re = 4 wt%, entry 3) was similar to that over ReO_x-Pd/CeO_2 (Re = 2 wt%, entry 5). These data suggest that the Re surface concentration on CeO_2 was similar between CeO_2 + ReO_x/C-BP (Re = 4 wt%) and ReO_x-Pd/CeO_2 (Re = 2 wt%); it is interpreted that half of Re species in CeO_2 + ReO_x/C-BP (Re = 4 wt%) move from C-BP to CeO_2 surfaces. In the case of lower Re loading amount in CeO_2 + ReO_x/C-BP, the TOF value became larger than the case of CeO_2 + ReO_x/C-BP (Re = 4 wt%), suggesting that more than half of Re species move from C-BP to CeO_2 surfaces (entries 1-3).

As discussed for Figure 3-3, the reaction rate per weight of CeO_2 over ReO_x-Au/CeO_2 (Re = 1 wt%) + ReO_x/C-BP (Re = 3 wt%) was lower than that over CeO_2 + ReO_x/C-BP (Re = 4 wt%). One possible cause of the difference is the lower reduction temperature (level off temperature <400 K in TPR [9]) for Re species in Au-promoted system. An important point is that low-valent Re species are not mobile (soluble) according to the previous study [11]: when the ReO_x/C-BP was reduced by H_2 before reaction, the conversion of 1,4-AHERY over Au/CeO_2 + reduced ReO_x/C-BP (Re = 3 wt%) dramatically dropped to 8% from 80% over Au/CeO_2 + unreduced ReO_x/C-BP. Therefore, the mobility of Re species can be influenced by the catalyst reducibility. The reduction of components on the catalyst can proceed during the reduction pretreatment. In the present experiment, the prepared catalysts, 1,4-dioxane and substrate are put into the reactor. Air in the reactor is purged with H_2 and 6 MPa H_2 is introduced to the reactor after purging at room temperature. The reactor is heated from room temperature to the reaction temperature. Under these conditions, the Re species can be reduced at lower temperature on the catalyst with high catalyst reducibility. It is interpreted that the amount of mobile Re species can be smaller with higher catalyst reducibility.

3.3.4 Applications to other diols or polyols

Over ReO_x-Au/CeO_2 and ReO_x-Pd/CeO_2 catalysts, various substrates with vicinal OH groups can be respectively converted to corresponding alkenes and alkanes in DODH reaction [9]-[13]. In order to know whether or not the ReO_x/CeO_2 + ReO_x/C-BP system is applicable to DODH of other diols or polyols, some substrates with vicinal OH groups were tested over ReO_x/CeO_2 and ReO_x/C-BP catalysts, and the results are listed in Table 3-9. In the case of *cis*-1,2-cyclohexanediol, the main products were *trans*-1,2-cyclohexanediol by isomerization and cyclohexane by DODH + hydrogenation over ReO_x/CeO_2 + ReO_x/C-BP (entry 1). DODH product, cyclohexene, was not formed in the reaction. Single ReO_x/C-BP catalyzed the isomerization of *cis*-1,2-cyclohexanediol (entry 3). Single ReO_x/CeO_2 showed very low activity in *cis*-1,2-cyclohexanediol conversion (entry 2), and very small amount of cyclohexene was detected as the DODH product. Therefore, the DODH was surely catalyzed by ReO_x/CeO_2 + ReO_x/C-BP, and the hydrogenation was catalyzed by ReO_x/C-BP, and all components of ReO_x/CeO_2 and ReO_x/C-BP are necessary in the catalysis. As a similar cyclic substrate, *cis*-1,2-cyclopentanediol was mainly converted to the *trans*-isomer, the DODH product (cyclopentene), and the DODH + hydrogenation product (cyclopentane) over ReO_x/CeO_2 + ReO_x/C-BP (entry 4) as well. Single ReO_x/C-BP showed activity only in the isomerization of *cis*-1,2-cyclopentanediol to *trans*-1,2-cyclopentanediol (entry 6). From *cis*-1,2-cyclohexanediol, higher yield of isomerized product was obtained than that from *cis*-1,2-cyclopentanediol over ReO_x/C-BP or over ReO_x/CeO_2 + ReO_x/C-BP. On the other hand, the sum yields of DODH and DODH + hydrogenation product from *cis*-1,2-cyclopentanediol was clearly higher than that from *cis*-1,2-cyclohexanediol over ReO_x/CeO_2 + ReO_x/C-BP. These indicate that the reactivity of *cis*-1,2-cyclopentanediol in the DODH reaction is higher than that of *cis*-1,2-cyclohexanediol. The trend of higher reactivity of 5-membered ring *cis*- cyclic diols than 6-membered ring ones in DODH has been reported in other DODH systems [8],[9],[13],[18]. This reactivity difference can be explained by the angle between the two C-OH bonds. At the same time, the reactivity of *cis*-1,2-cyclopentanediol over ReO_x/C-BP in the isomerization reaction is significantly lower than that of *cis*-1,2-cyclohexanediol, which is also contributable to higher yield of DODH (+ hydrogenation) products over ReO_x/CeO_2 + ReO_x/C-BP.

As a straight chain substrate with vicinal OH groups, 1,2-octanediol was mainly converted to DODH + hydrogenation product *n*-octane over ReO_x/CeO_2 + ReO_x/C-BP (entry 7). The activity of single ReO_x/CeO_2 or ReO_x/C-BP was very low in the reaction of 1,2-octanediol (entries 8 and 9). However, single ReO_x/C-BP had relatively high activity of the hydrogenation and isomerization of 1-octene to *n*-octane and 2- and 3-octenes, respectively (Table 3-10, entry 3) even at 2 MPa of H_2. High hydrogenation activity of ReO_x/C-BP limits the production of DODH product (alkene) over the mixture of ReO_x/CeO_2 + ReO_x/C-BP in the reaction of 1,2-octanediol. Another interesting point is higher yield of *n*-octane on ReO_x/CeO_2 (Re = 1 wt%) + ReO_x/C-BP (Re = 3 wt%) (Table 3-10, entry 1) than that on ReO_x/C-BP (Table 3-10, entry 3). It seems that the presence of CeO_2 or ReO_x/CeO_2 promotes the hydrogenation of 1-octene over ReO_x/C-BP on the basis that ReO_x/CeO_2 showed almost no activity of 1-octene hydrogenation (Table 3-10, entry 2). Higher activity of ReO_x/CeO_2 + ReO_x/C-BP than ReO_x/CeO_2 or ReO_x/C-BP alone in alkene hydrogenation was actually observed for trans-2-octene as a substrate (Table 3-10, entries 5-7). One possible explanation is the decrease of the coverage of Re cation on the Re metal surface over ReO_x/C-BP with the move of Re species from C-BP to CeO_2. High coverage of metal cation on metal surface can decrease the number of active metal site and the hydrogenation activity.

Glycerol was converted to hydrogenated DODH product (1-propanol) over ReO_x/CeO_2 + ReO_x/C-BP (Table 3-9, entry 10), and allyl alcohol (DODH product) yield was very low. The formation of 1,2-propanediol might be due to the dehydration and hydrogenation of glycerol [10]. Single ReO_x/CeO_2 or ReO_x/C-BP also had difficulty to catalyze the reaction of glycerol.

ReO_x/C-BP or ReO_x/CeO_2 + ReO_x/C-BP showed the activity to catalyze the isomerization of the *trans*-1,2-cyclohexanediol to *cis*-1,2-cyclohexanediol (entries 13 and 15), therefore, they might have possibility to isomerize the OH groups in *trans*- to *cis*- position in other sugar alcohols such as methyl glucoside. The extension of the substrate scope is needed to be further investigated. According to the results in Table 3-9 and Table 3-10, ReO_x/C-BP can catalyze the

C=C hydrogenation of various substrates. On the other hand, the yield of THF in the reaction of 1,4-AHERY over $(ReO_x)/CeO_2$ + ReO_x/C-BP is much lower than 1,4-BuD, and this indicates that the reactivity of 2,5-DHF and 2,3-DHF in the hydrogenation to THF is much lower than in the hydration of 2,3-DHF to 2-HTHF.

3.3.5 Catalyst stability

The deactivation of ReO_x-Au/CeO_2 + ReO_x/C-BP was reported in my previous study [11]: The conversion of 1,4-AHERY was decreased from 100% to 65% in the second run, and the selectivity also decreased from 86% to 71%. Similarly, the ReO_x/CeO_2 + ReO_x/C-BP co-catalyst was also difficult to be reused due to the catalyst deactivation. Table 3-11 shows the reusability of CeO_2 and ReO_x/C-BP mixture. The activity (conversion) and selectivity to 1,4-BuD of the used catalyst mixture sharply decreased from 100% and 89% to 64% and 64%, respectively, after first run (entry 2). One reason of the deactivation of the co-catalyst might be that a part of monomeric active Re species became polymeric inactive ones. Therefore, adding fresh catalysts (entries 3 and 4) could effectively recover the activity of reused catalyst mixture. The yield of 1,4-BuD in the second run was comparable to that in the first run by replenishing the weight loss in recycling with fresh ReO_x/C-BP. However, the activity still obviously dropped in the third run even the fresh ReO_x/C-BP was added (entry 5). Pretreatments such as heating in N_2 at 773 K for 1 h presented some effect on the regeneration of the used catalyst (entry 6), because the organic deposits on catalyst surface could be removed by heating [11]. The conversion of 1,4-AHERY can be recovered to be 91% by heating in N_2 at 773 K for 1 h in the case of the ReO_x-Au/CeO_2 + ReO_x/C-BP. However, in the case of CeO_2 + ReO_x/C-BP, the conversion was 71% after the same regeneration. The selectivity of 1,4-BuD was lower than the catalyst combinations in the presence of Au promoter as well. The combination of replenishing fresh ReO_x/C-BP with the N_2 heating pretreatment effectively increased the catalytic activity of the used catalyst mixture (entry 7). The conversion (activity) and selectivity to 1,4-BuD were almost the same as that in the first run. Nevertheless, the yield of 1,4-BuD slightly decreased in the third use (entry 8). Due to the combustibility of carbon support, the reusability of ReO_x/C-BP in the co-catalysis system should be further studied in the future.

3.3.6 Models of ReO_x-Au/CeO_2 + ReO_x/C-BP and CeO_2 + ReO_x/C-BP

Based on the above considerations, the models of structure change of ReO_x-Au/CeO_2 + ReO_x/C-BP and CeO_2 + ReO_x/C-BP during reaction are shown in Figure 3-8. Before reaction, the Re species on CeO_2 and C-BP are in high-valent state of +7, which is derived from the precursor of NH_4ReO_4. During heating in the reaction mixture under H_2 ("reduction pretreatment"), the high-valent Re species on C-BP can take two different routes. One is the reduction to low-valent Re species with H_2 and the other is leaching to the solvent and the move to CeO_2 surface. Since the low-valent Re species, which is formed by the reduction of high-valent Re species on C-BP, is not soluble, the catalyst reducibility can affect the degree of the move of high valent Re species. Re species on CeO_2 can be reduced to +4 even in the presence of highly dispersed Pd metal particles according to the previous works [12],[13]. On the other hand, Re species on inert supports such as SiO_2 and C can be reduced to metallic state or lower-valent state (< 4) [16],[17],[22]. When the catalyst system has high reducibility, high-valent Re species on C-BP is reduced at lower temperature during the heating for the reduction pretreatment, and the amount of soluble and mobile Re species can be smaller. ReO_x-Au/CeO_2 catalyst has higher reducibility than ReO_x/CeO_2 and ReO_x/C-BP, due to high activation ability of H_2 of Au and its ability to supply activated hydrogen species by spillover, which is demonstrated by H_2-TPR. Therefore, high valent Re species tends to be reduced on C-BP rather than the move to CeO_2 surface in the case of ReO_x-Au/CeO_2 + ReO_x/C-BP. In contrast, in the case of CeO_2 + ReO_x/C-BP, the catalysts have lower reducibility and high-valent Re species tends to move to CeO_2 surface rather than to be reduced on C-BP. The model schemes of the high-valent Re species on C-BP in the case of ReO_x-Au/CeO_2 + ReO_x/C-BP and CeO_2 + ReO_x/C-BP are shown in Figure 3-8. The distributions of Re species on CeO_2 and C-BP supports can be determined by the catalyst reducibility.

The DODH activity is controlled by the amount of monomeric ReO_x species on CeO_2, which is strongly affected by loading amount of Re on CeO_2, and it should be optimized. In the present case, the amount of Re species on CeO_2 is optimized by the catalyst reducibility. As reported previously, ReO_x/C-BP is not so an effective catalyst in DODH reaction using H_2 as a reductant [11], which is explained by the reduction to low-valent Re species with low-DODH activity. In contrast, CeO_2 has a function to suppress the formation of low-valent Re species and maintain the high-valent state of Re species ($\geq +4$). In the previous works, the combination of Pd and Au with high-valent Re species enables the high DODH activity, where the important role of Pd and Au is the H_2 activation to promote the reduction of Re species. Based on the present work, the reduced Re species on C-BP has the role of H_2 activation and promotes the DODH reaction on high-valent Re species on CeO_2. In other words, the combinations of supports for Re loading can omit the utilization of Pd and Au, and to give monometallic Re catalyst using H_2 as a reductant. Another important point is the preparation method. The impregnation of the premixed CeO_2 + C-BP with the aqueous solution of Re precursor is not effective at all. (Table 3-2, entry 6). At present, the reason for low activity of this catalyst system is not clear. Further investigation is necessary. In fact, the high performance of CeO_2 + ReO_x/C-BP indicates that *in-situ* preparation using the move of Re species is very effective.

3.4 Conclusions

1,4-Butanediol can be produced from 1,4-anhydroerythritol (1,4-AHERY) over the co-catalysis of ReO_x/CeO_2 and ReO_x/C-BP (C-BP: carbon black BP2000) in one-pot reaction using H_2 as a reductant without Au promoter for ReO_x/CeO_2. The products pattern in the reaction of 1,4-AHERY over ReO_x/CeO_2 + ReO_x/C-BP is very similar to that over the co-catalyst with Au, and the reaction mechanism is supposed to start with the deoxydehydration (DODH) of 1,4-anhydroerythritol to 2,5-dihydrofuran over ReO_x/CeO_2 + ReO_x/C-BP. ReO_x/C-BP can promote the reduction of Re species on CeO_2, similarly to Au promoter on ReO_x-Au/CeO_2. Then 2,5-dihydrofuran is further converted to 1,4-butanediol over ReO_x/C-BP. In addition, it is found that physical mixture of CeO_2 and ReO_x/C-BP shows high activity in the conversion of 1,4-AHERY to 1,4-BuD, and the activity is clearly higher than that of ReO_x-Au/CeO_2 + ReO_x/C. High activity of CeO_2 + ReO_x/C-BP can be due to the mobility of high-valent Re species from

C-BP to CeO_2 surface to give catalytically active Re species for the DODH reaction. Considering that high-valent Re species tends to be present on the catalysts before reduction, the Re species can move during the heating for catalyst reduction. Therefore, the catalyst reducibility can influence the mobility of high-valent Re species, and higher catalyst reducibility can be connected to lower mobility of the Re species. According to the profiles of the temperature programmed reduction with H_2, CeO_2 + ReO_x/C-BP showed lower reducibility than ReO_x-Au/CeO_2, which enables the move of Re species from C-BP to CeO_2. About half of Re species can be moved from ReO_x/C-BP (Re = 4 wt%) to mixed CeO_2 (weight ratio of CeO_2 : ReO_x/C-BP = 1 : 1). High activity can be explained by larger amount of catalytically active Re species on CeO_2 in CeO_2 + ReO_x/C-BP than that of ReO_x-Au/CeO_2 + ReO_x/C-BP at the same total Re loading amount. The performance of CeO_2 + ReO_x/C-BP was comparable to ReO_x-Au/CeO_2 + ReO_x/C-BP in terms of the yield of 1,4-BuD (~85%) and the catalyst reusability. Another important aspect in the present study is to demonstrate that heterogeneous DODH or DODH + hydrogenation catalysts can be prepared from only Re species by utilizing Re species for DODH reaction and low valent Re species for H_2 activation on different supports.

References

[1] A. M. Ruppert, K. Weinberg, R. Palkovits, Angew. Chem. 2012, vol. 51, pp. 2564-2601.

[2] Y. Kobayashi, H. Iwata, D. Mizushima, J. Ogihara, T. Kasumi, Lett. Appl. Microbiol. 2015, 60, 475-480.

[3] D. Sun, Y. Yamada, S. Sato, W. Ueda, Appl. Catal. B 2016, 193, 75-92.

[4] J. R. Dethlefsen, P. Fristrup, ChemSusChem 2015, 8, 767-775.

[5] A. R. Petersen, P. Fristrup, Chem. Eur. J. 2017, 23, 10235-10243.

[6] S. Raju, M. Moret, R. J. M. K. Gebbink, ACS Catal. 2015, 5, 281-300.

[7] J. R. Dethlefsen, D. Lupp, A. Teshome, L. B. Nielsen, P. Fristrup, ACS Catal. 2015, 5, 3638-3647.

[8] S. Raju, J. T. B. H. Jastrzebski, M. Lutz, R. J. M. K. Gebbink, ChemSusChem 2013, 6, 1673-1680.

[9] S. Tazawa, N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, ACS Catal. 2016, 6, 6393-6397.

[10] Y. Nakagawa, S. Tazawa, T. Wang, M. Tamura, N. Hiyoshi, K. Okumura, K. Tomishige, ACS Catal. 2018, 8, 584-595.

[11] T. Wang, S. Liu, M. Tamura, Y. Nakagawa, N. Hiyoshi, K. Tomishige, Green Chem. 2018, 20, 2547-2557.

[12] N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, Angew. Chem. 2015, vol. 54, pp. 1897-1900.

[13] N. Ota, M. Tamura, Y. Nakagawa, K. Tomishige, ACS Catal. 2016, 6, 3213-3226.

[14] M. Tamura, N. Yuasa, J. Cao, Y. Nakagawa, K. Tomishige, Angew. Chem. 2018, vol. 57, pp. 8058-8062.

[15] Y. Xi, W. Yang, S. C. Ammal, J. Lauterbach, Y. Pagan-Torresb, A. Heyden, Catal. Sci. Technol. 2018, 8, 5740-5752.

[16] Y. Takeda, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, ACS Catal. 2015, 5, 7034-7047.

[17] Y. Takeda, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, Catal. Sci. Technol. 2016, 6, 5668-5683.

[18] Y. Amada, N. Ota, M. Tamura, Y. Nakagawa, K. Tomishige, ChemSusChem 2014, 7, 2185-2192.

[19] M. Tamura, K. Tokonami, Y. Nakagawa, K. Tomishige, Chem. Commun. 2013, 49, 7034-7036.

[20] M. Tamura, K. Tokonami, Y. Nakagawa, K. Tomishige, ACS Catal. 2016, 6, 3213-3226.

[21] M. Tamura, K. Tokonami, Y. Nakagawa, K. Tomishige, ACS Sustain. Chem. Eng. 2017, 5, 3685-3697.

[22] B. Zhang, Z. Qi, X. Li, J. Ji, W. Luo, C. Li, A. Wang, T. Zhang, ACS Sustainable Chem. Eng. 2019, 7, 208-215.

Table 3-1 Reaction of 1,4-AHERY over various Re catalysts physically mixed with ReO_x/CeO_2 [a]

Entry	Catalyst 1	Catalyst 2	Conv.	Product selectivity /%							
			/%	1,4-BuD	THF	GBL	1-BuOH	2,5–DHF	2,3–DHF	Acetal	Others
1	ReO_x/CeO_2	ReO_x/C-BP	97	86	7	2	2	0	0	0	2
2[b]	ReO_x-Au/CeO_2[c]	ReO_x/C-BP	100	86	8	2	2	0	0	0	3
3	ReO_x/CeO_2	—	4	0	41	7	0	0	1	0	51
4[b]	—	ReO_x/C-BP	2	18	10	0	4	4	0	0	65
5	ReO_x/CeO_2	ReO_x/C-NR	67	60	1	2	0	2	0	26	8
6	ReO_x/CeO_2	ReO_x/HZSM-5	11	0	1	1	0	3	1	0	94
7	ReO_x/CeO_2	ReO_x/Al_2O_3	2	0	0	0	0	41	0	0	59
8	ReO_x/CeO_2	ReO_x/SiO_2	7	0	0	0	0	80	0	0	20
9	ReO_x/CeO_2	ReO_x/TiO_2	5	0	1	0	0	66	0	0	32
10	ReO_x/CeO_2	ReO_x/ZrO_2	4	0	0	0	0	60	0	0	40
11	ReO_x/CeO_2	C-BP	24	72	2	2	0	1	0	14	9
12	CeO_2	ReO_x/C-BP	91	90	5	1	1	0	0	0	3
13	CeO_2	ReO_x/C-BP[d]	4	53	6	0	4	0	0	4	33
14[e]	ReO_x/CeO_2	ReO_x/C-BP	8	4	0	23	0	9	0	60	3

[a] 1,4-AHERY = 0.5 g, catalyst 1 = 0.15 g (Re = 1 wt%), catalyst 2 = 0.15 g (Re = 3 wt%), 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. [b] Reported in ref. [11] (reaction conditions were the same). [c] Au = 0.3 wt%. [d] ReO_x/C-BP was reduced by H_2 in 1,4-dioxane at 413 K for 1 h before reaction, then it was mixed with CeO_2 without exposing to air. [e] P_{Ar} = 5 MPa (zero hydrogen pressure). AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, GBL: γ-butyrolactone, BuOH: butanol, DHF: dihydrofuran, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran. C-BP: carbon black BP2000, C-NR: activated carbon Norit RX3 extra.

Table 3-2 Reaction of 1,4-AHERY over ReO_x/CeO_2 + ReO_x/C-BP with various Re loading amount [a]

Entry	Catalyst 1	Catalyst 2	Conv.	Product selectivity /%					
			/%	1,4-BuD	THF	GBL	1-BuOH	Acetal	Others
1	CeO_2	ReO_x/C-BP (Re = 4 wt%)	100	89	6	1	2	0	2
2	ReO_x/CeO_2 (Re = 1 wt%)	ReO_x/C-BP (Re = 3 wt%)	97	86	7	2	2	0	2
3	ReO_x/CeO_2 (Re = 2 wt%)	ReO_x/C-BP (Re = 2 wt%)	100	82	13	1	2	1	1
4	ReO_x/CeO_2 (Re = 3 wt%)	ReO_x/C-BP (Re = 1 wt%)	100	73	24	0	2	0	1
5	ReO_x/CeO_2 (Re = 4 wt%)	C-BP	100	75	22	1	1	0	1
6	$ReO_x/(CeO_2$ + C-BP$)_{mixture}$ (Re = 2 wt%) [b]		60	75	7	2	2	11	3

[a] 1,4-AHERY = 0.5 g, catalyst 1 = 0.15 g, catalyst 2 = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h.

[b] Catalyst = 0.3 g, CeO_2 and C-BP (1:1 in weight) were mixed before Re loading in the preparation. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, GBL: γ-butyrolactone, BuOH: butanol, DHF: dihydrofuran, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran. C-BP: carbon black BP2000.

Table 3-3 Time course of the reaction of 1,4-AHERY over the mixture of CeO_2 + ReO_x/C-BP (Re = 4 wt%) [a]

Entry	Time /h	Conv. /%	Product selectivity /%							
			1,4-BuD	THF	2,5-DHF	2,3-DHF	GBL	1-BuOH	Acetal	Others
1	0	33	46	1	2	1	2	0	41	8
2	2	60	70	4	2	1	1	0	17	5
3	4	73	85	4	2	1	0	0	5	3
4	7.5	86	86	5	0	0	2	1	3	2
5	12	95	88	6	0	0	1	2	1	2
6	24	100	89	6	0	0	1	2	0	1
7	48	100	83	14	0	0	0	2	0	1

[a] 1,4-AHERY = 0.5 g, CeO_2 = 0.15 g, ReO_x/C-BP (Re = 4 wt%) = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 0 to 48 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran, C-BP: carbon black BP2000.

Table 3-4 Reaction of 1,4-AHERY and the intermediates over related catalysts [a]

Entry	Substrate	Catalyst	Catalyst weight /g	Products (yield /%)	Conv. /% (C.B. /%)
1	1,4-AHERY	ReO$_x$/CeO$_2$ + ReO$_x$/C-BP	0.15 + 0.15	1,4-BuD (91), THF (5), others (4)	100
2		ReO$_x$/CeO$_2$	0.15	2,5-DHF (4), GBL (0.2), others (2)	6
3 [b]		ReO$_x$/C-BP	0.15	1,4-BuD (1), THF (0.3), others (1)	33 (68)
4	2,5-DHF	ReO$_x$/CeO$_2$ + ReO$_x$/C-BP	0.15 + 0.15	1,4-BuD (68), GBL (9), THF (8), others (4)	96
5		ReO$_x$/CeO$_2$	0.15	THF (2), 2,3-DHF (1), Furan (1)	3
6 [b]		ReO$_x$/C-BP	0.15	1,4-BuD (39), THF (9), GBL (8), others (9)	94 (70)
7		ReO$_x$/C-BP [c]	0.15	1,4-BuD (38), THF (17), GBL (6), others (5)	98 (67)
8 [b]		C-BP	0.15	Furan (3), 2,2'-oxybis(tetrahydrofuran) (1), THF (1)	4
9	2,3-DHF	ReO$_x$/CeO$_2$ + ReO$_x$/C-BP	0.15 + 0.15	1,4-BuD (52), GBL (7), 2-HTHF (5), others (9)	99 (80)
10		ReO$_x$/CeO$_2$	0.15	2-HTHF (13), 2,2'-oxybis(tetrahydrofuran) (7), others (7)	45 (81)
11 [b]		ReO$_x$/C-BP	0.15	1,4-BuD (24), GBL (6), THF (2), others (6)	100 (38)
12		ReO$_x$/C-BP [c]	0.15	1,4-BuD (23), GBL (4), THF (5), others (1)	100 (33)
13 [b]		C-BP	0.15	2,2'-oxybis(tetrahydrofuran) (46), 2-HTHF (18), 3-HTHF (8), others (5)	98 (80)

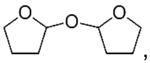
[a] Substrate = 0.15 g, water = 0.03 g (water : substrate molar ratio = 1 : 1), catalyst = 0.15 g for single, or 0.15 + 0.15 g for mixture (ReO$_x$/CeO$_2$ (Re = 1 wt%); or ReO$_x$/C-BP (Re = 3 wt%); or C-BP), 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 4 h. [b] Reported in ref. [11]. [c] ReO$_x$/C-BP (Re = 6 wt%). AHERY: anhydroerythritol; BuD: butanediol; GBL: γ-butyrolactone; THF: tetrahydrofuran; DHF: dihydrofuran; HTHF: hydroxytetrahydrofuran; 2,2'-oxybis(tetrahydrofuran) , C-BP: carbon black BP2000.

Table 3-5 Summary of TPR results in Figure 3-4

Entry	Profiles in Figure 3	Catalyst	Re loading amount /wt%	Catalyst weight /mg	Re amount /mmol	H_2 consumption /mmol	
						500 – 600 K	500 – 900 K
1	(a)	CeO_2 + ReO_x/C-BP	4	25 + 25	0.005	0.028	0.054
2	(b)	CeO_2	—	50	—	0.001	0.035
3	(c)	ReO_x/CeO_2	1	50	0.003	0.001	0.052
4	(d)	C-BP	—	50	—	0.001	0.004
5	(e)	ReO_x/C-BP	3	50	0.008	0.014	0.035
6	(f)	Au/CeO_2 + ReO_x/C-BP	3	25 + 25	0.004	0.010 0.013 (350 – 500 K)	0.027
7 [a]		ReO_x-Au/CeO_2	1	50	0.003	0.050 (350 – 600 K)	
8 [b]		ReO_x-Pd/CeO_2	2	50	0.005	0.031 (450 – 600 K)	

[a] Reported in ref. [10]. [b] Reported in ref. [13]. C-BP: carbon black BP2000.

Table 3-6 Detailed data of Figure 3-7 (Effect of hydrogen pressure on the reaction of 1,4-AHERY over CeO_2 + ReO_x/C-BP [a])

Entry	H_2 pressure /MPa	Reaction time /h	Conv. /%	Product selectivity /%							
				1,4-BuD	THF	GBL	1-BuOH	2,5-DHF	2,3-DHF	Acetal	Others
1	1	0	< 1	—	—	—	—	—	—	—	—
2		1	17	25	2	2	0	1	1	63	6
3		2	27	55	4	2	1	0	1	34	4
4	2	0	3	14	0	0	0	11	7	62	6
5		1	25	39	1	3	1	1	0	49	7
6		2	37	49	2	4	1	1	0	39	5
7	4	0	15	45	1	4	0	2	0	43	5
8		1	32	49	2	4	1	1	2	35	7
9		2	47	66	2	3	1	0	0	22	6
10	8	0	33	46	1	2	1	2	0	41	8
11		1	47	69	3	1	1	1	0	22	4
12		2	60	70	4	2	1	1	0	17	5

[a] 1,4-AHERY = 0.5 g, CeO_2 = 0.15 g, ReO_x/C-BP = 0.15 g (Re = 4 wt%), 1,4-dioxane = 4 g, P_{H2} = 1, 2, 4, 8 MPa, T = 413 K, t = 0 ~ 2 h (0 h was defined as the time when the temperature reached 413 K). AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, GBL: γ-butyrolactone, BuOH: butanol, DHF: dihydrofuran, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran, C-BP: carbon black BP2000.

Table 3-7 Comparison of initial conversion rates between various Re catalyst combinations in the reaction of 1,4-AHERY [a]

Entry	Catalyst	Re loading amount /wt%	CeO_2 amount /g	Reaction rate /mmol· $g_{CeO_2}^{-1}$· h^{-1}	TOF /h^{-1}	Ref.
1	CeO_2 + ReO_x/C-BP	1	0.15	1.8	33	This work
2		2	0.15	2.8	26	
3		4	0.15	3.2	15	
4	ReO_x/CeO_2 + ReO_x/C-BP	1+3	0.15	2.1	10	This work
5 [b]	ReO_x-Pd/CeO_2	2	0.15	3.7	34	[12], [13]
6 [c]	ReO_x-Au/CeO_2 + ReO_x/C-BP	1+3	0.15	1.3	5	[11]

[a] 1,4-AHERY = 0.5 g, CeO_2 = 0.15 g, ReO_x/C-BP = 0.15 g (Re = 1, 2, 4 wt%), 1,4-dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 4 h. [b] 1,4-AHERY = 1 g, ReO_x-Pd/CeO_2 = 0.15 g (Re = 2 wt%, Pd/Re = 0.25). [c] ReO_x-Au/CeO_2 = 0.15 g (Re = 1 wt%, Au = 0.3 wt%), ReO_x/C-BP = 0.15 g (Re = 3 wt%). AHERY: anhydroerythritol, C-BP: carbon black BP2000. It has been confirmed that the rate is independent of the substrate concentration in this concentration range. The detailed data are shown in Table 3-8

Table 3-8 Detailed data of Table 3-7

Entry	Catalyst	Re loading amount /wt%	Time /h	Conv. /%	Main product selectivity /%				Ref.
					1,4-BuD	THF	Acetal	Others	
1-1 [a]	CeO_2 + ReO_x/C-BP	1	0	4	9	0	65	26	This work
1-2 [a]			2	15	50	4	39	7	
2-1 [a]		2	0	15	33	6	54	7	
2-2 [a]			4	50	73	2	19	6	
3-1 [a]		4	0	33	46	1	41	12	
3-2 [a]			4	73	85	4	5	6	
4-1 [a]	ReO_x/CeO_2 + ReO_x/C-BP	1 + 3	0	38	43	4	40	13	This work
4-2 [a]			2	51	52	4	27	17	
5-1 [b]	ReO_x-Pd/CeO_2	2	0	15	0	98	0	2	[12], [13]
5-2 [b]			4	38	0	100	0	0	
6-1 [c]	ReO_x-Au/CeO_2 + ReO_x/C-BP	1 + 3	0	33	28	3	55	14	[11]
6-2 [c]			4	49	55	4	28	13	

[a] 1,4-AHERY = 0.5 g, CeO_2 = 0.15 g, ReO_x/C-BP = 0.15 g (Re = 1, 2, 4 wt%), 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 4 h. [b] 1,4-AHERY = 1 g, ReO_x-Pd/CeO_2 = 0.15 g (Re = 2 wt%, Pd/Re = 0.25). [c] ReO_x-Au/CeO_2 = 0.15 g (Re = 1 wt%, Au = 0.3 wt%), ReO_x/C-BP = 0.15 g (Re = 3 wt%). AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, C-BP: carbon black BP2000.

Table 3-9 Reaction of diols and polyols over ReO_x/CeO_2 (Re = 1 wt%) and ReO_x/C-BP (Re = 3 wt%) catalysts [a]

Entry	Substrate	Catalyst	Main products (yield /%)	Conv. /% (C.B. /%)
1	*cis*-1,2-cyclohexanediol	ReO_x/CeO_2 + ReO_x/C-BP	*trans*-1,2-cyclohexanediol (52), cyclohexane (19), others (1)	71
2		ReO_x/CeO_2	cyclohexene (2), others (1)	3
3		ReO_x/C-BP	*trans*-1,2-cyclohexanediol (43), others (1)	43
4	*cis*-1,2-cyclopentanediol	ReO_x/CeO_2 + ReO_x/C-BP	cyclopentane (32), *trans*-1,2-cyclopentanediol (11), cyclopentene (6), others (1)	71 (79)
5		ReO_x/CeO_2	cyclopentene (4), others (1)	5
6		ReO_x/C-BP	*trans*-1,2-cyclopentanediol (17), others (1)	18
7	1,2-octanediol	ReO_x/CeO_2 + ReO_x/C-BP	*n*-octane (85), others (2)	100 (88)
8		ReO_x/CeO_2	1-octene (3), others (3)	7
9		ReO_x/C-BP	1-octene (1), others (1)	3
10	glycerol	ReO_x/CeO_2 + ReO_x/C-BP	1-propanol (34), 1,2-propanediol (18), allyl alcohol (3), others (2)	73 (83)
11		ReO_x/CeO_2	allyl alcohol (2), others (1)	3
12		ReO_x/C-BP	1-propanol (1), others (1)	2
13	*trans*-1,2-cyclohexanediol	ReO_x/CeO_2 + ReO_x/C-BP	*cis*-1,2-cyclohexanediol (21), cyclohexane (3), others (1)	25
14		ReO_x/CeO_2	*cis*-1,2-cyclohexanediol (0.1), cyclohexene (0.1), others (0.8)	1
15		ReO_x/C-BP	*cis*-1,2-cyclohexanediol (13), others (1)	14

[a] Substrate = 0.5 g, ReO_x/CeO_2 (Re = 1 wt%) = 0.15 g, ReO_x/C-BP (Re = 3 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. C-BP: carbon black BP2000.

Table 3-10 Reaction of 1-octene and *trans*-2-octene over ReO_x/CeO_2 (Re = 1 wt%) and ReO_x/C-BP (Re = 3 wt%) catalysts [a]

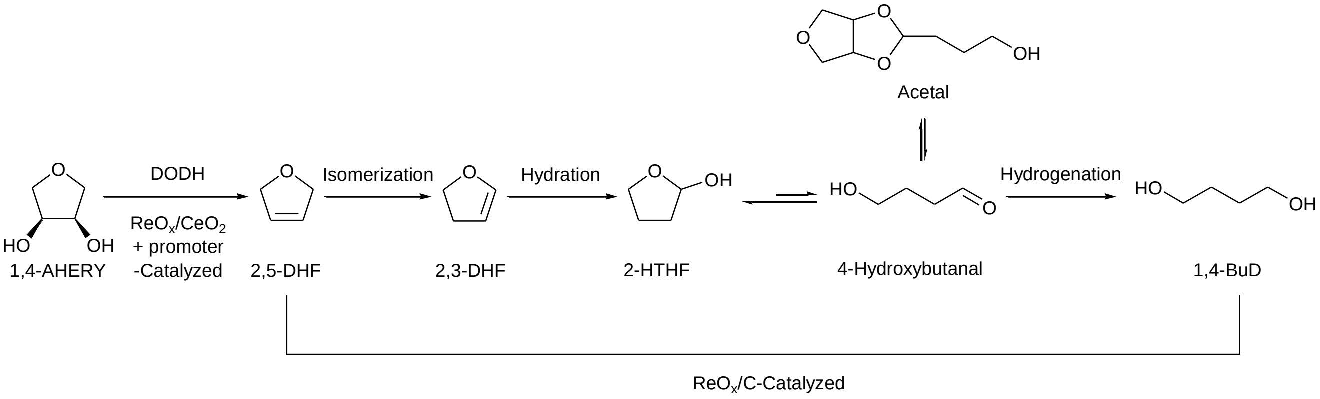
Entry	Substrate	Catalyst	Main products (yield /%)	Conv. /% (C.B. /%)
1	1-octene	ReO_x/CeO_2 + ReO_x/C-BP	*n*-octane (85), *cis*-3-octene (2), *trans*-3-octene (2)	99
2		ReO_x/CeO_2	*n*-octane (0.2), *cis*-2-octene (0.2), *trans*-2-octene (0.1), others (1)	2
3		ReO_x/C-BP	*n*-octane (51), *trans*-3-octene (14), *trans*-2-octene (12), *cis*-3-octene (8), *cis*-2-octene (4), others (1)	97
4		C-BP	—	<1
5	*trans*-2-octene	ReO_x/CeO_2 + ReO_x/C-BP	*n*-octane (63), *cis*-2-octene (0.2), *cis*-3-octene (0.2), *trans*-3-octene (0.3), others (0.4)	64
6		ReO_x/CeO_2	*cis*-2-octene (0.4), *n*-octane (0.1), 1-octent (0.1), *cis*-3-octene (0.1), *trans*-3-octene (0.3), others (0.8)	2
7		ReO_x/C-BP	*cis*-2-octene (6), *n*-octane (0.5), 1-octent (0.4), *cis*-3-octene (0.1), *trans*-3-octene (0.5), others (0.4)	8

[a] Substrate = 0.15 g, ReO_x/CeO_2 (Re = 1 wt%) = 0.15 g, ReO_x/C-BP (Re = 3 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 2 MPa, T = 413 K, t = 4 h. C-BP: carbon black BP2000.

Table 3-11 Reusability of CeO_2 + ReO_x/C-BP (Re = 4 wt%) in the reaction of 1,4-AHERY [a]

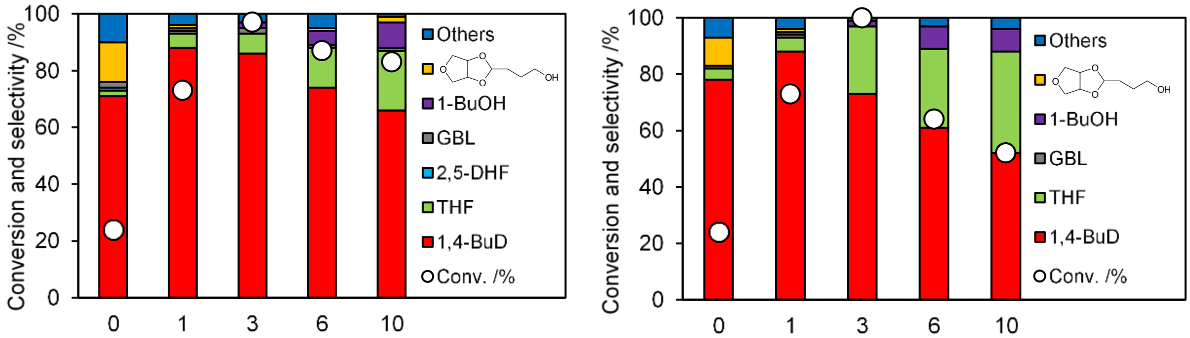
Entry	Usage time	Conv. /%	Selectivity /%							
			1,4-BuD	THF	GBL	1-BuOH	2,5-DHF	2,3-DHF	Acetal	Others
1	1	100	89	6	1	2	0	0	0	1
2 [b]	2	64	64	5	2	1	5	0	18	5
3 [c]	2	91	84	5	2	1	1	0	4	3
4 [d]	2	100	84	7	2	2	1	0	1	3
5 [d]	3	67	79	8	3	1	1	0	6	3
6 [e]	2	71	76	9	2	1	0	0	7	4
7 [f]	2	100	89	5	2	1	0	0	1	2
8 [f]	3	92	81	7	4	1	0	0	2	5

[a] 1,4-AHERY = 0.5 g, CeO_2 = 0.15 g, ReO_x/C-BP (Re = 4 wt%) = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h (the conversion of 1,4-AHERY approximately reached 100% at 24 h). [b] Recycled CeO_2 + ReO_x/C-BP (Re = 4 wt%) = 0.3 g. [c] Recycled CeO_2 + ReO_x/C-BP (Re = 4 wt%) = 0.28 g, and fresh CeO_2 = 0.0.1 g, ReO_x/C-BP (Re = 4 wt%) = 0.01 g were replenished. [d] Recycled CeO_2 + ReO_x/C-BP (Re = 4 wt%) = 0.28 g, and fresh ReO_x/C-BP (Re = 4 wt%) = 0.02 g was replenished. [e] Recycled catalyst mixture was heated in N_2 at 773 K for 1 h, CeO_2 + ReO_x/C-BP (Re = 4 wt%) = 0.3 g, [f] Recycled catalyst mixture was heated in N_2 at 773 K for 1 h, CeO_2 + ReO_x/C-BP (Re = 4 wt%) = 0.24 g, fresh CeO_2 = 0.03 g, ReO_x/C-BP (Re = 4 wt%) = 0.03 g, were replenished. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran. C-BP: carbon black BP2000.



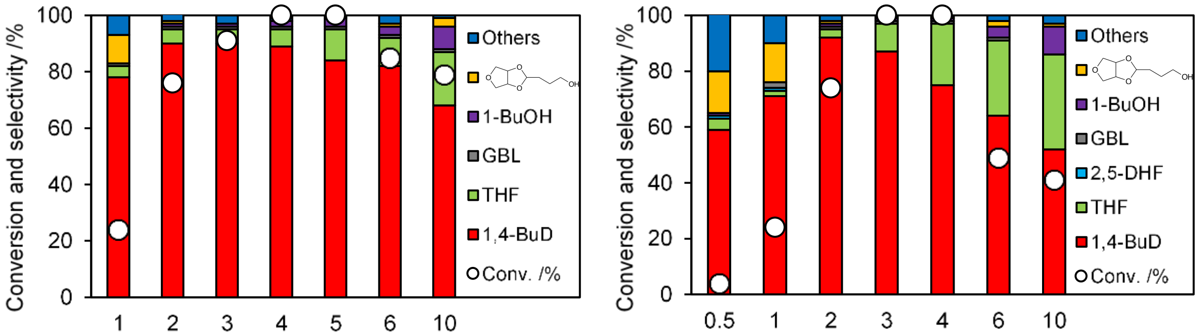
Scheme 3-1 Reaction route from 1,4-AHERY to 1,4-BuD over the mixture of ReO$_x$/CeO$_2$ and ReO$_x$/C-BP

AHERY: anhydroerythritol, BuD: butanediol, DHF: dihydrofuran, THF: tetrahydrofuran, HTHF: hydroxytetrahydrofuran.



(a) Loading amount of Re (wt%) of ReO$_x$/C-BP (combined with ReO$_x$/CeO$_2$, Re = 1%)

(b) Loading amount of Re (wt%) of ReO$_x$/CeO$_2$ (combined with ReO$_x$/C-BP, Re = 1%)



(c) Loading amount of Re (wt%) of ReO$_x$/C-BP (combined with CeO$_2$)

(d) Loading amount of Re (wt%) of ReO$_x$/CeO$_2$ (combined with C-BP)

Figure 3-1 Effect of Re loading amount of ReO$_x$/C-BP ((a) and (c)) or ReO$_x$/CeO$_2$ ((b) and (d)) in the reaction of 1,4-AHERY [a]

[a] 1,4-AHERY = 0.5 g, ReO$_x$/CeO$_2$ = 0.15 g, ReO$_x$/C-BP = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, GBL: γ-butyrolactone, BuOH: butanol, DHF: dihydrofuran, C-BP: carbon black BP2000.

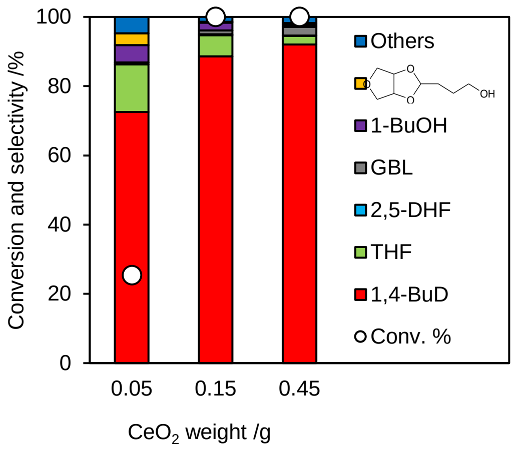


Figure 3-2 Effect of CeO_2 amount in the reaction of 1,4-AHERY with ReO_x/C-BP [a]

[a] 1,4-AHERY = 0.5 g, CeO_2 = 0.05 ~ 0.45 g, ReO_x/C-BP (Re = 4 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, C-BP: carbon black BP2000.

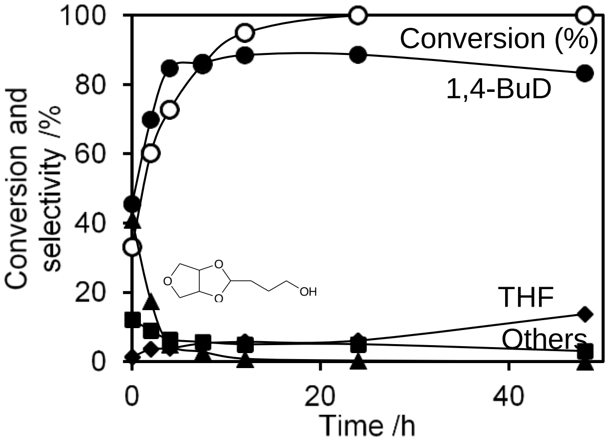


Figure 3-3 Time course of the reaction of 1,4-AHERY over CeO_2 + ReO_x/C-BP (Re = 4 wt%) [a]

[a] 1,4-AHERY = 0.5 g, CeO_2= 0.15 g, ReOx/C-BP (Re = 4 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 0 ~ 48 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, C-BP: carbon black BP2000. The detailed data are shown in Table 3-3.

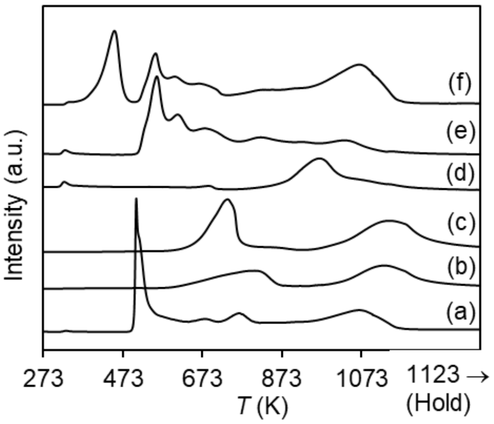


Figure 3-4 H_2-TPR profiles of (a) CeO_2 + ReO_x/C-BP (Re = 4%), physically mixed in 1,4-dioxane and then dried, (b) CeO_2 [9], (c) ReO_x/CeO_2 (Re = 1 wt%) [9], (d) C-BP [11], (e) ReO_x/C-BP (Re = 3%) [11], (f) Au/CeO_2 + ReO_x/C-BP (Re = 3%). Total sample weight = 50 mg (25 mg for each catalyst in the mixture). H_2/Ar (5% v/v, 30 cc/min) at heating rate of 10 K/min. C-BP: carbon black BP2000.

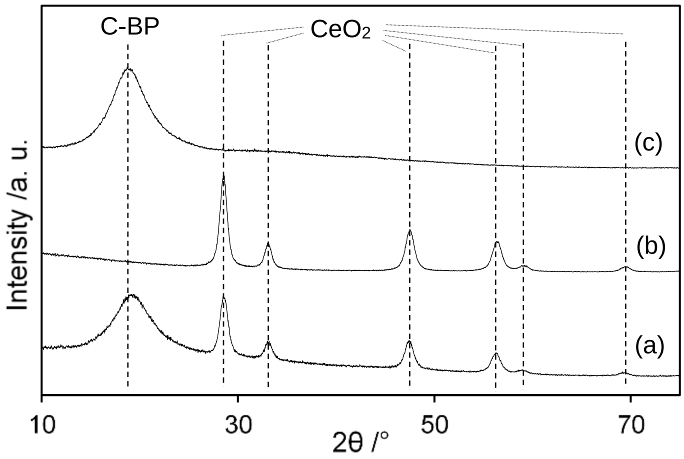


Figure 3-5 XRD patterns of Re catalysts. (a) CeO_2 + ReO_x/C-BP (Re = 4 wt%) after reaction, (b) ReO_x/CeO_2 (Re = 1 wt%), (c) ReO_x/C-BP (Re = 3 wt%) after reaction. Reaction conditions: 1,4-AHERY = 0.5 g, ReO_x/CeO_2 = 0.15 g, ReO_x/C-BP = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 4 h. AHERY: anhydroerythritol, C-BP: carbon black BP2000.

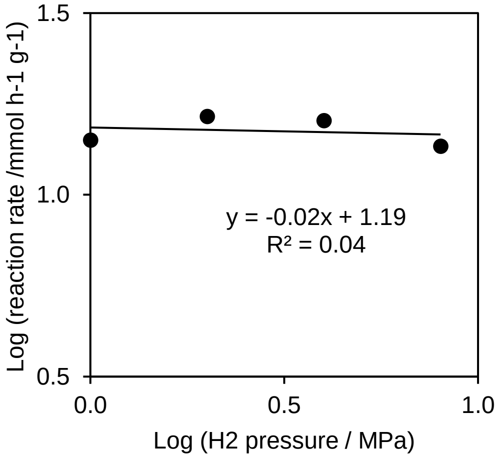


Figure 3-6 Effect of hydrogen pressure on the reaction of 1,4-AHERY over CeO_2 + ReO_x/C-BP [a]

[a] 1,4-AHERY = 0.5 g, CeO_2 = 0.15 g, ReOx/C-BP (Re = 4 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 1, 2, 4, 8 MPa, T = 413 K, t = 0 ~ 2 h. AHERY: anhydroerythritol, C-BP: carbon black BP2000. The detailed data are shown in Figure 3-7 and Table 3-6

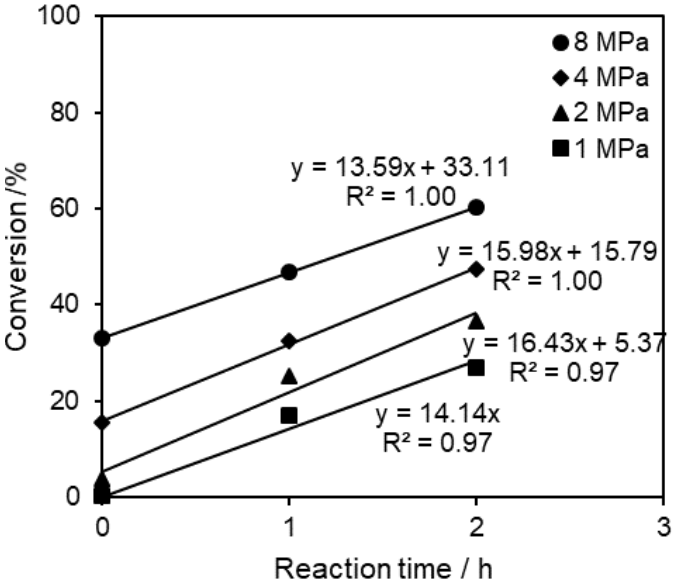
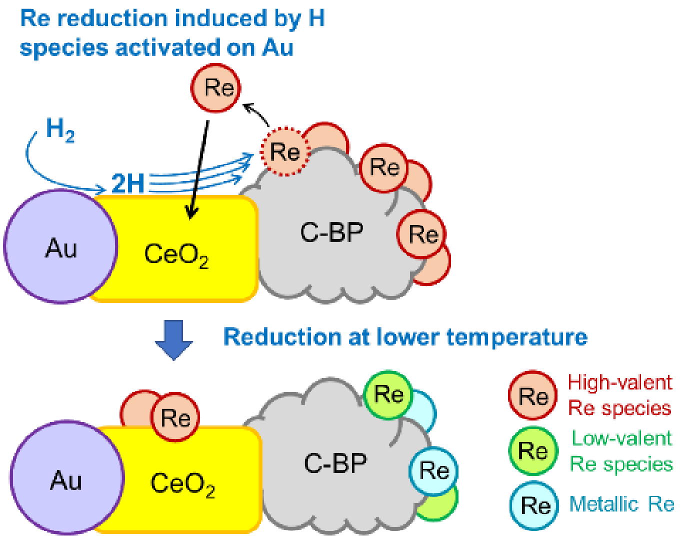


Figure 3-7 Detailed data of Figure 3-6 (Effect of hydrogen pressure on the reaction of 1,4-AHERY over CeO_2 + ReO_x/C-BP (Re = 4 wt%) [a])

[a] 1,4-AHERY = 0.5 g, CeO_2 = 0.15 g, ReO_x/C-BP (Re = 4 wt%) = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 1, 2, 4, 8 MPa, T = 413 K, t = 0 ~ 2 h (0 h was defined as the time when the temperature reached 413 K). AHERY: anhydroerythritol, BuD: butanediol, C-BP: carbon black BP2000.

(a) ReO_x-Au/CeO_2 with higher catalyst reducibility



(b) CeO_2 + ReO_x/C-BP with lower catalyst reducibility

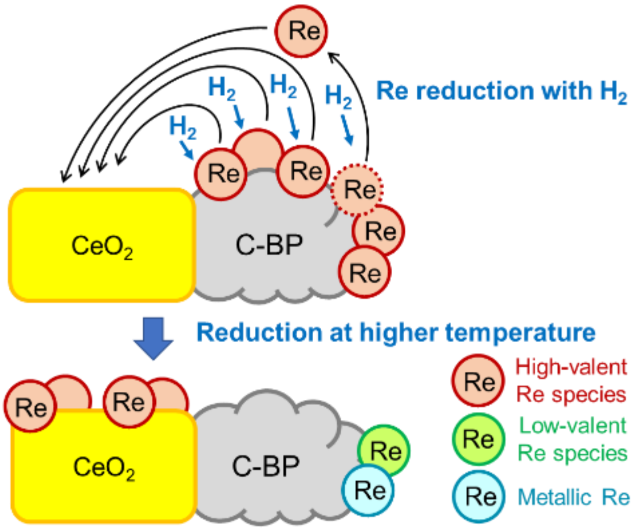


Figure 3-8 Models of (a) ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) + ReO_x/C-BP (Re = 3 wt%) and (b) CeO_2 + ReO_x/C-BP (Re = 4 wt%) in the reaction of 1,4-anhydroerythritol. C-BP: carbon black BP2000.

Chapter 4

Tungsten-zirconia-supported Rhenium Catalyst in the Synthesis of 1,4-Butanediol from 1,4-Anhydroerythritol

4.1 Introduction

Biomass plays an increasingly significant role as chemical feedstocks and energy resource instead of fossil fuels, while its high oxygen content is not convenient and economical for energy generation or industrial chemical synthesis. Catalytic conversions such as deoxydehydration (DODH) which can simultaneously remove the vicinal OH groups in biomass-based products such as sugar alcohols and form corresponding alkenes, can effectively reduce the oxygen content and increase their commodity value [1]-[3]. Tomishige laboratory found ReO_x-Au/CeO_2 and ReO_x-Pd/CeO_2 are heterogenous DODH catalysts high activity and product selectivity with the reductant of H_2 [4]-[9]. The author further developed a co-catalyst system which combined ReO_x-Au/CeO_2 and ReO_x/C catalysts for producing value-added product 1,4-butanediol (1,4-BuD) from biomass-derived product 1,4-anhydroerythritol (1,4-AHERY) in one-pot reaction [10], reported in Chapter 2. The yield of 1,4-BuD was about 90% which was the highest from C4 sugar alcohol erythritol or its dehydrated product. In Chapter 3, the author also found that 1,4-AHERY still could produce 1,4-BuD over the combination of ReO_x/CeO_2 and ReO_x/C even without Au promotor. The yield of 1,4-BuD was as high as 85% similar to the one with Au promotor, because the reduced Re species on C might act as the promotor instead of Au in the reaction [11]. According to the previous studies in Chapter 2 and 3, the only drawback of this co-catalyst system was a deactivation of the catalyst mixture after reaction. The conversion of 1,4-AHERY sharply dropped from 100% to 65% after the first run, and the selectivity to 1,4-BuD also decreased. Although the CeO_2 supported Re catalyst could be regenerated by calcination to recover the activity [6], due to the combustibility of carbon support, the recycled catalyst mixture of ReO_x(-Au)/CeO_2 and ReO_x/C is infeasible to regenerate by calcination. Pretreatments such as heating the recycled catalyst mixture in N_2 for removing the deposits on the catalyst surface, as well as replenishment of fresh catalyst, could regenerate the activity to some extent, however, the activity still decreased significantly with time of use. Due to the difficulty for the reuse of carbon-supported Re catalyst, other Re catalyst with regenerable support was studies as an alternative instead of ReO_x/C in the co-catalyst system in this study. Tungsten-zirconia-supported Re catalyst was found to be possible to reuse by calcination after reaction, combined with ReO_x-Au/CeO_2 in the production of 1,4-BuD from 1,4-AHERY. The activity of used catalyst mixture of ReO_x/WO_3-ZrO_2 and ReO_x-Au/CeO_2 could be comparable to the fresh one by calcination.

4.2 Experimental

The chemicals used in this chapter were the same as used in Chapter 2 and 3.

4.2.1 Catalyst preparation

The ReO_x/Support catalysts were prepared by impregnating support materials with NH_4ReO_4 aqueous solution at 353 K. Support materials included ZrO_2, TiO_2, SiO_2, Al_2O_3, MgO, HZSM-5 (JRC-Z5-90H(1), Süd-Chemie Catalysts and Catalysis Society of Japan, Si/Al_2 = 90, BET surface area: 390 m^2/g), TiO_2-ZrO_2 (TiO_2 = 30 wt%, Daiichi Kigenso Kagaku Kogyo Co., Ltd., BET surface area: 148 m^2/g), SiO_2-ZrO_2 (SiO_2 = 10 wt%, Daiichi Kigenso Kagaku Kogyo Co., Ltd., BET surface area: 136 m^2/g), CeO_2-ZrO_2 (CeO_2 = 50 wt%, Daiichi Kigenso Kagaku Kogyo Co., Ltd., BET surface area: 136 m^2/g), WO_3-ZrO_2 (WO_3 = 10 wt%, Daiichi Kigenso Kagaku Kogyo Co., Ltd., BET surface area: 103 m^2/g), $^{cp}WO_3$-ZrO_2 (W = 5 wt%, prepared by co-precipitation method, BET surface area: 68 m^2/g). Ammonia solution (Wako Pure Chemical Ind. Ltd.) (0.1 M) was added to the stirring aqueous solution of zirconium nitrate oxide dihydrate (Kanto Chemical Co. Inc.) and ammonium metatungstate hydrate (Strem Chemicals Inc.) aqueous solution to co-precipitate $^{cp}WO_3$-ZrO_2 at 353 K, and then the deposition was filtrated and dried in oven at 373 K for 12 h. All supports were calcinated at 773 K for 3 h before impregnation. ReO_x/WO_3/Support catalysts were prepared by sequential impregnation method. WO_3/Support was firstly prepared by impregnating supports, including ZrO_2, Al_2O_3, and TiO_2, with ammonium metatungstate hydrate aqueous solution at 353 K. The dried (373 K, 12 h) then calcinated (773 K, 3 h) WO_3/Support was impregnated by NH_4ReO_4 aqueous solution at 353 K, and dried then calcinated again at the same conditions. All the impregnated catalysts were dried in oven at 373 K for 12 h, and then calcinated 773 K for 3 h. The ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) catalyst was prepared by deposition-precipitation method for Au loading and subsequent impregnation for Re loading according to the report [6].

4.2.2 Activity test

The activity test was conducted with autoclave reactor equipped with an inner glass cylinder as mentioned in Chapter 2 and 3. The standard conditions for the reaction of 2,5-DHF were: 0.15 g 2,5-DHF, 0.03 g water, 0.15 g ReO_x-Au/CeO_2, 0.15 g ReO_x/WO_3-ZrO_2, 0.1 g dodecane (internal standard), 4 g 1,4-dioxane, 413 K reaction temperature, 8 MPa H_2 pressure (at reaction temperature), and 4 h reaction time; and for the reaction of 1,4-AHERY were: 0.3 g 1,4-anhydroerythritol, 0.15 g ReO_x-Au/CeO_2, 0.15 g ReO_x/WO_3-ZrO_2, 0.1 g dodecane (internal standard), 4 g 1,4-dioxane, 413 K reaction temperature, 8 MPa H_2 pressure (at reaction temperature), and 24 h reaction time. The parameters were changed appropriately for investigating the effects of reaction conditions. Details of the reaction conditions are described in each result.

The products were analyzed by FID-GC, and calculated as the same method in Chapter 2 and 3. The carbon balance (C.B.) of each analysis result was calculated using eq (4-1). When the C.B. is in the range of 100 ± 10% considering the experimental error, the conversion and selectivity on the carbon basis are calculated by eq (4-2) and (4-3), respectively. When the C.B. is clearly lower than <90%, the conversion and selectivity on carbon basis are calculated by eq (4-4) and (4-5). The yield was calculated by eq (4-6) for both cases.

$$\text{C. B. (\%)} = \frac{\text{Amount of remaining substrate (C-mol) + Total amount of detected products (C-mol)}}{\text{Amount of initial substrate (C-mol)}} \times 100 \qquad (4\text{-}1)$$

$$\text{Conversion (\%)} = \frac{\text{Total amount of detected products (C-mol)}}{\text{Amount of remaining substrate (C-mol) + Total amount of detected products (C-mol)}} \times 100 \qquad (4\text{-}2)$$

$$\text{Selectivity of product A (\%)} = \frac{\text{Amount of A (C-mol)}}{\text{Total amount of detected products (C-mol)}} \times 100 \qquad (4\text{-}3)$$

$$\text{Conversion (\%)} = 100 - \frac{\text{Amount of remaining substrate (C-mol)}}{\text{Amount of initial substrate (C-mol)}} \times 100 \qquad (4\text{-}4)$$

$$\text{Selectivity of product A (\%)} = \frac{\text{Amount of A (C-mol)}}{\text{Amount of initial substrate (C-mol) - Amount of remaining substrate (C-mol)}} \times 100 \qquad (4\text{-}5)$$

$$\text{Yield (\%)} = \frac{\text{Conversion (\%)} \times \text{Selectivity (\%)}}{100} \qquad (4\text{-}6)$$

The reuse procedure of catalysts was as the same method mentioned in Chapter 2 and 3. The mixture of ReO_x-Au/CeO_2 and ReO_x/WO_3-ZrO_2 after reaction was washed and dried at 373 K for 12 h, and then treated with various regeneration. The regeneration methods included calcination in air at 573 K or 773 K for 1 or 3 h, respectively. Due to the weight loss of the catalyst mixture during the recovery process, the lost weight was replenished by fresh catalysts or the catalyst mixture recovered by the same method.

4.2.3 Catalyst characterization

The samples of ReO_x/CeO_2 and ReO_x/C-BP were characterized by X-ray diffraction (XRD), temperature-programmed reduction (H_2-TPR), thermogravimetric-differential thermal analysis (TG-DTA), and scanning transmission electron microscope (STEM), using the same analytical apparatuses and methods as Chapter 2.

4.2.4 Products identification

Most products were identified by commercially available chemicals include tetrahydrofuran, 2,5-DHF, 2,3-DHF, γ-butyrolactone (GBL), 1-butanol (1-BuOH), 3-hydroxytetrahydrofuran (3-HTHF), and furan. The intermediate acetals which are commercially unavailable were described in Chapter 2.

4.3 Results and discussion

4.3.1 Screening of catalysts

In the one-pot reaction of 1,4-AHERY to 1,4-BuD over the co-catalyst system of ReO_x-Au/CeO_2 and ReO_x/C, the ReO_x/C was mainly catalyzed the conversion of 2,5-DHF to 1,4-BuD. Therefore, in order to find a replacement of ReO_x/C catalyst, I tested various Re catalysts in the reaction of 2,5-DHF (Table 4-1) with 1 equivalent of water and the reductant of H_2. ReO_x/TiO_2 was reported to catalyze the conversion of 2,5-DHF to 1,4-BuD in flow reactor with 80% yield [12]. However, in my reaction conditions, the ReO_x/TiO_2 (entry 2) showed much lower performance (selectivity to 1,4-BuD and its precursors < 40%) than the report. Nevertheless, ReO_x/TiO_2 and ReO_x/ZrO_2 (entries 2 and 3) showed relatively higher conversion and selectivity to 1,4-BuD compared with Re catalysts on other oxide supports such as ReO_x/Al_2O_3, ReO_x/SiO_2, ReO_x/HZSM5, and ReO_x/MgO (entries 4-7). The main products over ReO_x/Al_2O_3 and ReO_x/HZSM5 were THF and furan which were the disproportionated products from DHFs (2,5-DHF and 2,3-DHF). THF was also the main product over ReO_x/SiO_2 and ReO_x/MgO. 2,3-DHF, isomerized from 2,5-DHF, was another main product over ReO_x/MgO, and also formed over ReO_x/SiO_2 and ReO_x/Al_2O_3. Addition products of 2,3-DHF with water or alcohols (acetals) were also detected over ReO_x/Al_2O_3, ReO_x/SiO_2 and ReO_x/MgO. However, ReO_x/MgO and ReO_x/Al_2O_3 showed very low activity in the conversion of 2,3-DHF to 1,4-BuD. ReO_x/HZSM5 performed lack of activity in isomerization of 2,5-DHF to 2,3-DHF which was the first step of 1,4-BuD formation. The ReO_x/ZrO_2 showed slightly higher activity of 2,5-DHF conversion than that of ReO_x/TiO_2. However, the selectivity to 1,4-BuD over either ReO_x/TiO_2 or ReO_x/ZrO_2 was just around 20%, as same to their selectivity to THF.

All the Re catalysts with single oxide support showed lower activity and 1,4-BuD selectivity than those of carbon support (entry 1). Therefore, the Re catalysts with mixed oxide supports were test in the reaction of 2,5-DHF. Zirconia was selected as one of components because of the variety of available mixed oxides and relatively good performance of ReO_x/ ZrO_2. The ReO_x/WO_3-ZrO_2 (entry 11) catalyst showed the highest conversion of 2,5-DHF and the highest selectivity to 1,4-BuD among all the non-carbon supported Re catalysts. The conversion over

ReO_x/WO_3-ZrO_2 was as high as that obtained over ReO_x/C, and the selectivity to 1,4-BuD was slightly lower than that of ReO_x/C due to the higher selectivity to THF. Other Re catalysts with bi-oxide supports such as ReO_x/TiO_2-ZrO_2, ReO_x/SiO_2-ZrO_2, ReO_x/CeO_2-ZrO_2, ReO_x/WO_3-TiO_2, and $ReO_x/WO_3-Al_2O_3$ (entries 8-10, 12-13) showed lower activity in the conversion of 2,5-DHF and selectivity to 1,4-BuD than those of ReO_x/WO_3-ZrO_2. The reduced ReO_x/WO_3-ZrO_2 before using (entry 14) showed lower activity than the non-pretreated one, and the selectivity to 1,4-BuD also decrease, as well as the selectivity of other intermediates such as 2-HTHF and acetals increased meanwhile, indicating that the high-valent Re species of ReO_x/WO_3-ZrO_2 might be the active sites which showed higher catalytical activity in the isomerization of 2,5-DHF to 2,3-DHF.

Figure 4-1 shows the effect of Re loading amount of ReO_x/WO_3-ZrO_2 in the reaction of 2,5-DHF. The optimized Re loading amount was 1 wt% based on the 2,5-DHF conversion and 1,4-BuD selectivity. The conversion and selectivity to 1,4-BuD dramatically increased with increasing the Re loading amount from 0 to 1 wt%. However, the formation of THF increased when the Re loading amount was over 1 wt%, as well as the conversion of 2,5-DHF decreased at the same time. The decrease of conversion probably due to the aggregation of catalytically active sites of monomeric Re species to be inactive polymeric Re species (in isomerization of 2,5-DHF to 2,3-DHF). The increase of THF selectivity with increase of Re amount can be due to the hydrogenation ability of polymerized Re species as well.

Even though 1,4-BuD was formed over the ReO_x/ZrO_2 catalyst, adding WO_3 to ZrO_2 support improved the conversion and the selectivity to 1,4-BuD dramatically. In addition to commercial WO_3-ZrO_2 (10 wt% WO_3) support, WO_3/ZrO_2 supports with various W amount were prepared and tested as $ReO_x/WO_3/ZrO_2$ catalysts for the reaction of 2,5-DHF (Figure 4-2). Up to 5 wt% W, the activity of $ReO_x/WO_3/ZrO_2$ catalyst increased with increasing W amount. The selectivity to 1,4-BuD and its precursors (acetals and 2-HTHF) became higher when W amount was between 3-5%. The THF formation was sharply increased at higher W loading amount than 5 wt%. The conversion of 2,5-DHF also decreased dramatically when the W loading amount was higher than 5 wt%. Tungsten-zirconia supports prepared by different methods showed different performance.

In tungsten-zirconia supported Re catalysts, the homemade WO_3/ZrO_2 (W = 5 wt%) (Table 4-1, entry 15) showed similar activity to the commercial WO_3-ZrO_2 (WO_3 = 10 wt%) (entry 11). When the WO_3-ZrO_2 (W = 5 wt%) support was prepared by co-precipitation, the activity of ReO_x/WO_3-ZrO_2 (W = 5 wt%) (entry 16) was lower than the ReO_x/WO_3-ZrO_2 with commercial support (entry 11). I used commercial WO_3-ZrO_2 (WO_3 = 10 wt%) support in the following studies due to the convenience of accessibility.

4.3.2 Optimization of reaction conditions

The reaction temperature of 413 K (Figure 4-3) for the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2 was optimized based on the yield of 1,4-BuD. The conversion and selectivity to 1,4-BuD increased with lifting the reaction temperature from 393 to 413 K, while the selectivity to 1,4-BuD sharply decreased when the temperature was over 413 K because of the selectivity to THF dramatically increased due to the dehydration of 1,4-BuD at higher temperature.

Figure 4-4 showed the effect of H_2 pressure in the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2 (the detailed data are in Figure 4-5 and Table 4-2). The conversion and selectivity to 1,4-BuD increased with increasing the hydrogen pressure from 2 to 8 MPa (Figure 4-4 (a)). Although the THF selectivity increased at the same time, the reaction rate was much higher under 8 MPa hydrogen pressure. The total selectivity to 1,4-BuD + acetals + 2-HTHF + GBL and the sum of selectivity to furan + THF were similar under different H_2 pressure, even though the 1,4-BuD selectivity was lower and GBL selectivity was higher under lower H_2 pressure. Therefore, the GBL may be an intermediate of 1,4-BuD like 2-HTHF and acetals in the conversion of 2,5-DHF.

The reaction rate increased with increasing the H_2 pressure in the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2. The reaction order with respect to hydrogen pressure was 0.94 (Figure 4-4 (b)), indicating that the rate-determination step was hydrogen species involved reactions, which might be the activation of H_2, or the reduction with the hydrogen species.

As above, the optimized reaction conditions were temperature of 413 K for 1,4-BuD production from 2,5-DHF under H_2 pressure of 8 MPa, which were the same reaction conditions used in the reaction of 1,4-AHERY over the combination of ReO_x-Au/CeO_2 (or ReO_x/CeO_2) and

ReO_x/C catalysts as reported in my previous reports [10],[11].

4.3.3 Reaction mechanism

The optimized ReO_x/WO_3-ZrO_2 catalyst was applied to the reaction of 1,4-AHERY combined with ReO_x-Au/CeO_2 or ReO_x/CeO_2 catalysts under the standard reaction conditions. 1,4-BuD could be produced from 1,4-AHERY over the physical mixture of ReO_x-Au/CeO_2 and ReO_x/WO_3-ZrO_2 catalysts (Table 4-3, entry1). However, the combination of ReO_x/CeO_2 and ReO_x/WO_3-ZrO_2 showed very low activity in the conversion of 1,4-AHERY (entry 2). This indicates that the Au promoter is necessary for the activation of H_2 in the DODH reaction of 1,4-AHERY to 2,5-DHF, because single ReO_x/WO_3-ZrO_2 catalyst also showed very low activity to 1,4-AHERY (entry 4). Unlike the mechanism of the co-catalyst of ReO_x/CeO_2 and ReO_x/C, the Re species on CeO_2 could not be reduced by hydrogen species activated on ReO_x/WO_3-ZrO_2 support. The difference between C and WO_3-ZrO_2 supports as the promoting ability of ReO_x/CeO_2 reduction may be related to the electrical conductivity: C support can more easily transport electron which is produced from H_2 along with H^+ than oxide support. Therefore, the ReO_x/WO_3-ZrO_2 catalyst only has the function of converting 2,5-DHF to 1,4-BuD. The DODH reaction of 1,4-AHERY to 2,5-DHF was entirely catalyzed by ReO_x-Au/CeO_2.

In the conversion of 2,5-DHF, single WO_3-ZrO_2 (entry 7) or ZrO_2 (entry 8) without Re loading showed very low activity, and the main products were THF and furan, which were co-produced by disproportionation of DHFs. Furthermore, the conversion and selectivity to THF and furan were not so changed by H_2 pressure (Table 4-4) in the reaction of 2,5-DHF over WO_3-ZrO_2, indicating that the H_2 pressure had no effect on the disproportionation of DHFs. Although a very small amount of 2,3-DHF and its hydration products (acetals) were detected over WO_3-ZrO_2 under higher H_2 pressure, these intermediates were not able to open ring for further steps in the absence of Re. Generally, furan is easily hydrogenated to THF over metal catalyst and H_2, therefore, furan is an unfavorable by-product. The higher THF selectivity of ReO_x/WO_3-ZrO_2 was due to the activity of WO_3-ZrO_2 support to some extent. The formation of 2,3-DHF and 1,4-BuD was negligible over the WO_3-ZrO_2 support without Re, indicating that the

Re species have the function of catalyzing the conversion of 2,5-DHF to 2,3-DHF which was the first step in the production of 1,4-BuD from 2,5-DHF. Although the ReO_x-Au/CeO_2 could catalyze a part of conversion of 2,5-DHF to 2,3-DHF (entry 5), it is difficult to catalyze hydration of 2,3-DHF to 2-HTHF. The total yield of 1,4-BuD and other precursors over ReO_x/WO_3-ZrO_2 was higher than that over ReO_x-Au/CeO_2, indicating that the isomerization of 2,5-DHF to 2,3-DHF was mainly catalyzed by the Re species on WO_3-ZrO_2 support.

In the reaction of 2,3-DHF (entries 9-13), the low carbon balance was low might be due to the formation of polymers from 2,3-DHF over ReO_x/WO_3-ZrO_2, WO_3-ZrO_2, and ZrO_2 (entries 10-12), as well as the evaporation of 2,3-DHF (boiling point: 328 K). This indicates that ReO_x-Au/CeO_2 could suppress the formation of polymers from 2,3-DHF in the reaction of 1,4-AHERY combined with ReO_x/WO_3-ZrO_2. Similar to the reaction of 2,5-DHF, although ReO_x-Au/CeO_2 could partially catalyze the hydration of 2,3-DHF to 2-HTHF and the acetals (entry 9), the activity and the yield of 2-HTHF-derived products were lower than those of ReO_x/WO_3-ZrO_2 (entry 10), suggesting that the hydration of 2,3-DHF was mainly catalyzed by ReO_x/WO_3-ZrO_2. Acidity is necessary in the hydration of 2,3-DHF to 2-HTHF and its derivatives. Basic support such as MgO (entry 13) showed much lower activity than the that over acid supports ZrO_2 (entry 12) and WO_3-ZrO_2 (entry 11). Furthermore, the addition of WO_3 to ZrO_2 increased the conversion probably due to the stronger acidity of WO_3-ZrO_2 than ZrO_2. Meanwhile, THF formed by adding WO_3, which might be due to the acid-catalyzed dehydration of 1,4-BuD, because furan was not detected. The acid-catalyzed dehydration also might be the reason for the increment of the GBL selectivity and decline of the 2-HTHF selectivity. The selectivity of 1,4-BuD was dramatically increased when the Re species were loaded on the WO_3-ZrO_2, indicating that the hydrogenation of 2-HTHF-derived products to 1,4-BuD was mainly catalyzed by the Re species on WO_3-ZrO_2, because the Re species on the CeO_2 surface showed much lower hydrogenation activity.

The time course of the reaction of 1,4-AHERY over the mixture of ReO_x-Au/CeO_2 and ReO_x/WO_3-ZrO_2 was shown in Figure 4-6 and detailed data were shown in Table 4-5. The selectivity to 1,4-BuD and THF increased with the growth of conversion. At the beginning of the reaction, the intermediates of 2,5-DHF and the acetal from 4-hydroxybutanal and 1,4-AHERY were detected, and they were gradually converted with time. Unlike the time course of 1,4-AHERY reduction over the combination of ReO_x-Au/CeO_2 and ReO_x/C, 2,5-DHF as an intermediate was detected in significant amount at shorter reaction time, indicating that the ReO_x/WO_3-ZrO_2 catalyst has lower ability of the isomerization of 2,5-DHF to 2,3-DHF than ReO_x/C. The DHFs were quickly converted over the ReO_x/C catalyst, and the rate-determining step of ReO_x(-Au)/CeO_2 + ReO_x/C system for 1,4-AHERY reduction was the DODH catalyzed by ReO_x(-Au)/CeO_2. In the co-catalyst system of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2, the rate-determining step in the conversion of 1,4-AHERY was the reduction of 2,5-DHF over ReO_x/WO_3-ZrO_2. The highest yield of 1,4-BuD was 55% obtained at 32 h, which was much lower than that of 90% over the co-catalyst of ReO_x-Au/CeO_2. and ReO_x/C, due to the high selectivity to THF in the reaction. Because THF was formed from several pathways (DHFs hydrogenation, DHFs disproportionation, and 1,4-BuD dehydration), the increase of 1,4-BuD yield in the reaction of 1,4-AHERY over the co-catalyst of ReO_x-Au/CeO_2. and ReO_x/WO_3-ZrO_2 might be difficult.

Similar to the reaction mechanism of 1,4-AHERY to 1,4-BuD over the combination of ReO_x-Au/CeO_2 and ReO_x/C-BP, the proposed reaction route over ReO_x-Au/CeO_2 and ReO_x/WO_3-ZrO_2 (Scheme 4-1) was composed of ReO_x-Au/CeO_2-catalyzed DODH of 1,4-AHERY to 2,5-DHF and ReO_x/WO_3-ZrO_2-catalyzed reduction of 2,5-DHF to 1,4-BuD. In the conversion 2,5-DHF, the Re species of ReO_x/WO_3-ZrO_2 firstly catalyzed the isomerization of 2,5-DHF to 2,3-DHF, and then the WO_3-ZrO_2 catalyzed the hydration of 2,3-DHF to 2-HTHF-derivatives; finally the Re species on ReO_x/WO_3-ZrO_2 catalyzed the hydrogenation of the 2-HTHF-derived intermediates to 1,4-BuD.

4.3.4 Catalyst stability

The co-catalyst of ReO_x-Au/CeO_2 + ReO_x/C was unable to be reused due to the deactivation after catalytic use, as well as the difficulty for regeneration because of the combustibility of carbon support by heating. Therefore, the reusability of the ReO_x/WO_3-ZrO_2 catalyst combined with ReO_x-Au/CeO_2 was the most important part in this study. Table 4-6 shows the reuse tests of the co-catalyst mixture of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 in the reaction of 1,4-AHERY to 1,4-BuD. The selectivity to 1,4-BuD of the ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 mixture dramatically decreased from 53% in the first run to 25% in the second run (entries 1-2), even though the conversion was almost the same. The decrease of the 1,4-BuD selectivity due to the increase of total intermediates selectivity, indicating the catalytic activity of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 decreased after reaction. Due to the oxide support, the ReO_x/WO_3-ZrO_2 catalyst could be calcinated to remove the deposits on the catalyst surface to recover the catalytic activity. According to the TG-DTA graph of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 mixture after use (Figure 4-7), the deposits on the catalyst surface could be removed from 450 K to 650 K. Therefore, the calcination temperature was tested at 573 K (entries 3-6) and 773 K (entries 7-9). The calcination conditions were optimized as 573 K for 3 h. The conversion and selectivity to 1,4-BuD were almost same in the reaction of 1,4-AHERY over the recycled catalyst mixture of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 calcinated at 573 K for 1 or 3 h in the second run (entries 3 and 5, respectively). However, the conversion of 1,4-AHERY obviously dropped in the third run over the recycled catalyst mixture calcinated at 573 K for 1 h, and the selectivity to 1,4-BuD also decreased with increasing the THF selectivity (entry 4). On the other hand, the conversion was still 100% in the third run over the recycled catalyst mixture calcinated at 573 K for 3 h, and the selectivity to 1,4-BuD was similar to the fresh one (entry 6). Therefore, the co-catalyst system of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 showed potential to be reused by calcination at 573 K for 3 h to regenerate the catalytic activity. The conversion and 1,4-BuD selectivity sharply decreased in the reuse tests over the recycled catalyst mixture calcinated at higher temperature of 773 K for 3 h (entries 7-8), indicating that the higher calcination temperature also caused the deactivation of the catalyst mixture. The replenishment of fresh ReO_x-Au/CeO_2 catalyst to the recycled mixture of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 could recover the activity to the fresh level (entry 9), indicating that the main deactivation of the catalyst mixture after use caused by the ReO_x-Au/CeO_2 catalyst. Single ReO_x-Au/CeO_2 catalyst could be reused for times without deactivation by the pretreatment of calcination [6]. On the contrary, the replenishment of fresh

ReO_x/WO_3-ZrO_2 to the used catalyst mixture dramatically decreased the conversion of 1,4-AHERY as well as the 1,4-BuD selectivity which was due to the addition of fresh ReO_x/WO_3-ZrO_2 caused the increase the formation of THF. The ReO_x/WO_3-ZrO_2 was not the reason of the deactivation of co-catalyst mixture. Therefore, the calcination mainly recovers the activity of ReO_x-Au/CeO_2 in the mixture. The reuse of the co-catalyst mixture of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 was possible by the calcination at 573 K for 3 h.

4.3.5 Characterization

The H_2-TPR profiles of WO_3-ZrO_2 and ReO_x/WO_3-ZrO_2 are shown in Figure 4-8, and Table 4-7 shows the H_2 consumption amount in the H_2-TPR. The WO_3-ZrO_2 showed a broad peak at 723-1000 K, which was the reduction of WO_3 in WO_3-ZrO_2. The H_2 consumption of the broad peak was 0.007 mmol/50 mg (entry 1), which was the same to the H_2 consumption in 723-1000 K (entry 2). The reduction of Re species showed two peaks at 585 K and 690 K. The H_2 consumption of ReO_x/WO_3-ZrO_2 at 500-723 K was 0.008 mmol/50 mg, this H_2 consumption was mainly the reduction of Re species. The reduction of Re species could take place in the reaction temperature due to the higher H_2 pressure. The Re species could be reduced from +7 to +4 on average in the reaction.

Figure 4-9 shows the Re L_3-edge XANES spectra of ReO_x/WO_3-ZrO_2 and reference compounds. The detailed linear relationship between white line areas and average valence were shown in Table 4-8 and Figure 4-10. The average Re valence of ReO_x/WO_3-ZrO_2 was +3.1 after reaction. The average Re valance was reduced from +7 to +3. Therefore, a part of Re species were reduced to be metallic state for the hydrogenation of 4-hydroxybutanal to 1,4-BuD, and another part of high-valent Re species were not reduced for the isomerization of 2,5-DHF to 2,3-DHF.

Acidity of supports measured by NH_3-TPD were shown in Table 4-9. The NH_3 amount of WO_3-ZrO_2 was larger than that of carbon support, indicating the acidity of WO_3-ZrO_2 is stronger than that of carbon. However, the activity of ReO_x/C combined with ReO_x-Au/CeO_2 in the reaction of 1,4-AHERY is much higher than that of ReO_x/WO_3-ZrO_2. As mentioned above, while in the catalyst acidity is necessary in the hydration of 2,3-DHF to 2-HTHF-derivatives, it was might not significant factor on the catalyst activity.

XRD patterns of the tungsten-zirconia supported Re catalysts were shown in Figure 4-11. The Re species did not show peaks due to the low loading amount and highly spread on the support surface. The commercial ZrO_2 was monoclinic crystalline structure (m-ZrO_2) showed peaks at 28 and 32° (Figure 4-11 (a)), and ZrO_2 of WO_3-ZrO_2 prepared by co-precipitation method formed the tetragonal crystalline structure (t-ZrO_2) which showed a peak at 30° (Figure 4-11 (d)). The BET surface area of ReO_x/WO_3/m-ZrO_2 (Table 4-10, entry 3) and $ReO_x/^{cp}WO_3$-t-ZrO_2 (entry 4) was similar. The ReO_x/WO_3-ZrO_2 containing m-ZrO_2 performed better activity in the reaction of 2,5-DHF than that containing t-ZrO_2 (Table 4-1, entry 16), while the selectivity to 1,4-BuD + its precursors or that to THF + furan were similar between two types of catalysts. The crystalline structure of ZrO_2 does not have critical role in the catalysts; the activity difference can be explained by the surface concentration of W species (WO_3/ZrO_2 prepared by impregnation has higher surface concentration of W than WO_3-ZrO_2 prepared by co-precipitation).

4.4 Conclusions

1,4-Butanediol can be produced from 1,4-anhydroerythritol (1,4-AHERY) over the co-catalysis of ReO_x/CeO_2 and ReO_x/C-BP (C-BP: carbon black BP2000) in one-pot reaction using H_2 as a reductant without Au promoter for ReO_x/CeO_2. The products pattern in the reaction of 1,4-AHERY over ReO_x/CeO_2 + ReO_x/C-BP is very similar to that over the co-catalyst with Au, and the reaction mechanism is supposed to start with the deoxydehydration (DODH) of 1,4-anhydroerythritol to 2,5-dihydrofuran over ReO_x/CeO_2 + ReO_x/C-BP. ReO_x/C-BP can promote the reduction of Re species on CeO_2, similarly to Au promoter on ReO_x-Au/CeO_2. Then 2,5-dihydrofuran is further converted to 1,4-butanediol over ReO_x/C-BP. In addition, it is found that physical mixture of CeO_2 and ReO_x/C-BP shows high activity in the conversion of 1,4-AHERY to 1,4-BuD, and the activity is clearly higher than that of ReO_x-Au/CeO_2 + ReO_x/C. High activity of CeO_2 + ReO_x/C-BP can be due to the mobility of high-valent Re species from C-BP to CeO_2 surface to give catalytically active Re species for the DODH reaction. Considering that high-valent Re species tends to be present on the catalysts before reduction, the Re species can move during the heating for catalyst reduction. Therefore, the catalyst reducibility can influence the mobility of high-valent Re species, and higher catalyst reducibility can be connected to lower mobility of the Re species. According to the profiles of the temperature programmed reduction with H_2, CeO_2 + ReO_x/C-BP showed lower reducibility than ReO_x-Au/CeO_2, which enables the move of Re species from C-BP to CeO_2. About half of Re species can be moved from ReO_x/C-BP (Re = 4 wt%) to mixed CeO_2 (weight ratio of CeO_2 : ReO_x/C-BP = 1 : 1). High activity can be explained by larger amount of catalytically active Re species on CeO_2 in CeO_2 + ReO_x/C-BP than that of ReO_x-Au/CeO_2 + ReO_x/C-BP at the same total Re loading amount. The performance of CeO_2 + ReO_x/C-BP was comparable to ReO_x-Au/CeO_2 + ReO_x/C-BP in terms of the yield of 1,4-BuD (~85%) and the catalyst reusability. Another important aspect in the present study is to demonstrate that heterogeneous DODH or DODH + hydrogenation catalysts can be prepared from only Re species by utilizing Re species for DODH reaction and low valent Re species for H_2 activation on different supports.

References

[1] J. R. Dethlefsen and P. Fristrup, ChemSusChem, 2015, 8, 767-775.

[2] A. R. Petersen and P. Fristrup, Chem. Eur. J., 2017, 23, 10235-10243.

[3] S. Raju, M. Moret and R. J. M. K. Gebbink, ACS Catal., 2015, 5, 281-300.

[4] N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, Angew. Chem. 2015, vol. 54, pp. 1897-1900.

[5] N. Ota, M. Tamura, Y. Nakagawa, K. Tomishige, ACS Catal. 2016, 6, 3213-3226.

[6] S. Tazawa, N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, ACS Catal. 2016, 6, 6393-6397.

[7] Y. Nakagawa, S. Tazawa, T. Wang, M. Tamura, N. Hiyoshi, K. Okumura, K. Tomishige, ACS Catal. 2018, 8, 584-595.

[8] M. Tamura, N. Yuasa, J. Cao, Y. Nakagawa, K. Tomishige, Angew. Chem. 2018, vol. 57, pp. 8058-8062.

[9] J. Cao, M. Tamura, Y. Nakagawa, K. Tomishige, ACS Catal. 2019, 9, 3725-3729.

[10] T. Wang, S. Liu, M. Tamura, Y. Nakagawa, N. Hiyoshi, K. Tomishige, Green Chem. 2018, 20, 2547-2557.

[11] T. Wang, M. Tamura, Y. Nakagawa, K. Tomishige, ChemSusChem, 2019, 12, DOI: 10.1002/cssc.201900900

[12] R. Pinkos, R. H. Fischer, B. Breitscheidel, P. Polanek, CA Pat., 2168458C, 2004.

Table 4-1 Reaction of 2,5-DHF over various Re catalysts [a]

Entry	Catalyst	Re loading amount /wt%	Conv. /%	Selectivity /%									
				1,4-BuD	THF	2,3–DHF	1-BuOH	GBL	Furan	2-HTHF	Acetal A	Acetal B	Others
1[b]	ReO_x/C	3	94	60	14	0	2	12	2	0	0	5	5
2	ReO_x/TiO_2	3	43	21	22	3	18	6	9	2	2	5	11
3	ReO_x/ZrO_2	3	62	19	20	6	3	17	7	4	1	16	6
4	ReO_x/Al_2O_3	3	23	1	27	11	1	2	26	5	4	1	24
5	ReO_x/SiO_2	3	25	13	48	11	8	0	9	11	0	0	0
6	ReO_x/HZSM5	3	26	2	45	0	7	0	32	1	0	0	12
7	ReO_x/MgO	3	25	0	35	46	0	0	11	8	0	0	0
8	ReO_x/TiO_2-ZrO_2 [c]	1	57	21	30	10	2	7	4	4	1	17	4
9	ReO_x/SiO_2-ZrO_2 [d]	1	52	22	36	1	3	6	6	2	1	17	2
10	ReO_x/CeO_2-ZrO_2 [e]	1	17	2	37	28	0	0	0	21	0	0	12
11	ReO_x/WO_3-ZrO_2 [f]	1	94	43	38	0	4	5	2	1	0	6	1
12	$ReO_x/WO_3/TiO_2$ [g]	1	26	3	31	0	5	0	28	5	0	0	27
13	$ReO_x/WO_3/Al_2O_3$ [g]	1	22	9	38	1	2	1	21	10	2	6	9
14	ReO_x/WO_3-ZrO_2 [f h]	1	63	18	39	1	3	10	3	3	0	12	9
15	$ReO_x/WO_3/ZrO_2$ [g]	1	93	40	45	0	5	3	3	0	0	3	1
16	ReO_x/WO_3-ZrO_2 [g i]	1	46	26	36	3	4	5	10	2	1	10	4

[a] 2,5-DHF = 0.15 g, water = 0.03 g, catalyst (Re = 1 or 3 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 4 h.

[b] Previously Reported. Commercial supports: [c] TiO_2 = 30 wt%, [d] SiO_2 = 10 wt%, [e] CeO_2 = 50 wt%, [f] WO_3 = 10 wt%. Homemade supports: [g] W = 5 wt%. [h] ReO_x/WO_3-ZrO_2 was reduced in solvent at 413 K for 1 h before the reaction.

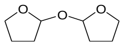
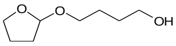
[i] WO_3-ZrO_2 was prepared by co-precipitation method. BuD: butanediol, DHF: dihydrofuran, THF: tetrahydrofuran, BuOH: butanol, GBL: γ-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A: ; Acetal B: .

Table 4-2 Detailed data of Figure 4-4 (b). (Effect of hydrogen pressure on the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2 catalyst [a])

Entry	H_2 Pressure /MPa	Reaction time /h	Conv. /%	Selectivity /%									
				1,4-BuD	THF	2,3–DHF	1-BuOH	GBL	Furan	2-HTHF	Acetal A	Acetal B	Others
1	2	0	2	0	26	0	0	0	74	0	0	0	0
2	2	1	10	0	31	0	0	0	69	0	0	0	0
3	2	2	19	16	33	3	2	10	12	0	0	16	2
4	4	0	15	0	44	0	0	0	56	0	0	0	0
5	4	1	32	15	32	2	2	8	17	4	0	16	2
6	4	2	44	18	39	2	3	7	9	2	0	17	2
7	8	0	44	15	52	5	4	7	10	0	0	8	0
8	8	0.5	60	29	48	2	4	4	5	0	0	8	0
9	8	1	75	31	45	0	4	6	3	1	0	8	1

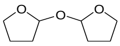
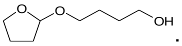
[a] 2,5-DHF = 0.15 g, water = 0.04 g, ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 2 or 4 or 8 MPa, T = 413 K, t = 0 or 1 or 2 or 4 h. DHF: dihydrofuran, BuD: butanediol, THF: tetrahydrofuran, BuOH: butanol, GBL: γ-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A: ; Acetal B: .

Table 4-3 Reaction of 1,4-AHERY and the intermediates over related catalysts [a]

Entry	Substrate	Catalyst	Conv. /% (C. B. /%)	Selectivity /%											
				1,4-BuD	THF	2,5–DHF	2,3–DHF	1-BuOH	GBL	Furan	2-HTHF	Acetal A	Acetal B	Acetal C	Others
1	1,4-AHERY	ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2	100	53	35	3	0	2	1	0	0	0	1	6	0
2		ReO_x/CeO_2 + ReO_x/WO_3-ZrO_2	1	0	0	64	0	0	0	0	0	0	0	0	36
3 [b]		ReO_x-Au/CeO_2 [b]	64	0	1	89	5	0	0	0	1	0	0	0	3
4		ReO_x/WO_3-ZrO_2	1	0	0	0	0	0	63	0	0	0	0	0	37
5 [b d]	2,5-DHF	ReO_x-Au/CeO_2	45	4	34	—	54	2	0	2	2	0	0	—	1
6 [d]		ReO_x/WO_3-ZrO_2	94	43	38	—	0	4	5	2	1	0	6	—	1
7 [d]		WO_3-ZrO_2	7	0	30	—	1	0	0	56	7	3	0	—	3
8 [d]		ZrO_2	5	0	36	—	5	1	4	29	8	2	0	—	16
9 [e]	2,3-DHF	ReO_x-Au/CeO_2 [b]	49 (71)	8	6	0	—	0	3	2	41	23	2	—	13
10 [e]		ReO_x/WO_3-ZrO_2	100 (20)	32	6	0	—	0	15	0	3	0	15	—	30
11 [e]		WO_3-ZrO_2	98 (21)	9	6	0	—	0	21	0	18	5	18	—	23
12 [e]		ZrO_2	76 (62)	4	0	0	—	0	12	0	30	18	16	—	19
13 [e f]		MgO	32 (79)	0	0	3	—	0	5	0	64	23	0	—	6

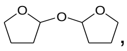
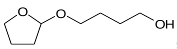
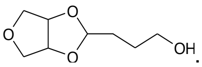
[a] 1,4-AHERY = 0.3 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, or ReO_x/CeO_2 (Re = 1 wt%) = 0.15 g, ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) = 0.15 g, or WO_3-ZrO_2 (WO_3 = 10 wt%) = 0.15 g, or ZrO_2 = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. [b] Reported in ref. [10], [c] 1,4-AHERY = 0.5 g. [d] 2,5-DHF = 0.15 g, t = 4 h. [e] 2,3-DHF = 0.15 g, t = 4 h, [f] MgO = 0.15 g. C. B.: carbon balance. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, BuOH: butanol, GBL: γ-butyrolactone, Acetal A: , Acetal B: , Acetal C: .

Table 4-4 Effect of hydrogen pressure on the reaction of 2,5-DHF over WO_3-ZrO_2 support [a]

Entry	H_2 Pressure /MPa	Conv. /%	Selectivity /%									
			1,4–BuD	THF	2,3–DHF	1–BuOH	GBL	Furan	2-HTHF	Acetal A	Acetal B	Others
1	2	2	0	37	0	0	0	63	0	0	0	0
2	4	3	0	29	0	0	0	71	0	0	0	0
3	8	7	0	30	1	0	0	56	7	3	0	3

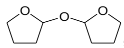
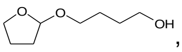
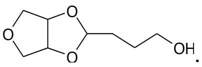
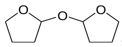
[a] 2,5-DHF = 0.15 g, water = 0.03 g, WO_3-ZrO_2 (WO_3 = 10 wt%) = 0.15 g, 1,4-Dioxane = 4 g, P_{H2} = 2 or 4 or 8 MPa, T = 413 K, t = 4 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, BuOH: butanol, GBL: γ-butyrolactone, Acetal A: , Acetal B: , Acetal C: .

Table 4-5 Time course of the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 [a]

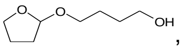
Entry	Reaction time /h	Conv. /%	Selectivity /%									
			1,4-BuD	THF	GBL	1-BuOH	2,5-DHF	2,3-DHF	Acetal A	Acetal B	Acetal C	Others
1	1	45	7	22	0	1	26	1	0	1	37	4
2	4	90	18	25	1	1	25	2	0	3	23	3
3	12	100	42	33	2	1	6	1	0	3	11	1
4	24	100	53	35	1	2	3	0	0	1	6	0
5	32	100	55	35	0	2	1	0	0	0	5	1
6	48	100	54	40	0	2	0	0	0	0	3	0

[a] 1,4-AHERY = 0.3 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 1 ~ 48 h.

AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, BuOH: butanol, GBL: γ-butyrolactone, Acetal A:



, Acetal B:



, Acetal C:

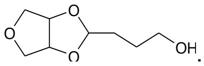


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Table 4-6 Reuse of ReO$_x$-Au/CeO$_2$ + ReO$_x$/WO$_3$-ZrO$_2$ catalyst mixture in the reaction of 1,4-AHERY [a]

Entry	Calcination conditions	Time of use	Conv. /%	Selectivity /%									
				1,4-BuD	THF	GBL	1-BuOH	2,5-DHF	2,3-DHF	Acetal A	Acetal B	Acetal C	Others
1		1	100	53	31	1	2	5	0	0	1	6	0
2 [b]	—	2	97	25	23	4	1	12	2	0	20	8	5
3 [b]	573 K, 1 h	2	100	46	38	0	2	1	0	0	1	11	1
4 [b]	573 K, 1 h	3	84	35	44	0	2	2	0	0	1	13	3
5 [b]	573 K, 3 h	2	100	49	39	0	2	5	0	0	0	4	1
6 [b]	573 K, 3 h	3	100	43	34	1	2	13	1	0	3	2	1
7 [b]	773 K, 3 h	2	80	38	41	0	2	1	1	0	1	14	2
8 [b]	773 K, 3 h	3	68	26	18	6	1	26	1	0	8	6	9
9 [c]	—	2	100	51	35	1	2	0	0	0	1	10	1
10 [d]	—	2	68	32	36	0	2	2	0	0	3	23	2

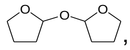
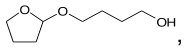
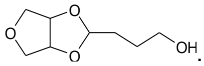
[a] 1,4-AHERY = 0.3 g, ReO$_x$-Au/CeO$_2$ (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO$_x$/WO$_3$-ZrO$_2$ (Re = 1 wt%, WO$_3$ = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 24 h. [b] Recycled ReO$_x$-Au/CeO$_2$ + ReO$_x$/WO$_3$-ZrO$_2$ mixture = 0.3 g. [c] Recycled ReO$_x$-Au/CeO$_2$ + ReO$_x$/WO$_3$-ZrO$_2$ mixture = 0.24 g, and fresh ReO$_x$-Au/CeO$_2$ (Re = 1 wt%, Au = 0.3 wt%) = 0.06 g was added. [d] Recycled ReO$_x$-Au/CeO$_2$ + ReO$_x$/WO$_3$-ZrO$_2$ mixture = 0.24 g, and fresh ReO$_x$/WO$_3$-ZrO$_2$ (Re = 1 wt%, WO$_3$ = 10 wt%) = 0.06 g was added. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, BuOH: butanol GBL: γ-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A: , Acetal B: , Acetal C: .

Table 4-7 TPR results in Figure 4-8

Entry	Profiles in Figure 4-8	Catalyst	Re loading amount /wt%	Catalyst weight /mg	Re amount /mmol	H_2 consumption /mmol		
						500 – 723 K	723 – 1000 K	500 – 1000 K
1	(a)	WO_3-ZrO_2	-	50	-	0.001	0.007	0.008
2	(b)	ReO_x/WO_3-ZrO_2	1	50	0.003	0.008	0.007	0.015

Table 4-8 Average valence of Re determined from white line intensity

Entry	Profiles in Figure 4-9	Sample	Valence of Re	White line intensity
1	(a)	Re powder	0	15.70
2	(b)	ReO_2	4	19.41
3	(c)	ReO_3	6	21.55
4	(d)	Re_2O_7	7	22.08
5	(e)	ReO_x/WO_3-ZrO_2 (after reaction [a])	3.1	18.50

[a] Reaction conditions: 2,5-DHF = 0.15 g, water = 0.03 g, ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T =413 K, t = 4 h.

Table 4-9 Acidic property of various catalyst supports measured by NH_3-TPD

Entry	Catalyst	NH_3 amount /mmol·g^{-1}
1	WO_3-ZrO_2	0.22
2	ReO_x/C	0.058

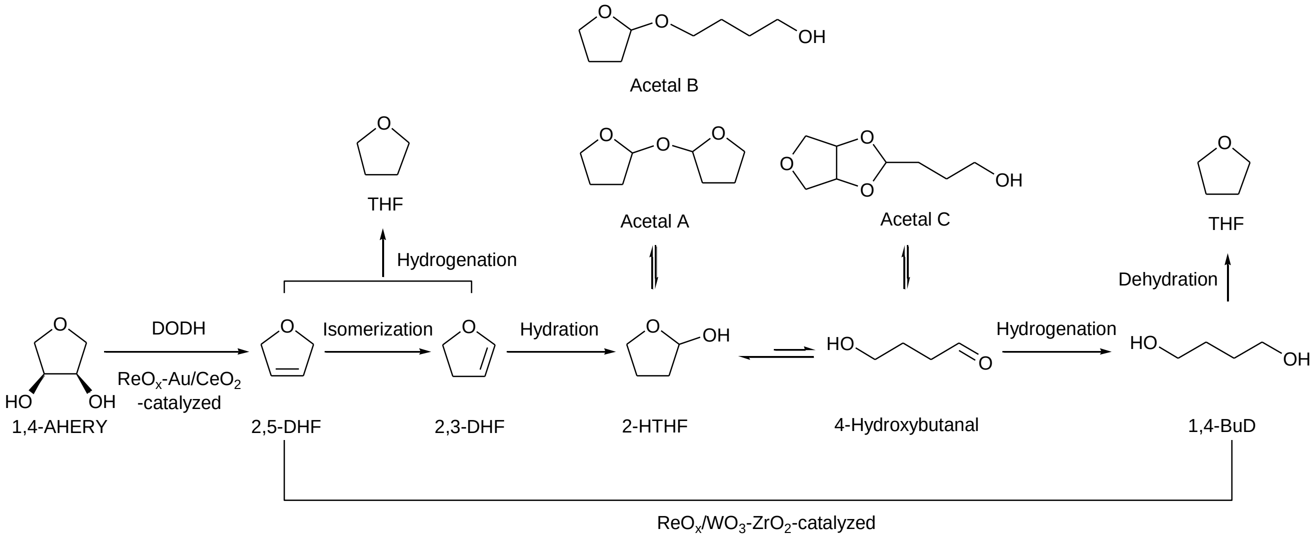
Table 4-10 BET surface area of various catalyst supports

Entry	Support	BET surface area /$m^2 \cdot g^{-1}$
1	ZrO_2	62
2	WO_3-ZrO_2 [a]	103
3	WO_3/ZrO_2 [b]	63
4	$^{cp}WO_3$-ZrO_2 [c]	68
5	C	1282

[a] WO_3-ZrO_2 (WO_3 = 10 wt%), commercially available.

[b] WO_3/ZrO_2 (W = 5 wt%) was prepared by impregnation method.

[c] $^{cp}WO_3$-ZrO_2 (W = 5 wt%) was prepared by co-precipitation method.



Scheme 4-1 Reaction route from 1,4-AHERY to 1,4-BuD over the mixture of ceria-supported Re catalyst and carbon-supported Re catalyst. AHERY: anhydroerythritol, BuD: butanediol, DHF: dihydrofuran, THF: tetrahydrofuran, HTHF: hydroxytetrahydrofuran.

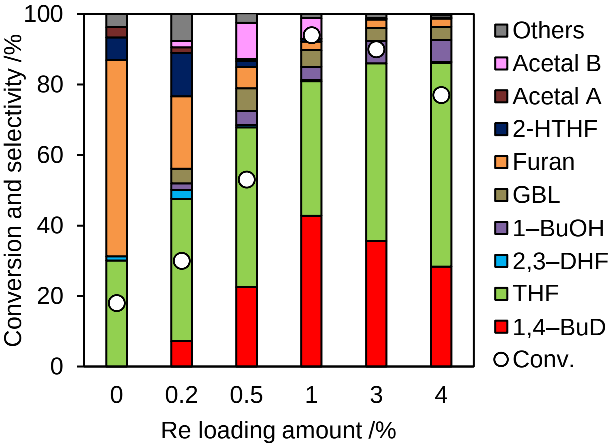
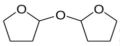
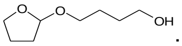


Figure 4-1 Effect of Re loading amount of ReO$_x$/WO$_3$-ZrO$_2$ in the reaction of 2,5-DHF [a]

[a] 2,5-DHF = 0.15 g, water = 0.04 g, ReO$_x$/WO$_3$-ZrO$_2$ (Re = 0 ~ 4 wt%, WO$_3$ = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 4 h. DHF: dihydrofuran, BuD: butanediol, THF: tetrahydrofuran, BuOH: butanol, GBL: *γ*-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A: ; Acetal B: .

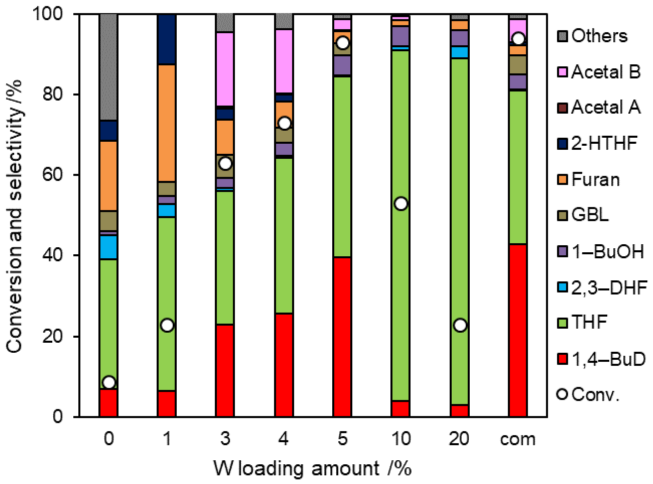
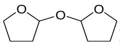
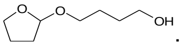


Figure 4-2 Effect of W loading amount of $ReO_x/WO_3/ZrO_2$ in the reaction of 2,5-DHF [a]

[a] 2,5-DHF = 0.15 g, water = 0.04 g, $ReO_x/WO_3/ZrO_2$ (Re = 1 wt%, W = 1 ~ 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 4 h. DHF: dihydrofuran, BuD: butanediol, THF: tetrahydrofuran, BuOH: butanol, GBL: γ-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A: ; Acetal B: 
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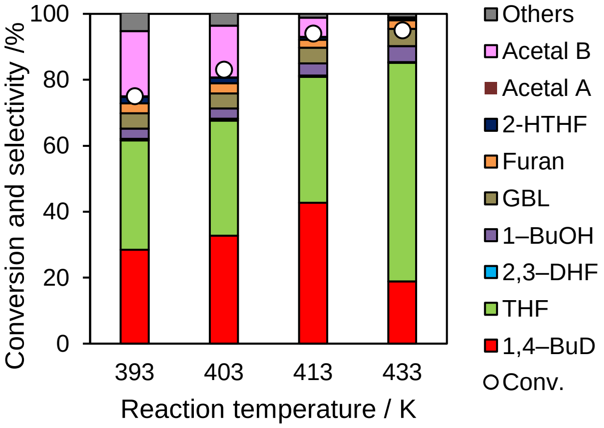
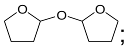
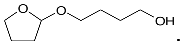


Figure 4-3 Effect of reaction temperature in the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2 [a]

[a] 2,5-DHF = 0.15 g, water = 0.04 g, ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 393 ~ 433 K, t = 4 h. DHF: dihydrofuran, BuD: butanediol, THF: tetrahydrofuran, BuOH: butanol, GBL: γ-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A: ; Acetal B: .

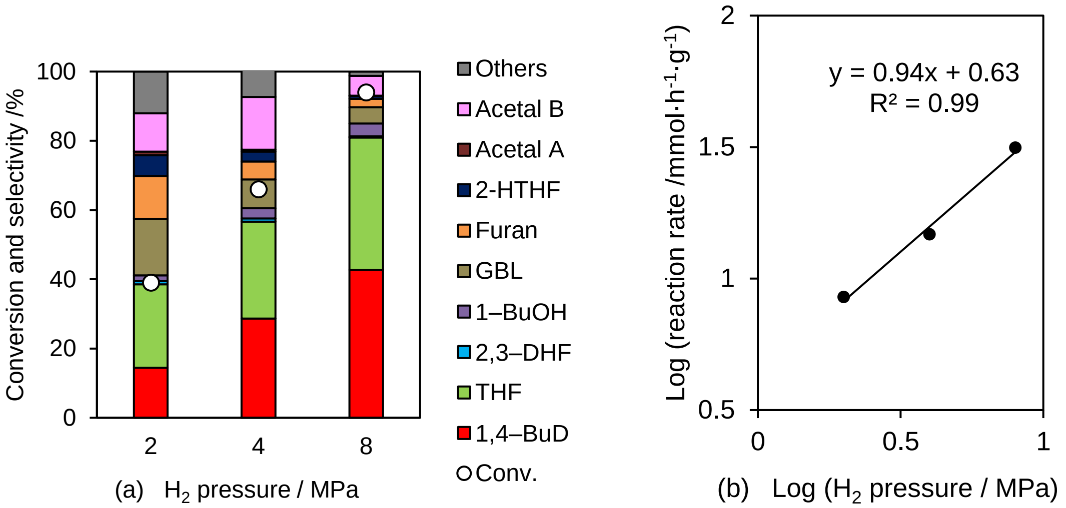
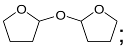
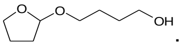


Figure 4-4 Effect of H_2 pressure in the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2 [a]

[a] 2,5-DHF = 0.15 g, water = 0.04 g, ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 2 or 4 or 8 MPa, T = 413 K, t = 0 or 1 or 2 or 4 h. DHF: dihydrofuran, BuD: butanediol, THF: tetrahydrofuran, BuOH: butanol, GBL: γ-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A: ; Acetal B: .

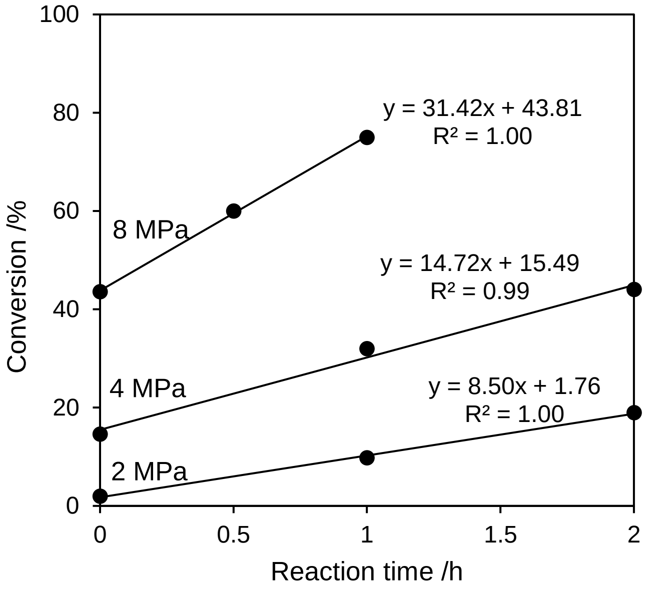


Figure 4-5 Detailed data of Figure 4 (b). (Effect of hydrogen pressure on the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2 catalyst [a])

[a] 2,5-DHF = 0.15 g, water = 0.04 g, ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 2 or 4 or 8 MPa, *T* = 413 K, *t* = 0 or 1 or 2 or 4 h.

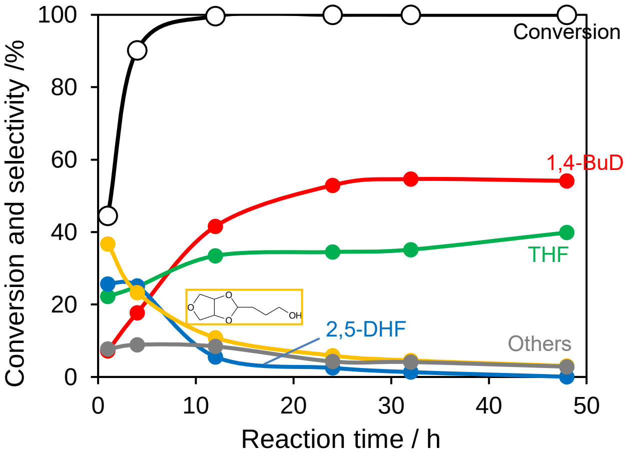


Figure 4-6 Time course of the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 [a]

[a] 1,4-AHERY = 0.3 g, ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) = 0.15 g, ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T = 413 K, t = 1 ~ 48 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran.

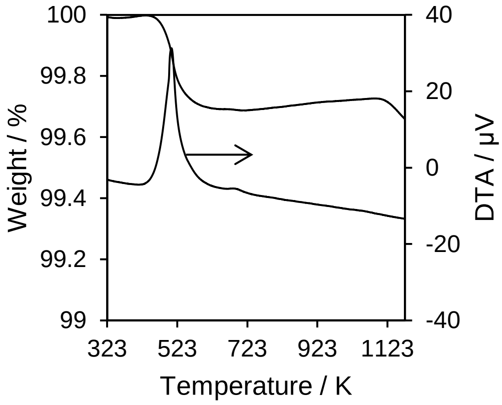


Figure 4-7 TG-DTA graph of the 1:1 mixture of ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) and ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) (after 1st use). Heating rate = 10 K/min, sample weight = 10 mg.

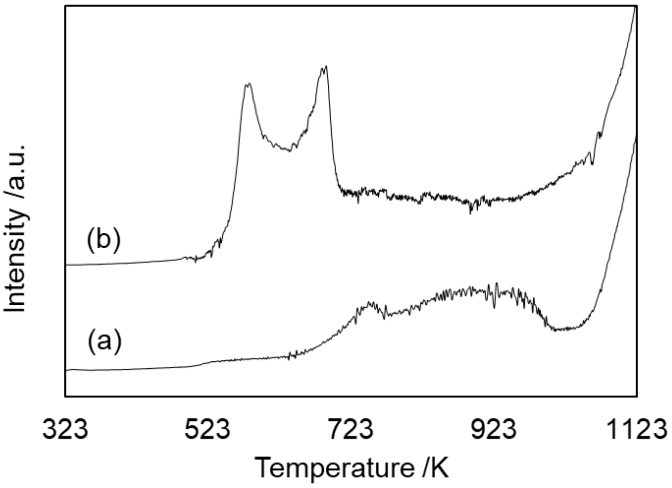


Figure 4-8 H_2-TPR profiles of (a) WO_3-ZrO_2, (b) ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%).

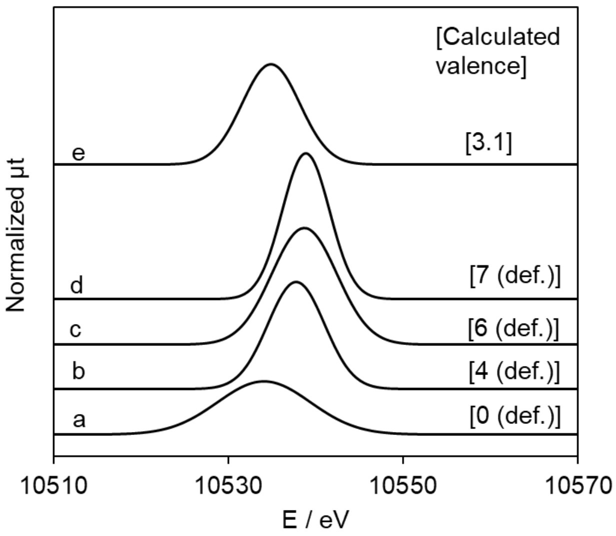


Figure 4-9 Re L_3-edge XANES spectra and the Re valence calculated by white line area. (a) Re powder, (b) ReO_2, (c) ReO_3, (d) Re_2O_7, (e) ReO_x/WO_3-ZrO_2 after reaction (reaction conditions: 2,5-DHF = 0.15 g, water = 0.03 g, catalyst = 0.15 g, 1,4-dioxane = 4 g, P_{H2} = 8 MPa, T =413 K, t = 4 h).

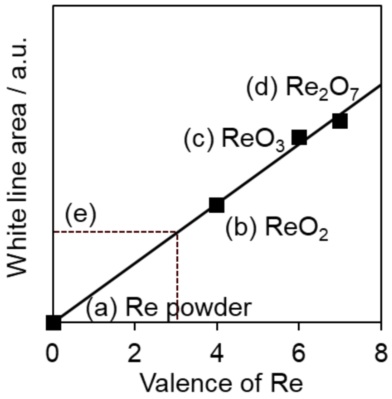


Figure 4-10 White line area of Re L_3-edge XANES vs. valence of Re plot in reference samples.

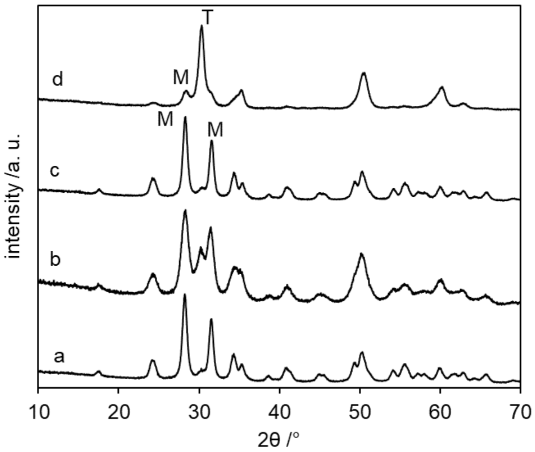


Figure 4-11 XRD pattern of tungsten-zirconia-supported Re catalysts. (a) ReO_x/ZrO_2 (Re = 3 wt%), (b) ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%), (c) $ReO_x/WO_3/ZrO_2$ (Re = 1 wt%, W = 5 wt%, W was loaded by impregnation method), (d) ReO_x/WO_3-ZrO_2 (Re = 1 wt%, W = 5 wt%, WO_3-ZrO_2 was prepared by co-precipitation method). T: tetragonal, M: monoclinic.

Chapter 8

Summary

For this thesis, the author investigated a heterogenous co-catalyst system for one-pot catalytic selective synthesis of biomass-based C4 sugar alcohol 1,4-anhydroerythritol (1,4-AHERY) to valuable non-natural fine chemical 1,4-butanediol (1,4-BuD) with the reductant of hydrogen.

The combination of ReO_x-Au/CeO_2 and ReO_x/C (C-BP, carbon black 2000) catalysts effectively converted 1,4-AHERY to 1,4-BuD with a very high yield of ~90% at the reaction temperature of 413 K in the presence of H_2. The mechanism of this reaction is composed of ReO_x-Au/CeO_2-catalyzed deoxydehydration (DODH) of 1,4-AHERY to 2,5-DHF, and ReO_x/C-catalyzed 2,5-DHF to 1,4-BuD. In the reduction of 2,5-DHF to 1,4-BuD, 2,5-DHF firstly isomerized to 2,3-DHF catalyzed by Re species on C; then over the C support of ReO_x/C, 2,3-DHF hydrated to 2-HTHF which could convert to 4-hydroxybutanol; finally 4-hydroxybutanol hydrogenated to be 1,4-BuD catalyzed by Re species on C. The use of ReO_x-Au/CeO_2 and ReO_x/C catalysts in one-pot synthesis effectively suppressed the formation of by-products such as THF derived from reactive intermediates such as 2,3- and 2,5-DHF. (Chapter 2)

The co-catalyst system using ReO_x-Au/CeO_2 + ReO_x/C was improved to be ReO_x/CeO_2 + ReO_x/C without Au which could decrease the cost of expensive metal. The author found that 1,4-BuD could be produced from 1,4-AHERY even without Au promoter over the co-catalyst of be ReO_x/CeO_2 + ReO_x/C using H_2 as a reductant with a good yield as high as ~80% which was comparable to that over the co-catalyst with Au promotor. The reactivity trends of possible intermediates suggest that the reaction mechanism over ReO_x/CeO_2 + ReO_x/C catalysts is similar to that over ReO_x-Au/CeO_2 + ReO_x/C, including DODH of 1,4-AHERY to 2,5-DHF over ReO_x species on CeO_2 support with the promotion of H_2 activation by ReO_x/C as the similar promotor function of Au on ReO_x-Au/CeO_2. Then 2,5-DHF isomerized to 2,3-DHF catalyzed by ReO_x on C support, hydration of 2,3-DHF catalyzed by C, and hydrogenation to 1,4-butanediol catalyzed by ReO_x/C. The reaction order of conversion of 1,4-AHERY with respect to H_2 pressure is almost zero and this indicates that the rate-determining step is the formation of 2,5-DHF from the coordinated substrate with reduced Re in the DODH step. In addition, physical mixture of CeO_2 + ReO_x/C showed almost the same performance as ReO_x/CeO_2 + ReO_x/C combination, giving 89% yield of 1,4-BuD from 1,4-AHERY in the same reaction conditions. CeO_2 + ReO_x/C also shows higher activity in the conversion of 1,4-AHERY than that of ReO_x-Au/CeO_2 + ReO_x/C. High activity of CeO_2 + ReO_x/C can be due to the mobility of high-valent Re species from C to CeO_2 surface to give catalytically active Re species for the DODH reaction. About half of Re species can be moved from ReO_x/C (Re = 4 wt%) to mixed CeO_2. The high-valent Re species such as Re^{7+} on CeO_2 and C supports are mobile in the solvent; however, the low-valent Re species including metal Re species have much lower mobility. Metallic Re and cationic low-valent Re species with high reducibility and low mobility can be present on carbon support as a trigger for H_2 activation and promoter of the reduction of Re species on CeO_2. The presence of noble metals such as Au can enhance the reducibility through the activation of H_2 molecule on noble metal and the formation of spilt-over hydrogen over noble metal/CeO_2, as indicated by H_2-TPR. The higher reducibility of ReO_x-Au/CeO_2 lowers the DODH activity of ReO_x-Au/CeO_2 + ReO_x/C in comparison with ReO_x/CeO_2 + ReO_x/C by restricting the move of Re species from C to CeO_2. (Chapter 3)

The biggest problem of this co-catalyst system was the deactivation of the catalyst mixture after reaction. Due to the combustibility of carbon support which makes ReO_x/C infeasible to regenerate by calcination, tungsten-zirconia-supported Re catalyst was found to be an alternative instead of ReO_x/C combined with ReO_x-Au/CeO_2 catalyst for the production of 1,4-BuD from 1,4-AHERY in one-pot reaction. Although the highest yield of 1,4-BuD was about 55% over the co-catalyst of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 which was lower than that over the co-catalyst of ReO_x-Au/CeO_2 + ReO_x/C, the activity of recycled mixture of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 could be regenerated by calcination. The conversions of 1,4-AHERY and the selectivity to 1,4-BuD over the calcinated mixture of ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 did not decrease significantly in the second or third runs. The optimized calcination conditions for the activity regeneration of ReO_x/WO_3-ZrO_2 + ReO_x-Au/CeO_2 mixture were temperature at 573 K for 3 h. Similar to the reaction mechanism in the co-catalyst system of ReO_x-Au/CeO_2 + ReO_x/C, ReO_x-Au/CeO_2 catalyzed the DODH reaction of 1,4-AHERY to 2,5-DHF, and ReO_x/WO_3-ZrO_2 catalyzed the successive reactions including isomerization, hydration, hydrogenation of 2,5-DHF to 1,4-BuD. The relatively lower yield of 1,4-BuD was mainly due to the high selectivity to THF, which could be produced by several pathways such as the disproportionation of DHFs to THF and furan, the hydrogenation of DHFs to THF, as well as the dehydration of 1,4-BuD to THF. (Chapter 4)

The innovation and importance of the co-catalyst system combining ceria-supported Re catalyst and carbon-supported Re catalysts in one-pot reaction for the production of 1,4-BuD from 1,4-AHERY are the high yield of 1,4-BuD (~90%) produced from erythritol or its derivates, which was the highest compared with reported articles so far, because the selective OH groups removal in C4 or larger sugar alcohols is difficulty and the studies of production of 1,4-BuD from erythritol or 1,4-AHERY are very limited. In addition, the combination of DODH reaction catalyzed by ceria-supported Re catalyst and reduction by carbon-supported Re catalyst in one-pot reaction created a new pathway to synthesis 1,4-BuD from biomass-based feedstocks. Changing the carbon-supported Re catalyst to tungsten-zirconia-supported Re catalyst combined with ceria-supported Re catalyst in the co-catalyst system improved the reusability of co-catalyst mixture, expending application of the co-catalyst system due to the variety of catalyst species.

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Finally, I thank my family and friends for their supports and encouragements.

August, 2019
School of Engineering
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Tianmiao Wang

List of Publications

1. Tianmiao Wang, Sibao Liu, Masazumi Tamura, Yoshinao Nakagawa, Norihito Hiyoshi, Keiichi Tomishige, "*One-pot Catalytic Selective Synthesis of 1,4-Butanediol from 1,4-Anhydroerythritol and Hydrogen*", Green Chem., 2018, 20, 2547-2557.

2. Tianmiao Wang, Masazumi Tamura, Yoshinao Nakagawa, Keiichi Tomishige, "*Preparation of Highly Active Monometallic Rhenium Catalyst for Selective Synthesis of 1,4‐Butanediol from 1,4‐Anhydroerythritol*", ChemSusChem, 2019, 12, 3615-3626.