Erythritol: Another C4 Platform Chemical in Biomass Refinery

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ABSTRACT: The potential of erythritol as a platform chemical in biomass refinery is discussed in terms of erythritol production and utilization. Regarding erythritol production, fermentation of sugar or starch has been already commercialized. The shift of the carbon source from glucose to inexpensive inedible waste glycerol is being investigated, which will decrease the price of erythritol. The carbon-based yield of erythritol from glycerol is comparable to or even higher than that from glucose. The metabolic pathway of erythritol biosynthesis has become clarified: erythrose-4-phosphate, which is one of the intermediates in the pentose phosphate pathway, is dephosphorylated and reduced to erythritol. The information about the metabolic pathway may give insights to improve the productivity by bleeding. Regarding erythritol utilization, chemical conversions of erythritol, especially deoxygenation, have been investigated in these days. Erythritol is easily dehydrated to 1,4-anhydroerythritol, which can be also used as the substrate for production of useful C4 chemicals. C=O hydrogenolysis and deoxydehydration using heterogeneous catalysts are effective reactions for erythritol/1,4-anhydroerythritol conversion.

1. INTRODUCTION

The use of biomass as a source of chemicals has been very important because of global warming and depletion of crude oil. Biomass such as lignocellulose is a complex mixture of polymers with various minor components, and thus the main approach of the biomass conversion is the utilization of “platform chemicals” as intermediates. The platform chemicals are small molecules which can be synthesized in pure form from biomass via chemical conversion or fermentation, and they included sugar alcohols, furanic compounds, and carboxylic acids. The platform chemicals correspond to building blocks in petrorefinery such as alkenes and BTX, and the approach of biomass conversion using platform chemicals as intermediates is called biomass refinery (or biorefinery). Both production of platform chemicals and conversion to each target product have been intensively investigated.

C4 compounds are an important class of chemicals consumed in large scale. Butadiene is a monomer for rubber and ABS resin. 1,4-Butanediol (1,4-BuD) and THF are also used as a monomer. Other C4 oxygenates such as butanones, butanols, and other butanediols are common chemicals used in many fields. The main source of such C4 compounds in petrochemistry is butadiene, butenes, and maleic anhydride. Butadiene and butenes are coproducts of naphtha cracking whose main targets are ethylene and propylene. However, recently lighter hydrocarbons such as associated petroleum gas and shale gas than naphtha have become inexpensive substrates of cracking or dehydrogenation for ethylene production. From these lighter hydrocarbons, the yield of C4 compounds is much lower. In addition to global warming as a long-term issue, the shift of carbon source in petrochemistry may increase the competitiveness of C4 biomass refinery.

The widely recognized C4 platform chemicals in biomass refinery are fermentation-derived dicarboxylic acids, especially the most simple form, succinic acid. Hydrogenation of succinic acid to γ-butyrolactone or 1,4-BuD has been a hot topic in biomass refinery. Other dicarboxylic acids, namely, fumaric acid, malic acid, and aspartic acid, and some other C4 compounds (acetoin, 3-hydroxybutyrolactone, and threonine) are also listed in the screening report by the National Renewable Energy Laboratory (NREL), U.S. Department of Energy; however, they can be mainly used for fine chemical production, and the conversion to commodity chemicals has not been focused on. In comparison with the C3, C5, and C6 biomass refinery where there are versatile platform chemicals such as glycerol (C3), furfural (C5), levulinic acid (C5), 5-hydroxymethylfurfural (C6), and sorbitol (C6), the C4 biomass refinery has limited product scope and has been less investigated.
Rather, production of C4 compounds from non-C4 platform chemicals can also be practical, such as butadiene production from ethanol and decarbonylation of furfural to furan.

Erythritol (meso,1,2,3,4-butanetetraol) is a C4 sugar alcohol which is distributed widely in fruits, fermented foods, and animals. Like other sugar alcohols, erythritol is stable and durable to decay with heat treatment. Erythritol has a moderate and plain sweetness of 70–80% of sucrose. In addition, erythritol has extremely low energy value as food, 0.2–0.4 kcal/g, because the majority of erythritol (ca. 90%) is not metabolized in the human body and is excreted into urine within 48 h after oral intake without affecting blood glucose and insulin levels. Based on these characteristics, erythritol has been used as an excellent additive (sweetener) to food, cosmetics, and pharmaceuticals. The current world production of erythritol is about 60 000 t/year, and the price is comparable to other compounds produced by fermentation such as glutamic acid and citric acid. However, erythritol has been less recognized as a “platform chemical”; the report by U.S. Department of Energy did not mention erythritol at all even as one of 47 potential building block candidates, while C3, C5, and C6 sugar alcohols (glycerol, xylitol, and sorbitol) and glutamic acid were regarded as “Top 12” building blocks; the revised list in 2010 also included glycerol, xylitol, and sorbitol but not erythritol. Nevertheless, the utilization of erythritol as a platform chemical began to be carried out, by our groups and some other groups. In this paper, we introduce the potential of erythritol as a platform chemical in biomass refinery by discussing the science and technologies of erythritol production (section 2) and various conversion routes from erythritol to useful chemicals (section 3).

2. PRODUCTION OF ERYTHRITOL

2.1. Fermentative Production Using Glucose. Fermentative production of erythritol has over 50 years of history. Hajny et al. reported in 1964 that Tolura yeast produced a substantial amount of erythritol in liquid media when glucose was supplied as a carbon source. Then, Ohnishi described that yeast genera produce several kinds of sugar alcohols: mannotiol, arabitol, and erythritol. Currently, a wide variety of yeasts and yeast-like fungi such as Moniliella, Torula, Candida, Pichia, Trichoderma, and Yarrowia are found to produce erythritol. In 1988, Kasumi et al. isolated a yeast-like fungus that produced a large amount of erythritol and originally designated Aureobasidium sp. SN-124A. This strain was then identified as Trichosporonoides megachiliensis, and together with reclassification of yeast, it was incorporated in a group of genera Moniliella as M. megachiliensis SN-124A. M. megachiliensis SN-G42, the mutant strain of SN-124A, showed excellent productivity of erythritol under stressing high glucose concentration with a small amount of nitrogen source. Using this strain, industrial production of erythritol was initially established in Japan in 1990. Currently, microorganisms used for the commercial base of erythritol production are Moniliella pollinis, Moniliella megachiliensis, and Yarrowia lypolitica. In contrast to ethanol, erythritol hardly suppresses the growth of yeasts, and a high concentration of erythritol (>200 g/L) can be obtained in a batch fermenter. The concentration of erythritol after fermentation is higher than that of succinic acid (ca. 150 g/L). Essentially, erythritol is one of the compatible solutes responding to environmental hyperosmotic or oxidative stress for erythritol-producing yeasts. Hence, reasonably stressing culture conditions are necessary to enhance erythritol yield.

Erythritol has good crystallinity and can be obtained in pure crystals (Figure 1).

2.2. Glycerol to Erythritol. Fermentation uses edible sugars as the carbon source. Large-scale fermentation may affect the food price, which has been actually pointed out for the ethanol production for biogasoline. The use of cheap and inedible biomass as a carbon source is preferable in biomass refinery. Glycerol is generated as a waste material from biodiesel fuel manufacturing which has been already carried out in large scale. Raw glycerol from biodiesel fuel manufacturing is normally devolatilized and purified. However, in the case of beef tallow glycerol, the yield was significantly low compared to palm oil, due to high pH value 11.0; however, it was recovered after pH adjustment to neutral using diluted sulfuric acid. Cell growth on glycerol was almost the same as on glucose, and the cells could grow in up to 300 g/L of glycerol. When 200 g/L of nonrefined glycerol was supplied, the carbon-based yield of erythritol was approximately 60% in a 500 mL flask batch culture after 3 days, which is slightly higher than that obtained with glucose. Regarding wild-type M. megachiliensis SN-124A, cell growth and erythritol yield were deficient compared to SN-G42, and in addition, the color of the culture broth changed from dark brown to an initial yellowish brown along with culture time because of the melaninoid pigment formation. Further improvement in cell growth and erythritol might be possible.

2.3. Metabolic Pathway of Erythritol Biosynthesis. The metabolic pathway and related important enzymes of erythritol biosynthesis are illustrated in Figure 2. In eukaryotes, erythritol works in various biosyntheses such as those of pentose derivatives (e.g., nucleotide). In the case of erythritol-producing
yeasts, erythrose-4-phosphate, which is one of the intermediates in the pentose phosphate pathway, is specifically dephosphorylated to erythrose. Then, erythrose is enzymatically reduced to erythritol by NADP+-dependent erythrose reductase (ER). Among three sER isogenes (er1, er2, er3) of M. megachiliensis, er3 was highly responsive to hyper-osmotic stress than er1 and er2. The two STREs (stress response elements: AGGGG or CCCCT) which existed upstream of er3 were considered closely related to stress response and erythritol production.

The dephosphorylation step of erythrose-4-phosphate with erythrose-4-phosphate phosphatase (or erythrose-4-phosphate kinase) should also be important; however, the details have not yet been clarified for the erythritol-producing yeasts. Since the pentose phosphate pathway is closely linked with a glycolytic pathway, a lot of enzymes involved in both pathways take part in erythritol biosynthesis. Especially, transketolase (TKL) or transaldolase (TAL) that plays an important role in the pentose phosphate pathway is also considered to be key enzymes.

Similarly, two isogenes were present in TKL (tkl1, tkl2). The tkl1 expression increased rapidly under osmotic stress, while tkl2 showed no significant increase. In contrast, oxidative stress induced a considerable increase in tkl2, while tkl1 expression remained low. These profiles are related to the existence of STRE in isogenes: two STREs in tkl1 and no STRE in tkl2. Meanwhile, two AP-1 elements (activator protein 1 response element) were found in tkl2, but none were detected in tkl1. The AP-1 element is suggested as a binding site involved in oxidative stress. The amount of erythritol produced was parallel to expression profiles of these isogenes. Thus, erythritol was considered to be generated in cooperation with isogenes of metabolic enzymes under osmotic or oxidative stress in M. megachiliensis.

MAPK Hog1 (mitogen activated protein kinase Hog1) plays an important role in signal response regulation during osmotic stress as well as heat shock, oxidative stress, or cell mitosis. Hog1 phosphorylated by MAPKK rapidly translocates to the nucleus and then stimulates transcription of target genes involved in osmotic adaptation together with other transcription factors. Compared with Hog1 from Saccharomyces cerevisiae, response to osmotic stress of M. megachiliensis Hog1 was highly sensitive. Moreover, retention time in the nucleus was significantly longer. The identity of an amino acid sequence between two strains was as high as 79%. Hence, it is probably due to the distinct substitution in dozens of amino acid sequences in the C-terminal region.

In the case of using glycerol as the carbon source, glycerol is reportedly metabolized through dihydroxyacetone phosphate, which is formed by the oxidation of glycerol and successive phosphorylation. Glycerol is also consumed through glycerol-3-phosphate formed via phosphorylation by glycerol kinase. Glycerol-3-phosphate is transformed to glyceraldehyde-3-phosphate and then dihydroxyacetone phosphate by glycerol-3-phosphate dehydrogenase and triose phosphate isomerase, respectively. These two triose isomers are then aldolized to fructose-6-phosphate via a gluconeogenetic enzyme. Erythritol is possibly produced via two paths: oxidation of glucose-6-phosphate as the starting material in the pentose phosphate pathway or by transaldolization between glyceraldehyde-3-phosphate and fructose-6-phosphate which is the reverse reaction of the consumption step of erythrose-4-phosphate in the pentose phosphate pathway. Besides erythritol, M. megachiliensis intracellularly accumulates a substantial amount of trehalose, which is produced from glucose-6-phosphate, when cultured in a glycerol medium. It is suggested that M. megachiliensis possesses a metabolic pathway from glycerol to glucose-6-phosphate, similar to the gluconeogenetic metabolism in S. cerevisiae.

Although the majority of metabolic mechanisms of erythritol from glycerol is still unclear, the proposed production routes in Figure 2 suggest that inherent carbon loss during production of erythritol by M. megachiliensis was minimized.
erythritol from glycerol is smaller than that from glucose: The carbon loss occurs during the pentose phosphate formation in the pentose phosphate pathway. From glucose, two molecules of C6 glucose are first converted to two C5 pentose phosphates and two CO2 (C1). The two pentose phosphates are finally converted to one C4 erythritol and one C6 hexose phosphate. The C6 hexose phosphate can also be used as the source of pentose phosphate. The net reaction can be C6 → C4 + 2C1, and the theoretical carbon-based erythritol yield from glucose is 67%. On the other hand, from glycerol, one C3 phosphate and one C6 phosphate (derived from two C3) are converted to one erythritol and one C5 xylulose-5-phosphate. The C5 xylulose-5-phosphate reacts with C5 ribose-5-phosphate which is produced by the pentose phosphate pathway (C6 → C5 + C1) to give finally erythritol and C6 hexose phosphate. The coproduced C6 hexose phosphate can be used in other steps. The net reaction can be 3C3 → 2C4 + C1, and the theoretical carbon-based erythritol yield from glycerol is 89%. Further comprehensive study is anticipated to elevate erythritol production yield.

3. CONVERSION OF ERYTHRITOL TO VALUABLE CHEMICALS

Erythritol has as much as 52 wt % oxygen content, and therefore the decrease of oxygen atoms is essential in the conversion to valuable chemicals. There are two general methods to decrease oxygen atoms in compounds: dehydration and deoxygenation.

3.1. Dehydration of Erythritol to 1,4-Anhydroerythritol (1,4-AHERY). A dehydration product of erythritol is 1,4-anhydroerythritol (cis-3,4-dihydroxytetrahydrofuran; 1,4-AHERY) (eq 1). Strong Brønsted acid catalyzes this dehydration, such as mineral acids and ion-exchange resin.16 Because of the much different boiling points between erythritol and 1,4-AHERY, the reactive distillation system is effective in collecting 1,4-AHERY product. The yield reaches 90% or even higher. The distillation may also be effective to remove nonvolatile impurities of erythritol such as salt used in the salting-out process for the collection of erythritol. The yield of 70–75% was obtained in a simple batch reactor without a reactive distillation system.16a Because of the relatively easy synthesis of 1,4-AHERY, it can also be used as a reactant for the production of useful C4 chemicals.

3.2. Step-by-Step Hydrodeoxygenation of Erythritol and 1,4-AHERY. Deoxygenation of erythritol involves dissociation of C–O bonds, and the C–O bonds are replaced with C–H bonds. This is a reduction reaction requiring some reducing agents. Molecular hydrogen (H2) is the best reducing agent in view of price, atom efficiency, and availability from renewable resources. Deoxygenation using molecular hydrogen as a reducing agent is called hydrodeoxygenation. There is a similar term to hydrodeoxygenation: C–O hydrogenolysis. C–O hydrogenolysis means the dissociation of a C–O bond and capping with H atoms from the H2 molecule (R–OR′ + H2 → RH + R′OH). C–O hydrogenolysis of alcohols (R′ = H) is hydrodeoxygenation, while that of ethers is not because it does not decrease the oxygen amount in organic molecules.

Hydrodeoxygenation products of erythritol and 1,4-AHERY are summarized in Figure 3. Potential products include two butanetriols, four butanediols (BuDs), and two butanols. Among these compounds, BuDs are attractive targets because of the larger demand than triols and a smaller amount of H2 to produce than butanols. However, selective production of one specific BuD is difficult because of a large number of isomers and the presence of overreaction to butanols.

Tomishige et al. applied an Ir-ReOx/SiO2 catalyst to erythritol hydrodeoxygenation.17 This Ir-ReOx/SiO2 catalyst is a very active C–O

![Figure 3. Hydrodeoxygenation products of erythritol and 1,4-anhydroerythritol (1,4-AHERY). BuT = butanetriol, BuD = butanediol, BuOH = butanol. Reproduced from ref 17. Copyright 2012 Wiley-VCH.](https://dx.doi.org/10.1021/acsomega.9b04046)
hydrogenolysis catalyst, especially in selective dissociation of C−O bonds neighboring the −CH2OH group; i.e., R-CCHOHCH2OH can be converted into R-CH2CH2OH.18 Based on the selectivity, erythritol is expected to be converted into 1,4-BuD. After optimization of reaction conditions, the maximum yield of 1,4-BuD was 25% (74% conversion, 33% selectivity).17 Longer reaction time increased the selectivity to 1-butanol instead (Figure 4). The low selectivity was reasonable considering that even in simpler glycerol hydrodeoxygenation the maximum 1,3-propanediol yield was below 40% over the Ir-ReOx/SiO2 catalyst because of the overreaction to 1-propanol (initial selectivity was ~70%).18 Pinel and Besson et al. reported erythritol hydrodeoxygenation over Rh-ReOx catalysts,19 which are also active in C−O dissociation (C−O hydrogenolysis) but less regioselective than Ir-ReOx catalysts.18 A yield of BuDs (~35%) similar to the case of Ir-ReOx/ SiO2 catalyst (34%) was obtained, while the distribution of isomers was different (mixture of 1,4-, 2,3-, and 1,2-BuDs over Rh-ReOx/ZrO2 catalyst; mainly 1,4-BuD with a small amount of 1,3-BuD over the Ir-ReOx/SiO2 catalyst). In contrast to the Ir-ReOx/SiO2 catalyst which showed a typical step-by-step consecutive reaction profile, the selectivity to BuDs was little changed over the Rh-ReOx/ZrO2 catalyst during the conversion range of 20−80%. BuDs were probably formed before desorption of the formed butanetriols from the catalyst surface.

In contrast to erythritol which contains 4 OH groups, 1,4-AHERY has two sets of much different types of C−O bonds: two ether bonds in the THF ring and two secondary OH groups. Therefore, selectivity control is easier in 1,4-AHERY conversion than in erythritol conversion.20 Tomishige et al. reported 1,4-AHERY hydrodeoxygenation over Rh-MoOx/SiO2 catalyst.20a 2-Butanol was obtained in good yield (51%) at the optimized conditions. Other M-MoOx/SiO2 (M = Pt, Pd, Ir) catalysts, other Rh-M’Ox/SiO2 (M’ = W, Re, Nb, Cr, Mn) catalysts, and Ir-ReOx/SiO2 catalysts showed lower selectivity to 2-butanol or no activity. The time course of 1,4-AHERY hydrodeoxygenation over Rh-MoOx/ZrO2 catalyst during the conversion range of 20−80%. BuDs were probably formed before desorption of the formed butanetriols from the catalyst surface.

Figure 4. Hydrogenolysis of erythritol over Ir-ReOx/SiO2 catalyst.17,18b Reaction conditions: erythritol 1 g, water 4 g, Ir-ReOx/SiO2 (Ir 4 wt %, Re/Ir = 1) 0.3 g, H2SO4 (H+/Ir = 1), H2 8 MPa, 373 K. BuT = butanetriol, BuD = butanediol, BuOH = butanol. Reproduced from ref 18b. Copyright 2017 The Royal Society of Chemistry.

Figure 5. Time course of the hydrogenolysis of 1,4-anhydroerythritol (1,4-AHERY) over Rh-MoOx/SiO2 catalyst. Reaction conditions: 20 wt % of 1,4-AHERY 1 g, water 4 g, Rh-MoOx/SiO2 (Rh 4 wt %, Mo/Rh = 0.13) 0.1 g, H2 8 MPa, 393 K. BuT = butanetriol, BuD = butanediol, BuOH = butanol, 3-HTHF = 3-hydroxytetrahydrofuran. Reproduced from ref 20a. Copyright 2016 Wiley-VCH.

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As shown above, Rh and Ir catalysts modified with reducible metal oxides (MoOx, ReOx) are active in hydrodeoxygenation. Typically, under the reaction conditions, the metal oxide species are partially reduced, and a direct bond with a noble metal (Rh
or Ir) surface is formed. The attached metal oxide species activates the substrate molecule and/or affects the electronic state of the noble metal surface to increase the activity. The noble metal activates the H₂ molecule. Typically first-order dependence with respect to H₂ pressure was observed, and probably hydride-like active species were formed with 1:1 stoichiometry from H₂ on the catalyst surface.

3.3. Deoxydehydration (DODH). The C–O hydrogenolysis reactions introduced above dissociate C–O bonds step by step, and the regioselectivity is generally not high. Recently, another deoxygenation reaction, deoxydehydration (DODH), has attracted attention for the conversion of biomass-derived polyols. DODH is the reverse reaction of cis-dihydroxylation of alkenes (i.e., osmium oxidation): cis-vicinal diols are converted to alkenes with 2-electron-reducing agents (Scheme 1). Typical DODH catalysts are homogeneous Re species such as methyltrioxorhenium (MTO; CH₃ReO₃) and Cp*ReO₃. The reaction is believed to proceed via redox of Re species between +5 and +7 valence states. Erythritol and 1,4-AHERY have been frequently used as reactants for DODH. Even the first report of DODH in 1996 used erythritol as one of the tested reactants, giving ca. 80% yield of butadiene with Cp*ReO₃ catalyst, PPh₃ reducing agent, and chlorobenzene solvent. Shiramizu and Toste reported a more practical system using CH₃ReO₃ catalyst and 3-octanol as both a solvent and a reducing agent. Erythritol and 1,4-AHERY were converted to butadiene and 2,5-dihydrofuran with 89% and 91% yield, respectively (Scheme 2). Gebbink et al. developed Cp²ReO₃ catalyst (Cp² = 1,3-di-tert-butylcyclopentadienyl) and obtained 90% butadiene yield from erythritol using 3-octanol. Bergman et al. reported direct conversion of erythritol to 2,5-dihydrofuran via acid-catalyzed cyclization and DODH with 62% yield using TsOH, Re₂(CO)₁₀ and 3-octanol as an acid catalyst, a DODH catalyst, and a reducing agent, respectively.

The problems of these typical DODH systems include difficult recovery of used catalyst (homogeneous system), low turnover number (<50), the use of non-H₂ reducing agent, and the price of Re catalyst. The development of cheaper catalysts such as Mo than Re has been a hot topic in DODH studies; however, both activity (higher reaction temperature by >50 K) and product yield (<75% 2,5-dihydrofuran from 1,4-AHERY; very low butadiene yield (<3%) from erythritol) were lower than those in the case of Re catalysts. The use of H₂ as a reducing agent is generally difficult in DODH probably because of the over-reduction of the active Re (or Mo) species to inactive low valent species.

Tomishige et al. developed a ReOₓ/CeO₂-based new heterogeneous DODH catalyst, overcoming these problems. First, the ReO₂-Pd/CeO₂ catalyst was developed, which is active in hydrodeoxygenation of cis-vicinal diols (−CHOH−CHOH− + 2H₂ → −CH₂−CH₂− + 2H₂O). This is a variant of DODH because this reaction is composed of DODH and Pd-catalyzed hydrogenation of the produced alkene. 1,4-AHERY was efficiently converted to THF with H₂ as a reducing agent (Figure 6). This system showed very high THF yield (>99%), good reusability (activity totally recovered after calcination), and very large TON (>10⁴). From erythritol, 1,2-butanediol was obtained in good yield (77%) at an appropriate reaction time (eq 4), while too long reaction time led to overreaction to butane. This is the first and only report in the literature to obtain 1,2-butanediol in good yield from erythritol. The activity trends of related catalysts and various characterizations suggested that monomeric Re species with a +4 or +6 valence state on the CeO₂ crystal surface was the active site for DODH. Higher Re loading rather decreased the activity because the major Re species was shifted from monomeric ones.

Scheme 1. Deoxydehydration (DODH) Catalyzed by Re Species

Scheme 2. DODH of Erythritol and 1,4-AHERY with CH₃ReO₃ Catalyst

Figure 6. Time course of 1,4-AHERY hydrodeoxygenation over ReO₂-Pd/CeO₂ catalyst (C: conversion, S: selectivity). 1,4-AHERY 1 g, 1,4-dioxane 4 g, ReO₂-Pd/CeO₂ (Re 2 wt %, Pd 0.3 wt %) 0.15 g, H₂ 8 MPa, 413 K. Reproduced from ref 22a. Copyright 2015 Wiley-VCH.
to inactive polymeric ones. The Pd species activate H₂ molecules to supply Re species with hydrogen species to reduce the Re species. In addition, Pd catalyzes hydrogenation of the C=\(\text{C}\) bond formed by DODH. The rate-determining step is the formation of alkene and oxidized Re species, and the steps of reduction of Re species and hydrogenation of the C=\(\text{C}\) bond are fast, which has been shown by the small effect on activity by both the Pd loading amount and H₂ pressure. The main role of CeO₂ support is the stabilization of Re species with higher valence state: on other supports such as SiO₂ the Re species are easily reduced to a lower valence state (\(0 \sim +3\)).

Next, ReOₓ-Au/CeO₂ was developed which catalyzes DODH without hydrogenation. ReOₓ-Au/CeO₂ showed very high selectivity to an alkene product from vicinal diols. The ReOₓ-Au/CeO₂ catalyst is the only DODH catalyst that can use H₂ as a reducing agent with good yield in the literature. Butadiene (81% yield) and 2,5-dihydrofuran (80% yield) were obtained from erythritol and 1,4-AHERY, respectively (Scheme 3). Although the activity of the ReOₓ-Au/CeO₂ catalyst was lower than that of ReOₓ-Pd/CeO₂ because of the very small number of H₂ activation sites, the ReOₓ-Au/CeO₂ catalyst showed similarly good stability. The good yield of butadiene from erythritol is attractive because butadiene is a very important monomer in industry. There are several other production routes of butadiene from biomass, such as succinic acid hydrogenation + dehydration and ethanol dimerization. The production routes will be compared economically. In view of consumed H₂ amount, the erythritol DODH (2 equiv of H₂ consumed) is better than succinic acid hydrogenation to 1,4-BuD + dehydration (4 equiv of H₂ consumed), while both erythritol and succinic acid are compounds produced by fermentation.

A variant of ReOₓ-Au/CeO₂-catalyzed DODH has been further developed. When ReOₓ-Au/CeO₂ catalyst was mixed with ReOₓ/C catalyst, 1,4-AHERY was reduced to 1,4-BuD in good yield (~90%) (Scheme 4). The reactivities of possible intermediates showed that the 1,4-BuD formation is composed of several steps: DODH of 1,4-AHERY to 2,5-dihydrofuran, isomerization of 2,5-dihydrofuran to 2,3-dihydrofuran, hydration of 2,3-dihydrofuran to 2-hydroxytetrahydrofuran, hydrogenation of 2-hydroxytetrahydrofuran or the ring-opened form (4-hydroxybutanal) to 1,4-BuD. The second DODH step is catalyzed by ReOₓ-Au/CeO₂. The isomerization step is catalyzed by ReOₓ on ReOₓ/C. The hydration step of 2,3-dihydrofuran is catalyzed by a weak acid and proceeds over the C support. The final hydrogenation step is catalyzed by ReOₓ on ReOₓ/C. 2-Hydroxytetrahydrofuran or 4-hydroxybutanal reversibly reacted with 1,4-AHERY to form acetal, which was actually detected at short reaction time. The key to obtain 1,4-BuD is the selection of the support of the second catalyst for the isomerization step. The ReOₓ catalyst on the carbon support was active in isomerization, while ReOₓ/oxide support catalysts showed low activity. The type of carbon also affected the activity: carbon black BP2000 showed good performance. Later, it was found that the Au promoter is not necessary in the mixture catalysts. A simple mixture of ReOₓ/CeO₂ + ReOₓ/C showed almost the same activity and selectivity in the reduction of 1,4-AHERY to 1,4-BuD. The catalyst stability is an unsolved issue in this system: while ReOₓ(-Au)/CeO₂ can be regenerated by calcination, the mixture with ReOₓ/C cannot be calcined because of the combustibility of carbon support. The production route of 1,4-BuD from erythritol via 1,4-AHERY will also be compared with that from succinic acid, as well as the case of butadiene production.

Tungsten (W) can form reducible oxide with high valence, like Mo and V. While Mo and V have been investigated as catalysts for DODH, W has not been regarded as an active element for DODH. However, we think that the catalysis of WOₓ-Pd/support described in the above section is a variant of DODH, namely, DODH + hydration, because of the similar

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**Scheme 3. DODH of Erythritol and 1,4-AHERY over Heterogeneous ReOₓ-Au/CeO₂ Catalyst**

![Scheme 3. DODH of Erythritol and 1,4-AHERY over Heterogeneous ReOₓ-Au/CeO₂ Catalyst](image)

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**Scheme 4. One-Pot Production of 1,4-BuD from 1,4-AHERY over ReOₓ-Au/CeO₂ + ReOₓ/C Mixed Catalyst**

![](image)

*(1,4-BuD was obtained with 90% yield in the conditions of 0.15 g of 1,4-AHERY, ReOₓ-Au/CeO₂ (Re 1 wt %, Au 0.3 wt %) 0.15 g, ReOₓ/C (BP2000 support (C-BP), Re 3 wt %) 0.15 g, 1,4-dioxane 4 g, H₂ 8 MPa, 413 K, 4 h. DHF = dihydrofuran. Reproduced from ref 24a. Copyright 2018 The Royal Society of Chemistry.)*
reactivity trends of various substrates to those of DODH: only cis-vicinal diols were converted. The alkene intermediate was probably quickly hydrated over the acidic W center before desorption, and the cis-vicinal diols were converted to monoalcohols.

Another variant of DODH is the reaction of diols with formic acid. At high temperature (around 500 K), cis-vicinal diols react with formic acid to give alkenes, water, and CO2 (Scheme 5). An orthoester-type intermediate has been proposed, and the thermal decomposition of this intermediate gives the products. 2,5-Dihydrofuran can be obtained in 87% isolated yield from erythritol at 483 K. From erythritol, a substantial amount of erythritol was first dehydrated to 1,4-AHERY and then reacted with formic acid. 2,5-Dihydrofuran was obtained in 39% isolated yield from erythritol + formic acid (2 equiv). The strong acidity of formic acid led to dehydration of erythritol. The use of formic acid orthoester instead of formic acid itself can suppress the dehydration. With 2 equiv of triethyl orthoformate in DMSO solvent at 588 K, butadiene was obtained at 42% yield. The absence of expensive metal catalysts in a formic-acid-based system is attractive; because this is a noncatalyzed system.

4. SUMMARY AND OUTLOOK

Erythritol has already been manufactured by fermentation in a large scale. While the current use of erythritol is sweeter, erythritol can be regarded as a platform chemical in biomass refinery. The production cost is a limiting factor to use erythritol as a source of chemicals such as monomers for plastics. The production cost will be lowered by the use of a cheaper carbon source such as waste glycerol and/or further breeding of the microorganisms for erythritol production. The biosynthesis mechanism of erythritol is being clarified, and the insights will help the bleeding. Erythritol can be readily converted to 1,4-anhydroerythritol (1,4-AHERY) by acid-catalyzed dehydration, and 1,4-AHERY can also be regarded as a platform chemical. Because of the large amount of oxygen in erythritol, reduction with hydrogen (hydrodeoxygenation) is the main method to synthesize useful compounds from erythritol or 1,4-AHERY. The main targets of erythritol conversion have been butadiene, 1,4-butanediol, 2,5-dihydrofuran, and THF. Except 2,5-dihydrofuran which is not a commodity chemical, these compounds can also be synthesized from succinic acid which has been already recognized as a C4 platform chemical. The reaction routes from erythritol and succinic acid will be compared. Different from succinic acid, erythritol can serve as a source of other butanediols: 1,2-, 1,3-, and 2,3-. However, the reports for the productions of these butanediols from erythritol or 1,4-AHERY are very limited: only 1,2-butanediol could be obtained in good yield from erythritol over ReOx-Pd/CeO2 catalyst. Catalysts for the reduction of erythritol or 1,4-AHERY can be classified to two types: noble-metal-catalyzed C=O hydrogenolysis and deoxydehydration (DODH). Noble-metal-catalyzed C=O hydrogenolysis can give various types of products including 1,3-butenediol; however, the selectivity control is difficult. More catalyst development is necessary in view of precise control of active sites, in addition to selection of appropriate components (active metal, additives, and support) of catalyst. DODH has simpler product pattern and can give higher selectivity to one specific product. ReOx/CeO2-based catalysts are promising DODH catalysts because of the heterogeneous nature, use of H2 as a reducing agent, and good stability.

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Notes

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**ACKNOWLEDGMENTS**

Part of this work was carried out on commission by the Ministry of the Environment, Japan, as “Demonstration project for plastics resource circulation system for decarbonized society”.

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