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Hydrodeoxygenation of potential platform chemicals derived from biomass to fuels and chemicals†

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Biomass valorization has emerged as a promising and sustainable means of accommodating value-added chemicals. To produce such chemicals, various transformation methods of the top biomass-derived platform chemicals nominated by the U.S. Department of Energy (DOE) have been extensively investigated in recent decades. However, as represented by 5-hydroxymethylfurfural, which is one of the most widely investigated top platform chemicals, their use is still under development due to difficulties in their production, handling, and selective transformation. In this context, revisiting the U.S. DOE's lists and refocusing on other potent platform chemicals are beneficial for this research field. This review introduces such platform chemicals, *viz.*, levoglucosan (+levoglucosenone), alkyl glycosides, glucaric acid, erythritol (+1,4-anhydroerythritol), and *N*-acetylglucosamine. Hydrodeoxygenation to remove oxygenated functionalities partially or completely using hydrogen as a reductant is a promising means of upgrading these compounds to fuels and useful chemicals, whose production is difficult from conventional top platform chemicals. Herein, a variety of catalytic systems to achieve the selective hydrodeoxygenation of the compounds introduced above are summarized with a description of their features, including catalytic performance, active sites, and mechanism.

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1. Introduction

Decreasing CO_2 emission is one of the urgent tasks for the prevention of global warming. Much attention has been recently paid to the concept of "carbon recycling", which can include CO_2 conversion to fuels and chemicals by renewable energies.[1–3] A typical method for CO_2 conversion is the reduction of CO_2 with renewable hydrogen to CO, formic acid, formaldehyde, methanol, methane, ethanol, longer chain hydrocarbons, and so on. CO_2 contains carbon atoms with the highest oxidation state, meaning that a large amount of renewable hydrogen is required for CO_2 reduction to hydrocarbons. The availability of renewable hydrogen influences the feasibility of these CO_2 hydrogenation processes significantly. A variety of useful oxygenates have been produced by the oxidation and/or hydration of hydrocarbons in the petroleum refining industry. It is thought that the production of such oxygenates by the oxidation/hydration of hydrocarbons from CO_2 reduction is not energy-efficient. Oxygenates can be produced by the reduction of biomass-derived platform chemicals with renewable hydrogen because the oxygen content of biomass-derived platform chemicals is clearly higher than that of oxygenates produced in the petrochemical industry. The reduction of biomass-derived platform chemicals is more favorable than CO_2 hydrogenation because a lower amount of H_2 is necessary for the former case. The more energy efficient production of value-added chemicals *via* biomass-derived platform chemicals than those *via* CO_2-derived hydrocarbons will maintain the importance of biomass utilization.

Two famous lists of biomass-derived platform chemicals were issued by the U.S. Department of Energy (DOE) in 2004 and 2010, and the newer one was published in this journal.[4,5] The older list was made by the screening of various compounds that can be obtained from carbohydrates. Twenty-eight carbohydrate-derived compounds, many of which were fermentation products, were selected, and the combination of these compounds with CO and synthesis gas (syngas) gave the "Top 30" candidates. Further refinement gave the "Top 15" candidates. They are sometimes also called the "Top 12" by combining three C4 dicarboxylic acids (succinic acid, malic acid, and fumaric acid) and C5 sugar alcohols (xylitol and arabinitol) into their respective groups, and they are even colloquially called the "Top 10". The newer list was re-compiled from compounds in a wider range, including those derived from vegetable oil and algae. The manufacturing cost and availability were more focused on for the newer list, and compounds synthesized by chemical processes, rather than fermentation,

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†Electronic supplementary information (ESI) available: Discussion about the model reactions of single-hydrodeoxygenation, energy profiles for the hydrogenolysis of glycerol and erythritol, and the hydrogenolysis of glycerol to 1,3-propanediol. See DOI: https://doi.org/10.1039/d2gc01289h

tended to be selected. Numerous studies on the synthesis and conversion of these platform chemicals have been carried out in this decade on the basis of these lists.[6] The compounds introduced as top biomass-derived platform chemicals in the two lists are shown in Table 1.

As the sole C2 platform chemical, ethanol can be easily converted into ethylene, meaning that ethanol can play similar roles to ethylene as an intermediate in petrochemical production. Glycerol can give a variety of C3 chemicals such as propanols, propanediols, and acrolein, suggesting that glycerol will be able to act as a substitute for propylene in the petrochemical industry. It is expected that C2 and C3 chemicals can be sufficiently supplied from these present platform chemicals. For C4 platform chemicals, various compounds were introduced in the older list;[4] however, only one compound, succinic acid, remained a top platform chemical in the newer list.[5] This is because the fermentative production of these C4 platform chemicals is inefficient and costly. The petrochemical industry finds it difficult to produce a C5 platform chemical, and thus, the accessibility of C5 platform chemicals is the advantage of the biomass refinery because of hemicellulose and natural rubber. One of the major strategies for the utilization of such C5 platform chemicals relies on furfural and its derivatives.[7–11] In the petrochemical industry, a variety of C6 aliphatic and aromatic chemicals are produced mainly *via* benzene. Because of the importance of many C6 compounds in the chemical industry, biomass-derived platform chemicals for C6 compounds should be diverse with respect to functionality and feedstock, and we propose several new C6 platform chemicals.

A biomass-derived candidate for a C6 platform chemical with wide applicability is 5-hydroxymethylfurfural (HMF). HMF has been recognized as one of the most typical lignocellulosic biomass-derived platform chemicals, since this compound can be derivatized into valuable chemicals including 2,5-dimethylfuran (diesel fuel) and 2,5-furandicarboxylic acid (FDCA; building block of polyethylene furanoate),[12–15] the latter of which is also listed in the top bio-based chemicals derived from sugars by the U.S. DOE along with HMF (Table 1).[4,5] However, regardless of their attractive applications, the mass production of these furanic compounds inevitably faces serious and fundamental obstacles arising from the chemical nature of HMF, namely its reactive formyl and hydroxymethyl groups (Fig. 1), as described

Keiichi Tomishige

Keiichi Tomishige received his B.S., M.S., and Ph.D. from the Graduate School of Science, Department of Chemistry, The University of Tokyo, under the guidance of Prof. Y. Iwasawa. During his Ph.D. course in 1994, he moved to the Graduate School of Engineering, The University of Tokyo, as a research associate and worked with Prof. K. Fujimoto. In 1998, he became a lecturer, and then he moved to the Institute of Materials Science, University of Tsukuba, as a lecturer in 2001. Since 2004 he has been an associate professor at the Graduate School of Pure and Applied Sciences, University of Tsukuba. Since 2010 he has been a professor at the School of Engineering, Tohoku University. His research interests are the development of heterogeneous catalysts for (1) the production of biomass-derived chemicals, (2) the non-reductive conversion of CO_2 with alcohols/amines into organic carbonates, carbamates, and ureas, and (3) the reforming of hydrocarbons such as biomass tar and methane. He received a Catalysis Society of Japan Award (Academic field) in 2021. He is a member of the editorial boards of Green Chemistry (since Aug., 2017) and Applied Catalysis A (since Apr., 2009), a member of the international advisory boards of ChemSusChem (since Jan., 2015) and ChemCatChem (since Jan., 2021), a member of the editorial advisory board of ACS Omega (since Jan., 2018), and a member of the editorial boards of Catalysis Surveys from Asia (since Oct., 2021), Sustainable Chemistry for Climate Action (since Jan., 2022) and Current Opinion in Chemical Engineering (since Jan., 2022).

Mizuho Yabushita

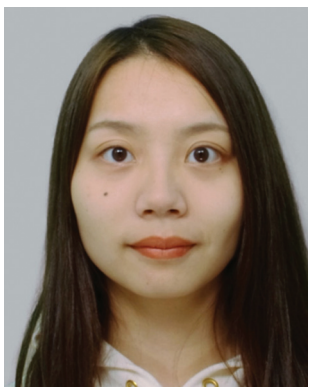
Mizuho Yabushita received his Ph.D. in 2015 from the Graduate School of Chemical Sciences and Engineering, Hokkaido University under the guidance of Prof. A. Fukuoka. From 2015 to 2018, he worked as a postdoctoral fellow at the University of California, Berkeley, with Prof. A. Katz and at Hokkaido University with Prof. A. Fukuoka. After two years as an assistant professor in Prof. A. Muramatsu's group at Tohoku University, he moved to the research group led by Prof. K. Tomishige as an assistant professor. His current research interests are the catalytic conversion of biomass-derived compounds and the synthesis and application of zeolites.

in a previous essay by Galkin and Ananikov.[16] A well-known issue is the difficulty in the selective production of HMF from biomass-derived sugars. The most attractive substrate for synthesizing HMF is glucose, which is the most accessible monosaccharide in nature and typically undergoes a two-step transformation to yield HMF (isomerization of glucose to fructose catalyzed by a base or Lewis acid and subsequent dehydration of fructose to HMF in the presence of acids).[12] However, due to the presence of reactive functional groups (formyl and hydroxymethyl groups) in both the substrate and HMF molecules, this reaction always suffers from side reactions, as exemplified by the intermolecular condensation of HMF and/or reactive intermediate compounds to produce insoluble humins and the hydrolysis of HMF to levulinic acid and formic acid.[17–19] Low substrate concentration conditions and biphasic systems comprising water, sometimes containing salts, which are required for the dissolution of sugar substrates, and organic solvent, which extracts and stabilizes produced HMF, are effective for the suppression of undesired side reactions.[20–22] However, the dilution of HMF and the use of additional solvents and additives require energy-consuming condensation, separation, and/or purification steps. Such additional steps make the entire HMF production process more complicated and costlier. What is worse, HMF degrades spontaneously to be polymerized even during storage.[23] Therefore, to establish efficient commercial plants for manufacturing HMF derivatives, these fundamental limitations need to be solved. The protection of the reactive groups of HMF, *e.g.*, acetalization of the formyl group by 1,3-propanediol,[24,25] silylation of the hydroxymethyl group by the *tert*-butyldiphenylsilyl group,[23] or etherification of the hydroxymethyl group,[26] should be a promising approach (Fig. 1) and is in progress. More detailed protection strategies were summarized in a very recent review.[27] Another issue for handling HMF arises from the negative effect of trace impurities on the catalytic conversions of HMF.[28] HMF synthesis typically uses unconventional solvents such as dimethyl sulfoxide (DMSO), and the presence of trace DMSO greatly affects the hydrogenation of HMF.[29]

As mentioned above, some difficulties of HMF operation arise from the presence of the formyl group; this is common when handling sugar compounds. It is known that formyl groups can be protected by acetal formation. Sugars are usually present as cyclic hemiacetals through the intramolecular addition reaction of the OH group at the 4- or 5-position to the formyl group (Fig. 2). Further reaction of the hemiacetal with another OH group in the sugar molecule gives an acetal. A representative of such an acetal is levoglucosan, which is the acetal of β-glucose cyclized between the 1- and 6-positions *via* an O atom. Another type of acetal is that of external alcohols, alkyl glycosides. Here, we discuss the potential of these acetals (levoglucosan: section 2; alkyl glycosides: section 3) as C6 platform chemicals.

Carboxylic groups can be formed *via* simple oxidation of formyl and primary hydroxy groups. The reactivity of the carboxylic group is not as high as that of the formyl group, leading to the ease of handling such compounds containing a carboxylic group(s). Therefore, sugar acids can be also considered as C6 platform chemicals (section 4).

Another problem of the platform-chemical list from 2010[4] is that C4 platform chemicals are limited to dicarboxylic acids, and the most easily accessible one is succinic acid. This is connected to the difficulty in functionalizing the 2-position. Syntheses of C4 chemicals from C5 platform chemicals have even been investigated recently, for example, the decarboxylation of levulinic acid.[30] Considering that sugar alcohols (glycerol, xylitol, and sorbitol) are listed as C3, C5, and C6 platform chemicals, respectively, erythritol can also be a C4 platform chemical because it is produced by the fermentation of glucose and (crude) glycerol.[31,32] All the carbon atoms in erythritol are functionalized and this enables derivatization to a variety of C4 chemicals. While the possibility of erythritol as a platform chemical was discussed in our previous review paper,[33] the chemistry of hydrodeoxygenation of erythritol and its dehydrated derivative (1,4-anhydroerythritol (1,4-AHERY)) has been growing rapidly. Here we summarize recent developments in section 5.



Ji Cao

Ji Cao is an assistant professor at the School of Engineering, Tohoku University. She received her B.E degree in 2014 from Taiyuan University of Technology, and her M.ScT. degree in 2016 from Hirosaki University. She obtained her Ph.D. in 2020 from the Graduate School of Engineering at Tohoku University under the guidance of Prof. K. Tomishige. Her current research focuses on the development of heterogeneous catalysts for the conversion of biomass-related compounds into value-added chemicals.

Yoshinao Nakagawa

Yoshinao Nakagawa received his Ph.D. in 2005 from the Graduate School of Engineering, The University of Tokyo, under the guidance of Prof. N. Mizuno. After 4 years of postdoctoral research in the same group, he joined the research group of Keiichi Tomishige at the University of Tsukuba. He moved to Tohoku University and became an assistant professor in 2010. Since 2013, he has been an associate professor. His current research interests are catalytic oxidations and reductions of bio-related chemicals.

Table 1 Platform chemicals introduced in reports by the U.S. DOE and discussed in this review

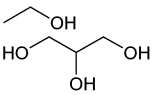
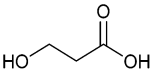
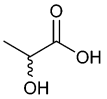
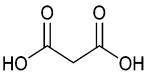
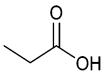
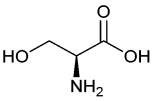
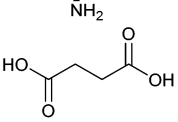
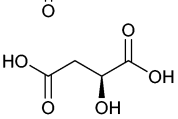
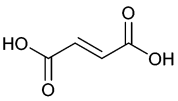
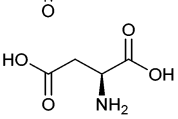
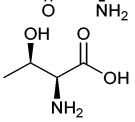
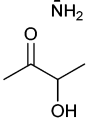
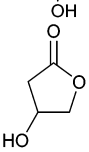
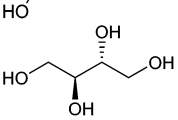
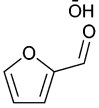
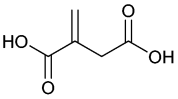
Compound name	Chemical formula	Feedstock, type of production process[a]	Carbon number	DOE report in 2004 [b]		Green Chem. in 2010[c]	This review
				"Top 12 (or 15)"	"Top 30"		
Carbon monoxide, syngas		Lignocellulose, C	1	—	X	—	—
Ethanol		Sugars, B	2	—	—	X	—
Glycerol		Oil/fat, C	3	X	X	X	—
3-Hydroxypropionic acid		Sugars, B	3	X	X	X	—
Lactic acid		Sugars, B	3	—	X	X	—
Malonic acid		Sugars, B	3	—	X	–	—
Propionic acid		Sugars, B	3	—	X	–	—
Serine		Sugars, B	3	—	X	–	—
Succinic acid		Sugars, B	4	X	X	X	—
Malic acid		Sugars, B	4	X	X	—	—
Fumaric acid		Sugars, B	4	X	X	—	—
Aspartic acid		Sugars, B	4	X	X	—	—
Threonine		Sugars, B	4	—	X	—	—
Acetoin		Sugars, B	4	—	X	—	—
3-Hydroxybutyrolactone		Sugars, B	4	X	X	—	—
Erythritol		Sugars, B	4	—	—	—	X
Furfural		Hemicellulose, C	5	—	X	X	–
Itaconic acid		Sugars, B	5	X	X	—	—

Table 1 *(Contd.)*

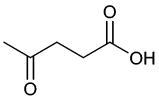
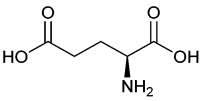
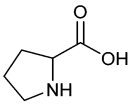
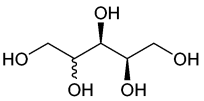
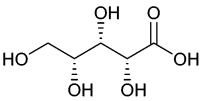
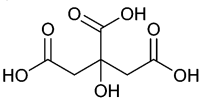
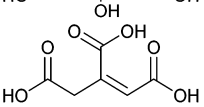
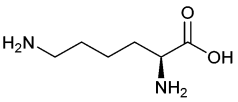
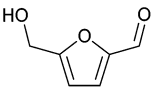
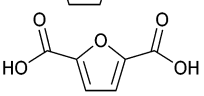
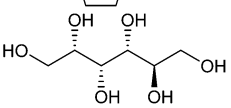
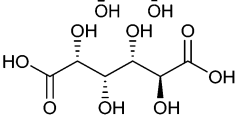
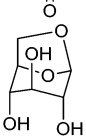
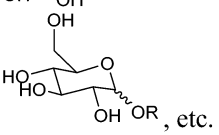
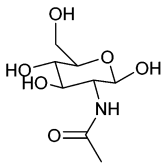
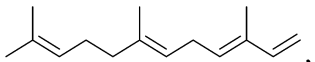
Compound name	Chemical formula	Feedstock, type of production process[a]	Carbon number	DOE report in 2004 [b]		Green Chem. in 2010[c]	This review
				"Top 12 (or 15)"	"Top 30"		
Levulinic acid		Sugars, C	5	X	X	X	–
Glutamic acid		Sugars, B	5	X	X	—	—
Proline		Sugars, B	5	—	X	—	—
Xylitol and arabinitol		Hemicellulose, C	5	X	X	X	—
Xylonic acid		Hemicellulose, C	5	—	X	—	—
Isoprene		Sugars, B	5	—	—	X	—
Citric acid, aconitic acid	 	Sugars, B	6	—	X	—	—
Lysine		Sugars, B	6	—	X	—	—
5-Hydroxymethylfurfural (HMF)		Sugars, C	6	—	—	X	—
2,5-Furandicarboxylic acid (FDCA)		Sugars, C	6	X	X	X	—
Sorbitol		Sugars, C	6	X	X	X	—
Glucaric acid		Sugars, C	6	X	X	—	X
Levoglucosan		Cellulose, C	6	—	X	—	X
Alkyl glycosides		Sugars, C	6[d]	—	—	—	X

Table 1 *(Contd.)*

Compound name	Chemical formula	Feedstock, type of production process[a]	Carbon number	DOE report in 2004 [b] "Top 12 (or 15)"	DOE report in 2004 [b] "Top 30"	Green Chem. in 2010[c]	This review
N-Acetylglucosamine		Chitin, C	6[d]	—	—	—	X
Heavy biohydrocarbons	 etc.	Sugars, B or algae, C	≥15	—	—	X	—

[a] B: Produced by biological or biochemical processes such as fermentation; C: produced by chemical or physical processes. [b] Ref. 4. [c] Ref. 5. [d] Carbon atoms in the alkyl or acetyl group are not included.

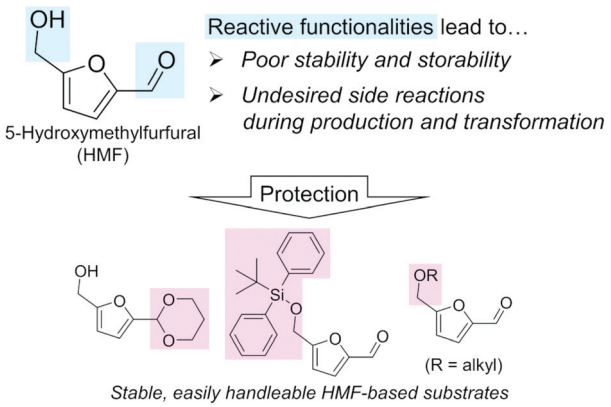


Fig. 1 Origins of the difficulty in using HMF as a platform chemical and promising approaches for its protection.

In addition, we mention the possibility of *N*-acetylglucosamine as an N-containing C6 platform chemical because its polymer, chitin, is regarded as an abundant biomass resource (section 6).

2. Levoglucosan and levoglucosenone

Levoglucosan can be produced by the pyrolysis of cellulose in good yields. The yield varies depending on the reactor type and conditions, and there are several reports with yields higher than 60%.[34] High temperature, such as 773 K, has been applied. As shown by the high temperature required for synthesis, levoglucosan is thermally stable and easy to handle. The production of levoglucosan from starch is also possible;[35] however, production from cellulose is preferable because the use of starch as a source of chemicals competes with food supply. Levoglucosan is also one of the main components of the pyrolysis product of raw lignocellulose (bio-oil).[36,37] The relatively easy production from biomass makes levoglucosan a potential platform chemical. In the DOE report from 2004, levoglucosan was selected as one of the top 30 candidates; however, it was not selected as a final top 12 building block because it has "somewhat lower potential" in transformation to useful products.[4] After publication of the DOE report, more and more research was carried out for the transformation of any biomass-derived molecules including levoglucosan and its derivatives. A comprehensive review paper on the synthesis and application of levoglucosan was published in this journal in 2020.[38] Fermentation is the main transformation method of levoglucosan. There are two major pathways of levoglucosan metabolism: one is the combination of oxidation, hydrolysis and reduction to glucose, and the other is direct phosphorylation to glucose-6-phosphate (Fig. 3). Both products are further consumed in the same way as that in the fermentation of glucose.

Levoglucosan can be re-hydrated to glucose over acid catalysts. Many of the products of the chemical transformation of levoglucosan are compounds that can also be produced from glucose. This is true for the reductive conversion of levoglucosan. Heeres *et al.* reported the conversion of levoglucosan into sorbitol over a mesoporous-carbon-supported Ru catalyst with H_2 in high yield (96%) at 453 K.[39] On the other hand, sorbitol can be produced by the hydrogenation of glucose or even cellulose.[40,41] The production of sorbitol by the hydrogenation of glucose can proceed almost quantitatively. Although the sorbitol yield from cellulose was generally not high (typically around 60%), the performance of direct cellulose hydrogenation to sorbitol has been steadily improved in extensive recent studies.[42,43] Bindwal and Vaidya reported the hydrogenolysis of levoglucosan over a Ru/C catalyst in water as a solvent.[44] The main products were 1,2-propanediol and ethylene glycol with a combined yield of 35%-C (94.8% conversion) at 413 K. These glycols can also be produced by the hydrogenolysis of various sugars and sugar alcohols such as cellulose,[45,46] sorbitol,[47–49] xylitol,[50] and glycerol.[51,52] The combined yields

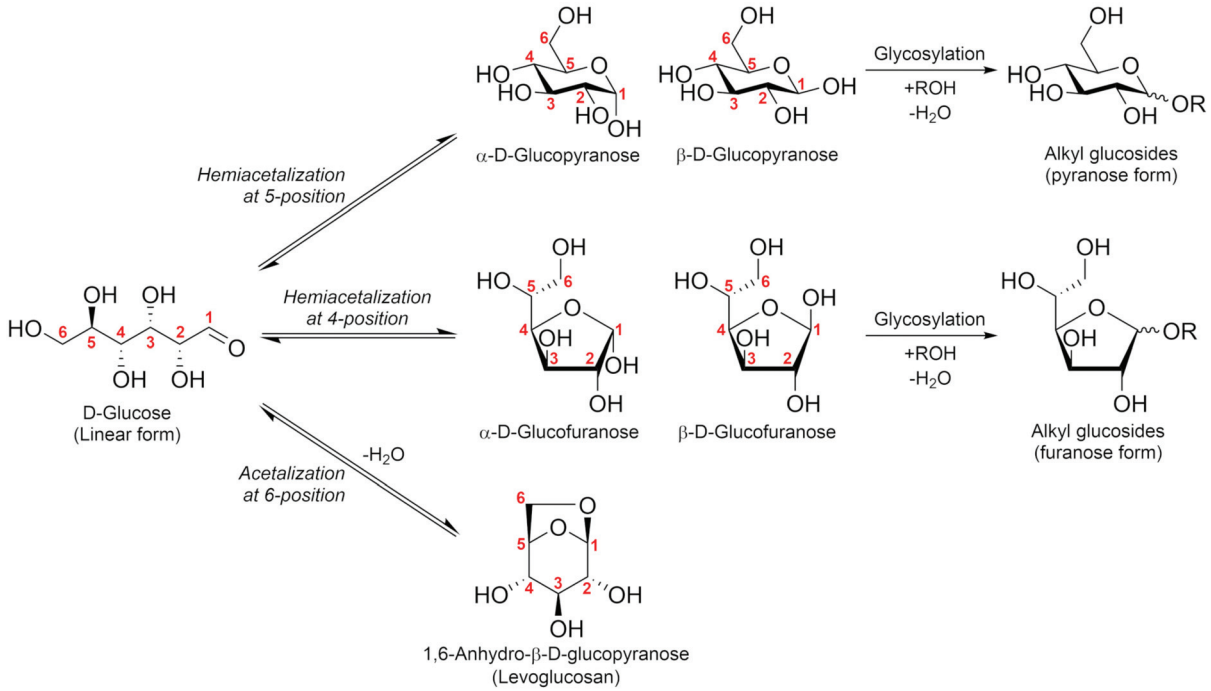


Fig. 2 Hemiacetalization and acetalization of sugar compounds, as exemplified by D-glucose.

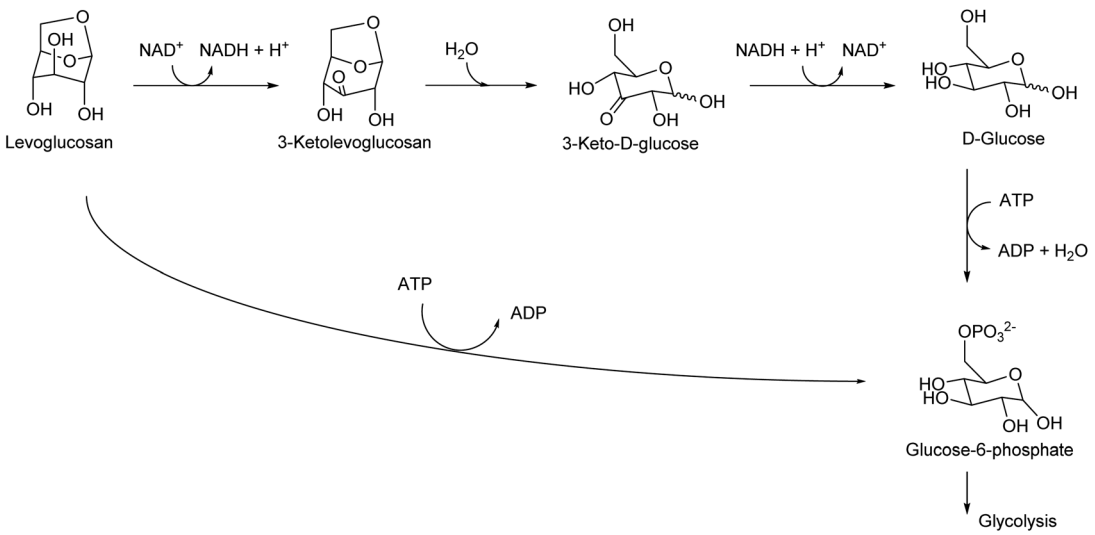


Fig. 3 Pathways of levoglucosan metabolism.

of glycols from cellulose and sugar alcohols reached over 80%, and that from levoglucosan was still significantly lower.

Levoglucosan has three OH groups, and regioselective derivatization is not easy. The selective hydrogenolysis of levoglucosan at a specific C–OH group has not yet been reported. Limited examples of the regioselective derivatization of OH groups in levoglucosan include enzymatic acylation[53] and continuous-flow benzylation over a BaO catalyst.[54] However, the products of these systems are not useful as substrates for reductive conversions. Deoxydehydration (DODH) and double-hydrodeoxygenation reactions, which have been recently attracting much attention in the reductive conversion of sugar-derived compounds and are explained later, cannot be applied to levoglucosan because both pairs of vicinal OH groups (*i.e.* 2- and 3-positions as well as 3- and 4-positions) have the *trans* configuration.

On the other hand, double-dehydration of levoglucosan over acid catalysts can selectively produce the enone product, levoglucosenone (Fig. 4). The direct production of levoglucosenone from cellulose is also possible by pyrolysis in the pres-

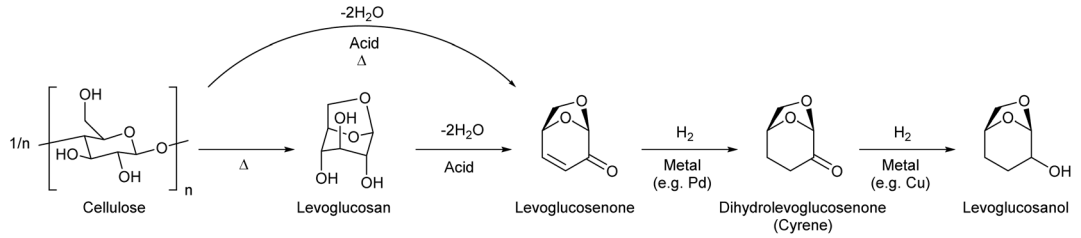


Fig. 4 Production route for levoglucosanol from cellulose.

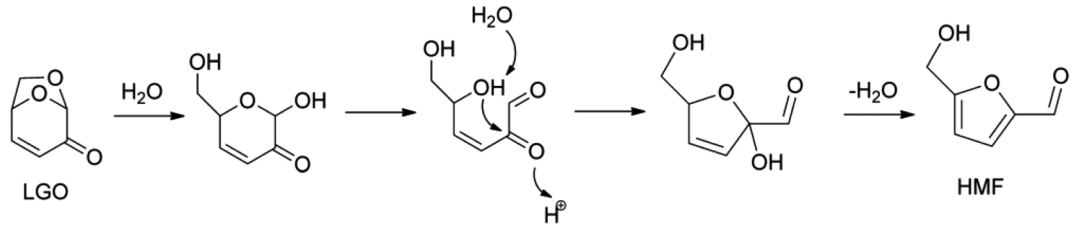


Fig. 5 Proposed mechanism for levoglucosenone (LGO) isomerization to HMF. Reprinted from ref. 60 with permission from John Wiley and Sons, copyright 2016.

ence of acid catalysts, and this reaction has been investigated intensively in recent years.[55–57] The yield of levoglucosenone from levoglucosan and cellulose reached 48% (propylsulfonic-acid-functionalized silica catalyst, 483 K)[58] and 51% (H_2SO_4 catalyst, 483 K),[59] respectively. Levoglucosenone also has potential as a platform chemical. Levoglucosenone has only one reactive functional group in each category (OH and C=C), and therefore, selective conversions of levoglucosenone are easier than those of levoglucosan.

The treatment of levoglucosenone in acidic hot water gives HMF (Fig. 5), and then HMF is hydrolyzed to levulinic acid and formic acid.[60–62] The yield of HMF was about 60%. This isomerization reaction may be regarded as an indirect synthesis of HMF from cellulose, while it is a side reaction in the conversion of levoglucosenone into another product.

The reduction of levoglucosenone first hydrogenates the C=C bond to give dihydrolevoglucosenone (Cyrene),[63] and further C=O hydrogenation gives levoglucosanol.[64–66] Cyrene has been used as a nontoxic renewable dipolar aprotic solvent. These hydrogenation reactions are not difficult and good yields (≥90%) have been reported.

Huber *et al.* have intensively investigated the hydrogenolysis of levoglucosanol. The hydrogenolysis of levoglucosanol in water over supported Pt catalysts combined with acidic components such as Pt/SiO_2–Al_2O_3 gave 1,2,5,6-hexanetetraol, which is a potential polymer precursor,[67] in excellent yield (maximum 94%; Fig. 6).[68] A more recent paper reported a slightly lower yield (*ca.* 90% selectivity at 91% conversion) with a Pt–WO_x/TiO_2 catalyst; however, the stability of this catalyst was higher than that of Pt/SiO_2–Al_2O_3.[69] 1,2,5,6-Hexanetetraol production from sorbitol by Cu-catalyzed hydrogenolysis has been reported in patents with about 40% yield.[70,71] While the overall yields from cellulose with these two routes, *via* sorbitol

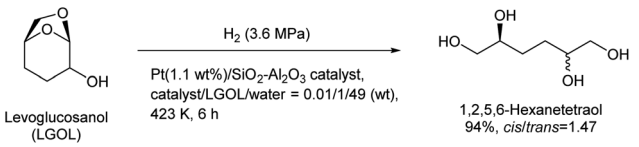


Fig. 6 Levoglucosanol hydrogenolysis in water as a solvent.[68]

and *via* levoglucosanol, are comparable, the high selectivity to 1,2,5,6-hexanetetraol in levoglucosanol hydrogenolysis can decrease the cost of separation from byproducts with high boiling points such as polyols. The hydrogenolysis of levoglucosanol in a non-water solvent produces the dehydrated form of 1,2,5,6-hexanetetraol, tetrahydrofuran-2,5-dimethanol.[72–74] Both Pd/SiO_2–Al_2O_3 and Pt/SiO_2–Al_2O_3 catalysts have been tested, and slightly higher selectivity was reported with Pt/SiO_2–Al_2O_3 (73%) (Fig. 7).[75] The main byproducts were 2-hydroxymethyltetrahydropyran-5-one and 2-hydroxymethyltetrahydropyran-5-ol. Tetrahydrofuran-2,5-dimethanol can be further converted into 1,2,6-hexanetriol and 1,6-hexanediol by selective hydrogenolysis.[76,77] Tetrahydrofuran-2,5-dimethanol and its hydrogenolysis products are also potential monomers. Tetrahydrofuran-2,5-dimethanol can also be synthesized through the total hydrogenation of HMF,[78,79] although the *cis*/*trans* ratio was different for these two methods (mostly *cis* (*ca.* 90%) by hydrogenation of HMF; mixture of similar amounts by hydrogenolysis of levoglucosanol). When searching the literature, care must be taken to note that tetrahydrofuran-2,5-dimethanol is sometimes called by other names such as 2,5-bis(hydroxymethyl) tetrahydrofuran and 2,5-dihydroxymethyltetrahydrofuran.

The mechanisms of the hydrogenolysis reactions of levoglucosanol in both water and non-water solvents have been

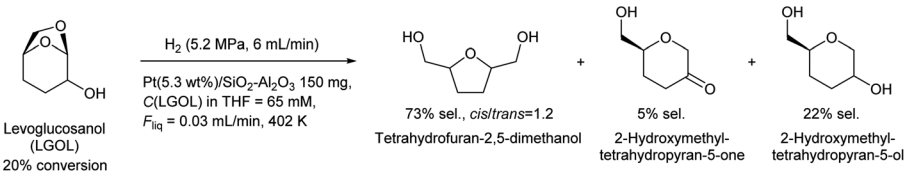


Fig. 7 Levoglucosanol hydrogenolysis in a non-water solvent.[75]

investigated in detail (Fig. 8). The reaction starts with protonation of the oxygen atom bridging the 1- and 6-positions, because of the large distortion of the 7-membered ring structure. The O–C bond at the 1-position is dissociated to produce a cationic intermediate. Dissociation at the 6-position does not occur because this dissociation would produce a less stable primary carbocation. In water as a solvent, the produced cationic intermediate quickly reacts with water to give 3,4-dideoxysugars (3,4-dideoxyglucose or 3,4-dideoxymannose, depending on the stereochemistry of the levoglucosanol substrate).[68,80] The hydrogenation of 3,4-dideoxysugars over metal catalysts gives the target product 1,2,5,6-hexanetetraol. In non-water solvents, the cationic intermediate is rearranged.[73] There are two pathways: one is hydride transfer from the 2-position to the 1-position. Subsequent deprotonation gives 2-hydroxymethyltetrahydropyran-5-one. Further hydrogenation over metal catalysts produces 2-hydroxymethyltetrahydropyran-5-ol. The other pathway is the dissociation of the C–O bond at the 5-position, which is facilitated by the oxocarbenium ion resonance state. The recombination of the carbocation at the 5-position with the OH group at the 2-position produces a tetrahydrofuran ring. Further deprotonation and hydrogenation give tetrahydrofuran-2,5-dimethanol.

The catalyst for levoglucosanol hydrogenolysis is bifunctional: it has Brønsted acidity to activate the C–O bond and a noble metal surface to hydrogenate the unsaturated bond(s). This combination, as exemplified by Pt/SiO_2–Al_2O_3 and metal/acidic zeolite, is also the most typical class of catalysts in many C–O hydrogenolysis reactions.[81,82] Although it is difficult to change largely the selectivity pattern of the main reaction paths over these catalysts, tuning the acidity appropriately as well as selecting the reaction conditions can control undesirable side reactions derived from the unsaturated intermediates.

Selective functionalization and C–C bond formation of levoglucosenone and its hydrogenation product, Cyrene, are possible. In particular, elongation of the carbon framework by C–C bond formation can enlarge the scope of the products. Useful reactions for C–C bond formation include the Michael addition[83] and the Diels–Alder reaction[84,85] of levoglucosenone at the electron-deficient C=C moiety and the condensation of Cyrene with another Cyrene molecule or an aldehyde (Fig. 9).[86] The products of these reactions can be used as intermediates in the syntheses of fine chemicals and as the substrates of total hydrodeoxygenation toward branched hydrocarbons, which can be blended into aviation fuel.[87]

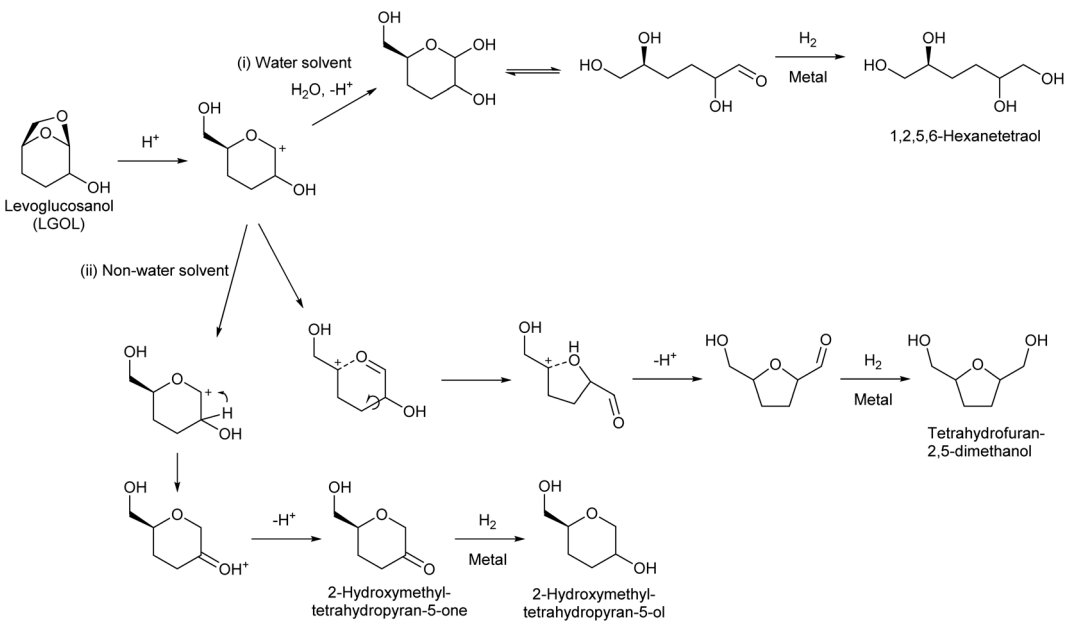


Fig. 8 Reaction routes for levoglucosanol hydrogenolysis.

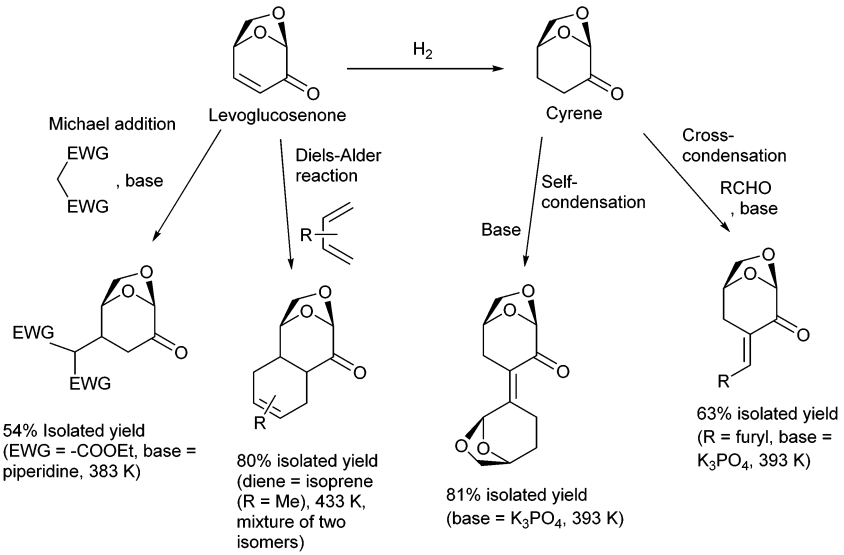


Fig. 9 C–C bond formation reactions on levoglucosenone and Cyrene.[83,84,86]

As described above, the hydrogenolysis of levoglucosan/levoglucosenone and their derivatives with the same bicyclic structure can convert them into various products; however, most of them can also be synthesized from sugars *via* other methods starting from sorbitol and HMF. Levoglucosan and levoglucosenone are cellulose-derived molecules, and the amount of hydrogen consumed in the total reaction routes involving levoglucosan or levoglucosenone as an intermediate is the same as that required for other routes to the same target from sugars. The answer to the question of which route is more competitive depends on the yield of each step and the energy consumption, especially during separation. Generally, the levoglucosan/levoglucosenone-based routes have an advantage in view of the separation cost because of the lower polarity than sugars and sugar alcohols and the high thermal stability. Improvement of the product yield is necessary for both steps of levoglucosan/levoglucosene production and their conversion.

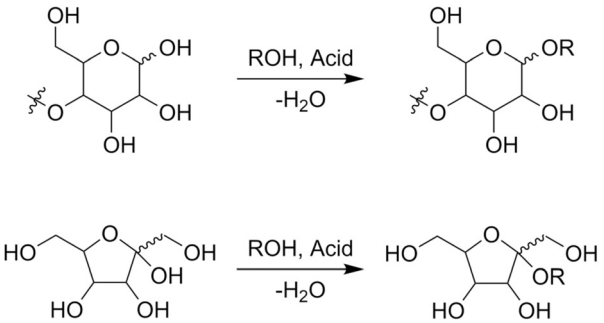


Fig. 10 Fischer glycosylation of sugars to alkyl glycosides, as exemplified by (poly)aldohexopyranose (upper) and ketohexofuranose (lower).

3. Alkyl glycosides

3.1. Production of alkyl glycosides

Alkyl glycosides are acetal compounds that are synthesized from sugars and alcohols and have been used as non-ionic, biodegradable, and environmentally benign surfactants due to their hydrophilic and hydrophobic properties resulting from sugar and alkyl moieties, respectively.[88,89] The worldwide market for natural surfactants, which include alkyl glycosides, was 18.16 billion USD in 2020 and is projected to grow to 24.78 billion USD in 2028.[90] The traditional approach for synthesizing alkyl glycosides is known as Fischer glycosylation (also called Fischer glycosidation, Fig. 10), where a sugar compound is reacted directly with an alcohol (used as both a solvent and reactant).[91] Hydrochloric acid is a classical catalyst for Fischer glycosylation,[91] and other homogeneous strong acids including trifluoromethanesulfonic acid[92] and dodecylbenzenesulfonic acid[93] are also effective for this type of glycosylation. Besides, to improve the reusability of catalysts and/or efficiency of the reaction, heterogeneous catalysts such as sulfuric acid immobilized on silica,[94] silica-alumina,[95] strongly acidic resin,[96] and sulfonated mesoporous carbons[97] as well as microwave-assisted reaction systems[96] have been developed thus far. In all cases, a mixture of α- and β-anomers is obtained, and their molar ratio is dependent on the class of alcohols and heating methods (*i.e.*, typical heating in an oil bath and microwave irradiation). Instead of a leaving group in the Fischer glycosylation (*i.e.* hydroxide), more reactive leaving groups as exemplified by bromide and chloride (Koenigs–Knorr glycosylation),[98] fluoride (Mukaiyama–Suzuki glycosylation),[99–101] and trichloroimidate (Schmidt glycosylation)[102] have also been used in the field of organic chemistry to synthesize a variety of glycosides with precisely designed molecular structures.[103] For these types of glycosylation, heavy metal salts consisting of Ag, Hg, and Sn play key roles as Lewis

acidic activators toward such leaving groups.[104,105] From the viewpoints of ease of operation and unnecessity of harmful heavy metals, among the glycosylation techniques described above, Fischer glycosylation is a more practically applicable means especially in the large-scale production of alkyl glycosides. The combination with epimerization of naturally abundant sugars should pave the way to using naturally rare or even inaccessible sugar-based alkyl glycosides.

Another possible approach for synthesizing alkyl glycosides is the alcoholysis of oligo- and poly-saccharides. In this type of reaction, *O*-glycosidic bonds originally present in such saccharides are cleaved and alkoxide species then attack oxocarbenium ions, which are intermediate species typically found in a variety of glycosylation reactions,[106] to form alkyl glycosides. The most attractive substance for alcoholysis is cellulose, which is a polymer of glucose linked by β-1,4-glycosidic bonds, and this polysaccharide was converted in various alcohols with 1–12 carbon atom(s) into the corresponding alkyl glucosides (Fig. 11). Similar to the hydrolysis of cellulose in water,[107–110] alcoholysis is also accelerated in the presence of acid catalysts such as heteropolyacids,[111] sulfonated carbon,[112] and mesoporous zeolite.[113] Likewise, the combination of acid catalysts and ionic liquids, the latter of which are effective for improving the reactivity of cellulose, has achieved outstanding yields of alkyl glucosides;[114–116] for example, a hydrophobic and acidic bifunctional ionic liquid produced 93.1% yield of methyl glucosides including both α- and β-anomers from ball-milled cellulose (*i.e.*, amorphous cellulose) at 413 K for 4 h.[115] Jérôme *et al.* reported that after the sulfuric acid-assisted mechanochemical reaction of cellulose induced by ball-milling, which was the same procedure first reported for cellulose hydrolysis,[117–119] the resulting cello-oligosaccharides were easily converted in 1-butanol into *n*-butyl glucosides in 70% yield at a relatively low temperature of 390 K for 3 h.[120] Such mild alcoholysis conditions are favorable for the production of desired alkyl glucosides, since under harsh conditions in the presence of acids, alkyl glucosides undergo further transformation into 5-alkoxymethylfurfural and alkyl levulinate.[121,122] The direct production of alkyl glycosides *via* alcoholysis has also been reported for other poly- or oligo-saccharides such as starch,[123,124] which consists of glucose linked by α-1,4-glycosidic bonds and is known to undergo depolymerization more easily than cellulose,[108] and mannotetraose,[125] which is a tetramer of mannose connected by β-1,4-glycosidic bonds and a model compound of naturally occurring β-mannan. For the alcoholysis of starch, sub-critical alcohols, methanol[124] and isooctyl alcohol,[123] were applied to the synthesis of methyl glucosides and isooctyl glucosides, respectively; these reactions proceeded without any catalysts, because of the high reactivity of both starch and sub-critical alcohols. In the case of mannotetraose, β-mannase from *Trichoderma reesei*, which is a hydrolase for β-1,4-glycosidic bonds in β-mannan, was employed in 1-hexanol.[125] This enzyme cleaved the glycosidic bonds in mannotetraose partially to produce *n*-hexyl mannobioside and *n*-hexyl mannotrioside, but the yield of the former product was at most 1.9% (the yield of the

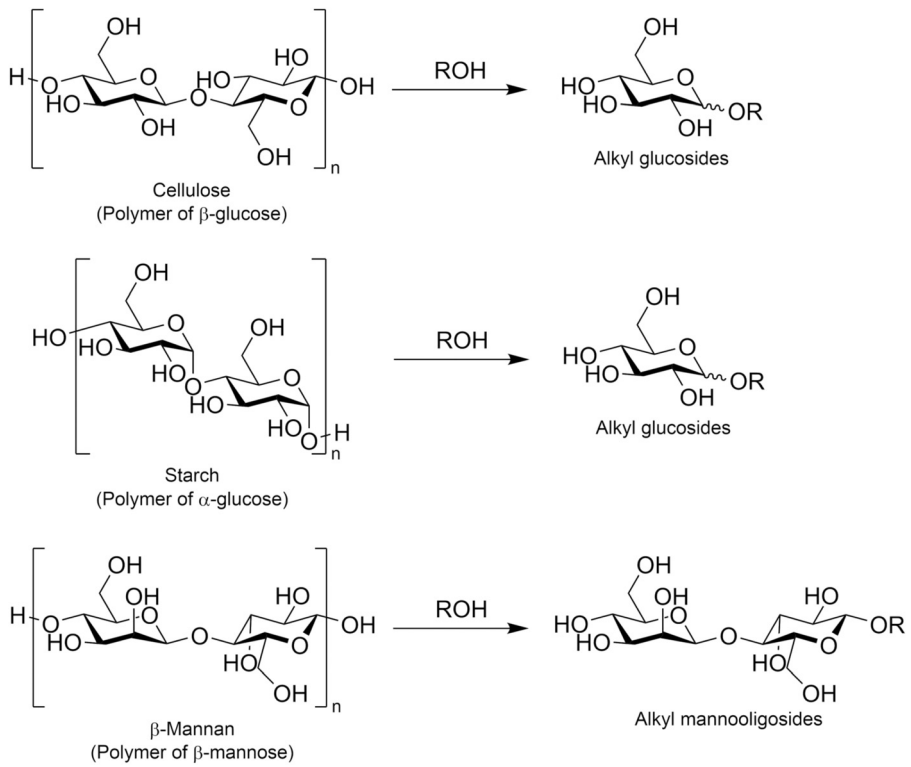


Fig. 11 Alcoholysis of polysaccharides to alkyl glycosides.

latter product was not reported in the cited reference). As described here, the variation of poly- and oligo-saccharides investigated as substrates for alcoholysis has been limited thus far, yet these examples imply the possibility of the alcoholysis of other naturally occurring poly- and oligo-saccharides to produce a variety of alkyl glycosides.

3.2. Single-hydrodeoxygenation of related substrates

There are a variety of advantages of the hydrodeoxygenation of alkyl glycosides compared to that of monosaccharides. In the case of monosaccharides, the hydrogenation of monosaccharides into the corresponding sugar alcohols readily proceeds; this means that the hydrodeoxygenation of monosaccharides provides very similar results to that of the corresponding sugar alcohols. In addition, monosaccharides have high reactivity due to the presence of formyl or carbonyl groups in their structure. These highly reactive groups are protected almost completely in alkyl glycosides, which leads to the suppression of side reactions and high selectivity to the target product in the case of alkyl glycosides. Another advantage is due to maintaining the ring structure in alkyl glycosides; the well-organized geometry (*cis*, *trans*) of OH groups and other substituents in the ring structure is beneficial for selective transformation. In contrast, once the deprotection of ring-structural alkyl glycosides (*i.e.*, hydrolysis of alkoxy group) proceeds to form sugars and/or sugar alcohols, subsequent epimerization, hydrogenation, or dehydrogenation occurs easily over a suitable catalyst.[126]

Monodeoxysugars and dideoxysugars are typical target products for the hydrodeoxygenation of alkyl glycosides. This is because mono- and dideoxy-sugars occupy the core structure of natural products and are important intermediates for the synthesis of rare sugars,[127] medicines (*e.g.*, antibiotics and antitumor agents),[128,129] and insecticides.[130] In addition, the alkyl monodeoxy/dideoxy glycosides can be further converted into the corresponding partially deoxygenated chiral acyclic polyols with high yield and high stereoselectivity; these compounds can be used for the production of fine chemicals (*e.g.*, cosmetics, food additives, and surfactants) and polymers (*e.g.*, alkyd resins, polyurethanes, and polyesters) due to their stereochemistry and multiple functional groups. One problem in the synthesis of monodeoxy- and dideoxy-sugars is the high *E*-factor of the overall process containing multi-step reactions, a variety of reagents, and protection and deprotection of functional groups.[131–133] Therefore, environmentally benign synthesis methods should be developed, and one promising means is the hydrodeoxygenation of alkyl glycosides.

Generally speaking, the reaction temperature for hydrodeoxygenation is comparable to or higher than 373 K, and the stability of alkyl glycosides at this temperature enables their selective transformation into the desired products. Yet, the development of highly active hydrodeoxygenation catalysts that can work at lower reaction temperatures is always desired.

A variety of catalysts have been proposed for the hydrodeoxygenation of polyols and other substrates, as mentioned later, while the application of such catalysts to the hydrodeoxygenation of other substrates is not easy. The Ir–ReO_x and Pt–WO_x catalysts, which are typical hydrodeoxygenation catalysts that have been developed mainly for glycerol hydrogenolysis, exhibited a high catalytic performance in aqueous solutions.[134,135] However, water is not a suitable solvent for the hydrodeoxygenation of alkyl glycosides because the alkoxy group (RO–) in alkyl glycosides is readily hydrolyzed to the hydroxy group (HO–) in water, resulting in the opening of their ring structure to cause hydrogenation of the formyl group. Yet, the electron-withdrawing nature of the –OH group at the 2-position on the ring destabilizes the carbocation transition state and results in the low reactivity of alkyl glycosides toward hydrolysis.[136] These could be the reasons for the lack of reports on the hydrodeoxygenation of alkyl glycosides to the corresponding monodeoxysugars using the developed hydrodeoxygenation catalysts and H_2 reductant. Therefore, in section S1 (ESI†), we mentioned the reported results on the hydrodeoxygenation of model diols with cyclic structures.

3.3. Double-hydrodeoxygenation of alkyl glycosides with *cis*-vicinal OH groups

Double-hydrodeoxygenation of alkyl glycosides is easier than single-hydrodeoxygenation when the alkyl glycosides possess *cis*-vicinal OH groups because there is an effective reaction for the removal of *cis*-vicinal OH groups, deoxydehydration (DODH). Various catalysts and reductants have been proposed for DODH and there are many good review papers that summarize general DODH reactions.[137–143] In this review, we focus on cases using H_2 as a reductant. The general scheme of DODH with H_2 reductant is shown in Fig. 12, and the reported catalysts for this type of reaction are ReO_x–Au/CeO_2,[144–146] ReO_x–Ag/CeO_2,[147] MoO_x–Au/TiO_2,[148] ReO_x/C,[149] and CH_3ReO_3.[150] Most of these catalysts are bimetallic. In these bimetallic catalysts, the role of added metal (Au and Ag) is the activation of H_2 molecules to reduce DODH-active species such as Re and Mo. In the case of Au- and Ag-added catalysts, DODH products (alkenes) become major products since the consecutive hydrogenation of C=C in DODH products does not proceed over Au[144–146] or Ag.[147] In contrast, ReO_x–Pd/CeO_2 catalysts, in which Pd species have the same role as Au and Ag to reduce Re, gave the saturated products through the high hydrogenation activity of Pd.[151–154] This reaction system is called "DODH + hydrogenation", and the reaction scheme is shown in Fig. 13. The overall reaction for DODH + hydrogenation is regarded as simultaneous hydrodeoxygenation of vicinal OH groups, which is called double-hydrodeoxygenation in this review.

It is known that DODH is catalyzed by homogeneous Re and Mo complexes with high valence states, and the reaction

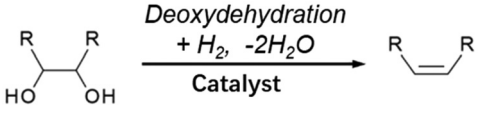


Fig. 12 Generalized scheme for DODH with H_2 reductant.

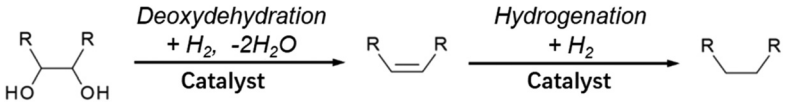


Fig. 13 Generalized scheme for DODH + hydrogenation (double-hydrodeoxygenation) with H_2 reductant.

proceeds by the redox cycle between the higher valent species (Re^{7+} and Mo^{6+}) and lower valent ones (Re^{5+} and Mo^{4+}). An important point is that typical reductants are secondary alcohols and triphenylphosphine, and H_2 cannot be used with these homogeneous catalysts. It is characteristic that the reported heterogeneous DODH catalysts such as ReO_x–Au/CeO_2, ReO_x–Ag/CeO_2, MoO_x–Au/TiO_2, and ReO_x–Pd/CeO_2 enable the use of H_2 reductant. Based on characterization of the catalyst and the dependence of the Re loading amount on the catalytic performance, it has been proposed that monomeric Re species on CeO_2 were the active sites for DODH. The catalytic cycles for DODH on heterogeneous Re species on CeO_2 and homogeneous Re species are illustrated in Fig. 14. All the steps in Fig. 14 do not require acids, and therefore, the use of strong acids, which may lead to side reactions, can be avoided in DODH (+hydrogenation). DODH systems do not need water as a solvent (rather, water generally retards DODH reactions significantly), and many organic solvents such as hydrocarbons, ethers, and alcohols can be used, enabling the conversion of a wide range of substrates.

Another important feature of the DODH of cyclic vicinal diols is the much higher reactivity of *cis*-vicinal diols than that of *trans*-vicinal diols. The reactivity tendency of *cis*- and *trans*-vicinal diols can be explained by the stability of the DODH products, as illustrated in Fig. 15, where the DODH of 1,2-cyclohexanediols is used as a model reaction. The reactivity difference between *cis*- and *trans*-vicinal OH groups in DODH is very useful for the selective transformation of methyl glycosides. Alkyl glucoside, whose availability is the highest among alkyl glycosides, contains only *trans*-vicinal OH groups, and unfortunately, it has very low reactivity in DODH. In contrast, the DODH of alkyl glycosides with *cis*-vicinal OH groups is possible. In particular, the combination of ReO_x–M/CeO_2 (M = Pd, Ag, and Au) catalysts with H_2 reductant enhances the DODH activity and decreases the reaction temperature, which allows the application of ReO_x–M/CeO_2 (M = Pd,[156,157] Ag,[147] and Au[146]) to the DODH of methyl glycosides with *cis*-vicinal OH groups.

Table 2 lists the results for the DODH (+hydrogenation) of several methyl glycosides with *cis*-vicinal OH groups using ReO_x–M/CeO_2 (M = Pd, Au, and Ag) catalysts and H_2 reductant. It is demonstrated that the corresponding saturated and unsaturated dideoxy-products are synthesized in high yields in one step using suitable catalysts and H_2 reductant. Generally speaking, the protection and deprotection of OH groups are required for the transformation of specific OH groups of sugars. In contrast, the present method relying on DODH does not need the protection or deprotection of OH groups. The highly selective conversion of methyl glycosides with *cis*-vicinal OH groups in Table 2 is due to the selective recognition of *cis*-vicinal OH groups as illustrated in Fig. 16.

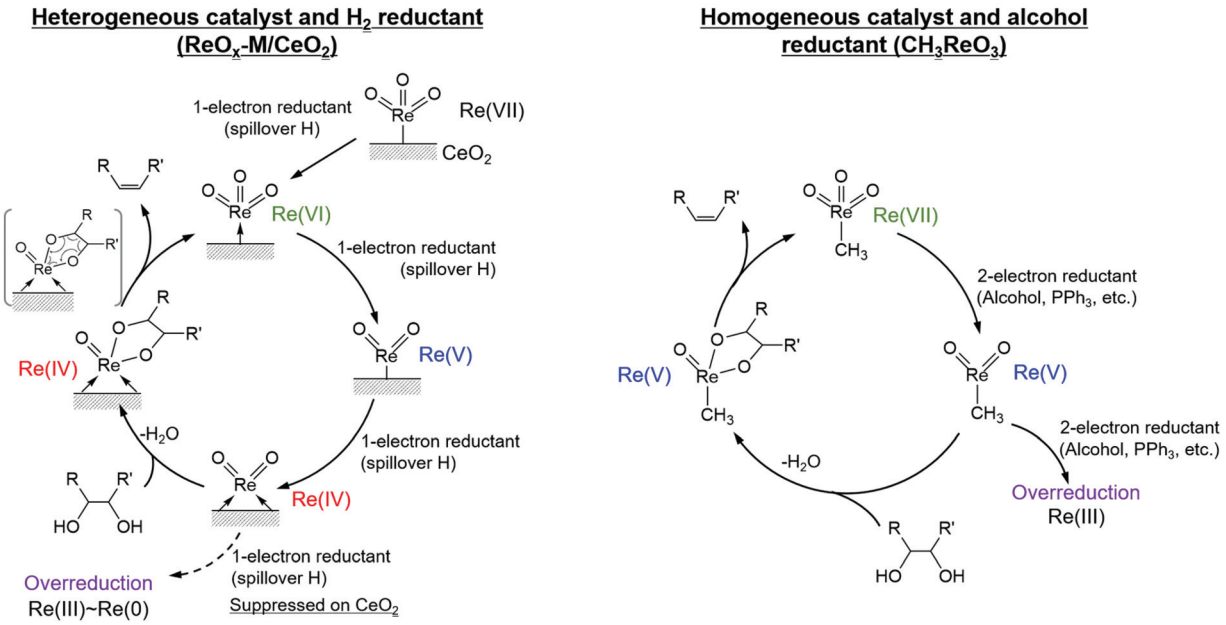


Fig. 14 Catalytic cycles for DODH on heterogeneous Re on CeO_2 and homogeneous Re species. Reproduced from ref. 155 with permission from Elsevier, copyright 2020.

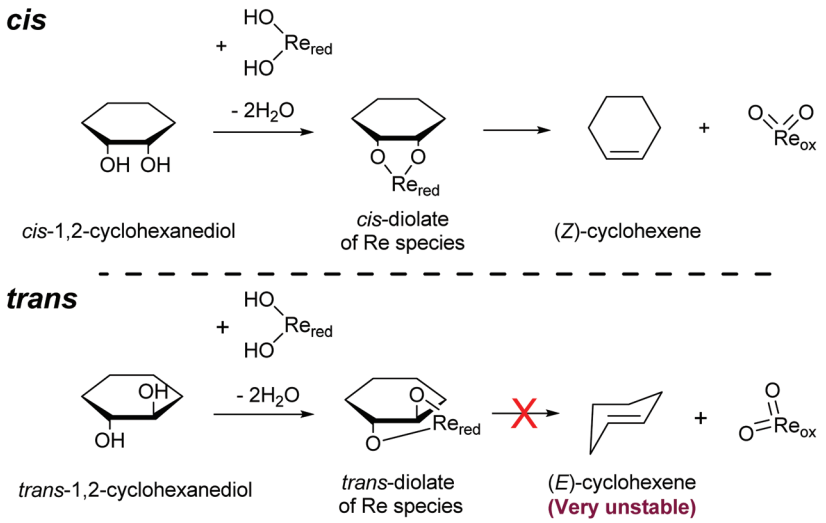


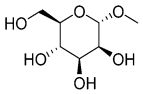
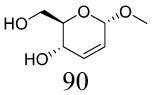
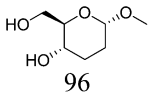
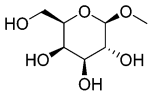
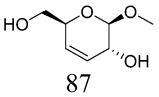
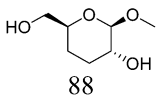
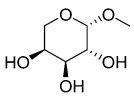
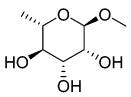
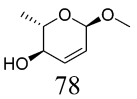
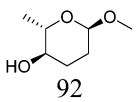
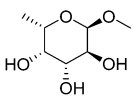
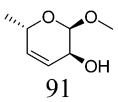
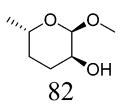
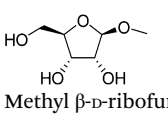
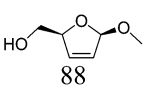
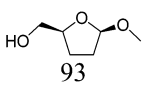
Fig. 15 DODH of *cis*- and *trans*-1,2-cyclohexanediols.

In addition, the obtained saturated dideoxy methyl glycosides can be further converted into valuable chiral acyclic polyols *via* hydrolysis of the methoxy moiety and hydrogenation steps (Fig. 17). (2*S*)-1,2,5-Pentanetriol was obtained from methyl β-D-ribofuranoside in a yield of 97% with 95% ee through a one-pot two-step reaction over ReO_x–Pd/CeO_2 as the common catalyst for both steps.[156] Meanwhile, the DODH by the same ReO_x–Pd/CeO_2 catalyst and subsequent transformation over Rh–ReO_x/SiO_2 produced (2*R*)-1,2,5-pentanetriol from methyl β-L-arabinopyranoside in a yield of 95% with 95% ee. Moreover, the hexane-tetraols and -triols with fixed OH group positions and stereochemistry could be obtained over Pt-based catalysts (Pt/SiO_2 or Pt/SiO_2–Al_2O_3) in 77–95% yield with >92% diastereoselectivity from the synthesized saturated dideoxy methyl glycosides.[136]

Based on data for catalyst amounts and reaction times in Table 2, it is expected that the reactivity would be different for different substrates. Therefore, the reactivity of the substrates was compared on the basis of the results of reaction rate measurements for the DODH + hydrogenation of 6-membered ring methyl glycosides with *cis*-vicinal OH groups on ReO_x–Pd/CeO_2 as listed in Table 3. The obtained reaction orders with respect to substrate concentration and H_2 pressure are also listed in Table 3. Both reaction orders with respect to the substrate concentration and H_2 pressure in the DODH + hydrogenation on ReO_x–Pd/CeO_2 were almost zero in all cases, suggesting that the reaction mechanism for the DODH + hydrogenation was the same. The DODH of the diolate formed from the substrate and ReO_x species was the rate-determining step and the coverage of the catalytic active sites by diol molecules was close to the saturation level. Therefore, the reactivity difference cannot be explained by the difference in the reaction mechanism and/or the rate-determining step. More reactive methyl glycosides commonly have substituents juxtaposed to *cis*-vicinal OH groups on the opposite side, and less reactive methyl glycosides have substituents neighboring *cis*-vicinal OH groups on the same side. A detailed comparison was carried out by using more reactive methyl α-L-rhamnopyranoside and less reactive methyl α-L-fucopyranoside. The apparent activation energies of the reaction of methyl α-L-rhamnopyranoside and methyl α-L-fucopyranoside were found to be 63 and 73 kJ mol^{-1}, respectively. The adsorption and transition states of these two methyl glycosides were also analyzed by density functional theory (DFT) calculations, and the results are shown in Fig. 18. The energy difference between these two substrates at their transition states was about 10 kJ mol^{-1}, which agreed well with the difference in the experimentally obtained activation energies. In contrast, the energy difference at the adsorbed states was much smaller. The energy difference at the transition states can be explained by steric hindrance, as illustrated in Fig. 19. The angles between the substituent neighboring *cis*-vicinal OH groups and C–OH in the *cis*-vicinal OH groups in the Re diolate from methyl α-L-rhamnopyranoside at the transition state were calculated to be 72.4° and 155.8°, while the angles in the case of Re diolate from methyl α-L-fucopyranoside were 37.6° and 73.7°. It is clear that the angles are wider for methyl α-L-rhamnopyranoside than methyl α-L-fucopyranoside, meaning that less steric hindrance gives a lower energy at the transition state.

Compared to conventional organochemical approaches described roughly in section 3.2, one-pot DODH + hydrogenation using heterogeneous catalysts is a more useful and environmentally benign means of synthesizing dideoxysugars from alkyl glycosides. The use of hydrogen as a reducing agent in the synthesis of dideoxysugars is favorable in terms of the reagent cost and atom efficiency, which are especially important in the chemical industry operating on a large scale, while the use of high-pressure H_2 is a barrier to laboratory-scale syntheses. Considering that dideoxysugars are fine chemicals, expanding the scope of the reducing agents may have merit. The use of homogeneous catalysts may also be acceptable in the synthesis of fine chemicals, although the turnover number

Table 2 DODH (+hydrogenation) of methyl glycosides with *cis*-vicinal OH groups using ReO_x–M/CeO_2 catalysts and H_2 reductant[147,152,156]

					Main product yield [%]	
Entry	Substrate	Catalyst [amount per g]	t [h]	Conv. [%]	DODH product	Dideoxy product
1[a]		ReO_x–Au/CeO_2 (0.50)	8	99	 90	
2[b]	Methyl α-D-mannopyranoside	ReO_x–Pd/CeO_2 (0.15)	51	99		 96
3[a]		ReO_x–Au/CeO_2 (0.50)	48	>99	 87	
4[b]	Methyl β-D-galactopyranoside	ReO_x–Pd/CeO_2 (0.30)	72	94		 88
5[a]		ReO_x–Au/CeO_2 (0.50)	8	97	 90	
6[b]	Methyl β-L-arabinopyranoside	ReO_x–Pd/CeO_2 (0.15)	72	>99		 93
7[a]		ReO_x–Au/CeO_2 (0.50)	16	93	 78	
8[b]	Methyl α-L-rhamnopyranoside	ReO_x–Pd/CeO_2 (0.15)	36	>99		 92
9[c]		ReO_x–Ag/CeO_2 (1.00)	20	94	 91	
10[b]	Methyl α-L-fucopyranoside	ReO_x–Pd/CeO_2 (0.45)	95	97		 82
11[c]		ReO_x–Ag/CeO_2 (0.25)	10	99	 88	
12[b]	Methyl β-D-ribofuranoside	ReO_x–Pd/CeO_2 (0.10)	24	>99		 93

Reaction conditions: methyl glycoside (1.29 mmol), 1,4-dioxane (10 g), 413 K. [a] ReO_x–$^{dp}Au^{0.3}$/CeO_2 (1 wt% Re, Au/Re = 0.3, prepared *via* deposition precipitation method), H_2 (1.7 MPa) (at 413 K). [b] ReO_x–Pd/CeO_2 (2 wt% Re, Pd/Re = 0.25), H_2 (8.0 MPa) (at 413 K). [c] ReO_x–Ag/CeO_2 (1 wt% Re, Ag/Re = 0.3).

(TON) of typical homogeneous DODH catalyst systems is not large (<10^2) especially when using an inexpensive reducing agent such as simple secondary alcohols and H_2.[138] Meanwhile, the substrate scope is an apparent issue: it is limited to sugars (and sugar derivatives) that possess *cis*-vicinal diols in their structure. This fact means that the most common naturally occurring monosaccharide, glucose, cannot be transformed into dideoxysugars due to the lack of a *cis*-vicinal diol structure. In this respect, different types of reaction that enable epimerization of glucose to access rare sugars containing a *cis*-vicinal diol are necessary. Mannose has been reported to be synthesized from glucose directly *via* epimerization by Mo-based catalysts[158,159] and Sn-beta zeolites,[160,161] while other rare sugars are difficult to produce from glucose except for biochemical methods using epimerase. In order to make DODH + hydrogenation more useful and attractive,

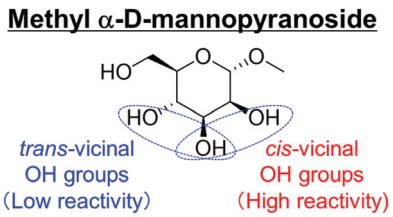


Fig. 16 Reactive *cis*- and unreactive *trans*-vicinal OH groups of methyl α-D-mannopyranoside in DODH.

highly efficient chemical techniques, which have been very limited thus far,[162,163] need to be devised.

4. Glucaric acid and mucic acid

Glucaric acid is the most popular aldaric acid (aldose-derived dicarboxylic acid), an oxidized derivative of glucose. Glucaric acid has been industrially manufactured on the order of 10^4 t per year and used for a number of purposes such as a food additive and a corrosion inhibitor.[164] Glucaric acid was selected for the "Top 12" in the DOE report in 2004 (see Table 1).[4] The expected utilization of glucaric acid is as a monomer of polyamides and polyesters. However, because of "limited research activity" in the utilization of glucaric acid, it was not selected for the revised 2010 list.[5]

Aldaric acids including glucaric acid are generally synthesized by nitric acid oxidation of the corresponding sugars. Modest yields (40–45%) of glucaric acid are obtained.[165,166] Catalytic oxidation with molecular oxygen is preferable to traditional nitric acid oxidation. An excess amount of base is frequently added to the oxidation systems for sugars and sugar alcohols;[167] however, neutralization is necessary to obtain the free acid, leaving a large amount of salt. Therefore, base-free systems are preferable. Up to about 70% yield of glucaric acid through the base-free catalytic oxidation of glucose with O_2 was reported in the literature.[168–170] It is generally energy-consuming to separate sugar acids from an aqueous reaction mixture containing various compounds with high boiling points. Biocatalytic, electrocatalytic and photocatalytic oxidation systems have also been investigated;[166,171] however, these systems tend to be energy consuming. Energy consumption should be carefully assessed for the practical application of any systems.

The recent development of the deoxydehydration (DODH) reaction has again shed light on the use of glucaric acid as a source of chemicals. DODH of glucaric acid produces *cis*,*trans*-muconic acid (2,4-hexadienedioic acid). The most stable isomer of muconic acid (*trans*,*trans*) is also produced.[172] The hydrogenation of muconic acids produces adipic acid, which is a very important monomer for a polyamide, 6,6-nylon, in industry.[173] Currently, adipic acid is manufactured by the hydrogenation of petroleum-derived benzene and subsequent stepwise oxidations. The final step of adipic acid manufacture

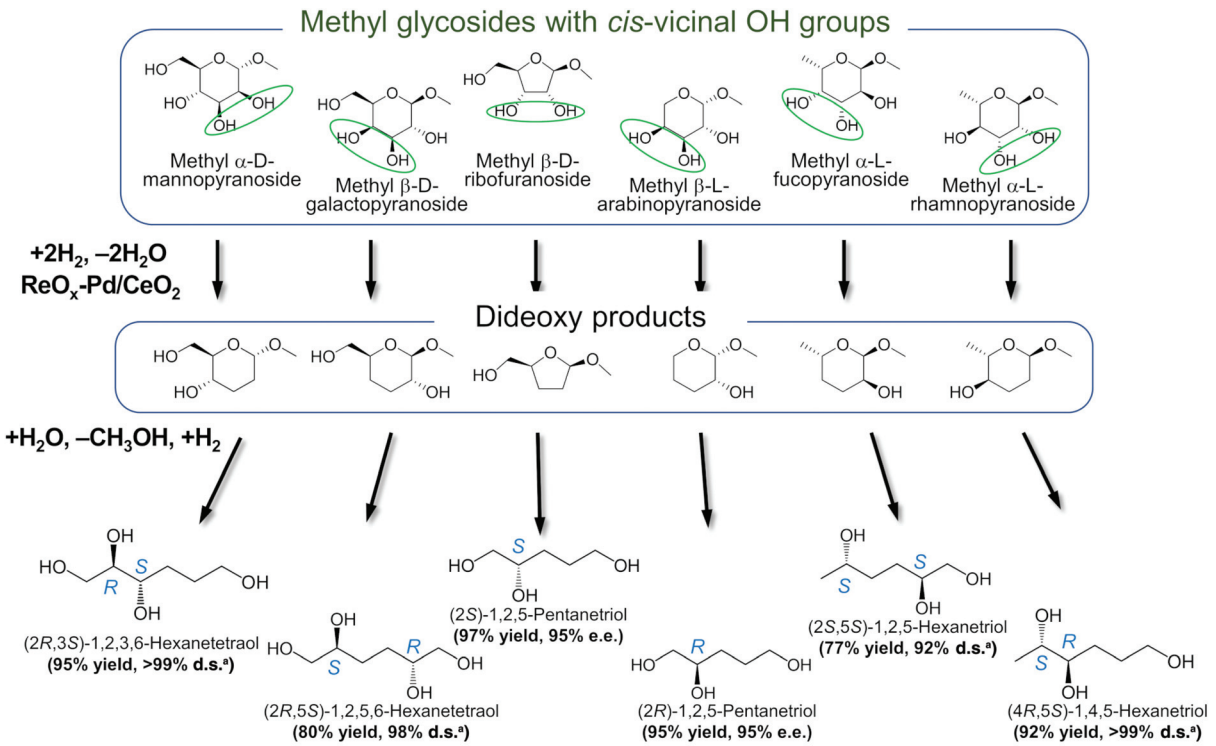
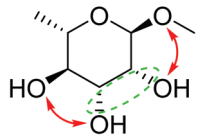
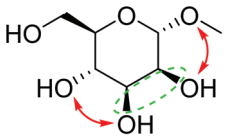
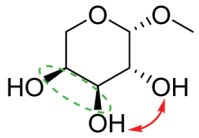
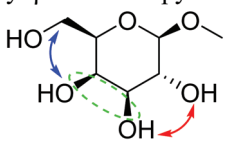
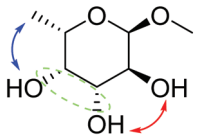


Fig. 17 Conversion of methyl glycosides into chiral pentanetriols, hexanetriols, and hexanetetraols.[136,156] [a] Diastereoselectivity measured by ^{13}C NMR.

Table 3 Results of reaction rate measurements for the DODH + hydrogenation of 6-membered ring methyl glycosides with *cis*-vicinal OH groups on ReO_x–Pd/CeO_2 [146]

Entry	Substrate	Reaction rate [mmol g_{cat}^{-1} h^{-1}]	Reaction order	
			Concentration	H_2 pressure
1	 Methyl α-L-rhamnopyranoside	1.9	0.1	0.2
2	 Methyl α-D-mannopyranoside	1.7	−0.1	0.3
3	 Methyl β-L-arabinopyranoside	1.7	0.0	0.2
4	 Methyl β-D-galactopyranoside	0.73	−0.1	0.2
5	 Methyl α-L-fucopyranoside	0.38	0.0	0.3

Reaction conditions: ReO_x–Pd/CeO_2 catalyst (0.15 g) (Re = 2 wt%, Pd/Re = 0.25), substrate (1.3 mmol), 1,4-dioxane (10 g), 7.7 MPa H_2 at 413 K (initial 1.0 MPa H_2 at r.t.), 413 K. Red arrows: opposite direction between the functional group and its adjacent *cis*-vicinal OH group, blue arrows: same direction between the functional group and its adjacent *cis*-vicinal OH groups.

uses nitric acid. The manufacture of adipic acid has low atom efficiency in the overall process, and an efficient synthesis method for adipic acid from renewable resources is highly desirable.

Reports on the DODH of glucaric acid and its related reactions are summarized in Table 4. Examples of the DODH of glucaric acid are rather limited, and the DODH of mucic acid (galactaric acid), which is the galactose-derived aldaric acid, is more frequently carried out. The product of the DODH of mucic acid is *trans*,*trans*-muconic acid, which is the most stable isomer. Mucic acid is more reactive in DODH than glucaric acid[172,174] probably because of the higher stability of the DODH product. Typical systems used a homogeneous Re catalyst and an alcohol as both a reductant and solvent.[172,175–182] Because of the excess use of alcohol, the product is usually obtained in the form of an ester. A one-pot system using the combination of a DODH catalyst (Re) + alcohol and hydrogenation catalyst + H_2 to directly obtain adipic acid from aldaric acids was also reported.[174,183,184] Bimetallic solid catalysts containing both Re and a noble metal for hydrogenation have been reported recently.[185,186] Considering that adipic acid is a bulk chemical, it is also better to use H_2 as a reducing agent in the DODH step. However, the use of H_2 as a reducing agent for the DODH of aldaric acids is difficult; the ReO_x–M/CeO_2 system mentioned in the previous section does not work probably because of the strong adsorption of the carboxylate group on the basic CeO_2 surface. Toste *et al.* reported the production of adipic acid from glucarodilactone, where the OH groups at the 3- and 4-positions in glucaric acid are condensed with the carboxylic groups at the 6- and 1-positions, respectively, by DODH + hydrogenation with H_2 as a reducing agent.[183] This system used water as a solvent, which generally retards DODH reactions significantly, although a large amount of catalyst and additives such as active carbon were necessary. The TONs of all the reported systems for the DODH of aldaric acid or its ester were still low. As another approach, the hydrodeoxygenation of glucaric acid using a large amount of halogen ions, where nucleophilic substitution of an alcohol with a halogen

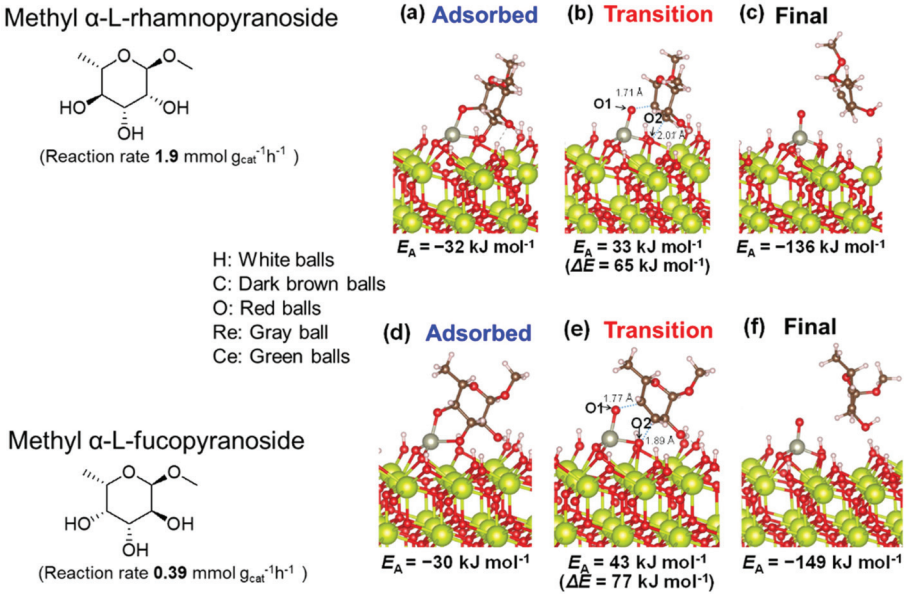


Fig. 18 DFT calculations of the adsorption and transition states of the DODH of methyl α-L-rhamnopyranoside and methyl α-L-fucopyranoside on ReO_x/CeO_2(111). Reproduced from ref. 157 with permission from the American Chemical Society, copyright 2020.

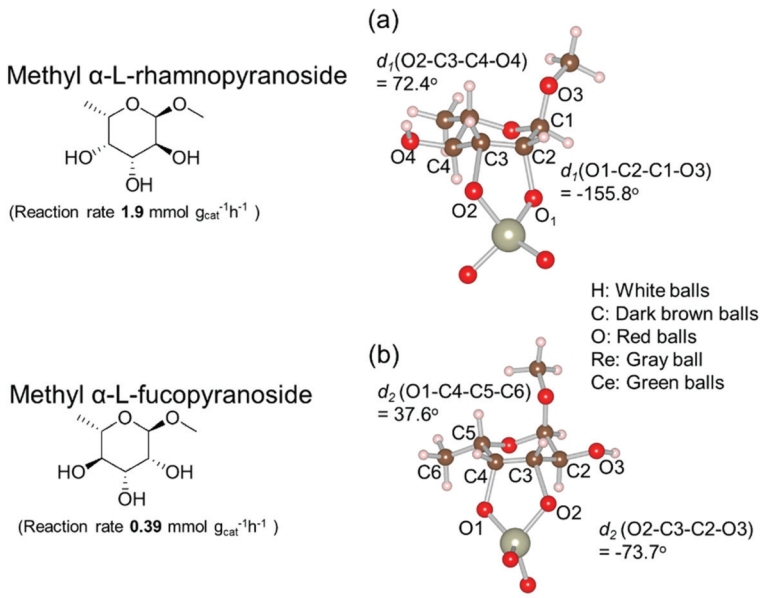
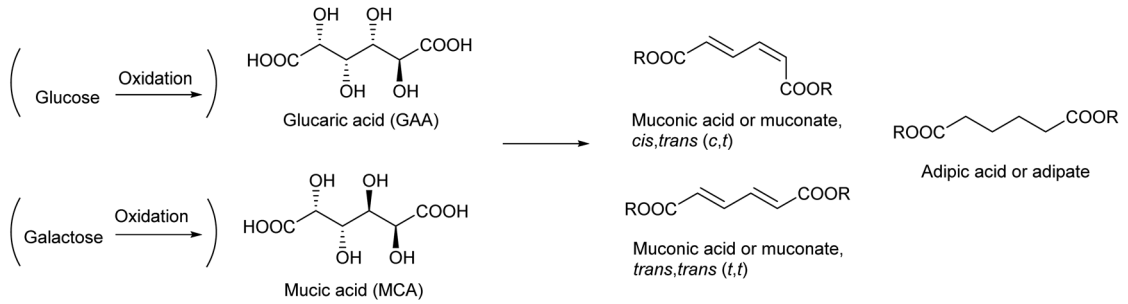


Fig. 19 Structure of the transition states of diolates from methyl α-L-rhamnopyranoside and methyl α-L-fucopyranoside on ReO_x/CeO_2(111). Reproduced from ref. 157 with permission from the American Chemical Society, copyright 2020.

ion and subsequent hydrogenolysis of an alkyl halide proceed, has been reported.[187] The use of a large amount of corrosive acid is a problem for this halogen-mediated hydrodeoxygenation system. Grilc *et al.* reported the hydrodeoxygenation of mucic acid by a commercial sulfided $NiMo/Al_2O_3$ catalyst, and a small amount of adipic acid was obtained.[188]

There are many issues for the industrialization of adipic acid production by DODH + hydrogenation of aldaric acids, considering that adipic acid is a commodity chemical with a low price, in contrast to the deoxysugars discussed in the previous section. The catalyst life (*i.e.*, TON) should be much improved. The cost of Re catalysts is very high, and their replacement with a less expensive active metal such as Mo is desirable. The use of H_2 as a reducing agent is essential. Tolerance to water content in the reaction media may be necessary. The substrate should be glucose-derived (glucaric acid), or at least the system should accept a mixture of glucaric acid and mucic acid as substrates because the main natural

Table 4 DODH and hydrodeoxygenation of aldaric acids



Substrate	Catalyst	Reducing agent	Temp. [K]	Product (yield [%])	TON[a]	Average TOF[a] [h^{-1}]	Ref.
GAA	$HReO_4$	1-Butanol	433	Muconate, *c*,*t* : *t*,*t* = 18 : 7 (25)	3.1	0.21	172
MCA	$HReO_4$	1-Butanol	433	Muconate, *t*,*t* (62)	8.9	0.59	172
MCA	CH_3ReO_3	3-Pentanol	428	Muconate, *t*,*t* (57)	11	0.76	172
MCA	CH_3ReO_3	3-Pentanol	393	Muconate, *t*,*t* (99)	20	0.83	175
MCA	CH_3ReO_3 + TsOH + Pt/C	3-Pentanol	473	Adipate (75)	15	0.31	175
MCA	NH_4ReO_4	Indoline + 1-butanol	423	Muconate, *t*,*t* (57)	5.7	0.24	176
MCA	NH_4ReO_4	3-Pentanol	393	Mucic acid, *t*,*t* (82) + muconate, *t*,*t* (16)	20	0.82	177
Glucarate-6,3-lactone	$KReO_4$ + Pd/C + H_3PO_4 + C	Methanol + H_2 (0.5 MPa)	423	Adipate (88)	88	4.9	183
Glucarodilactone	$KReO_4$ + Pd/C + C + DMAP	H_2 (0.5 MPa)	423	Adipic acid (72)	7.2	0.5	183
Dibutyl mucate	Re_2O_7 + TsOH + [BMIM]OTf	1-Butanol	Reflux	Muconate, *t*,*t* (>99)	20	1.7	178
MCA	$Cp^{tt}ReO_3$	3-Pentanol	393	Muconate, *t*,*t* (75)	15	1.3	179
MCA	CH_3ReO_3	Indoline + 1-butanol	463	Muconate, *t*,*t* (36)	3.6	0.075	180
MCA-1,4-lactone	ReO_x/ZrO_2, Pd/C	1-Butanol + H_2 (0.1 MPa)	393, 393	Adipate (82) after two DODH + hydrogenation cycles	8.3	0.35	184
MCA	$L^{(NNO)}Re(CO)_3$	3-Octanol	453	Muconate, *t*,*t* (46)	23	3.8	181
MCA	$[L^{(py4)}ReO_2]^+$	3-Pentanol	453	Muconate, *t*,*t* (65)	33	11	182
MCA	Pt-ReO_x/C	2-Propanol	443	Adipate (85)	24	0.98	185
GAA	Re/C + Pd/C	Methanol + H_2 (0.5 MPa)	393	Adipate (25)	2.1	0.030	174
MCA	Re/C + Pd/C	Methanol + H_2 (0.5 MPa)	393	Adipate (58)	6.8	0.094	174
GAA	Pd–ReO_x/C + Amberlyst	Methanol + H_2 (2 MPa)	383	Adipate (95)	18	0.74	186
MCA	Pd–ReO_x/C + Amberlyst	Methanol + H_2 (2 MPa)	383	Adipate (95)	18	0.74	186
MCA	$NiMoS/Al_2O_3$	H_2 (5 MPa)	498	Adipic acid (4.3)	—	—	188
GAA	Rh/C + HI	H_2 (2.8 MPa)	403	3-Iodoadipic acid (67) + adipic acid (9)	—	—	187

TsOH = trifluoromethanesulfonic acid; DMAP = 4-dimethylaminopyridine; [BMIM]OTf = 1-butyl-3-methylimidazolium trifluoromethanesulfonate; Cp^{tt} = 1,3-di-*tert*-butylcyclopentadienyl. [a] Based on Re amount. One turnover means two DODH reactions (*e.g.*, mucic acid to muconate).

source of galactose is lactose, which is composed of galactose and glucose units.

Because of the importance of adipic acid, there are several other approaches to synthesizing adipic acid from renewable resources: direct production by fermentation,[189] fermentative muconic acid production and subsequent hydrogenation,[177,190] hydrodeoxygenation of 2,5-furandicarboxylic acid,[15,191,192] carbonylation of C5 platform chemicals,[193] and oxidative cleavage of lignin-derived di-functionalized cyclohexanes.[194] The feasibility of each method depends on various factors: in addition to the yield and separation cost of each conversion step, the amount of H_2 and other reagents (CO in carbonylation) and availability of substrates (intermediates from raw biomass) affect the feasibility. The availability of the substrate in the future will depend on the utilization scope of the same compound for other purposes; for example, future wide use of polyethylene furanoate, which is a co-polymer of 2,5-furandicarboxylic acid and ethylene glycol, will enlarge the supply of 2,5-furandicarboxylic acid and encourage the production of adipic acid from 2,5-furandicarboxylic acid.

Similarly, once the polyester or polyamide of glucaric acid is commercialized, the use of glucaric acid as the source of adipic acid will be spotlighted.

5. Erythritol and 1,4-anhydroerythritol (1,4-AHERY)

Erythritol is already commercially manufactured by fermentation as a sweetener. The fermentation process is not so difficult because of various factors: (i) erythrose-4-phosphate, which is a precursor of erythritol, is involved in the pentose phosphate pathway of metabolism and is a common compound in nature; (ii) yeasts can withstand high concentrations of erythritol; and (iii) erythritol has good crystallinity.[33] Furthermore, the recent development of the fermentative production of erythritol showed that glycerol can also be used as the feed.[31,32,195] It is known that glycerol is the main byproduct in the large-scale production of biodiesel fuel through the transesterification of vegetable oils with methanol or ethanol, and glycerol is a waste product that is not fully utilized. Crude glycerol obtained from biodiesel fuel manufacturing is normally strongly alkaline and contains various minor impurities derived from the mother oil. Generally speaking, the purification of glycerol is energy consuming; this can be connected to the high price of glycerol and its chemically transformed products as chemicals. On the other hand, the removal of impurities from crude glycerol may not be necessary for the fermentative production of erythritol since it has been found that *Moniliella megachiliensis* SN-G42 assimilates nonrefined glycerol derived from palm oil and converts it efficiently into erythritol.[196] For example, the carbon-based yield of erythritol was approximately 60% in a 500 mL flask batch culture after 3 days; this yield was slightly higher than that obtained with glucose. Further improvement in cell growth and erythritol production might be possible. In addition, a synthetic enzyme cascade was developed for the production of the functional C4 sugar erythrulose by utilizing formaldehyde as a C1 carbon source, where formaldehyde could be sustainably derived from other C1 feedstocks.[197] The conversion of erythrulose into the corresponding sugar alcohols is easy like in the cases of xylose to xylitol and glucose to sorbitol. Based on this and related reports, we believe that erythritol will be able to be regarded as a platform chemical in the biomass refinery.[33] Although erythritol itself can be used as a raw material for the production of polymers and chemicals,[198–200] examples are very limited.

The dehydration of erythritol gives 1,4-anhydroerythritol (1,4-AHERY), which is catalyzed by a strong Brønsted acid such as mineral acids and ion-exchange resin.[201,202] A reactive distillation system for collecting the 1,4-AHERY product in high yield (~90%) has been reported.[201] The dehydration of erythritol proceeded effectively in carbonated water to give >70% yield of 1,4-AHERY at 573 K, and this could be catalyzed by protons generated from carbonic acid in the presence of high-pressure CO_2.[203] The relatively easy conversion of erythritol into 1,4-AHERY is thought to enable the utilization of 1,4-AHERY as a biomass-derived platform chemical. The hydrodeoxygenation of erythritol and 1,4-AHERY gives a variety of chemicals as shown in Fig. 20 and 21, where the reducing agent is hydrogen. Butanediols are important targets for erythritol hydrodeoxygenation (Fig. 20) because they have higher demands than butanetriols and also a lower amount of H_2 is required for their production compared to butanols. However, the separation of one specific butanediol from a mixture of butanediols is difficult, and high selectivity is especially necessary from a practical viewpoint.

5.1. Hydrogenolysis of erythritol as a variant of glycerol

The hydrogenolysis of C–O bonds in erythritol potentially produces a variety of products; for example, two triols (1,2,3- and 1,2,4-), four diols (1,2-, 1,3-, 1,4-, and 2,3-), and two mono-alcohols are possibly produced from erythritol, even though side reactions such as C–C dissociation and cyclization are excluded. This means that the control of regio-selectivity is essential. On the other hand, the hydrogenolysis of C–O bonds in glycerol has been intensively investigated because of the large supply of glycerol as a byproduct in the biodiesel industry. Glycerol hydrogenolysis can be used as a model reaction of erythritol hydrogenolysis, and some catalysts developed for glycerol hydrogenolysis have been applied to erythritol hydrogenolysis. Although the hydrogenolysis of glycerol has also been achieved by the combination of homogeneous acid catalysts and Ru complex catalysts, examples of such systems are very limited and mainly produce 1-propanol or propane.[204–206] In a related reaction of biomass-derived furanic compounds, Pd/C combined with metal triflates, which act as homogeneous Lewis acids, accelerated the complete hydrogenolysis to give alkanes.[207–209] These examples indicate that the use of homogeneous catalysts has great potential for the complete removal of OH groups from biomass-derived substrates, while the regioselective transformation is rather difficult. Therefore, from the viewpoint of the regioselective hydrogenolysis of biomass-derived substrates, we focus on the reaction systems using heterogeneous catalysts in this review.

There are two important mechanisms of indirect hydrogenolysis of glycerol that can work over a broad range of catalysts:[51] dehydration + hydrogenation, which mainly proceeds over metal + acid catalysts, and dehydrogenation + dehydration + hydrogenation, which mainly occurs over non-acidic metal catalysts (Fig. 22). A key reaction in the latter mechanism is the second step, dehydration at C–H and C–OH at the α- and β-positions, respectively, of the carbonyl group. The acidic nature of C–H at the α-position of the carbonyl group promotes dehydration. A similar dehydration process also occurs during the dehydration + hydrogenation mechanism, which directly forms dideoxygenated products. We calculated the energy profiles of both mechanisms by DFT and details are shown in section S2 (ESI†). Here we only provide a summary: in the dehydration + hydrogenation mechanism, the main product is 1,2-propanediol *via* removal of the OH group at the 1-position. However, the energy difference between the removal of the OH group at the 1- and 2-positions is not so sig-

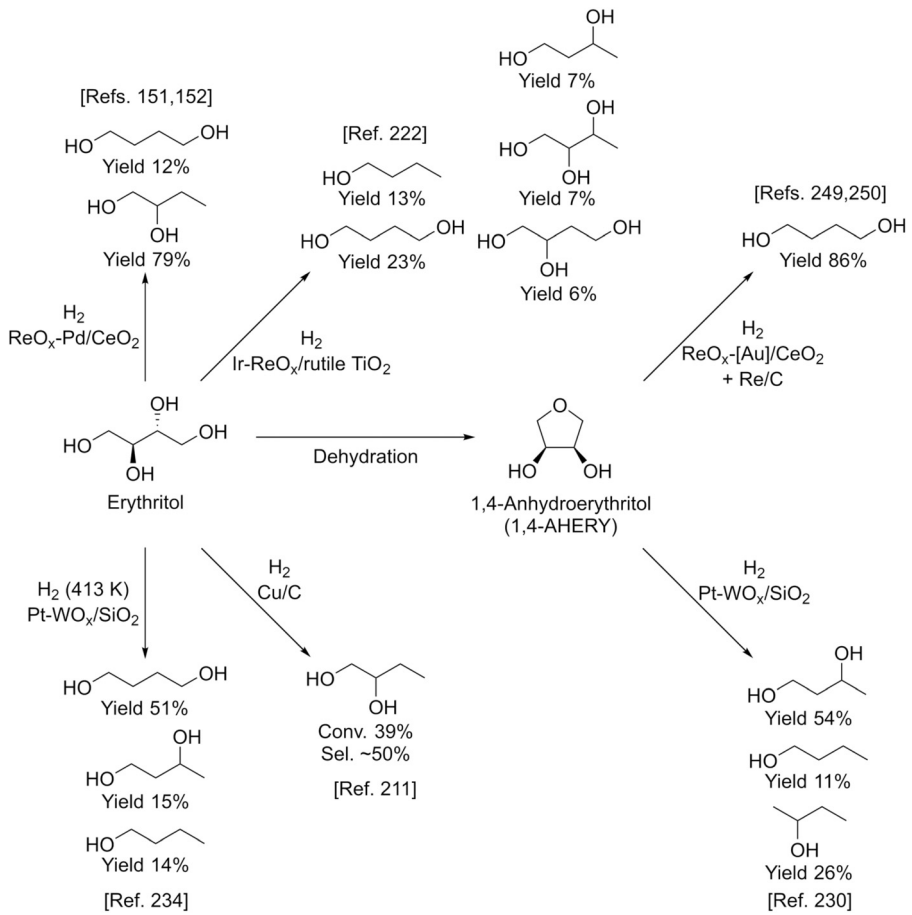


Fig. 20 Transformation of erythritol and 1,4-AHERY into C4 diols with H_2.

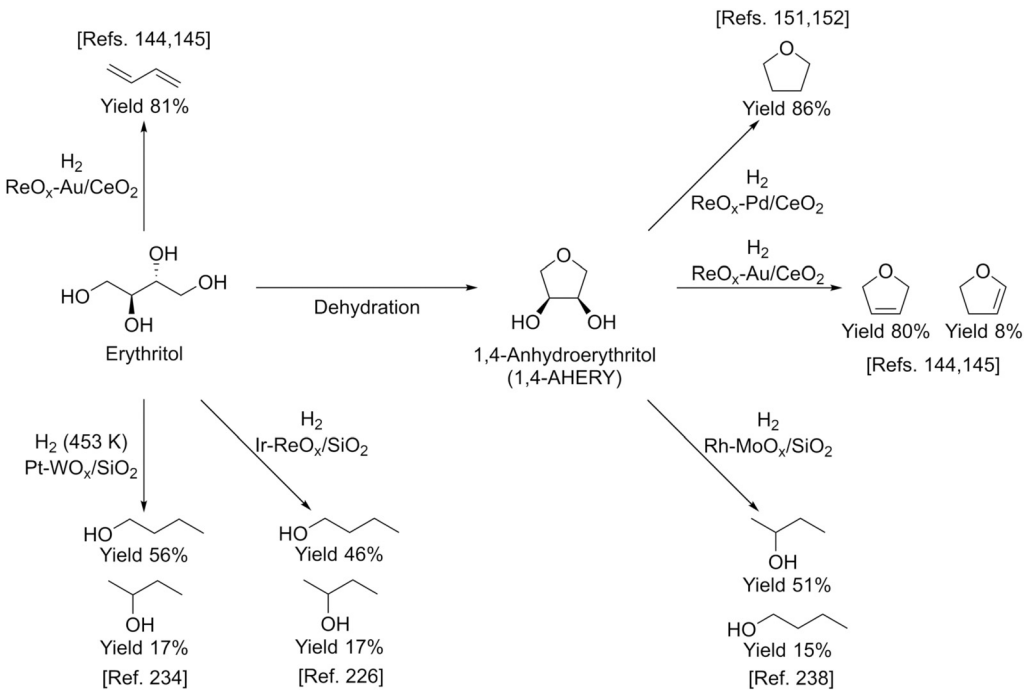


Fig. 21 Transformation of erythritol and 1,4-AHERY into C4 monoalcohols and other products with H_2.

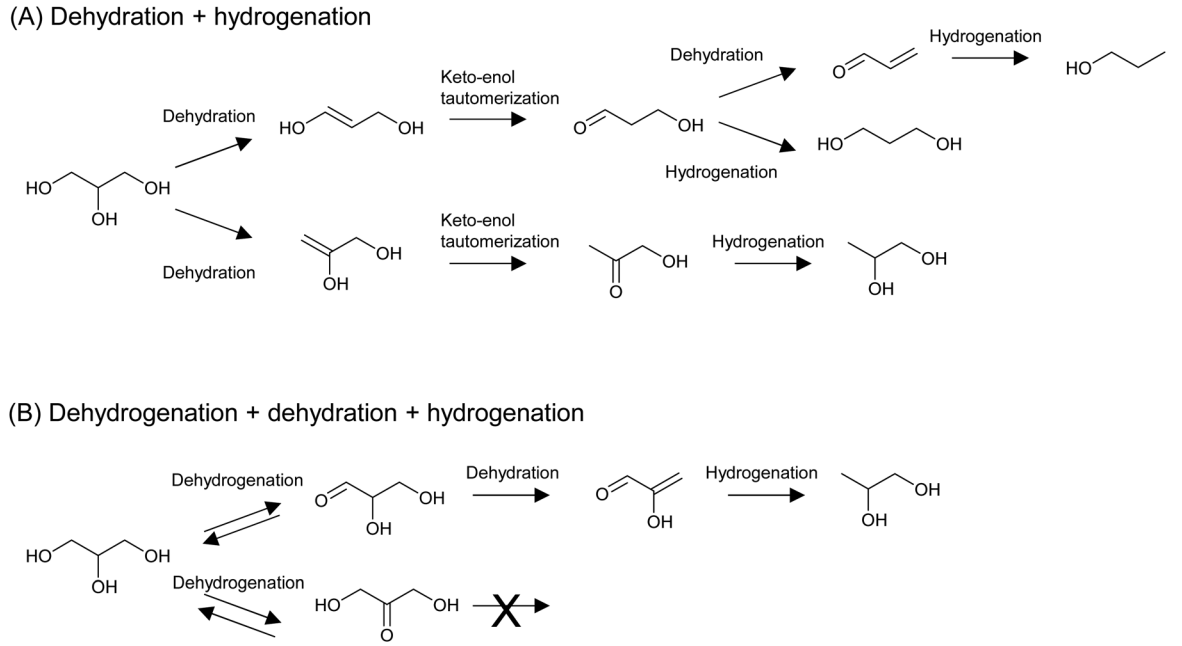


Fig. 22 Typical mechanisms of the indirect hydrogenolysis of glycerol: dehydration + hydrogenation (A) and dehydrogenation + dehydration + hydrogenation (B).

nificant. In addition, when removal of the OH group at the 2-position occurs, further dehydration of 3-hydroxypropanal to acrolein easily proceeds because of the presence of C–H and C–OH at the α- and β-positions of the carbonyl group in 3-hydroxypropanal. Therefore, 1,3-propanediol and 1-propanol can also be produced. In the case of the dehydrogenation + dehydration + hydrogenation mechanism, only 1,2-propanediol can be produced. Furthermore, 1,2-propanediol is not reactive in the dehydrogenation + dehydration + hydrogenation mechanism, but it can be further hydrodeoxygenated to propanols and propane by the dehydration + hydrogenation mechanism.

Similar analyses of the energy profiles for erythritol hydrogenolysis by the two indirect different mechanisms (dehydration + hydrogenation, dehydrogenation + dehydration + hydrogenation) were carried out and detailed results are shown in section S2 (ESI†). The reaction routes are more complicated than those for glycerol hydrogenolysis; in addition to an increase in the number of possible intermediates, the possible involvement of cyclization complicates the reaction. In summary, in the dehydration + hydrogenation mechanism, the reaction is unselective to form various products or even does not proceed by the formation of 1,4-AHERY. In fact, typical catalyst systems with the dehydration + hydrogenation mechanism such as Ru + acidic resin have not been tested for erythritol hydrogenolysis. In the dehydrogenation + dehydration + hydrogenation mechanism for erythritol hydrogenolysis, dehydrogenation at a terminus in the initial step produces 1,2,4-butanetriol + 1,2-butanediol while that at an internal position provides 1,2,3-butanetriol. The ratio of 1,2,4-butanetriol + 1,2-butanediol to 1,2,3-butanetriol may depend on the catalyst. Further conversions of both triols are possible through this mechanism because both triols have a 1,3-diol structure, while 1,2-butanediol is not reactive due to the lack of such a structure.

Erythritol hydrogenolysis was reported over Cu catalysts, which are typically utilized in glycerol hydrogenolysis to 1,2-propanediol through the dehydrogenation + dehydration + hydrogenation mechanism.[210,211] The reported results for erythritol and related substrates over the Cu/C catalyst are shown in Fig. 23.[211] The main products of erythritol hydrogenolysis were 1,2,4-butanetriol and 1,2-butanediol. An important point is that data were recorded at a low conversion level and it appeared that 1,2-butanediol was also a primary product. The reaction temperature was rather high (453 K) and a negative reaction order with respect to H_2 pressure was mentioned in the same report. This suggests that the reaction of erythritol over Cu/C proceeds through the dehydrogenation + dehydration + hydrogenation route, which also opens the reaction of erythritol to 1,2-butanediol through the dehydrogenation + (double) dehydration + hydrogenation route as described above. The reactivity of 1,2-butanediol was much lower than that of erythritol, 1,2,3- and 1,2,4-butanetriols over Cu/C, which was also in agreement with the discussion above for the dehydrogenation + dehydration + hydrogenation route.

Neither of the indirect mechanisms in Fig. 22 give 1,3-propanediol as the main product from glycerol, and another mechanism is necessary for its production. Indeed, there are systems for selective glycerol hydrogenolysis to 1,3-propanediol.[212,213] Typical catalysts are supported Pt–WO_x and Ir–ReO_x, and selected systems with high yields are summarized in section S3 (ESI†). Generally, Ir–ReO_x catalysts have an advantage in terms of catalytic activity, which permits hydroge-

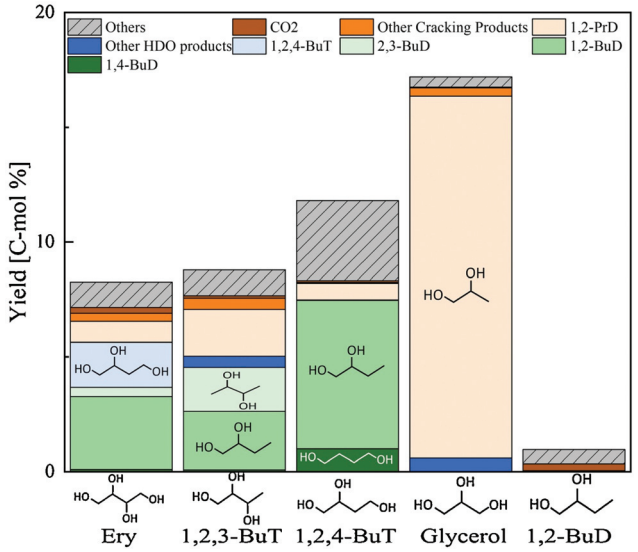


Fig. 23 Hydrogenolysis of various substrates over Cu/C. Reaction conditions: substrate (4.5 g), water (25.5 g), catalyst (0.9 g-Cu), H_2 (1.8 MPa), 453 K, 24 h. Ery = erythritol; BuT = butanetriol; BuD = butanediol; PrD = propanediol; HDO = hydrodeoxygenation. Reprinted from ref. 211 with permission from Elsevier, copyright 2021.

nolysis at lower reaction temperatures, while Pt–WO_x catalysts have an advantage from the viewpoint of high yield and selectivity of the target products. One proposed mechanism is the acidic activation of a secondary C–O bond combined with S_N2-like hydride attack on a secondary carbon (Fig. 24) in the 1,2-diol moiety of the substrate.[214] With this mechanism, erythritol will be converted into 1,2,4-butanetriol and then 1,4-butanediol, while the selective production of 1,4-butanediol from erythritol is very difficult with the two indirect mechanisms outlined in Fig. 22.

The structure of the Ir–ReO_x/SiO_2 catalyst has been reported to be Ir metallic nanoparticles partially covered with three-dimensional ReO_x clusters.[215] There are direct bonds between the Ir metal surface and Re atoms in the ReO_x clusters, as expected from observation of the Re–Rh bond in Rh–ReO_x catalysts[216] and the Re–Pt bond in Pt–ReO_x catalysts[217] by extended X-ray absorption fine structure (EXAFS) analysis. The direct interaction between Ir and ReO_x is strongly connected to the reaction mechanism of C–O hydrogenolysis outlined in Fig. 24. The Ir–ReO_x/SiO_2 catalysts maintain very small Ir metal particles (*ca.* 2–3 nm) even when the loading amount of Ir is increased (from 4 wt% to 20 wt%).[218] Interestingly, the Ir-amount-based catalytic activity for glycerol hydrogenolysis slightly increased and the optimum Re addition amount per Ir decreased with an increase of the Ir loading amount. The catalytically active site (the interface between Ir metal surfaces and ReO_x clusters) effectively formed with a high loading amount of Ir and Re species. Based on this finding, the preparation of Ir–ReO_x species on oxide supports with a much lower surface area than SiO_2 has been attempted, and rutile TiO_2 (6 m^2 g^{-1}) was found to be a suitable support.[219] The transmission electron microscope (TEM) images and model structures are shown in Fig. 25 and 26, respectively. Ir nanoparticles attach to the rutile TiO_2 surface strongly, maintaining a small particle size even when the density is high. The advantage of the formation of dense metallic particles is a reduction in the amount of modifier (ReO_x clusters in this case) by sharing it between two metal particles as illustrated in Fig. 26. In particular, this kind of catalyst design is more efficient in the case of the expensive modifier such as Re. The TiO_2 support has also been proposed to have a role in the suppression of the over-reduction of Re species, leading to the interaction between an erythritol molecule and catalytic active site.[220,221]

Fig. 27 shows the conversion and selectivity as a function of reaction time for erythritol hydrogenolysis over Ir–ReO_x/rutile TiO_2 (4 wt% Ir, Re/Ir = 0.25) at 353 K.[222] The reaction temperature (353 K) for the Ir–ReO_x catalyst was clearly lower than that (453 K) for the Cu catalyst, which was due to the very high activity of Ir–ReO_x catalysts for C–O hydrogenolysis of various polyfunctionalized compounds such as sugars,[223,224] sugar alcohols,[222,225–227] and cyclic ones.[228] The selectivity of the primary products can be estimated from the data at a lower conversion level (*i.e.*, shorter reaction time) (Fig. 27). The selectivities of 1,2,4-butanetriol, 1,2,3-butanetriol, 1,4-butanediol, and 1,3-butanediol in the initial stage were estimated to be 55%, 20%, 15%, and 10%, respectively, at 373 K.[222] The C–O bond at the 2-position of erythritol was mainly dissociated first over Ir–ReO_x/rutile TiO_2. In the case of glycerol hydrogenolysis, the initial selectivities of 1,3-propanediol and 1-propanol were estimated to be 70% and 20%, respectively, at 393 K over the same Ir–ReO_x/rutile TiO_2 catalyst.[219] The reactivity of erythritol is lower (about half) than that of glycerol under similar reaction conditions over Ir–ReO_x/rutile TiO_2. An important feature of the Ir–ReO_x/TiO_2-catalyzed hydrogenolysis of erythritol and glycerol was the relatively high selectivity of 1,4-BuD and 1-propanol, respectively, even at a low conversion level. Similar behavior was observed in the cases of erythritol and glycerol hydrogenolysis over Ir–ReO_x/SiO_2 catalysts.[226,227] This behavior suggests that 1,4-butanediol is produced directly on the active site from erythritol without desorption of 1,2,4-butanetriol as

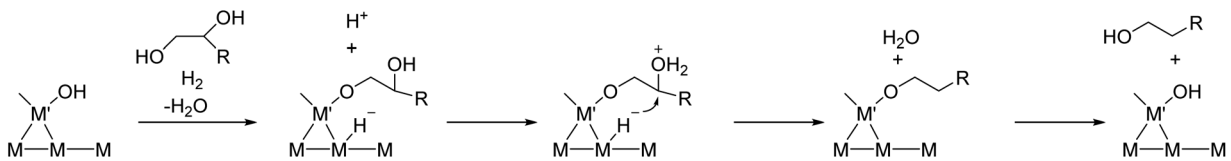


Fig. 24 Proposed reaction mechanism for glycerol hydrogenolysis to 1,3-propanediol over M–M′O_x. R = CH_2OH.

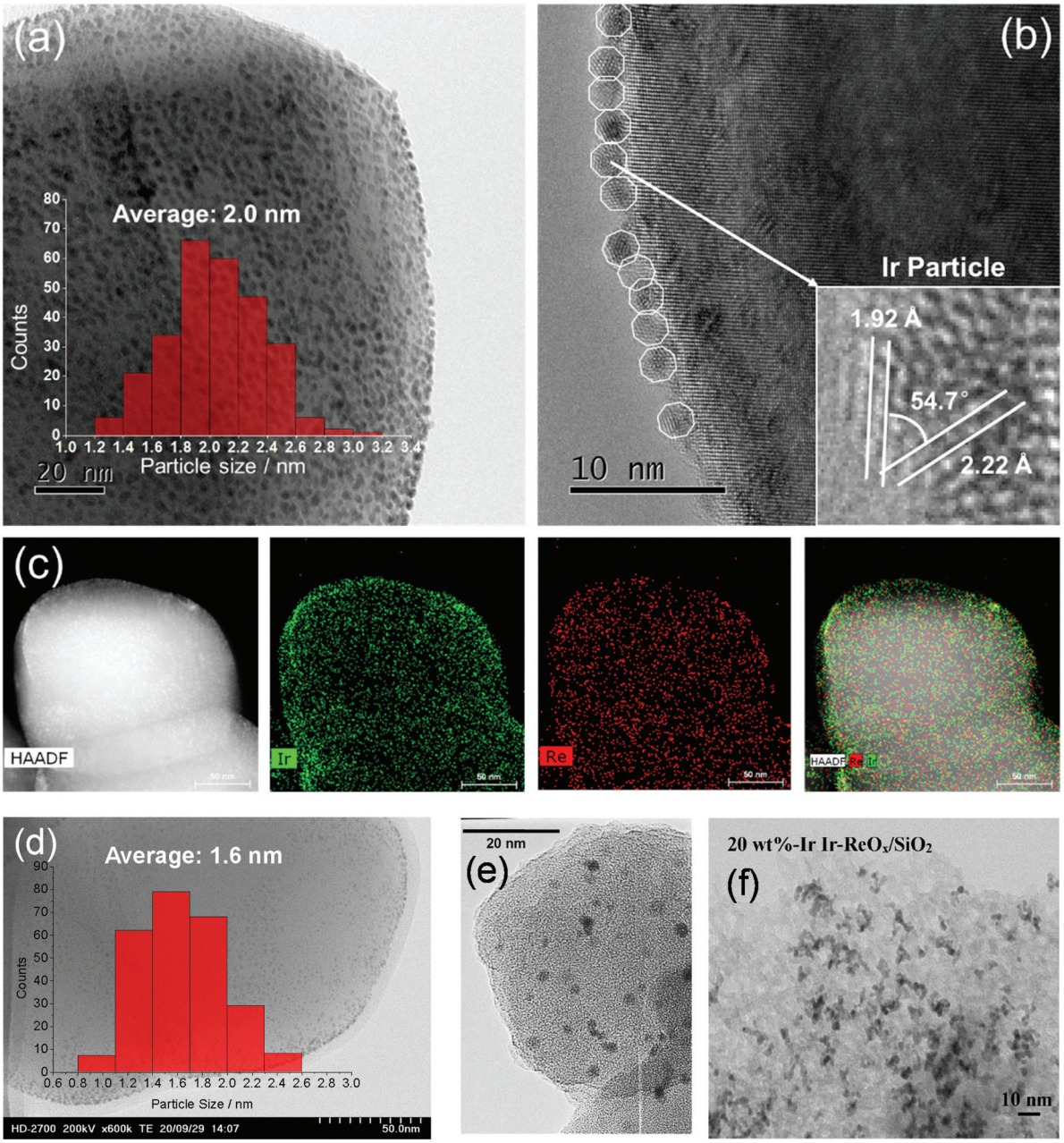


Fig. 25 TEM images of Ir–ReO_x/rutile TiO_2 (4 wt% Ir, Re/Ir = 0.24) (a–c), Ir–ReO_x/rutile TiO_2 (1 wt% Ir, Re/Ir = 0.24) (d), Ir–ReO_x/SiO_2 (4 wt% Ir, Re/Ir = 0.83) (e), and Ir–ReO_x/SiO_2 (20 wt% Ir, Re/Ir = 0.34) (f). Reprinted from ref. 222 with permission from John Wiley and Sons, copyright 2020, for (a–d). Reproduced from ref. 225 with permission from Elsevier, copyright 2010, for (e) and from ref. 218 with permission from Elsevier, copyright 2019, for (f).

an intermediate. The product distribution over Ir–ReO_x was clearly different from the case of Cu/C; this could be related to direct C–O hydrogenolysis by S_N2 attack of the hydride. The highest yield of 1,4-butanediol was 23%, which is far from satisfactory.[222] From the viewpoint of the yield of 1,3-propanediol in glycerol hydrogenolysis, Pt–WO_x catalysts are superior to Ir–ReO_x catalysts.[212,229] The applicability of Pt–WO_x catalysts to erythritol hydrogenolysis should be mentioned.

For Pt–WO_x catalysts, there are many reports on glycerol hydrogenolysis to 1,3-propanediol;[135] however, the relationship between structure and performance is complex because the reported performance varies extensively even among catalysts with similar supports and compositions. Nonetheless, recent developments in this research area show that silica-based supports and a low W amount are effective in terms of both activity at low reaction temperature and selectivity to 1,3-propanediol.[230–233] Therefore, Pt–WO_x/SiO_2 is one of the most suitable model catalysts and it is thought to be possible to reveal the essence of Pt–WO_x catalysts. The Pt–WO_x/SiO_2 (4 wt% Pt, W/Pt = 0.25) catalyst after the reaction contains

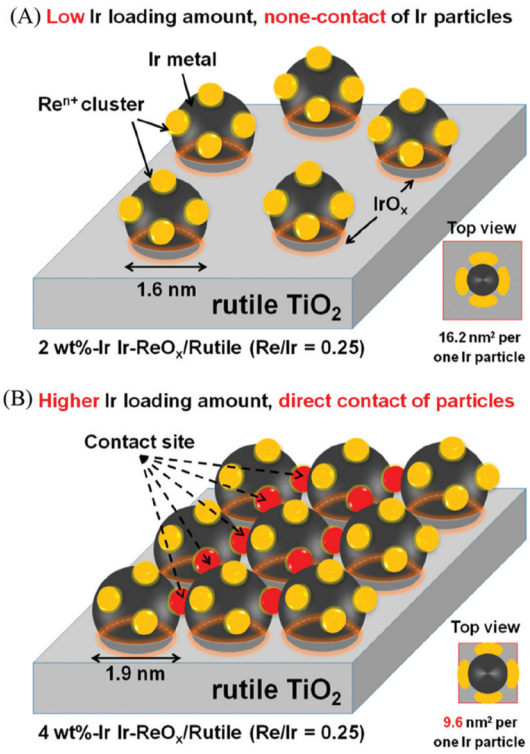


Fig. 26 Model structure of Ir–ReO_x/rutile TiO_2 catalysts. Reprinted from ref. 219 with permission from the American Chemical Society, copyright 2019.

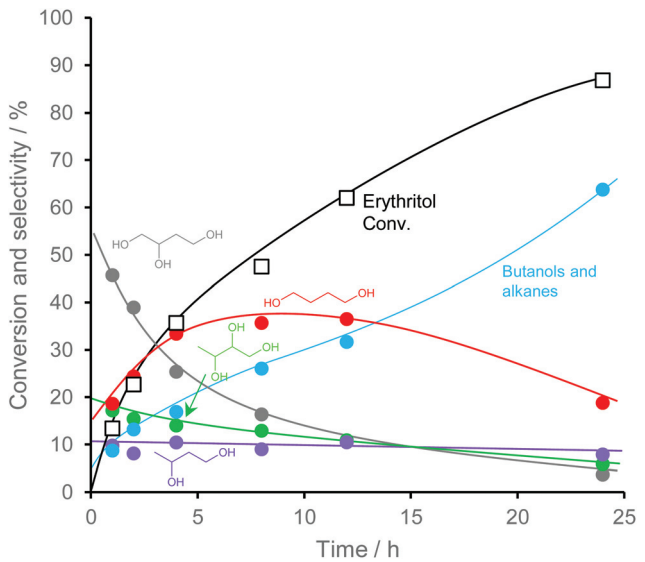


Fig. 27 Time course of erythritol hydrogenolysis over Ir–ReO_x/TiO_2 (4 wt% Ir, Re/Ir = 0.25).[222] Reaction conditions: 20 wt% aqueous solution of erythritol (5 g), catalyst (300 mg), 353 K, H_2 (8 MPa), 373 K.

about 5 nm Pt metal particles, and the presence of the direct W–Pt bond is strongly suggested by EXAFS analysis.[231] Elemental mapping in the TEM observation indicates that the W species are located around Pt metal particles. An interesting result is that the signal intensity ratio of W to Pt in the X-ray photoelectron spectroscopy (XPS) results is much lower than that of the catalyst composition (W/Pt = 0.25). At present, it is interpreted as W species (W^{4+}) being located between the Pt metal and SiO_2 surface selectively as illustrated in Fig. 28. The structure of Pt–WO_x/SiO_2 is rather different from that of Ir–ReO_x catalysts; however, the reaction kinetics such as the reaction orders with respect to the concentrations of the substrates and H_2 pressure is similar, suggesting that the reaction mechanisms over these two catalyst systems are also similar. The catalytically active site of Pt–WO_x/SiO_2 is the interface between the Pt metal surface and WO_x species and the mechanism could be S_N2-like hydride attack on the secondary carbon as shown in Fig. 24.[231]

Fig. 29 shows the time course of erythritol hydrogenolysis over Pt–WO_x/SiO_2 (4 wt% Pt, W/Pt = 0.25).[234] The selectivities of 1,2,4- and 1,2,3-butanetriols at the initial stage were about 80% and 20%, respectively. The very high selectivity of 1,3-pro-

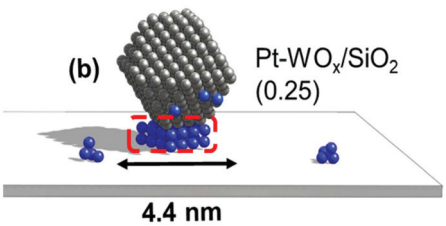


Fig. 28 Proposed structure of Pt–WO_x/SiO_2. Reprinted from ref. 231 with permission from Elsevier, copyright 2021.

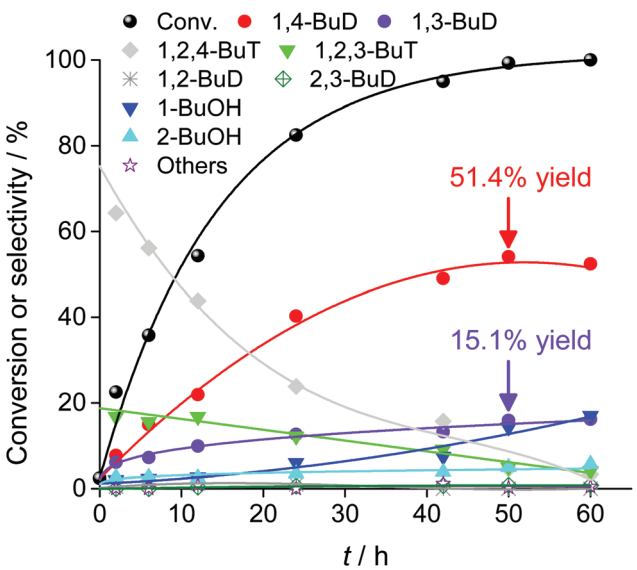


Fig. 29 Time course of erythritol hydrodeoxygenation over Pt–WO_x/SiO_2 (4 wt% Pt, W/Pt = 0.25). Reaction conditions: erythritol (0.5 g), H_2O (4 g), catalyst (0.2 g), H_2 (8 MPa), 413 K. Reduction conditions: liquid-phase reduction at 473 K. BuT = butanetriol, BuD = butanediol, BuOH = butanol. Reprinted from ref. 234 with permission from the Royal Society of Chemistry, copyright 2021.

panediol from glycerol (57% yield of 1,3-propanediol)[230] is connected to that of 1,2,4-butanetriol from erythritol. This excellent selectivity of Pt–WO_x/SiO_2 in the C–O hydrogenolysis of the C–O bond neighboring –CH_2OH enables a high yield (51%) of 1,4-butanediol. Another important point is that 1,4-butanediol is formed by consecutive C–O hydrogenolysis of erythritol (erythritol → 1,2,4-butanetriol → 1,4-butanediol), considering the very low initial selectivity of 1,4-butanediol formation.

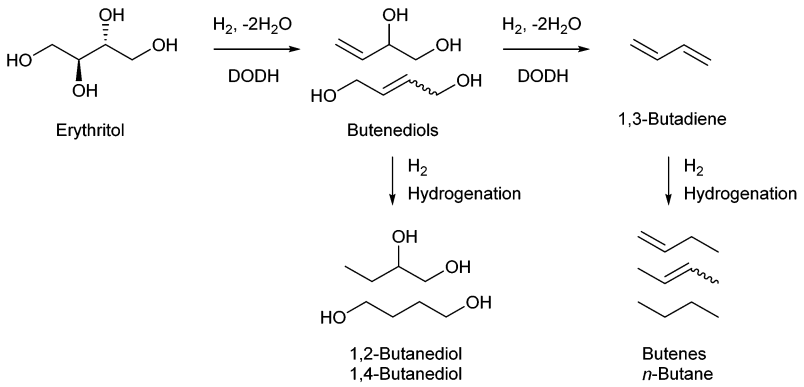
The above results of erythritol hydrogenolysis over Ir–ReO_x and Pt–WO_x catalysts are directed to the synthesis of butanediols. On the other hand, Ir–ReO_x and Pt–WO_x catalysts are also effective for the synthesis of butanols when the catalysts are applied to more severe reaction conditions such as higher reaction temperature and longer reaction time. This is because butanols are formed by the further hydrogenolysis of butanediols. When the Ir–ReO_x/SiO_2 catalyst was used, 43% yield of 1-butanol and 17% yield of 2-butanol were reported.[226] Meanwhile, the Pt–WO_x/SiO_2 catalyst was reported to produce 57% yield of 1-butanol and 18% yield of 2-butanol.[234] It should be noted that Ir–ReO_x/SiO_2 catalysts were also effective for producing hexanols (3-hexanol 41% yield, 2-hexanol 18% yield, 1-hexanol 1% yield) from mechanocatalytically depolymerized cellulose in a biphasic reaction system (*n*-decane and H_2O) with the aid of H_2SO_4.[223] These high yields of mono-alcohols in the hydrogenolysis of polyols are due to the lower reactivity of mono-alcohols over Ir–ReO_x/SiO_2 [134] and Pt–WO_x/SiO_2.[230]

5.2. Deoxydehydration (DODH) and DODH + hydrogenation of erythritol

DODH is also a useful reaction in the conversion of erythritol, although examples are limited especially for those using H_2 as a reducing agent. The results for the DODH and DODH + hydrogenation of erythritol with H_2 as a reducing agent are summarized in Table 5. 1,2-Butanediol can be synthesized from erythritol by the DODH of erythritol to 1-butene-3,4-diol and the consecutive hydrogenation of the C=C bond in 1-butene-3,4-diol to 1,2-butanediol. These two reactions proceed in one pot over ReO_x–Pd/CeO_2.[151,152] The reaction time should be carefully controlled in order to obtain 1,2-butanediol in high yield, because 1,2-butanediol is converted into *n*-butane after consumption of erythritol. Still, the 1,2-butanediol yield for DODH + hydrogenation over ReO_x–Pd/CeO_2 was much higher than that obtained with other systems such as Cu catalysts as described in section 5.1.

The DODH of erythritol was catalyzed by ReO_x–Au/CeO_2 and a high yield of 1,3-butadiene (~80%) was achieved (see Table 5).[144,145] It has been recently reported that ReO_x–Ag/CeO_2 exhibited a higher activity than ReO_x–Au/CeO_2 and a comparably high yield of 1,3-butadiene.[147] Furthermore, the application of "solventless" conditions further increased the yield of 1,3-butadiene, probably due to the efficient transfer of 1,3-butadiene from the liquid phase (erythritol and butenediols for the "solventless" conditions) to the gas phase. In addition, the "solventless" conditions greatly improved the *E*-factor.

Table 5 DODH and DODH + hydrogenation of erythritol with H_2 as a reducing agent



Catalyst	Solvent	$P(H_2)$ [MPa]	Temp. [K]	Time [h]	Conv. [%]	Selectivity [%]				TON[a]	Ref.
						1,3-Butadiene	1,2-BuD	1,4-BuD	Butenes and butane		
ReO_x–Pd/CeO_2	1,4-Dioxane	8	433	24	98	0	79	12	5	249	151
ReO_x–Au/CeO_2	1,4-Dioxane	8	413	60	97	83	0	1	3	426	144
ReO_x–Ag/CeO_2	1,4-Dioxane	8	413	20	>99	86	0	0	6	245	147
ReO_x–Ag/CeO_2	None	8	413	24	>99	91	0	0	3	240	147
ReO_x–Cu/CeO_2	1,4-Dioxane	8	413	24	>99	0	50	4	22	129	147
ReO_x–Ni/CeO_2	1,4-Dioxane	8	413	24	25	0	0	0	0	26	147

BuD: butanediol. [a] TON = ((mol of hydrocarbons) × 2 + (mol of butanediols) + (mol of butenediols))/(mol of Re).

5.3. Production of 1,3-butanediol: hydrogenolysis of 1,4-anhydroerythritol (1,4-AHERY)

The main primary product in the hydrogenolysis of erythritol is 1,2,4-butanetriol on both Ir–ReO_x and Pt–WO_x catalysts as well as Cu catalysts. This means that it is difficult to obtain a high yield of 1,3-butanediol from erythritol because the hydrogenolysis of primary C–OH bonds in glycols is very challenging and suitable catalysts for this hydrogenolysis are too limited. A recent example was the hydrogenolysis of 1,2-propanediol to 2-propanol catalyzed by Ru–ReO_x/SiO_2; however, the obtained yield of 2-propanol was as low as 23% and not satisfactory.[235] The selective hydrogenolysis of 1,2,4-butanetriol to 1,3-butanediol is regarded to be very challenging at present. 1,3-Butanediol is a possible target from 1,4-AHERY. One of the possible routes is the conversion of 1,4-AHERY to 3-hydroxytetrahydrofuran[236] and the consecutive conversion of 3-hydroxytetrahydrofuran to 1,3-butanediol.[237] The conversion of 1,4-AHERY into 3-hydroxytetrahydrofuran was catalyzed by the WO_x–Pd/C catalyst and the yield of 3-hydroxytetrahydrofuran was 72% (Fig. 30).[236] The hydrogenolysis of 3-hydroxytetrahydrofuran to 1,3-butanediol was catalyzed by Ir–ReO_x/SiO_2 and the selectivity of 1,3-butanediol formation was 81% at 24% conversion.[237] The overall selectivity of 1,3-butanediol from 1,4-AHERY was calculated to be 58%. It has been recently reported that the hydrogenolysis of 3-hydroxytetrahydrofuran to 1,3-butanediol was also catalyzed by Pt–WO_x/SiO_2 and the selectivity of 1,3-butanediol formation was 90% at 40% conversion,[230] and the overall selectivity of 1,3-butanediol from 1,4-AHERY increased to 65%. Actually, the solvent for the conversion of 1,4-AHERY into 3-hydroxytetrahydrofuran over WO_x–Pd/C was 1,4-dioxane, and that for the hydrogenolysis of 3-hydroxytetrahydrofuran to 1,3-butanediol over Ir–ReO_x/SiO_2 and Pt–WO_x/SiO_2 was water. The difference in suitable solvents for the process including a series of two reactions decreases the feasibility of the conversion process of 1,3-butanediol from 1,4-AHERY. The one-pot conversion of 1,4-AHERY was thus desired.

A possible one-pot route is the combination of the hydrogenolysis of 1,4-AHERY to 1,2,3-butanetriol and the successive one of 1,2,3-butanetriol to 1,3-butanediol. It has been reported that Rh–MoO_x/SiO_2 catalyzed the one-pot hydrogenolysis of 1,4-AHERY to 2-butanol with the highest yield of 2-butanol (51%).[238] Such Rh–MoO_x catalysts were also found to be effective for the C–O hydrogenolysis of related compounds.[238–241] It has been proposed that the primary ring-opening C–O hydrogenolysis of 1,4-AHERY over Rh–MoO_x/SiO_2 gave 1,2,3-butanetriol, and the reaction mechanism was thought to be similar to that of glycerol hydrogenolysis over Ir–ReO_x catalysts. From the viewpoint of the synthesis of 1,3-butanediol from 1,2,3-butanetriol, Rh–MoO_x/SiO_2 is not suitable on the basis of the low selectivity to 1,3-propanediol through glycerol hydrogenolysis.[242] Ir–ReO_x/SiO_2 was also investigated for the hydrogenolysis of 1,4-AHERY,[238] as listed in Table 6. The selectivity to 1,2,3-butanetriol + 1,3-butandiol was around 60%; however, the selectivity to 2-butanol was 14% even at a

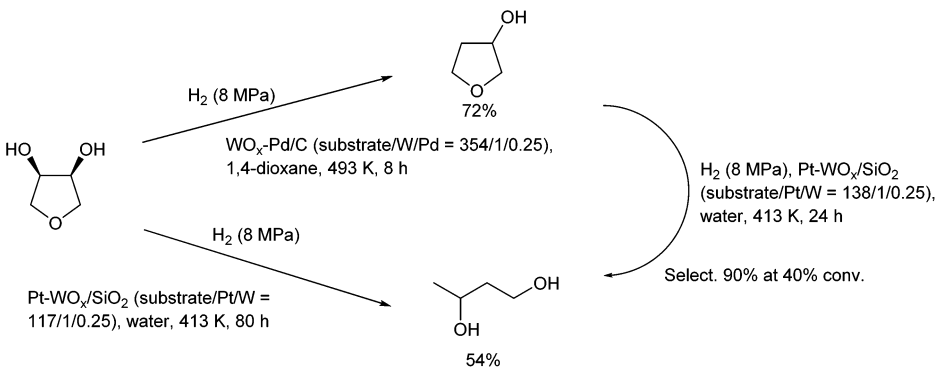


Fig. 30 Selective hydrogenolysis systems of 1,4-AHERY.[230,236]

Table 6 Hydrogenolysis of 1,4-AHERY over Rh- and Ir-based catalysts[238]

				Selectivity [%]								
Entry	Catalyst	Time [h]	Conv. [%]	1,2,3-BuT	3-HTHF	1,2-BuD	2,3-BuD	1,3-BuD	1-BuOH	2-BuOH	Alkanes	Others
1	Rh–MoO_x/SiO_2	1	21	37	9	9	12	2	4	23	2	2
2	Rh–MoO_x/SiO_2	48	100	<1	<1	<1	8	<1	15	51	24	2
3	Ir–ReO_x/SiO_2	1	8	43	8	4	2	25	3	14	1	<1
4	Ir–ReO_x/SiO_2	24	63	35	4	4	2	23	11	19	3	1

BuT: butanetriol; HTHF: hydroxytetrahydrofuran; BuD: butanediol; BuOH: butanol. Reaction conditions: catalyst (0.1 g) (Rh or Ir 4 wt%, Mo/Rh = 0.13 or Re/Ir = 1), 1,4-AHERY (1 g), water (4 g), H_2 (8 MPa), 393 K.

low conversion level, suggesting that a high yield of 1,3-butanediol is difficult on the Ir–ReO_x/SiO_2 catalyst. This can be explained by the not so high yield of 1,3-propanediol through glycerol hydrogenolysis on Ir–ReO_x catalysts due to the consecutive hydrogenolysis of 1,3-propanediol to 1-propanol as mentioned above. Based on this discussion, it is thought that Pt–WO_x is more suitable than Ir–ReO_x in the one-pot hydrogenolysis of 1,4-AHERY to 1,3-butanediol.

It has been recently demonstrated that Pt–WO_x/SiO_2, which is the same catalyst for erythritol hydrogenolysis to 1,4-butanediol (Fig. 29), was effective for the one-pot synthesis of 1,3-butanediol by 1,4-AHERY hydrogenolysis[230] and 54% yield of 1,3-butanediol from 1,4-AHERY was achieved (Fig. 30). Fig. 31 shows the time course of the hydrogenolysis of 1,4-AHERY over Pt–WO_x/SiO_2 (4 wt% Pt, W/Pt = 0.25). The selectivity of 1,2,3-butanetriol was high (about 80%) at a low conversion level.

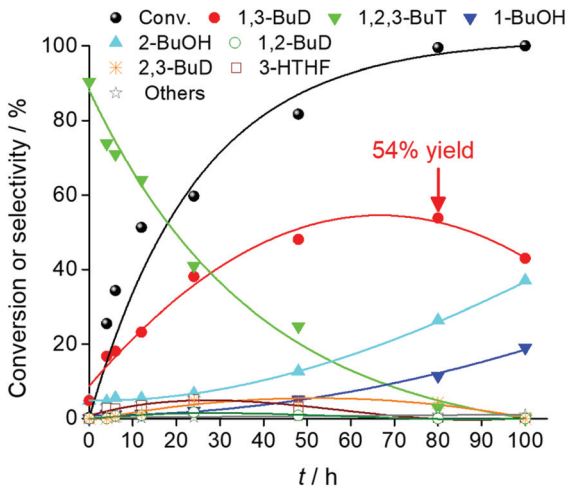


Fig. 31 Time course of the hydrogenolysis of 1,4-AHERY over 4 wt% Pt–WO_x/SiO_2 (W/Pt = 0.25). Reaction conditions: 1,4-AHERY (0.5 g), H_2O (4 g), catalyst (0.2 g), H_2 (8 MPa), 413 K. BuD: butanediol; BuT: butanetriol; BuOH: butanol; HTHF: hydroxytetrahydrofuran. Reprinted from ref. 230 with permission from the Royal Society of Chemistry, copyright 2020.

The reaction routes for 1,4-AHERY and erythritol over Pt–WO_x/SiO_2 indicated that the key intermediates were 1,2,3-butanetriol and 1,2,4-butanetriol, respectively, as shown in Fig. 32. Regarding the formation of 1,3-butanediol, the reaction proceeds *via* the ring-opening hydrogenolysis of 1,4-AHERY followed by selective removal of secondary OH groups in 1,2,3-butanetriol. In the mechanism of the ring-opening hydrogenolysis of 1,4-AHERY, the *anti*-conformation of C–O in the tetrahydrofuran ring with C–OH is connected to high selectivity to the formation of 1,2,3-butanetriol. It is necessary to suppress the further hydrogenolysis of 1,3-butanediol in order to increase the yield of 1,3-butanediol from 1,4-AHERY.

5.4. Deoxydehydration (DODH) and DODH + hydrogenation of 1,4-anhydroerythritol (1,4-AHERY)

1,4-AHERY has *cis*-vicinal OH groups with a 5-membered ring structure. Compared to the 6-membered ring structure, the angle between the C–OH bonds is much smaller in the 5-membered ring structure, which leads to a higher DODH reactivity of 1,4-AHERY. Therefore, 1,4-AHERY is a typical model substrate in the DODH. Table 7 summarizes the DODH of 1,4-AHERY and its related reactions using H_2 as a reducing agent. The DODH of 1,4-AHERY gives 2,5-dihydrofuran, and the consecutive hydrogenation of 2,5-dihydrofuran gives tetrahydrofuran. Homogeneous catalysts such as CH_3ReO_3 are not effective, while good 2,5-dihydrofuran yields have been reported when other reducing agents such as 3-octanol were used.[243] ReO_x–Pd/CeO_2 catalyzed the one-pot reaction of 1,4-AHERY with H_2 to tetrahydrofuran in high yield (>99%).[151,152] ReO_x–Au/CeO_2 catalyzed the DODH of 1,4-AHERY with H_2 to provide 2,5-dihydrofuran in high yield (~80%) with 8% yield of 2,3-dihydrofuran.[144,145] ReO_x–Ag/CeO_2 catalyzed the DODH of 1,4-AHERY with H_2 to produce 2,5-dihydrofuran in high yield (~88%) with 5% yield of 2,3-dihydrofuran.[147] It was also reported recently that MoO_x–Au/TiO_2 and MoO_x–Pd/TiO_2 emerged as good catalysts for the DODH of 1,4-AHERY with H_2 to form 2,5-dihydrofuran (77% yield)[148] and tetrahydrofuran,[148,244] respectively. Although high selectivity was reported, the activity of the MoO_x–M/TiO_2-catalyzed system was significantly lower than that of the ReO_x–M/

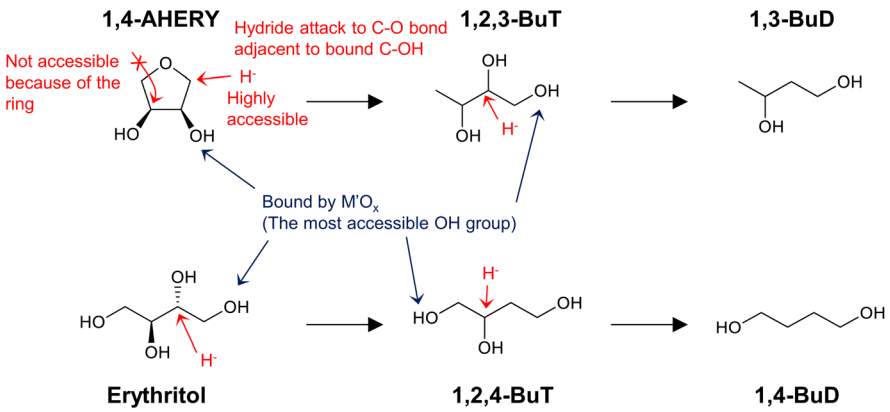


Fig. 32 Main reaction routes of 1,4-AHERY and erythritol over 4 wt% Pt–WO_x/SiO_2 (W/Pt = 0.25) catalyst. M': W; BuT: butanetriol; BuD: butanediol.

Table 7 DODH and its related reactions of 1,4-AHERY with H_2 as a reducing agent

Catalyst	Solvent	$P(H_2)$ [MPa]	Temp. [K]	Time [h]	Conv. [%]	Selectivity [%]				TON[a]	Ref.
						THF	2,5-DHF	2,3-DHF	1,4-BuD		
ReO_x–Pd/CeO_2	1,4-Dioxane	8	413	64	>99	>99	0	0	0	598	151
ReO_x–Au/CeO_2	1,4-Dioxane	8	413	24	93	3	86	9	0	269	144
ReO_x–Ag/CeO_2	1,4-Dioxane	8	413	2	98	4	90	5	0	149	147
ReO_x/CeO_2 + ReO_x/C	1,4-Dioxane	8	413	24	97	7	0	0	86	134	250
ReO_x–Au/CeO_2 + ReO_x/WO_3–ZrO_2	1,4-Dioxane	8	413	24	>99	35	3	0	53	174	252
ReO_x/C	None	0.4	473	2	74	0.1	34[b]	–	0.4	9	251
MoO_x–Au/TiO_2	1,2-DME	8	463	24	67	0.8	96	0.3	0.7	197	148
MoO_x–Pd/TiO_2	1,2-DME	8	463	24	65	98	0.4	0	0	192	148
MoO_x–Pd/TiO_2	1,4-Dioxane	5.2	413	8	29	98	<1	<1	0	44	244
CH_3ReO_3	1,4-Dioxane	3.4	423	16	n.r.	5[b]	25[c]	n.r.	n.r.	6	245
Ru(TMSO)$(DMSO)_4$	Benzene	6.8	463	48	n.r.	23[b]	n.r.	n.r.	n.r.	2	246
$[Cp^*Ru(CO)_3]_2$	Benzene	0.4	443	72	n.r.	12[b]	n.r.	n.r.	n.r.	0.6	247

DHF: dihydrofuran; BuD: butanediol; DME: dimethoxyethane; n.r.: not reported; TMSO: tetramethylene sulfoxide; Cp*: 1,2,3,4,5-pentamethylcyclopentadienyl. [a] TON = ((mol of THF) + (mol of dihydrofurans) + (mol of 1,4-BuD))/(mol of Re, Mo, or Ru). [b] Total yield of 2,5-DHF and 2,3-DHF. [c] Yield values.

CeO_2-catalyzed systems (higher reaction temperature or lower initial reaction rate), because of the intrinsic lower activity of Mo species in DODH than that of Re. Furthermore, the final yield was not high, suggesting that the MoO_x–M/TiO_2 catalysts tended to be deactivated rapidly. Further improvement of the performance of Mo-based heterogeneous DODH systems, especially at low reaction temperature, is necessary for their application to substrates with more complex structures such as erythritol and the alkyl glycosides mentioned in the previous section. Note that homogeneous catalysts combined with H_2 did not work well for this reaction,[245–247] demonstrating the superiority of heterogeneous catalytic systems to homogeneous ones.

5.5. 1,4-Anhydroerythritol (1,4-AHERY) to 1,4-butanediol *via* 2,5-dihydrofuran

The synthesis of 2,5-dihydrofuran in high yield enables the utilization of 2,5-dihydrofuran as an intermediate. Pinkos *et al.* at BASF found that 1,4-butanediol can be produced in high yield by hydration–reduction of 2,5-dihydrofuran over ReO_x/TiO_2 (Re = 6 wt%) catalysts with 1,4-dioxane–water or tetrahydrofuran–water as solvents and H_2 in a flow reactor.[248] The maximum yield of 1,4-butanediol was 85% at 427 K. Based on this previous work and reports on the selective synthesis of 2,5-dihydrofuran, the development of one-pot systems for the conversion of 1,4-AHERY to 1,4-butanediol has been attempted.

It is found that a physical mixture of ReO_x–Au/CeO_2 + ReO_x/C catalysts was effective at converting 1,4-AHERY to 1,4-butanediol in high yield (~90%) (Fig. 33).[249] Activity tests using possible intermediates as substrates suggested that the formation of 1,4-butanediol involved several steps: deoxydehydration (DODH) of 1,4-AHERY to 2,5-dihydrofuran (which is catalyzed by ReO_x–Au/CeO_2), isomerization of 2,5-dihydrofuran to 2,3-dihydrofuran, hydration of 2,3-dihydrofuran to 2-hydroxytetrahydrofuran, and hydrogenation of 2-hydroxytetrahydrofuran or the ring-opened form (4-hydroxybutanal) to 1,4-butanediol. The isomerization step is catalyzed by ReO_x on ReO_x/C. The hydration of 2,3-dihydrofuran is catalyzed by a weak acid and proceeds over the carbon support. The final hydrogenation step is catalyzed by metallic Re species on ReO_x/C. During the conversion of 1,4-AHERY into 1,4-butanediol, it is necessary to suppress the hydrogenation of unsaturated intermediates like 2,5- and 2,3-dihydrofurans, and promote higher activity for the hydrogenation of 4-hydroxybutanal.

Later, it was also found that the Au promoter is not necessary in the mixed catalysts.[250] A simple mixture of ReO_x/CeO_2 + ReO_x/C showed almost the same activity and selectivity in the conversion of 1,4-AHERY into 1,4-butanediol as the case of ReO_x–Au/CeO_2 + ReO_x/C, while ReO_x/C alone did not produce

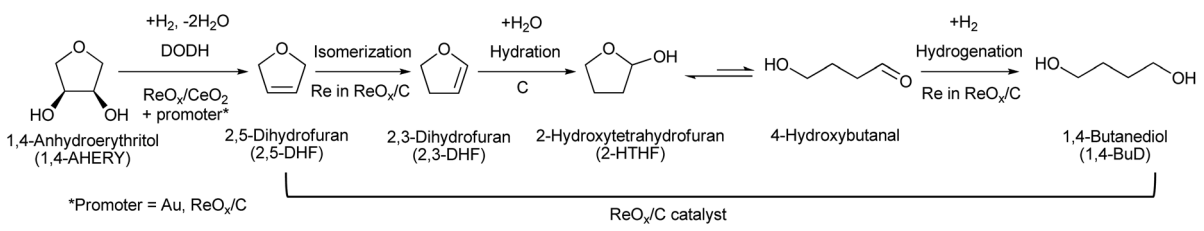


Fig. 33 One-pot conversion of 1,4-AHERY to 1,4-butanediol over ReO_x(–Au)/CeO_2 + ReO_x/C. Reprinted from ref. 252 with permission from the Royal Society of Chemistry, copyright 2020.

1,4-butanediol as a major product.[251] It is possible that metallic Re species on the carbon support help to reduce ReO_x species on CeO_2 *via* hydrogen spillover.

The bottleneck of the catalyst systems of ReO_x–Au/CeO_2 + ReO_x/C and ReO_x/CeO_2 + ReO_x/C is catalyst reusability because it is impossible to calcine carbon-supported catalysts for regeneration to remove deposited species from catalyst surfaces. In order to acquire catalyst reusability, the screening of oxides was conducted for the reaction of 2,5-dihydrofuran.[252] As a result, the ReO_x/WO_3–ZrO_2 catalyst showed a higher performance in the conversion of 2,5-dihydrofuran into 1,4-butanediol than other oxide-supported ReO_x catalysts, although its performance was clearly lower than that of ReO_x/C. Then, ReO_x/WO_3–ZrO_2 was used as a co-catalyst with ReO_x–Au/CeO_2 for the one-pot conversion of 1,4-AHERY. Fig. 34 shows the time courses of the reaction of 1,4-AHERY over ReO_x–Au/CeO_2 + ReO_x/C[249] and ReO_x–Au/CeO_2 + ReO_x/WO_3–ZrO_2.[252] The highest yield of 1,4-butanediol over ReO_x–Au/CeO_2 + ReO_x/WO_3–ZrO_2 was 55%, which was clearly lower than that over ReO_x–Au/CeO_2 + ReO_x/C. After a longer reaction time, the main byproduct was tetrahydrofuran in both cases. There are three formation routes for tetrahydrofuran: dihydrofuran hydrogenation, dihydrofuran disproportionation (to tetrahydrofuran and furan), and dehydration of 1,4-butanediol. At a low conversion level, in the case of ReO_x–Au/CeO_2 + ReO_x/C, the selectivity of the acetal (whose structure is shown in Fig. 34) and 1,4-butanediol was 55% and 28%, respectively, at 33% conversion.[249] The low selectivity of tetrahydrofuran at this stage and the low selectivity to furan suggest that the main formation route of tetrahydrofuran over ReO_x–Au/CeO_2 + ReO_x/C was the dehydration of 1,4-butanediol. In the case of ReO_x–Au/CeO_2 + ReO_x/WO_3–ZrO_2, the selectivities of the acetal, 2,5-dihydrofuran, tetrahydrofuran, and 1,4-butanediol were 37%, 26%, 22%, and 7%, respectively, at 45% conversion.[252] Furan, which is the byproduct co-produced by the disproportionation of dihydrofuran, was almost not formed. The higher levels of dihydrofuran and tetrahydrofuran selectivity at such low conversion suggested that dihydrofuran hydrogenation before hydration of dihydrofuran was the main formation route for tetrahydrofuran over ReO_x–Au/CeO_2 + ReO_x/WO_3–ZrO_2. On the other hand, the reuse of ReO_x–Au/CeO_2 + ReO_x/WO_3–ZrO_2 was almost possible (1,4-butanediol yield: 53% → 49% → 43%) by calcination at 573 K for 3 h, while the reuse of ReO_x–Au/CeO_2 + ReO_x/C was difficult (1,4-butanediol yield: 86% → 76% → 44%) by N_2 treatment at 773 K for 1 h.[252]

5.6. Summary of erythritol/1,4-anhydroerythritol hydrodeoxygenation

The number of research on the hydrodeoxygenation of erythritol and 1,4-AHERY is growing rapidly, because erythritol is now regarded as a platform chemical rather than a model substrate. Specific butanediols except 2,3-butanediol can be produced from erythritol by hydrodeoxygenation with >50% yield. A further increase of the yields and selectivities is expected, while an increase of selectivity is essential because of the difficulty in the separation of polyols. Tetrahydrofuran and 1,3-butadiene can also be produced in high yields (>80%). The hydrogen consumption amount for the production of these chemicals from erythritol or 1,4-AHERY is not high (2 equiv.) and lower than that for succinic acid reduction to 1,4-butanediol or tetrahydrofuran (4 equiv.).

Most chemicals synthesized *via* hydrodeoxygenation of erythritol or 1,4-AHERY can also be produced from biomass through another method such as direct fermentation (for buta-

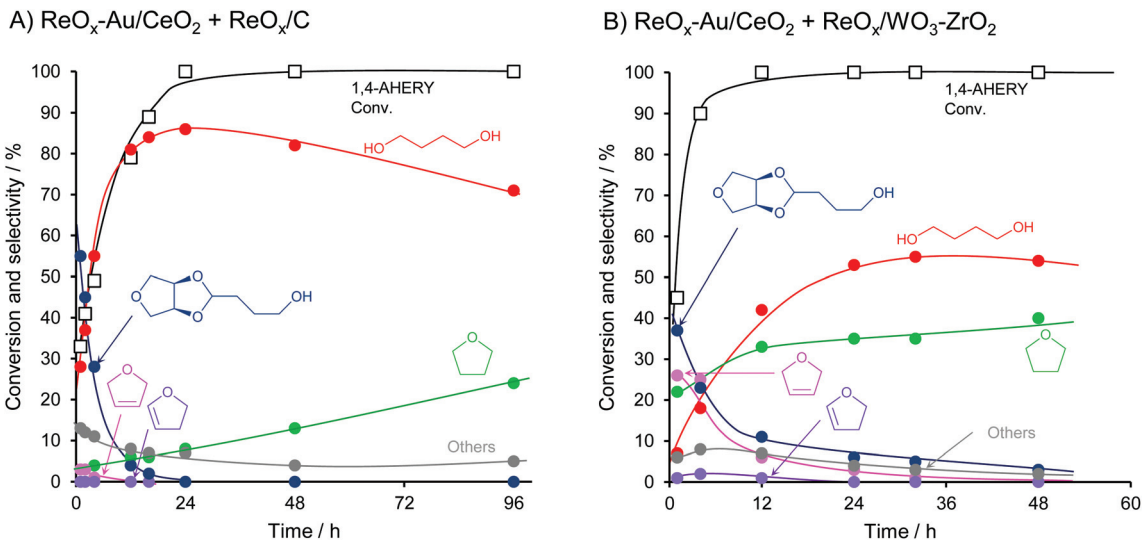


Fig. 34 Catalytic reduction of 1,4-AHERY to 1,4-butanediol.[249,252] (A) ReO_x–Au/CeO_2 + ReO_x/C catalyst mixture. Conditions: 1,4-AHERY (0.5 g), ReO_x–Au/CeO_2 (Re 1 wt%, Au 0.3 wt%) (0.15 g), ReO_x/C (Re 3 wt%) (0.15 g), 1,4-dioxane (4 g), H_2 (8 MPa), 413 K. (B) ReO_x–Au/CeO_2 + ReO_x/WO_3–ZrO_2 catalyst mixture. Conditions: 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), H_2 (8 MPa), 413 K. Others = 1-butanol, γ-butyrolactone, furan, 2-(4-hydroxybutyloxy)tetrahydrofuran and unidentified byproducts.

nediols[253] and 1-butanol[254]), ethanol conversion (for 1,3-butadiene[255]), succinic acid hydrogenation (for 1,4-butanediol and tetrahydrofuran[256,257]) and decarbonylation/decarboxylation of C5 platform molecules (for tetrahydrofuran and 2-butanol[30,258]). The costs can be compared for erythritol-based and other methods. There is uncertainty in the future price of erythritol because the main use of erythritol is as a low-calorie sweetener, the demand for which significantly depends on its reputation for consumers. Nevertheless, the versatile nature of erythritol as a platform chemical is attractive and we hope many researchers will join the study of erythritol/1,4-AHERY conversions.

6. *N*-Acetyl-D-glucosamine (NAG)

Next to cellulose, chitin is the second most abundant biomass resource found in crustacean shells and the exoskeletons of insects and has emerged as a core compound in the "shell biorefinery" for this decade due to its attractive N-containing structure.[259–261] The extraction and purification of this polysaccharide from natural sources requires excess amounts of HCl and NaOH for demineralization and deproteinization, respectively, and is still under development due to its low efficiency and high environmental impact.[262,263] Yet, the use of chitin as a source of N-containing chemicals has been examined in recent decades. Chitin is initially depolymerized into NAG, whose structure is identical to that of glucose (monomer of cellulose) except for an acetamide group at the 2-position, *via* traditional enzymatic hydrolysis[264] and H_2SO_4-assisted mechanochemical depolymerization + subsequent thermal hydrolysis.[265] Note that the undesired deacetylation to form glucosamine did not occur in these cases. In the former case, NAG could be produced in excellent yields of over 90 wt% even from untreated chitin,[266,267] which typically requires pretreatment to improve its poor reactivity due to the robust crystalline structure of chitin. Although conventional hydrolysis in a concentrated HCl solution also provided a good yield of NAG (65%),[268,269] a large amount of acidic waste was co-produced and needed to be neutralized. A diluted HCl solution led to the deacetylation of NAG along with the hydrolysis of β-glycosidic bonds, to yield glucosamine as a major product. Likewise, a mechanochemical technique using NaOH caused depolymerization accompanied by partial deacetylation, which produced low molecular weight chitosan.[270] Such deacetylation led to the production of mixtures containing NAG-rich and glucosamine-rich polysaccharides, making their further utilization complicated.

In recent years, the transformation of NAG into a variety of N-containing compounds has been explored. Similar to the glucose-to-HMF transformation, the most extensively investigated route for NAG is dehydration to 2-acetamido-2,3-dideoxy-D-*erythro*-hex-2-enofuranose (Chromogen I), 3-acetamido-5-(1′,2′-dihydroxyethyl)furan (Chromogen III), and 3-acetamido-5-acetylfuran (3A5AF). Due to the reaction scheme depicted in Fig. 35, the good yields of two Chromogen compounds (37.0% and 34.5% for Chromogen I and III, respectively) were achieved in subcritical water in the absence of catalysts;[271] the presence of acid catalysts decreased the yield of Chromogen III because of its further dehydration to 3A5AF. Due to the presence of vicinal hydroxy groups, both Chromogen I and III can be assumed to undergo further transformation into

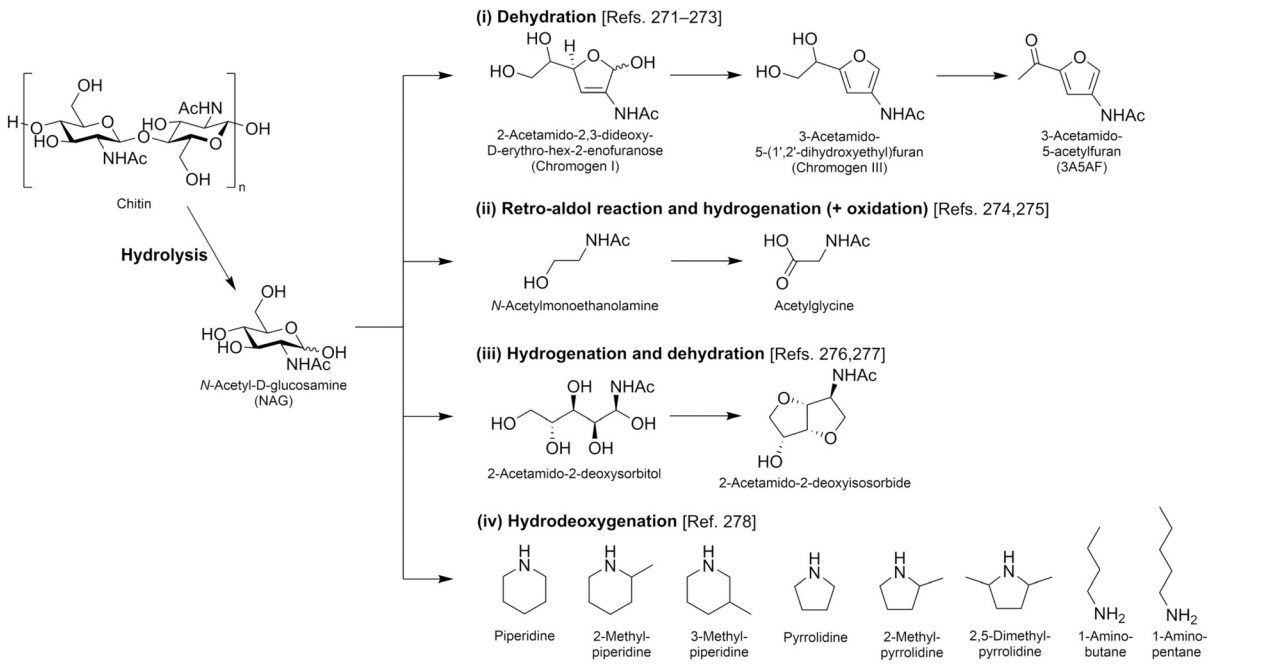


Fig. 35 Derivatization of chitin-derived *N*-acetyl-D-glucosamine (NAG).

N-containing unsaturated products *via* deoxydehydration (DODH) reactions. The use of the appropriate combination of solvent(s) and additive(s) in NAG transformation provided 3A5AF as a major product; for example, the system using boric acid in 1-butyl-3-methylimidazolium ([BMIM]) chloride afforded 60.0% yield of 3A5AF[272] and a different system employing boric acid and sodium chloride in a mixture of [BMIM]Cl and [BMIM]HSO_4 with ethyl acetate as an *in situ* extractant produced 3A5AF in 55.6%.[273] Other routes for NAG transformation into N-containing chemicals have also been developed as exemplified by the retro-aldol reaction + hydrogenation to *N*-acetylmonoethanolamine,[274] its further oxidation to acetylglycine,[275] and hydrogenation + dehydration to 2-acetamide-2-deoxyisosorbide[276,277] (see Fig. 35(ii) and (iii)).

The hydrodeoxygenation of NAG has recently been achieved by using a 3 mol% Ru/C catalyst in a 0.6 M phosphoric acid solution, by which a mixture of various aliphatic amines were produced in *ca.* 50% of their total yield under optimized conditions (Fig. 35(iv)).[278] In this system, both Ru/C and phosphoric acid played important roles: the Ru/C catalyst promoted the hydrodeoxygenation of NAG to form aliphatic amines and phosphoric acid was proposed to form adducts with such amine products and stabilize them. When the system lacked either Ru/C or phosphoric acid, the total yield of aliphatic amines became less than half or even zero. Although the yield and selectivity toward desired amine(s) need to be improved, this report demonstrated the possibility of the production of useful amines from chitin-derived NAG. By contrast, the removal of all the hydroxy groups from NAG requires a lot of hydrogen and also narrows the application of NAG-derived compounds. In this context, the partial and selective removal of specific hydroxy group(s) from NAG molecules can be invoked as a promising means. For this objective, we infer that the examples of the hydrodeoxygenation of cellulose-derived compounds in the previous sections as well as the ones summarized in our previous review[214] will be helpful for the precise design of catalysts and reaction systems due to the structural similarity between glucose and NAG.

The characteristics of chitin—which occurs naturally and abundantly as well as containing nitrogen atoms—make it attractive as a source of valuable N-containing chemicals. Yet, all the reactions of NAG exemplified above still suffer from low yield and/or selectivity of the desired products and necessitate further improvement by modifying and optimizing the catalytic systems. Considering that N-containing compounds are often used as fine chemicals, the well-controlled and selective (*i.e.*, site-specific) transformation of chitin-derived compounds is required. For such an objective, homogeneous catalysts, which can be designed and synthesized to gain specific function(s) more precisely than heterogeneous catalysts, should have great potential. Yet, when there is the desire to convert chitin-derived compounds into bulk chemicals like building blocks for polymers due to the presence of both N- and O-containing functionalities, heterogeneous catalysts, which enable the large-scale production of desired products using continuous flow-type reactors, are worth investigating. We further note that in some cases, chitin and NAG have been converted into non-N-containing chemicals as summarized in previous review papers;[260,264] however, without a specific reason, such transformations accompanied by denitrogenation should be avoided since non-N-containing products can also be synthesized from cellulosic biomass.

7. Conclusion and outlook

Hydrodeoxygenation is a common method for biomass valorization to fuels and chemicals, and remarkable progress has been achieved in the field for the development of heterogeneous catalysts and reaction routes. This review focuses on heterogeneous catalysts, which are generally more suitable than homogeneous catalysts because hydrogen molecules can be activated easily on a solid metal surface. For the production of bulk chemicals, heterogeneous catalysts are advantageous over homogeneous ones because of the ease of separation and applicability to continuous flow-type reactors. In most cases, a liquid-phase reaction is inevitable because of the low vapor pressure of the biomass-derived substrates. Mass transfer is sometimes problematic in the case of heterogeneous catalysts and needs to be improved by altering their structures such as morphology and pores (from micropores in crystals to macropores in pelletized catalysts). Leaching and in the worse case the involvement of leached species in the reaction are critical issues in liquid-phase heterogeneous catalysis and should be carefully checked. Meanwhile, the production of fine chemicals from biomass-derived compounds that typically possess multiple functionalities requires site-specific and/or chemoselective transformation. For such selective transformation, homogeneous catalysts, which can be designed and synthesized more precisely than heterogeneous ones, are promising candidates. Another advantage of homogeneous catalytic systems is the ease of scale up at the level of productivity for fine chemicals and a lack of mass transfer issues. In contrast, the development of highly durable homogeneous catalysts for selective hydrodeoxygenation is very challenging because of the reactivities of C–X (X = O, N, halogen, *etc.*) bonds in ligands and the difficulty of hydrogen activation. Alcohols are relatively inexpensive reducing agents that can be utilized in homogeneous catalysis; however, their use as reducing agents for deoxygenation reactions leads to a loss of selectivity because the biomass-derived substrates also contain alcoholic OH groups. The combination of homogeneous catalyst complexes for C–O bond activation with metallic catalysts for hydrogen activation is also a possible approach, although examples of such systems are limited thus far.

As mentioned in previous sections, a variety of reaction routes such as direct C–O hydrogenolysis, dehydration + hydrogenation, dehydrogenation + dehydration + hydrogenation, and deoxydehydration (+ hydrogenation) are regarded as one-pot hydrodeoxygenation. Appropriate catalysts for each reaction process that give high yields of target products have also been developed, and progress will contribute to the wider

scope of biomass-derived platform chemicals and products. Therefore, we selected and proposed potential platform chemicals for the biomass refinery in this review article, which included erythritol (+1,4-anhydroerythritol), levoglucosan (+levoglucosenone), glucaric acid, alkyl glycosides, and *N*-acetylglucosamine.

Practically feasible methods for the production of potential platform chemicals from biomass have not yet been established, but are under development. However, we believe that progress in efficient conversion technology for the potential platform chemicals introduced here will also promote the development of upstream processes for producing such platform chemicals. Of course, the efficiency of the current conversion technology of potential platform chemicals is not satisfactory and needs to be improved. One of the important future tasks is the substitution of noble metal catalyst components with non-noble metal ones; even if noble metal species are used, the development of catalysts with a very large TON, good reusability, and regenerability is necessary. From the viewpoint of catalytic processes, namely those using heterogeneous catalysts, the proposed catalysts are more applicable to continuous flow reactors, where leaching of the catalyst components must be completely suppressed. These tasks are very challenging and will be connected to decarbonization without using fossil resources.

Conflicts of interest

There are no conflicts to declare.

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