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

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Abstract

The physical mixture of ReO_x-Au/CeO_2 and carbon-supported rhenium catalysts effectively converted 1,4-anhydroerythritol to 1,4-butanediol with H_2 as a reductant. The combination of these two catalysts in one-pot reaction dramatically increased selectivity of 1,4-butanediol as well as conversion of 1,4-anhydroerythritol. The yield of 1,4-butanediol reached ~90%, which is the highest yield from erythritol and 1,4-anhydroerythritol so far, furthermore, at relatively low reaction temperature of 413 K. This reaction is composed of ReO_x-Au/CeO_2-catalyzed deoxydehydration of 1,4-anhydroerythritol to 2,5-dihydrofuran and ReO_x/C-catalyzed successive isomerization, hydration and reduction reactions of 2,5-dihydrofuran.

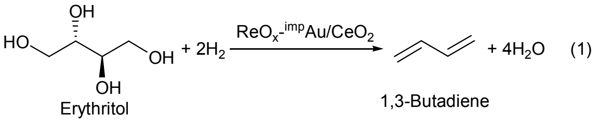
Keywords: Heterogenous catalysis, deoxydehydration, rhenium oxide, gold, one-pot reaction

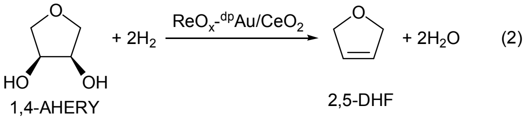
Introduction

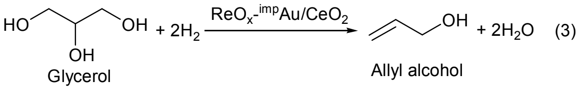
Renewable biomass-based products as energy resources and feedstocks are in increasing demand as replacements of fossil resources.[1-5] However, due to the high oxygen content of biomass-derived platform compounds such as sugar alcohols, selective oxygen removal is one of the most important processes to produce biomass-based chemicals.[4,5] Among sugar alcohols, glycerol and sorbitol have been frequently used as substrates of catalytic hydrodeoxygenation because of their large potential supply.[1-3] While selective oxygen removal of glycerol is possible to produce propanediols as main target chemicals,[6-7] selective oxygen removal of sorbitol is much more difficult, and the main products are deeply deoxygenated ones such as hexane and smaller (≤ C3) compounds such as propylene glycol.[1,8-13] Erythritol is a C4 sugar alcohol which is already produced as a sweetener in industrial scale by fermentation.[14-17] Production of erythritol by fermentation of glycerol, even non-refined one, is also possible.[18] However, erythritol has been less investigated as a substrate of deoxygenation than glycerol and sorbitol. This is because selective oxygen removal of erythritol is more difficult than that of glycerol: the deeply deoxygenated products such as butanols and *n*-butane are coproduced, and high yield of the value-added target products such as butanediols are not achieved.[19-21]

Deoxydehydration (DODH) reaction is an attractive method to decrease the oxygen content of biomass-derived molecules by simultaneously removing vicinal diols to C=C bond.[22-24] Erythritol and its dehydrated product 1,4-anhydroerythritol (1,4-AHERY) are frequently used as substrates for DODH, and their products are 1,3-butadiene and 2,5-dihydrofuran (2,5-DHF), respectively (eqn (1)-(2)).[25-29] Typical DODH systems use homogenous Re catalysts such as CH_3ReO_3 and non-H_2 reductants such as secondary alcohol,[22] while development of heterogeneous DODH catalysts has also been carried out.[30,31] Recently, we reported ReO_x-Au/CeO_2 catalysts as effective H_2-driven heterogeneous DODH catalysts.[32,33] It has been proposed that CeO_2 support plays an important role in the suppression of deep reduction of Re species to low valent Re species such as Re metal and maintaining high valence ($\geq +4$) of the Re species, which can be an active Re species for the DODH reaction, under the DODH reaction conditions. The studies on the effect of loading amount of Re on CeO_2 and the catalyst characterization suggest that monomeric Re species attached on the surface of CeO_2 support is a catalytically active species and polymeric Re species is inactive species in the DODH reaction. Moreover, the DODH reaction is suggested to proceed by the redox mechanism between Re^{4+} and Re^{6+}. On the other hand, the Au particles have a role on the activation of molecular hydrogen, and the activated hydrogen species are supplied from Au surface to Re species via the CeO_2 surface, to reduce the oxidized Re species (Re^{6+}) to the reduced Re species (Re^{4+}). We prepared two types of ReO_x-Au/CeO_2 catalysts: Au loading by deposition-precipitation (ReO_x-^{dp}Au/CeO_2) and Au loading by impregnation (ReO_x-^{imp}Au/CeO_2).[32,33] The former has smaller Au particles (3 nm) and higher activity, and the latter has larger Au particles (12 nm) and lower activity. However, the ReO_x-^{imp}Au/CeO_2 is preferable for the polyol substrates such as glycerol and erythritol (eqn (3) and (1)) due to the higher yield of DODH product (allyl alcohol and 1,3-butandiene, respectively), because the low H_2 activation ability of ^{imp}Au slows down the hydrogenation of alkenes. On the other hand, the ReO_x-^{dp}Au/CeO_2 is good for the DODH reaction of diol substrates such as 1,4-AHERY (eqn (2)), because the selectivity of DHFs of ReO_x-^{dp}Au/CeO_2

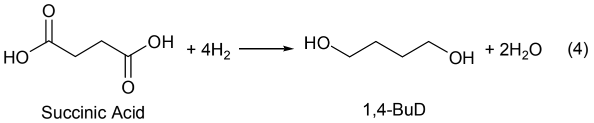
(98%) is similar to that of ReO_x-^{imp}Au/CeO_2 (98%), while the reaction rate of ReO_x-^{dp}Au/CeO_2 is 6 times higher than that ReO_x-^{imp}Au/CeO_2. We also reported a variant of DODH using heterogeneous ReO_x-Pd/CeO_2 catalyst which converted 1,4-AHERY to tetrahydrofuran (THF) via DODH and hydrogenation with high activity and selectivity (99%).[34,35] The structure of Re species is the same as that in ReO_x-Au/CeO_2, the high activity of ReO_x-Pd/CeO_2 is derived from the high H_2 activation ability of Pd, and high dispersion of Pd metal particles (<1 nm).

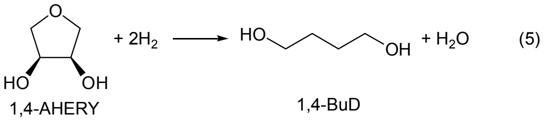




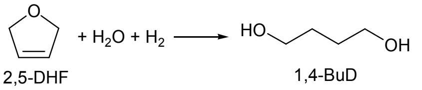


As well as 1,3-butadiene and THF, 1,4-butanediol (1,4-BuD), used as an important monomer and a solvent for synthesis in industry[20], can be a reduction product from erythritol or 1,4-AHERY. A number of studies about production of 1,4-BuD by reduction of succinic acid (eqn (4)), which can be obtained by fermentation from glucose, has been reported.[1,36] Over 80% yields of 1,4-BuD from succinic acid have been reported.[1,36,37] The production of 1,4-BuD from succinic acid requires 4 equiv. of H_2 (eqn (4)). On the other hand, the production of 1,4-BuD from 1,4-AHERY requires only 2 equiv. of H_2 (eqn (5)), and this route is more economical in terms of the reductant cost. However, the production system of 1,4-BuD from erythritol are very limited.





Rh or Ir catalysts modified with group 6-7 metal oxides are known to be active in C-O hydrogenolysis of polyols,[19,21,37] however, it is difficult to remove secondary OH groups consecutively without producing butanols over these catalysts. Only 25% yield of 1,4-BuD is obtained by erythritol hydrogenolysis over Ir-ReO_x/SiO_2 catalyst.[19] Hydrogenolysis of 1,4-AHERY over Ir-ReO_x/SiO_2 and Rh-MO_x/SiO_2 (M = Mo, W, Re) does not produce 1,4-BuD at all.[19,39] On the other hand, Pinkos et al. of BASF found that 1,4-BuD with high yield can also be produced by hydration-reduction of 2,5-DHF over ReO_x/TiO_2 (Re = 6 wt%) catalysts (eqn (6)) with 1,4-dioxane-water or THF-water solvent and H_2 in a flow reactor.[40] The maximum yield of 1,4-BuD was 85% at 427 K. As mentioned above, 2,5-DHF is the product in the Re-catalyzed DODH reaction of 1,4-AHERY (eqn (2)). Thus, 1,4-AHERY may be possible to be converted to 1,4-BuD over Re catalysts. On the basis of the selective conversion of 1,4-AHERY to 2,5-DHF catalyzed by ReO_x-Au/CeO_2, it seems that the tandem process consisting of 1,4-AHERY to 2,5-DHF (413 K, H_2, 1,4-dioxane solvent) and 2,5-DHF to 1,4-BuD catalyzed by ReO_x/TiO_2 (427 K, H_2, 1,4-dioxane + water solvent) in different reactors can produce 1,4-BuD from 1,4-AHERY. Considering that two systems have common reaction conditions such as reaction temperature, H_2 reductant, and the main component of solvent, the one-pot conversion of 1,4-AHERY to 1,4-BuD is promising. Manzer of DuPont reported in the patent that 30% yield of 1,4-BuD is obtained from 1,4-AHERY with ReO_x/C (Re = 5 wt%) catalysts and H_2 at 473 K.[41] The selectivity of 1,4-BuD was as low as 41%, and the main by-products were γ-butyrolactone (GBL) and THF. THF can be formed by hydrogenation of DHF or dehydration of 1,4-BuD.[41] GBL may be formed by disproportionation of the precursor aldehyde of 1,4-BuD (eqn (7)). The low selectivity might be due to the high reaction temperature for ReO_x/C-catalyzed H_2-driven DODH with low activity.[34] Milder reaction conditions may be better for 1,4-BuD production to suppress such side-reactions, and ReO_x-Au/CeO_2 with the DODH activity at low temperature (413 K) is contributable to the one-pot conversion of 1,4-AHERY to 1,4-BuD. In addition, the 1,4-dioxane-water solvent was used for the conversion of 2,5-DHF to 1,4-BuD because H_2O is also a reactant as well as H_2 (eqn (6)). On the other hand, water is not suitable solvent for the DODH reaction catalyzed by ReO_x-M/CeO_2 (M = Au, Pd).[32-35] However, the conversion of 1,4-AHERY to 2,5-DHF gives water as a product (eqn (2)). Therefore, the addition of water can be omitted in principle (eqn (5)) when the product water becomes a reactant in the conversion of 2,5-DHF regardless of low concentration of water.



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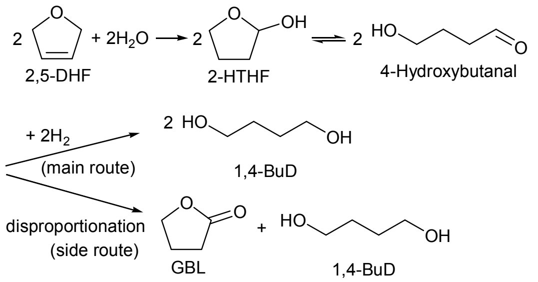

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This one-pot system can decrease the requirement of reactors, separation of intermediates, and solvent, maintaining high yield and productivity of the target product. In this study, we combine the two catalyses within one-pot reaction: the DODH of 1,4-AHERY to 2,5-DHF over ReO_x-Au/CeO_2 and the conversion of 2,5-DHF to 1,4-BuD over another Re catalyst. Over the combination of ReO_x-Au/CeO_2 and ReO_x/C catalysts, we obtained ~90% yield of 1,4-BuD from 1,4-AHERY and H_2 at 413 K (eqn (5)). This yield is much higher than the literature ones of 1,4-BuD from 1,4-AHERY.

Results and Discussion

Production of 1,4-butanediol

Various supported Re catalysts were tested for the co-catalysis with ReO_x-Au/CeO_2 (ReO_x-^{dp}Au/CeO_2) in the reaction of 1,4-AHERY (Table 1). We selected ReO_x-^{dp}Au/CeO_2 because of the higher activity than ReO_x-^{imp}Au/CeO_2.[32,33] The combination of carbon-supported rhenium catalysts with ReO_x-Au/CeO_2 (entries 1-2) showed good selectivity of 1,4-BuD. The ReO_x/C-BP (carbon black BP2000) performed higher conversion and better 1,4-BuD selectivity than ReO_x/C-NR (activated carbon Norit RX3 extra). The combinations of ReO_x/SiO_2, ReO_x/TiO_2, ReO_x/ZrO_2, ReO_x/Al_2O_3, and ReO_x/MgO with ReO_x-Au/CeO_2 (entries 3-7) showed very low yield of 1,4-BuD. The main products of these Re catalysts were 2,5-DHF and 2,3-DHF, indicating that they have low activity in the conversion of DHFs. Single ReO_x-Au/CeO_2 had high selectivity of 2,5-DHF by DODH of 1,4-AHERY (entry 8).[32] Single ReO_x/C-BP showed very low activity in the reaction of 1,4-AHERY (entry 9), and the products include THF and 1,4-BuD. This indicates that ReO_x/C-BP and ReO_x/C-NR have high activity of DHFs ring-opening reaction to 1,4-BuD. Adding ReO_x/C-BP or ReO_x/C-NR to ReO_x-Au/CeO_2 increased the selectivity of 1,4-BuD and effectively decreased the selectivity of other products such as DHFs which were rapidly converted to 1,4-BuD over ReO_x/C-BP and ReO_x/C-NR during the reaction (entries 1 and 2). Meanwhile, the addition also increased the conversion of 1,4-AHERY probably due to the move of some Re species from carbon support to the surface of CeO_2 (entry 12), thereby increasing the number of active site of

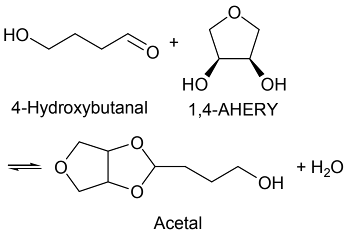
ReO_x-Au/CeO_2 catalyst (discussed below). Because ReO_x/C-BP co-catalyst showed the best selectivity of 1,4-BuD with ReO_x-Au/CeO_2 catalyst in the reaction of 1,4-AHERY, it was used in the following studies. The reaction over the catalyst mixture under Ar atmosphere (entry 10) gave low conversion and many types of products, probably via dehydrogenation and reduction with hydrogen produced by the dehydrogenation.

The optimizations of Re loading amount of ReO_x/C-BP (Fig. 1 (a)), weight ratio of ReO_x/C-BP to ReO_x-Au/CeO_2 (Fig. 1 (b) and (c)), H_2 pressure (Fig. 1 (d)), and reaction temperature (Fig. 2) were carried out. The best result was obtained with the conditions in Table 1: 3 wt% Re for ReO_x/C-BP, 1:1 catalysts weight ratio, 8 MPa H_2, and 413 K. Addition of Re on carbon dramatically increased the selectivity of 1,4-BuD, as well as the conversion of 1,4-AHERY. In the case of ReO_x-Pd/CeO_2 catalyst for DODH + hydrogenation, the weight-based activity is increased until the Re loading of 2 wt%, and then it is decreased with further Re loading, because the amount of monomeric Re species was maximized at 2 wt% of Re.[35] In our previous study on ReO_x-Au/CeO_2,[32] the leaching of Re and Au to the liquid phase was negligible in glycerol DODH. On the other hand, metals on carbon support are easier to escape including ReO_x/C, especially at high temperature.[42] The Re loading in ReO_x-Au/CeO_2 is 1 wt%, and thus the move of some Re species from C-BP to CeO_2 can increase the DODH activity and that from CeO_2 to C-BP can decrease the DODH activity. The stability of Re species and the move between supports will be also discussed later. When the Re amount on ReO_x/C-BP was higher than 3%, the THF selectivity slightly increased (Fig. 1 (a) and (b)). Lower conversion of ReO_x-Au/CeO_2 + C-BP (Fig. 1 (a)) than that of ReO_x-Au/CeO_2 (Fig. 1 (b)) can be explained by the move of some Re species from CeO_2 to C-BP. The amount of

ReO_x-Au/CeO_2 significantly affected the conversion of the reaction, while the selectivity was not so affected (Fig. 1 (c)), indicating that the rate of DODH catalyzed by ReO_x-Au/CeO_2 controls the reaction rate of 1,4-AHERY to 1,4-BuD. In the DODH reaction of polyols over single ReO_x-Au/CeO_2, the formation of alkene from the diolate complex is the rate-determining step.[33] Therefore, this step is also the rate-determining step in the conversion of 1,4-AHERY to 1,4-BuD.

At higher temperature of 443 K (Fig. 2), the selectivity of 1,4-BuD decreased and that to THF increased with the reaction time. The yield of 1,4-BuD at 1 h was 43%, and the yield decreased to be 37% after 4 h reaction time. This behavior suggested that 1,4-BuD is consecutively dehydrated to THF before total conversion of 1,4-AHERY. Thus, lower temperature of 413 K is more suitable for 1,4-BuD formation. This reaction temperature is also lower than those in the patent using ReO_x/C catalyst (473 K), where THF formation decreased the yield of 1,4-BuD.[41] The TOF based on the conversion and total Re amount of the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP at 413 K is calculated to be 5 h^{-1} using the conversion increase during 2 - 4 h reaction time (41% → 49%; Table S1, entries 2 and 3, ESI), which is comparable to that on ReO_x/C at 473 K (13 h^{-1}). High activity of ReO_x-Au/CeO_2 in DODH can decrease the reaction temperature maintaining the productivity.

Fig. 3 and Table S1 (ESI) show the time course of the reaction of 1,4-AHERY over the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. The selectivity of 1,4-BuD increased until 1,4-AHERY was totally converted. The selectivity of DHFs was kept low, indicating that DHFs were rapidly converted. At short reaction time, the acetal from 4-hydroxybutanal and 1,4-AHERY (eqn (8)) (identified by GC-MS and NMR, ESI) was detected in significant selectivity. 4-Hydroxybutanal is thought to be in the equilibrium by the intramolecular acetalization with 2-hydroxytetrahydrofuran (2-HTHF) (eqn (9)). 2-HTHF can be formed by the hydration reaction of 2,3-DHF (eqn (7)). In fact, 4-hydroxybutanal and 2-HTHF were not detected as products in the reaction of 1,4-AHERY. On the other hand, the selectivity of the acetal at low conversion of 1,4-AHERY was rather high and 4-hydroxybutanal is thought to be trapped by acetalization and this decreases in the reactivity of formyl group. While the formation of the acetal can be rather preferable in the reaction equilibrium, the hydrogenation of 4-hydroxybutanal to 1,4-BuD gradually proceeds and the selectivity of the acetal decreases, and finally the acetal was not detected at longer reaction time. The overreaction of 1,4-BuD to 1-butanol or THF was slow under these reaction conditions. The yield of 1,4-BuD reached 85% at 24 h, and this yield value is much higher than the literature values of erythritol or 1,4-AHERY conversions.[19,35]



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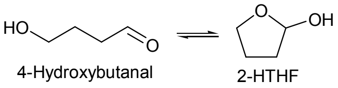

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It should be noted that the conversion of 1,4-AHERY to 1,4-BuD involves H_2O release and consumption together with H_2 consumption (eqn (2) and (6)). In the case of the conversion of 2,5-DHF to 1,4-BuD using ReO_x/TiO_2, THF-water or 1,4-dioxane-water solvents were used, and the water was also a reactant as well as the solvent.[40] In contrast, water is not added at all in this work, and this means that the produced water can react selectively even at the low concentration of H_2O during the reaction of 1,4-AHERY.

Therefore, we also tested the effect of water in the solvent in our system (Table 2). The addition of water to solvent sharply decreased the conversion, indicating that the DODH activity of ReO_x-Au/CeO_2 is suppressed by the presence of water. The conversion of 1,4-AHERY was very low in water solvent (Table S2, entry 4, ESI), and similar behavior was observed in the reaction of 1,4-AHERY to THF over ReO_x-Pd/CeO_2.[35] The conversion of 1,4-AHERY was very low in pure water solvent (Table S2, entry 4, ESI). The interpretation is that higher concentration of water suppresses the formation of Re diolate which is the very important surface intermediate species in DODH. The use of water solvent in DODH with good yield has been only recently reported with the combination of $KReO_4$, Pd/C, 4-(dimethylamino)pyridine ligand and large amount of activated carbon.[43] In addition, the formation of acetal was suppressed by the presence of water (entries 3 and 4, and Fig. 3), and the selectivity of 1,4-BuD was slightly higher than the case in the absence of water. This suggests that 4-hydroxybutanal and 2-HTHF intermediates were rapidly hydrogenated to 1,4-BuD in the presence of water. The reaction can be conducted in THF solvent or even without solvent (Table S2, entries 1 and 3, ESI). The selectivity of 1,4-BuD was almost same although the activity was slightly lower than that in the 1,4-dioxane solvent.

Catalyst characterization

Because the catalysts were well mixed in the reaction, the characterization of used catalyst was rather difficult. In our previous reports, the reduction of Re species on CeO_2 is dramatically promoted by addition of promoters such as Au and Pd.[32-35] High valence Re species on CeO_2 can be easily reduced to Re^{4+} with H_2 in presence of promoters. In the

DODH reaction of 1,4-AHERY to 2,5-DHF, Re species in ReO_x-Au/CeO_2 may have the redox pair of Re^{4+} and Re^{6+}, and Re^{6+} reduced to Re^{4+} with H_2 after the reaction.[32-35]

The H_2-TPR profiles of ReO_x/C-BP and C-BP support are shown in Fig. 4. The reduction of C-BP started about 700 K, suggesting that C-BP support was not reduced in the reaction conditions (413 K). The reduction of Re species started around 500 K. Although the temperature was higher than reaction temperature, reduction of supported Re to the mixture of Re^0 and Re^{n+} can take place in the solvent at lower temperature than the TPR peak,[37,44,45] which can be explained by much higher H_2 pressure under the reaction conditions than that under TPR conditions. When ReO_x/C-BP was pre-reduced at 673 K, the H_2 consumption amount was decreased by 0.41 $mmol \cdot g^{-1}$, which corresponds to the reduction of Re from +7 to average valence +2, suggesting that the part of Re species on C-BP is reduced to metallic state. The formation of Re metal on ReO_x/C-BP is also supported by the data that ReO_x/C-BP alone has some activity in hydrogenation as discussed later.

The XRD patterns (Fig. S1, ESI) only showed CeO_2 peaks in fresh or used catalyst mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. This indicates that Au and ReO_x particles were highly dispersed on both CeO_2 and/or carbon surfaces,[32-35] and suggesting that the aggregation of particles is not so significant.

The TEM images of used catalyst mixture are shown in Fig. 5. CeO_2 particles were located on the C-BP support as small aggregates composed of a few CeO_2 crystallites. The aggregate size (10-20 nm) was much smaller than that on the CeO_2 alone or ReO_x-Au/CeO_2 alone (0.2-1 μm),[33] while the primary crystallite size of CeO_2 (8 nm) is similar for CeO_2 alone,[33] ReO_x-Au/CeO_2 alone,[33] and ReO_x-Au/CeO_2 + ReO_x/C-BP. This suggests that the aggregates of CeO_2 are dispersed by the interaction between CeO_2 crystallite and the carbon surface. In our recent paper, we found that the ReO_x species on CeO_2 can be reduced by H_2 even when the promotor Au is absent on the same CeO_2 particle.[33] The active hydrogen species is supposed to move from particle to particle via proton and electron. As well as CeO_2, carbon can carry electrons, and thus the active hydrogen species can move from promotor (Au) to Re in the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. On the C-BP support (Fig. 5C), Re species existed as highly dispersed state.

Reaction mechanism

To study the possible route of the reaction from 1,4-AHERY to 1,4-BuD and the role of catalyst components, reactions of different substrates (or possible intermediates) were tested over various related catalysts (Table 3). In this experiment, small amount of water was added to the system (water: substrate = 1:1) because the DODH step of 1,4-AHERY co-produces water, and formed water is used as a reactant for the subsequent steps. The substrate amount (0.15 g) was set lower than the standard runs (0.5 g, Table 1) because the concentration of possible intermediates was low in the standard runs for the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/C-BP, for example Table 1, entry 1. The combination of ReO_x-Au/CeO_2 and ReO_x/C-BP (Table 3, entry 1) gave high yield of 1,4-BuD (90%), which is similar to the case of standard conditions (Table 1, entry 1). It should be noted that this yield is clearly higher than the yield of 1,4-BuD by the reaction of 2,5-DHF over ReO_x/TiO_2 (85%),[40] indicating the superiority of the one-pot system. Single ReO_x-Au/CeO_2 (Table 3, entry 2) gave higher yield of THF and 2,3-DHF than the result under the standard conditions in

Table 1, entry 8, indicating that the successive reactions of 2,5-DHF to THF by hydrogenation and to 2,3-DHF by isomerization are also catalyzed by ReO_x-Au/CeO_2. In spite of this activity of ReO_x-Au/CeO_2 in hydrogenation of 2,5-DHF to THF, very high yield of 1,4-BuD and very low yield of THF over ReO_x-Au/CeO_2 + ReO_x/C-BP were observed, which suggests that the activity of ReO_x/C-BP in the successive reactions of 2,5-DHF can be much higher than that of ReO_x-Au/CeO_2. Single ReO_x/C-BP (Table 3, entry 3) showed very low yield of 1,4-BuD, THF and so on, while the conversion was significantly higher than the total yield of detected products. This suggests that polymerized products are formed from 1,4-AHERY or the reduced compounds such as DHFs. The difference between the conversion and the sum of the detected products' yield was also observed over ReO_x/C-BP in the reaction of 2,5-DHF (Table 3, entry 6). Medium yield of 1,4-BuD was obtained, indicating that ReO_x/C-BP catalyzes the conversion of 2,5-DHF to 1,4-BuD, although high concentration of 2,5-DHF can promote the polymerization of 2,5-DHF and hydrogenation to THF and can cause the decrease in the yield of 1,4-BuD. The combination of ReO_x/C-BP with ReO_x-Au/CeO_2 enhanced the yield of 1,4-BuD and suppressed the polymerization (Table 3, entry 4). The activity of ReO_x-Au/CeO_2 was not so high in the reaction of 2,5-DHF (Table 3, entry 5), indicating that the reaction of 2,5-DHF is mainly catalyzed by ReO_x/C-BP (Table 3, entry 6). An important point is that single C-BP has almost no activity in the reaction of 2,5-DHF (Table 3, entry 7) and Re species supported on C-BP catalyzes the reaction of 2,5-DHF.

Next, the reactions of 2,3-DHF over various catalysts were also tested because 2,3-DHF is a possible intermediate for the formation of 1,4-BuD. It should be noted that the difference between the sum of the detected products' yield and the conversion in the reaction of

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

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

Catalyst stability

The drawback of this co-catalysis of ReO_x-Au/CeO_2 + ReO_x/C-BP is the decrease of catalytic activity after usage (Table 4). The activity of the catalyst mixture dropped from 100% conversion (fresh) to 65% in the 2nd run, and the selectivity of 1,4-BuD also decreased. The carbon balance was about 90%, suggesting that a small amount of products was adsorbed on the catalysts. The carbonaceous deposits on catalyst surface might cover the active sites leading the deactivation of catalysts. The leached amount of Re from the mixture of ReO_x-Au/CeO_2 + ReO_x/C-BP in the absence of air was below 0.01% of total Re amount in the catalysts by ICP analysis (filtration after cooling), indicating that Re in both catalysts was almost not dissolved in the solution during the reaction. However, when the reaction solution was collected in air, the Re leaching amount from the catalyst mixture increased to 0.25%. This is probably due to oxidation of some of Re species and dissolution into the solution. The move of Re species from ReO_x/C-BP in oxidized state was also suggested by the reaction tests with Au/CeO_2 + ReO_x/C-BP (Table 1, entry 12). When the ReO_x/C-BP was reduced before mixing, the activity of the mixture was very low (Table 1, entry 13). This suggests that the move of Re species is suppressed during the reaction, which agrees with that the leaching of Re from the standard mixture was negligible. Anyway, the leached Re amount was too small to be the reason for the deactivation of catalysts. On the other hand, the Re leaching amount of single ReO_x/C-BP (0.39%) was higher than that of the mixture of ReO_x-Au/CeO_2 + ReO_x/C-BP showing that the Re species on C is more labile than that on CeO_2. The Re species can to move from C surface to CeO_2 surface, which might be a reason for the deactivation of ReO_x/C-BP. In our previous paper, used ReO_x-Au/CeO_2 catalyst can perform almost the same activity after regeneration by calcination after each usage.[32] However, the combustibility of carbon support makes such regeneration difficult. We tested heating the used catalyst mixture at 573 K in air. At this temperature, the combustion of carbon support is minimal based on TG-DTA profile (Fig. S2, ESI). Nevertheless, the activity was further decreased (44% conv.), and the main product was 2,5-DHF, indicating that both ReO_x/C-BP and ReO_x-Au/CeO_2 were deactivated by air treatment. Then we tested the regeneration under N_2 or H_2. H_2 regeneration had little effect on increasing the activity of used catalyst mixture (66% conv.). Regeneration with N_2 at 773 K for 1 h gave better result of 91% conversion and 83% 1,4-BuD selectivity. However, the activity was further decreased by further uses, and it dropped to 54% conversion after 4th run. The decline of selectivity was lower than the decrease of activity, indicating that ReO_x-Au/CeO_2 was more severely deactivated than ReO_x/C-BP. The low carbon balance of entries 9 and 10 might be due to the deactivation of ReO_x/C-BP.

Conclusions

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

Experimental

The ReO_x-Au/CeO_2 (1 wt% Re, 0.3 wt% Au) catalyst was prepared by deposition-precipitation method for Au loading and subsequent impregnation for Re loading according to our previous report.[32] The activity test was conducted with autoclave reactor equipped with an inner glass cylinder. After reaction, both gas and liquid phases were analyzed by FID-GC. The carbon balance (C.B.) of each analysis result was calculated using eqn (10). The sum of the detected but unidentified products is denoted as “others” in results. The FID sensitivity of “others” was assumed to be the same as that of 1,4-butanediol (1,4-BuD) unless denoted. When the C.B. is in the range of 100 ± 10% considering the experimental error, the conversion and selectivity on the carbon basis are calculated by eqn (11) and (12), respectively, and the data of C.B. are not shown in each result. In contrast, when the C.B. is clearly lower than 100% (<90%), the conversion and selectivity on carbon basis are calculated by eqn (13) and (14) as below. The selectivity of "others" is the same as the above case. The data of C.B. are shown in each result when clearly below 100%. We think two reasons for low C.B. in the results. One is the use of substrate with low boiling point, in particular, 2,3-DHF. (b.p. 327 K). In the experiments of 2,3-DHF substrate (Table 3, entries 8-11), and in the results of significant yield of 2,3-DHF product in the reaction of 1,4-anhydroerythritol (Table 1, entries 3-5), it is thought that a part of 2,3-DHF can be lost during the purge of H_2 before reaction and the filtration after reaction. The other reason is the side reactions such as polymerization of unsaturated compounds like 2,5-DHF or 2,3-DHF giving undetected products, and this phenomenon seems to be observed remarkably on ReO_x/C-BP in Table 3, entries 1 and 4. The yield was calculated by eqn (15) for both cases. The detailed experimental procedures are also described in electronic supplementary information (ESI).

$$\text{C. B. (\%)}=\frac{\text{Amount of remaining substrate (C-mol) + Total amount of detected products (C-mol)}}{\text{Amount of initial substrate (C-mol)}}\times 100 \qquad (10)$$

$$\text{Conversion (\%)}=\frac{\text{Total amount of detected products (C-mol)}}{\text{Amount of remaining substrate (C-mol) + Total amount of detected products (C-mol)}}\times 100 \qquad (11)$$

$$\text{Selectivity of product A (\%)}=\frac{\text{Amount of A (C-mol)}}{\text{Total amount of detected products (C-mol)}}\times 100 \qquad (12)$$

$$\text{Conversion (\%; low C. B.)}=100-\frac{\text{Amount of remaining substrate (C-mol)}}{\text{Amount of initial substrate (C-mol)}}\times 100 \qquad (13)$$

$$\text{Selectivity of product A (\%; low C. B.)}=\frac{\text{Amount of A (C-mol)}}{\text{Amount of initial substrate (C-mol) - Amount of remaining substrate (C-mol)}}\times 100 \qquad (14)$$

$$\text{Yield (\%)}=\frac{\text{Conversion (\%)} \times \text{Selectivity (\%)}}{100} \qquad (15)$$

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

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

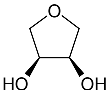
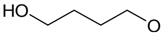
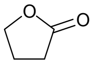
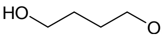
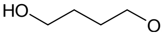
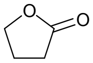
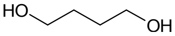
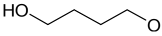
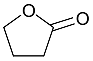
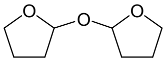
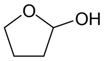
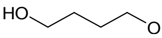
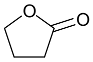
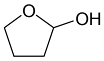
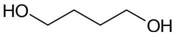
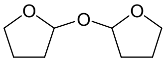
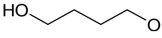
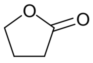
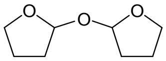
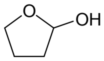
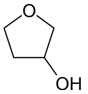
[a] 1,4-AHERY = 0.5 g, $W_{\mathrm{cat\,1}}$ = 0.15 g (Re = 1 wt%, Au = 0.3 wt%), $W_{\mathrm{cat\,2}}$ = 0.15 g (Re = 3 wt%), 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 24 h. [b] P_{Ar} = 5 MPa. [c] ReO_x/C-BP was reduced by H_2 in 1,4-dioxane at 413 K for 1 h before reaction. AHERY: anhydroerythritol,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

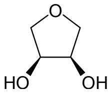
Table 2 Effect of water addition to the1,4-dioxane solvent in the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 and ReO_x/C-BP catalysts [a]

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

[a] 1,4-AHERY = 0.5 g, water = 0 to 0.3 g, $W_{\mathrm{cat\ (ReO_x\text{-}Au/CeO_2,\ Re\ =\ 1\ wt\%,\ Au\ =\ 0.3\ wt\%)}}$ = 0.15 g, $W_{\mathrm{cat\ (ReO_x/C\text{-}BP,\ Re\ =\ 3\ wt\%)}}$ = 0.15 g, 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran.

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

Entry	Substrate	Catalyst	Catalyst weight /g	Products (yield /%)	Conv. /% (C.B. /%)
1		ReO_x-Au/CeO_2 + ReO_x/C-BP	0.15 + 0.15	 (90),  (4),  (4), others (2)	100
2		ReO_x-Au/CeO_2	0.15	 (32),  (27),  (25), others (6)	100
3		ReO_x/C-BP	0.15	 (1),  (0.3), others (1)	33 (69)
4		ReO_x-Au/CeO_2 + ReO_x/C-BP	0.15 + 0.15	 (80),  (13),  (4), others (3)	98
5		ReO_x-Au/CeO_2	0.15	 (23),  (13),  (2), others (3)	45
6		ReO_x/C-BP	0.15	 (39),  (9),  (8), others (9)	94 (70)
7		C-BP	0.15	 (3),  (1),  (1),  (0.5), others (0.5)	4
8		ReO_x-Au/CeO_2 + ReO_x/C-BP	0.15 + 0.15	 (60),  (12), others (6)	100 (78)
9		ReO_x-Au/CeO_2	0.15	 (5),  (3),  (2), others (10)	49 (71)
10		ReO_x/C-BP	0.15	 (24),  (6),  (2), others (6)	100 (38)
11		C-BP	0.15	 (46),  (18),  (8), others (5)	98 (80)

[a] Substrate = 0.15 g, water = 0.03-0.04 g (water : substrate molar ratio = 1 : 1), W_{cat} = 0.15 g for single, or 0.15 + 0.15 g for mixture (ReO_x–Au/CeO_2, Re = 1 wt%, Au = 0.3 wt%; or ReO_x/C-BP, Re = 3 wt%; or C-BP), 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 4 h.  1,4-AHERY: 1,4-anhydroerythritol;

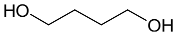
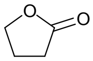
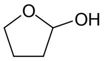
 1,4-BuD: 1,4-butanediol;  GBL: γ-butyrolactone;  THF: tetrahydrofuran;  2,5-DHF: 2,5-dihydrofuran;  2,3-DHF: 2,3-dihydrofuran;  2-HTHF: 2-hydroxytetrahydrofuran.

Table 4 Reusability of the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP catalysts [a]

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

[a] 1,4-AHERY = 0.5 to 0.3 g (based on the weight of catalysts), $W_{\text{cat mixture}}$ = 0.3 to 0.18 g (ReO_x–Au/CeO_2, Re = 1 wt%, Au = 0.3 wt%; ReO_x/C-BP, Re = 3 wt%), 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol, Acetal: 3,4-(4-hydroxybutylidenedioxy)-tetrahydrofuran.

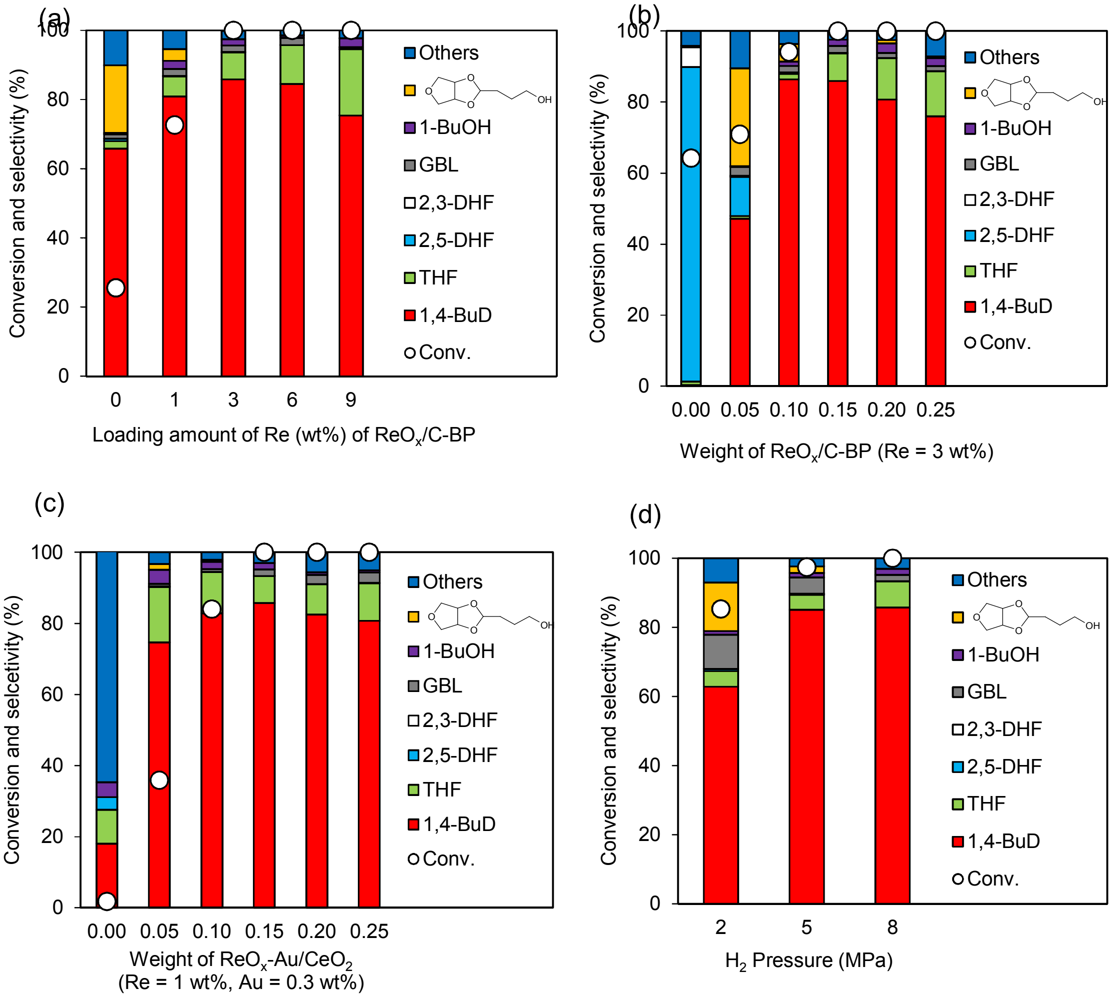


Fig. 1 Effect of (a) Re loading amount of ReO_x/C-BP (0.15 g) in the reaction of 1,4-AHERY with ReO_x-Au/CeO_2 (0.15 g); (b) weight of ReO_x/C-BP (Re = 3 wt%) in the mixture with ReO_x-Au/CeO_2 (0.15 g) in the reaction of 1,4-AHERY; (c) weight of ReO_x-Au/CeO_2 in the mixture with ReO_x/C-BP (Re = 3 wt%, 0.15 g) in the reaction of 1,4-AHERY; (d) hydrogen pressure in the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 (0.15 g) + ReO_x/C-BP (Re = 3 wt%, 0.15 g).

Standard conditions: 1,4-AHERY = 0.5 g, $W_{\text{cat (ReO}_x\text{-Au/CeO}_2\text{, Re = 1 wt\%, Au = 0.3 wt\%)}}$ = 0.15 g, $W_{\text{cat (ReO}_x\text{/C-BP, Re = 3 wt\%)}}$ = 0.15 g, 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol.

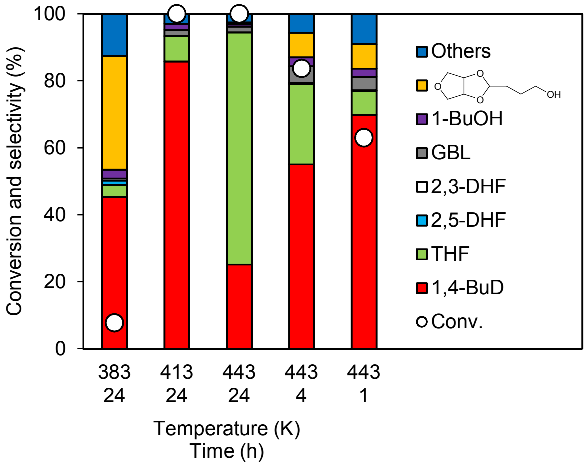


Fig. 2 Effect of reaction temperature and reaction time in the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/C-BP. 1,4-AHERY = 0.5 g, $W_{cat\ (ReO_x\text{-}Au/CeO_2,\ Re\ =\ 1\ wt\%,\ Au\ =\ 0.3\ wt\%)}$ = 0.15 g, $W_{cat\ (ReO_x/C\text{-}BP,\ Re\ =\ 3\ wt\%)}$ = 0.15 g, 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 383 to 443 K, t = 1 to 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, GBL: γ-butyrolactone, BuOH: butanol.

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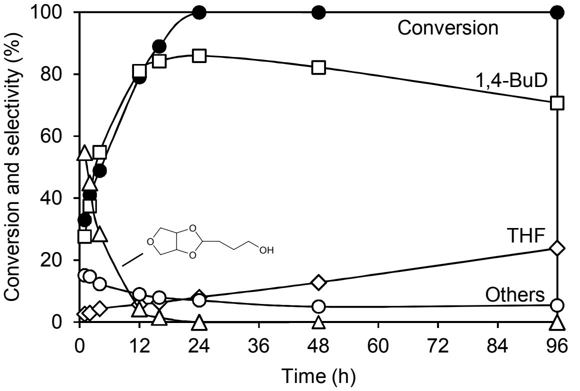


Fig. 3 Time course of the reaction of 1,4-anhydroerythritol over the mixture of ReO_x-Au/CeO_2 and ReO_x/C-BP. 1,4-AHERY = 0.5 g, $W_{\mathrm{cat}\ (\mathrm{ReO_x\text{-}Au/CeO_2,\ Re = 1\ wt\%,\ Au = 0.3\ wt\%})}$ = 0.15 g, $W_{\mathrm{cat}\ (\mathrm{ReO_x/C\text{-}BP,\ Re = 3\ wt\%})}$ = 0.15 g, 1,4-Dioxane = 4 g, $P_{\mathrm{H_2}}$ = 8 MPa, T = 413 K, t = 1 to 96 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, “others” also include 2,5-DHF (2,5-dihydrofuran), 2,3-DHF (2,3-dihydrofuran), GBL (γ-butyrolactone) and BuOH (butanol), as well as by-products shown as “others” in Table S1, ESI.

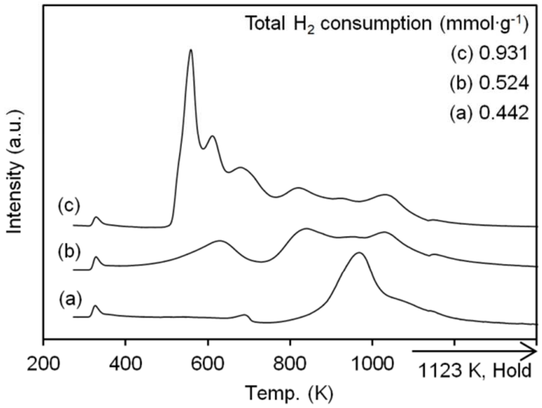


Fig. 4 H_2-TPR profiles of ReO_x/C-BP (Re = 3 wt%; 0.16 mmol·g^{-1}). (a) C-BP, (b) ReO_x/C-BP after reduction in H_2 flow (30 cc/min) at 673 K for 1 h (at heating rate of 10 K/min), (c) ReO_x/C-BP. Sample weight = 50 mg.

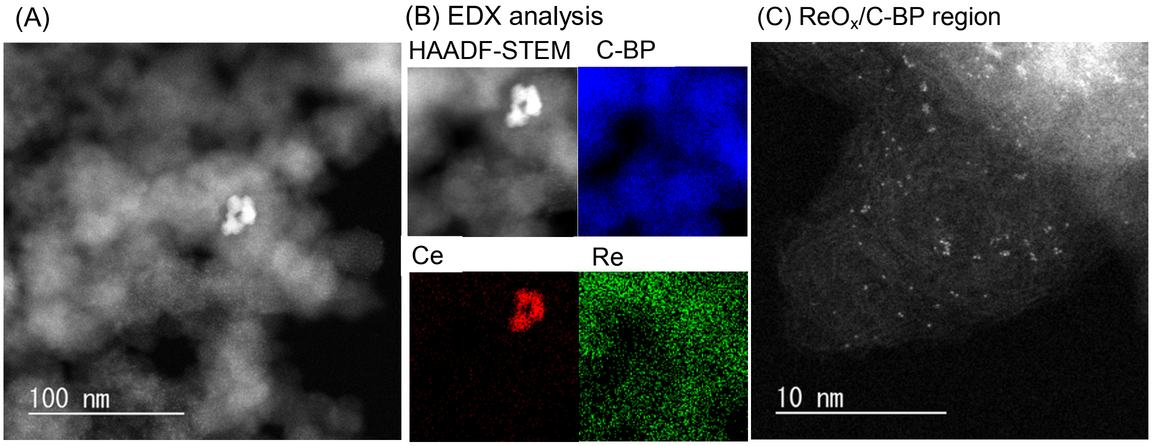
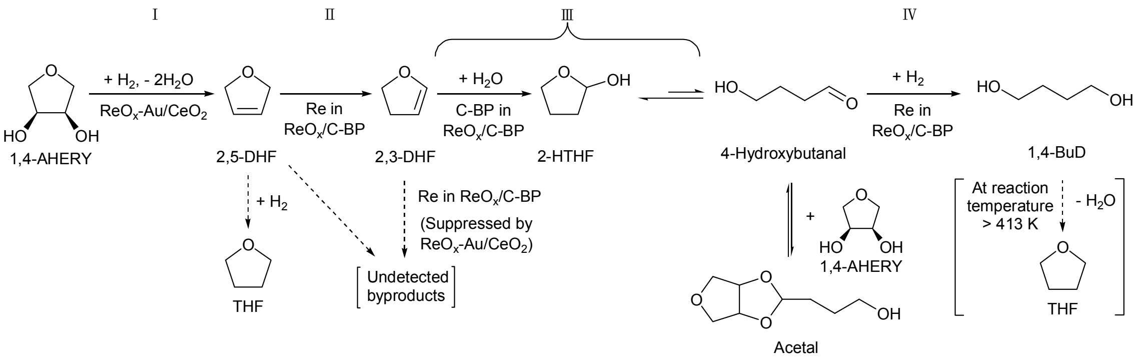


Fig. 5 HAADF-STEM images of the mixture of ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) and ReO_x/C-BP (Re = 3 wt%) after catalytic use. The conditions for catalytic reaction: 1,4-AHERY = 0.5 g, $W_{ReO_x\text{-}Au/CeO_2}$ = 0.15 g, $W_{ReO_x/C\text{-}BP}$ = 0.15 g, 1,4-Dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 24 h.



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