

# Article

# Mechanistic Study of Hydrogen-driven Deoxydehydration over Ceria-supported Rhenium Catalyst Promoted by Au Nanoparticles

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# **ACS** Catalysis

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Mechanistic Study of Hydrogen-driven Deoxydehydration over Ceria-supported Rhenium Catalyst **Promoted by Au Nanoparticles** Yoshinao Nakagawa, \*<sup>[a,b]</sup> Shuhei Tazawa, <sup>[a]</sup> Tianmiao Wang, <sup>[a]</sup> Masazumi Tamura, <sup>[a,b]</sup> Norihito Hiyoshi, <sup>[c]</sup> Kazu Okumura,<sup>[d]</sup> Keiichi Tomishige\*<sup>[a,b]</sup> <sup>[a]</sup> Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan <sup>[b]</sup> Research Center for Rare Metal and Green Innovation, Tohoku University, 468-1, Aoba, Aramaki, Aoba-ku, Sendai 980-0845, Japan <sup>[c]</sup> Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), 4-2-1 Nigatake, Miyagino-ku, Sendai 983-8551, Japan <sup>[d]</sup> Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, 2665-1 Nakano-machi, Hachioji, Tokyo 192-0015, Japan \*Corresponding author: Yoshinao Nakagawa and Keiichi Tomishige School of Engineering, Tohoku University, 6-6-07, Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan E-mail: yoshinao@erec.che.tohoku.ac.jp, tomi@erec.che.tohoku.ac.jp

# Abstract

Structure and activity of ReOx-Au/CeO2 catalysts for deoxydehydration (DODH) of polyols to alkenes with H<sub>2</sub> were investigated in detail. Based on XRD and TEM, the size of Au particles is in a similar scale to CeO<sub>2</sub> support particles, and the number of Au particles is much smaller than that of  $CeO_2$  support particles. Nevertheless, the catalytic activity and TPR data of the physical mixture of Re/CeO<sub>2</sub> and Au/CeO<sub>2</sub> indicate that Re species on all the CeO<sub>2</sub> particles can be reduced with H<sub>2</sub> and can work as a catalytic center. The H<sub>2</sub> activation ability of the catalyst with larger (~12 nm) Au particles (<sup>imp</sup>Au; "imp" means impregnation for loading) is lower than that with smaller (~3 nm) Au particles (<sup>dp</sup>Au; "dp" means deposition-precipitation for loading), and the DODH reaction rate over ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> is limited by the H<sub>2</sub> activation rate. The CeO<sub>2</sub>-supported <sup>dp</sup>Au particles have also higher activity in C=C hydrogenation, C=C migration and *cis/trans* isomerization of diols. The C=C hydrogenation and C=C migration are side reactions in DODH, and in the DODH reaction of polyols, such as glycerol and erythritol, ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> shows higher yield of DODH products than ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>. In contrast, in the case of diols, the selectivity decrease by these side reactions is small, and ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> is better catalyst than ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> because of the higher activity. In addition, the cis/trans isomerization activity of ReOx-dpAu/CeO2 enables the DODH of trans-1,2-cyclohexanediol, which is usually unreactive in DODH, into cyclohexene via isomerization to cis-1,2-cyclohexanediol and the subsequent DODH.

#### Keywords

Deoxydehydration, hydrogen spillover, heterogeneous catalysis, isomerization, rhenium

# Introduction

Applying a heterogeneous catalytic system to reactions that have been carried out with a homogeneous catalytic system is important in view of industrialization.[1] One of the chemical transformations that are desired to industrialize is the deoxygenation of poly-functionalized compounds such as polyols to unsaturated alcohols and alkenes.[2] Polyols are typically derived from sugars or vegetable oils in large scale, while unsaturated alcohols and alkenes are especially important platform chemicals because of the reactivity toward versatile addition reactions. Deoxygenation requires reductants, and the most inexpensive and greenest reductant in industry is molecular hydrogen (H<sub>2</sub>); however, deoxygenation with H<sub>2</sub> typically produces saturated compounds and selective production of unsaturated target compound is generally difficult.[3]

Deoxydehydration (DODH) is one kind of deoxygenation reactions and has received increasing attention during the past few years (Scheme 1).[4] This reaction transforms *cis*-vicinal OH groups into C=C bond accompanying the consumption of a reductant. High-valent Re catalysts have been most investigated as an active center in DODH, while there are also Mo [5-7] and V [8,9] catalysts for DODH. As variants of DODH, deepoxidation,[4b,10] reductive coupling of alcohols [11] and monodeoxygenation of vicinal OH groups [12] have been also reported. The widely accepted mechanism of DODH (Scheme 1) is that diolate complex with metal center reduced by two electrons is transformed into product (alkene) and fully oxidized metal center. As reductants, alcohols have been most used, while PPh<sub>3</sub>,[13,14] sulfite,[15] metal,[16] hydroaromatics,[17] and CO [8b] have been also used to give high yields of DODH products. One of the most typical DODH systems with high selectivity to olefins and wide substrate scope is the combination of CH<sub>3</sub>ReO<sub>3</sub> catalyst and a secondary alcohol reductant reported by Toste et al.[18]

Development of heterogeneous catalysts using H<sub>2</sub> reductant is one of the current topics in the

research field of DODH. Jentoft, Nicholas and co-workers reported a  $H_2$ -driven DODH over ReO<sub>x</sub>-C as a heterogeneous catalyst in 2013.[19] However, there is room for improvement in the catalytic performance, such as the low activity and the leaching of Re. After that, ReO<sub>x</sub>/TiO<sub>2</sub> was reported as a recyclable solid catalyst for DODH using 3-octanol as a reductant, but the yields of DODH products were moderate (~50%).[20] Recently, HReO<sub>4</sub> immobilized on poly-benzylamine was reported to exhibit high selectivity in the DODH of tartaric acid, but the serious leaching of Re was observed.[21] Moreover, the latter two DODH systems with solid catalysts were driven by a secondary alcohol reductant. There are two issues in the use of H<sub>2</sub> as reductant for DODH: (i) it is difficult to keep high valence of supported Re species when H<sub>2</sub> is used as reductant [22] and (ii) the unsaturated product is easily hydrogenated.[14a,23]

We have recently discovered that CeO<sub>2</sub> is an appropriate support for Re center for DODH with H<sub>2</sub> as a reductant.[24-26] We first reported heterogeneous ReO<sub>x</sub>-Pd/CeO<sub>2</sub> catalyst for the simultaneous removal of vicinal OH groups (DODH + hydrogenation) such as 1,4-anhydroerythritol and glycerol to tetrahydrofuran and 1-propanol, respectively.[24] ReO<sub>x</sub>-Pd/CeO<sub>2</sub> exhibited much higher activity (TOF) than all the previously reported homogeneous and heterogeneous DODH catalysts, and very high yields of the hydrogenated DODH products are obtained with H<sub>2</sub> as a reductant. The supported Re species are highly dispersed, and monomeric Re species with +4 or +6 valence, which is different from the valence (+5 or +7) of homogeneous Re catalysts for DODH, are supposed to be the active center.[25] Higher loading of Re decreases the number of monomeric Re species, decreasing TOF and even weight-based activity. The decrease of activity by excess loading, as well as the higher activity than homogeneous catalysts, also supports the heterogeneous nature of ReO<sub>x</sub>-Pd/CeO<sub>2</sub> catalyst. The Pd species is present as metal clusters having low Pd-Pd coordination number (~3) on the CeO<sub>2</sub> surface, activating H<sub>2</sub> for the promotion of the Re reduction and the hydrogenation of

DODH products. To obtain DODH products without hydrogenation such as 2,5-dihydrofuran and allyl alcohol from 1,4-anhydroerythritol and glycerol, respectively, we later found that Au particles are very effective promoters, and ReOx-Au/CeO2 catalyst exhibited high yields of olefinic compounds in H<sub>2</sub>-driven DODH.[26] We tested two preparation methods for Au loading: deposition-precipitation (dp) and impregnation (imp). Similarly to the numerous studies on Au catalysts,[27]  $^{dp}Au/CeO_2$  has smaller Au particles (~3 nm) than  $^{imp}Au/CeO_2$  (~12 nm). Both the Au/CeO<sub>2</sub> catalysts have almost no activity in glycerol reduction with H<sub>2</sub>. On the other hand,  $ReO_x$ -Au/CeO<sub>2</sub> catalysts prepared by impregnating Au/CeO<sub>2</sub> with Re (1 wt% Re, Au/Re = 0.3 mol/mol) have DODH activity of glycerol to allyl alcohol with H<sub>2</sub>. Similarly to many Au-catalyzed reactions including hydrogenation and H<sub>2</sub>/D<sub>2</sub> exchange, [27,28] ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> with smaller Au particles showed higher activity than ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub>. However, because of the overreduction of allyl alcohol to 1-propanol over dispersed Au in  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub>, the final allyl alcohol yield (91%) was higher in the case of  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub>. In this system, the large size of Au particles, even larger than CeO<sub>2</sub> support particles, raises questions: how the activated H<sub>2</sub> is transferred from Au (or Au-support interface site)[29] to distant Re species? In this study, we discuss the details of  $ReO_x$ -Au/CeO<sub>2</sub> catalysis especially in view of H<sub>2</sub> activation. We found that the hydrogen species are surely transferred from Au/CeO<sub>2</sub> to Re species on different CeO<sub>2</sub> particles. The difference in the performance between ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> and ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> was investigated in detail, and in some cases ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> is found to be better catalyst: DODH of reactive diol substrates such as 1,4-anhydroerythritol and that of *trans*-diols which need isomerization before DODH.

## **Results and discussion**

Structure model of the catalysts

We used two  $ReO_x$ -Au/CeO<sub>2</sub> catalysts,  $ReO_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> and  $ReO_x$ -<sup>dp</sup>Au/CeO<sub>2</sub>, the same catalysts

in our previous report.[26] For both catalysts, Au/CeO<sub>2</sub> was first prepared by impregnation (<sup>imp</sup>Au/CeO<sub>2</sub>) or deposition-precipitation (<sup>dp</sup>Au/CeO<sub>2</sub>), and then Re was loaded by impregnation. The loading amount of Au was set 0.32 wt%, since more amount of Au loading further increases the Au particle size in <sup>imp</sup>Au/CeO<sub>2</sub>.[26] The Re amount was set at Au/Re=0.3 mol/mol, corresponding to Re 1 wt%, unless noted. The XRD patterns of ReOx-Au/CeO2 catalysts after use in glycerol DODH are reprinted in Figure 1,[26] and now the particle sizes of the crystallites of each component including CeO<sub>2</sub> are compared. As described in the Introduction, the Au particles in ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> and ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> have 12 and 3 nm sizes, respectively. The formation of Au particles with such sizes has been also supported by Au  $L_2$ -edge XAFS (coordination number of Au-Au shell = 11.6±1.7 and 8.9±1.5 in ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> and ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>, respectively),[26] and the presence of XRD-insensitive monomeric Au or small Au clusters is unlikely based on the coordination numbers. The XRD patterns of <sup>imp</sup>Au/CeO<sub>2</sub> and <sup>dp</sup>Au/CeO<sub>2</sub> are shown in Figure S1, and the structures of Au species are similar to those in Re-loaded catalysts. There are no peaks for Re species in both catalysts, which supports the high dispersion of  $ReO_x$ . The  $CeO_2$  support has 8 nm size of crystallites in all samples. The Au particles in ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> are clearly larger than CeO<sub>2</sub> particles. The TEM images and the EDX analysis results of  $\text{ReO}_x$ -Au/CeO<sub>2</sub> catalysts are shown in Figure 2. Unfortunately, very few Au particles were observed in both ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> (Figure 2A) and ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> (Figure 2B) due to the small contrast between CeO<sub>2</sub> support and Au particles, and it was not possible to count the Au particles with each particle size. Few large spherical Au particles were observed in ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> (Figure 2B); however, the number of such large particles was much smaller than that in ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> with higher Au loading amount (0.64 wt% Au; double amount of standard catalyst) (Figure 2C). According to our previous paper, the catalyst with higher

Au loading amount has large average Au particle size ( $d_{XRD} = 25 \text{ nm}$ ),[26] which agreed with the TEM image (Figure 2C). The much smaller number of large Au particles in standard ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> (Figure 2B), even considering the lower loading amount, indicates that most Au species were not observed in the TEM image. The characterization of Re species was conducted with XAFS. The Re  $L_3$ -edge XANES spectra of ReO<sub>x</sub>-Au/CeO<sub>2</sub> and reference compounds are shown in Figure 3. The average Re valence was estimated by the relationship between the white line area and the valences of reference compounds (the relationship is shown in Figure S2), and the estimated values are added to Figure 3. The average valence of the Re species in both ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> and  $ReO_x$ - $^{dp}Au/CeO_2$  after calcination was +7.0, and that in  $ReO_x$ - $^{imp}Au/CeO_2$  and  $ReO_x$ - $^{dp}Au/CeO_2$  after glycerol DODH was +5.9 and +5.3, respectively. These values are similar to the result of  $ReO_x$ -Pd/CeO<sub>2</sub> after 1,4-anhydroerythritol reduction under similar conditions (average valence = 5.1).[25] The slightly higher valence of Re in  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> may be related to the limited supply of activated hydrogen, as discussed later. The curve fitting results of Re  $L_3$ -edge EXAFS are summarized in Table 1, and the details are shown in Figure S3 (spectra) and Table S1 (curve fitting results). The results for ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> and ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> are similar to those for ReO<sub>x</sub>-Pd/CeO<sub>2</sub>. These XAFS data suggest that the structure of Re species in ReO<sub>x</sub>-Au/CeO<sub>2</sub> is similar to that in ReO<sub>x</sub>-Pd/CeO<sub>2</sub> where Re<sup>IV</sup> and Re<sup>VI</sup> species are dispersed on CeO<sub>2</sub> surface.[25]

Now we calculate the number of particles in the catalysts. Based on the weight ratio (CeO<sub>2</sub>: Au = 99: 0.3), densities ( $\rho$ (CeO<sub>2</sub>) = 7.22 g cm<sup>-3</sup>;  $\rho$ (Au) = 19.3 g cm<sup>-3</sup>) and particle sizes, the number ratios of Au particles to CeO<sub>2</sub> particles are calculated to be about 1 to 3000 and 1 to 40 in ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> and ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>, respectively. Assuming that Re atoms in ReO<sub>x</sub>-Au/CeO<sub>2</sub> are randomly dispersed on the surface of CeO<sub>2</sub> support, which is the proposed structure in ReO<sub>x</sub>-Pd/CeO<sub>2</sub>,[25] the average number of Re atoms on one CeO<sub>2</sub> particle is calculated to be about

60. Some of Re species have monomeric structure with catalytic activity, and some of Re species inevitably have polymeric structure because of the limitation of CeO<sub>2</sub> surface sites (BET surface area:  $84 \text{ m}^2 \text{ g}^{-1}$ ; 1.1 mmol g<sup>-1</sup> surface sites for Re<sup>n+</sup> adsorption, corresponding to 20 wt% loading of Re).[25] The polymeric Re species are supposed to be inactive based on the stoichiometric DODH reaction of reduced ReO<sub>x</sub>-Pd/CeO<sub>2</sub>.[25] According to our previous paper,[25] 75% of Re species in ReO<sub>x</sub>(-M)/CeO<sub>2</sub> with 1 wt% Re (0.05 mmol-Re g<sup>-1</sup>) are monomeric based on the randomly-located model. The structure models of ReO<sub>x</sub>-Au/CeO<sub>2</sub> catalysts in the reduced form (Re<sup>IV</sup>) are shown in Figure 4. The active monomeric Re<sup>IV</sup> species is coordinated with substrate as diolate complex. This complex can release alkene product and the Re species becomes the oxidized form (Re<sup>VI</sup>) without move on the CeO<sub>2</sub> surface. The catalytic cycle is completed by re-reduction of the oxidized form of Re species and coordination of substrate (Scheme 1).

Most CeO<sub>2</sub> support particles are located far from the Au particles in both ReO<sub>x</sub>-Au/CeO<sub>2</sub> catalysts. On the other hand, in ReO<sub>x</sub>-Pd/CeO<sub>2</sub> (Re 2 wt%, Pd/Re=0.25), the average number of Pd atoms on one CeO<sub>2</sub> particle is about 30. Considering the very low Pd-Pd coordination number (~3),[24,25] the Pd particles are composed of few (<10) Pd atoms. Therefore, most CeO<sub>2</sub> particles support Pd particles as well as ReO<sub>x</sub> species.

# Reduction of Re catalyzed by distant Au particles: mixture of $ReO_x/CeO_2$ and $Au/CeO_2$

It seems questionable that reduction of Re species with H<sub>2</sub> is indeed catalyzed by distant Au particles. Although EXAFS data do not suggest, is there the effect of very small XRD-insensitive Au species loaded on every Re/CeO<sub>2</sub> particle? Although the leached amount of metal species from ICP analysis (0.2% Re and Au; filtration was carried out after cooling)[26] was very small and can be explained by limitation of filterable size, is there a possibility that dissolved Re species are involved

in the reduction of Re species? To clarify the former point, we tested the catalysis of the mixture of  $ReO_x/CeO_2 + Au/CeO_2$ , and the results are shown in Table 2. The physical mixture of  $ReO_x/CeO_2 + i^{imp}Au/CeO_2$  (entry 5) and that of  $ReO_x/CeO_2 + d^pAu/CeO_2$  (entry 6) exhibited comparable activity to  $ReO_x-i^{imp}Au/CeO_2$  (entry 2) and  $ReO_x-d^pAu/CeO_2$  (entry 3), respectively. The effect of increasing  $CeO_2$  amount was checked by the mixture of  $ReO_x-i^{imp}Au/CeO_2 + CeO_2$  (entry 4), and it is negligible. The physical mixture of  $ReO_x/CeO_2 + Pd/CeO_2$  also showed comparable activity to  $ReO_x-Pd/CeO_2$  (entries 7 and 8). These data indicate that Re species located far from noble metal particles can work as catalytic center.

We further carried out TPR measurements of the mixtures of ReO<sub>x</sub>/CeO<sub>2</sub> + Au/CeO<sub>2</sub> to check that reduction of Re species is indeed catalyzed by distant Au particles. The TPR experiments do not use solvent, and therefore there is no dissolution and deposition of metal species during TPR. The results are shown in Figure 5. Our previous paper already showed that ReO<sub>x</sub>-Au/CeO<sub>2</sub> catalysts have reduction peaks of Re species at lower temperature than  $\text{ReO}_x/\text{CeO}_2$ , [26] and the data are also shown for comparison. The TPR profiles of the physical mixtures of ReO<sub>x</sub>/CeO<sub>2</sub> + Au/CeO<sub>2</sub> ((e) and (f) for <sup>imp</sup>Au and <sup>dp</sup>Au, respectively) have low-temperature signals (420-710 K and 330-580 K, respectively) at similar positions to those of the corresponding  $ReO_x$ -Au/CeO<sub>2</sub> ((c) and (d), respectively). These low-temperature signals can be assigned to reduction of Re and some CeO<sub>2</sub>. Only weak broad signal was observed in the 600-800 K range profiles of ReO<sub>x</sub>/CeO<sub>2</sub> + Au/CeO<sub>2</sub>, and the broad signal can be assigned to CeO<sub>2</sub>-derived one because both CeO<sub>2</sub> (a) and ReO<sub>x</sub>/CeO<sub>2</sub> (b) have such signal. In the profile of  $\text{ReO}_x/\text{CeO}_2$  (b), sharper strong signal assignable to Re reduction (and some  $\text{CeO}_2$ ) was observed in 600-680 K range overlapping the weak broad signal, while this sharp signal was absent in the same range in  $\text{ReO}_x/\text{CeO}_2$  + Au/CeO<sub>2</sub> and  $\text{ReO}_x$ -Au/CeO<sub>2</sub> ((c)~(f)). These data indicate that Au/CeO<sub>2</sub> can catalyze the reduction of almost all of the Re species in the physically mixed  $Re/CeO_2$ .

The positions of the low-temperature signals are also similar to those of the corresponding Au/CeO<sub>2</sub> ((c), (e) and (g) for <sup>imp</sup>Au-containing sample; (d), (f) and (h) for <sup>dp</sup>Au-containing sample). The low-temperature signals in Au/CeO<sub>2</sub> can be assigned to the reduction of surface Ce, and therefore Re and surface Ce are reduced almost simultaneously by hydrogen species supplied by Au.

#### Kinetic studies

The effect of H<sub>2</sub> pressure in the DODH of 1,4-anhydroerythritol over ReO<sub>x</sub>-Au/CeO<sub>2</sub> catalysts was investigated (Figure 6; the detailed data are shown in Figure S4). The reactivity of 1,4-anhydroerythritol in DODH is generally high, [14a, 25, 26] and therefore the difference in the rate of Re reduction step can be more likely to affect the total reaction rate than the case of less reactive substrates. In our previous report for ReO<sub>x</sub>-Pd/CeO<sub>2</sub> catalyst system, [25] the reaction order with respect to H<sub>2</sub> pressure was estimated to be 0 in the range of 0.5-8 MPa, indicating that Re reduction step is faster than the latter step (release of alkene). On the other hand, the reaction rate over ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> (Figure 6(a)) was increased with increasing H<sub>2</sub> pressure in the range 1-8 MPa (reaction order: +0.6). The reaction rate over ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> showed saturation in the increase of  $H_2$  pressure: The reaction rate was increased until  $P(H_2) \sim 4$  MPa and it became almost constant above the pressure (Figure 6(b)). These results suggest that the rate-determination step under the standard conditions (H<sub>2</sub> 8 MPa, 413 K) in ReO<sub>x</sub>-Pd/CeO<sub>2</sub> and ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> system is the release of alkene, while that in the ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> system is the reaction steps associated with hydrogen, including the reduction of Re species. The promotional effect for the reduction of Re species decreases in the order of  $Pd > {}^{dp}Au/CeO_2 > {}^{imp}Au/CeO_2$ . The order between the two Au catalysts can be explained by the number of Au particles. The lower H<sub>2</sub> activation ability of  $ReO_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> may be related to the higher Re valence observed in Re  $L_3$ -edge XANES analysis (Figure 3; average

valence = 5.9).

The effect of substrate concentration in the DODH of 1,4-anhydroerythritol over  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> catalyst was also investigated (Figure 7; the detailed data are shown in Figure S5). The ratio of substrate to catalyst was set constant (substrate/Re =  $6 \times 10^2$  mol/mol) by only changing the solvent amount. The increase of reaction rate was almost saturated around 10 wt% substrate concentration. Therefore under standard conditions (20 wt% substrate) almost all the active Re species are coordinated with the substrate molecule. The saturation curve is very similar to the reduction of 1,4-anhydroerythritol over ReO<sub>x</sub>-Pd/CeO<sub>2</sub>,[25] which supports the idea that Re species is the same between ReO<sub>x</sub>-Pd/CeO<sub>2</sub> and ReO<sub>x</sub>-Au/CeO<sub>2</sub>.

Next, the reactivities of different substrates were compared (Figure 8; detailed data in Table S2). The tested substrates were 1,4-anhydroerythritol, glycerol and erythritol. The concentration was set at 5.4 mmol in 4 g 1,4-dioxane, which corresponds to 20 wt% for 1,4-anhydroerythritol. Considering the more number of vicinal OH groups in glycerol and erythritol molecules than 1,4-anhydroerythritol, the substrate concentration is enough to reach saturation in the reaction rate. The H<sub>2</sub> pressure was set 8 MPa where the effect of H<sub>2</sub> pressure is saturated for ReO<sub>x</sub>-Pd/CeO<sub>2</sub> and ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>. The amount of Re was set constant for all runs. The conversions of glycerol, 1,4-anhydroerythritol and erythritol over ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> were similar (Figure 8(I)), which agreed with that the rate-determining step is the reduction of Re species as suggested by the reaction orders. On the other hand, the reaction rate over ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> and ReO<sub>x</sub>-Pd/CeO<sub>2</sub> (Figure 8(II and III)) is dependent on the substrate, and the reactivity order is the same between these two catalysts: 1,4-anhydroerythritol > erythritol > glycerol. These results agree with that the rate-determining step over ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> was about 1.5 times of the

conversion exhibited by  $\text{ReO}_x$ -Pd/CeO<sub>2</sub>. The higher conversion over  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub> can be explained by the higher ratio of monomeric Re species to total Re species caused by the lower loading amount: 75% and 50% in 1 wt% and 2 wt% Re loading, respectively.[25] Thus, the reaction rate per active Re is constant regardless of the promoter metal (Pd or Au) if the promoter metal can sufficiently activates H<sub>2</sub>.

Based on the results above, the remote promotion of Re-catalyzed DODH on CeO<sub>2</sub> support by Au particles can be explained by the surface diffusion of active H species on CeO<sub>2</sub> support. The H<sub>2</sub> molecule is activated at some sites on Au particles such as defect sites and Au particle-CeO<sub>2</sub> interface sites.[29] The active H species is transferred onto CeO<sub>2</sub> surface followed by the spillover onto the surface of another  $CeO_2$  particle non-contacted with Au particle. The schematic representation is shown in Figure 9. It is well known that spillover of H atoms actually occurs from metal particles to various supports, such as reducible supports, carbon, and non-reducible supports with defects.[30,31] On reducible supports including  $Au/CeO_2$ , it is reported that the electron transfer process is most reasonable where H atoms migrate from a metal particle to the support as the protons and electrons on the surface and in the bulk of support, respectively.[32] Partial reduction of CeO<sub>2</sub> in ReO<sub>x</sub>-M/CeO<sub>2</sub> with H<sub>2</sub> is surely observed in TPR (Figure 5): the consumption amount of H<sub>2</sub> in the low-temperature peak is significantly larger than the reduction of Re (valence change:  $+7 \rightarrow +4$ ). Water molecules generated by the reduction of  $CeO_2$  or the OH group in substrates may help the move of proton on CeO<sub>2</sub> surface. The formed Re species with +4 valance will reduce the coordinated substrate, releasing alkene product and regenerating oxidized Re species with +6 valence. As discussed above, the rate-determining step is different between catalysts: the reduction of Re species is faster than the release of alkene in the case of ReOx-<sup>dp</sup>Au/CeO<sub>2</sub>, while the order is opposite in the case of  $\text{ReO}_{x}$ -<sup>imp</sup>Au/CeO<sub>2</sub>.

Comparison of the performance between  $ReO_x$ -Au/CeO<sub>2</sub> catalysts

In our previous paper we described that ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> gives higher yield of allyl alcohol by glycerol DODH than ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>.[25] However, because of the limiting H<sub>2</sub> activation ability of <sup>imp</sup>Au/CeO<sub>2</sub>, the activity is lower than that of ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>. Now we extend the substrate scope and check whether or not there are substrates that can utilize the higher activity of  $\text{ReO}_x$ - $^{dp}\text{Au}/\text{CeO}_2$ without loss of yield. The results are shown in Table 3. For polyol substrates with three or more number of OH groups (entries 1-6), ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> catalyst clearly showed higher selectivity to the corresponding alkene. The by-products over ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> catalyst are mainly DODH + hydrogenation products such as 1-propanol from glycerol, butanediols from erythritol, and 1-butanol from 1,2,4-butanetriol. In addition, isomerization of the DODH product via C=C migration also occurred over ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>, giving 2-buten-1-ol from 1,2,4-butanediol. On the other hand, in the cases of diol substrates, the selectivities to the DODH products are similar between  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> and  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub>. Considering the higher activity,  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub> is the better catalyst for diol substrates. A noteworthy result was obtained for trans-1,2-cyclohexanediol reduction. In contrast to general DODH reactions that cannot convert *trans*-diols,[4] ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> reduced *trans*-1,2-cyclohexanediol to cyclohexene in good yield (90%).

# Reactivity of DODH products

For further understanding of the selectivity, the reaction of DODH products themselves was investigated for  $ReO_x$ -Au/CeO<sub>2</sub> and Au/CeO<sub>2</sub> catalysts (Table 4). An important point is that there are two paths of hydrogenation of unsaturated alcohols (Scheme 2): (a) direct hydrogenation of C=C bond and (b) combination of C=C migration to enol, keto-enol tautomerization and hydrogenation of

C=O (indirect hydrogenation). In the case of allyl alcohol reduction (Table 4, entries 1-4), the activity was in the order of  $\text{ReO}_x$ - $^{dp}\text{Au}/\text{CeO}_2 \simeq {}^{dp}\text{Au}/\text{CeO}_2 > \text{ReO}_x$ - $^{imp}\text{Au}/\text{CeO}_2 > {}^{imp}\text{Au}/\text{CeO}_2$ . The main product was 1-propanol for all cases. Significant amount of propanal, which is an intermediate of indirect hydrogenation of allyl alcohol, was formed over <sup>imp</sup>Au-containing catalysts. The aldol condensation product of propanal, namely 2-methyl-2-pentenal, was also detected. C3 hydrocarbons, which are dehydration or overdeoxygenation products of 1-propanol, were also formed over Re-containing catalysts. The similar high activity of ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> and <sup>dp</sup>Au/CeO<sub>2</sub> catalysts indicates that <sup>dp</sup>Au is active in hydrogenation of allyl alcohol. The activity in hydrogenation of allyl alcohol agrees with the low selectivity of glycerol DODH to allyl alcohol over ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>. In view of the reaction path of 1-propanol formation (direct, indirect or both), the indirect route is likely to be involved because propanal was actually formed, although the involvement of the direct route cannot be excluded. The hydrogenation of 1-octene was carried out (Table 4, entries 5 and 6), where indirect hydrogenation involving C=O bond is impossible. Both the hydrogenation to *n*-octane and the C=C migration to 2-octene proceeded over ReOx-dpAu/CeO2, while ReOx-impAu/CeO2 showed almost no activity. Therefore both direct and indirect hydrogenations are catalyzed by <sup>dp</sup>Au/CeO<sub>2</sub>. The reduction rates of unsaturated compounds in entries 2, 4 and 6 are relatively high, in comparison with the DODH reactions (Table 3). The reduction of unsaturated compounds seems to be slowed down during DODH. To confirm this point, reaction of the mixture of allyl alcohol and 1,4-anhydroerythritol was carried out (Table 4, entries 7 and 8). The conversion of allyl alcohol was decreased from the case without 1,4-anhydroerythritol over both ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> and <sup>dp</sup>Au/CeO<sub>2</sub> (11% from 64% (entry 2), and 35% from 61% (entry 4), respectively). In <sup>dp</sup>Au/CeO<sub>2</sub>-catalyzed reaction (entry 8) where DODH of 1,4-anhydroerythritol was negligible, the conversion decrease of allyl alcohol ( $61\% \rightarrow 35\%$ ) is probably caused by the obstruction of the adsorption of allyl alcohol

onto catalyst (<sup>dp</sup>Au) by the competitive adsorption of 1,4-anhydroerytheritol. In  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub>-catalyzed reaction, the conversion of allyl alcohol was more decreased (64%  $\rightarrow$  11%). This result can be interpreted by that a part of active hydrogen species were consumed for 1,4-anhydroerythritol DODH instead of allyl alcohol hydrogenation. As shown in Table 3, selectivity of diol DODH is similar between  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub> and  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub>. Two factors may be involved in the suppression of side reactions in  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub>: competitive adsorption between diol and alkene and competitive use of active hydrogen between DODH and side reactions.

Reductions of 3-buten-1-ol and 2,5-dihydrofuran were also carried out (Table 4, entries 9-12). Similarly to the case of allyl alcohol reduction, <sup>dp</sup>Au/CeO<sub>2</sub> showed much higher activity in both hydrogenation and C=C migration than <sup>imp</sup>Au/CeO<sub>2</sub>. The reaction of 2,5-dihydrofuran was also tested with <sup>dp</sup>Au/CeO<sub>2</sub> under Ar atmosphere (Table 4, entry 13). The C=C migration as well as hydrogenation did not proceed at all, indicating that the C=C migration requires active hydrogen species, probably via the mechanism that addition of active hydrogen species to C=C and subsequent abstraction of hydrogen atom (Scheme 3).

The reaction of 1,2-cyclohexanediol over Au/CeO<sub>2</sub> catalysts was investigated in order to realize the trans-diol DODH (Table 5). The trans/cis isomerization of 1,2-cyclohexanediol readily proceeded over <sup>dp</sup>Au/CeO<sub>2</sub> (Table 5, entries 1 and 2) and the equilibrium was easily reached (Table 5, entries 3 and 4; the same *trans/cis* ratio from both *trans* and *cis* alone). The isomerization also proceeded under Ar atmosphere (Table 5, entry 5), in contrast to the case of C=C migration of 2,5-dihydrofuran (Table 4, entry 13). 2-Hydroxycyclohexanone, the dehydrogenation product of 1,2-cyclohexanediol, was detected in the reaction under Ar atmosphere. Based on these data, the reaction route of *trans*-1,2-cyclohexanediol DODH can be shown in Scheme 4: Dehydrogenation and <sup>dp</sup>Au hydrogenation trans-1,2-cyclohexanediol of over site reversibly produces

*cis*-1,2-cyclohexanediol, and then DODH of *cis*-1,2-cyclohexanediol over Au-promoted  $\text{ReO}_x/\text{CeO}_2$ produces cyclohexene. The consumption of *cis*-1,2-cyclohexanediol by DODH shifts the *trans/cis* equilibrium to the *cis* side, and finally *trans*-1,2-cyclohexanediol is totally converted into cyclohexene. The isomerization activity of <sup>imp</sup>Au/CeO<sub>2</sub> was very low (Table 5, entry 1), which agrees with the low activity of  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> in *trans*-diol DODH.

#### Conclusions

ReOx-Au/CeO2 catalysts which are active in deoxydehydration (DODH) with H2 as reductant contain much fewer Au particles than CeO<sub>2</sub> support particles. Au particles can promote the reduction of Re species on  $CeO_2$  support even when there are many other  $CeO_2$  particles located between Au and ReO<sub>x</sub>/CeO<sub>2</sub>, probably via diffusion of proton and electron on CeO<sub>2</sub> particles. CeO<sub>2</sub>-supported Au particles prepared by deposition-precipitation (<sup>dp</sup>Au/CeO<sub>2</sub>) have smaller size and higher activation ability of H<sub>2</sub> than those prepared by impregnation (<sup>imp</sup>Au/CeO<sub>2</sub>). The DODH activity of  $\text{ReO}_x$ - $^{\text{dp}}\text{Au}/\text{CeO}_2$  per active Re site is similar to that of  $\text{ReO}_x$ -Pd/CeO<sub>2</sub> where Pd clusters as well as  $\text{ReO}_x$  are present on most  $\text{CeO}_2$  particles. The activity of  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> in DODH is lower than ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> and is limited by the rate of H<sub>2</sub> activation. On the other hand, the rates of other reactions than DODH are higher in ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>: C=C hydrogenation, C=C migration and *cis/trans* isomerization. The former two reactions are side-reactions in DODH, and the high activity of ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> in these two reactions decreases the selectivity to the target alkene product in polyol DODH. These two reactions of C=C compounds are suppressed to some extent in the presence of diol/polyol substrate because of competitive adsorption and competitive consumption of active hydrogen species. In diol DODH, these side reactions are suppressed enough to obtain similar yield of the target alkene with ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> to that with ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub>. The *cis/trans* 

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isomerization can be useful: it enables *trans*-diol DODH which is difficult with literature systems of Re-catalyzed DODH such as those with homogeneous Re complex catalysts. Therefore,  $ReO_x$ -<sup>dp</sup>Au/CeO<sub>2</sub> is better DODH catalyst for simple diols, while  $ReO_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> is better for polyols with three or more OH groups and unsaturated diols.

# **Experimental section**

**Catalyst preparation.** The catalysts were prepared with the same procedure as our previous works.[24-26] ReO<sub>x</sub>/CeO<sub>2</sub>, <sup>imp</sup>Au/CeO<sub>2</sub> and Pd/CeO<sub>2</sub> catalysts were prepared by impregnating CeO<sub>2</sub> powder (Daiichi Kigenso Co., Ltd., HS, BET surface area: 84 m<sup>2</sup> g<sup>-1</sup>, after calcination at 873 K for 3 h) with an aqueous solution of NH<sub>4</sub>ReO<sub>4</sub>, HAuCl<sub>4</sub> and Pd(NO<sub>3</sub>)<sub>2</sub>. ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> catalyst was prepared by impregnation of 383 K-dried <sup>imp</sup>Au/CeO<sub>2</sub> with an aqueous solution of NH<sub>4</sub>ReO<sub>4</sub>. d<sup>p</sup>Au/CeO<sub>2</sub> catalyst was prepared by slow addition of aqueous solutions of HAuCl<sub>4</sub> for 4 h at 353 K with pH adjustment to 8 by addition of aqueous ammonia. The catalysts were dried at 383 K for 12 h and then calcined in air at 673 K for 4 h. ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> catalyst was prepared by impregnating calcined <sup>dp</sup>Au/CeO<sub>2</sub> with aqueous solution of NH<sub>4</sub>ReO<sub>4</sub>, followed by further drying and calcination at 673 K.

Activity test. Activity tests were performed in a 190 mL stainless steel autoclave. Substrate, internal standard (dodecane) and solvent (1,4-dioxane) was placed into the autoclave containing an inner glass cylinder with a spinner and appropriate amount of catalysts. After sealing the reactor, the air content was purged by flushing three times with H<sub>2</sub>, and H<sub>2</sub> pressure was increased to appropriate value (typically 5.7 MPa, for 8.0 MPa at 413 K). The autoclave was then heated to the reaction temperature. The temperature was monitored using a thermocouple inserted in the autoclave. Counting the reaction time started when the temperature reached the set value. The heating took

about 40 min. During the experiment, the stirring rate was fixed at 250 rpm (magnetic stirring). After an appropriate reaction time, the autoclave was cooled down with running water. The gases were collected in a gas bag. The autoclave contents and the washing solvent (methanol or 1,4-dioxane, 15 mL) were transferred to vials, and the catalyst was separated by centrifugation and filtration.

The reaction conditions for the various spectroscopic measurements of used catalyst were as follows: 0.5 g (5.4 mmol) glycerol, 300 mg catalyst, 0.1 g dodecane, 4 g 1,4-dioxane, 413 K reaction temperature, 8 MPa initial hydrogen pressure (at reaction temperature) and 2 h reaction time. The reaction conditions of activity tests are described in each result. In the reaction with a physical mixture of catalysts, the catalysts were sequentially placed into a glass cylinder without pre-mixing of catalysts.

**Product analysis.** The products in both gas and liquid phases were analyzed using a gas chromatograph (Shimadzu GC-2025) equipped with FID and an HPLC (Shimadzu LC-10A) equipped with a refractive index detector. A TC-WAX capillary column (diameter 0.25 mm, 30 m) and an Aminex HPX-87C column (diameter 7.8 mm, 300 mm) were used for GC and HPLC, respectively. For the reaction of erythritol, 1,2,4-butanetriol and 3-buten-1-ol, a GC equipped with Rtx<sup>®</sup>-1 PONA capillary column (diameter 0.25 mm, 100 m) was used for the gas phase analysis. Products were also identified using GC-MS (QP5050, Shimadzu). The conversion and the selectivities were calculated on the carbon-basis. The mass balance was also confirmed in each result and the difference in mass balance was always in the range of the experimental error (±10% except in the cases of erythritol at almost full conversion where the mass balance was lower (87% in the worst case) probably because of the difficulty in capturing all the C4 hydrocarbons).

**Catalyst characterization.** The surface areas of the catalysts were measured using BET method (N<sub>2</sub> adsorption) with an apparatus (Micromeritics Gemini). Powder X-ray diffraction (XRD) patterns

were recorded by a diffractometer (Rigaku MiniFlex600) with Cu K $\alpha$  radiation. When Scherrer's equation was applied to the Au peak, the XRD peaks of CeO<sub>2</sub> support were removed using the pattern of CeO<sub>2</sub> powder after calcination at 873 K for 3 h, and then the Au (fcc) peak at 38.2° in the obtained patterns was fitted by a Gaussian function. Scanning transmission electron microscope (STEM) images were taken by JEOL ARM-200F with Cu grids.

Temperature-programmed reduction ( $H_2$ -TPR) was carried out in a fixed-bed reactor equipped with a thermal conductivity detector (TCD) using 5%  $H_2$  diluted with Ar (30 mL/min). The amount of catalyst or physical mixture of catalysts was 100 mg, and temperature was increased from room temperature to 1173 K at a heating rate of 10 K/min. The sample of physical mixture was prepared by mixing catalysts in an agate mortar with an agate pestle for 15 min.

The X-ray absorption fine structure (EXAFS and XANES) spectra were measured at the BL01B1 station at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2016A1352). The storage ring was operated at 8 GeV, and a Si(111) single crystal was used to obtain a monochromatic X-ray beam. The spectra of reference compounds (Re powder, ReO<sub>2</sub>, ReO<sub>3</sub> and NH<sub>4</sub>ReO<sub>4</sub>) were obtained in a transmission mode. Ion chambers for  $I_0$  and I were filled with 100 % N<sub>2</sub> and 30% Ar + 70% N<sub>2</sub>, respectively. The edge jumps were in the range of 0.1-1. The catalyst samples were prepared after catalytic use by transferring the used catalyst powder to a measurement cell after reaction and cooling in a gas bag filled N<sub>2</sub> to avoid exposure to air. The data were collected in a fluorescence mode using a 19-element Ge solid-state detector (19-SSD). An ion chamber for  $I_0$  was filled with 100 % N<sub>2</sub>. The edge jumps were in the range of 0.0022-0.0024. For EXAFS analysis, the oscillation was first extracted from the EXAFS data using a spline method [33]. Fourier transformation of the  $k^3$ -weighted EXAFS oscillation from the k space to r space was carried out to obtain a radial distribution function. The inversely Fourier filtered data were analyzed using a

usual curve-fitting method [34]. For curve-fitting analysis, the empirical phase shift and amplitude functions for the Au–Au and Re–O bonds were extracted from data for Au metal and NH<sub>4</sub>ReO<sub>4</sub>, respectively. Analyses of EXAFS data were carried out using a computer program REX2000, ver. 2.6 (Rigaku Corp.). Error bars for each parameter, while optimizing the others parameter, until the residual factor becomes 2 times its minimum value [35]. In the analysis of XANES spectra, the normalized spectra were obtained by subtracting the pre-edge background from the raw data with a modified Victoreen equation and normalizing them by the edge height [36-38].

# **Associated content**

Supporting information: XRD patterns of Au/CeO<sub>2</sub> (Figure S1), detailed data of XANES (Figure S2), EXAFS (Figure S3 and Table S1), kinetics (Figures S4 and S5) and activity comparison between catalysts (Table S2).

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5	Table 1. Curve fitting	Results of Re L	-edge EX
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7	$\text{ReO}_{x}$ -Pd/CeO <sub>2</sub> (2 wt%)	Re, Pd/Re = $0.25$ )	
8	Sample	Condition	shells
9	$\mathbf{R}_{2}\mathbf{O}_{1}$ imp $\mathbf{A}_{11}/\mathbf{C}_{2}\mathbf{O}_{1}$	Calainad	Do-O
10	$\text{KeO}_{x}$ - $^{1}\text{Au}/\text{CeO}_{2}$	Calcined	Re-O
11	ReO <sub>x</sub> - <sup>dp</sup> Au/CeO <sub>2</sub>	Calcined	Re=O
12	$\text{ReO}_{x}$ -Pd/CeO <sub>2</sub> <sup>c</sup>	Calcined	Re=O
13	$ReO - \frac{imp}{2}Au/CeO_2$	$Used^d$	Re=0
14		0300	Re O
15			Re–O
16	$\text{ReO}_{x}$ - <sup>dp</sup> Au/CeO <sub>2</sub>	$\operatorname{Used}^d$	Re=O
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Used<sup>e</sup>

ReO<sub>x</sub>-Pd/CeO<sub>2</sub><sup>c</sup>

NH<sub>4</sub>ReO<sub>4</sub>

Table 1. Curve fitting Results of Re  $L_3$ -edge EXAFS of ReO<sub>x</sub>-Au/CeO<sub>2</sub> (1 wt% Re, Au/Re = 0.3) and ReO<sub>x</sub>-Pd/CeO<sub>2</sub> (2 wt% Re, Pd/Re = 0.25)

 $CN^{a}$ 

4.0

4.0

4.0

1.9

4.2

1.7

4.0

1.3

4.2

0.4

4

 $R / 10^{-1} \text{ nm}^{b}$ 

1.74

1.74

1.74

1.74

1.96

1.74

1.96

1.74

1.94

2.66

1.73

<sup>*a*</sup>CN = Coordination number. <sup>*b*</sup>R = Bond distance. <sup>*c*</sup> Ref. 25. <sup>*d*</sup> Reaction conditions: glycerol 0.5 g, catalyst 0.3 g, 1,4-dioxane 4 g, H<sub>2</sub> 8 MPa, 413 K, 2 h. <sup>*e*</sup> Reaction conditions: 1,4-anhydroerythritol 1 g, catalyst 0.15 g, 1,4-dioxane 4 g, H<sub>2</sub> 8 MPa, 413 K, 4 h. <sup>*f*</sup> This shell is added based on the Pd-Re coordination number in Pd *K*-edge EXAFS.

Re=O

Re-O

Re–Pd<sup>f</sup>

Re=O

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Entry	Catalyst	Conv.	v. Selectivity / %							
		/ %	Allyl	1-PrOH	2-PrOH	1,2-PrD	1,3-PrD	Propanal	Others	
			alcohol							
1	ReO <sub>x</sub> /CeO <sub>2</sub>	6	90	2	<1	<1	<1	3	3	
2	ReO <sub>x</sub> - <sup>imp</sup> Au/CeO <sub>2</sub>	57	95	3	<1	<1	<1	1	1	
3	$ReO_x$ - <sup>dp</sup> Au/CeO <sub>2</sub>	72	62	30	<1	4	<1	1	2	
4	$ReO_x$ -imp $Au/CeO_2 + CeO_2$	54	91	3	<1	1	<1	3	2	
5	$\text{ReO}_{x}/\text{CeO}_{2} + {}^{\text{imp}}\text{Au}/\text{CeO}_{2}$	38	95	1	<1	1	<1	1	2	
6	$\text{ReO}_{x}/\text{CeO}_{2} + {}^{dp}\text{Au}/\text{CeO}_{2}$	81	83	12	<1	2	<1	1	2	
$7^b$	ReO <sub>x</sub> -Pd/CeO <sub>2</sub>	37	<1	83	<1	15	<1	<1	2	
$8^b$	$ReO_x/CeO_2 + Pd/CeO_2$	43	<1	86	<1	13	<1	<1	1	

Table 2. Reduction of glycerol over the physical mixture of various catalysts<sup>*a*</sup>

<sup>*a*</sup> Glycerol (0.5 g), 1,4-dioxane (4 g),  $W_{cat} = 0.3$  g or 0.3 + 0.3 g (30 mg Re, Au/Re = 0.3), H<sub>2</sub> (8 MPa), 413 K, 24 h. PrOH = propanol, PrD = propanediol. <sup>*b*</sup>  $W_{cat} = 0.15$  g or 0.15 + 0.15 g (30 mg Re, Pd/Re = 0.25).

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Table 3. Reduction of diols and polyols over ReO<sub>x</sub>-Au/CeO<sub>2</sub> catalysts<sup>a</sup>

Entry	Substrate	Catalyst	t /	Conv.	Products (Selectivity / %)
			h	/ %	
1 <sup>b</sup>	но он он	ReO <sub>x</sub> - <sup>imp</sup> Au/CeO <sub>2</sub>	52	>99	но (91), но (5), о (1), он
	Glycerol				(<1), hydrocarbons (1), others (2)
2		ReO <sub>x</sub> - <sup>dp</sup> Au/CeO <sub>2</sub>	24	72	но (62), но (30), о (1), он
					(5), hydrocarbons (1), others (1)
3 <sup>b</sup>		ReO <sub>x</sub> - <sup>imp</sup> Au/CeO <sub>2</sub>	60	97	(83), butenes (3), HO, OH (7),
	Erythritol				$\stackrel{\text{OH}}{\stackrel{\text{HO}}{}} (<1),  \stackrel{\text{HO}}{} (1),  \stackrel{\text{OH}}{} (1),  (1),  \stackrel{\text{OH}}{} (1),$
	2				mono-ols (1), C $\leq$ 3 hydrocarbons (<1), others (3)
4		ReO <sub>x</sub> - <sup>dp</sup> Au/CeO <sub>2</sub>	16	94	(57), butenes (5), HO, OH (8),
					$\stackrel{\text{OH}}{\stackrel{\text{HO}}{\longrightarrow}} (9), \stackrel{\text{HO}}{\stackrel{\text{OH}}{\longrightarrow}} (5), \stackrel{\text{OH}}{\stackrel{\text{OH}}{\longrightarrow}} (9),$
					mono-ols (3), C $\leq$ 3 hydrocarbons (<1), others (3)
5 <sup><i>b</i></sup>	он но ОН	ReO <sub>x</sub> - <sup>imp</sup> Au/CeO <sub>2</sub>	72	80	но (80), но (7), но (4),
	1,2,4-Butanetr				Ho (6), 0 (1), others (1)
6	iol	ReO <sub>x</sub> - <sup>dp</sup> Au/CeO <sub>2</sub>	24	65	но (30), но (19), но (7),
					Ho (38), 0 (2), others (5)
$7^b$	$\langle \circ \rangle$	ReO <sub>x</sub> - <sup>imp</sup> Au/CeO <sub>2</sub>	24	93	$\begin{pmatrix} 0 \\ - \end{pmatrix}$ (86) $\begin{pmatrix} 0 \\ - \end{pmatrix}$ (9) $\begin{pmatrix} 0 \\ - \end{pmatrix}$ (3) others (2)
8	нотон	ReO - <sup>dp</sup> Au/CeO	2	>99	
0	1,4-Anhydroer		-		(86), (10), (3), (3), (1)
	ythritol				
9	1,2-Octanedio	$\text{ReO}_{x}$ - <sup>imp</sup> Au/CeO <sub>2</sub>	48	42	1-Octene (76), <i>n</i> -octane (8), others (16)
10	1	ReO <sub>x</sub> - <sup>dp</sup> Au/CeO <sub>2</sub>	4	74	1-Octene (84), 2-octenes (9), <i>n</i> -octane (7), others (<1)
11 <sup><i>b,c</i></sup>	ОН	ReO <sub>x</sub> - <sup>imp</sup> Au/CeO <sub>2</sub>	8	91	$\bigcirc (94), \bigcirc (1), \bigcirc (2), \text{ others } (3)$
12 <sup>c</sup>	<i>cis</i> -1,2-cycloh exanediol	ReO <sub>x</sub> - <sup>dp</sup> Au/CeO <sub>2</sub>	2	>99	$\bigcirc (92), \bigcirc (6), \text{ others } (2)$
13 <sup>c</sup>	ОН	ReO <sub>x</sub> - <sup>imp</sup> Au/CeO <sub>2</sub>	8	9	(31) $(<1)$ $(<1)$ $(<1)$ $()$ $()$ others $(11)$
14 <sup>c</sup>	<i>trans</i> -1,2-cycl ohexanediol	ReO <sub>x</sub> - <sup>dp</sup> Au/CeO <sub>2</sub>	8	98	(92), (1), (1), (1), (1), (1), (1)

<sup>*a*</sup> Substrate (0.5 g), 1,4-dioxane (4 g),  $W_{cat} = 0.3$  g (1 wt% Re, Au/Re = 0.3), H<sub>2</sub> (8 MPa), 413 K. <sup>*b*</sup> Ref. 26. <sup>*c*</sup> Substrate (0.25 g), 443 K.

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<sup>*a*</sup> Substrate (5.4 mmol), 1,4-dioxane (4 g),  $W_{cat} = 0.3$  g (0 or 1 wt% Re, 0.32 wt% Au (Au/Re = 0.3)), H<sub>2</sub> (8 MPa), 413 K, 1 h. <sup>*b*</sup> Based on 1,4-anhydroerythritol. <sup>*c*</sup> The catalyst was pre-reduced in 1,4-dioxane under 8 MPa H<sub>2</sub> at 413 K for 0.5 h with stirring, and the reaction was conducted under Ar atmosphere (1 MPa).

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Entry	Catalyst	$W_{\rm cat}$	<i>t</i> /	Conv.	Selectiv	vity / %			
		/ g	h	/ %	$\bigcirc$	$\bigcirc$	OH	ОН	Others
1	<sup>imp</sup> Au/CeO <sub>2</sub>	0.15	1	3	<1	<1	90	7	3
2	<sup>dp</sup> Au/CeO <sub>2</sub>	0.15	1	19	<1	<1	99	<1	1
3	<sup>dp</sup> Au/CeO <sub>2</sub>	0.3	2	33	<1	<1	99	<1	1
$4^b$	<sup>dp</sup> Au/CeO <sub>2</sub>	0.3	2	62	<1	<1	99 (trans)	<1	1
$5^c$	<sup>dp</sup> Au/CeO <sub>2</sub>	0.15	1	21	<1	<1	75	24	1

Table 5. Reaction of *trans*-1,2-cyclohexanediol over  $Au/CeO_2^a$ 

<sup>*a*</sup> Substrate (0.25 g), 1,4-dioxane (4 g), catalyst (0.32 wt% Au), H<sub>2</sub> (8 MPa), 443 K. <sup>*b*</sup> Substrate: *cis*-1,2-cyclohexanediol. <sup>*c*</sup> The catalyst was pre-reduced in 1,4-dioxane under 8 MPa H<sub>2</sub> at 413 K for 0.5 h with stirring, and the reaction was conducted under Ar atmosphere (1 MPa).



Scheme 1. General mechanism of deoxydehydration.  $M^{n+} = Re^{5+}$ ,  $Re^{4+}$ ,  $Mo^{4+}$  and  $V^{3+}$ .



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Scheme 2. Two paths of allyl alcohol hydrogenation.



Scheme 3. Mechanism of C=C migration.



Scheme 4. Reaction path of *trans*-1,2-cyclohexanediol DODH.





Figure 1. XRD patterns of  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub> and  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub> (1 wt% Re, Au/Re = 0.3) after use in glycerol DODH. Reprinted with permission from ref. 26. Copyright 2016 American Chemical Society.



Figure 2. TEM images of  $\text{ReO}_x$ - $^{dp}\text{Au}/\text{CeO}_2$  (A) and  $\text{ReO}_x$ - $^{imp}\text{Au}/\text{CeO}_2$  (B and C) after catalytic use. (A) and (B): 1 wt% Re, Au/Re = 0.3; (C): 1 wt% Re, Au/Re = 0.6. The conditions for catalytic reaction: glycerol 0.5 g, catalyst 0.3 g, 1,4-dioxane 4 g, H<sub>2</sub> 8 MPa, 413 K, 2 h.



Figure 3. Re  $L_3$ -edge XANES spectra and the Re valence calculated by white line area. The relationship between Re valence and white line area is shown in Figure S2. (a) Re powder, (b) ReO<sub>2</sub>, (c) ReO<sub>3</sub>, (d) Re<sub>2</sub>O<sub>7</sub>, (e) ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> after calcination, (f) ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> after calcination, (g) ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> after use in glycerol DODH, (h) ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> after use in glycerol DODH. The conditions for glycerol DODH: glycerol 0.5 g, catalyst 0.3 g, 1,4-dioxane 4 g, H<sub>2</sub> 8 MPa, 413 K, 2 h.



Figure 4. Structure models of  $\text{ReO}_x$ -Au/CeO<sub>2</sub> catalysts (1 wt% Re, Au/Re = 0.3) in reduced form. (I)  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub>, (II)  $\text{ReO}_x$ -<sup>dp</sup>Au/CeO<sub>2</sub>.





Figure 5. TPR profiles of catalysts. Conditions: sample (0.1 g or 0.05 + 0.05 g) and H<sub>2</sub>/Ar (5% v/v, 30 cc/min) at heating rate of 10 K/min. Dash lines represent the baselines for integration.  $\circ$ : Reduction of Ce;  $\blacksquare$ : reduction of Re accompanying reduction of Ce. (a) CeO<sub>2</sub>, (b) ReO<sub>x</sub>/CeO<sub>2</sub> (Re = 0.0054 mmol), (c) ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> (Re = 0.0054 mmol, Au/Re = 0.3), (d) ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> (Re = 0.0054 mmol, Au/Re = 0.3), (d) ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub> (Re = 0.0054 mmol, Au/Re = 0.3), (e) ReO<sub>x</sub>/CeO<sub>2</sub> + <sup>imp</sup>Au/CeO<sub>2</sub> (Re = 0.0027 mmol, Au/Re = 0.3), (f) ReO<sub>x</sub>/CeO<sub>2</sub> + <sup>dp</sup>Au/CeO<sub>2</sub> (Re = 0.0027 mmol, Au/Re = 0.3), (g) <sup>imp</sup>Au/CeO<sub>2</sub>, (h) <sup>dp</sup>Au/CeO<sub>2</sub>.

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ReO<sub>x</sub>-<sup>imp</sup>Au/CeO<sub>2</sub> and (b) ReO<sub>x</sub>-<sup>dp</sup>Au/CeO<sub>2</sub>. Conditions: 1,4-anhydroerythritol (0.5 g), 1,4-dioxane (2 g),  $W_{cat} = 0.15$  g (Re 1 wt%, Au/Re = 0.3), H<sub>2</sub> (1-8 MPa), 413 K, 0-1 h. The raw data are shown in Figure S4.

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Figure 7. Effect of substrate concentration on the DODH of 1,4-anhydroerythritol over  $\text{ReO}_x$ -<sup>imp</sup>Au/CeO<sub>2</sub>. Conditions: 1,4-anhydroerythritol (0.5 g), 1,4-dioxane (2-9.5 g),  $W_{\text{cat}} = 0.15$  g (Re 1 wt%, Au/Re = 0.3), H<sub>2</sub> (8 MPa), 413 K, 0-1 h. The raw data are shown in Figure S5.



Figure 8. Reactivity of various substrates in (I, II) DODH over  $\text{ReO}_x$ -Au/CeO<sub>2</sub> catalysts and (III) DODH + hydrogenation over  $\text{ReO}_x$ -Pd/CeO<sub>2</sub> catalyst. Conditions: substrate (5.4 mmol), 1,4-dioxane (4 g),  $W_{\text{cat}} = 0.3$  g (1 wt% Re, Au/Re = 0.3), H<sub>2</sub> (8 MPa), 413 K, 2 h.  ${}^aW_{\text{cat}} = 0.15$  g (2 wt% Re, Pd/Re = 0.25). The detailed data are shown in Table S2.



Figure 9. Schematic representation of reduction of Re species in  $ReO_x$ -Au/CeO<sub>2</sub>-catalyzed DODH. Note: the oxidized Re species (+6 valence) may be also coordinated with substrate. The coordinated state of oxidized Re species is omitted in this scheme for simplicity.

Graphical abstract

