**Hydrodeoxygenation** **Hot Paper**

DOI: 10.1002/anie.201410352

# Hydrodeoxygenation of Vicinal OH Groups over Heterogeneous Rhenium Catalyst Promoted by Palladium and Ceria Support**

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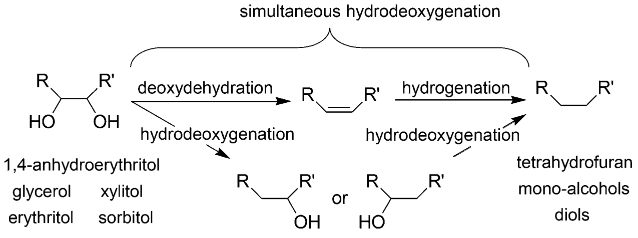
***Abstract:** Heterogeneous $ReO_x$–Pd/$CeO_2$ catalyst showed excellent performance for simultaneous hydrodeoxygenation of vicinal OH groups. High yield (> 99 %), turnover frequency (300 $h^{-1}$), and turnover number (10 000) are achieved in the reaction of 1,4-anhydroerythritol to tetrahydrofuran. This catalyst can be applied to sugar alcohols, and mono-alcohols and diols are obtained in high yields (≥ 85 %) from substrates with even and odd numbers of OH groups, respectively. The high catalytic performance of $ReO_x$–Pd/$CeO_2$ can be assigned to rhenium species with +4 or +5 valence state, and the formation of this species is promoted by $H_2$/Pd and the ceria support.*

Utilization of biomass as a source of chemicals becomes more and more important.[1] Since biomass contains a larger amount of oxygen than most chemicals, partial hydrodeoxygenation is a key reaction in the conversion of biomass to chemicals. For substrates with a few OH groups, a number of partial hydrodeoxygenation systems that selectively remove one OH group have been reported such as glycerol to 1,2-propanediol,[2–7] glycerol to 1,3-propanediol,[8–11] 1,2-alkanediol to 1-alcohol,[8,11,12] and 1,2-cycloalkanediol to 1-cycloalkanol.[13] However, it is much more difficult to selectively remove OH groups with these catalysts from substrates with four or more OH groups such as erythritol, xylitol, and sorbitol.[14] Other types of hydrodeoxygenation catalysts may be necessary. On the other hand, Re, V, and Mo homogeneous catalysts, especially Re, have been reported to be active in deoxydehydration (didehydroxylation) of vicinal OH groups to give alkenes.[15–25] In combination with the hydrogenation of the produced alkene, deoxydehydration transforms two vicinal OH groups to H atoms, and the reaction can be regarded as simultaneous hydrodeoxygenation (Scheme 1).[26] However, there are several problems in deoxydehydration systems in the literature (Table S1): 1) It is difficult to separate these homogeneous catalysts from the reaction mixture. 2) The turnover number (TON) and turnover frequency (TOF) per Re atom is not very high (TON: typically < 100, max. 1400;[16] TOF: max. 40 $h^{-1}$;[15a] Table S1, entries 1 and 4). 3) These systems typically use other reductants than $H_2$ and lower yields are obtained if $H_2$ is used as the reductant.[16,20] Simultaneous hydrodeoxygenation of straight-chain vicinal diols over heterogeneous Re catalysts has been reported; however, the yields of alkenes (≈ 50 %) were lower than those obtained with homogeneous catalysts (≈ 95 %), and the TON and TOF per Re atom were very low (< 20 and < 5 $h^{-1}$, respectively; Table S1, entries 27–30).[27,28] In addition, there are no reports on the reuse of heterogeneous catalysts for deoxydehydration without decrease in activity up to now. In this report, we developed an efficient heterogeneous catalyst for the simultaneous removal of vicinal OH groups with $H_2$. The applicability to sugar alcohols and the reaction mechanism are also discussed.



*Scheme 1.* Reduction of vicinal OH groups.

First, 1,4-anhydroerythritol (1,4-AHERY; Figure 1, inset) was used as a model substrate in a batch system with 1,4-dioxane solvent. 1,4-AHERY is the dehydration product of biomass-derived erythritol.[29] The target product is tetrahy-

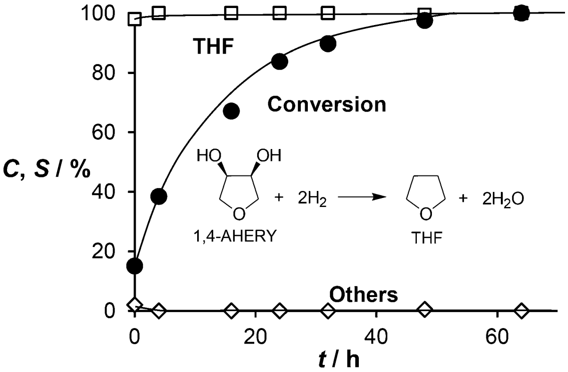


*Figure 1.* Time course of the simultaneous hydrodeoxygenation of 1,4-AHERY over $ReO_x$–Pd/$CeO_2$ (*C*: conversion, *S*: selectivity). 1,4-AHERY (1 g), 1,4-dioxane (4 g), $W_{cat} = 0.15$ g, $P_{H_2} = 8$ MPa, $T = 413$ K. THF = tetrahydrofuran.

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[**] This study was supported by the JSPS KAKENHI (grant number 26249121).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201410352.

drofuran (THF), which is used as an organic solvent. Re was selected as an active metal for deoxydehydration. Pd was used as an additive to activate $H_2$ and hydrogenate the "alkene" (2,5-dihydrofuran) intermediate. Among noble metals that can activate $H_2$, Pd itself has low activity in side reactions such as hydrodeoxygenation and degradation, and has been selected as the best additive for W- or Re-based reduction catalysts.[30,31] Indeed, we also tested various combinations of Group 5–7 metal ($MO_x$) + Pd (Figure S1) and $ReO_x$ + noble metal (Figure S2) using a silica support. Other combinations than $ReO_x$–Pd showed lower activity and/or lower selectivity to THF. The results of 1,4-AHERY reduction over $ReO_x$–Pd catalysts on various supports are shown in Table 1, entries 1 and 3–12. The $ReO_x$–Pd/$CeO_2$ catalyst gave by far the highest conversion (38%) and extremely high selectivity to THF (> 99%). $ReO_x/CeO_2$ catalyst showed a much lower activity and the main products were dihydrofuran and THF (entry 13). Pd/$CeO_2$ and $CeO_2$ alone were inactive (entries 14 and 15). These results indicate that all three components, $ReO_x$, Pd, and $CeO_2$, are essential in the high catalytic activity and selectivity to THF. In addition, mono-alcohols such as 1- and 2-hexanols were inert (conversion $< 1$%) under the same conditions as presented in Table 1.

The time course of the 1,4-AHERY hydrodeoxygenation over $ReO_x$–Pd/$CeO_2$ catalyst is shown in Figure 1. The very high selectivity to THF (> 99%) was maintained until complete conversion of 1,4-AHERY. The yield of THF reached > 99% ($t = 64$ h). Selectivity to THF was almost unchanged (> 99%) when the reaction temperature was in the range of 403–443 K (Table S2). The TOF per Re atom at 443 K was calculated to be about 300 $h^{-1}$, and this value was one order larger than those reported for homogeneous catalysts with non-$H_2$ reductant at the same temperature (Table S1).[15–20,23,24]

Next, the reusability of $ReO_x$–Pd/$CeO_2$ catalyst after regeneration by calcination was tested. The used catalyst gave the same activity and selectivity to THF within experimental errors as the fresh catalyst (Table 1, entry 2; Figures S3 and S4 for details). The stability of the $ReO_x$–Pd/$CeO_2$ catalyst was further investigated by using the catalyst with low Re loading (0.5 wt%). The total TON per Re atom reached about 10000 at 453 K for 96 h (Table S3). This value is much larger than those obtained on previously reported homogeneous and heterogeneous catalysts (Table S1).

The $ReO_x$–Pd/$CeO_2$ catalyst was applied to various sugar alcohol substrates (Table 2). C3 glycerol was converted to 1-propanol in 87% yield (entry 1). A small amount of 1,2-propanediol was formed, probably through a dehydrogenation–dehydration–hydrogenation mechanism, which is well known for glycerol conversion over noble metal catalyst in combination with base.[32] A small amount of propane was also formed, probably by the simultaneous hydrodeoxygenation of the produced 1,2-propanediol. C5 xylitol could be also converted to mono-alcohols (entry 2). The main product was 1-pentanol, which was formed by double simultaneous hydrodeoxygenation at the 2,3- and 4,5-position. 3-Pentanol was also produced through double simultaneous hydrodeoxygenation at the 1,2- and 4,5-position. In the case of erythritol and sorbitol, which contain an even number of OH groups, complete simultaneous hydrodeoxygenation can proceed to give *n*-alkanes, which are much less valuable than diols. After an optimization of the reaction conditions and in particular reaction time, diols can be produced in high yields ($\geq 85$%; entries 2 and 4). The high yields can be explained by the stronger adsorption of polyols compared with diols.[33] So far, no report in the literature shows good yield of diols from C4 or C6 sugar alcohols with Re catalysts such as $CH_3ReO_3$.

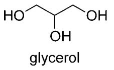
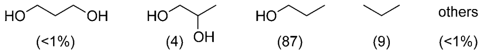
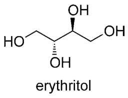
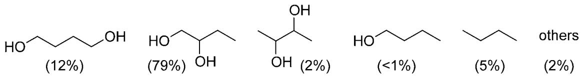
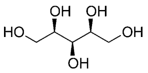
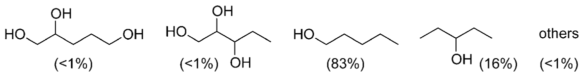
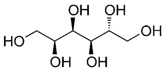
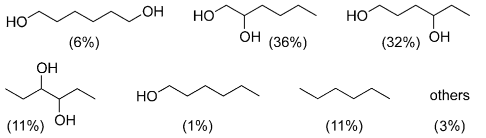
The $ReO_x$–Pd/$CeO_2$ catalyst was characterized with various techniques for both fresh (unreduced; after calcination) and reduced sample at 773 K with $H_2$. It was verified that $ReO_x$–Pd/$CeO_2$ catalyst reduced at 773 K gave similar conversion and selectivity to THF like the fresh one (Table S4). X-ray diffraction (XRD) patterns of reduced and calcined catalyst (Figure S5) were essentially identical, and only the peaks due to $CeO_2$ were observed. Considering that generally the Pd species can be fully reduced to the metallic state at

***Table 1:*** Reduction of 1,4-AHERY over various $ReO_x$–Pd catalysts.[a]

| Entry | Catalyst | Conv. [%] | Selectivity [%] THF | 3-Hydroxy-tetrahydrofuran | Butane-diols | Butanols | 1,4-Anhydro-threitol | Dihydrofuran | Others |
|---|---|---|---|---|---|---|---|---|---|
| 1 | $ReO_x$–Pd/$CeO_2$ | 38 | > 99 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 |
| 2[b] | $ReO_x$–Pd/$CeO_2$ | 38 | > 99 | < 1 | < 1 | < 1 | < 1 | < 1 | < 1 |
| 3 | $ReO_x$–Pd/$SiO_2$ | 1 | 74 | < 1 | < 1 | < 1 | 6 | < 1 | 20 |
| 4 | $ReO_x$–Pd/C | < 1 | – | – | – | – | – | – | – |
| 5 | $ReO_x$–Pd/AC | 2 | 81 | < 1 | 3 | 1 | < 1 | < 1 | 15 |
| 6 | $ReO_x$–Pd/$Al_2O_3$ | < 1 | – | – | – | – | – | – | – |
| 7 | $ReO_x$–Pd/$ZrO_2$ | 5 | 92 | 3 | < 1 | 1 | 2 | < 1 | 2 |
| 8 | $ReO_x$–Pd/$TiO_2$ | 2 | 77 | 2 | < 1 | 1 | 3 | < 1 | 17 |
| 9 | $ReO_x$–Pd/MgO | < 1 | – | – | – | – | – | – | – |
| 10 | $ReO_x$–Pd/CaO | < 1 | – | – | – | – | – | – | – |
| 11 | $ReO_x$–Pd/$La_2O_3$ | 1 | 92 | < 1 | < 1 | < 1 | < 1 | < 1 | 8 |
| 12 | $ReO_x$–Pd/$Y_2O_3$ | < 1 | – | – | – | – | – | – | – |
| 13[c] | $ReO_x/CeO_2$ | 1 | 48 | < 1 | < 1 | < 1 | 5 | 47[f] | < 1 |
| 14[d] | Pd/$CeO_2$ | < 1 | – | – | – | – | – | – | – |
| 15[e] | $CeO_2$ | < 1 | – | – | – | – | – | – | – |

[a] 1,4-AHERY (1 g), 1,4-dioxane (4 g), $W_{cat} = 0.15$ g (2 wt% Re, 0.3 wt% Pd), $P_{H_2} = 8$ MPa, $T = 413$ K, $t = 4$ h. AC = activated carbon. [b] 4th use. [c] $W_{cat} = 0.15$ g (2 wt% Re). [d] $W_{cat} = 0.15$ g (0.3 wt% Pd). [e] $W_{cat} = 0.15$ g. [f] Ratio of 2,3-dihydrofuran/2,5-dihydrofuran = 1/8.

***Table 2:*** Reduction of sugar alcohols over $ReO_x$–Pd/$CeO_2$ catalyst.[a]

| Entry | Substrate | Conv. [%] | Substrate/ 1,4-dioxane/ catalyst [g] | Product | Yield of diols or mono-ols [%] |
|---|---|---|---|---|---|
| 1 | <br>glycerol | >99 | 0.25/2/0.15 | <br>(<1%) (4) (87) (9) others (<1%) | 87 [mono-ols] |
| 2 | <br>erythritol | 98 | 0.5/4/0.15 | <br>(12%) (79%) (2%) (<1%) (5%) others (2%) | 91 [diols] |
| 3 | <br>xylitol | >99 | 1/2/0.3 | <br>(<1%) (<1%) (83%) (16%) others (<1%) | 98 [mono-ols] |
| 4[b] | <br>sorbitol | >99 | 0.5/4/0.15 | <br>(6%) (36%) (32%) (11%) (1%) (11%) others (3%) | 85 [diols] |

[a] $P_{H_2} = 8$ MPa, $T = 433$ K, $t = 24$ h. [b] $t = 72$ h.

much lower temperature than 773 K with $H_2$, the XRD result suggests that the Pd metal is highly dispersed. In addition, the XRD pattern of the used catalyst was also almost identical to that of the fresh one (Figure S5).

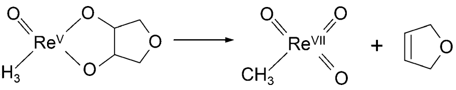
The average valence of Re was determined by the white-line area of Re $L_3$-edge XANES (Figures S6 and S7) on the basis of previous reports.[34,35] As a result, the average valence of the Re species on calcined and reduced $ReO_x$–Pd/$CeO_2$ was determined to be 7.0 and 3.7, respectively. Table 3 and Table S5 list the curve-fitting results of EXAFS (the spectra are shown in Figures S8 and S9). The curve-fitting analysis of Re $L_3$-edge EXAFS of $ReO_x$–Pd/$CeO_2$ after reduction indicates the presence of Re–O and Re–Re bonds. The presence of the Re–O bond indicates that the Re species is not fully reduced to the metallic state, which is in agreement with the Re $L_3$-edge XANES analysis. On the other hand, the curve-fitting analysis of the Pd K-edge EXAFS indicates the presence of the Pd–Pd bond with a coordination number (CN) of 2.1. This value is much smaller than the CN of bulk Pd metal species (12), agreeing with the absence of XRD peaks due to Pd metal (Figure S5). Based on the CN of the Pd–Pd bonds, the metal particle size of Pd is estimated to be at the subnanometer scale (< 1 nm). The Pd–Re bond was also observed, suggesting that a part of the Re species are attached on the Pd particles like it is the case for $ReO_x$-modified Ir, Pt, and Rh metal catalysts.[5,11,36]

***Table 3:*** Curve-fitting results of Re $L_3$-edge and Pd K-edge EXAFS of $ReO_x$–Pd/$CeO_2$ after reduction (773 K, 1 h).

| Edge | Sample | Shells | CN[a] | $R$ [$\times 10^{-1}$ nm][b] |
|---|---|---|---|---|
| Re $L_3$ | $ReO_x$–Pd/$CeO_2$ | Re–Re | $1.9 \pm 0.6$ | $2.69 \pm 0.01$ |
| | | Re–$O_{short}$ | $1.4 \pm 0.3$ | $1.97 \pm 0.01$ |
| | | Re–$O_{long}$ | $1.2 \pm 0.3$ | $2.45 \pm 0.02$ |
| | Re powder | Re–Re | 12 | 2.75 |
| | $NH_4ReO_4$ | Re=O | 4 | 1.73 |
| Pd $K$ | $ReO_x$–Pd/$CeO_2$ | Pd–Pd | $2.1 \pm 0.3$ | $2.74 \pm 0.01$ |
| | | Pd–Re | $0.6 \pm 0.2$ | $2.68 \pm 0.01$ |
| | Pd foil | Pd–Pd | 12 | 2.75 |

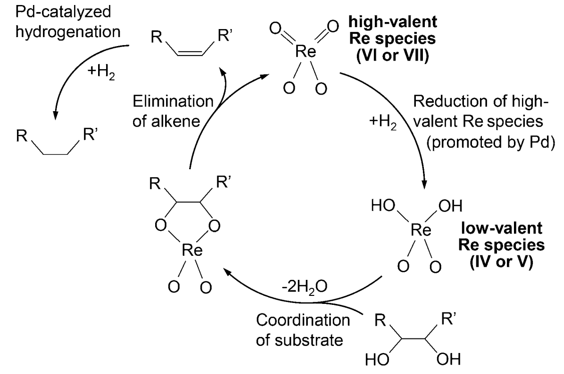
[a] CN = coordination number. [b] $R$ = bond length.

The reaction mechanism of the hydrodeoxygenation of 1,4-AHERY on $ReO_x$–Pd/$CeO_2$ is discussed here. Toste et al. have reported $CH_3ReO_3$-catalyzed deoxydehydration of 1,4-AHERY to 2,5-dihydrofuran.[15a] They proposed a mechanism in which pentavalent Re worked as a two-electron reducing agent [Eq. (1)].



(1)

Essentially the same mechanisms have been proposed by other researchers.[16,21,20,27] Because the substrate, main product, and active element of our system are similar to those of $CH_3ReO_3$-catalyzed deoxydehydration, the key steps can be similar in both systems. The proposed mechanism for simultaneous hydrodeoxygenation over $ReO_x$–Pd/$CeO_2$ catalyst is shown in Scheme 2. First, the high-valent Re species is reduced by $H_2$ as a reductant with the aid of Pd, and becomes the active low-valent Re species. Next, the substrate with vicinal OH groups is coordinated to the reduced low-valent Re species with the two OH groups as diolate. Then, alkene is released with the oxidation of Re. Finally, a Pd-catalyzed hydrogenation of the produced alkene gives the product. This mechanism can be regarded as deoxydehydration + hydrogenation. Considering the experimental error of the valence determination, at present, it is very difficult to determine the valence precisely and to distinguish between tetravalent (suggested by EXAFS and XANES analysis) and pentavalent Re species. Therefore, we think that the valence pair of high-valent and low-valent Re species can be 6 and 4 or 7 and 5. There are several reports for supported bimetallic noble metal–Re catalysts including $ReO_x$–Pd/$SiO_2$. Characterization with Re $L_3$-edge XANES of these catalysts shows that the average valence of Re is typically around 2.[5,9,37] This value is much lower than that found for our $ReO_x$–Pd/$CeO_2$ catalyst. According to the mechanism of $CH_3ReO_3$ catalyst and Scheme 2, the active species is Re with relatively high valences (+4–+7). Thus, overreduction of Re oxide can



**Scheme 2.** Simultaneous hydrodeoxygenation over ReO$_x$–Pd/CeO$_2$.

decrease the catalytic activity. The role of CeO$_2$ support could be to suppress the overreduction of Re probably by stabilizing Re by the interaction between Re species and the CeO$_2$ surface.

In summary, ReO$_x$–Pd/CeO$_2$ catalyst gave very high activity (TOF > $10^2$ h$^{-1}$) and selectivity to THF (> 99 %) in the selective simultaneous hydrodeoxygenation of 1,4-anhydroerythritol to tetrahydrofuran (THF). A relatively high-valent ReO$_x$ species is the active site. Pd and CeO$_2$ activate H$_2$ and keep the valence of Re high, respectively. The system can be applied to sugar alcohols. Mono-alcohols (from sugar alcohols which have an odd number OH groups) and diols (from sugar alcohols which have an even number of OH groups) are obtained in high yields (≥ 85 %).

Received: October 22, 2014
Published online: December 17, 2014

**Keywords:** heterogeneous catalysis · hydrodeoxygenation · palladium · rhenium oxide · sugar alcohols

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