# Structure and reaction mechanism of noble-metal-modified $ReO_x/CeO_2$ catalysts for deoxydehydration

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**Abstract:** The structure and deoxydehydration mechanism of $ReO_x$-M/$CeO_2$ (M=Pd, Au) catalysts were investigated. The XRD, XPS and XAFS characterization revealed that $ReO_x$-Au/$CeO_2$ catalysts are composed of very few Au particles and many $CeO_2$ particles supporting $Re^{6+/4+}$ species, while $ReO_x$-Pd/$CeO_2$ catalyst is composed of $CeO_2$ particles each of which supports both $Re^{6+/4+}$ species and Pd clusters. The activity of $ReO_x$-Au/$CeO_2$ is comparative to that of $ReO_x$-Pd/$CeO_2$, suggesting that supply of hydrogen from Au or Pd site to $Re^{6+}$ site is sufficiently fast in both catalysts.

**Keywords:** Deoxydehydration, Rhenium, hydrogen.

## 1. Introduction

Deoxydehydration (DODH), which converts diols to alkenes with appropriate catalyst and reducing agent, is a useful reaction in the field of biomass refinery. Typical DODH catalysts are homogeneous high-valent Re species, and non-$H_2$ reducing agent such as $PPh_3$ and secondary alcohols is used.[1] We have recently discovered that heterogeneous $ReO_x$-Pd/$CeO_2$ catalyst can remove vicinal OH groups with $H_2$ as reducing agent via DODH + hydrogenation,[2,3] and that $ReO_x$-Au/$CeO_2$ catalyst is an effective heterogeneous DODH catalyst with $H_2$.[4] In this study, the structure of these $ReO_x$-M/$CeO_2$ (M=Pd, Au) catalysts was determined, and the reaction mechanism, especially for the reduction of Re species, was discussed.

## 2. Experimental

$ReO_x$-Pd/$CeO_2$ catalyst was prepared by sequential impregnation of $CeO_2$ with $NH_4ReO_4$ and then $Pd(NO_3)_2$. The Re loading amount was 2 wt% and Pd/Re molar ratio was set as 0.25. The catalyst was calcined at 773 K after impregnation. Two types of $ReO_x$-Au/$CeO_2$ catalysts were prepared: $ReO_x$-$^{imp}$Au/$CeO_2$ and $ReO_x$-$^{dp}$Au/$CeO_2$. First, $^{imp}$Au/$CeO_2$ and $^{dp}$Au/$CeO_2$ catalysts were prepared by impregnation and deposition-precipitation, respectively. Then, Re was loaded by impregnation method. The catalysts were calcined at 673 K after impregnation of Re. The Re loading amount was 1 wt% and Au/Re molar ratio was set as 0.3. Activity tests were performed in a 190 mL autoclave with inserted glass vessel. Substrates and products were analyzed by GC (or HPLC for polyols) for both gas and liquid phases.

## 3. Results and discussion

The XRD pattern of used $ReO_x$-Pd/$CeO_2$ catalyst had only the peaks of $CeO_2$ support, and the crystallite size of $CeO_2$ was 8 nm. The XRD patterns of used $ReO_x$-Au/$CeO_2$ catalysts had Au peaks in addition to the peaks of $CeO_2$, and the crystallite size of Au was 12 and 3.3 nm for $ReO_x$-$^{imp}$Au/$CeO_2$ and $ReO_x$-$^{dp}$Au/$CeO_2$, respectively. These data indicate that $ReO_x$ and Pd species were highly dispersed. The XANES analysis showed that Pd and Au were in the metallic state. The Pd-Pd or Au-Au coordination number in EXAFS analysis was 3.1, 11.6 and 8.9 for $ReO_x$-Pd/$CeO_2$, $ReO_x$-$^{imp}$Au/$CeO_2$, and $ReO_x$-$^{dp}$Au/$CeO_2$, respectively. From these XRD and XAFS data, Pd species in $ReO_x$-Pd/$CeO_2$ formed metallic clusters composed of few Pd atoms, and Au species in $ReO_x$-Au/$CeO_2$ formed nanoparticles. The Re $L_3$-edge XANES of used catalysts showed that the Re valence of used catalysts were 5.1, 5.9 and 5.3 for $ReO_x$-Pd/$CeO_2$, $ReO_x$-$^{imp}$Au/$CeO_2$, and $ReO_x$-$^{dp}$Au/$CeO_2$, respectively. The XPS analysis of used $ReO_x$-Pd/$CeO_2$ showed that the Re species in the catalyst was the mixture of $Re^{4+}$ and $Re^{6+}$ species. These data suggest that the DODH reaction over $ReO_x$-M/$CeO_2$ catalysts involves $Re^{6+/4+}$ redox cycle.

Based on the particle/cluster sizes and the molar compositions, each $CeO_2$ particle in $ReO_x$-Pd/$CeO_2$ supports ~120 Re atoms and a few Pd particles (total ~30 Pd atoms). In the case of $ReO_x$-Au/$CeO_2$, each $CeO_2$ particles support ~60 Re atoms and the number ratio of Au particles to $CeO_2$ particles is about 1 to 3000 and 1 to 40 in $ReO_x$-$^{imp}$Au/$CeO_2$ and $ReO_x$-$^{dp}$Au/$CeO_2$, respectively. Therefore, most Re species in $ReO_x$-Au/$CeO_2$ are located far from the Au promoter particles, while most Re species in $ReO_x$-Pd/$CeO_2$ have Pd promoter clusters on the same $CeO_2$ support particle.

The reactivity of various substrates over $ReO_x$-M/$CeO_2$ is shown in Figure 1. The amount of Re was set constant for all catalysts. In spite of the sparsely distributed Au particles, the activities of $ReO_x$-Au/$CeO_2$ were similar to $ReO_x$-Pd/$CeO_2$. Nevertheless, $ReO_x$-$^{imp}$Au/$CeO_2$ showed lower activity than $ReO_x$-$^{dp}$Au/$CeO_2$, and the reactivities of substrates over ReOx-$^{imp}$Au/$CeO_2$ were similar among substrates. These data suggest that the reaction over $ReO_x$-$^{imp}$Au/$CeO_2$ is limited by $H_2$ activation, while the $H_2$ activation is fast over the other two catalysts with more condensed promoter noble metal particles/clusters.

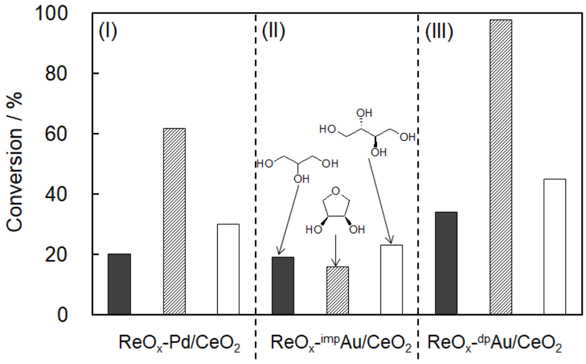

**Figure 1.** Reactivity of glycerol, 1,4-anhydroerythritol and erythritol over (I) $ReO_x$-Pd/$CeO_2$ and (II, III) $ReO_x$-Au/$CeO_2$ catalysts. Conditions: substrate (5.4 mmol), 1,4-dioxane (4 g), catalyst (I: 0.15 g, 2 wt% Re, Pd/Re = 0.25; II, III: 0.3 g, 1 wt% Re, Au/Re = 0.3), $H_2$ (8 MPa), 413 K, 2 h. The main product over $ReO_x$-Pd/$CeO_2$ (I) was 1-propanol, THF and 1,2-butanediol. The main product over $ReO_x$-Au/$CeO_2$ (II,III) was allyl alcohol, 2,5-dihydrofuran and 3-buten-1,2-diol.

Based on the proposed structure and reactivity data, the hydrogen species activated on Au particles (or the interface between Au and support) must be transferred to Re species from support particles to particles. To confirm the transfer of hydrogen species between multiple $CeO_2$ particles, TPR measurements of $ReO_x$/$CeO_2$, Au/$CeO_2$, $ReO_x$-Au/$CeO_2$, and the mixture of $ReO_x$/$CeO_2$ and Au/$CeO_2$ were carried out. The reduction of $ReO_x$/$CeO_2$ was surely promoted by being mixed with Au/$CeO_2$, and the pattern of the catalyst mixture was similar to that of $ReO_x$-Au/$CeO_2$.

The typical mechanism of DODH is composed of (i) reduction of active metal center such as $Re^{7+}$ by two electrons with reducing agent, (ii) coordination of diol to the metal center as diolate species, and (iii) the release of alkene from the diolate species. We propose the mechanism of $ReO_x$-M/$CeO_2$-catalyzed DODH as the combination of (i) reduction of $Re^{6+}$ species on $CeO_2$ to $Re^{4+}$ with hydrogen species which is produced from $H_2$ on M site, (ii) coordination of diol to $Re^{4+}$ species on $CeO_2$, and (iii) the release of alkene. In the case of M=Pd, the produced alkene is hydrogenated over Pd site to give saturated product.

## 4. Conclusions

$ReO_x$-Au/$CeO_2$ catalysts are composed of Au particles and $CeO_2$ particles with $Re^{6+/4+}$ species, and the Au particles is much fewer than $CeO_2$ particles. Nevertheless, the supply of hydrogen from Au site to active center $Re^{6+}$ site is sufficiently fast, similarly to $ReO_x$-Pd/$CeO_2$ catalyst.

## References

1. S. Raju, M. Moret, R. J. M. K. Gebbink, ACS Catal. 281 (2015) 281.
2. N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, Angew. Chem. Int. Ed. 54 (2015) 1897.
3. N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, ACS Catal. 6 (2016) 3213.
4. S. Tazawa, N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, ACS Catal. 6 (2016) 6393.