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$^{5+/4+}$ 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$_2$. 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$_4$ReO$_4$ 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$_x$-$^{\text{imp}}$Au/CeO$_2$ and ReO$_x$-$^{d_{\text{p}}}$Au/CeO$_2$. First, $^{\text{imp}}$Au/CeO$_2$ and $^{d_{\text{p}}}$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$_x$-$^{\text{imp}}$Au/CeO$_2$ and ReO$_x$-$^{d_{\text{p}}}$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$_x$-$^{\text{imp}}$Au/CeO$_2$, and ReO$_x$-$^{d_{\text{p}}}$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$_x$-$^{\text{imp}}$Au/CeO$_2$, and ReO$_x$-$^{d_{\text{p}}}$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 CeO₂ particle in ReOₓ-Pd/CeO₂ supports ~120 Re atoms and a few Pd particles (total ~30 Pd atoms). In the case of ReOₓ-Au/CeO₂, each CeO₂ particles support ~60 Re atoms and the number ratio of Au particles to CeO₂ particles is about 1 to 3000 and 1 to 40 in ReOₓ-imp/Au/CeO₂ and ReOₓ-xdp/Au/CeO₂, respectively. Therefore, most Re species in ReOₓ-Au/CeO₂ are located far from the Au promoter particles, while most Re species in ReOₓ-Pd/CeO₂ have Pd promoter clusters on the same CeO₂ support particle.

The reactivity of various substrates over ReOₓ-M/CeO₂ 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 ReOₓ-Au/CeO₂ were similar to ReOₓ-Pd/CeO₂. Nevertheless, ReOₓ-imp/Au/CeO₂ showed lower activity than ReOₓ-xdp/Au/CeO₂, and the reactivities of substrates over ReOₓ-imp/Au/CeO₂ were similar among substrates. These data suggest that the reaction over ReOₓ-imp/Au/CeO₂ is limited by H₂ activation, while the H₂ 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) ReOₓ-Pd/CeO₂ and (II, III) ReOₓ-Au/CeO₂ 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), H₂ (8 MPa), 413 K, 2 h. The main product over ReOₓ-Pd/CeO₂ (I) was 1-propanol, THF and 1,2-butanediol. The main product over ReOₓ-Au/CeO₂ (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 CeO₂ particles, TPR measurements of ReOₓ/CeO₂, Au/CeO₂, ReOₓ-Au/CeO₂, and the mixture of ReOₓ/CeO₂ and Au/CeO₂ were carried out. The reduction of ReOₓ/CeO₂ was surely promoted by being mixed with Au/CeO₂, and the pattern of the catalyst mixture was similar to that of ReOₓ-xdp/Au/CeO₂.

The typical mechanism of DODH is composed of (i) reduction of active metal center such as Re⁷⁺ 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 ReOₓ-M/CeO₂-catalyzed DODH as the combination of (i) reduction of Re⁵⁺ species on CeO₂ to Re⁴⁺ with hydrogen species which is produced from H₂ on M site, (ii) coordination of diol to Re⁴⁺ species on CeO₂, 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**

ReOₓ-Au/CeO₂ catalysts are composed of Au particles and CeO₂ particles with Re⁶⁺/⁵⁺ species, and the Au particles is much fewer than CeO₂ particles. Nevertheless, the supply of hydrogen from Au site to active center Re⁶⁺ site is sufficiently fast, similarly to ReOₓ-Pd/CeO₂ catalyst.

**References**