

Deoxydehydration of glycerol with H₂ to allyl alcohol catalyzed by heterogeneous ReO_x-Au/CeO₂

Keiichi Tomishige*, Yoshinao Nakagawa,
Masazumi Tamura

Department of Applied Chemistry, School of
Engineering, Tohoku University, Sendai,
Japan

*E-mail: tomi@erec.che.tohoku.ac.jp

Biomass-derived chemicals are attractive starting materials to substitute for unsustainable fossil resources. Since oxygen content is usually high in these biomass-derived materials compared with most value-added chemicals, deoxydehydration (DODH) is one of important reactions for the decrease of oxygen content, which converts vicinal two OH groups to one C=C double bond. One of typical DODH catalysts is homogeneous Re complex, where non-H₂ reductants such as PPh₃, sulfite, metal, hydroaromatics and alcohols have been used. Recently, our group has developed heterogeneous ReO_x-M/CeO₂ (M=Pd and Au) catalysts, where H₂ can be used as a reductant [1-3]. This presentation focuses the DODH of glycerol and erythritol with H₂ catalyzed by ReO_x-Au/CeO₂ catalyst.

CeO₂ (Daiichi Kigenso Co., Ltd., HS, BET surface area: 87 m² g⁻¹, after calcination at 873 K for 3 h) was used. The ReO_x/CeO₂ catalysts were prepared by impregnating CeO₂ with the aqueous solution of NH₄ReO₄. The ReO_x-Au/CeO₂ catalysts were prepared by impregnating ReO_x/CeO₂ after drying at 383 K for 12 h with aqueous solution of HAuCl₄. The activity tests were carried out using the autoclave reactor.

The addition of Au to ReO_x/CeO₂ enhanced the activity of the DODH reaction of glycerol [3]. The ReO_x-Au/CeO₂ catalyst (Re 1 wt%, Au/Re=0.3) has highly dispersed Re species on CeO₂ and 12 nm Au particles [3]. The main role of Au is to activate H₂ molecule and to promote the reduction of Re species probably by hydrogen spillover phenomenon. Figure 1 shows the reaction time dependence of DODH of glycerol with H₂ over ReO_x-Au/CeO₂. The selectivity to allyl alcohol is very high, and the yield of allyl alcohol reached 91% [3], which was clearly higher than those in previous

reports using H₂ as a reductant. The selectivity to allyl alcohol decreased significantly after the glycerol conversion reached about 100%, indicating the suppression of the consecutive hydrogenation of allyl alcohol to 1-propanol with the presence of glycerol.

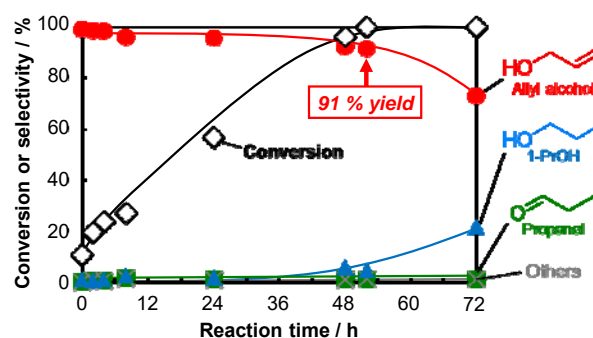
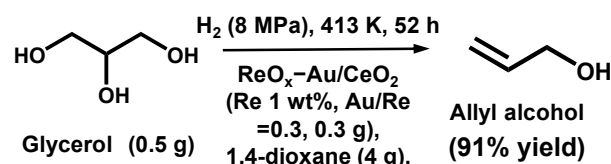
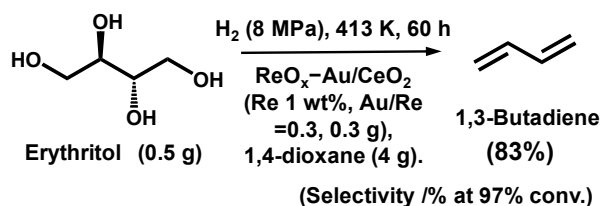


Fig. 1 Reaction time dependence of DODH of glycerol over ReO_x-Au/CeO₂ catalyst (Re 1 wt%, Au/Re=0.3)

Conditions: glycerol 0.5 g, 1,4-dioxane 4 g, W_{cat}=0.3 g, P(H₂) = 8 MPa, T = 413 K.

In addition, the DODH of erythritol was carried out using ReO_x-Au/CeO₂ catalyst, and 81% yield of 1,3-butadiene was obtained [3].



REFERENCES

- [1] N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, *Angew. Chem. Int. Ed.*, 54 (2015) 1897-1900.
- [2] N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, *ACS Catal.*, 6 (2016) 3213-3226.
- [3] S. Tazawa, N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, *ACS Catal.*, 6, (2016) 6393-6397.