

N°934 / OC

TOPIC(s) : Biomass conversion

Production of biomass-derived chemicals by deoxydehydration reaction using heterogenized Re oxide catalysts

AUTHORS

Keiichi TOMISHIGE / TOHOKU UNIVERSITY, 6-6-07, AOBAM, ARAMAKI, AOBA-KU, SENDAI, MIYAGI

PURPOSE OF THE ABSTRACT

Biomass is an attractive starting material in order to substitute fossil resources such as petroleum. Oxygen content is usually high in these biomass-derived materials compared with most useful petroleum-based chemicals. Therefore, the methods for the decrease of the oxygen content become more important. A typical method for the deoxygenation is hydrodeoxygenation such as C-O hydrogenolysis, for example, glycerol to 1,2- and 1,3-propanediols and so on. Another method is deoxydehydration (DODH), which converts vicinal OH groups to one C=C double bond. A typical DODH catalyst is homogeneous $\text{CH}_3\text{ReO}_3(1)$. The DODH reaction requires the reductant, and non- H_2 reductants such as PPh_3 or alcohols have been usually used, and H_2 is not suitable reductant from the viewpoint of yields of the DODH products. Recently, heterogeneous $\text{ReO}_x/\text{M}/\text{CeO}_2$ ($\text{M}=\text{Pd}$ and Au) catalysts have been developed and these enabled H_2 as a reductant (2-8).

CeO_2 (Daiichi Kigenso Co., Ltd., HS, BET surface area: $87 \text{ m}^2 \text{ g}^{-1}$, after calcination at 873 K for 3 h) was used. The $\text{ReO}_x/\text{CeO}_2$ catalyst were prepared by impregnating CeO_2 with the aqueous solution of NH_4ReO_3 . The $\text{ReO}_x/\text{M}/\text{CeO}_2$ ($\text{M}=\text{Pd}$, Au) catalysts were prepared by impregnating $\text{ReO}_x/\text{CeO}_2$ after drying at 383 K for 12 h with aqueous solution of $\text{Pd}(\text{NO}_3)_2$ and HAuCl_4 . The activity tests were carried out using the autoclave reactor.

The $\text{ReO}_x/\text{Pd}/\text{CeO}_2$ was effective to the conversion of 1,4-anhydroerythritol to tetrahydrofuran and erythritol to butanediols. These reactions contain the combination of the DODH catalyzed by ReO_x on CeO_2 and the subsequent hydrogenation of C-C double bond in the DODH products catalyzed by Pd metal particles. From the characterization results, it is found that the DODH reaction proceeds by the redox cycle of monomeric Re species on CeO_2 surface between Re^{4+} and Re^{6+} . At the same time, the Pd metal species promotes the reduction of Re species from Re^{6+} to Re^{4+} species by H_2 activation and spillover. An important role of CeO_2 is to stabilize Re^{4+} species to suppress the over-reduction to inactive Re species.

$\text{ReO}_x/\text{Pd}/\text{CeO}_2$ was also applied to the DODH+hydrogenation of various methyl glycoside with cis-vicinal OH groups to corresponding dideoxy derivatives, and obtained products were also converted to value-added chemicals such as chiral triols and so on.

The $\text{ReO}_x/\text{Au}/\text{CeO}_2$ catalyzed DODH of glycerol to allyl alcohol and erythritol to 1,3-butadiene with H_2 and high yields were obtained as shown below. The role of Au is to activate H_2 and to promote the reduction of Re species like the case of Pd-modified catalyst, however, the activity of C=C hydrogenation on Au is much lower than that on Pd, and the DODH products were obtained on $\text{ReO}_x/\text{Au}/\text{CeO}_2$. We recently reported that $\text{ReO}_x/\text{Au}/\text{CeO}_2$ also catalyzed DODH of methyl glycoside with cis-vicinal OH groups to corresponding unsaturated sugar derivatives. It is recently found that the combination of $\text{ReO}_x/\text{Au}/\text{CeO}_2$ with ReO_x/C enabled the one-pot conversion of 1,4-anhydroerythritol to 1,4-butanediol in high yield (~90%). The reaction route includes DODH of 1,4-anhydroerythritol, isomerization of 2,5-dihydrofuran to 2,3-dihydrofuran, H_2O addition of 2,3-dihydrofuran, ring-opening to 4-hydroxybutanal, and subsequent hydrogenation of 4-hydroxybutanal to 1,4-butanediol.

References

1. M. Shiramizu, F. D. Toste, *Angew. Chem. Int. Ed.* 32 (2012) 8082.
2. N. Ota, K. Tomishige, et al., *Angew. Chem. Int. Ed.* 54 (2015) 1897.
3. N. Ota, K. Tomishige, et al., *ACS Catal.* 6 (2016) 3213.
4. S. Tazawa, K. Tomishige, et al., *ACS Catal.* 6 (2016) 6393.

5. Y. Nakagawa, K. Tomishige, et al., *ACS Catal.* 8 (2018) 584
6. T. Wang, K. Tomishige, et al., *Green Chem.*, 20 (2018) 2574
7. M. Tamura, K. Tomishige, et al., *Angew. Chem. Int. Ed.* 57 (2018) 8058
8. J. Cao, K. Tomishige, et al., *ACS Catal.*, in press. (DOI: 10.1021/acscatal.9b00589).

FIGURES

FIGURE 1

FIGURE 2

KEYWORDS

biomass | heterogeneous catalysis | deoxydehydration

BIBLIOGRAPHY