One-pot Production of 1,4-Butanediol from 1,4-Anhydroerythritol Using the Deoxydehydration Reaction

Tianmiao Wang,[a] Sibao Liu,[a] Masazumi Tamura,[a,b] Yoshinao Nakagawa,[*,a,b] Keiichi Tomishige [*,a,b]

[a] Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

[b] Research center for Rare Metal and Green Innovation, Tohoku University, 468-1 Aoba, Aramaki, Aoba-ku, Sendai, 980-0845, Japan

** Corresponding Author: Yoshinao Nakagawa and Keiichi Tomishige, E-mail: yoshinao@erec.che.tohoku.ac.jp (Y. N.) tomi@erec.che.tohoku.ac.jp (K. T.)*

Abstract: The physical mixture of ReO_x-Au/CeO_2 and ReO_x/C catalysts effectively converted 1,4-anhydroerythritol to 1,4-butanediol with H_2 as a reductant at relatively low reaction temperature of 413 K. The combination of these two catalysts in one-pot reaction dramatically increased selectivity of 1,4-butanediol as well as conversion of 1,4-anhydroerythritol. The yield of 1,4-butanediol reached ~90%, which is the highest yield from erythritol and 1,4-anhydroerythritol so far. This reaction is composed of ReO_x-Au/CeO_2-catalyzed deoxydehydration of 1,4-anhydroerythritol to 2,5-dihydrofuran and ReO_x/C-catalyzed successive isomerization, hydration and reduction reactions of 2,5-dihydrofuran.

Keywords: Heterogenous catalysis, deoxydehydration, rhenium oxide, gold, one-pot reaction

1. Introduction

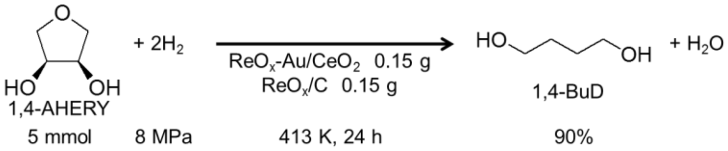
Renewable biomass-based products as energy resources and feedstocks are in increasing demand as replacements of fossil resources.[1,2] Deoxydehydration (DODH) reaction is an attractive selective oxygen removal process to decrease the oxygen content of biomass-derived polyols by simultaneously removing vicinal diols to C=C bond.[3-5] Recently, we reported heterogeneous ReO_x-Au/CeO_2 catalyst as an effective H_2-driven DODH catalyst.[6,7] In this DODH system, 1,4-anhydroerythritol (1,4-AHERY) as a dehydrated product from erythritol can be converted to 2,5-dihydrofuran (2,5-DHF).[6,7] 1,4-Butanediol (1,4-BuD) was reported to be able to be produced by hydration-reduction of 2,5-DHF over ReO_x/TiO_2 catalysts with H_2 in a flow reactor.[8] However, studies of 1,4-BuD production from erythritol or 1,4-AHERY are very limited. 1,4-BuD can be obtained from 1,4-AHERY with ReO_x/C catalysts and H_2 at 473 K,[9] nevertheless, the selectivity of 1,4-BuD is as low as 41%, and the yield is just 30%. In this study, we combine the two catalyses within one-pot reaction: the DODH of 1,4-AHERY to 2,5-DHF over ReO_x-Au/CeO_2 and the conversion of 2,5-DHF to 1,4-BuD over another Re catalyst. Over the combination of ReO_x-Au/CeO_2 and ReO_x/C catalysts, we obtained ~90% yield of 1,4-BuD from 1,4-AHERY and H_2 at 413 K. This yield is much higher than the literature ones of 1,4-BuD from 1,4-AHERY.

2. Experimental

The ReO_x-Au/CeO_2 (1 wt% Re, 0.3 wt% Au) catalyst was prepared by deposition-precipitation method for Au loading and subsequent impregnation for Re loading.[6] The ReO_x/C (3 wt% Re) catalyst was prepared by impregnation method using BP-2000 carbon black. The activity test was conducted with an autoclave reactor equipped with an inner glass cylinder. The optimized reaction conditions are 1:1 catalysts weight ratio, 8 MPa H_2, and 413 K. After reaction, both gas and liquid phases were analyzed by FID-GC, GC-MS, and NMR.

3. Results and discussion

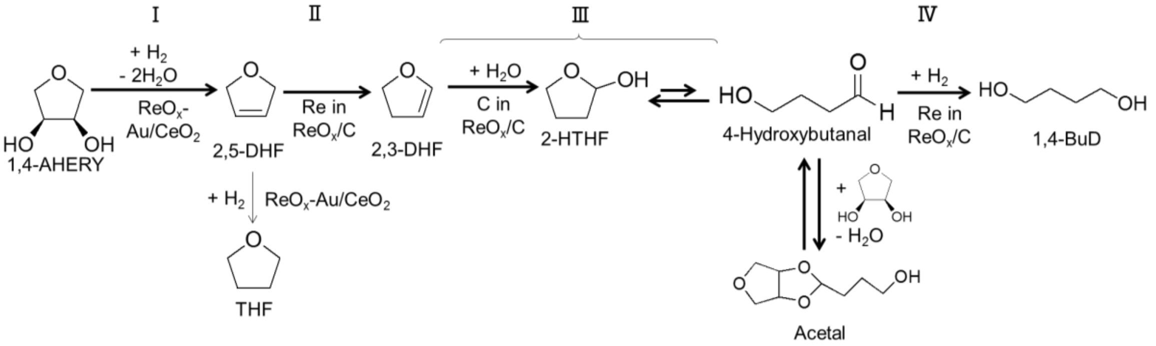
Various supported Re catalysts were tested for the co-catalysis with ReO_x-Au/CeO_2 in the reaction of 1,4-AHERY. The combination of carbon-supported rhenium catalysts with ReO_x-Au/CeO_2 showed the best selectivity of 1,4-BuD. The highest yield of 1,4-BuD reached ~90% (eq. (1)). Adding ReO_x/C to ReO_x-Au/CeO_2 dramatically increased the selectivity of 1,4-BuD and effectively suppressed the formation of by-products such as 2,5-DHF and 2,3-DHF; meanwhile, it also improved the 1,4-AHERY conversion (64% → 100%).



(1)

The use of ReO$_x$/C alone showed low conversion. The possible route of the reaction from 1,4-AHERY to 1,4-BuD and the role of catalyst components were studied by testing different substrates (or possible intermediates) over various related catalysts. Single ReO$_x$-Au/CeO$_2$ catalyzed the DODH conversion of 1,4-AHERY to 2,5-DHF and small amounts of 2,3-DHF and tetrahydrofuran (THF) which are successively produced by isomerization and hydrogenation of 2,5-DHF, respectively. Over ReO$_x$-Au/CeO$_2$ + ReO$_x$/C, very high yield of 1,4-BuD and low yield of THF were observed, suggesting that the activity of ReO$_x$/C in the successive reactions of 2,5-DHF can be much higher than that of ReO$_x$-Au/CeO$_2$. Over single ReO$_x$/C in the reaction of 2,5-DHF, medium yield of 1,4-BuD was obtained, indicating that ReO$_x$/C has high activity of DHFs ring-opening reaction to 1,4-BuD. The activity of ReO$_x$-Au/CeO$_2$ was not so high in the reaction of 2,5-DHF, indicating that the reaction of 2,5-DHF is mainly catalyzed by ReO$_x$/C. In the reaction of 2.3-DHF, single C showed activity to give 2-hydroxytetrahydrofuran (2-HTHF) and its addition product with 2,3-DHF. ReO$_x$-Au/CeO$_2$ + ReO$_x$/C gave high yield of 1,4-BuD in the reaction of 2,3-DHF. 1,4-BuD formed on ReO$_x$/C but did not form on C in the reaction of 2,3-DHF, indicating that Re species on ReO$_x$/C mainly catalyzes the hydrogenation of 2-HTHF (or 4-hydroxybutanal) to 1,4-BuD. Single C has almost no activity in the conversion of 2,5-DHF, indicating that Re species on C plays the key role in the reaction. At short reaction time in the reaction of 1,4-AHERY over ReO$_x$-Au/CeO$_2$ + ReO$_x$/C, an acetal formed by 4-hydroxybutanal and 1,4-AHERY was detected in significant selectivity (~55%). 4-Hydroxybutanal is thought to be in the equilibrium by the intramolecular acetalization with 2-HTHF.

Scheme 1 summarizes the proposed reaction route from 1,4-AHERY to 1,4-BuD. In this co-catalyzed reaction, the ReO$_x$-Au/CeO$_2$ catalyst is in charge of the high conversion of 1,4-AHERY to 2,5-DHF (step I). Meanwhile, the ReO$_x$/C catalyst is responsible for the isomerization of 2,5-DHF to 2,3-DHF (step II), hydration of 2,3-DHF to 4-hydroxybutanal or the hemiacetal/acetal (step III), as well as the hydrogenation to 1,4-BuD (step IV). Overall, the use of both ReO$_x$-Au/CeO$_2$ and ReO$_x$/C at once is effective in suppressing the side reaction of reactive intermediates, leading to high yield of 1,4-BuD from 1,4-AHERY.



Scheme 1. Proposed reaction route from 1,4-AHERY to 1,4-BuD over the mixture of ReO$_x$-Au/CeO$_2$ and ReO$_x$/C. AHERY: anhydroerythritol, BuD: Butanediol, DHF: dihydrofuran, THF: tetrahydrofuran. HTHF: hydroxytetrahydrofuran.

4. Conclusions

The physical mixture of ReO$_x$-Au/CeO$_2$ and ReO$_x$/C effectively converted 1,4-AHERY to 1,4-BuD with H_2 as reductant. The yield of 1,4-BuD reached ~90% at the reaction temperature of 413 K. In this reaction, ReO$_x$-Au/CeO$_2$ catalyzed DODH of 1,4-AHERY to 2,5-DHF, and ReO$_x$/C catalyzed successive isomerization, hydration and reduction reactions of 2,5-DHF. The use of both catalysts at once is effective in suppressing the formation of by-products derived from reactive intermediates such as 2,3- and 2,5-DHFs. We will develop the reusability of the catalyst mixture in the future study.

References

1. Besson, M.; Gallezot, P.; Pinel, C. *Chem. Rev.* **2014**, *114*, 1827-1870.
2. Schlaf, M. *Dalton Trans*., **2006**, 4645-4653.
3. Dethlefsen, J. R.; Fristrup, P. *ChemSusChem* **2015**, *8*, 767-775.
4. Petersen, A.R.; Fristrup, P. *Chem. Eur. J.* **2017**, *23*, 10235-10243.
5. Raju, S.; Moret, M.; Gebbink, R. J. M. K. *ACS Catal.* **2015**, *5*, 281-300.
6. Tazawa, S.; Ota, N.; Tamura, M.; Nakagawa, Y.; Okumura, K.; Tomishige, K. *ACS Catal.* **2016**, *6*, 6393-6397.
7. Nakagawa, Y.; Tazawa, S.; Wang, T.; Tamura, M.; Hiyoshi, N.; Okumura, K.; Tomishige, K. *ACS Catal.* in press.
8. Pinkos, R.; Fischer, R. H.; Breitscheidel, B.; Polanek, P. CA Patent 2168458C, May, 25, 2004.
9. Manzer, L. E. (E. I. du Pont de Nemours and Company). U.S. Patent 6593481B1, Jul. 15, 2003.