Catalytic production of chiral polyols using deoxydehydration of methyl glycosides over ReO_x-Pd/CeO_2 without protecting OH groups

Keiichi Tomishige*

School of Engineering, Tohoku University, Sendai, 980-8579, Japan

Abstract: Catalytic conversion methyl glycosides with maintaining the intrinsic stereostructure is desirable to make full use of sugars, however, it is not easy to apply the catalytic reactions to the conversion of sugars because of too high reactivity of sugars. Therefore, the protection and deprotection of the OH groups is needed for the transformation of sugars. In contrast, we found that ReO_x-Pd/CeO_2 catalyst was effective to deoxydehydration of methyl glycosides with *cis*-vicinal OH groups to corresponding dideoxy products in high yield, which can be easily converted to chiral polyols.

Keywords: Deoxydehydration, methyl glycosides, heterogeneous catalysts

1. Introduction

Biomass-derived chemicals are attractive starting materials to substitute fossil resources. Since oxygen content is usually high in these biomass-derived materials compared with most value-added chemicals, which have been produced mainly by petrochemical industries, deoxygenation is an important step in the conversion of biomass to value-added chemicals. 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[1]. Another method is deoxydehydration (DODH), which converts vicinal OH groups to one C=C double bond. It has been known that Re, V, and Mo homogeneous and heterogeneous catalysts, especially Re, have the catalytic activity in DODH reactions of polyols and so on. In these DODH reaction systems, non-H_2 reductants such as PPh_3, sulfite, metal, hydroaromatics and alcohols have been used, and this is because H_2 is not used as a reductant for much lower yields of the DODH products. In contrast, heterogeneous ReO_x–M/CeO_2 (M=Pd and Au) catalysts have been recently developed and these enabled H_2 as a reductant[2-6]. The catalysts are applicable to the conversion of 1,4-anhydroerythritol to tetrahydrofuran or 1,4-butanediol, erythritol to butanediols, glycerol to allyl alcohol, and erythritol to 1,3-butadiene and so on. Here, ReO_x–Pd/CeO_2 was applied to the deoxydehydration reaction of various methyl glycoside with cis-vicinal OH groups, and obtained dideoxy products were also converted to value-added chemicals such as chiral triols and so on.

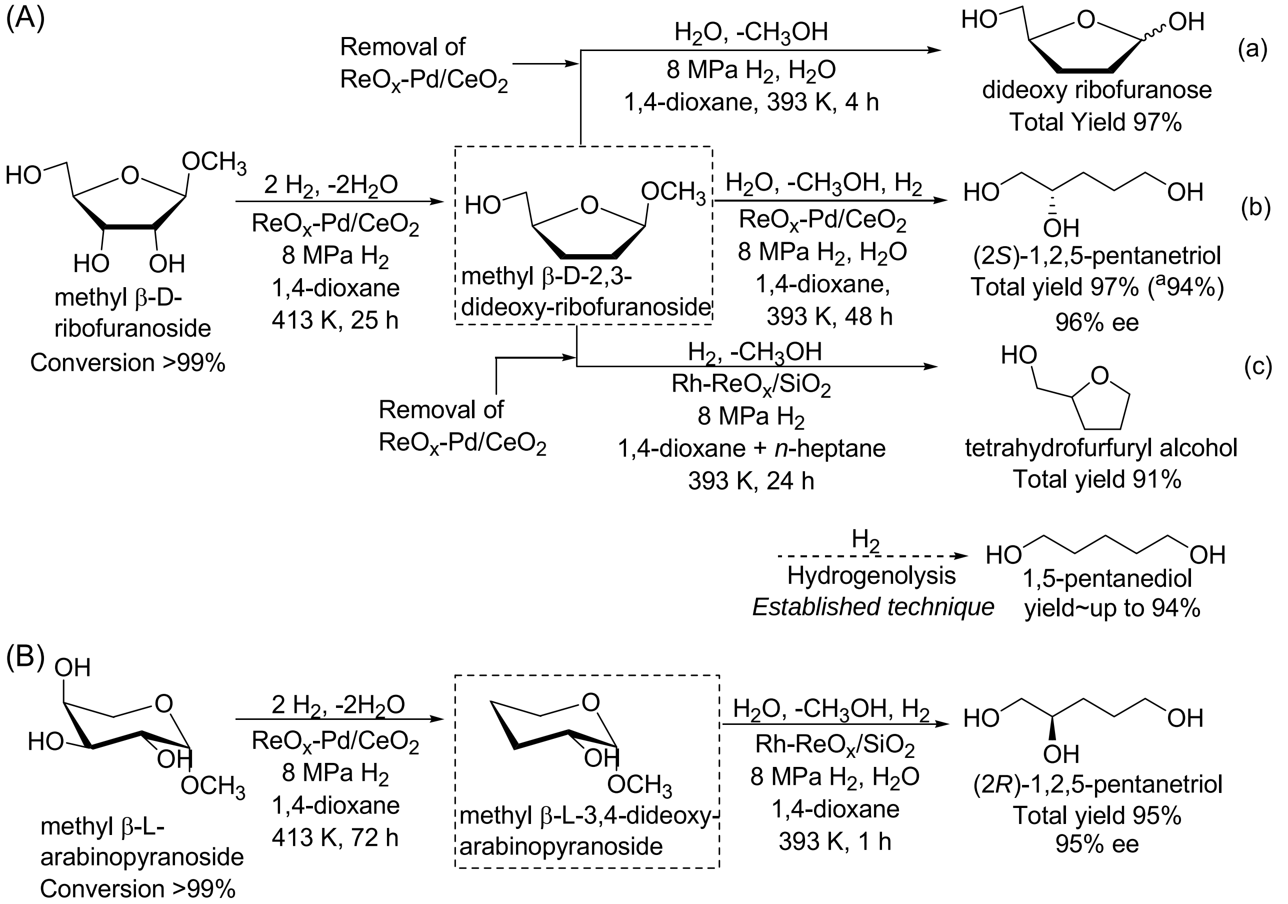
2. Experimental

CeO_2 (Daiichi Kigenso Co., Ltd., HS, BET surface area: 87 $m^2\,g^{-1}$, after calcination at 873 K for 3 h) was used. ReO_x–Pd/CeO_2 (Re=2 wt%, Pd/Re=1/4) was prepared by a sequential impregnation method on the basis of the previous reports[2, 3]. Rh–ReO_x/SiO_2 (Rh = 4 wt%, Re/Rh = 1/2) was prepared by a sequential impregnation method on the basis of the previous report[1]. The activity tests were carried out using the autoclave reactor.

3. Results and discussion

ReO_x–Pd/CeO_2 catalyst catalyzes DODH reaction and subsequent hydrogenation of C=C of the DODH product. Methyl β-D-ribofuranoside and methyl β-L-arabinopyranoside have cis-vicinal OH groups, and they were removed by the DODH and hydrogenation reactions over ReO_x–Pd/CeO_2 and corresponding dideoxyproducts were obtained in high yield (Scheme 1). An important point is that cyclic structure should be maintained for high selectivity, therefore, methyl glycosides were used for this reaction. After the DODH+hydrogenation reactions, H_2O was added to the solutions containing the dideoxyproducts and then

H_2 was pressurized. The dideoxy products were converted to (2S)-1,2,5-pentanetriol and (2R)-1,2,5-pentanetriol in high yield and high ee (Scheme 1). The high ee is due to the retention of stereostructure of the methyl glycoside substrates. Tetrahydrofurfuryl alcohol was also obtained from the dideoxyproduct of methyl β-D-ribofuranoside.



Scheme 1. Synthesis of chiral building blocks and α,ω-diol synthon. (A) Formation of dideoxy ribofuranose, (2*S*)-1,2,5-pentanetriol and tetrahydrofurfuryl alcohol from methyl β-D-ribofuranoside. (B) Formation of (2*R*)-1,2,5-pentanetriol from methyl β-L-arabinopyranoside.

4. Conclusions

ReO_x-Pd/CeO_2 was an effective heterogeneous catalyst for the direct and selective conversion of methyl glycosides with *cis*-vicinal OH groups to dideoxy glycosides without protection of OH groups by deoxydehydration and subsequential hydrogenation using gaseous H_2 as a reductant. Various methyl glycosides with *cis*-vicinal OH groups were converted to the corresponding dideoxy glycosides in high isolated yields with maintaining the intrinsic structure. The obtained dideoxy glycoside can be selectively transformed to the chiral polyols in high yield and high ee by hydration and hydrogenation.

References

1. K. Tomishige, Y. Nakagawa, M. Tamura, Green Chem. 19 (2017) 2876.
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.
5. Y. Nakagawa, S. Tazawa, T. Wang, M. Tamura, N. Hiyoshi, K. Okumura, K. Tomishige, ACS Catal. 8 (2018) 584.
6. T. Wang, S. Liu, M. Tamura , Y. Nakagawa, N. Hiyoshi, K. Tomishige, Green Chem. in press (DOI: 10.1039/C8GC00574E).
7. M. Tamura, N. Yuasa, J. Cao, Y. Nakagawa, K. Tomishige, Angew. Chem. Int. Ed. in press.