Hydrodeoxygenation of vicinal OH groups in methyl glycosides over palladium modified CeO_2 supported rhenium catalyst

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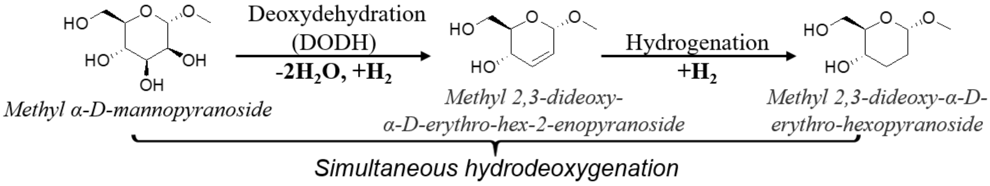
Abstract: Sugars are ubiquitous in nature, and are highly oxygen-rich compared with most chemicals and fuels, therefore it is necessary to develop deoxygenation of sugars and sugar-derived polyol compounds into valuable chemicals. Our previous work reported simultaneous removal of vicinal OH groups over ReO_x-Pd/CeO_2 catalyst. In this work, ReO_x-Pd/CeO_2 catalyst was applied to selective removal of *cis*-vicinal OH groups of methyl α-D-mannopyranoside with high selectivity of the corresponding dideoxy product, and the yield reached 96 %.

Keywords: Hydrodeoxygenation, Heterogeneous catalysis, Rhenium.

1. Introduction

The diversity of biomass feedstocks and the lack of conversion technology prevent increasing utilization of fossil resources. Since biomass, especially sugars and sugar-derived polyol compounds, contains a larger amount of oxygen atoms than petroleum derived chemicals, it is very important to develop a method for the conversion of oxygen-rich chemicals to fine chemicals. In our previous work, we reported that heterogeneous ReO_x-Pd/CeO_2 was an effective catalyst for simultaneous hydrodeoxygenation of 1,4-anhydroerythritol to tetrahydrofuran by using H_2 as a reductant[1,2]. In this system, two vicinal OH groups were transformed to H atoms by combination of deoxydehydration and hydrogenation step.

In this work, hydrodeoxygenation of methyl α-D-mannopyranoside was selected as a model reaction for the selective removal of *cis*-vicinal OH groups (Scheme 1). We found that ReO_x-Pd/CeO_2 catalyst showed high catalytic activity and selectivity for the reaction using H_2 as a reductant, providing the corresponding dideoxy product.



Scheme 1. Reaction pathway of simultaneous hydrodeoxygenation of vicinal OH groups in methyl α-D-mannopyranoside.

2. Experimental

Catalysts were prepared by sequential impregnation method. The MO_x-Pd/CeO_2 (M=Re, Mo, W, V M=2 wt%, Pd/M molar ratio =0.25) catalysts were prepared by impregnating MO_x/CeO_2 with corresponding precursor solution (NH_4ReO_4, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, $(NH_4)_6H_2W_{12}O_{40}\cdot xH_2O$, NH_4VO_3) and drying at 383 K for 12 h at first, then impregnating MO_x/CeO_2 with an aqueous solution of $Pd(NO_3)_2$ at 353 K in a similar way. The ReO_x-Pd/Support (Support=SiO_2, TiO_2, MgO, γ-Al_2O_3, ZrO_2) catalysts were prepared by impregnating ReO_x/Support after drying at 383 K for 12 h with an aqueous solution of $Pd(NO_3)_2$ in a similar way. The ReO_x/CeO_2 (Re=2 wt%) and Pd/CeO_2 (Pd=0.29 wt%) catalysts were prepared by impregnating CeO_2 powder with a aqueous solution of NH_4ReO_4 or $Pd(NO_3)_2$ at 353 K. The catalysts were further dried at 383 K for 12 h. The obtained catalyst precursors were dried at 383 K for 12 h, then calcined in air at 773 K for 3 h.

Activity tests were performed in a stainless-steel autoclave reactor. Substrate and solvent were placed into the autoclave containing an inner glass cylinder with a stirrer and appropriate amount of catalyst. The autoclave was then heated to the reaction temperature after being purged by hydrogen and increased to an appropriate hydrogen pressure. After reaction, the reactor was cooled down to room temperature. The substrates and products were analyzed by FID-GC, GC-MS and HPLC.

3. Results and discussion

Figure 1 showed the results about methyl α-D-mannopyranoside hydrodeoxygenation over ReO_x-Pd/Support, MO_x-Pd/CeO_2, Pd/CeO_2 and ReO_x/CeO_2 catalysts. During the reaction, the *cis*-vicinal OH groups at C-2 and C-3 positions of methyl α-D-mannopyranoside were removed, and methyl 2,3-dideoxy α-D-erythro-hexopytanoside was produced as a dideoxy product and methyl 2,3-dideoxy α-D-erythro-hex-2-enopyranoside was generated as an intermediate. After a 4 h reaction over ReO_x-Pd/CeO_2 catalyst, the conversion reached 35 % and the selectivity of dideoxy product was 96 %. For MO_x-Pd/CeO_2 catalysts, ReO_x-Pd/CeO_2 revealed the highest catalytic activity for hydrodeoxygenation of vicinal OH groups, while other metal oxides (MoO_x, WO_x, VO_x) modified Pd/CeO_2 catalysts showed almost no catalytic activity. While a quite low conversion (<5 %) and dideoxy product selectivity (<5 %) were observed in the case of using Pd/CeO_2 or ReO_x/CeO_2 catalyst. These results indicated that ReO_x-Pd worked as a responsible active species in this reaction. On the other hand, among various ReO_x-Pd/Support catalysts, CeO_2-supported ReO_x-Pd catalyst showed extremely higher conversion and dideoxy product selectivity than other metal oxide supported catalysts. These results demonstrated that, all three components, ReO_x, Pd and CeO_2, were essential for the high selectivity to dideoxy product with high activity on the hydrodeoxygenation of methyl α-D-mannopyranoside.

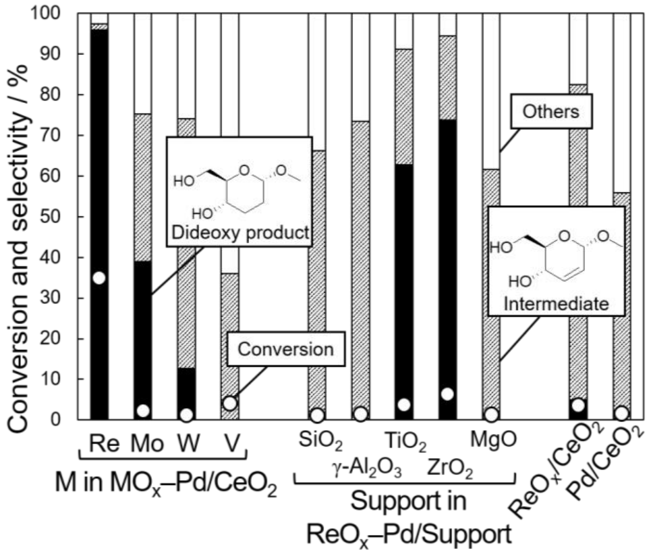


Figure 1. Hydrodeoxygenation of methyl α-D-mannopyranoside over various catalysts.
Reaction conditions: Methyl *a*-D-mannopyranoside 0.25 g, catalyst 0.15 g, 1,4-dioxane 10 g, reaction time 4 h, P_{H2} = 8 MPa, T = 413 K.

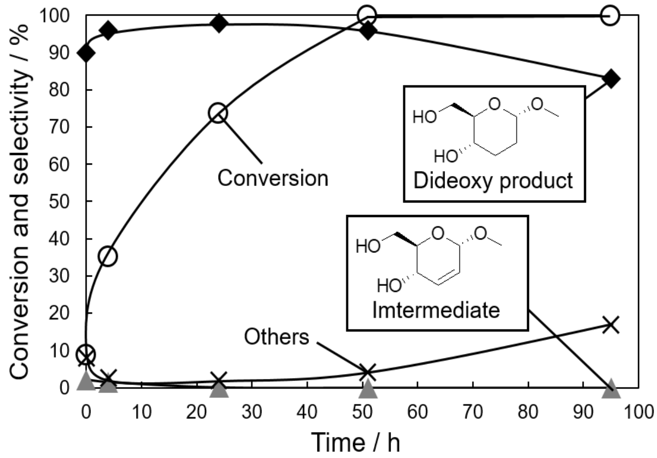


Figure 2. Time course of methyl α-D-mannopyranoside hydrodeoxygenation over ReO_x–Pd/CeO_2 catalyst.
Reaction conditions: Methyl *a*-D-mannopyranoside 0.25 g, catalyst 0.15 g, 1,4-dioxane 10 g, P_{H2} = 8 MPa, T = 413 K

Figure 2 showed the time course of methyl α-D-mannopyranoside hydrodeoxygenation over ReO_x-Pd/CeO_2 catalyst. The dideoxy product selectivity was maintained higher than 90 % and then decreased after 51 h due to the degradation the dideoxy product. The maximum yield reached 96 % at 51 h.

4. Conclusions

ReO_x, Pd and CeO_2 are essential for the high selectivity to dideoxy product with high activity on the hydrodeoxygenation of methyl α-D-mannopyranoside. The ReO_x-Pd/CeO_2 catalyst could selectively remove the *cis*-vicinal OH groups of methyl α-D-mannopyranoside and produced the dideoxy product in 96 % yield.

References

1. N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, Angew. Chem. Int. Ed. 54 (2015) 1897-1900.
2. N. Ota, M. Tamura, Y. Nakagawa, K. Okumura, K. Tomishige, ACS Catal. 6, (2016) 3213-3226.