Hydrogenolysis of glycerol to C_3 diols over $Pt/WO_3/Al_2O_3$ and Pd/*L*-Nb_2O_5

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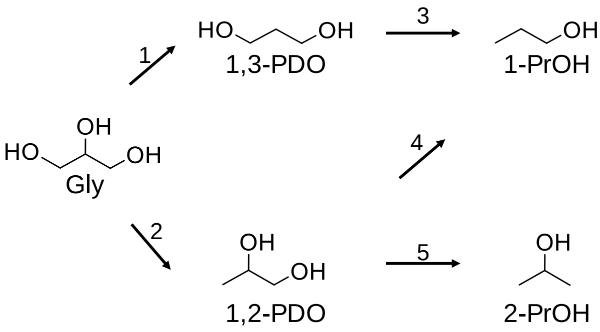
Highly efficient and selective transformations of glycerol (Gly) to valuable compounds such as 1,3- and 1,2-propanediol (PDO), using reusable heterogeneous catalysts are desired. Recently, we reported that 1,3- and 1,2-PDO were selectively formed by $Pt/WO_3/Al_2O_3$ with 7 wt% WO_3 loading [1] and Pd/layered Nb_2O_5 (*L*-Nb_2O_5) [2], respectively. In this work, hydrogenolysis of various diols and the competitive reaction between two kinds of alcohols over $Pt/WO_3/Al_2O_3$ and Pd/*L*-Nb_2O_5 catalysts were investigated.

$Pt/WO_3/Al_2O_3$ and Pd/*L*-Nb_2O_5 catalysts were prepared by the impregnation method. Hydrogenation of Gly was carried out in 50 mL autoclave at 453 K under 5 MPa H_2 for 15 h. The products were analyzed by FID-GC and TCD-GC.

Figure 1 shows the results of hydrogenolysis of various diols over $Pt/WO_3/Al_2O_3$ and Pd/*L*-Nb_2O_5. For $Pt/WO_3/Al_2O_3$, 1,2-PDO and EG, which have OH groups at 1,2-position, were selectively converted to 1-PrOH and EtOH, respectively. In contrast, Pd/*L*-Nb_2O_5 showed higher activity for hydrogenolysis of 1,3-PDO, which have OH groups at 1,3-position, than $Pt/WO_3/Al_2O_3$.

Furthermore the competitive reaction between two kinds of alcohols (molar ratio 1:1) was investigated. In the case of $Pt/WO_3/Al_2O_3$, competitive reaction of 1,3- and 1,2-PDOs showed that hydrogenolysis of 1,2-PDO to 1-PrOH (path 4 in Scheme 1) proceeded faster than path 3. On the other hand, on Pd/*L*-Nb_2O_5, the rate of hydrogenolysis of 1,3-PDO to 1-PrOH (path 3) was faster than path 2. The moderate yield of 1-PrOH on $Pt/WO_3/Al_2O_3$ in the hydrogenolysis of Gly can be explained by the stronger adsorption of 1,2-PDO compared with Pd/*L*-Nb_2O_5, and suggests that 1-PrOH was formed through the sequential hydrogenolysis of 1,2-PDO (path 2 and 4). On the other hand, the weak adsorption of 1,2-PDO on Pd/*L*-Nb_2O_5 compared with Gly and 1,3-PDO may inhibit the sequential hydrogenolysis of 1,2-PDO to 1-PrOH, resulting in a high selectivity to 1,2-PDO and 1-PrOH was formed from 1,3-PDO (path 1 and 3).



Scheme 1. Reaction path of glycerol hydrogenolysis.

On the basis of these results, we conclude that the adsorption structure of Gly and diols (1,3- and 1,2-PDOs) on WO_3/Al_2O_3 is different from that on *L*-Nb_2O_5, and strongly affects reaction rate and selectivity.

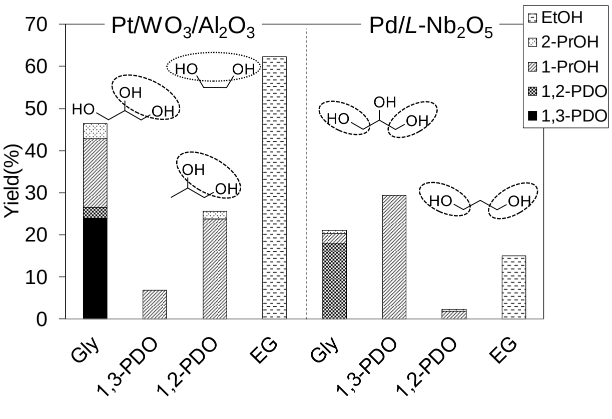


Fig.1. Regioselectivity of Hydrogenolysis.
Catalyst (100 mg), Substrate (3 mmol), H_2O (9mL), 453 K, H_2 (5 MPa), 15 h

REFERENCES

[1] H. Kobayashi, T. Aihara, H. Miura and T. Shishido, International Symposium on Catalytic Biomass Conversion 2016.

[2] T. Murayama, J. Chen, J.Hirata, K. Matsumoto, W. Ueda , Catal. Sci. Technol. 4 (2014) 4250.