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Synergistic Bimetallic Pd-Pt/TiO₂ Catalysts for Hydrogenolysis of Xylitol with In-Situ Formed H₂

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1. Introduction

Ethylene glycol (EG) and propylene glycol (PG) are widely used as value-added building blocks in various applications, such as antifreezes, solvents and pharmaceuticals. The global production of these glycols is currently based on petroleum-based olefins via epoxidation and dehydration technologies.^[1] Considering the diminishing supply of fossil fuels worldwide, conversion of bio-derived resources to industrial products is regarded to be a promising complementary process. Xylitol, which is obtained from hemicellulose biomass, could be hydrogenolysis into many types of renewables.^[2] At present, hydrogenolysis of xylitol is still conducted at relatively high hydrogen pressure (> 4 MPa). However, these harsh conditions caused considerable technological issues such as significant formation of less-valued CO₂ and CH₄, accelerated catalyst deactivation as well as high capital cost and energy consumption.^[3] Therefore, there demands alternative technologies which show both environmental and technological advantages over conventional ones.

In this work, we studied catalytic transfer hydrogenolysis (CTH) using *in-situ* formed H₂. A series of synergistic bifunctional Pd-based catalysts were designed for CTH of xylitol in aqueous medium. Based on experimental results, a selectivity of 41.1% to EG and 1,2-PDO was obtained over Pd-Pt/TiO₂ catalyst at 220 °C, 1.0 MPa N₂ atmosphere in absence of external H₂ with nearly 100% xylitol conversion. In our presentation, the structural properties including effect of particle size on catalytic activity and selectivity will be systematically studied, with the aim to establish structure-activity correlations for C-H/C-C/C-O cleavage of xylitol molecules. Moreover, the reaction pathways for CTH of xylitol will be qualitatively studied by analysis of substrate and intermediates at different experiment parameters.

2. Methods

Bimetallic Pd-Pt/TiO₂ catalysts were prepared *via* chemical reduction by deposition precipitation method.^[4] Bulk and surface characterization using ICP, XPS and TEM were employed to establish structure-performance correlations for CTH of xylitol on bimetallic Pd-Pt/TiO₂ catalysts. Activity tests were conducted in a 25 mL autoclave.^[5] The batch studies were carried out in the presence of N₂ atmosphere. After each study, the gas and liquid phase products were quantitatively assessed using GC (Scion GC-456) and Shimadzu HPLC (LC-20AT), equipped with both refractive index (RID-10A) and UV (SPD-20A) detectors.

3. Results and discussion

Among other bimetallic catalysts, it is found that bimetallic Pd-Pt/TiO₂ catalyst showed a superior CTH performance compared with other candidates under identical conditions (Figure 1(a)). In particular, combined selectivity of 41.1% to EG and 1,2-PDO was obtained on Pd-Pt/TiO₂ at 220 °C, 1.0 MPa after 6 h with almost complete conversion of xylitol.

We also found that activity and product distribution of xylitol conversion are strongly dependent on the size of Pd-Pt particles (Figure 1(b)), thus establishing structure-activity correlations for C-C, C-H and C-O cleavage of xylitol.

Based on experimental results, we proposed a plausible reaction network for CTH of xylitol over Pd-Pt/TiO₂ catalysts (Figure 2). Moreover, the reaction pathways for CTH of xylitol was qualitatively studied by analysis of substrate and intermediates at different experiment parameters. In particular, H₂ is generated from aqueous phase reforming of xylitol, while hydrogenolysis reaction of remaining substrate to glycols is realized with H₂ formed *in-situ* on catalyst surface.

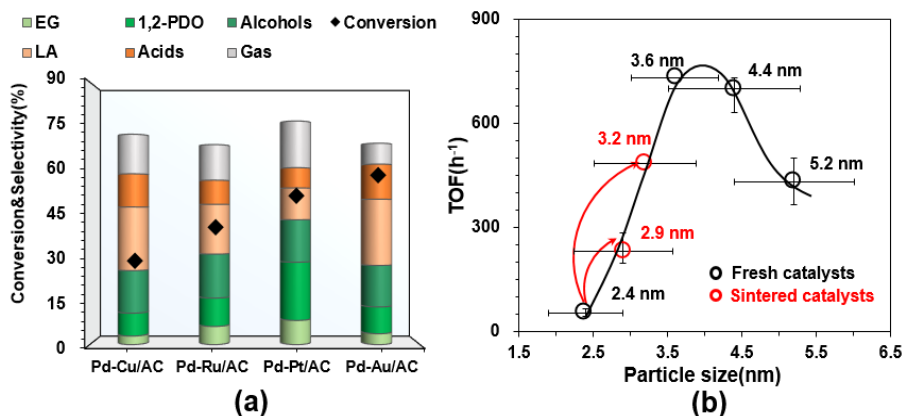


Figure 1. (a) Performance comparison of bimetallic Pd-based catalysts. (Temperature: 220 °C, P(N₂): 1 MPa, Reaction time: 6 h, Xylitol: 0.35 kmol/m³, Solvent: H₂O, Catalysts charge: 0.1 g, BaO/xylitol molar ratio: 1/8) (b) TOF-size trends for Pd-Pt/TiO₂ catalysts.

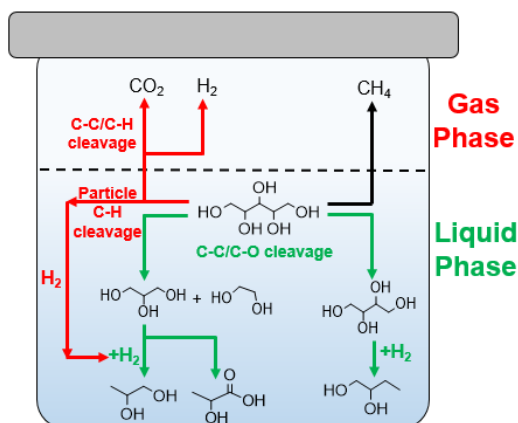


Figure 2. Proposed reaction pathways for transfer hydrogenolysis of xylitol

4. Conclusions

It is studied for the first time in literature that, catalytic transfer hydrogenolysis of xylitol can be achieved over synergistic Pd-Pt/TiO₂ catalysts. Experimental studies further confirmed that C-C, C-H and C-O cleavage of xylitol is strongly dependent on the size of bimetallic Pd-Pt nanoparticles.

References

- [1] Riviere, M, Perret, N, Delcroix, D, Cabiach, A, Pinel, C, Besson, M, Catalysts 2018, 8 (8).
- [2] Sun, J, Liu, H, Green Chem 2011, 13 (1), 135-142.
- [3] Jin, X, Thapa, P. S, Subramaniam, B, Chaudhari, R. V, Acs Sustain Chem Eng 2016, 4 (11), 6037-6047.
- [4] Murayama, T.; Haruta, M., Chinese J Catal 2016, 37 (10), 1694-1701
- [5] Li, S, Zan, Y, Sun, Y, Tan, Z, Miao, G, Kong, L. Z, Sun, Y, J Energy Chem 2019, 28, 101-106