**Heterogeneous Rhenium Catalysts supported on Ceria for Deoxydehydration of Polyols with Hydrogen**

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Chemical composition of the feedstock from biomass and biomass-based building blocks has much higher oxygen contents than that from crude oil. It has been known that the target products such as monomers for the polymer synthesis have comparatively lower oxygen content, and the reaction to decrease the oxygen content is important. It has been known that C3-C6 sugar alcohols (glycerol, erythritol, xylitol, and sorbitol) are regarded as promising building blocks in the biomass refinery, on the other hand, these compounds are over-functionalized. Therefore, the selective conversion is necessary to obtain appropriately functionalized compounds. A method is the selective C-O hydrogenolysis which demands the recognition of the target C-O bond among various kinds of C-O bonds. This enables the production of valuable chemicals such as diols, mono-ols, alkanes in high yield. ReOx-modified Ir metal catalyst (Ir-ReOx) is reported to be effective to the selective hydrogenolysis of polyols and cyclic ethers in water solvent as shown in Figure 1 [1]. The hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol proceeds over Ir-ReOx/SiO2 with high selectivity (Figure 1, [1]). In addition, the combination of Ir-ReOx/SiO2 with H-ZSM-5 gives *n*-alkanes and hexanols from cellulose, sugars, and sugar alcohols in high yield with the deep C-O hydrogenolysis and without C-C bond dissociation and skeletal isomerization (Figure 1, [1]). Ir-ReOx/SiO2 catalyzes the hydrogenolysis of glycerol to 1,3-propanediol with high selectivity (Figure 1 [1]). However, this Ir-ReOx/SiO2 was applied to the hydrogenolysis of erythritol, and the synthesis of the specific diol is much more difficult, and various kinds of products were co-produced [1]. The deoxydehydration is utilized for the selective conversion and we have developed the heterogeneous catalysts for the deoxydehydration reaction. Recently we found that ReOx-Pd/CeO2 showed excellent performance for simultaneous hydrodeoxygenation of vicinal OH groups in various substrates via deoxydehydration. High yield (>99%), turnover frequency, and turnover number were obtained in the reaction of 1,4-anhydroerythritol to tetrahydrofuran [2, 3]. This catalyst is also applicable to the conversion of sugar alcohols, and mono-alcohols and diols were obtained in high yields from substrates with even and odd numbers of OH groups, respectively [2]. In addition, ReOx-Au/CeO2 catalyzed the conversion of glycerol and erythritol to allyl alcohol and 1,3-butadiene in high yield (91% and 81%), respectively [4].

**Keywords:** biomass; sugar alcohol; cyclic ether; hydrogenolysis; hydrodeoxygenation; deoxydehydration.

**Reference**

[1] Tomishige, K.; Tamura, M.; Nakagawa, Y. *Chem. Rec.* 2014, 14, 1041-1054.

[2] Ota, N.; Tamura, M.; Nakagawa, K.; Okumura, K.; Tomishige, K. *Angew. Chem. Int. Ed.* 2015, 54, 1897-1900.

[3] Ota, N.; Tamura, M.; Nakagawa, K.; Okumura, K.; Tomishige, K. *ACS Catal.* 2016, 6, 3213-3226.

[4] Tazawa, S.; Ota, N.; Tamura, M.; Nakagawa, K.; Okumura, K.; Tomishige, K. *ACS Catal.* 2016, 6, 6393-6397

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