Co-catalysis of ReO_x-Au/CeO_2 and ReO_x/C in Hydrogenolysis of 1,4-Anhydroerythritol to 1,4-Butanediol

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Renewable biomass-based products are in increasing demand. However, as a chemical source, biomass contains higher oxygen content than fossil feedstocks. To deal with this drawback of biomass, the deoxydehydration (DODH) reaction would be a potential method to reduce the oxygen content in biomass products by removing vicinal diols in sugars simultaneously [1].

1,4-Anhydroerythritol can be produced by dehydration of erythritol which obtained from the fermentation of sugars. 1,4-Anhydroerythritol was able to be deoxygenated to 2,5-dihydrofuran and tetrahydrofuran in the DODH reaction over ceria-supported rhenium catalysts with gold and palladium promoters, respectively [2, 3]. In this study, we found that the physical mixture of ReO_x-Au/CeO_2 (Re = 1 wt %, Re/Au = 3 molar ratio) and carbon-supported rhenium (Re = 3%) catalysts showed high activity and good selectivity of 1,4-butanediol in the ring-opening reaction of 1,4-anhydroerythritol.

Various supported Re catalysts were tested for the co-catalysis with ReO_x-Au/CeO_2. Among them, the carbon black Black Pearls 2000 (BP2000), denoted as "C", was the best support to obtain 1,4-butanediol. Figure 1 showed the time course of ring-opening reaction of 1,4-anhydroerythritol over the mixture of ReO_x-Au/CeO_2 and ReO_x/C. The highest yield of 1,4-butanediol reached 82%, which is much higher than the existing report ($\leq$ 30%) [4].

In this co-catalyzed reaction, the ReO_x-Au/CeO_2 catalyst was in charge of the high conversion of 1,4-anhydroerythritol to dihydrofurans [2]. Meanwhile, the carbon-supported rhenium catalyst was probably responsible for the hydration of 2,3-dihydrofuran to 4-hydroxybutanal. Hydrogenation of 4-hydroxybutanal over either catalyst could give 1,4-butanediol (Scheme 1).

However, the activity of mixed ReO_x-Au/CeO_2 and ReO_x/C was decreased after usage. The reusability will be further investigated.

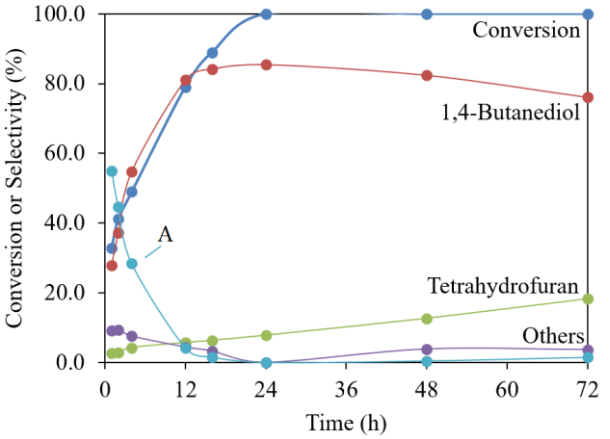
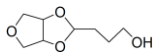
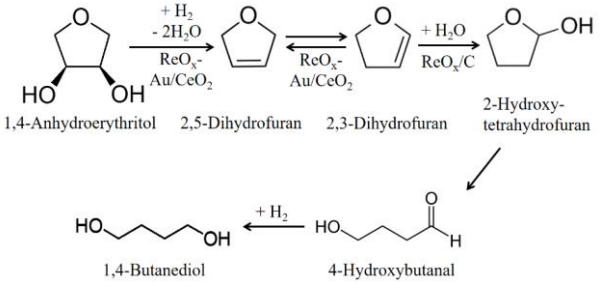


Fig. 1 Time course of the ring-opening reaction of 1,4-anhydroerythritol over the mixture of ReO_x-Au/CeO_2 and ReO_x/C. 1,4-Anhydroerythritol = 0.5 g, 1,4-dioxane = 4 g, $W_{cat.\ (ReO_x\text{-}Au/CeO_2)}$ = 0.15 g, $W_{cat.\ (ReO_x/C)}$ = 0.15 g, P_{H_2} = 8.0 MPa, T = 413 K. A: tentatively assigned as  .



Scheme. 1 Proposed reaction route from 1,4-anhydroerythritol to 1,4-butanediol over the mixture of ReO_x-Au/CeO_2 and ReO_x/C.

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