

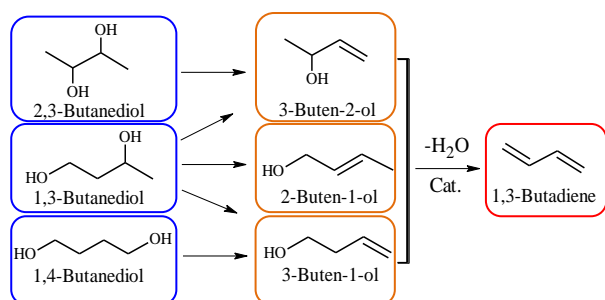
Efficient conversion of C4 unsaturated alcohols to 1,3-butadiene

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1,3-Butadiene (BD) is an important bulk chemical used for manufacturing rubber and polymers. Currently, BD is primarily produced as a by-product in ethylene plant through the naphtha steam cracking [1]. Because of the depletion of fossil resources, the production of BD from renewable biomass resources has attracted much attention. The catalytic conversion of bioethanol to BD is a well-known alternative route. On the other hand, butanediols such as 1,3-, 1,4- and 2,3-butenediol can be derivable from biomass by fermentation as well as catalytic conversion, and they also have potential as resources for producing biomass-derived BD.



Scheme.1 Production of 1,3-butadiene from butanediols via unsaturated alcohols.

Scheme 1 shows the expected production routes of BD from butanediols. It is obvious that the conversion of butanediols to BD requires two-step dehydration via unsaturated alcohols as intermediates. It was known that solid acids such as Al_2O_3 mainly convert 2,3-butenediol and 1,4-butenediol to 2-butanone and tetrahydrofuran, respectively [1], and convert 1,3-butenediol to a wide variety of products including 3-buten-1-ol, formaldehyde, and acetaldehyde [2,3]. The fact makes the direct conversion of butanediols to BD to be difficult. In contrast, we have found that rare earth metal oxides are effective for the selective dehydration of butanediols to

unsaturated alcohols [4]. Therefore, in this study, we focus on the second step, the dehydration of C4 unsaturated alcohols to BD.

The dehydration of unsaturated alcohols was performed in a fixed-bed down-flow glass reactor at a W/F of 0.34 in N_2 flow. Ordinary solid acid catalysts, such as Al_2O_3 , $SiO_2-Al_2O_3$, and TiO_2 , and rare earth metal oxides, such as Yb_2O_3 and CeO_2 , were tested in the dehydration of each unsaturated alcohol.

In the reaction of 3-buten-1-ol, the acid catalysts decomposed 3-buten-1-ol into propylene, therefore, BD could not be selectively produced. In contrast to the acid catalysts, CeO_2 inhibited the decomposition of 3-buten-1-ol, and gave a relatively high BD selectivity of 54.5% with 90% conversion at 400 °C. In the dehydration of 2-buten-1-ol and 3-buten-2-ol, however, acid catalysts were effective for the formation of BD. Among the tested catalysts, a commercial $SiO_2-Al_2O_3$ showed a relatively high catalytic performance, whereas it deactivated rapidly. We prepared a series of SiO_2/Al_2O_3 catalysts by depositing SiO_2 species onto Al_2O_3 support, and the SiO_2/Al_2O_3 with a SiO_2 content of 10 wt.% showed a more stable catalytic activity than the commercial $SiO_2-Al_2O_3$.

Furthermore, we tested metal-modified SiO_2/Al_2O_3 catalysts under H_2 flow conditions. The modification of SiO_2/Al_2O_3 by Ag with a loading of 3-5 wt.% was found to be efficient for inhibiting the coke formation as well as improving the catalytic stability of SiO_2/Al_2O_3 , and BD yields higher than 90% were achieved in the dehydration of both 2-buten-1-ol and 3-buten-2-ol at 260 °C. The loading of Ag on SiO_2/Al_2O_3 reduced the acid strength, which contributed to the stable activity of Ag-modified SiO_2/Al_2O_3 . It is concluded that the additive Ag would work at a metal state during the reaction, and inhibited the catalytic deactivation together with H_2 .

REFERENCES

- [1] H. Duan, Y. Yamada and S. Sato, *Chem. Lett.*, 45 (2016) 1036.
- [2] S. Sato, R. Takahashi, T. Sodesawa, N. Honda and H. Shimizu, *Catal. Commun.*, 4 (2003) 77.
- [3] D. Sun, S. Arai, H. Duan, Y. Yamada and S. Sato, *Appl. Catal. A: Gen.*, 531 (2017) 21.
- [4] S. Sato, F. Sato, H. Gotoh and Y. Yamada, *ACS Catal.*, 3 (2013) 721.