Efficient production of 1,3-butadiene in the dehydration of 1,4-butanediol over rare earth oxides

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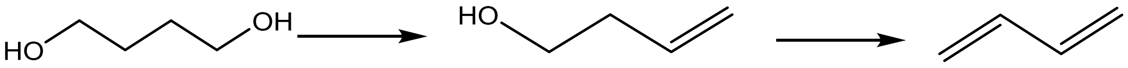
Abstract: Vapor-phase dehydration of 3-buten-1-ol and 1,4-butanediol to produce 1,3-butadiene was investigated over rare earth oxides, such as Yb_2O_3 and Er_2O_3. In the dehydration of 3-buten-1-ol, rare earth oxides showed high catalytic performance for the selective formation of 1,3-butadiene with small amount of propylene whereas acidic catalysts decomposed 3-buten-1-ol into propylene. In particular, 3-buten-1-ol was converted with a yield of 1,3-butadiene higher than 95% at 340°C over Yb_2O_3. In the dehydration of 1,4-butanediol, 1,3-butadiene was produced via an intermediate, 3-buten-1-ol, over Yb_2O_3 with an excellent yield of 96.6% at 360°C and a high contact time of 2.26 h.

Keywords: Dehydration of 1,4-butanediol, 1,3-Butadiene, 3-Buten-1-ol.

1. Introduction

To reduce the emission of carbon dioxide and other greenhouse gases resulted from human activity, biomass resources have been expected as an alternative to fossil fuels. In recent years, there is a growing worldwide interest in 1,3-butadiene (BD) as a platform chemical for producing a diversity of synthetic rubbers, elastomers and polymeric resins[1]. Recently, several butanediols are mostly reported to produce BD through a direct and a stepwise dehydration route because butanediols are the potential resources derived from renewable and waste feedstocks[2]. In our previous works, we have investigated a series of catalytic reaction of butanediols to BD including both the first step dehydration of butanediols to unsaturated alcohols (UOLs)[3, 4] and the second step dehydration of UOLs to BD[3,5]. It has been found that acid catalysts are effective for the production of BD from 3-buten-2-ol (3B2OL) and 2-buten-1-ol (2B1OL), and that a SiO_2-Al_2O_3 shows a high catalytic performance[5]. In the dehydration of 3-buten-1-ol (3B1OL), however, acid catalysts primarily transform 3B1OL into propylene through the C-C bond cleavage. In this work, to develop an efficient catalytic system for the production of BD from 1,4-butanediol (1,4-BDO), vapor-phase catalytic dehydration of 3B1OL was conducted over the rare earth oxide catalysts under different conditions, and the optimal catalytic conditions were investigated over Er_2O_3 and Yb_2O_3. Furthermore, the direct production of BD from 1,4-BDO over Yb_2O_3 was studied under the appropriate catalytic conditions obtained from the results of 3B1OL dehydration.



1,4-butanediol 3-buten-1-ol 1,3-butadiene

Scheme 1 Dehydration of 1,4-butanediol.

2. Experimental

The dehydration of UOLs as well as 1,4-BDO was performed in a fixed-bed down-flow glass reactor at an ambient pressure of N_2. Prior to the catalytic reaction, the catalyst was placed in the catalyst bed of the reactor and heated at the reaction temperature for 1 h. Then, a liquid reactant was fed at a flow rate of 1.75 $cm^3\ h^{-1}$, which is 1.47 $g\ h^{-1}$ for 3B1OL and 2B1OL; 1.77 $g\ h^{-1}$ for 1,4-BDO, together with an N_2 flow of 30 $cm^3\ min^{-1}$. The liquid effluents collected in an ice-water trap every hour were analyzed by an FID-GC (GC-2014, Shimadzu) with a 30-m capillary column of TC-WAX (GL-Science, Japan). The gaseous products were analyzed by an on-line gas chromatography (GC-8A, Shimadzu, Japan) with a 6-m packed column (VZ-7, GL-Science, Japan).

3. Results and discussion

Fig. 1 shows the changes in the selectivity with the 3B1OL conversion over Er_2O_3 and Yb_2O_3 at 360°C. The selectivity to BD increased with increasing the conversion of 3B1OL, while the selectivity to 2B1OL decreased. The positive influence of contact time indicates higher catalytic performance could be obtained by adjusting contact time. Hence, in an additional test, it was found that the higher BD selectivity of 96.7% was achieved over Yb_2O_3 at 99.6% conversion, a low temperature of 340°C, and W/F = 2.72 h, where W and F are the catalyst weight (g) and the feed rate of reactant (g h^{-1}), respectively. It is supposed that 2B1OL would be an immediate in the conversion of 3B1OL to BD, which means the mechanism of the dehydration of 3B1OL should be more complex than that supposed in the previous report[5]. Thus, we propose that the overall reaction routes consist of two main routes, a direct dehydration of 3B1OL to BD and a two-step dehydration, 3B1OL is isomerized into 2B1OL and then 2B1OL is further dehydrated into BD.

Fig. 2 shows the changes in the conversion of 1,4-BDO and the selectivity to each product over Yb_2O_3 at 360°C with W/F. The conversion of 1,4-BDO and the selectivity to BD increased with increasing W/F. The selectivity to 3B1OL was dramatically decreased along with monotonical increase in the selectivity to BD. The selectivity to 2B1OL was firstly increased with increasing the W/F, and then decreased at high W/F. The variation in the formation of 2B1OL indicates that 2B1OL is an intermediate to produce BD. The consumption of 3B1OL and the formation of BD infer that the formed 3B1OL was dehydrated into BD at high W/F in the dehydration of 1,4-BDO.

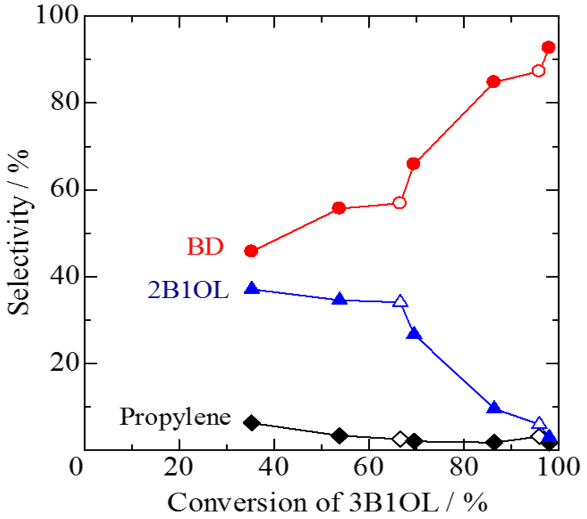


Fig. 1 Changes in selectivity with 3B1OL conversion in the dehydration of 3B1OL over Er_2O_3 (closed symbol) and Yb_2O_3 (open symbol) at 360 °C.

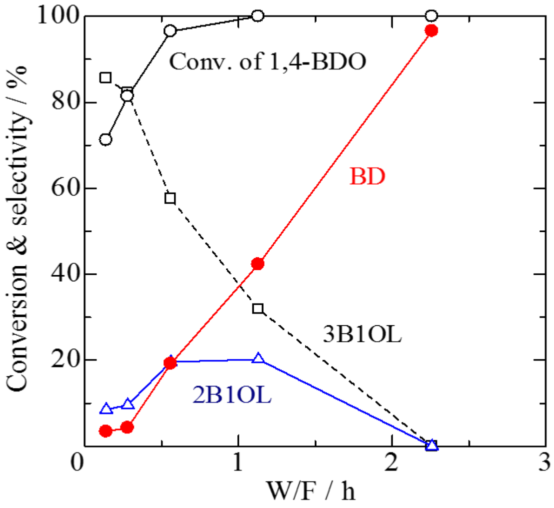


Fig. 2 Changes in conversion of 1,4-BDO and selectivity to BD and typical by-products in the dehydration of 1,4-BDO over Yb_2O_3 with W/F at 360°C.

4. Conclusions

Vapor-phase dehydration of 3B1OL to produce BD was investigated over REOs. In the dehydration of 3B1OL, an excellent catalytic performance with 99.6% conversion and a BD selectivity of 96.7% was obtained over Yb_2O_3 at 340°C and a W/F of 2.72 h. Vapor-phase dehydration of 1,4-BDO to produce BD was also investigated over Yb_2O_3. We successfully developed the direct BD production from 1,4-BDO with a yield of 96.6% over Yb_2O_3 at 360°C and a W/F of 2.26 h.

References

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