Vapor-phase catalytic dehydration of butanediols to unsaturated alcohols over yttria-stabilized zirconia catalysts

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Abstract: Vapor-phase catalytic dehydration of butanediols (BDOs) was investigated over yttria-stabilized zirconia (YSZ) catalysts. BDOs were converted to unsaturated alcohols (UOLs) with some by-products. It is suggested that YSZ is superior to monoclinic zirconia (MZ) in these reactions. Calcination temperature of YSZ greatly affected the selectivity to products: high selectivity to UOLs was obtained at high calcination temperatures. Conversion of BDO was also affected by calcination temperature. In the dehydration of 1,3-butanediol, the UOLs selectivity exceeded 95% over YSZ calcined at 900°C. In the conversion of 1,4-butanediol, the highest 3-buten-1ol selectivity of 75.3% was obtained over YSZ calcined at 1050°C.

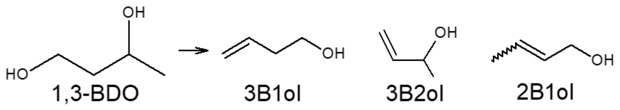
Keywords: Yttria-stabilized zirconia, Butanediol, Dehydration

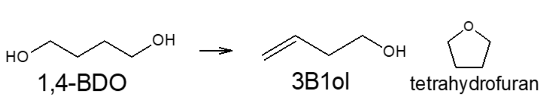
1. Introduction

Pure zirconia exhibits three polymorphs, monoclinic, tetragonal, and cubic phases[1]. The monoclinic, tetragonal, and cubic phases are thermodynamically stable at <1170°C, 1170-2370°C, and 2370°C-2680°C (melting point), respectively. These high temperatures of tetragonal and cubic phases cannot be retained upon rapid cooling to room temperature, resulting in a dislocation to monoclinic phase[2]. However, the tetragonal and cubic phases can be stabilized at room temperature by the addition of appropriate aliovalent cations, such as Y^{3+}, Sc^{3+}, La^{3+}, Ca^{2+}, and so on[3]. UOLs such as 3-buten-1-ol (3B1ol), 2-buten-1-ol (2B1ol), and 3-buten-2-ol (3B2ol) are valuable intermediates for the synthesis of medical drugs, agricultural chemicals and function polymers[4,5]. We have found that C4 UOLs can be synthesized from BDO derived from biomass over modified ZrO_2 catalysts[6,7]. In these works, it is suggested that crystalline phase of ZrO_2 catalyst is important for these reactions. However, types of effective crystalline phase for these reactions are not investigated specifically. In this paper, we examined the types of effective crystalline phase for these reactions, and found that YSZ had interesting features as catalysts and catalysis supports on these reactions.

2. Experimental

The reaction was carried out in a fixed-bed flow reactor under atmospheric pressure of N_2 carrier gas with a flow rate of 30 cm^3 min^{-1} at 325°C. A catalyst of 0.5 g was placed in the reactor. After the catalyst had been heated at the prescribed reaction temperature for 1 h, a reactant, either 1,3-BDO or 1,4-BDO, was fed into the reactor at a liquid feed rate of 1.60 g h^{-1}. The liquid effluent collected in a dry ice-acetone trap every hour was analyzed by gas chromatography (FID-GC-8A, Shimadzu, Japan) with a 30-m capillary column (InertCapWAX-HT) and identified by gas chromatography-mass spectrometry (GCMS-QP5050A, Shimadzu, Japan) with a 30-m capillary column (DB-WAX).





3. Results and discussion

In this work, YSZ catalysts as well as MZ catalysts were calcined at various temperatures. The catalysts were tested at 325°C. In the dehydration of 1,3-BDO, the conversion of 1,3-BDO and the selectivity to UOLs changed with the variation of calcination temperature, as shown in **Fig. 1**. It is suggested that, as a catalyst for this reaction, YSZ is superior to MZ. It is noted that calcination temperatures of at lowest 850°C would be needed to construct the active centers on the YSZ. At a calcination temperature higher than 850°C, however, the conversion of 1,3-BDO decreased with increasing the calcination temperature of YSZ because of decrease in the specific surface area. High selectivity to UOLs of 95.5% at the 1,3-BDO conversion of 54.0% was obtained at over YSZ calcined at 900°C.

In a similar manner, in the dehydration of 1,4-BDO, the conversion of 1,4-BDO and selectivity to 3B1ol changed with the variation of calcination temperature, as shown in **Fig. 2**. The selectivity to 3B1ol increased with increasing the calcination temperature. The conversion of 1,4-BDO decreased with increasing the calcination temperature, due to the decrease of specific surface area. The high selectivity to 3B1ol of 75.3% at the 1,4-BDO conversion of 26.1% was obtained over YSZ calcined at 1050°C. On the other hand, the highest selectivity to 3B1ol over MZ catalysts was 38.9% at the 1,4-BDO conversion of 77.5%. This indicates that, as a catalyst for this reaction, YSZ is better than MZ. In our previous work, high selectivity to 3B1ol of 89% at the 1,4-BDO conversion of 68% was obtained over CaO/MZ[6]. Therefore, it is suggested that YSZ is promising as a catalyst support.

For the dehydration of 1,5-pentanediol (1,5-PDO) and 2,3-butanediol (2,3-BDO), however, MZ is superior to YSZ. Selectivity to UOLs was not affected by the calcination temperature of YSZ. We reveal that depending on the position of OH group on BDOs, effective crystallite phase of ZrO_2 is different. This indicates that the mechanism of the dehydration of 1,5-PDO and 2,3-BDO are different from those of 1,3- and 1,4-BDO.

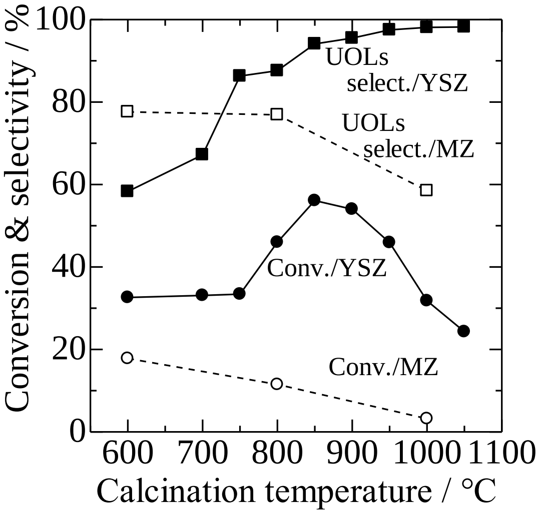


Figure 1. Dehydration of 1,3-BDO over YSZ catalysts calcined at different temperature (325℃)

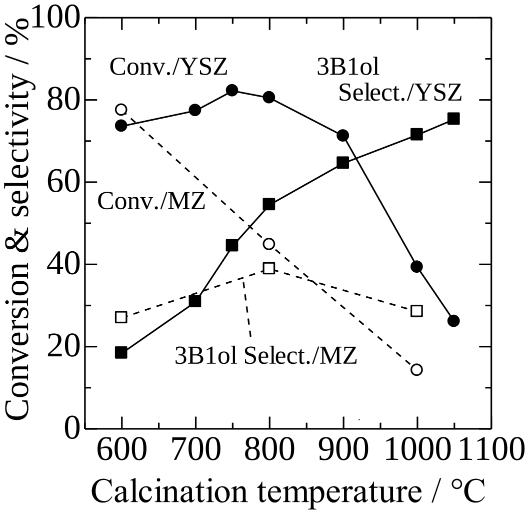


Figure 2. Dehydration of 1,4-BDO over YSZ catalysts calcined at different temperature (325℃)

4. Conclusions

Vapor-phase catalytic dehydration of BDOs was investigated over YSZ catalysts as well as MZ. It is suggested that, as a catalyst for the dehydration of 1,3-BDO and 1,4-BDO, YSZ is superior to MZ. In these reactions, the crystalline phase of zirconia is important for the activity of catalyst. Products selectivity and reactant conversion depended on the calcination temperature of YSZ. In the dehydration of 1,3-BDO at 325°C, the UOLs selectivity exceeded 95% at the 1,3-BDO conversion of 54.0% over YSZ calcined at 900°C. In the dehydration of 1,4-BDO at 325°C, the best selectivity to 3B1ol of 75.3% at the 1,4-BDO conversion of 26.1% was obtained over YSZ calcined at 1050°C.

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