Dehydration of 1,3-butanediol over Yb-Zr oxide catalysts

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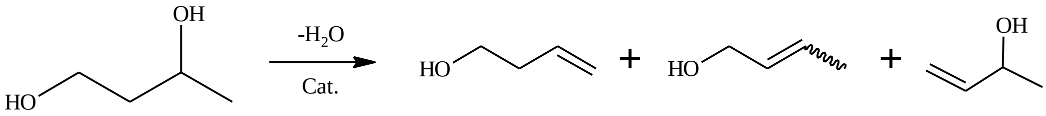
Abstract: Vapor-phase dehydration of 1,3-butanediol was performed over Yb-Zr oxide catalyst in an ambient nitrogen atmosphere. Catalysts were prepared by hydrothermal synthesis and coprecipitation methods. The sample prepared by coprecipitation was amorphous before calcination, while the sample prepared by hydrothermal synthesis was crystalline of cubic $Yb_{0.5}Zr_{0.5}O_{1.75}$ with high specific surface area. The best catalytic performance was obtained over hydrothermally synthesized Yb-Zr oxide catalyst: the selectivity to unsaturated alcohols was higher than 95% at a conversion of 82% at 325°C.

Keywords: Hydrothermal synthesis, 1,3-Butanediol, Unsaturated alcohols.

1. Introduction

Unsaturated alcohols are industrially important chemicals as starting materials of perfumes, medical drugs, agricultural chemicals, and polymers. It has been reported that CeO_2 catalyzes the dehydration of 1,3-diols into unsaturated alcohols[1], and pure Yb_2O_3 and Yb_2O_3 supported on monoclinic ZrO_2 are effective for the formation of 3-buten-1-ol from 1,4-butanediol[2]. It is also known that the selectivity to the products varies depending on the crystal structure[3]. In this study, we investigated the crystal structures of Yb-Zr oxide (Yb-Zr-O) prepared by hydrothermal synthesis (HTS) and coprecipitation (CP), and their catalytic activities in the vapor-phase reaction of 1,3-butanediol.



Scheme 1. Dehydration of 1,3-butanediol.

2. Experimental

Ytterbium(III) nitrate pentahydrate was purchased from Sigma-Aldrich Co. LLC. 1,3-Butanediol, zirconyl nitrate dihydrate and 10% ammonia solution, were purchased from Wako Pure Chemical Industries, Ltd. Equimolar $Yb(NO_3)_3 \cdot 5H_2O$ and $ZrO(NO_3)_2 \cdot 2H_2O$ were dissolved in 30 mL of distilled water. Then, the pH of the solution was adjusted to 10 with 10 wt% aqueous ammonia while stirring. The solution was transferred into a 100 cm^3 Teflon-lined pressured vessel. HTS treatment was carried out at 200°C for 24 h. The resulting precipitation was filtered, then washed, and dried at 110°C for 18 h, and finally calcined at a prescribed temperature for 3 h to obtain a Yb-Zr-O sample. The catalytic reaction of 1,3-butanediol was performed in a fix-bed flow reactor at ambient N_2 pressure. Prior to the reaction, a catalyst sample, 0.5 g, was preheated in the N_2 flow at 325°C for 1 h. 1,3-Butanediol was fed into the reactor at 325°C and a feed rate of 1.47 g h^{-1} together with an N_2 flow of 30 cm^3 min^{-1}. The reaction mixture recovered in a dry ice-acetone trap every hour was analyzed by a FID-GC (GC-8A, Shimadzu) with a 30-m capillary column (GL Science, Japan). A GCMS (QP5050A, Shimadzu) was used for identification of the products in the effluent.

3. Results and discussion

Figure 1 depicts XRD patterns of HTS and CP Yb-Zr-O catalysts used in this study. The uncalcined sample prepared by CP was amorphous, but the HTS samples were crystalline even when they were not calcined. HTS catalyst calcined at 800°C had a cubic $Yb_{0.5}Zr_{0.5}O_{1.75}$ structure with high crystallinity. Table 1 shows typical conversion and selectivity data in the dehydration of 1,3-butanediol at 325°C over HTS Yb-

Zr-O catalysts calcined at temperatures between 400 and 1000°C. The selectivities to unsaturated alcohols (UOLs) such as 3-buten-2-ol and 2-buten-1-ol increased with increasing calcination temperature, whereas the selectivities to 3-buten-1-ol and the oxidized products such as methylethylketone and methylvinylketone, decreased. In contrast, the catalytic reaction hardly proceeded over the CP Yb-Zr-O catalysts (Table 2). It is considered that the low activity of CP catalysts is caused by the small specific surface area. The catalytic activity of HTS catalysts was greatly increased by calcination temperatures. The formation rate of UOLs over HST Yb-Zr-oxide at 325°C was 231 g h^{-1} g_{-cat}^{-1}, while CeO_2 and Lu_2O_3 showed high catalytic activity: 445 for CeO_2[1] and 181 g h^{-1} g_{-cat}^{-1} for Lu_2O_3[3]. Although the activity of HTS did not reach that of CeO_2, it was the second-best activity among the catalysts that have reported in the past.

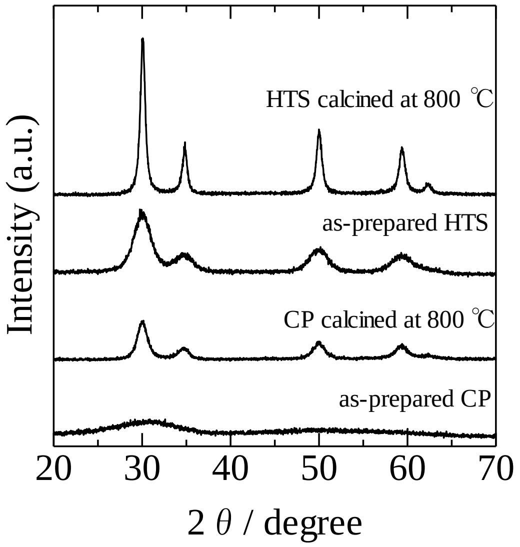


Figure 1. XRD patterns of Yb-Zr-O samples.

Table 1. Effect of calcination temperature of HTS catalysts at 325°C.

Calcination Temperature	SA (m²/g)	Conversion (mol%)	Selectivity (mol%)							
			3B1ol	3B2ol	trans-2B1ol	cis-2B1ol	sub total	MVK	MEK	others
as-prepared	141.4	62.2	2.4	39.8	23.8	4.3	70.3	6.5	14.2	9.0
400	127.8	64.4	2.3	41.3	24.8	4.4	72.8	6.1	13.7	7.4
600	93.6	81.2	2.1	45.5	29.6	5.4	82.6	4.0	8.5	4.9
800	48.9	74.3	1.6	52.9	33.4	6.3	94.2	1.8	2.3	1.7
900	40.6	82.7	1.0	52.6	35.8	6.0	95.4	1.3	2.0	1.3
1000	34.0	69.8	0.9	53.3	35.1	6.7	96.0	1.4	1.8	0.8

Catalyst weight, 0.5 g. Averaged conversion and selectivity between 0 h to 5 h. sub total = 3B1ol + 3B2ol + 2B1ol.
3B1ol, 3-butene-1-ol; 3B2ol, 3-butene-2-ol; 2B1ol, 2-butene-1-ol; MVK, methylvinylketone; MEK, methylethylketone.
SA: Specific surface area calculated by BET method.

Table 2. Effect of calcination temperature of CP catalysts at 325°C.

Calcination Temperature	SA (m²/g)	Conversion (mol%)	Selectivity (mol%)							
			3B1ol	3B2ol	trans-2B1ol	cis-2B1ol	sub total	MVK	MEK	others
as-prepared	30.9	2.6	0	8.2	1.0	0	9.2	35.3	6.9	48.6
400	6.3	1.1	1.7	44.7	33.2	1.9	81.5	14.1	0	4.4
600	—	1.9	2.8	42.2	32.8	6.8	84.6	4.8	0	10.6
800	—	<1	—	—	—	—	—	—	—	—
800*	—	33.9	1.9	50.3	36.6	6.7	95.5	1.3	1.2	2.0
1000	—	<1	—	—	—	—	—	—	—	—

Catalyst weight, 0.5 g. *Catalyst weight, 5.0 g. Averaged conversion and selectivity between 0 h to 5 h. sub total = 3B1ol + 3B2ol + 2B1ol.
3B1ol, 3-butene-1-ol; 3B2ol, 3-butene-2-ol; 2B1ol, 2-butene-1-ol; MVK, methylvinylketone; MEK, methylethylketone.
SA: Specific surface area calculated by BET method.

4. Conclusions

The vapor-phase conversion of 1,3-butanediol to produce unsaturated alcohols such as 3-buten-2-ol and 2-buten-1-ol was investigated over cubic $Yb_{0.5}Zr_{0.5}O_{1.75}$ catalysts prepared by hydrothermal synthesis and coprecipitation. The catalyst prepared by hydrothermal synthesis was crystalline even when it was not calcined, and the yield of unsaturated alcohol exceeded 79% over the catalyst calcined at 900°C.

References

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