Vapor-phase catalytic dehydration of 3-methyl-1,3-butanediol to unsaturated alcohols over ZrO_2 modified with calcium oxide

Kento Kurita, Yasuhiro Yamada, Satoshi Sato*
Graduate School of Engineering, Chiba University, Chiba, 263-8522, Japan
**Corresponding author: +81 43 2903376, satoshi@faculty.chiba-u.jp*

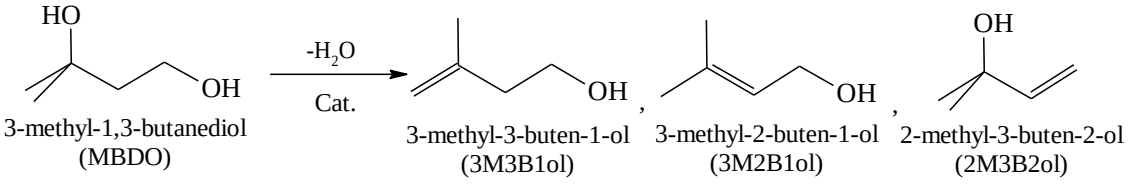
Abstract: Vapor-phase catalytic dehydration of 3-methyl-1,3-butanediol (MBDO) to unsaturated alcohols (UOLs) was investigated over CeO_2, ZrO_2, and several ZrO_2 catalysts modified with alkaline earth metal oxides, such as MgO, CaO, SrO, and BaO. It was found that only the ZrO_2 catalyst modified with CaO enhanced both of the conversion of MBDO and total selectivity to unsaturated alcohols. The best performance was obtained over 15mol% CaO/ZrO_2 catalyst calcinated at 800 °C: the total selectivity to unsaturated alcohols was 93% at a conversion of 94% at a weight hourly space velocity, WHSV of 0.57 h^{-1} and 300°C.
Keywords: 3-Methyl-1,3-butanediol, Tetragonal ZrO_2, Calcium oxide

1. Introduction

UOLs are important chemicals in chemical industry. UOLs are used as intermediate chemicals of medical drugs, agrichemicals, and perfume. Generally, UOLs can be made in the hydrogenation of unsaturated aldehydes. In this study, we highlighted MBDO. Previous work reveals that dehydration of MBDO with CeO_2 produces 3M2B1ol and 2M3B2ol (Scheme 1), the selectivity was 56.8% and 24.7%, respectively[1]. Another study indicates, with coke deposition on the Al_2O_3 catalyst, 3M3B1ol is generated with 83% of selectivity[2]. 3M3B1ol, one of the products of MBDO dehydration, is generated from isobutene and formaldehyde with $SnCl_4$[3].

Isoprene is an important raw material for various synthetic polymers and rubbers. Most of polyisoprene is used in the rubber industries. Copolymers of isoprene are also used as elastomers such as footwear, mechanical parts, medical supplies and latexes. Isoprene can be obtained by fractional distillation of petroleum. However, purification of isoprene is expensive because isoprene is obtained only about 15% in hydrocarbon C5 stream of petroleum cracking. All of the UOLs produced in this study can produce isoprene in further dehydration.

In this work, we investigated this reaction over several oxides such as CeO_2, ZrO_2 and ZrO_2 modified with alkaline earth oxides for the purpose of producing UOLs from MBDO.



Scheme 1 Dehydration of MBDO to produce UOLs.

2. Experimental

CaO/ZrO_2 catalysts were prepared by impregnation method and calcined at 800°C for 3 h. Calcium nitrate was used as the precursor of CaO. The catalytic reaction was performed in a fix-bed flow glass reactor at ambient N_2 pressure. After the catalyst had been heated at the reaction temperature for 30 min, MBDO was fed into the reactor and feed rate of 1.7 g h^{-1} together with 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 of Inert Cap WAX-HT (GL Science, Japan). A GCMS (QP5050A, Shimadzu, Japan) was used for identification of the products in the effluent.

3. Results and discussion

Several ZrO_2 catalysts modified with alkaline earth metal oxides were tested in the catalytic reaction of MBDO (Table 1). Although MgO/ZrO_2 catalyst and SrO/ZrO_2 catalyst raised the selectivity to UOLs, only the CaO/ZrO_2 catalyst exceeded the original ZrO_2 catalyst in terms of both the MBDO conversion and selectivity to UOLs. Modification of CaO shifted the main product from 3M3B1ol to 3M2B1ol and 2M3B2ol.

Table 1. Dehydration of 3-methyl-1,3-butanediol over ZrO_2 modified with various alkaline-earth oxides.

Catalysts	Conversion	Selectivity(mol%)								
	(mol%)	2M3B2ol	3M3B1ol	3M2B1ol	sum of UOLs	isobutene	isoprene	acetone	3M2BEA	others
ZrO_2	63.5	19.4	41.1	29.6	90.1	2.6	0.3	5.7	0.5	0.8
7 mol% MgO/ZrO_2	40.0	30.4	29.7	35.7	95.8	1.7	0.1	1.7	0.3	0.4
7 mol% CaO/ZrO_2	74.6	39.8	16.2	39.7	95.7	1.5	0.5	1.6	0.3	0.6
7 mol% SrO/ZrO_2	34.8	24.2	38.7	30.2	93.1	2.9	0.0	2.9	0.4	0.6
7 mol% BaO/ZrO_2	16.2	15.1	46.8	22.7	84.7	4.7	0.0	9.2	0.6	0.8

Average conversion and selectivity between 1-5 h; catalyst weight 0.5 g; N_2 flow rate 30 cm^3 min^{-1}; reaction temp. 325℃ ; calcinatinon temp. 800℃

The dehydration of MBDO was carried out using several catalysts with different CaO loading amounts (Fig. 1). 15 mol% CaO/ZrO_2 showed the best performance with the conversion of MBDO reached 80.5%. Fig. 1 also indicates the transition of the product selectivity: the selectivity of 2M3B2ol increased whereas its 3M3B1ol decreased with increase in the amount of CaO. This tendency was observed up to a CaO loading of 15 mol%, and the conversion came down with decreasing surface area. MBDO conversion decreased as the WHSV decreased and the maximum conversion, 94.6%, was obtained at WHSV=0.57 h^{-1}.

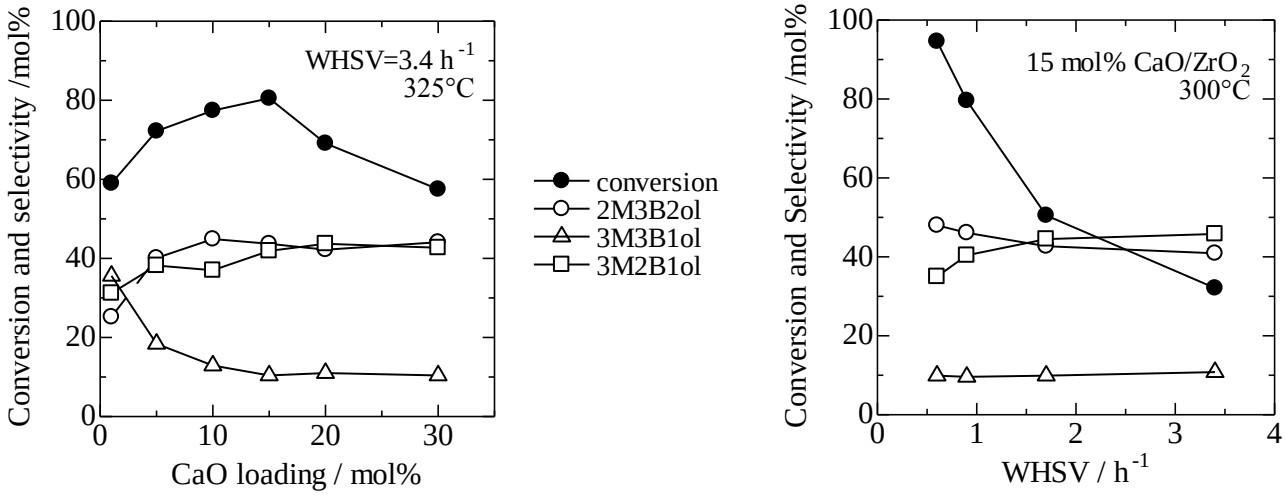


Figure 1 Changes in catalytic activity of CaO/ZrO_2 with CaO loading (right) and WHSV (left).

4. Conclusions

Vapor-phase catalytic dehydration of MBDO to UOLs was investigated over ZrO_2 catalysts modified with alkaline earth metal oxides, such as MgO, CaO, SrO, and BaO. Only the CaO/ZrO_2 enhanced the activity of MBDO dehydration and raised the unsaturated alcohol selectivity. At a WHSV of 0.57 h^{-1} and 300°C, MBDO conversion reached 94% and total selectivity to UOLs reached 93% with 15 mol% CaO/ZrO_2 catalyst.

References

1. S. Sato, R. Takahashi, T. Sodesawa, N. Honda, J. Mol. Catal. A: Chem. 221 (2004) 177-183.
2. Y. Morino, Y. Yamada, S. Sato, Appl. Catal. A: Gen. 475 (2014) 147-154.
3. S. Sato, F. Sato, H. Gotoh, Y. Yamada, ACS Catal. 3 (2013) 721-734.