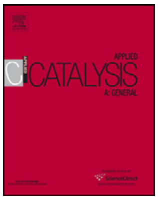
Applied Catalysis A: General 352 (2009) 66–73

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Dehydration of 1,4-butanediol over supported rare earth oxide catalysts

Hirotomo Inoue [a], Satoshi Sato [a,*], Ryoji Takahashi [a,b], Yusuke Izawa [c], Hironobu Ohno [c,d], Kazunari Takahashi [c]

[a] *Department of Applied Chemistry and Biotechnology, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan*
[b] *Graduate School of Science and Engineering, Ehime University, Bunkyo, Matsuyama 790-8577, Japan*
[c] *Petrochemicals Research Center, Mitsubishi Chemical Co., Ushiodori, Kurashiki, Okayama 712-8054, Japan*
[d] *Mitsubishi Chemical Group Science and Technology Research Center, Inc., Kamoshida, Aoba, Yokohama 227-8502, Japan*

ARTICLE INFO

Article history:
Received 25 May 2008
Received in revised form 28 September 2008
Accepted 29 September 2008
Available online 17 October 2008

Keywords:
Homoallyl alcohol
3-Buten-1-ol
1,4-Butanediol
Dehydration
Rare earth oxide
Yb_2O_3
Supported catalyst
ZrO_2

ABSTRACT

Vapor-phase catalytic dehydration of 1,4-butanediol was investigated over rare earth oxides supported on ZrO_2. In the dehydration of 1,4-butanediol, 3-buten-1-ol was mainly produced, together with tetrahydrofuran (THF) and γ-butyrolactone. The heavy group of rare earth oxides, such as Dy_2O_3, Ho_2O_3, Er_2O_3, Tm_2O_3, Yb_2O_3, and Lu_2O_3, supported on monoclinic ZrO_2 showed higher selectivity to 3-buten-1-ol than pure monoclinic ZrO_2 and supported light rare earth oxides, such as La_2O_3 and Pr_6O_{11}. Supported Yb_2O_3 catalysts dispersed on other oxides, such as alumina, silica, and tetragonal ZrO_2 catalyze the formation of THF. X-ray diffraction (XRD) measurements reveal that cubic Yb_2O_3 crystallites dispersed on monoclinic ZrO_2 provide active sites in the dehydration of 1,4-butanediol to produce 3-buten-1-ol.

1. Introduction

Unsaturated alcohols such as allylic and homoallylic alcohols are important chemicals as resources of aroma chemicals, medical drugs, agricultural chemicals and polymers. We have previously reported that CeO_2 catalyzes the dehydration of 1,3-diols into unsaturated alcohols [1–4]: 3-buten-2-ol and *trans*-2-buten-1-ol are produced from 1,3-buanediol at 325 °C with the selectivities of 57 and 36 mol%, respectively [1]. CeO_2 also catalyzes the dehydration of 1,4-butanediol into 3-buten-1-ol at 375–425 °C [2,4,5]: 3-buten-1-ol is produced with a maximum selectivity of 68 mol% at 400 °C [5]. Side reactions such as isomerization, dehydrogenation, hydrogenation and further dehydration of 3-buten-1-ol to produce 2-buten-1-ol, 2-butenal, 1-butanol, and 1,3-butadiene, respectively, and the cyclization of 1,4-butanediol into tetrahydrofuran (THF) and γ-butyrolactone (GBL) reduce the selectivity to 3-buten-1-ol at any temperature.

We have also found that ZrO_2 with monoclinic structure catalyzes the dehydration of 1,4-butanediol to produce 3-buten-1-ol together with THF at 300–375 °C [6,7]. The step-wise reactions, such as isomerization, dehydrogenation, hydrogenation, and further dehydration of 3-buten-1-ol, are completely suppressed over monoclinic ZrO_2 at a low temperature of 325 °C. In the formation of 3-buten-1-ol, the acid–base property of ZrO_2 plays an important role [7]: modification of ZrO_2 with sodium cation enhances the selectivity to 3-buten-1-ol to over 70 mol%.

Recently, we have reported that several rare earth oxides (REO), such as Tb_4O_7, Er_2O_3, and Yb_2O_3, are selective for the production of 3-buten-1-ol from 1,4-butanediol [8,9]. We have found an important issue that Yb_2O_3 shows different catalytic activities depending on the crystal structure [8]. The crystal structure of Yb_2O_3 varies from monoclinic to cubic structure at temperatures around 800 °C. Cubic Yb_2O_3 shows the selectivity to 3-buten-1-ol of higher than 80 mol%. In addition, cubic Yb_2O_3 as well as monoclinic ZrO_2 catalyzes the dehydration of 1,5-pentanediol into 4-penten-1-ol [10]: 4-penten-1-ol is produced with the selectivity of higher than 75 mol% over cubic Yb_2O_3. However, cyclic ethers such as THF and tetrahydropyrane are produced over monoclinic Yb_2O_3 [8,10]. The surface character of REOs is basic rather than acidic [9].

---

[*] Corresponding author. Tel.: +81 43 290 3376; fax: +81 43 290 3401.
E-mail address: satoshi@faculty.chiba-u.jp (S. Sato).

0926-860X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2008.09.039

REOs, especially heavy rare earth oxides, are as expensive as noble metals. In this paper, we aimed to prepare effective catalysts by dispersing REO on ZrO_2 to improve the catalytic activity by weight of REO, and we examined the dehydration of 1,4-butanediol over the REOs supported on ZrO_2. We also discussed the catalytic property as correlated with the changes in the structure and basicity of ZrO_2-supported Yb_2O_3 catalysts.

2. Experimental

2.1. Catalyst preparation

SiO_2 (CARiACT Q10), Al_2O_3 (DC2282), monoclinic ZrO_2 (RSC HP), and tetragonal ZrO_2 were supplied from Fuji Silycia Chemical Ltd., Dia Catalyst, Daiichi Kigenso Kagaku Kogyo Co., Ltd., and SAINT-GOBAIN, respectively. They were used as supports as well as catalysts. The support materials were crushed and sieved in the granule size of 0.25–1.00 mm. Rare earth metal nitrates were purchased from Wako Pure Chemical Co. Ltd. Yb_2O_3 was purchased from Kanto Chemical Co. Ltd.

Loading of REO on support material was done by incipient wetness impregnation. Each aqueous solution of nitrate with the prescribed amount of rare earth metal was impregnated on monoclinic ZrO_2. The resulting samples were calcined in air at a prescribed temperature for 3 h. Hereafter, the ZrO_2-supported REO is expressed as Ln/ZrO_2, where Ln means the atomic symbol of each rare earth element. Ln loading (wt.%) is defined as the following equation: $Ln/(Ln + ZrO_2)$ in weight percentage. Other catalysts were prepared in the same way as the Ln/ZrO_2 using SiO_2 and Al_2O_3, and tetragonal ZrO_2 instead of monoclinic ZrO_2.

2.2. Catalytic reaction

The dehydration of 1,4-butanediol was carried out in a fixed-bed flow reactor under atmospheric pressure of N_2 with a flow rate of 26 $cm^3\ min^{-1}$ at 325 °C. Prior to the reaction, a catalyst (0.574 g) was preheated in N_2 flow at 500 °C for 1 h. After the catalyst bed had been heated at the prescribed temperature, 1,4-butanediol was fed into the reactor at a liquid flow rate of 1.41 $cm^3\ h^{-1}$. An effluent collected hourly was analyzed by gas chromatography (GC-8A, Shimadzu, Japan) with a 30-m capillary column (TC-WAX, GL Science, Japan). Gaseous products such as 1,3-butadiene were analyzed by on-line gas chromatography (GC-8A) with a 1-m packed column (Porapack Q).

2.3. Characterization

The specific surface area (SA) of each catalyst was calculated by the BET method using the N_2 isotherm at −196 °C. X-ray diffraction (XRD) patterns were recorded on an XRD7000 (Shimadzu, Japan) using Cu Kα radiation (λ = 0.15 nm) to detect the crystal structure of the samples. The tube voltage and current were 40 kV and 30 mA, respectively.

Temperature-programmed desorption (TPD) profiles of NH_3 and CO_2 were measured to estimate the acidity and the basicity of the catalysts, respectively [7,9]. The numbers of acid and base sites were estimated from neutralization–titration curves of diluted H_2SO_4 and NaOH solution, respectively. A sample (ca. 50 mg) was preheated at 500 °C for 1 h under a reduced pressure. In NH_3-TPD, NH_3 at 13 kPa was introduced to the sample at room temperature for 1 h. In CO_2-TPD, CO_2 was adsorbed on the sample at room temperature for 72 h. Then, each sample was evacuated for 1 h. After no adsorbate had been observed in N_2 flow, the sample was heated from room temperature to 800 °C at a heating rate of 10 °C min^{-1} under an N_2 flow of 15 $cm^3\ min^{-1}$. The desorbed adsorbate molecules, together with N_2 gas, were bubbled into an electric conductivity cell containing a dilute H_2SO_4 or NaOH solution (50 cm^3). The conductivity of the solution was monitored, and the obtained conductivity curve was differentiated to provide a distribution curve of adsorbate desorbed from adsorbent.

3. Results

3.1. Dehydration of 1,4-butanediol over supported rare earth oxide catalysts

Table 1 lists the catalytic results of several supported Yb_2O_3 catalysts in the reaction of 1,4-butanediol at 325 °C. Over Al_2O_3, THF was dominantly produced regardless of Yb loading. Yb/SiO_2 completely converted 1,4-butanediol to THF, while pure silica was not active for the reaction of 1,4-butanediol under the present conditions. It is known that acids catalyze the formation of THF from 1,4-butanediol [11,12]. It is reasonable that Al_2O_3 enhances the THF formation since it is acidic [5,13]. Because Yb/SiO_2 is selective for the THF formation, acidic sites could be generated on the surface of Yb/SiO_2. On the other hand, 3-buten-1-ol was produced over Yb/ZrO_2, while THF was formed over pure ZrO_2. Particularly, Yb_2O_3 supported on monoclinic ZrO_2 catalyzed the selective dehydration of 1,4-butanediol into 3-buten-1-ol. Thus, the monoclinic ZrO_2 was selected as the catalyst support in the following research.

Table 1
Dehydration of 1,4-butanediol over several supported Yb_2O_3 catalysts at 325 °C[a].

Catalyst[b]	Yb loading (wt.%)	SA[c] ($m^2\ g^{-1}$)	Conversion (%)	Selectivity (mol%)[d]			
				3-Buten-1-ol	THF	GBL	Others
Al_2O_3	0	205	100	0.1	97.4	0.0	2.5
Yb/Al_2O_3	30	115	99.8	1.3	96.4	0.5	1.8
SiO_2	0	316	1.6	0.0	26.5	0.0	73.5
Yb/SiO_2	30	149	100	0.2	98.3	0.1	1.4
m-ZrO_2	0	56	94.4	34.1	65.9	0.0	0.0
Yb/m-ZrO_2	20	40	50.8	86.5	4.3	1.1	8.1
t-ZrO_2	0	91	99.9	0.7	96.8	0.2	2.3
Yb/t-ZrO_2	20	43	77.1	39.4	50.7	0.8	9.1
Yb_2O_3[e]	0	30	57.8	84.8	1.4	1.1	12.7

[a] Conversion and selectivity were averaged in the initial 5 h. W/F = 0.407 g h cm^{-3} where W and F are catalyst weight and flow rate of reactant fed, respectively, reaction temperature = 325 °C, N_2 carrier flow rate = 26 $cm^3\ min^{-1}$.

[b] Calcined at 400 °C. m-ZrO_2 means monoclinic ZrO_2, and t-ZrO_2 means tetragonal ZrO_2.

[c] SA, specific surface area.

[d] THF, tetrahydrofuran; GBL, γ-butyrolactone. Others include 1,3-butadiene, 2-buten-1-ol, and 1-butanol.

[e] Calcined at 800 °C.