



Vapor-phase catalytic dehydration of terminal diols

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ABSTRACT

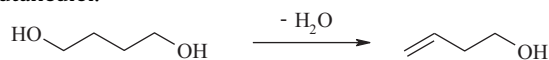
Vapor-phase catalytic reactions of several terminal diols were investigated over several rare earth oxides, such as Sc₂O₃, Y₂O₃, CeO₂, Yb₂O₃, and Lu₂O₃. Sc₂O₃ showed selective catalytic activity in the dehydration of terminal diols with long carbon chain, such as 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, and 1,12-dodecanediol, to produce the corresponding unsaturated alcohols. In the dehydration of 1,6-hexanediol, 5-hexen-1-ol was produced with selectivity over 60 mol%, together with by-products such as ε-caprolactone and oxacycloheptane. In the dehydration of 1,10-decanediol, 9-decen-1-ol was produced with selectivity higher than 70 mol%. In addition to Sc₂O₃, heavy rare earth oxides such as Lu₂O₃ as well as monoclinic ZrO₂ showed moderate selectivity in the dehydration of the terminal diols.

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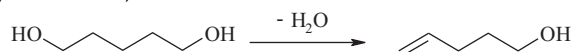
1. Introduction

More than four decades ago, it was discovered that rare earth oxides (REOs) promote the Hofmann elimination reaction in the dehydration of 2-alcohols such as 4-methyl-2-pentanol [1]. An α-olefin, such as 1-butene, is formed with selectivity higher than 80% in the dehydration of 2-butanol over REOs, except La₂O₃ and CeO₂ [2]. We have previously investigated the catalytic performance of REOs [3–11], and reported that several REOs, such as CeO₂, Tb₄O₇, Er₂O₃, and Yb₂O₃, are effective for the dehydration of diols, such as 1,3-, 1,4, and 1,5-diols, to produce unsaturated alcohols. CeO₂ catalyzes the dehydration of 1,3-diols into unsaturated alcohols [3–5]: 3-buten-2-ol and *trans*-2-buten-1-ol are produced from 1,3-buanediol at 325 °C. CeO₂ is the most active catalyst for the formation of the unsaturated alcohols from 1,3-buanediol [11].

In the dehydration of 1,4-butanediol over CeO₂ at 400 °C, 3-buten-1-ol is produced with maximum selectivity of 68 mol%, together with the formation of tetrahydrofuran (THF) [6]. Heavy REO catalysts, such as Tb₄O₇, Er₂O₃, and Yb₂O₃, are also selective for the production of 3-buten-1-ol from 1,4-butanediol [7]: the selectivity to 3-buten-1-ol exceeds 80 mol% over cubic Yb₂O₃. The surface character of REOs is basic rather than acidic [8,10]. In the reaction of 1,4-butanediol, the catalytic function of REOs is related to the basic properties of REO originated in lanthanide contraction [8]. Yb₂O₃ is more active than CeO₂ in the dehydration of 1,4-butanediol.



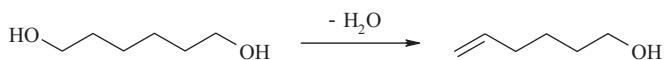
We have also found that Yb₂O₃ shows different catalytic activities depending on its crystal structure [7], which varies from monoclinic to cubic at temperatures around 800 °C. Yb₂O₃ with the cubic bixbyite structure shows higher selectivity to 3-buten-1-ol than the monoclinic one. Yb₂O₃ also works as an effective catalyst in the dehydration of 1,5-pentanediol to produce 4-penten-1-ol [9]. In addition to REOs, monoclinic ZrO₂ [12,13] and In₂O₃ [14] also show the catalytic activity for the formation of 3-buten-1-ol in the dehydration of 1,4-butanediol.



It is known that scandium trifluoromethanesulfonate is used for a reusable Lewis acid catalyst in organic synthesis such as Diels–Alder reaction [15]. On the other hand, there are a few studies on the catalytic property of Sc₂O₃. In heterogeneous catalysis, it is reported that pure Sc₂O₃ as well as Sm₂O₃ is selective for C2 formation in the oxidative coupling of methane [16]. Sc₂O₃ and Y₂O₃ are active for the reduction of nitric oxide with methane [17]. Scandium is an expensive metal, so that catalytic performance of Sc₂O₃ has rarely been investigated.

9-Decen-1-ol is synthesized in the decomposition of monoesters of 1,10-decanediol and carboxylic acids, such as palmitic acid and stearic acid, at temperatures of 330–345 °C [18]. In the dehydration of terminal diols, there is no research report on the direct synthesis of long-chain unsaturated alcohols, such as 5-hexen-1-ol and 9-decen-1-ol. We preliminarily found that Sc₂O₃ was active for the formation of unsaturated alcohols from terminal diols with long carbon chain. In this paper, we investigated catalytic activity of pure Sc₂O₃ as well as several REOs for the reactions of diols with carbon chains of 6–12 and of cyclohexanol as a reference of monoalcohol. Then, we discussed the catalytic properties of Sc₂O₃ in connection with the radius of cation in the REOs.

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2. Experimental

2.1. Samples

REO samples, such as Sc_2O_3 , Y_2O_3 , Yb_2O_3 , CeO_2 , and Lu_2O_3 , were purchased from Kanto Kagaku Co. Ltd., Japan. The commercial REO samples were prepared by decomposing the corresponding chlorides at temperatures $>2000^\circ\text{C}$ for ca. 2 s in the vapor phase, and their physical properties used in this study are listed in tables of Ref. [19]. Monoclinic ZrO_2 (RSC-HP) was supplied by Daiichi Kigenso Kagaku Kogyo Co. Ltd. Al_2O_3 was supplied by Dia Catalyst, DC-2282. The samples used for the catalytic reactions were calcined at an appropriate temperature between 500 and 1000°C for 3 h [10]. The specific surface area of the catalysts, SA, was calculated with the BET method using N_2 isotherm at -196°C .

1,6-Hexanediol, cyclohexanol, and ethanol were purchased from Wako Pure Chemical Industries, Japan. The other diols, such as 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, and 1,12-dodecanediol, were purchased from Tokyo Kasei Kogyo Ltd., Japan. The alcohols were used for the catalytic reaction without further purification.

2.2. Catalytic reaction

The catalytic reactions were performed in a fixed-bed down-flow reactor. Prior to the reactions, a catalyst sample (weight, $W=0.50$ g) was preheated in the flow reactor in N_2 flow at 500°C for 1 h. After the temperature of catalyst bed was set at a prescribed temperature between 325 and 425°C , a reactant solution was fed through the reactor top at a liquid feed rate, F , of $1.80\text{ cm}^3\text{ h}^{-1}$ together with N_2 flow of $27\text{ cm}^3\text{ min}^{-1}$. The reactant diol dissolved in ethanol at 20 wt.% was used as a reactant solution. The effluent collected every hour was analyzed by gas chromatography (GC-8A, Shimadzu, Japan) with a flame ionization detector and a 30-m capillary column (TC-WAX, GL Science Inc., Japan) and by gas chromatography with a mass spectrometer (GCMS-QP-5050A, Shimadzu, Japan) and a 30-m capillary column (DB-WAX, Agilent Technologies, USA).

In this paper, the catalytic activity was evaluated by averaging the conversion data in the initial 5 h. The conversion of alcohol is defined as the amount of alcohol consumed in the reaction. The selectivity to each product is defined as molar selectivity.

3. Results and discussion

3.1. Reaction of diols over several oxide catalysts

Table 1 shows catalytic activity of several REOs in the dehydration of 1,6-hexanediol. The REO samples were calcined at either 800 or 1000°C . Among the catalysts compared in Table 1, Sc_2O_3 showed the highest selectivity in the dehydration of 1,6-hexanediol into 5-hexen-1-ol, and the conversion over Sc_2O_3 was higher than those over the other REOs. Although Yb_2O_3 and Y_2O_3 show high selectivity to 3-buten-1-ol in the dehydration of 1,4-butanediol in our previous work [7,10], they were less selective than Sc_2O_3 in the formation of 5-hexen-1-ol from 1,6-hexanediol. In addition, CeO_2 , which is an excellent catalyst for the formation of 2-propen-1-ol from 1,3-propenediol [3], was also less selective to 5-hexen-1-ol than the other REOs, and CeO_2 produced cyclohexanone and 1-hexanol as by-products. Over the catalysts we tested, several cyclic compounds such as oxacycloheptane, cyclopentanone, cyclopentanemethanol were observed. During the reactions in the initial 5 h, the conversion of 1,6-hexanediol was decreased by 10–20% with time on stream, while the selectivity to 5-hexen-1-ol was hardly changed. As a reference catalyst, monoclinic ZrO_2 showed the conversion higher than Sc_2O_3 , whereas the selectivity to 5-hexen-1-ol is low. Al_2O_3 was also active but not selective in the dehydration of 1,6-hexanediol: a lot of by-products were observed.

Table 2 shows catalytic performance of REOs on the dehydration of several terminal diols at 350°C , except 1,12-dodecanediol. The dehydration of 1,12-dodecanediol was conducted at a high temperature of 400°C , and so the conversion of 1,12-dodecanediol was higher than those of the other terminal diols. In a similar way to the dehydration of 1,6-hexanediol, Sc_2O_3 showed high conversion and selectivity to the corresponding unsaturated alcohols from the terminal diols we tested. The other REOs such as Yb_2O_3 and Y_2O_3 showed lower selectivity to unsaturated alcohols than Sc_2O_3 . Cyclic ketones such as cyclohexanone and cyclopentanone were produced from 1,7-heptanediol and 1,8-octanediol. Fig. 1 summarizes selectivity to the corresponding unsaturated alcohol in the dehydration of terminal diols over REOs. Although the selectivity was obtained at different conversions, it is meaningful: the highest selectivity was obtained at high conversion over Sc_2O_3 , while the low selectivity was at low conversion over CeO_2 . The terminal diols with carbon chains between 6 and 10 had a similar reactivity over the REO catalysts. The conversion and selectivity in Table 2 is strongly dependent on the catalysts. Because the interaction between the two OH groups in the long chain diols is weak, the conversion and selectivity would be similar in the reaction of various long diols over the same catalyst.

Table 1
Catalytic conversion of 1,6-hexanediol over several oxides at 350°C .^a

Catalyst (calcination/ $^\circ\text{C}$)	SA ^b ($\text{m}^2\text{ g}^{-1}$)	Conversion (%)	Selectivity (mol%)					
			5Hx1ol	HxOH	OCH	CHN	Dienes	CPNs
Sc_2O_3 (800)	51.5	47.8	60.9	0	4.4	0	0	3.7
CeO_2 (800)	34.3	45.2	4.8	9.4	4.3	25.2	0	11.0
Y_2O_3 (1000)	21.8	20.0	26.3	0.3	8.4	2.4	1.9	8.8
Yb_2O_3 (1000)	15.7	29.8	17.6	0.3	11.7	2.5	0.1	6.9
Lu_2O_3 (1000)	14.1	32.9	32.2	0.3	9.9	2.8	0.1	7.0
ZrO_2^c (800)	29.0	52.9	32.6	0.5	22.4	1.9	1.2	9.4
Al_2O_3^d (600)	205.0	99.9	2.1	0	14.3	0	21.0	0

^a Conversion and selectivity were averaged in the initial 5 h. $W/F=1.39\text{ g h cm}^{-3}$ where W and F are catalyst weight and feed rate of reactant diol, respectively. 1,6-Hexanediol dissolved in ethanol at 20 wt.% was fed through the reactor top. N_2 carrier flow rate = $27\text{ cm}^3\text{ min}^{-1}$.

5Hx1ol, 5-hexen-1-ol; HxOH, 1-hexanol; OCH, oxacycloheptane; CHN, cyclohexanone; Dienes, 1,5-hexadiene + 1,4-hexadiene; CPNs, cyclopentanone + cyclopentanol. Other by-products are 4-hexen-1-ol, ϵ -caprolactone, cyclohexanol, cyclopentylmethanol, 2-cyclopentenylmethanol, cyclohexene, cyclohexane, and several unidentified products.

^b Specific surface area.

^c Monoclinic ZrO_2 .

^d Reacted at 300°C .

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