



## Vapor-phase catalytic dehydration of terminal diols

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### ABSTRACT

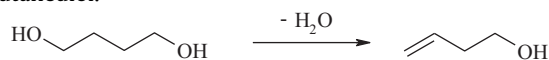
Vapor-phase catalytic reactions of several terminal diols were investigated over several rare earth oxides, such as Sc<sub>2</sub>O<sub>3</sub>, Y<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Yb<sub>2</sub>O<sub>3</sub>, and Lu<sub>2</sub>O<sub>3</sub>. Sc<sub>2</sub>O<sub>3</sub> showed selective catalytic 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 Sc<sub>2</sub>O<sub>3</sub>, heavy rare earth oxides such as Lu<sub>2</sub>O<sub>3</sub> as well as monoclinic ZrO<sub>2</sub> showed moderate selectivity in the dehydration of the terminal diols.

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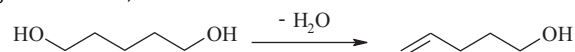
### 1. Introduction

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 La<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub> [2]. We have previously investigated the catalytic performance of REOs [3–11], and reported that several REOs, such as CeO<sub>2</sub>, Tb<sub>4</sub>O<sub>7</sub>, Er<sub>2</sub>O<sub>3</sub>, and Yb<sub>2</sub>O<sub>3</sub>, are effective for the dehydration of diols, such as 1,3-, 1,4, and 1,5-diols, to produce unsaturated alcohols. CeO<sub>2</sub> 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. CeO<sub>2</sub> 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 CeO<sub>2</sub> 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 Tb<sub>4</sub>O<sub>7</sub>, Er<sub>2</sub>O<sub>3</sub>, and Yb<sub>2</sub>O<sub>3</sub>, 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 Yb<sub>2</sub>O<sub>3</sub>. 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]. Yb<sub>2</sub>O<sub>3</sub> is more active than CeO<sub>2</sub> in the dehydration of 1,4-butanediol.



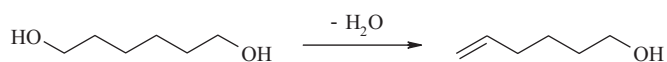
We have also found that Yb<sub>2</sub>O<sub>3</sub> shows different catalytic activities depending on its crystal structure [7], which varies from monoclinic to cubic at temperatures around 800 °C. Yb<sub>2</sub>O<sub>3</sub> with the cubic bixbyite structure shows higher selectivity to 3-buten-1-ol than the monoclinic one. Yb<sub>2</sub>O<sub>3</sub> 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 ZrO<sub>2</sub> [12,13] and In<sub>2</sub>O<sub>3</sub> [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 Sc<sub>2</sub>O<sub>3</sub>. In heterogeneous catalysis, it is reported that pure Sc<sub>2</sub>O<sub>3</sub> as well as Sm<sub>2</sub>O<sub>3</sub> is selective for C2 formation in the oxidative coupling of methane [16]. Sc<sub>2</sub>O<sub>3</sub> and Y<sub>2</sub>O<sub>3</sub> are active for the reduction of nitric oxide with methane [17]. Scandium is an expensive metal, so that catalytic performance of Sc<sub>2</sub>O<sub>3</sub> 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 Sc<sub>2</sub>O<sub>3</sub> was active for the formation of unsaturated alcohols from terminal diols with long carbon chain. In this paper, we investigated catalytic activity of pure Sc<sub>2</sub>O<sub>3</sub> 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 Sc<sub>2</sub>O<sub>3</sub> in connection with the radius of cation in the REOs.

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## 2. Experimental

### 2.1. Samples

REO samples, such as  $\text{Sc}_2\text{O}_3$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ ,  $\text{CeO}_2$ , and  $\text{Lu}_2\text{O}_3$ , 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  $\text{ZrO}_2$  (RSC-HP) was supplied by Daiichi Kigenso Kagaku Kogyo Co. Ltd.  $\text{Al}_2\text{O}_3$  was supplied by Dia Catalyst, DC-2282. The samples used for the catalytic reactions were calcined at an appropriate temperature between 500 and  $1000^\circ\text{C}$  for 3 h [10]. The specific surface area of the catalysts, SA, was calculated with the BET method using  $\text{N}_2$  isotherm at  $-196^\circ\text{C}$ .

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,  $W=0.50\text{ g}$ ) was preheated in the flow reactor in  $\text{N}_2$  flow at  $500^\circ\text{C}$  for 1 h. After the temperature of catalyst bed was set at a prescribed temperature between 325 and  $425^\circ\text{C}$ , 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  $\text{N}_2$  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  $1000^\circ\text{C}$ . Among the catalysts compared in Table 1,  $\text{Sc}_2\text{O}_3$  showed the highest selectivity in the dehydration of 1,6-hexanediol into 5-hexen-1-ol, and the conversion over  $\text{Sc}_2\text{O}_3$  was higher than those over the other REOs. Although  $\text{Yb}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  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  $\text{Sc}_2\text{O}_3$  in the formation of 5-hexen-1-ol from 1,6-hexanediol. In addition,  $\text{CeO}_2$ , 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  $\text{CeO}_2$  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  $\text{ZrO}_2$  showed the conversion higher than  $\text{Sc}_2\text{O}_3$ , whereas the selectivity to 5-hexen-1-ol is low.  $\text{Al}_2\text{O}_3$  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  $350^\circ\text{C}$ , except 1,12-dodecanediol. The dehydration of 1,12-dodecanediol was conducted at a high temperature of  $400^\circ\text{C}$ , 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,  $\text{Sc}_2\text{O}_3$  showed high conversion and selectivity to the corresponding unsaturated alcohols from the terminal diols we tested. The other REOs such as  $\text{Yb}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$  showed lower selectivity to unsaturated alcohols than  $\text{Sc}_2\text{O}_3$ . 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  $\text{Sc}_2\text{O}_3$ , while the low selectivity was at low conversion over  $\text{CeO}_2$ . 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  $350^\circ\text{C}$ .<sup>a</sup>

Catalyst (calcination/ $^\circ\text{C}$ )	SA <sup>b</sup> ( $\text{m}^2\text{ g}^{-1}$ )	Conversion (%)	Selectivity (mol%)					
			5Hx1ol	HxOH	OCH	CHN	Dienes	CPNs
$\text{Sc}_2\text{O}_3$ (800)	51.5	47.8	60.9	0	4.4	0	0	3.7
$\text{CeO}_2$ (800)	34.3	45.2	4.8	9.4	4.3	25.2	0	11.0
$\text{Y}_2\text{O}_3$ (1000)	21.8	20.0	26.3	0.3	8.4	2.4	1.9	8.8
$\text{Yb}_2\text{O}_3$ (1000)	15.7	29.8	17.6	0.3	11.7	2.5	0.1	6.9
$\text{Lu}_2\text{O}_3$ (1000)	14.1	32.9	32.2	0.3	9.9	2.8	0.1	7.0
$\text{ZrO}_2^c$ (800)	29.0	52.9	32.6	0.5	22.4	1.9	1.2	9.4
$\text{Al}_2\text{O}_3^d$ (600)	205.0	99.9	2.1	0	14.3	0	21.0	0

<sup>a</sup> 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.  $\text{N}_2$  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,  $\epsilon$ -caprolactone, cyclohexanol, cyclopentylmethanol, 2-cyclopentenylmethanol, cyclohexene, cyclohexane, and several unidentified products.

<sup>b</sup> Specific surface area.

<sup>c</sup> Monoclinic  $\text{ZrO}_2$ .

<sup>d</sup> Reacted at  $300^\circ\text{C}$ .

**Table 2**  
Catalytic conversion of diols over several oxides at 350 °C.<sup>a</sup>

Catalyst (calcination/°C)	1,7-Hexanediol		1,8-Octanediol		1,9-Nonanediol		1,10-Decanediol		1,12-Dodecanediol	
	Conv.	Selec. <sup>b</sup>	Conv.	Selec. <sup>c</sup>	Conv.	Selec. <sup>d</sup>	Conv.	Selec. <sup>e</sup>	Conv. <sup>f</sup>	Selec. <sup>f</sup>
Sc <sub>2</sub> O <sub>3</sub> (800)	42.3	59.6	55.8	65.0	55.9	57.6	59.7	74.0	93.4	60.1
CeO <sub>2</sub> (800)	25.5	2.6	27.0	7.7	26.8	5.2	24.1	6.6	73.6	13.1
Y <sub>2</sub> O <sub>3</sub> (1000)	26.4	19.0	33.5	22.6	26.0	29.4	26.0	16.9	70.2	37.4
Yb <sub>2</sub> O <sub>3</sub> (1000)	37.2	18.0	29.2	40.0	20.7	34.0	26.8	29.4	70.8	42.1
Lu <sub>2</sub> O <sub>3</sub> (1000)	28.9	38.7	35.0	59.0	25.2	56.6	33.8	49.7	76.1	56.2
ZrO <sub>2</sub> <sup>g</sup> (800)	44.2	37.2	27.5	46.7	26.3	55.2	32.1	51.1	96.2	36.5

<sup>a</sup> Diol dissolved in ethanol at 20 wt.% was fed through the reactor top. Conversion (%) and selectivity (mol%) were averaged in the initial 5 h. Reaction conditions are the same as those in Table 1.

<sup>b</sup> Selectivity to 6-hepten-1-ol.

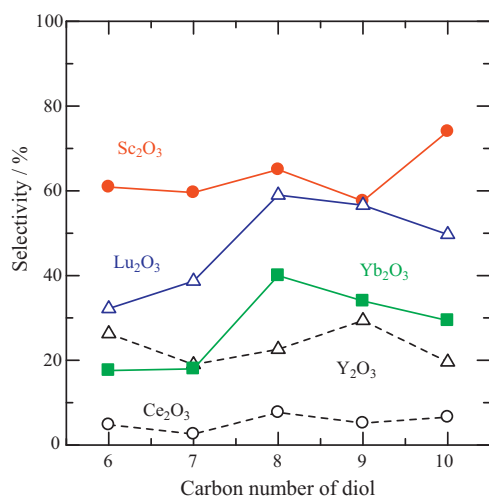
<sup>c</sup> Selectivity to 7-octen-1-ol.

<sup>d</sup> Selectivity to 8-nonen-1-ol.

<sup>e</sup> Selectivity to 9-decen-1-ol.

<sup>f</sup> Reacted at 400 °C. Selectivity to 11-dodecen-1-ol.

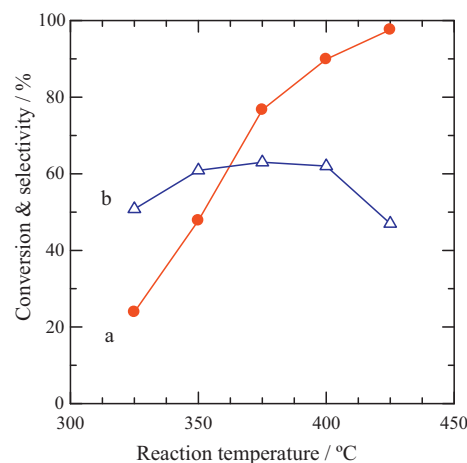
<sup>g</sup> Monoclinic ZrO<sub>2</sub>.



**Fig. 1.** Changes in the selectivity to unsaturated alcohols in the dehydration of terminal diols over several oxide catalysts, such as Sc<sub>2</sub>O<sub>3</sub>, CeO<sub>2</sub>, Y<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, and Lu<sub>2</sub>O<sub>3</sub>. The data are cited from Tables 1 and 2.

### 3.2. Reaction of 1,6-hexanediol over Sc<sub>2</sub>O<sub>3</sub>

Calcination temperatures of REO greatly affect the catalytic performance, especially product selectivity [4,5,10,11]. Table 3 shows effects of calcination temperature of Sc<sub>2</sub>O<sub>3</sub> on the dehydration of 1,6-hexanediol at 400 °C. The conversion of 1,6-hexanediol was slightly decreased with the decrease in SA of Sc<sub>2</sub>O<sub>3</sub>. The selectivity to 5-hexen-1-ol was maximized at a calcination temperature of 800 °C. At higher calcination temperatures than 800 °C, the selec-



**Fig. 2.** Changes in conversion and selectivity in the dehydration of 1,6-hexanediol over Sc<sub>2</sub>O<sub>3</sub> calcined at 800 °C with reaction temperature. (a) Solid circle, conversion of 1,6-hexanediol; (b) open triangle, selectivity to 5-hexen-1-ol. 1,6-Hexanediol dissolved in ethanol at 20 wt.% was fed through the reactor top. Reaction temperature, 400 °C; W/F = 1.39 g h cm<sup>-3</sup>.

tivity to 5-hexen-1-ol was decreased because of the increase in  $\epsilon$ -caprolactone as a dehydrogenated product.

Fig. 2 shows a change in the catalytic activity with reaction temperature in the dehydration of 1,6-hexanediol over Sc<sub>2</sub>O<sub>3</sub> calcined at 800 °C. The conversion of 1,6-hexanediol was increased with increasing reaction temperature. The selectivity to 5-hexen-1-ol was maximized at reaction temperatures between 375 and 400 °C. A main by-product at low reaction temperature was oxacycloheptane, which is decreased at high temperature, while dienes, cyclic

**Table 3**  
Dehydration of 1,6-hexanediol over Sc<sub>2</sub>O<sub>3</sub> calcined at different temperatures.<sup>a</sup>

Calcination (°C)	SA <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	Conversion (%)	Selectivity (mol%) <sup>c</sup>					
			5-Hexen-1-ol	OCH	$\epsilon$ -Caprolactone	Dienes	CPMs	CPNs
As-obtained	98.4	93.3	38.4	2.1	0.5	7.0	8.2	4.0
500	81.8	95.6	41.4	2.2	0.5	3.8	10.3	4.2
600	72.1	94.6	41.9	1.6	0.5	6.1	8.0	4.1
700	64.6	93.1	53.7	2.0	0.6	6.5	4.1	2.9
800	51.5	94.6	62.0	2.1	0.8	5.2	3.2	2.2
900	45.4	87.6	57.6	2.1	1.5	7.2	2.5	1.9
1000	30.9	82.2	49.8	3.0	4.7	7.5	2.3	1.9

<sup>a</sup> Conversion and selectivity at 400 °C were averaged in the initial 5 h. Reaction conditions are the same as those in Table 1.

<sup>b</sup> Specific surface area.

<sup>c</sup> OCH, oxacycloheptane; CPMs, cyclopentylmethanol + 2-cyclopentenylmethanol; CPNs, cyclopentanone + cyclopentanol; other by-products are 4-hexen-1-ol, 1-hexanol, cyclohexanone, cyclohexanol, cyclohexene, and several unidentified products.

ketones, and cyclic alcohols such as cyclopentanone and cyclopentanemethanol were increased at high reaction temperatures. In the reactions over  $\text{Sc}_2\text{O}_3$ , cyclohexanol and cyclohexene were observed as very minor by-products. Thus, we tested the catalytic reaction of cyclohexanol as a reference monoalcohol over REOs in the following section.

### 3.3. Reactivity of cyclohexanol over the REO catalysts

Table 4 shows catalytic performance of REOs on cyclohexanol at 350 °C in order to compare with the reactivity of diols. Cyclohexanone and cyclohexene were detected in the reaction through dehydrogenation and dehydration, respectively.  $\text{Sc}_2\text{O}_3$  and  $\text{Lu}_2\text{O}_3$  showed a comparable product ratio of cyclohexanone to cyclohexene. Over the other REOs such as  $\text{Yb}_2\text{O}_3$  and  $\text{Y}_2\text{O}_3$ , cyclohexanone was produced more than cyclohexene.

Product selectivity in the reaction of cyclohexanol over REOs would be an indicator to evaluate the dehydration ability of REO, and to differentiate the reactivity between the diol and monoalcohol in the dehydration (Table 4). In other words, the abilities for the dehydration and for the dehydrogenation can be determined by product ratio in such a way that cyclohexene is hydration product and cyclohexanone is hydrogenation product. The results in Table 4 indicate that  $\text{Sc}_2\text{O}_3$  has higher ability of dehydration and lower dehydrogenation ability than the other REOs. Namely, dehydration ability of  $\text{Sc}_2\text{O}_3$  is superior to that of other REOs.

At 350 °C, the dehydration product was only cyclohexene over  $\text{Sc}_2\text{O}_3$ , while the conversion was low. The reactivity of cyclohexanol was lower than those of terminal diols over  $\text{Sc}_2\text{O}_3$  by comparison of the conversion at the same temperature (Tables 1 and 4). In the present reactions, ethanol is used as a solvent for the reactants. Ethanol is hardly reacted over REOs at 350 °C. Thus, it also indicates that monoalcohol is much less reactive than diols and cyclohexanol.

### 3.4. Catalytic activities of $\text{Sc}_2\text{O}_3$ compared to the other REOs

Ionic radii of rare earth metals are reported to be 0.0745 nm ( $\text{Sc}^{3+}$ ), 0.0900 nm ( $\text{Y}^{3+}$ ), 0.0970 nm ( $\text{Ce}^{4+}$ ), 0.0868 nm ( $\text{Yb}^{3+}$ ), and 0.0861 nm ( $\text{Lu}^{3+}$ ), where the trivalent ions have 6 coordination number except for  $\text{Ce}^{4+}$  with 8 coordination number [20].  $\text{In}_2\text{O}_3$  with cubic bixbyite crystal structure is reported to be active in the dehydration of diols [14]: the formation of unsaturated alcohols is considered to proceed via tridentate coordination of diol on the surface of  $\text{In}_2\text{O}_3$ . It is also speculated that the tridentate adsorption of diols on the surface of cubic bixbyite  $\text{Sc}_2\text{O}_3$  could be an intermediate during catalysis.

The dehydration ability of REOs would be related to the ionic radius of metal cations in REOs. Therefore, the selectivity to unsaturated alcohol and the formation rate of unsaturated alcohols in the dehydration of various diols with the number of carbon atom from 6 to 10 were plotted in the relation with ionic radius of rare earth cations in Fig. 3A and B, respectively. Both the selectivity and the formation rate decreases with increasing the ionic radius. The terminal diols have the same tendency of increasing the selectivity and the formation rate as the ionic radius decreases. In other words, REO with small ionic diameter of rare earth metal cation is effective in the formation of unsaturated alcohol.

In Table 4, the selectivity to cyclohexene in the dehydration of cyclohexanol is in the order of  $\text{Sc} > \text{Lu} > \text{Ce} > \text{Y} > \text{Yb}$ . The order in the selectivity is not always the same as the order in the selectivity to 5-hexen-1-ol in the dehydration of 1,6-hexanediol (Fig. 1),  $\text{Sc} > \text{Lu} > \text{Yb} > \text{Y} > \text{Ce}$ . Table 4 also lists the formation rate of cyclohexene, which is in the order of  $\text{Lu} > \text{Sc} > \text{Yb} > \text{Y} > \text{Ce}$ . The order is quite the same as the order in the formation rate of 5-hexen-1-ol per unit surface area shown in Fig. 3C. Since the formation rate based on unit surface area means the intrinsic activity, it can be estimated

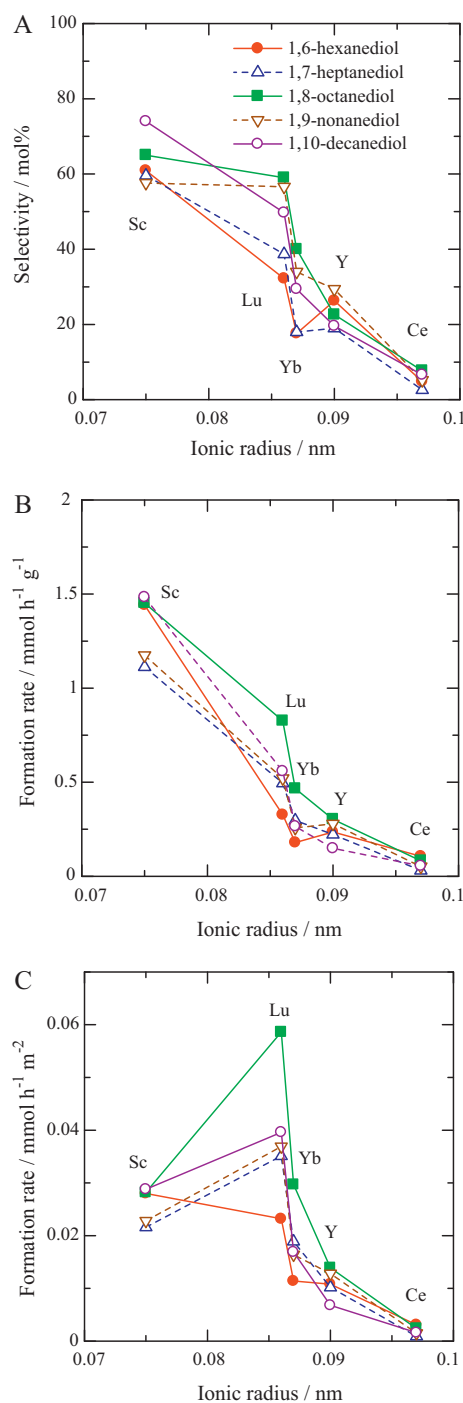


Fig. 3. Changes in the selectivity to unsaturated alcohol (A) and the formation rate of unsaturated alcohol (B and C) in the dehydration of several terminal diols, such as 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, and 1,10-decanediol, over oxide catalysts at 350 °C with ionic radius of rare earth cation.

the ability of dehydration. Comparing the values of formation rate in Fig. 3C with those in Table 4, diols are much more reactive than monoalcohol such as cyclohexanol.

### 3.5. Probable reaction route over REOs

1,6-Hexanediol produces various by-products, whereas 1,4-butanediol produces only several by-products [12,13]. One of the most important factors of this difference is the stability of cyclic compounds. Two cyclic compounds with 5-membered ring,

**Table 4**  
Catalytic conversion of cyclohexanol at 350 °C.<sup>a</sup>

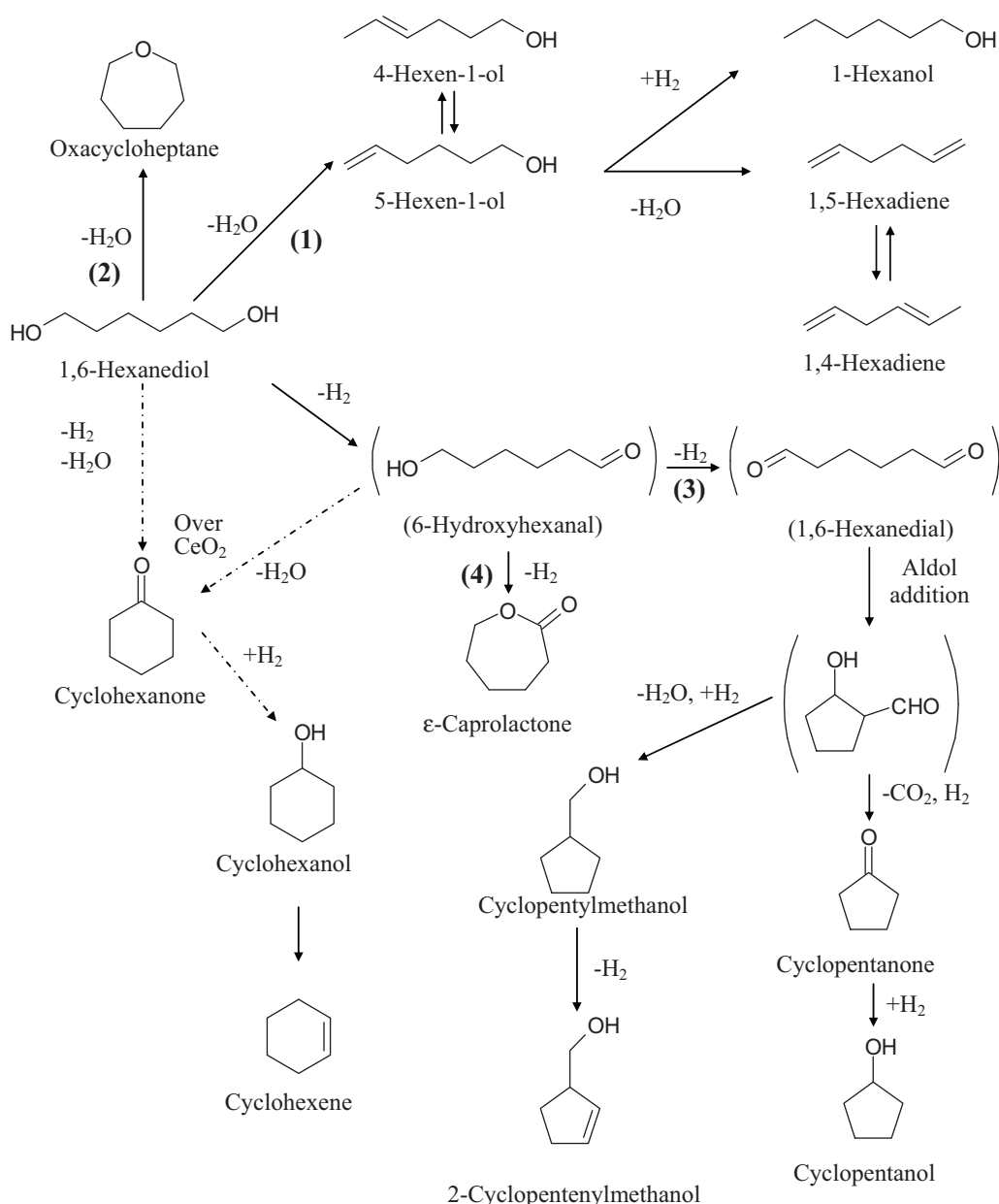
Catalyst (calcination/°C)		Conversion (%)	Selectivity (mol%) <sup>b</sup>	
			Cyclohexene	Cyclohexanone
Sc <sub>2</sub> O <sub>3</sub>	(800)	14.7	33.1 (0.0071)	31.0 (0.0066)
CeO <sub>2</sub>	(800)	14.8	13.0 (0.0041)	23.6 (0.0075)
Y <sub>2</sub> O <sub>3</sub>	(1000)	12.7	10.7 (0.0046)	27.4 (0.0117)
Yb <sub>2</sub> O <sub>3</sub>	(1000)	16.5	8.4 (0.0065)	40.8 (0.0315)
Lu <sub>2</sub> O <sub>3</sub>	(1000)	13.0	16.8 (0.0113)	31.7 (0.0215)

<sup>a</sup> Reaction conditions are the same as those in Table 1. Cyclohexanol dissolved in ethanol at 20 wt.% was fed through the reactor top.

<sup>b</sup> Data in the parentheses mean the formation rate (mmol h<sup>-1</sup> m<sup>-2</sup>).

tetrahydrofuran and  $\gamma$ -butyrolactone, can be produced from 1,4-butanediol, while no 4-membered ring compounds were observed due to the low stability of 4-membered ring. 1,6-Hexanediol, on the other hands, produces various cyclic products such as 5- and 6-membered rings, and 7-membered ring including oxygen within the ring (Tables 1 and 3).

Taking into account the by-products listed in Table 3, Fig. 4 suggests possible reaction routes from 1,6-hexanediol. There are possibly four main reaction routes. The first route produces 5-hexen-1-ol via dehydration, in which reaction route involves production of 4-hexen-1-ol by isomerization, or production of by-products such as 1-hexanol or dienes by hydrogenation



**Fig. 4.** Proposed reaction pathway of 1,6-hexanediol over REOs.

or excessive dehydration, respectively. The second route produces oxacycloheptane via intramolecular etherification. Over  $\text{Sc}_2\text{O}_3$ , however, a little amount of oxacycloheptane is produced from 1,6-hexanediol, whereas 1,4-butanediol mainly produces tetrahydrofuran in the dehydration. The third route produces cyclopentanol and cyclopentanone in the dehydrogenation of 1,6-hexanediol to 6-hydroxyhexanal and to 1,5-hexanediol followed by the formation of cyclic intermediate via aldol addition. Since the ratio of cyclopentanone in the cyclic compounds is large, this reaction preferably proceeds over  $\text{Sc}_2\text{O}_3$ . The last route is similar to the third route:  $\epsilon$ -caprolactone is produced via 6-hydroxyhexanal as an intermediate. Since a little amount of  $\epsilon$ -caprolactone is produced, this route does not proceed favorably over  $\text{Sc}_2\text{O}_3$ .

Over  $\text{CeO}_2$ , cyclohexanone and cyclohexanol are observed. They would be produced from 6-hydroxyhexanal, but the mechanism is unclear. However, cyclopentanone is a major product over  $\text{CeO}_2$  in the reaction using aqueous 1,6-hexanediol as a feed solution instead of ethanol solution [21]. Although pure ethanol does not react over REOs at 350 °C, ethanol solvent used in the feed solution may affect the catalytic dehydration. We need further investigation on the dehydration of terminal diols using direct feed of terminal diols melted.

#### 4. Conclusions

The catalytic activity of several REOs such as  $\text{Sc}_2\text{O}_3$ ,  $\text{CeO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$ , and  $\text{Lu}_2\text{O}_3$  was investigated in the vapor-phase catalytic reactions of terminal diols with carbon numbers from 6 to 12, such as 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol, and 1,12-dodecanediol.  $\text{Sc}_2\text{O}_3$  showed the highest selectivity to the corresponding unsaturated alcohols in the dehydration of the terminal diols. For instance, 5-hexen-1-ol was produced as a dehydration product of 1,6-hexanediol with the selectivity over 60 mol%, together with by-products of  $\epsilon$ -caprolactone and oxacycloheptane. In the dehydration of 1,10-decanediol over  $\text{Sc}_2\text{O}_3$ , 9-decen-1-ol was produced

with the selectivity higher than 70 mol%. Heavy REOs such as  $\text{Lu}_2\text{O}_3$  as well as monoclinic  $\text{ZrO}_2$  show moderate catalytic activity in the dehydration of the terminal diols, while their selectivity was lower than  $\text{Sc}_2\text{O}_3$ .  $\text{CeO}_2$ , which is an excellent catalyst in the formation of 2-propen-1-ol from 1,3-propanediol, was less selective in the dehydration of terminal diols than the other REOs. In the reaction of cyclohexanol,  $\text{Sc}_2\text{O}_3$  was the most selective catalyst for the dehydration to produce cyclohexene, while the other REOs predominantly catalyzed the dehydrogenation to produce cyclohexanone.

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