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# Dehydration of 1,5-pentanediol over bixbyite Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> catalysts

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# ABSTRACT

Vapor-phase dehydration of 1,4- and 1,5-alkanediols was investigated over three scandium ytterbium mixed oxides,  $Sc_{2-x}Yb_xO_3$  (x = 0.5, 1.0, and 1.5), to produce the corresponding unsaturated alcohols. In the dehydration of 1,5-pentanediol,  $Sc_{0.5}Yb_{1.5}O_3$  was more active than simple rare earth oxides such as  $Sc_2O_3$ ,  $Lu_2O_3$ ,  $Yb_2O_3$ , and  $Tm_2O_3$ . The selectivity to 4-penten-1-ol surpassed 80 mol% over the  $Sc_{2-x}Yb_xO_3$  catalysts. The highest formation rate of 4-penten-1-ol was obtained at x = 1.5 and affected by lattice parameter of cubic bixbyite  $Sc_{2-x}Yb_xO_3$ . In the dehydration of 1,4-butanediol, however,  $Tm_2O_3$  was the most active among the catalysts.

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## 1. Introduction

Rare earth mixed oxides are important materials such as catalysts [1,2] as well as laser sources [3], pigments [4,5], dielectric [6], and fluorescent materials [7]. Lattice parameter of the mixed oxides can be controlled by regulating the composition. For instance, it is reported that lattice parameter (LP) *a* of cubic scandium ytterbium mixed oxide,  $Sc_{2-x}Yb_xO_3$ , is linearly increased from 0.9845 to 1.0435 nm with increasing x from 0 to 2.0 [7].

In the catalytic dehydration of alkanediol to the corresponding unsaturated alcohol, formation rate of unsaturated alcohol varies with ionic radius of rare earth cation of rare earth oxide catalyst [8–11]. The LP of cubic bixbyite rare earth oxide, RE<sub>2</sub>O<sub>3</sub>, is correlated with ionic radius of rare earth cation. In the dehydration of 1,5-pentanediol, Lu<sub>2</sub>O<sub>3</sub> is the most active in the simple cubic RE<sub>2</sub>O<sub>3</sub> catalysts [8]. Since surface geometry reflects the bulk structure, the LP should affect the catalytic activity. Unfortunately, there is no simple RE<sub>2</sub>O<sub>3</sub> with a LP value between 0.9845 nm of Sc<sub>2</sub>O<sub>3</sub> and 1.0391 nm of Lu<sub>2</sub>O<sub>3</sub> [12]. It is expected that a catalyst with a LP between Sc<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub> could surpass the highest Lu<sub>2</sub>O<sub>3</sub> in the dehydration of 1,5-pentanediol. However, cubic Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> samples have LP values that comfortably fit into the missing LP region.

We have recently reported that the reactivity of alkanediols into corresponding unsaturated alcohols over  $Yb_2O_3$  calcined at 800 °C is affected by carbon length [8]: the order of reactivity at <350 °C is 1,6-hexanediol<<1,5-pentanediol<<1,3-propanediol<1,4-butanediol. The reactivity of 1,3-propanediol lower than that of 1,4-butanediol is

due to the fact that 1,3-propanediol is readily dehydrogenated to 3hydroxypropanal, which is decomposed though retro-aldol addition.

In this work, we investigated the dehydration of 1,5-pentanediol as well as 1,4-butanediol over cubic  $Sc_{2-x}Yb_xO_3$  catalysts. We selected Yb rather than the smallest Lu among the rare earth elements because Yb is more inexpensive than Lu. We also discussed the correlation between the LP value and the catalytic activity of  $Sc_{2-x}Yb_xO_3$  samples.

#### 2. Experimental

## 2.1. Catalyst samples

Three Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> catalyst samples with x = 0.5, 1.0, and 1.5, namely Sc<sub>1.5</sub>Yb<sub>0.5</sub>O<sub>3</sub>, Sc<sub>1.0</sub>Yb<sub>1.0</sub>O<sub>3</sub>, and Sc<sub>0.5</sub>Yb<sub>1.5</sub>O<sub>3</sub>, were supplied by Daiichi Kigenso Kagaku Kogyo Co., Ltd., Japan. Outline of the sample preparation is as follows: a Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> sample was prepared from mixed nitrate solution at an appropriate composition by using ammonia as a precipitation reagent, and the resulting precipitate after washing was calcined in air at 400 °C for 10 h to obtain a Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> catalyst. Simple Lu<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, Tm<sub>2</sub>O<sub>3</sub> were supplied by Kanto Kagagu Co., Ltd., Japan. All the catalyst samples were calcined at 800 °C in air for 3 h prior to the catalytic reaction.

### 2.2. Characterization of catalysts

The specific surface area of the catalyst was calculated by the Brunauer–Emmett–Teller (BET) method using the N<sub>2</sub> isotherm at -196 °C. Transmission electron microscope (TEM) image was taken on a JEM-2100F microscope (JEOL, Japan) operating at 120 kV. X-ray diffraction (XRD) patterns were recorded on a NEW D8 ADVANCE (Bruker,

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Germany) using Cu K $\alpha$  radiation ( $\lambda$  = 0.15 nm). Tube voltage and current were 40 kV and 40 mA, respectively. Lattice parameter *a* of cubic Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> was calculated from the following equation:

$$\frac{1}{d} = \frac{h^2 + k^2 + l^2}{a^2} = \frac{2^2 + 2^2 + 2^2}{a^2} \quad (h = k = l = 2)$$
(1)

using the lattice spacing of  $\{222\}$  facet, *d*, where *h*, *k*, and *l* are Miller indices.

Temperature-programmed desorption (TPD) of CO<sub>2</sub> adsorbed at 25 °C was examined by neutralization titration using an electric conductivity cell immersed in aqueous NaOH solution, and the detail procedure has been described elsewhere [13,14]. CO<sub>2</sub> that desorbed with N<sub>2</sub> carrier gas was bubbled into a dilute NaOH solution. The amount of desorbed CO<sub>2</sub> was monitored from the change in conductivity of the solution. The sample was heated from 25 to 800 °C at a rate of 10 °C min<sup>-1</sup> in N<sub>2</sub> flow of 50 cm<sup>3</sup> min<sup>-1</sup>. The density of basic sites is defined as the number of CO<sub>2</sub> molecules desorbed in the temperature range of 25–500 °C on the assumption that one CO<sub>2</sub> molecule adsorbs on one basic site of the catalyst surface. The TPD of NH<sub>3</sub> adsorbed at 25 °C was also measured in the same apparatus as the CO<sub>2</sub>-TPD, as has been described previously [13]. N<sub>2</sub> gas with the desorbed NH<sub>3</sub> was monitored from the change in conductivity of the solution, and the amount of desorbed NH<sub>3</sub> was monitored from the change in conductivity of the solution.

#### 2.3. Catalytic reactions

The dehydration of alkanediols, such as 1,5-pentanediol and 1,4butanediol, was carried out in a fixed-bed down-flow glass tube reactor with an inner diameter of 17 mm and a length of 300 mm under the atmospheric pressure of nitrogen gas at the flow rate of 30 cm<sup>3</sup> min<sup>-1</sup>. In each test, 0.3 g of catalyst was loaded in the reactor. After the catalyst bed had been heated in nitrogen flow at 500 °C for 1 h, the catalytic reaction was performed at 350 or 400 °C. An alkanediol was fed into the reactor at a liquid flow rate of 1.8 cm<sup>3</sup> min<sup>-1</sup> (17 mmol h<sup>-1</sup> for 1,5-pentanediol). A reaction effluent recovered every hour was analyzed by gas chromatography (GC-2014, Shimadzu, Japan) with a 30-m capillary column (Rtx-Wax, RESTEK, USA). A gas chromatography mass spectrometer (GCMS-QP5050A, Shimadzu, Japan) equipped with a 30-m capillary column (DB-WAX, Agilent Technologies, USA) was used for identification of compounds in the effluent.

Since the catalytic activity is stable, as a previous paper has reported [11], both the conversion of diol and the selectivity to each product are averaged in the initial 5 h to evaluate the catalytic activity. The conversion of diol is defined as the amount of diol consumed in the reaction, and the selectivity to each product is defined as the molar selectivity.

#### 3. Results and discussion

#### 3.1. Characterization of catalyst samples

Fig. 1 shows XRD profiles of  $Sc_{2-x}Yb_xO_3$  ( $0 \le x \le 2$ ) calcined at 800 °C. All the samples had cubic bixbyite phase: the largest diffraction appeared at  $2\theta = ca$ . 30°, which is assigned {222} facet (Fig. 1A). The diffractions assigned {211}, {400}, {440}, and {622} facets also appeared. Fig. 1B shows enlarged view of Fig. 1A around the main diffraction peak of {222} facet. Diffraction angle of {222} facet, 2 $\theta$ , was decreased from 31.56 to 29.60° with increasing x from 0 to 2.0. In the sample at x = 0.5 and 1.0 (Fig. 1B, b and c), however, a small peak at  $2\theta = ca$ . 29.6° was observed, and this could be attributed to the segregation of Yb<sub>2</sub>O<sub>3</sub> phase in the samples. Diffraction angle of other facets also depended on Yb content. We calculated a LP value from the diffraction angle of {222} facet.

Table 1 summarizes the calculated LP values of  $Sc_{2-x}Yb_xO_3$ . LP values of  $Sc_{0.5}Yb_{1.5}O_3$  and  $Sc_{1.0}Yb_{1.0}O_3$  are close to the values ( $Sc_{1.494}Yb_{0.506}O_3$ , 1.0009 nm;  $Sc_{1.015}Yb_{0.985}O_3$ , 1.0149 nm) reported previously [7]. LP values of  $Sc_2O_3$  and  $Yb_2O_3$  correspond with the reported values of



**Fig. 1.** XRD profiles of  $Sc_{2-x}Yb_xO_3$  mixed oxides at x = (a) 0, (b) 0.5, (c) 1.0, (d) 1.5, and (e) 2.0. Diffraction data of  $Sc_2O_3$  and  $Yb_2O_3$  were the same as those of Refs. [14] and [18], respectively.

0.9845 and 1.0435 nm [7]. The LP value of Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> was linearly increased from 0.9812 nm of Sc<sub>2</sub>O<sub>3</sub> to 1.0445 nm of Yb<sub>2</sub>O<sub>3</sub> with increasing x from 0 to 2.0 (Figure not shown). The tendency is consistent with the previous report [7]. As we expected, we obtained Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> samples with LP values between those of Sc<sub>2</sub>O<sub>3</sub> and Lu<sub>2</sub>O<sub>3</sub>.

Table 1 also displays specific surface area (SA) of catalysts. SA of  $Sc_{2-x}Yb_xO_3$  was decreased from 53.2 to 26.2  $m^2g^{-1}$  with increasing x from 0.5 to 1.5. Particle size, *D*, of  $Sc_{1.0}Yb_{1.0}O_3$  was calculated by the following equation, assuming that the particles are spherical:

$$D = \frac{6}{d' \cdot SA} \tag{2}$$

where *d'* is an estimated density of  $Sc_{1.0}Yb_{1.0}O_3$ , *d'* = [(density of  $Sc_2O_3$ , 3.864 g cm<sup>-3</sup> [15]) + (density of  $Yb_2O_3$ , 9.2 g cm<sup>-3</sup> [15])]/ 2 = 6.5 g cm<sup>-3</sup>. The *D* of  $Sc_{1.0}Yb_{1.0}O_3$  was estimated to be 26 nm. Fig. 2 shows TEM images of  $Sc_{2-x}Yb_xO_3$ . Judging from the TEM images, the  $Sc_{2-x}Yb_xO_3$  samples were composed of nanoparticles with the particle size ranging from 20 nm to 40 nm. Table 1 also summarizes particle size, on the other hand, is smaller than the size observed in TEM photos of Fig. 2. The size is similar to the *D* value calculated from the SA value (Table 1). Thus, it is reasonable that the nanoparticles observed in Fig. 2 are composed of primary particles of  $Sc_{1.0}Yb_{1.0}O_3$ .

Fig. 3 shows TPD profiles of NH<sub>3</sub> and CO<sub>2</sub> adsorbed on Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> catalysts. In the NH<sub>3</sub>-TPD (Fig. 3a–c), NH<sub>3</sub> was not adsorbed on the samples even at 25 °C. This indicates that Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> samples have no acidic sites which can be estimated by NH<sub>3</sub> adsorption. This is consistent with the previous TPD results of Yb<sub>2</sub>O<sub>3</sub> [13]. In contrast, CO<sub>2</sub> was adsorbed on the samples, and desorption profiles were obtained (Fig. 3d–h). Table 1 lists density of basic sites and desorption temperature observed in the CO<sub>2</sub>-TPD profiles. The density of basic sites of Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> is ca. 5 µmol m<sup>-2</sup>, which is comparable to that of Yb<sub>2</sub>O<sub>3</sub>. The basic sites, estimated by desorption temperature around 130 °C, is regarded as weak basic sites. The TPD results indicate that Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> surface is weak basic rather than acidic.

#### 3.2. Catalytic reactions

Table 2 summarizes catalytic activities of various catalysts in the dehydration of 1,5-pentanediol at 400 °C.  $Sc_{2-x}Yb_xO_3$  catalysts showed high selectivity to 4-penten-1-ol higher than 80% at the conversion ranging from 57% to 68% regardless of Yb content. Over  $Sc_{2-x}Yb_xO_3$ , the selectivity to 4-penten1-ol was higher than those of simple  $Sc_2O_3$  and  $Yb_2O_3$ ,

Catalyst <sup>a</sup>	R <sub>i</sub> (nm)	LP, a <sup>d</sup> (nm)	$SA (m^2g^{-1})$	Particle size <sup>f</sup> (nm)	Density of basic sites $(\mu mol m^{-2})$	$T_d \text{ of } CO_2$ (°C)
$Sc_2O_3$	0.0745 <sup>b</sup>	0.9812	51.5 <sup>e</sup>	37.5	2.3 <sup>g</sup>	146 <sup>g</sup>
Sc <sub>1.5</sub> Yb <sub>0.5</sub> O <sub>3</sub>	0.0776 <sup>c</sup>	0.9976	53.2	12.2	4.7	131
Sc <sub>1.0</sub> Yb <sub>1.0</sub> O <sub>3</sub>	0.0807 <sup>c</sup>	1.0153	35.9	13.3	5.4	132
Sc <sub>0.5</sub> Yb <sub>1.5</sub> O <sub>3</sub>	0.0837 <sup>c</sup>	1.0318	26.2	19.7	5.1	134
$Lu_2O_3$	0.0861 <sup>b</sup>	1.0391	27.8 <sup>e</sup>	20.5	7.0 <sup>g</sup>	123 <sup>g</sup>
Yb <sub>2</sub> O <sub>3</sub>	0.0868 <sup>b</sup>	1.0445	28.8 <sup>e</sup>	36.2	5.3 <sup>g</sup>	124 <sup>g</sup>
$Tm_2O_3$	0.0880 <sup>b</sup>	1.0488	27.0 <sup>e</sup>	17.9	8.3 <sup>g</sup>	145 <sup>g</sup>

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Physical	and	chemical	properties	of	cataly	st.

R<sub>i</sub>, average ionic radius; LP, lattice parameter; SA, specific surface area; T<sub>d</sub>, desorption temperature.

<sup>a</sup> Catalyst calcined at 800 °C.

<sup>b</sup> Ionic radius of trivalent rare earth cation with coordination number 6 cited from Ref. [14,17].

<sup>c</sup> Calculated by using Eq. (3).

<sup>d</sup> Calculated by using Eq. (1) and the lattice spacing of {222} facet.

e Cited from Ref. [14].

<sup>f</sup> Calculated by using Scherrer's equation and the diffraction peak of {222} facet.

<sup>g</sup> Estimated from the TPD profile in Ref. [14].

because the selectivity to tetrahydropyran (THP) and  $\delta$ -valerolactone (DVL) was lower. Table 2 also shows formation rate of 4-penten-1-ol per unit surface area at 400 °C as an intrinsic catalytic activity. Intrinsic catalytic activity showed the highest value of 1.106 mmol h<sup>-1</sup> m<sup>-2</sup> at x = 1.5.

Fig. 4A shows a change in the formation rate of 4-penten-1-ol with LP of catalyst. At LP of 1.0318 nm (Sc<sub>0.5</sub>Yb<sub>1.5</sub>O<sub>3</sub>), the intrinsic catalytic activity showed a maximum. This indicates that oxide surface with LP of Sc<sub>0.5</sub>Yb<sub>1.5</sub>O<sub>3</sub> is suitable for the dehydration of 1,5-pentanediol. In other words, LP values of Sc<sub>2</sub>O<sub>3</sub>, Sc<sub>1.5</sub>Yb<sub>0.5</sub>O<sub>3</sub>, and Sc<sub>1.0</sub>Yb<sub>1.0</sub>O<sub>3</sub> were low for the dehydration of 1,5-pentanediol, while those of Lu<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, and Tm<sub>2</sub>O<sub>3</sub> were too high.

As shown in Fig. 1, all  $Sc_{2-x}Yb_xO_3$  catalysts had cubic bixbyite phase. One of the authors has reported a surface structure of {222} facet of cubic bixbyite, such as  $In_2O_3$  [16]: a bixbyite phase intrinsically has asterism-like oxygen defects on the surface (Fig. 5 in Ref. [16]). We have also proposed an adsorption model of 1,4-butanediol on acid–base pair sites of RE<sub>2</sub>O<sub>3</sub> (Fig. 7 in Ref. [9]). We consider that the asterism-like oxygen defects sites of bixbyite RE<sub>2</sub>O<sub>3</sub> provide acid–base pair sites. This will be discussed in the next Section 3.3.

Table 3 summarizes catalytic activities of various catalysts in the dehydration of 1,4-butanediol at 350 °C. The highest conversion of 1,4-butanediol of 86.5% was obtained at x = 1.0. The selectivity to 3-buten-1-ol was decreased from 76.2 to 69.6% with increasing x from 0.5 to 1.5. Over Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub>, 2-buten-1-ol and tetrahydrofuran produced as by-products with the total selectivity of ca. 20–25% decrease the selectivity to 3-buten-1-ol. In Table 3, Tm<sub>2</sub>O<sub>3</sub> shows the highest selectivity to 3-buten-1-ol.

Fig. 4B shows a change in the formation rate of 3-buten-1-ol with LP of catalyst. Intrinsic catalytic activity at 350 °C was simply increased from 0.66 to 1.67 mmol  $h^{-1}$  m<sup>-2</sup> with increasing LP from 0.9812 to 1.0488 nm: Tm<sub>2</sub>O<sub>3</sub> was the most active. This result has a

difference from the finding reported previously at a reaction temperature of 375 °C (Fig. 5 in Ref. [9]): Tm<sub>2</sub>O<sub>3</sub> calcined at 800 °C is less reactive than Er<sub>2</sub>O<sub>3</sub>, Yb<sub>2</sub>O<sub>3</sub>, and Lu<sub>2</sub>O<sub>3</sub> calcined at 800 °C. In any case, the most active of the catalyst considered for the dehydration of 1,4butanediol is different from that in the dehydration of 1,5-pentanediol. In other words, the most suitable lattice parameter in the dehydration of 1,4-butanediol is different from the value in the dehydration of 1,5-pentanediol. This result suggests that positions of hydroxyl groups of alkanediol affect the most suitable lattice parameter of catalyst in its dehydration. In our previous work [8], on the other hand, the reactivity of alkanediols to produce the corresponding unsaturated alcohols is affected by carbon length: 1,4-butanediol is more reactive than 1,5-pentanediol at the same temperature. Therefore, catalytic activity of cubic Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> catalysts could be determined according to the compatibility between the position of hydroxyl groups of alkanediol and the distance between oxygen defects on the catalyst, which is strongly related to lattice parameter.

#### 3.3. Effect of ionic radius in the dehydration of 1,5-pentanediol

As described in the previous section, LP value of catalyst influences the catalytic activity. Unfortunately, it is impossible that the catalytic activities of other rare earth oxides with monoclinic and hexagonal phases such as Dy<sub>2</sub>O<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> are plotted in Fig. 4A because the crystal phases have different lattice parameters in the different directions. As shown in Fig. 4A, there are few plots to understand the tendency in a large sense. In the latest work, catalytic activity of RE<sub>2</sub>O<sub>3</sub> varied with ionic radius of rare earth cation in the dehydration of 1,5-pentanediol (Fig. 4 in Ref. [8]). However, catalytic activity of Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> cannot simply be compared with those of simple cubic RE<sub>2</sub>O<sub>3</sub> samples because Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> includes two types of cations such as Sc<sup>3+</sup> and Yb<sup>3+</sup>. Since the LP value of Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> linearly varies



Fig. 2. TEM image of  $Sc_{2-x}Yb_xO_3$  calcined at 800 °C. x = (A) 0.5, (B) 1.0, and (C) 1.5.



**Fig. 3.** TPD profiles of NH<sub>3</sub> and CO<sub>2</sub> adsorbed on  $Sc_{2-x}Yb_xO_3$ . NH<sub>3</sub> adsorbed on the samples at x = (a) 0.5, (b) 1.0, and (c) 1.5; CO<sub>2</sub> adsorbed on the samples at x = (d) 0, (e) 0.5, (f) 1.0, (g) 1.5, and (h) 2.0. TPD profiles d and h were the same as those of Ref. [14].

with Yb content, an average ionic radius of  $Sc_{2-x}Yb_xO_3$  was calculated. Here, arithmetic average of cationic radius in  $Sc_{2-x}Yb_xO_3$  can be described in the following equation:

$$R(\mathrm{Sc}_{2-x}\mathrm{Yb}_{x}\mathrm{O}_{3}) = \left\{ r\left(\mathrm{Sc}^{3+}\right) \times (2-x) + r\left(\mathrm{Yb}^{3+}\right) \times x \right\} / 2 \tag{3}$$

where  $R(Sc_{2-x}Yb_xO_3)$  is average cationic radius of  $Sc_{2-x}Yb_xO_3$ ,  $r(Sc^{3+})$ is ionic radius of  $Sc^{3+}$  (0.0745 nm, 6-coordinated [17]), and  $r(Yb^{3+})$ is that of  $Yb^{3+}$  (0.0868 nm, 6-coordinated [17]). Table 1 lists the average ionic radius in Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> as well as ionic radius of Sc<sup>3+</sup>, Lu<sup>3+</sup>, Yb<sup>3+</sup>, and Tm<sup>3+</sup>. As shown in Table 1, LP value of Sc<sub>2-x</sub>Yb<sub>x</sub>O<sub>3</sub> catalyst is linearly correlated with average ionic radius. Fig. 5 shows a change in the formation rate of 4-penten-1-ol with average ionic radius of rare earth cation in the dehydration of 1,5-pentanediol at 400 °C. The formation rate of 4-penten-1-ol showed the highest at a average ionic radius of 0.0837 nm (Sc<sub>0.5</sub>Yb<sub>1.5</sub>O<sub>3</sub>). As a comparison, over a  $ZrO_2$  with monoclinic phase (ionic radius of  $Zr^{4+}$  is 0.0840 nm, 8-coordinated [17]), the formation rate of 4-penten-1-ol is calculated to be at most 0.225 mmol  $h^{-1}$  m<sup>-2</sup> at 400 °C [11]. Catalytic activity of monoclinic  $ZrO_2$  is much lower than  $Sc_{0.5}Yb_{1.5}O_3$  which has a similar average ionic radius to that of ZrO<sub>2</sub>. There is a significant difference between  $ZrO_2$  and  $Sc_{0.5}Yb_{1.5}O_3$ :  $ZrO_2$  intrinsically has no oxygen defects, while cubic Sc<sub>0.5</sub>Yb<sub>1.5</sub>O<sub>3</sub> has oxygen defects on the surface.

It is well known that dehydration of alcohols usually proceeds over acidic sites of oxides. The present TPD results, however, do not

Table 2	
Dehydration of 1,5-butanediol at 400 °C <sup>a</sup> .	



**Fig. 4.** Formation rate of the unsaturated alcohols at different lattice parameters of (closed circle)  $Sc_{2-x}Yb_xO_3$  and (open triangle) simple rare earth oxides in the dehydration of (A) 1,5-pentanediol at 400 °C and (B) 1,4-butanediol at 350 °C.

explain the high catalytic activity of  $Sc_{2-x}Yb_xO_3$  in dehydration of diols to produce unsaturated alcohols. The dehydration of diols into unsaturated alcohols would be catalyzed not by simple acid sites but probably by acid–base pair sites. We have already reported that the catalytic activity of rare earth oxides is not correlated with the density of basic sites and basic strength, and proposed a concerted acid–base mechanism in the formation of unsaturated alcohols [9]. It can be understood that the adsorption energy of 1,5-pentanediol could be the highest on  $Sc_{0.5}Yb_{1.5}O_3$ with the most appropriate surface geometry, and that the bulk structure

Catalyst	Conversion (%)	Selectivity (	(mol%) <sup>c</sup>		Formation rate of 4P1OL (mmol $h^{-1} m^{-2}$ )		
		4P10L	THP	DVL	13PDE	Others <sup>d</sup>	
Sc <sub>2</sub> O <sub>3</sub> <sup>b</sup>	63.3	75.5	7.5	1.6	0.4	14.9	0.530
Sc <sub>1.5</sub> Yb <sub>0.5</sub> O <sub>3</sub>	57.4	81.5	4.1	0.6	1.2	12.4	0.503
$Sc_{1.0}Yb_{1.0}O_3$	68.4	80.9	4.2	0.3	2.4	10.8	0.882
Sc <sub>0.5</sub> Yb <sub>1.5</sub> O <sub>3</sub>	62.8	80.8	3.7	0.3	2.5	14.5	1.106
Lu <sub>2</sub> O <sub>3</sub> <sup>b</sup>	55.3	77.8	7.5	1.6	0.9	14.8	0.884
Yb <sub>2</sub> O <sub>3</sub> <sup>b</sup>	50.9	74.0	8.3	2.8	0	18.5	0.747
Tm <sub>2</sub> O <sub>3</sub> <sup>b</sup>	44.9	64.0	10.7	6.4	0	13.9	0.608

<sup>a</sup> Conversion and selectivity were averaged in the initial 5 h.

<sup>b</sup> Data cited from Ref. [8].

<sup>c</sup> 4P10L: 4-penten-1-ol, THP: tetrahydropyran, DVL: δ-valerolactone, and 13PDE: 1,3-pentadiene.

<sup>d</sup> Include 1-pentanol, cis- and trans-3-penten-1-ol, 3,4-dihydropyran, and pentanal.

Table 3	
Dehydration of 1,4-butanediol at 350	°Ca

Catalyst	Conversion (%)	Selectivity (mol%) <sup>b</sup>						Formation rate <sup>d</sup> (mmol $h^{-1} m^{-2}$ )
		3B1OL	2B1OL	THF	GBL	13BDE	Others <sup>c</sup>	
Sc <sub>2</sub> O <sub>3</sub>	67.3	69.0	5.3	19.8	1.4	0.1	4.4	0.66
Sc <sub>1.5</sub> Yb <sub>0.5</sub> O <sub>3</sub>	85.1	76.2	13.9	6.3	0.4	0.3	3.0	0.98
Sc <sub>1.0</sub> Yb <sub>1.0</sub> O <sub>3</sub>	86.5	72.8	14.6	8.8	0.8	0.8	2.3	1.43
Sc <sub>0.5</sub> Yb <sub>1.5</sub> O <sub>3</sub>	63.2	69.6	10.3	14.9	1.2	0.5	3.5	1.31
$Lu_2O_3$	74.6	72.5	15.2	2.8	0.9	0.4	8.1	1.60
Yb <sub>2</sub> O <sub>3</sub>	74.5	80.1	12.7	4.6	0.6	0.2	1.0	1.64
$Tm_2O_3$	74.0	80.3	9.5	7.2	0.8	0.1	2.1	1.67

<sup>a</sup> Conversion and selectivity were averaged in the initial 5 h.

<sup>b</sup> 3B10L: 3-buten-1-ol, 2B10L: 2-buten-1-ol, THF: tetrahydrofuran, GBL: γ-butyrolactone, 13BDE: 1,3-butadiene.

<sup>c</sup> Include 1-butanol and several unknown products.

<sup>d</sup> Total formation rate of 3B1OL and 2B1OL.

provide an active center on the surface to fit the concerted acid-base mechanism. The adsorption of diol could be stabilized by the most suitable coordination structure. We will clarify the catalytic nature of rare earth oxides through quantum calculation in the future.

## 4. Conclusions

Vapor-phase catalytic dehydration of 1,5-pentanediol to 4-penten-1-ol was investigated over three  $Sc_{2-x}Yb_xO_3$  samples. In the dehydration of 1,5-pentanediol,  $Sc_{0.5}Yb_{1.5}O_3$  was more active than simple rare earth oxides such as  $Sc_2O_3$ ,  $Lu_2O_3$ , and  $Yb_2O_3$ . Formation rate of 4-penten-1-ol was affected on lattice parameter of catalyst. In contrast,  $Lu_2O_3$ ,  $Yb_2O_3$ , and  $Tm_2O_3$  were more active than  $Sc_{2-x}Yb_xO_3$  in the dehydration of 1,4-butanediol to produce 3-buten-1-ol. These results indicate that cubic  $Sc_{0.5}Yb_{1.5}O_3$  with the most appropriate surface geometry to adsorb a reactant is catalytically active in the dehydration of 1,5-pentanediol.

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**Fig. 5.** Formation rate of 4-penten-1-ol in the dehydration of 1,5-pentanediol at 400 °C with average ionic radii of rare earth cations. (Red filled circle)  $Sc_{2-x}Yb_xO_3$  with cubic bixbyite phase, (blue open triangle) cubic bixbyite, (purple open diamond) coexistence of cubic bixbyite and monoclinic, (black open square) monoclinic, (brown open circle) cubic fluorite, and (green filled square) hexagonal.