

Dehydration of diols catalyzed by CeO₂

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Abstract

Dehydration of several 1,3-diols into unsaturated alcohols was investigated over pure CeO₂ at 325–425 °C. 1,3-Diols are more reactive than other diols and monoalcohols over CeO₂. In the dehydration of 1,3-propanediol, 1,3-butanediol, 3-methyl-1,3-butanediol, 2,4-pentanediol, and 2-methyl-2,4-pentanediol, unsaturated alcohols are selectively produced at 325 °C. In the dehydration of 2-methyl-1,3-propanediol, the corresponding unsaturated alcohol is produced with low selectivity: decomposition simultaneously proceeds. TPR experiment reveals that active CeO₂ surface is maintained at high valence of Ce⁴⁺ in the water-producing reaction. It is speculated that redox nature between Ce⁴⁺–Ce³⁺ affects the dehydration of 1,3-diols.

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1. Introduction

Cerium(IV) oxide itself has attractive features in catalyses such as CO hydrogenation to hydrocarbons [1], *ortho*-selective alkylation of phenol with alcohols [2–4], and ketone formation through dimerization of alcohol [4–9], aldehyde, ester [9], and carboxylic acid [10,11]. In the reaction of 1-propanol, 1-propanol was converted into 3-pentanone with high selectivity over pure CeO₂ catalyst [4]. In the vapor-phase conversion of 1,6-hexanediol over CeO₂, cyclopentanone is formed with high selectivity [12].

We have recently reported that pure CeO₂ selectively catalyzes the formation of unsaturated alcohols in the dehydration of 1,3-diols [13]. In the dehydration of 1,3-propanediol, 2-propen-1-ol is produced with 98.9 mol% selectivity over CeO₂ at 325 °C. In the catalytic reaction of 1,3-butanediol over Al₂O₃ and MgO, 1,3-butanediol decomposes to gaseous hydrocarbons such as 1,3-butadiene without producing unsaturated alcohols. Only CeO₂ has specific catalytic activity for the selective dehydration of 1,3-butanediol to 2-buten-1-ol and 3-buten-2-ol with a small amount of 3-buten-2-one.

Syntheses of unsaturated alcohols have been widely investigated. It is known that both isomerization of epoxy compounds such as 1,2-epoxypropane [14,15] and partial hydrogenation of unsaturated aldehydes such as 2-butenal [16–18] are efficient for the synthesis. However, some epoxides and unsaturated aldehydes are expensive as raw materials. As long as using inexpensive diols, we expect that the dehydration of diols is an alternative for the production of unsaturated alcohols.

It is well known that CeO₂ component with oxygen storage capacity plays an important redox role in automotive exhaust catalysts [19,20]. Both the redox ability and the basicity of CeO₂ cooperate to catalyze the ketone formation at temperatures >400 °C [8,9]: dehydrogenation of alcohol is the initial reaction, followed by aldol addition of the resulting aldehyde, and the aldol is finally decomposed into ketone. CeO₂ catalyzes dehydrogenation of primary alcohol to aldehyde, while it does not catalyze the dehydration of the primary alcohol into olefin and ether even at high temperatures >400 °C. In contrast, 1,3-diols are readily dehydrated into unsaturated alcohols over CeO₂ at low temperatures <400 °C [13].

However, we have observed several by-products, which had not been detected in the previous report [13], in reactions of 1,3-diols in GC analysis using a different capillary column.

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In this paper, we describe catalytic feature of CeO₂ in dehydration of various monoalcohols and diols at 325–425 °C. We also examined the effect of reduction of CeO₂ on the catalytic activity, and characterized the CeO₂ by using temperature-programmed reduction (TPR). Then, we discussed active centers of CeO₂ in the vapor-phase dehydration of 1,3-diols to unsaturated alcohols.

2. Experimental

2.1. Catalyst samples

A reagent-grade powder of cerium(IV) oxide was purchased from Wako Pure Chemical Industry Ltd., Japan. The specific surface area (SA) of the CeO₂ was 20 m² g⁻¹ by the calculation with BET method using N₂ isotherm at -196 °C. Zirconium(IV) oxide, ZrO₂, with SA of 44 m² g⁻¹ was prepared by conventional precipitation using zirconyl nitrate and ammonia solution, followed by calcination in air at 500 °C for 3 h.

A temperature-programmed reduction measurement was done with a stepwise temperature program for the samples of both fresh and treated with water vapor after reduction, and the details are described elsewhere [21,22]. A mixture of H₂/N₂ (1/9) was flowed at rate of 10 cm³ min⁻¹ at ambient pressure over a catalyst sample (30 mg) charged in a quartz tube. The temperature was raised from 25 °C to a prescribed temperature at heating rate of 5 K min⁻¹, and kept at the temperature for 1 h. An amount of H₂ consumed for reduction of the sample was monitored with a thermal conductivity detector, and was calibrated by using complete reduction of a reference NiO sample. Average oxidation number of Ce in CeO₂ was calculated from the consumption of H₂ during the TPR process.

2.2. Catalytic reactions

Prior to the reaction, a CeO₂ sample (0.15 g) was preheated in a usual fixed bed flow reactor in an N₂ flow typically at 500 °C for 1 h. A reactant fed into the reactor at flow rate of 2.01 cm³ h⁻¹ together with an N₂ flow of 73 mmol h⁻¹ was contacted with the catalyst at a prescribed temperature between 325 and 425 °C. The effluent collected periodically 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 (Porapak Q).

3. Results

3.1. Dehydration of alcohols

Table 1 lists results of the reactions of several monoalcohols such as 1-butanol, 2-butanol, 2-buten-1-ol, and 3-methoxy-1-butanol over CeO₂ at 325–425 °C. In the reaction of 2-butanol, CeO₂ catalyzes the dehydrogenation to produce butanone, while butenes are formed at higher temperatures. In the conversion of 1-butanol and 3-methoxy-1-butanol, CeO₂ catalyzes only the dehydrogenation to produce butanal and 2-butenal. These monoalcohols are not dehydrated to butenes at temperatures of 325–425 °C. In the conversion of 2-buten-1-ol, dehydration to 1,3-butadiene proceeds in addition to dehydrogenation. In contrast, 3-oxo-1-butanol is readily dehydrated into 3-buten-2-one at temperatures lower than 300 °C, together with decomposition into propanone.

Table 2 summarizes results of the reactions of different butanediols such as 1,2-, 1,3-, 1,4-, and 2,3-butanediol over CeO₂ at 325–425 °C. CeO₂ catalyzes the dehydration of

Table 1
Dehydration of monoalcohols over CeO₂

Reactant	Temperature (°C)	Conversion (%)	Selectivity ^a
1-Butanol	325	0.4	1 (68)
	375	0.8	1 (36)
	425	2.2	1 (41)
2-Butanol	325	2.3	2 (95)
	375	8.2	2 (30), 3 (63)
	425	40.4	2 (17.6), 3 (76.3)
2-Buten-1-ol	325	2.4	Unidentified
	375	20.9	1 (19.4), 4 (19.1), 5 (12.9)
	425	29.1	1 (12.7), 4 (12.5), 5 (15.5)
3-Methoxy-1-butanol	325	2.0	1 (7), 4 (47)
	375	7.5	1 (12), 4 (7)
	425	15.1	1 (13), 4 (9)
3-Oxo-1-butanol	275	51.8	6 (87.2), 7 (10.0)
	325	87.2	6 (67.0), 7 (29.7)

Products: (1) butanal; (2) butanone; (3) 1-butene; (4) 2-butenal; (5) 1,3-butadiene; (6) 3-buten-2-one; (7) propanone.

^a Number in parenthesis indicates the selectivity (mol%) to the product.

Table 2
Dehydration of butanediols over CeO₂

Reactant	Conversion (%)	Selectivity ^a
1,2-Butanediol	6.4 ^b	2 (14)
	15.7 ^c	1 (23), 2 (19), 8 (17), 9 (2)
	53.1 ^d	1 (28.4), 2 (26.4), 8 (12.7), 9 (2.2)
1,3-Butanediol	36.9 ^b	10 (56.9), 11 (35.5), 12 (2.2), 6 (1.8), 2 (1.3), 7 (0.8), 8 (0.5)
	61.0 ^c	10 (41.8), 11 (28.2), 12 (3.7), 6 (6.0), 2 (4.3), 7 (4.5), 8 (1.2), 4 (0.7), 5 (0.7)
	96.5 ^d	10 (47.9), 11 (19.4), 12 (2.1), 6 (4.1), 2 (2.5), 7 (4.9), 8 (1.6), 4 (1.3), 5 (4.6)
	33.5 ^{c,e}	10 (15.3), 11 (11.2), 12 (3.7), 6 (10.6), 2 (10.6), 7 (2.8), 8 (2.1), 5 (3.7), 13 (25.5)
1,4-Butanediol	2.6 ^b	13 (84)
	19.0 ^c	13 (36.2), 11 (1.1), 12 (1.7), 8 (1.9), 14 (2.7), 15 (50.4), 5 (3.0)
	74.0 ^d	13 (57.1), 11 (2.8), 12 (4.7), 8 (3.5), 14 (3.0), 15 (17.4), 5 (3.2)
2,3-Butanediol	1.5 ^b	2 (18), 10 (3)
	10.3 ^c	2 (48), 7 (7), 10 (5), 6 (1)
	51.1 ^d	2 (64.0), 7 (9.4), 10 (2.7), 6 (1.3)

Products: (**1**) butanal; (**2**) butanone; (**4**) 2-butenal; (**5**) 1,3-butadiene; (**6**) 3-buten-2-one; (**7**) propanone; (**8**) 1-butanol; (**9**) 2-butanol; (**10**) 3-buten-2-ol; (**11**) *trans*-2-buten-1-ol; (**12**) *cis*-2-buten-1-ol; (**13**) 3-buten-1-ol; (**14**) γ -butyrolactone; (**15**) tetrahydrofuran.

^a Number in parenthesis indicates the selectivity (mol%) to the product.

^b Reacted at 325 °C.

^c Reacted at 375 °C.

^d Reacted at 425 °C.

^e Catalyzed by ZrO₂ prepared by precipitation.

1,2-butanediol to produce mainly butanal and butanone, where an enol form of the carbonyl products would be an intermediate. 2,3-Butanediol is also converted to butanone over CeO₂. It is remarked that 2-buten-1-ol and 3-buten-2-ol are rarely produced in the dehydration of 1,2-butanediol and 2,3-butanediol. In addition, 1,4-butanediol is converted to 3-buten-1-ol with a small amount of tetrahydrofuran and 1,3-butadiene at high temperature as 425 °C. In the conversion of 1,3-butanediol over CeO₂, however, 3-buten-2-ol and *trans*-2-buten-1-ol are selectively produced while *cis*-2-buten-1-ol is minimally formed. In contrast to CeO₂, ZrO₂ has dehydration ability for 1,3-butanediol at 375 °C, while 3-buten-1-ol is the major product together with other unsaturated alcohols such as 3-buten-2-ol, *trans*-, and *cis*-2-buten-1-ol.

Fig. 1 depicts the time dependence of conversion of 1,3-butanediol over CeO₂ at 325 °C. CeO₂ shows attractive cat-

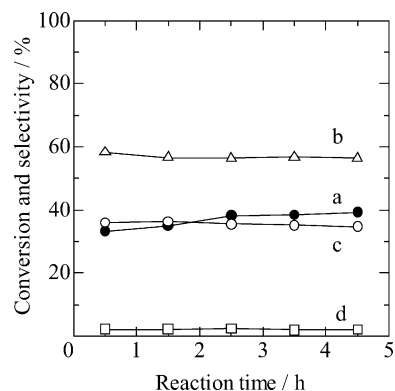


Fig. 1. Time dependence of conversion in the dehydration of 1,3-butanediol over CeO₂ at 325 °C: (a) conversion of 1,3-butanediol; (b) selectivity to 3-buten-2-ol; (c) selectivity to *trans*-2-buten-1-ol; (d) selectivity to *cis*-2-buten-1-ol.

alytic performance without decay of the conversion within the initial 5 h. Both the conversion of 1,3-butanediol and the selectivities to 3-buten-2-ol, *trans*-, and *cis*-2-buten-1-ol are stabilized. In contrast, slight decays in the conversion are observed at 375 and 425 °C.

Table 3 lists results of the reactions of reactive diols such as 1,3-propanediol, 2,4-pentanediol, 3-methyl-1,3-butanediol, and 2-methyl-2,4-pentanediol over CeO₂ at 325–425 °C. In the reactions, CeO₂ effectively catalyzes the dehydration to unsaturated alcohols even at 325 °C. Table 4 summarizes results of the reactions of other diols such as 1,2-propanediol, 2-methyl-1,3-propanediol, and 2-ethyl-1,3-hexanediol, together with 1,2,3-propanetriol over CeO₂. In the conversion of 1,2-propanediol, propanal and propanone are formed through enols. 1,2,3-Propanetriol is converted into hydroxypropanone with moderate selectivity, and several unknown products are detected. In the conversion of 2-methyl-1,3-propanediol and 2-ethyl-1,3-hexanediol, the corresponding unsaturated alcohols are produced with moderate selectivity. However, the 1,3-diols with alkyl group at 2-position are less reactive than the 1,3-diols having no alkyl side chain listed in Table 3.

3.2. Dehydration of 1,3-butanediol over reduced CeO₂ and its redox nature

Fig. 2 shows TPR profiles of CeO₂. H₂ consumption in the TPR up to the prescribed temperature increases with raising the reduction temperature: CeO₂ is readily reduced at higher temperature. Since the H₂ consumption in the TPR can be calibrated by the amount of H₂ consumption in a reference NiO, oxidation state of CeO₂ treated at different temperatures can be estimated by the H₂ consumption. For example,

Table 3
Dehydration of other reactive diols over CeO₂

Reactant	Temperature (°C)	Conversion (%)	Selectivity ^a
1,3-Propanediol	325	50.6	16 (98.9)
	375	59.6	16 (65.5), 17 (4.3), 18 (3.1), 19 (7.6)
	425	78.1	16 (54.0), 17 (6.2), 18 (5.5), 19 (10.1)
2,4-Pentanediol	325	47.2	20 (86.8), 21 (7.4), 22 (1.4)
	375	79.2	20 (78.9), 21 (7.5), 22 (2.9)
	425	97.3	20 (60.6), 21 (7.1), 22 (8.3)
3-Methyl-1,3-butanediol	325	42.3	23 (56.8), 24 (24.7)
	375	75.4	23 (59.1), 24 (25.5)
	425	87.3	23 (44.3), 24 (16.3)
2-Methyl-2,4-pentanediol	325	28.3	25 (48.9), 26 (5.8), 27 (28.3), 28 (5.7), 29 (5.6)
	375	59.7	25 (46.9), 26 (7.4), 27 (27.9), 28 (4.6), 29 (5.5)
	425	81.8	25 (22.6), 26 (5.8), 27 (11.9), 28 (22.2), 29 (10.5)

Products: (**16**) 2-propen-1-ol; (**17**) 1-propanol; (**18**) propanal; (**19**) ethanol; (**20**) *trans*-3-penten-2-ol; (**21**) *cis*-3-penten-2-ol; (**22**) 1,3-pentadiene; (**23**) 2-methyl-3-buten-2-ol; (**24**) 3-methyl-2-buten-1-ol; (**25**) *trans*-2-methyl-3-penten-2-ol; (**26**) *cis*-2-methyl-3-penten-2-ol; (**27**) 4-methyl-3-penten-2-ol; (**28**) 2-methyl-1,3-pentadiene; (**29**) propanone.

^a Number in parenthesis indicates the selectivity (mol%) to the product.

CeO₂ is reduced to CeO_{1.79} at 900 °C, where the average oxidation number of Ce is estimated to be 3.58. This means that 42% of the total Ce⁴⁺ cations is reduced to Ce³⁺. The reduction treatment at >500 °C changes the sample color from yellow to gray. Table 5 lists the average oxidation number of Ce in the CeO₂ reduced at different temperatures. The average oxidation number decreases with raising the reduction temperature.

Table 5 also summarizes the effect of CeO₂ pretreatment on the catalytic activity in the conversion of 1,3-butanediol, together with the selectivities to 3-buten-2-ol and *trans*-2-buten-1-ol. In the samples reduced by H₂ at >500 °C, the average conversion level in the initial 5 h decreases with raising reduction temperature while the SA decreases steeply. In the N₂-pretreatment of CeO₂ at >700 °C, the average con-

version decreases with raising pretreatment temperature. The decrease in the catalytic activity is also caused by the decrease in SA of the samples heated at high temperature. In addition, H₂ used as a carrier gas does not affect the catalytic activity of CeO₂.

Fig. 3 shows TPR profiles of CeO₂ samples treated under different conditions. When the sample reduced at 600 °C are contacted with H₂O at 325 °C for 1 h, it has a reduction peak similar to the original CeO₂ sample (Fig. 3b). The reduction peak at <600 °C decreases with increasing reduction temperature (Fig. 3c and d), and TPR profile at >600 °C is recovered. In addition, the H₂O treatment changes the sample color from gray to yellow. This indicates that the reduced CeO₂ surface is readily oxidized by H₂O at 325 °C.

Table 4
Dehydration of less reactive polyols over CeO₂

Reactant	Conversion (%)	Selectivity ^a
1,2-Propanediol	3.3 ^b	17 (21), 29 (5), 18 (3), 30 (2), 31 (31)
	11.3 ^c	17 (23), 29 (14), 18 (11), 30 (3), 31 (18)
	47.4 ^d	17 (18.7), 29 (19.0), 18 (18.2), 30 (2.2), 31 (4.7)
2-Methyl-1,3-propanediol	6.8 ^b	32 (61), 33 (4), 34 (7), 18 (6), 17 (23)
	48.0 ^c	32 (64.9), 33 (6.4), 34 (8.4), 18 (7.4), 17 (12.0)
	85.4 ^d	32 (36.4), 33 (17.2), 34 (11.4), 18 (13.6), 17 (17.3)
2-Ethyl-1,3-hexanediol	19.0 ^b	35 (54.1), 36 (22.5), 8 (3.6), 1 (3.8)
	40.7 ^c	35 (47.2), 36 (22.1), 8 (7.3), 1 (3.0)
	81.9 ^d	35 (37.3), 36 (18.2), 8 (9.9), 1 (9.2)
1,2,3-Propanetriol	3.9 ^b	31 (50)
	21.6 ^c	31 (36.8)
	49.7 ^d	31 (26.0)

Products: (**1**) butanal; (**8**) 1-butanol; (**17**) 1-propanol; (**18**) propanal; (**29**) propanone; (**30**) 2-propanol; (**31**) 1-hydroxy-2-propanone; (**32**) 2-methyl-2-propen-1-ol; (**33**) 2-methylpropanal; (**34**) 2-methylpropanol; (**35**) 2-ethyl-1-hexen-3-ol; (**36**), 2-ethyl-2-hexen-1-ol.

^a Number in parenthesis indicates the selectivity (mol%) to the product.

^b Reacted at 325 °C.

^c Reacted at 375 °C.

^d Reacted at 425 °C.

Table 5
Effect of pretreatment of CeO₂ on the catalytic reaction of 1,3-butanediol at 325 °C

Pretreatment ^a (°C)	Valence of Ce in CeO _x ^b	Conversion ^c (%)	Selectivity (mol%)		SA ^d (m ² g ⁻¹)	
			3-Buten-2-ol	<i>trans</i> -2-Buten-1-ol		
H ₂	100	4.000	61.6	56.1	35.6	20.4
H ₂	250	4.000	60.0	56.2	34.9	–
H ₂	325	3.994	60.3	56.2	34.9	–
H ₂	500	3.940	59.4	56.1	35.4	20.3
H ₂	600	3.910	57.5	54.5	35.3	18.4
H ₂	700	3.762	41.0	53.9	36.7	9.0
H ₂	800	3.658	29.6	52.3	36.4	2.3
H ₂	900	3.582	10.8	51.8	35.2	2.1
H ₂	325	3.994	61.4 ^e	55.8	35.2	–
H ₂	600	3.910	56.3 ^e	53.9	35.0	–
H ₂	700	3.762	40.0 ^e	54.3	36.5	–
H ₂	800	3.658	29.9 ^e	51.3	36.8	–
N ₂	325	–	58.2	55.9	35.8	–
N ₂	500	–	56.3	56.0	35.7	20.1
N ₂	700	–	58.1	57.5	35.4	17.1
N ₂	800	–	48.4	55.6	34.7	8.4
N ₂	900	–	24.7	56.9	35.2	4.2

^a The pretreatment of catalyst samples was performed at the prescribed temperature for 1 h.

^b Average oxidation number of Ce in CeO_x, calculated from the consumption of H₂ during the TPR process (Fig. 2).

^c The catalytic reaction was performed over 0.3 g of CeO₂ catalyst in N₂ flow of 73 mmol h⁻¹.

^d Specific surface area.

^e The catalytic reaction was carried out in H₂ carrier gas of 73 mmol h⁻¹.

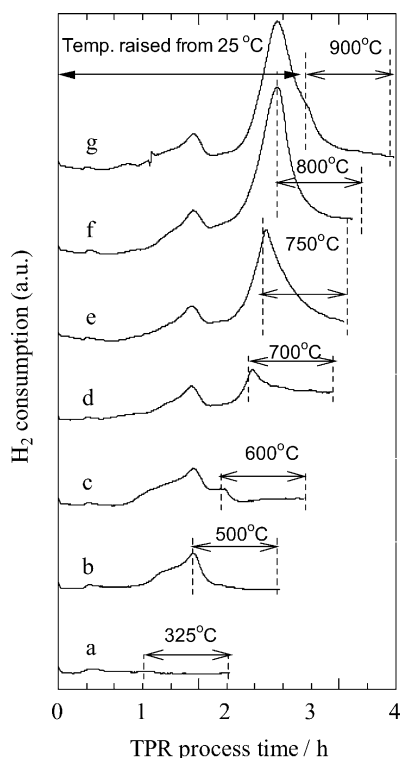


Fig. 2. Stepwise TPR profiles of CeO₂. The TPR was performed at the temperature-rising rate of 5 K min⁻¹ and then the temperature was held at a prescribed temperature for 1 h: (a) 325 °C; (b) 500 °C; (c) 600 °C; (d) 700 °C; (e) 750 °C; (f) 800 °C; (g) 900 °C.

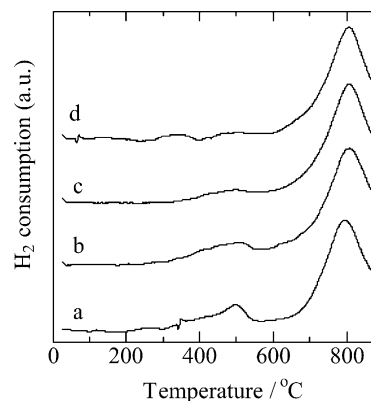


Fig. 3. TPR profiles of CeO₂ treated under different conditions. The TPR was performed at the temperature-rising rate of 5 K min⁻¹ and then the temperature was held at 900 °C for 1 h: (a) fresh CeO₂; (b) treated with H₂O at 325 °C for 1 h after being reduced by H₂ at 600 °C; (c) 700 °C; (d) 800 °C.

4. Discussion

4.1. Reactivity of alcohols over CeO₂

In the dehydration over CeO₂, alcohol reactants are categorized into four types: monoalcohols, 1,3-diols, 1,4-diol, and others. Monoalcohols are less reactive, and they are dehydrogenated into aldehyde and ketone at higher temperatures (Table 1). 1-Butanol is less reactive even at 425 °C, and it produces butanal not olefin: 1-butanol can be converted to 4-heptanone through dimerization of butanal at 450 °C [7,8]. It is noted that further dehydration of 2-buten-1-ol, a product

in the dehydration of 1,3-butanediol, does not proceed over CeO_2 , and that monoalcohols such as 1-butanol and 2-butanol were not dehydrated to butenes over CeO_2 at low temperatures $<375^\circ\text{C}$. 1-Butene is a major product in the dehydration of 2-butanol over CeO_2 at $\geq 375^\circ\text{C}$. It is also known that lanthanide oxides including CeO_2 catalyze Hoffman elimination to produce α -olefin [23].

Diols are more reactive than monoalcohols, and they are dehydrated to either unsaturated alcohols or saturated ketones (Tables 2–4). 1,3-Diols are basically reactive in the dehydration to produce unsaturated alcohols. 1,4-Butanediol has specific reactivity: CeO_2 catalyzes dehydration of 1,4-butanediol to 3-buten-1-ol, which is not further dehydrated to 1,3-butadiene, at 425°C . Polyols such as 1,2- and 2,3-butanediol, and 1,2,3-propanetriol are dominantly dehydrated into ketone through the enol form. Butanone would be directly formed via 2-buten-2-ol in the dehydration of 2,3-butanediol: 3-buten-2-ol is not an intermediate because it is observed as a stable product in the reaction of 1,3-butanediol over CeO_2 (Table 2).

CeO_2 works with different catalytic functions depending on the temperature as well as on the reactant (Tables 1–4). It can be summarized that CeO_2 catalyzes dehydration of 1,3-diols to unsaturated alcohols at $<400^\circ\text{C}$ and dehydration of 1,4-butanediol to 3-buten-1-ol at $>400^\circ\text{C}$. It also catalyzes dehydration of 1,2- and 2,3-diols to aldehyde and ketone.

4.2. Activation of alcohols over CeO_2 and its redox property

We suggested that the catalytic activity of CeO_2 in the activation of alcohols would be correlated with the redox feature [4,8,9]. In the alkylation of phenol with 1-propanol catalyzed by $\text{CeO}_2\text{-MgO}$ at 475°C , it has been suggested that redox sites, not acid sites, activate the alkylating reagent of 1-propanol [4]. A hydrogen atom is eliminated from 1-propanol to produce radical species such as 1-hydroxypropyl radical rather than propoxy radical. The hydrogen atom can reduce Ce^{4+} into Ce^{3+} : Ce^{4+} cation oxidatively eliminates hydrogen from 1-propanol to form proton. The 1-hydroxypropyl radical attacks the electron-rich *ortho*-positions of phenol adsorbed perpendicularly on the weak basic sites in the $\text{CeO}_2\text{-MgO}$ because the α -position of 1-hydroxypropyl radical is slightly positive. A hydroxyl radical is readily eliminated from the alkylated intermediate to produce 2-*n*-propylphenol and water, together with the oxidation of Ce^{3+} to Ce^{4+} .

In the TPR profile (Fig. 2), CeO_2 is severely reduced at $>600^\circ\text{C}$. Both the average oxidation number of Ce and the catalytic activity of CeO_2 in the dehydration of 1,3-diols decreased with raising the reduction temperature above 600°C (Table 5). Because SA also decreases with treatment temperature, the reduced CeO_2 seems to have the intrinsic catalytic activity as active as the non-reduced one: the catalytic activity could be proportional to the SA. Unexpectedly, we still have a question whether the oxidation state of CeO_2 affects

the intrinsic catalytic activity of CeO_2 for the dehydration of 1,3-butanediol or not.

Then, we examined another TPR experiment for samples with different treatment (Fig. 3). Contact of water with the reduced CeO_2 surface regenerates the reduction peak at around 500°C , and it induces the oxidation of Ce^{3+} cations into Ce^{4+} . This is consistent with the reports of Otsuka et al. [24,25]: a reduced CeO_2 powder is oxidized to CeO_2 by water even at 300°C , and the oxidation by water occurs not only on the surface but also in the bulk. The reduction peak at $<600^\circ\text{C}$ would be concerned with surface CeO_2 because reduction at high temperatures reduces both the reduction peak (Fig. 3) and the specific surface area (Table 5). Since the surface Ce^{3+} is readily oxidized to Ce^{4+} by H_2O produced in the dehydration, it is reasonable that the CeO_2 surface is maintained at high oxidation state in the working state of the dehydration.

4.3. Reaction model in the dehydration of 1,3-diol over CeO_2

ZrO_2 and CeO_2 have different catalytic features in dehydration of 4-methylpentan-1-ol, while ZrO_2 is much more acidic and basic than CeO_2 [26]. ZrO_2 has a fluorite (CaF_2) structure similar to CeO_2 , and it also has ability for the dehydration of 1,3-butanediol, while 3-buten-1-ol is formed in addition to 3-buten-2-ol, *trans*-, and *cis*-2-buten-1-ol (Table 2). The product distribution over ZrO_2 is explained by another mechanism that an OH anion is initially eliminated; acidic sites of ZrO_2 probably activate the OH group of 1,3-butanediol.

In contrast, CeO_2 produces only 3-buten-2-ol and 2-buten-1-ol without producing 3-buten-1-ol. If an OH group on the 3-position is eliminated first as an OH anion, 3-buten-1-ol has to be formed together with 2-buten-1-ol. Thus, the product distribution cannot be explained by the acid-catalyzed mechanism mentioned above. We speculate that redox nature of CeO_2 initially activates hydrogen in the 2-position of 1,3-butanediol [13]: the dehydration of 1,3-diols over CeO_2 follows a radical mechanism; a hydrogen atom located on the 2-position is abstracted first, followed by the elimination of an OH radical (Fig. 4). Then, it is reasonable that Ce^{4+} is reducible by the eliminated hydrogen radical in the catalytic cycle.

Here, we have a significant question: even monoalcohols, instead of diols, may be dehydrated into olefin according to the radical mechanism (Fig. 4). Actually, monoalcohols including unsaturated alcohol are less reactive for dehydration (Table 1). Dehydration of 1,3-diol proceeds at temperature as low as 325°C , while much higher temperatures are needed for the activation on monoalcohols. Since 1,3-diols are more stabilized and activated than monoalcohols on the CeO_2 surface, both of the OH groups in 1,3-diol could be interacted with the surface of CeO_2 . We can correct the reaction image of the dehydration of 1,3-diols (Fig. 5). It is remarkable that 2-methyl-1,3-propanediol is less reactive than

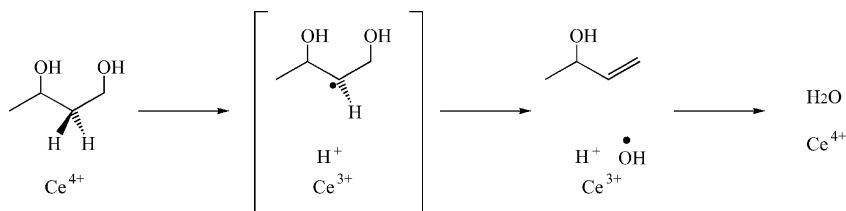
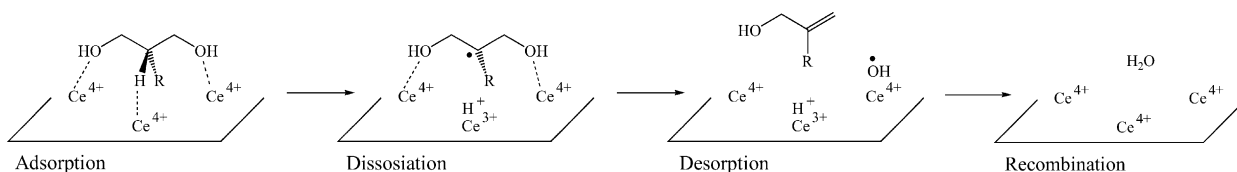


Fig. 4. Possible mechanism of dehydration of 1,3-diol.

Fig. 5. Probable mechanism in the dehydration of 1,3-propanediol over CeO_2 ($R = \text{H}$ or CH_3).

1,3-butanediol and 1,3-propanediol (Table 4). The methyl group on 2-methyl-1,3-propanediol would obstruct the adsorption on the surface because of the steric hindrance (Fig. 5).

There still remains a question: why are not the most acidic protons on the OH groups eliminated from 1,3-diols? The speculative mechanism needs further investigation.

5. Conclusions

The dehydration of monoalcohols and diols catalyzed by CeO_2 was investigated. The dehydration of 1,3- and 2,4-diols produces selectively unsaturated alcohols over CeO_2 at 325 °C. CeO_2 has attractive performance without decay at lower temperatures, while other alcohols such as 1,2- and 1,4-butanediol are activated at higher temperature. In the reaction of monoalcohols such as 1-butanol, 2-butanol, 2-buten-1-ol, and 3-methoxy-1-butanol, they are dehydrogenated into aldehyde and ketone at higher temperatures.

TPR measurement combined with H_2O treatment of the reduced CeO_2 reveals that active CeO_2 surface is maintained at high valence of Ce^{4+} . The redox cycle of Ce^{4+} – Ce^{3+} on the surface would play a role for the dehydration concerning the activation of diols in the form of radicals, as shown in Fig. 5.

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