

Surface-structure sensitivity of CeO₂ for several catalytic reactions

Mika Kobune, Satoshi Sato*, Ryoji Takahashi¹

Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan

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Abstract

Vapor-phase catalytic reactions of several reactants were investigated over CeO₂ with different particle sizes, and the surface-structure sensitivity, i.e. crystal plane dependency, was discussed. The particle size of CeO₂ was regulated by the calcination temperature. In dehydration of 1,4-butanediol and 1,3-butanediol into unsaturated alcohols, and ketonization of propanoic acid, the activities increased with increasing the CeO₂ particle size. CeO₂ {111} facets became predominant on the large particles. This indicates that CeO₂ {111} facets have active sites for the reactions of butanediols and of propanoic acid. Therefore, dehydration of 1,4-butanediol and 1,3-butanediol, and ketonization of propanoic acid are categorized into surface-structure-sensitive reaction. The structure-sensitive reactions have feature that the main product is formed with high selectivity at temperatures lower than 400 °C. In contrast, activities of dehydration of 2-heptanol, methylation of phenol with methanol, and ketonization of propanal and 1-propanol were independent of the CeO₂ particle size. These reactions are categorized into structure-insensitive reaction. © 2007 Elsevier B.V. All rights reserved.

Keywords: CeO₂; Surface-structure sensitivity; Particle size; Crystal face

1. Introduction

Heterogeneous catalytic reactions are classified into two types of reactions: one is the reaction in which the activity of catalyst depends on surface-structure of the catalyst, i.e. surface-structure-sensitive reaction, which is catalyzed by a specific active site located on corner, edge or particular surface of crystallites. The other is the reaction in which the catalytic activity does not depend on surface-structure of the catalyst, i.e. structure-insensitive reaction, which is promoted by all the surface of catalyst. Thus, the catalytic activity proportionally changes with surface area of catalyst. In contrast, relation between the catalytic activity and surface area shows complicated manner in the structure-sensitive reaction. Various structure-sensitive and insensitive reactions have been reported since 1970's. As structure-sensitive reactions, ammonia synthesis [1,2], oxidation of CO [1], methane [3] and propane [4], CO hydrogenation [5,6], and aromatization of hexane [1], over either single crystal metals such as Pt, Rh and Fe or their metal-based catalysts

have been reported. Somorjai et al. reported that Fe (111) and Fe (211) crystal faces are more active than Fe (110) face in ammonia synthesis [1,2]. They also reported that the hexagonal (111) surface dominantly produces benzene in the conversion of *n*-hexane, while the (100) face prefers to catalyze isomerization [1]. In the structure-sensitive reaction, the activity depends on particular facets of single crystal. In contrast, cyclohexane dehydrogenation [7] and ethylene hydrogenation [8] over Pt are structure-insensitive reaction.

Wang et al. observed the growth of CeO₂ particles under hydrothermal conditions, and reported that the surface of the particles in the size range of 3–10 nm was dominated by the {111} and {100} facets [9]. As the particles grew larger, the {100} facets disappeared, and the octahedral shape with flat surfaces, which are {111} facets, dominated the larger CeO₂ particles. A similar observation has been reported in CeO₂ particles calcined at temperatures of 500 and 1000 °C [10]: a well-grown shape with clear edges is observed in the CeO₂ particles calcined at 1000 °C, whereas the shape of particles calcined at 500 °C seems to be more spherical without clear edges.

We have also reported structure-sensitive dehydration of butanediols such as 1,3-butanediol and 1,4-butanediol over CeO₂ with different particle sizes [10,11]. In the dehydration of butanediols over CeO₂, both the conversion and selectivity to unsaturated alcohol increased with increasing the CeO₂ par-

* Corresponding author. Tel.: +81 43 290 3376; fax: +81 43 290 3401.

E-mail address: satoshi@faculty.chiba-u.jp (S. Sato).

¹ Present address: Department of Chemistry, Faculty of Science, Ehime University, Bunkyo, Matsuyama 790-8577, Japan.

ticle size. Because the larger CeO₂ particles are dominated by the {1 1 1} facets, CeO₂ {1 1 1} facets have active sites for the formation of unsaturated alcohols, and the other surfaces catalyze the side reactions such as decomposition of 1,3-butanediol and cyclization of 1,4-butanediol. We have proposed that three Ce cations exposed at an oxygen-defect site of the CeO₂ (1 1 1) surface are the active center for the dehydration of diols [12–14].

We have reported that CeO₂ is an attractive catalyst in *ortho*-selective alkylation of phenol [15–17], and ketone formation through dimerization of alcohols [17–19] and of carboxylic acids [20,21]. Based on our recent results on the reaction of butanediols over CeO₂ with different surface character [10,11], these reactions can be categorized into either surface-structure-sensitive or insensitive reaction. In this paper, we investigated catalytic activity of CeO₂ with different particle sizes in the reaction of various reactants such as 1,3-butanediol, 1,4-butanediol, 2-heptanol, propanoic acid, propanal, 1-propanol, phenol and methanol. We carried out the catalytic reactions at a constant surface area of CeO₂ catalyst to evaluate intrinsic activity of the catalyst, and discussed CeO₂–surface-structure sensitivity, i.e. crystal plane dependency, of the reactions.

2. Experimental

2.1. Samples and characterization

Organic reactants such as 1,4-butanediol, 1,3-butanediol, propanoic acid, propanal, 1-propanol, phenol and methanol were purchased from Wako Pure Chemical Industries, Ltd., Japan. 2-Heptanol was purchased from Tokyo Kasei Kogyo Co., Ltd., Japan. CeO₂ samples were supplied by Daiichi Kigenso Co. Ltd., Japan. Five CeO₂ samples were prepared by calcinating a CeO₂ precursor at 500, 600, 800, 900 and 1000 °C. These samples are the same as those reported in the previous work [10].

Specific surface area (SA) of catalyst was calculated by the BET method using the N₂ adsorption isotherm at –196 °C. Particle size of CeO₂, *D*, was calculated by the following equation, assuming that the particles are spherical:

$$D = \frac{6}{d \text{ SA}} \quad (1)$$

where *d* is the density of CeO₂, *d* = 7.1 g cm^{–3}. Table 1 summarizes the SA and *D* of CeO₂ samples used in this work calcined at

Table 1
CeO₂ samples used in this study and their physical properties

Calcination (°C)	SA (m ² g ^{–1}) ^a	<i>D</i> (nm) ^b	Catalyst (g) ^c
500	140.8	6.0	0.15
600	73.9	11.4	0.29
800	41.9	20.2	0.50
900	22.6	37.4	0.93
1000	13.0	65.0	1.62

^a Specific surface area calculated by BET method using N₂ adsorption isotherm at –196 °C, reported in Ref. [10].

^b Particle size of CeO₂ is calculated by Eq. (1).

^c Catalyst weight used in this study.

temperatures between 500 and 1000 °C [10]. The SA decreases and the *D* increases with raising the calcination temperature. The *D* values are in the range of 6.0–65.0 nm. Transmission electron microscopy (TEM, JEM-2010, JEOL) was employed to observe the morphology of crystallites in the CeO₂ samples calcined at 600, 800 and 900 °C.

2.2. Catalytic reactions

All reactions were carried out in a fixed-bed flow reactor under the atmospheric pressure of N₂ at the flow rate of 30 cm³ min^{–1}. Prior to the reaction, a CeO₂ sample was preheated in the N₂ gas at the reaction temperature for 1 h. Table 1 also shows catalyst weight of each sample used in this study. Catalyst weight was calculated in order that the surface area of the catalyst placed in the reactor became constant at 21.1 m². Reactants were fed into the reactor at the following liquid flow rate: propanal and 2-heptanol, 1.7 cm³ h^{–1}; 1-propanol, 2.5 cm³ h^{–1}; 1,3-butanediol, 1,4-butanediol and propanoic acid, 6.5 cm³ h^{–1}. In the alkylation of phenol with methanol, a mixture of phenol and methanol was fed at flow rate of 6.5 cm³ h^{–1} where the mole ratio of mixture solution is methanol/phenol = 20. A reaction temperature for each reactant was prescribed between 325 and 450 °C in order to obtain a low conversion (10–30%) over the sample of CeO₂ calcined at 500 °C.

Effluent collected periodically was analyzed by gas chromatography (GC-8A, Shimadzu, Japan) with a capillary column of Inert Cap WAX (60 m, GL Science Inc., Japan) over temperature range controlled from 40 to 210 °C at a heating rate of 8 K min^{–1}. The conversion of reactant and the selectivity to each product were averaged in the initial 2.5 h, when a liquid flow rate was 6.5 cm³ h^{–1}. When a liquid flow rate was 1.7 or 2.5 cm³ h^{–1}, they were averaged in the initial 5 h.

In the dehydration of butanediols, the conversion of butanediol is defined as the consumption of butanediol. The selectivity to each product is defined as a carbon-based molar selectivity: the selectivity to a C4 product, *S*_{C4}, is calculated from the equation: *S*_{C4} = (product/mol)/(consumed butanediol/mol); the selectivity to a C3 product, *S*_{C3}, is calculated from the equation: *S*_{C3} = (3/4)(product/mol)/(consumed butanediol/mol); the selectivity to a C2 product, *S*_{C2}, is calculated from the equation: *S*_{C2} = (2/4)(product/mol)/(consumed butanediol/mol); the selectivity to a C1 product, *S*_{C1}, is calculated from the equation: *S*_{C1} = (1/4)(product/mol)/(consumed butanediol/mol).

In the dehydration of 2-heptanol, conversion of 2-heptanol is defined as the consumption of 2-heptanol. In this reaction, all products are C7 compounds. The selectivity to each product is calculated from the equation: *S* = (product/mol)/(consumed 2-heptanol/mol).

In the ketonization of propanoic acid, propanal and 1-propanol, the conversion is defined as the consumption of reactant. In the reaction, 3-pentanone is formed by decarboxylation. The selectivity to each product is defined as a reactant-based selectivity: a C5 or C6 product is produced by two C3 reactants. The selectivity to a C5 or C6 product, *S*_{C5} or *S*_{C6} is calculated from the equation: *S*_{C5}, *S*_{C6} = 2(product/mol)/(consumed reactant/mol); a C7 or C8

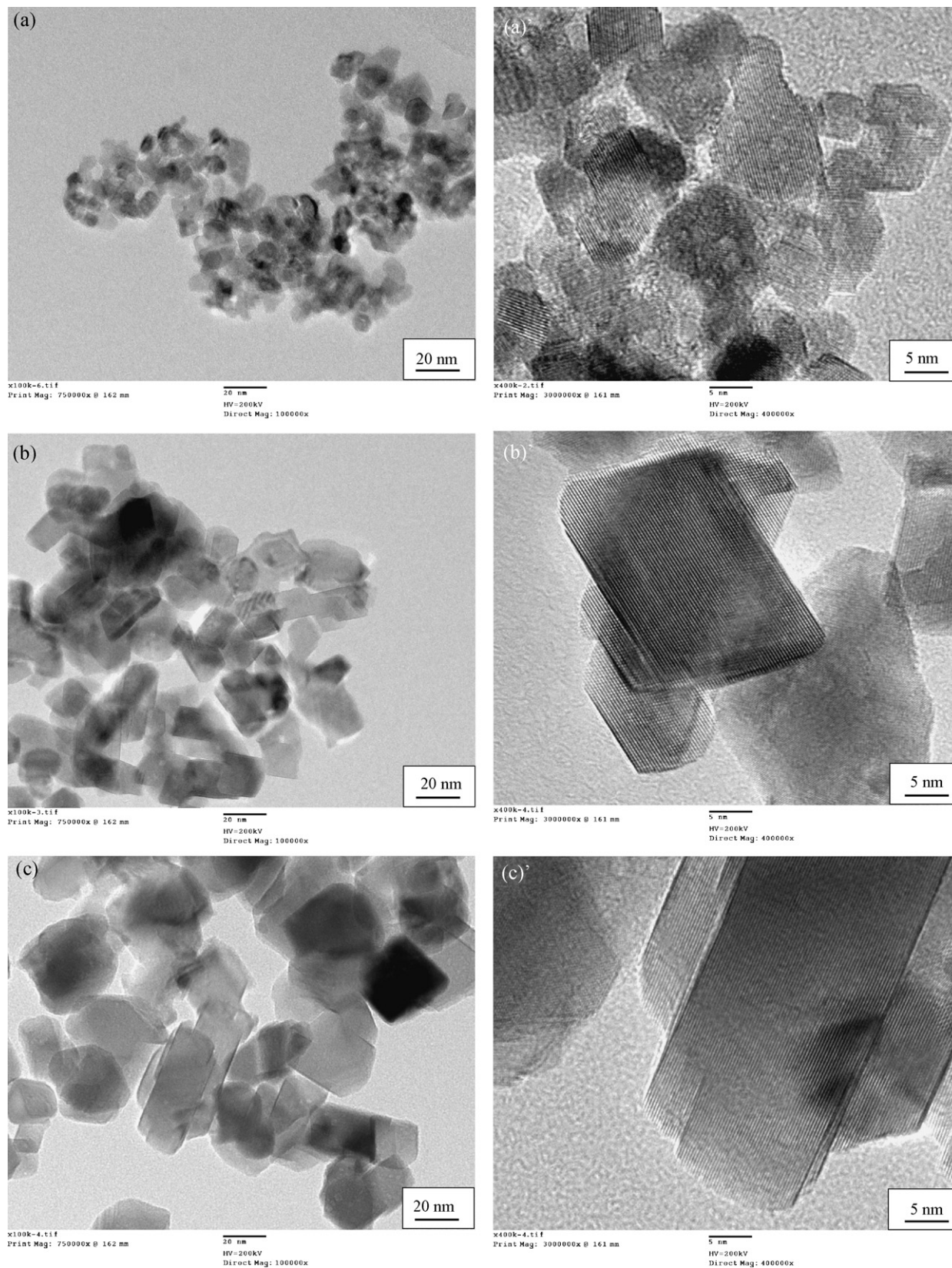


Fig. 1. TEM photographs of CeO₂: (a, a') calcined at 600 °C; (b, b') 800 °C; (c, c') 900 °C.

product is produced by three C3 reactants. The selectivity to a C7 or C8 product, S_{C7} or S_{C8} is calculated from the equation: $S_{C7}, S_{C8} = 3(\text{product/mol})/(\text{consumed reactant/mol})$; a C4 product is produced by a C3 reactant and a C1 intermediate. The selectivity to a C3 or C4 product, S_{C3}, S_{C4} is calculated from the equation: $S_{C3}, S_{C4} = (\text{product/mol})/(\text{consumed reactant/mol})$.

In the alkylation of phenol with methanol, the conversion and selectivity are defined as a phenol-based. The conversion is consumption of phenol. The selectivity to each product, S_i , is calculated from the equation: $S_i = (\text{product/mol})/(\text{consumed phenol/mol})$.

3. Results

3.1. Characterization of CeO_2

Fig. 1 shows TEM photographs of CeO_2 particles calcined at 600, 800 and 900 °C. TEM photographs of CeO_2 particles at 500 and 1000 °C have been shown in Fig. 2 of Ref. [10]. In the samples, aggregation of crystallites forming secondary particles rarely occurs, and the crystallites seem to expose most of their outer surface. The crystallite size increases with increasing calcination temperature. This change is consistent with the change in particle size, D (Table 1), which is geometrically calculated from specific surface area assuming a spherical particle. The agreement between TEM crystallite size and D also supports that most of crystallite surfaces are exposed. Since the growth of the CeO_2 crystallites is accompanied with the change in their shape, particles with clear sharp edges and flat surfaces became dominant with increasing the calcination temperature.

Wang et al. observed that the large CeO_2 particles prepared under hydrothermal conditions are dominated by octahedral

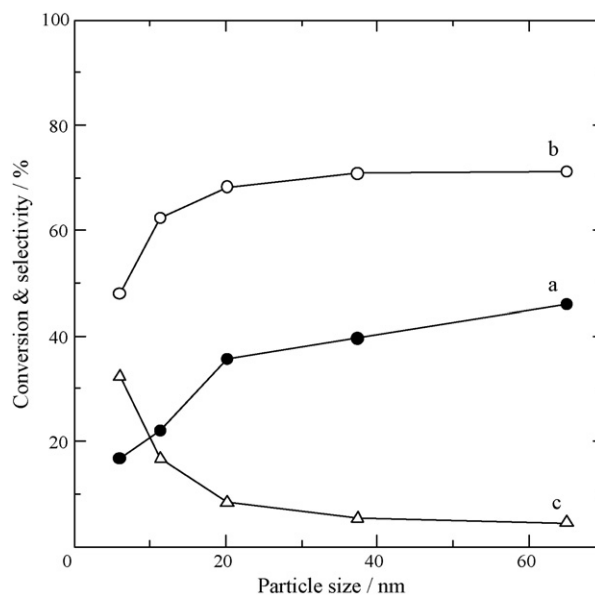


Fig. 2. Changes in conversion and selectivity in the dehydration of 1,4-butanediol over CeO_2 with different particle sizes at 375 °C. (a) Conversion of 1,4-butanediol, (b) selectivity to 3-buten-1-ol, and (c) selectivity to THF.

shape with flat surfaces composed of $\{111\}$ facets with decrease in $\{100\}$ facets [9]. Flat surfaces in TEM photographs would be $\{111\}$ facets, as shown in Fig. 1c. As the particles became larger, the $\{100\}$ facets disappeared. The large CeO_2 particles are dominated by $\{111\}$ facets.

3.2. Dehydration of butanediols

Table 2 summarizes the conversion and selectivity in the dehydration of 1,4-butanediol (375 °C) and 1,3-butanediol (325 °C) over CeO_2 with different particle sizes. Here, the

Table 2
Dehydration of butanediols over CeO_2

D (nm)	Conversion (%)	Selectivity (mol%) ^a			STY ($\text{mmol m}^{-2} \text{h}^{-1}$) ^b
		3-Buten-1-ol	THF	GBL	
1,4-Butanediol (375 °C) ^c					
6.0	16.7	48.0	32.4	8.9	0.29
11.4	22.0	62.3	16.7	7.6	0.52
20.2	35.7	68.2	8.4	5.8	0.97
37.4	39.6	70.8	5.4	5.3	1.10
65.0	46.0	71.2	4.5	4.6	1.32
D (nm)	Conversion (%)	Selectivity (mol%) ^d			STY ($\text{mmol m}^{-2} \text{h}^{-1}$) ^e
		3-Buten-2-ol	2-Buten-1-ol	MEK + MVK	
1,3-Butanediol (325 °C) ^c					
6.0	25.2	49.6	34.4	9.8	0.72
11.4	51.9	55.0	36.4	5.3	1.62
20.2	59.0	59.2	36.7	2.2	1.94
65.0	82.2	60.0	36.5	1.7	2.72

^a THF, tetrahydrofuran; GBL, γ -butyrolactone. Other by-products are 2-buten-1-ol and 1-butanol.

^b Space time yield (STY) of unsaturated alcohols: 3-buten-1-ol and 2-buten-1-ol.

^c Conversion and selectivity were averaged in the initial 2.5 h. $F = 6.5 \text{ cm}^3 \text{ h}^{-1}$.

^d MEK, butanone; MVK, 3-buten-2-one. Other by-products are propanone, ethanol, methanol, 1-butanol, 2-butanol, 3-buten-1-ol and butanal.

^e STY of unsaturated alcohols: 3-buten-2-ol, 2-buten-1-ol and 3-buten-1-ol.

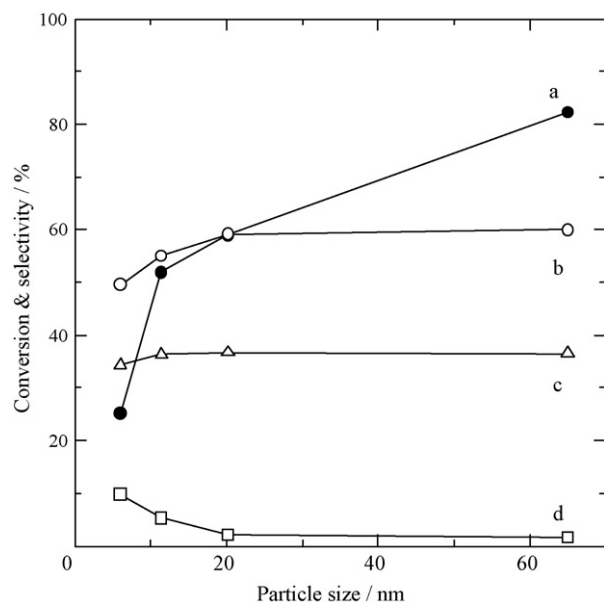


Fig. 3. Changes in conversion and selectivity in the dehydration of 1,3-butanediol over CeO₂ with different particle sizes at 325 °C. (a) Conversion of 1,3-butanediol, (b) selectivity to 3-buten-2-ol, (c) selectivity to 2-buten-1-ol, and (d) selectivity to MEK + MVK.

difference in the reaction temperature between the reactions reflects the reactivity of each reactant. Conversion and selectivity to major products are also plotted in Figs. 2 and 3 for the reaction of 1,4-butanediol and 1,3-butanediol, respectively. In the dehydration of 1,4-butanediol, a major product is 3-buten-1-ol with by-products such as tetrahydrofuran (THF), γ -butyrolactone (GBL), *cis*- and *trans*-2-buten-1-ol, and 1-butanol. The conversion increases with increasing the CeO₂ particle size, it reaches a maximum value of 46.0% at 65.0 nm. The selectivity to 3-buten-1-ol increases with increasing the CeO₂ particle size. In contrast, selectivity to THF decreases with increasing the CeO₂ particle size. In the dehydration of 1,3-butanediol, the major products are 3-buten-2-ol, *cis*- and *trans*-2-buten-1-ol with by-products such as butanone (MEK), 3-buten-2-one (MVK), propanone and ethanol. The conversion of 1,3-butanediol increases with increasing the CeO₂ particle size, it reaches a maximum value of 82.2% at 65.0 nm. The selectivity to 3-buten-2-ol or 2-buten-1-ol also increases with increasing the CeO₂ particle size, while the selectivity to MEK and MVK decreases.

Table 3
Dehydration of 2-heptanol over CeO₂ at 375 °C

<i>D</i> (nm)	Conversion (%) ^a	Selectivity (mol%) ^a			STY (mmol m ⁻² h ⁻¹) ^b
		1-Heptene	2-Heptene	2-Heptanone	
6.0	25.4	59.7	8.9	31.4	0.099
11.4	38.4	65.2	12.0	22.8	0.168
20.2	37.7	67.5	12.6	19.9	0.172
37.4	35.3	62.4	13.1	24.5	0.151
65.0	38.4	55.9	12.1	32.0	0.149

^a Conversion and selectivity were averaged in the initial 5 h, $F = 1.7 \text{ cm}^3 \text{ h}^{-1}$.

^b STY of heptenes: 1-heptene and 2-heptene.

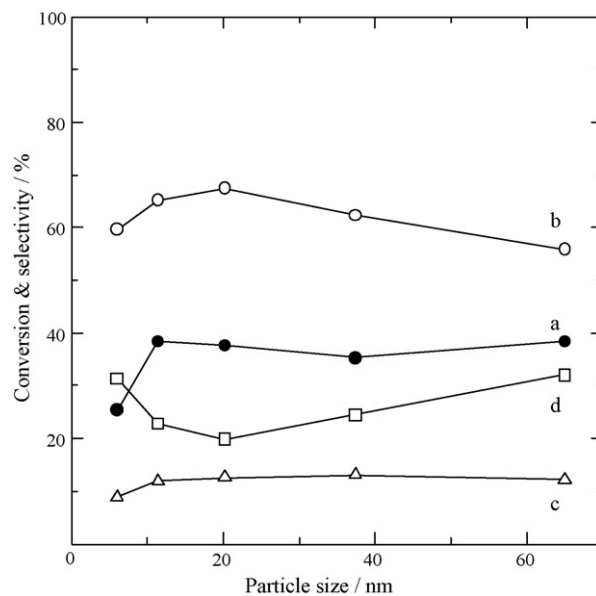


Fig. 4. Changes in conversion and selectivity in the dehydration of 2-heptanol over CeO₂ with different particle sizes at 375 °C. (a) Conversion of 2-heptanol, (b) selectivity to 1-heptene, (c) selectivity to 2-heptene, and (d) selectivity to 2-heptanone.

Space-time yield (STY/mm² h⁻¹) is defined as a formation rate of major products per unit surface area. The STY data is also listed in the last column of Table 2. For example, 1.3 mmol of unsaturated alcohols was produced over a unit surface area for an hour in the dehydration of 1,4-butanediol over CeO₂ with particle size of 65.0 nm, when a reactant was fed into the reactor at 73.6 mmol h⁻¹ (6.5 cm³ h⁻¹).

3.3. Dehydration of 2-heptanol

Table 3 lists the conversion and selectivity in the dehydration of 2-heptanol over CeO₂ with different particle sizes at 375 °C. In the dehydration of 2-heptanol, a major product is 1-heptene with by-products such as 2-heptanone and, *cis*- and *trans*-2-heptene. Fig. 4 shows changes in conversion of 2-heptanol and selectivity to major products with the CeO₂ particle size. The conversion is almost constant, about 37% at 11.4–65.0 nm, except for 6.0 nm. Selectivity slightly varies with the CeO₂ particle size: the selectivity to 1-heptene is maximized at 20.2 nm, 67.5%, and the selectivity to 2-heptanone

Table 4
Ketonization of propanoic acid, propanal and 1-propanol over CeO₂

Reactant	<i>D</i> (nm)	Conversion (%)	Selectivity (mol%)		STY (mmol m ⁻² h ⁻¹) ^a
			3-Pentanone	Butanone	
Propanoic acid (350 °C) ^b	6.0	10.0	99.9	0.1	0.20
	11.4	26.6	99.8	0.2	0.55
	20.2	36.3	99.7	0.3	0.75
	65.0	49.7	99.8	0.2	1.02

Reactant	<i>D</i> (nm)	Conversion (%)	Selectivity (mol%)				STY (mmol m ⁻² h ⁻¹) ^a
			3-Pentanone	Ketones ^c	1-Propanol	Aldehydes ^d	
Propanal (400 °C) ^e	6.0	16.1	48.5	23.3	5.0	11.4	0.043
	11.4	21.9	43.4	28.0	4.4	13.4	0.053
	20.2	19.3	34.4	22.1	8.3	21.1	0.037
	37.4	21.8	27.4	23.9	8.2	19.4	0.033
	65.0	28.8	26.8	27.0	5.8	16.8	0.043

Reactant	<i>D</i> (nm)	Conversion (%)	Selectivity (mol%)				STY (mmol m ⁻² h ⁻¹) ^a
			3-Pentanone	Ketones ^f	Alcohols ^g	Propanal	
1-Propanol (450 °C) ^h	6.0	21.3	63.6	8.9	15.8	5.7	0.101
	11.4	23.9	62.3	13.7	13.0	4.2	0.118
	20.2	25.2	62.5	16.2	8.8	5.9	0.124
	65.0	18.2	56.7	19.6	9.7	6.2	0.081

^a STY of 3-pentanone.

^b Conversion and selectivity were averaged in the initial 2.5 h, $F = 6.5 \text{ cm}^3 \text{ h}^{-1}$.

^c Ketones: 2-methyl-3-pentanone, 3-heptanone, 4-methyl-3-heptanone, 2-butanone, 3-methyl-2-butanone.

^d Aldehydes: 2-methylpropanal, 2-methylpentanal, 2-methyl-2-pentenal.

^e Conversion and selectivity were averaged in the initial 5 h, $F = 1.7 \text{ cm}^3 \text{ h}^{-1}$.

^f Ketones: 2-methyl-3-pentanone, 3-heptanone, 4-methyl-3-heptanone, 2-butanone.

^g Alcohols: 3-pentanol, 2-methylpentanol, methanol, 2-methylpropanol.

^h Conversion and selectivity were averaged in the initial 5 h, $F = 2.5 \text{ cm}^3 \text{ h}^{-1}$.

that is a dehydrogenation product is minimized at 20.2 nm, 19.9%.

3.4. Ketonization of propanoic acid, propanal and 1-propanol

Table 4 summarizes the conversion and selectivity in the ketonization of propanoic acid (350 °C), propanal (400 °C) and 1-propanol (450 °C) over CeO₂ with different particle sizes. In the ketonization of propanoic acid, a major product is 3-pentanone with high selectivity of >99%. A small amount of butanone was observed as a by-product. Fig. 5 shows change in conversion of propanoic acid and selectivity to 3-pentanone with the CeO₂ particle size. The conversion of propanoic acid increases with increasing the CeO₂ particle size, and it reaches a maximum value of 49.7% with maintaining high selectivity to 3-pentanone.

In the ketonization of propanal, the major product is also 3-pentanone with by-products such as 4-methyl-3-heptanone, 2-methylpropanal, 3-heptanone, 1-propanol and 2-methyl-3-pentanone (Table 4). The conversion of propanal moderately increases with increasing the CeO₂ particle size. The selectivity to 3-pentanone decreases with increasing the CeO₂ particle size. In the reaction, there are several unknown products, which could be formed by step-wise condensation, and the selectivity to the

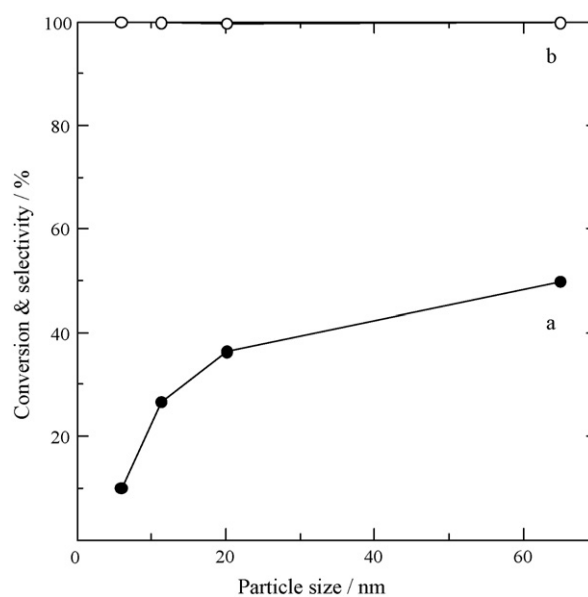


Fig. 5. Changes in conversion and selectivity in the ketonization of propanoic acid over CeO₂ with different particles sizes at 350 °C. (a) Conversion of propanoic acid and (b) selectivity to 3-pentanone.

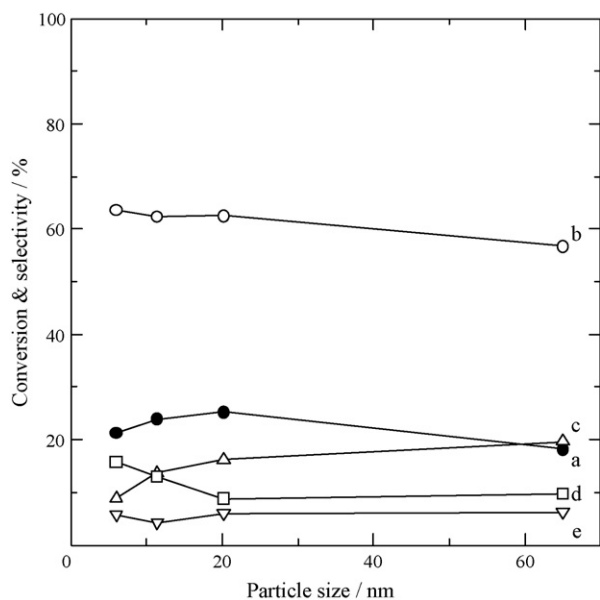


Fig. 6. Changes in conversion and selectivity in the ketonization of 1-propanol over CeO_2 with different particle sizes at 450°C . (a) Conversion of 1-propanol, (b) selectivity to 3-pentanone, (c) selectivity to ketones except 3-pentanone, (d) selectivity to alcohols, and (e) selectivity to propanal.

unknown products increases with increasing the CeO_2 particle size (data not shown).

In the ketonization of 1-propanol, a major product is 3-pentanone with by-products such as 3-pentanol, propanal, 3-heptanone, 4-methyl-3-heptanone and 2-methyl-3-pentanone (Table 4). Fig. 6 shows change in conversion of 1-propanol and selectivity to 3-pentanone with the CeO_2 particle size. Level of the conversion of 1-propanol and the selectivity to main products is almost constant at the different particle sizes.

3.5. Methylation of phenol

Table 5 lists the conversion and selectivity in the alkylation of phenol with methanol over CeO_2 at 450°C . In the alkylation of phenol, a major product is *o*-cresol with by-products such as 2,6-xyleneol and anisole. Fig. 7 shows changes in conversion of phenol and selectivity to the by-products with the CeO_2 particle size. The values of conversion and selectivity are almost constant at the different particle sizes.

Table 5
Alkylation of phenol with methanol over CeO_2 at 450°C

<i>D</i> (nm)	Conversion (%) ^a	Selectivity (mol%) ^a			STY ($\text{mmol m}^{-2} \text{h}^{-1}$) ^b
		<i>o</i> -Cresol	2,6-Xyleneol	Anisole	
6.0	28.7	85.3	9.4	3.6	0.084
11.4	33.0	85.7	9.0	4.0	0.097
20.2	31.9	87.7	7.6	3.8	0.096
37.4	36.1	88.9	6.5	2.5	0.110
65.0	37.4	88.4	7.5	2.6	0.113

^a Conversion and selectivity were averaged in the initial 2.5 h, $F = 6.5 \text{ cm}^3 \text{ h}^{-1}$. Phenol: methanol = 1:20 (molar ratio).

^b STY of *o*-cresol.

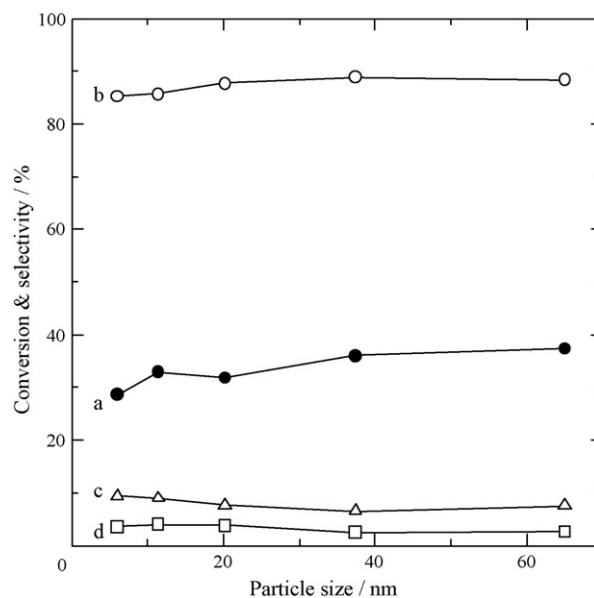


Fig. 7. Changes in conversion and selectivity in the alkylation of phenol with methanol over CeO_2 with different particle sizes at 450°C . (a) Conversion of phenol, (b) selectivity to *o*-cresol, (c) selectivity to 2,6-xyleneol, and (d) selectivity to anisole.

4. Discussion

4.1. Dehydration of alcohols

In the structure-insensitive reaction, we can expect the proportional relation between the catalytic activity and surface area of pure CeO_2 . In this work, we carried out the reactions using catalyst with the same surface area by adjusting catalyst weight for the CeO_2 with different particle sizes. If a reaction is structure-insensitive, the catalytic activity is not affected by the particle size of CeO_2 . On the other hand, growth of CeO_2 particles enhances the formation of clear facets, as shown in Fig. 1. This change is related to the change in the surface density of (1 1 1) face. That is, the density of (1 1 1) face increases with increasing the particle size. If a reaction is promoted by a specific surface configuration, i.e. if the reaction is structure-sensitive, the change in such surface-structure with increasing the particle size will affect the reaction.

Fig. 8 shows relative STY of main products in the reactions over CeO_2 . A relative STY was calculated the STY based on the

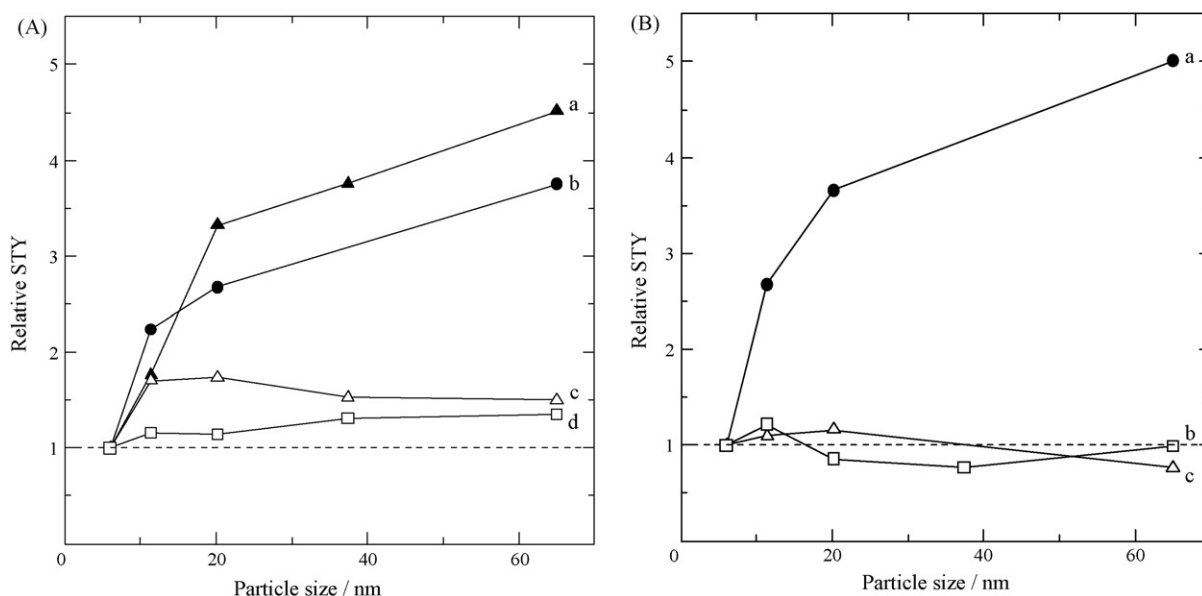


Fig. 8. Relative STY of main products in various reactions over CeO₂. A: (a) STY of unsaturated alcohols in the dehydration of 1,4-butanediol; (b) STY of unsaturated alcohols in the dehydration of 1,3-butanediol; (c) STY of heptenes in the dehydration of 2-heptanol; (d) STY of *o*-cresol in the alkylation of phenol with methanol. B: STY of 3-pentanone in the ketonization of (a) propanoic acid, (b) propanal and (c) 1-propanol.

value of CeO₂ with the *D* of 6.0 nm. In the dehydration of 1,4-butanediol, the relative STY of unsaturated alcohols increases by ca. 4.5 times with increasing CeO₂ particle size (Fig. 8A(a)). In the dehydration of 1,3-butanediol, relative STY also increases by ca. 3.8 times with increasing CeO₂ particle size (Fig. 8A(b)). The reaction was carried out under the same surface area of catalyst used, and activity based on unit surface area was improved by the calcination at high temperature. This means that the dehydration of butanediols is catalyzed by {1 1 1} facets of CeO₂. That is, the dehydration of butanediols is a structure-sensitive reaction over CeO₂.

We have already reported a structure-sensitive catalysis in the dehydration of butanediols over CeO₂ [10]. In order to compare the previous results with the present ones, we re-calculated the conversion of 1,4-butanediol per unit surface area from the data of Table 3 in Ref. [10]. Fig. 9 shows the conversion per unit surface area with different CeO₂ particle sizes relative to the value of CeO₂ with the *D* of 6.0 nm. Although we had used a constant weight of catalyst in the experiment, the activity in dehydration of 1,4-butanediol based on unit surface area increased greatly with increasing CeO₂ particle size (Fig. 9a): the relative conversion increases by ca. 6.8 times with increasing CeO₂ particle size. The relative conversion based on unit surface area for the large particles must be overestimated. This is because the relative conversion is divided by small specific surface area. Intrinsic activity should be estimated at a constant surface area, as demonstrated in this work. On the other hand, there could be a possibility that underestimation in this work: the conversion should be lowered at the level as low as 10% in the catalyst with small particles.

In the dehydration of 2-heptanol, relative STY of heptenes is almost constant at 11.4–65.0 nm, except for 6.0 nm (Fig. 8A(c)). We do not know the reason why the STY of the 6.0-nm sample is less active, but the catalyst may contain amorphous compo-

nent or not be fully dehydrated. However, the selectivities to 1-heptene and 2-heptanone are slightly changed with the CeO₂ particle size (Fig. 4). Although the change in the selectivity may remind us of the structure-sensitive reaction, we can judge that the dehydration of 2-heptanol is structure-insensitive because of the constant conversion at 11.4–65.0 nm.

We can summarize that the dehydration of alcohols is surface-structure-sensitive for the reaction of diols, and insensitive for the reaction of mono alcohols. As demonstrated previously [10], a diol molecule preferentially adsorbs on defect sites on CeO₂

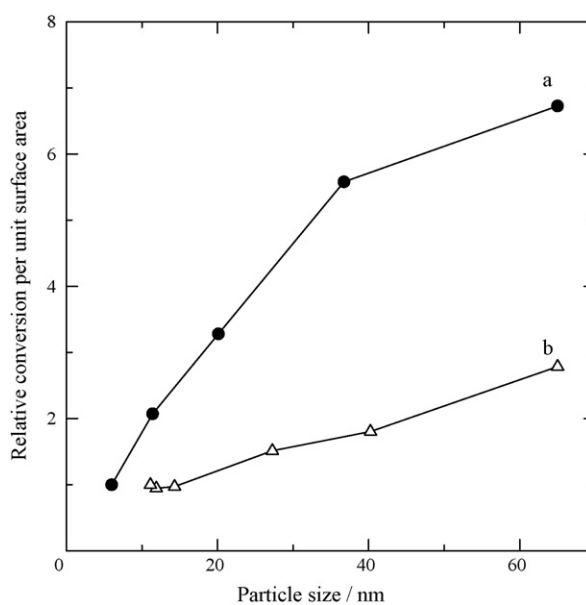


Fig. 9. Relative conversion per surface area with CeO₂ particle size. (a) Dehydration of 1,4-butanediol. The data cited from Ref. [10]. (b) Methylation of phenol. The data cited from Ref. [15].

{1 1 1} surface. This would be the origin of the difference in the reaction trend.

4.2. Alkylation of phenol with methanol

In the methylation of phenol, relative STY of *o*-cresol is almost constant at different CeO₂ particle sizes (Fig. 8A(d)). Because the activity based on unit surface area changes little, we can judge that the methylation of phenol does not depend on surface-structure of CeO₂ particles, and the reaction is structure-insensitive.

On the other hand, we have tested several CeO₂ catalysts with different specific surface areas in the methylation of phenol [15]. In order to check the results, we re-calculated relative conversion of phenol per unit surface area and particle size from the data of Table 1 in Ref. [15]. The relative conversion of phenol per unit surface area slightly increased with increasing CeO₂ particle size (Fig. 9b). The result does not seem to agree with the present results. However, we have to notice the difference in the nature of CeO₂ used. Although the specific surface area of CeO₂ was systematically controlled by changing calcination temperature in the present work, the samples used in the pioneering work were prepared by thermal decomposition of different precursors such as acetate, nitrate, carbonate, and oxalate [15]. CeO₂ prepared by such method would have different surface morphology and/or contain impurities depending on the precursors used. We need to observe the morphology of the samples to discuss the surface-structure sensitivity.

4.3. Ketonization of carboxylic acid, aldehyde and alcohol

Fig. 8B shows relative STY of 3-pentanone in ketonization of propanoic acid, propanal and 1-propanol. In the ketonization of propanoic acid, relative STY of 3-pentanone increases by ca. 5 times with increasing CeO₂ particle size (Fig. 8B(a)). In the ketonization of propanal and 1-propanol, relative STYs of 3-pentanone are constant (Fig. 8 B(b and c)). These results suggest that the formation of 3-pentanone from propanoic acid proceeds via different reaction mechanism from the reaction of 1-propanol and propanal. The formation of 3-pentanone from 1-propanol and propanal proceeds via aldol addition of propanal into 3-hydroxy-2-methylpentanal, followed by the decomposition into 3-pentanone [19]. In contrast, the formation of 3-pentanone from propanoic acid proceeds via the following mechanism [20]: first, surface carboxylates are formed, and an α -hydrogen atom is abstracted to form an anion radical, which is then added to another carboxylate to produce a β -ketocarboxylic acid, followed by decarboxylation to form a ketone. Thus, the formation of 3-pentanone from propanoic acid via β -ketocarboxylic acid depends on the CeO₂ particle size. In contrast, the ketonization from propanal via aldol is independent of the CeO₂ particle size. This suggests that CeO₂ {1 1 1} facets have active sites for the ketonization via β -ketocarboxylic acid, and that the active sites of ketonization via aldol addition are not related to the facets of CeO₂ surface.

Stubenrauch et al. investigated the formation of propanone from acetic acid over crystal surfaces of CeO₂ [22]. Propanone

is formed from acetic acid on CeO₂ (1 1 1) plane, whereas the (1 0 0) plane rarely catalyzes the ketone formation. The difference indicates that the catalytic activity depends on the CeO₂ crystal faces.

4.4. Structure-sensitive and insensitive reactions

As described above, dehydration of butanediols (325, 375 °C) and ketonization of propanoic acid (350 °C) are structure-sensitive reactions. The catalytic activities for these reactions increase with the increase in the exposure ratio of CeO₂ {1 1 1} facets. In contrast, dehydration of 2-heptanol (375 °C), methylation of phenol (450 °C), and ketonization of propanal (400 °C) and 1-propanol (450 °C) are structure-insensitive reactions. It is obvious that structure sensitivity is dependent on the reactant. We should notice that structure-sensitive reactions have some features: one is that structure-sensitive reactions proceed at lower temperatures, 325–375 °C. In contrast, the structure-insensitive reactions proceed at relatively high temperatures, 375–450 °C. The other feature is that a structure-sensitive reaction proceeds with high selectivity to the major product. We can judge that a reaction with high selectivity to a specific product over CeO₂ at lower temperatures would be a structure-sensitive reaction.

5. Conclusions

Vapor-phase catalytic reactions of various reactants were investigated over CeO₂ with different particle sizes. The particle size of CeO₂ was controlled by the calcination temperature. In the dehydration of 1,4-butanediol and 1,3-butanediol, and ketonization of propanoic acid, the activities increased with increasing the CeO₂ particle size. These reactions can be categorized into structure-sensitive reaction. In contrast, dehydration of 2-heptanol, methylation of phenol, and ketonization of propanal and 1-propanol are structure-insensitive reaction.

In the structure-sensitive reactions, the catalytic activity increases with increasing the particle size. Since CeO₂ {1 1 1} facets become predominant on the large particles, CeO₂ {1 1 1} facets have the active sites for the ketonization of carboxylic acid and dehydration of butanediol into unsaturated alcohol. These structure-sensitive reactions have feature that the major product is formed at high selectivity at lower temperatures. It is concluded that a reaction having these feature over CeO₂ is the structure-sensitive reaction.

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