

Synthesis of 3-buten-1-ol from 1,4-butanediol over ZrO₂ catalyst

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Abstract

Dehydration of 1,4-butanediol was investigated over ZrO₂ at temperatures of 325–375 °C. Modification of ZrO₂ with a small amount of sodium hydroxide greatly enhanced the selectivity to 3-buten-1-ol. Temperature-programmed desorption of adsorbed NH₃ and CO₂ elucidated acidity and basicity of the catalysts, respectively. The number of acidic sites on the ZrO₂ decreased with increasing Na content, and disappeared at Na content of 1.0 mol%, whereas the number of basic sites increased with increasing Na content. In the relationship between Na content and the selectivity to products, selectivities to tetrahydrofuran and γ -butyrolactone simply increased with the number of acidic and basic sites, respectively. However, the selectivity to 3-buten-1-ol was maximized at an appropriate Na content. 3-Butan-1-ol is possibly formed by acid–base-concerted catalysis of monoclinic ZrO₂ in the dehydration of 1,4-butanediol.

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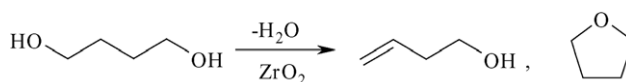
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1. Introduction

Recently, we have reported that homoallyl alcohol such as 3-buten-1-ol is produced in the dehydration of 1,4-butanediol over pure CeO₂ at temperatures of 400–425 °C [1]. 3-Buten-1-ol is synthesized with the maximum selectivity of 68 mol% and the yield of 60% at 400 °C. In the reaction, however, consecutive reactions such as isomerization of 3-buten-1-ol, dehydrogenation and hydrogenation proceed. CeO₂ also catalyzes the formation of allylic alcohols from 1,3-diols at 325 °C [2–4]: 3-buten-2-ol and 2-buten-1-ol are produced with the sum of the selectivity >99 mol% from 1,3-butanediol. 1,4-Butanediol, however, is rarely dehydrated to 3-buten-1-ol over CeO₂ at such low temperature of 325 °C [1].

In the latest paper, we have reported that ZrO₂ with monoclinic crystal phase also catalyzes the dehydration of 1,4-butanediol into 3-buten-1-ol at 325–375 °C [5]. In the dehydration, tetrahydrofuran (THF) is competitively produced, while other by-products such as 2-buten-1-ol, 2-butenal, and 1-butanol, which are observed over CeO₂, are suppressed over ZrO₂ at 325 °C. The selectivity to 3-buten-1-ol over the ZrO₂,

however, is lower than that over CeO₂ because of a moderate amount of THF produced. 1,4-Butanediol is readily dehydrocyclized into THF over solid acids such as SiO₂–Al₂O₃, Al₂O₃ [1], cation exchange resin [6], and heteropoly acids [7]. Thus, we speculated that acid–base property of ZrO₂ influences the selectivity to products in the dehydration of 1,4-butanediol.



ZrO₂ shows attractive catalyses for various reactions such as isosynthesis from synthesis gas [8–10], dehydration of secondary alcohols [11,12], hydrogenation of conjugated dienes [13], isomerization of 1-butene [14], ketonization of alcohols, aldehydes [15] and carboxylic acids [16–18], dehydrogenation of alkylamines into nitriles [19]. ZrO₂ is also known as a bifunctional catalyst with acidic and basic sites [20]. ZrO₂ catalysts modified with Al₂O₃ and KOH have acidic and basic sites, respectively, and are effective for the isosynthesis from synthesis gas [9]: a ratio of basic to acidic sites on the catalysts determines the percentage of *iso*-C₄ in the total C₄ hydrocarbons.

In this paper, we investigated catalytic activity of sodium-modified ZrO₂ in the dehydration of 1,4-butanediol, to improve the selectivity to 3-buten-1-ol. We also examined acid–base properties of the catalysts using temperature-programmed desorption (TPD) of adsorbed NH₃ and CO₂. Then, we discussed

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the catalysis of ZrO_2 in the dehydration of 1,4-butanediol in connection with the acid–base properties.

2. Experimental

2.1. Catalyst preparation

A monoclinic ZrO_2 with the average particle size of $5\ \mu\text{m}$ was supplied by Daiichi Kigenso Chemical Industry, Japan. Sodium-modified ZrO_2 samples were prepared by impregnation, incipient wetness. Sodium hydroxide (NaOH) solution with the concentration of $3\text{--}40\ \text{mmol dm}^{-3}$ was impregnated to the monoclinic ZrO_2 to obtain precursors. Other modified ZrO_2 were prepared by the impregnation using either LiOH , KOH , or H_3PO_4 solution with the concentration of $8\ \text{mmol dm}^{-3}$ instead of using NaOH . Finally, the precursors were dried at $100\ ^\circ\text{C}$ for 24 h and calcined at $400\ ^\circ\text{C}$ for 3 h in air. The ZrO_2 catalysts, which are modified with NaOH , LiOH , KOH , and H_3PO_4 , are abbreviated as Na- ZrO_2 , Li- ZrO_2 , K- ZrO_2 , and P- ZrO_2 , respectively.

A tetragonal ZrO_2 was prepared by adding a $0.5\ \text{mol dm}^{-3}$ NaOH solution into a solution of zirconyl nitrate ($\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$) with the concentration of 5 mass% under stirring at room temperature. The mixture was further stirred at room temperature for 1 h and allowed to stand at room temperature for 24 h. The resulting precipitate was filtered and washed with distilled water until the pH of the solution became ca. 9.5. The precipitate was dried at $110\ ^\circ\text{C}$ for 24 h to obtain a precursor. Finally, a tetragonal ZrO_2 was obtained by calcinating the precursor at $500\ ^\circ\text{C}$ for 3 h in air.

CeO_2 was a commercially available reagent and was purchased from Wako Pure Chemical Industry Ltd., Japan. Al_2O_3 was supplied by Dia Catalyst, DC-2282.

2.2. Catalytic reaction

The dehydration of 1,4-butanediol was carried out in a fixed-bed flow reactor, which was made of glass with inside diameter of 20 mm, under atmospheric pressure of He at temperatures of $325\text{--}375\ ^\circ\text{C}$. Prior to the reaction, a catalyst sample, 0.3–1.0 g, was preheated in the He flow at $500\ ^\circ\text{C}$ for 1 h. After the catalyst bed had been set at a prescribed temperatures between 325 and $375\ ^\circ\text{C}$, 1,4-butanediol was fed into the reactor at a liquid flow rate of $1.77\ \text{cm}^3\ \text{h}^{-1}$ together with a He gas flow of $73\ \text{mmol h}^{-1}$. An effluent collected periodically was analyzed by gas chromatography (GC-8A, Shimadzu, Japan) with a 30-m capillary column (TC-WAX, GL Science, Japan) and GC-MS (GCMS-QP5050A, Shimadzu, Japan) with a 30-m capillary column (DB-WAX, Agilent Technologies, USA). Gaseous products such as 1,3-butadiene were analyzed by on-line gas chromatography (GC-8A) with a 1-m packed column (Porapak Q).

As has been shown in Fig. 2 of Ref. [5], ZrO_2 catalysts have stable conversion of 1,4-butanediol at $325\ ^\circ\text{C}$ with time on stream after the initial 3 h. Then, we evaluated the catalytic activity using the average conversion and selectivity in the initial 5 h.

2.3. Characterization

The TPD of adsorbed NH_3 was measured by neutralization titration using an electric conductivity cell immersed in an aqueous solution of H_2SO_4 to estimate acidity of the catalysts, as has been described in the TPD experiment of adsorbed NH_3 [21–26]. A sample (ca. 50 mg) was preheated in a quartz tube at $500\ ^\circ\text{C}$ for 1 h under a reduced pressure of 1.3 Pa. NH_3 vapor with 13 kPa was introduced to the sample at $100\ ^\circ\text{C}$ for 30 min, and then evacuated at $100\ ^\circ\text{C}$ for 1 h to remove the physisorbed NH_3 on the catalyst. After no NH_3 had been observed in N_2 flow, the sample was heated from 100 to $600\ ^\circ\text{C}$ at a heating rate of $10\ ^\circ\text{C min}^{-1}$ under N_2 flow of $15\ \text{ml min}^{-1}$. The desorbed NH_3 , together with N_2 gas, was bubbled into an electric conductivity cell containing a $0.5\ \text{mmol dm}^{-3}$ H_2SO_4 solution ($50\ \text{cm}^3$). The amount of desorbed NH_3 was monitored by the change in the conductivity of the solution. A cumulative amount of desorbed NH_3 was obtained as a function of the desorbed temperature and then differentiated to give a TPD profile as an acid strength distribution. In this paper, the number of the acidic sites is calculated in the temperature range from 100 to $600\ ^\circ\text{C}$ by an assumption in which one NH_3 molecule adsorbs to one acidic site on the catalyst surface.

The TPD of adsorbed CO_2 was also examined by neutralization titration in $2.0\ \text{mmol dm}^{-3}$ of an NaOH solution to estimate basicity of the catalyst, as has been described elsewhere [26]. The catalyst loaded in a quartz tube was preheated at $500\ ^\circ\text{C}$ for 1 h under a reduced pressure in the same way as the NH_3 adsorption described above. After the pretreatment, the quartz tube was filled with CO_2 gas at room temperature for 72 h. The following procedures for TPD experiment of adsorbed CO_2 were performed according to the TPD of adsorbed NH_3 , except for using an NaOH solution to titrate the desorbed CO_2 . The number of the basic sites is defined as the number of desorbed CO_2 in the temperature range from 25 to $600\ ^\circ\text{C}$.

The specific surface areas of samples were calculated with BET method using nitrogen adsorption isotherm at $-196\ ^\circ\text{C}$. XRD patterns were recorded with M18XHF (Mac Science).

3. Results

3.1. Dehydration of 1,4-butanediol over modified ZrO_2

Table 1 lists distribution of products in the dehydration of 1,4-butanediol over various catalysts. Over phosphorous-modified ZrO_2 (P- ZrO_2) and tetragonal ZrO_2 , THF is mainly produced together with a small amount of 3-buten-1-ol at $325\ ^\circ\text{C}$, while γ -butyrolactone is hardly produced. Over CeO_2 at $425\ ^\circ\text{C}$, 3-buten-1-ol is produced with a small amount of THF and γ -butyrolactone. Al_2O_3 selectively catalyzes the dehydrative cyclization of 1,4-butanediol into THF at $275\ ^\circ\text{C}$. 3-Buten-1-ol and THF are produced from 1,4-butanediol at a ratio of ca. 1:1 over monoclinic ZrO_2 at $325\ ^\circ\text{C}$.

In the dehydration of 1,4-butanediol over sodium-modified ZrO_2 (Na- ZrO_2) at $325\ ^\circ\text{C}$, the conversion of 1,4-butanediol gradually decreases with increasing Na content (Table 1). Fig. 1 shows the relationship between Na content and the selectiv-

Table 1
Distribution of products in the dehydration of 1,4-butanediol over various catalysts at 325 °C

Catalyst ^a	Conversion (%)	Selectivity (mol%)			
		3-Buten-1-ol	THF	GBL	Others ^b
Monoclinic ZrO ₂	39.1	45.7	51.1	0.4	2.8
0.3 Na-ZrO ₂	37.1	51.4	37.7	1.3	9.6
0.5 Na-ZrO ₂	24.1	64.5	31.0	1.4	3.1
1.0 Na-ZrO ₂	18.5	70.6	21.5	1.8	6.1
1.5 Na-ZrO ₂	18.7	71.8	20.8	2.1	5.3
3.0 Na-ZrO ₂	12.7	67.2	7.9	5.3	19.6
5.0 Na-ZrO ₂	7.0	61.8	6.5	16.1	15.6
1.5 Li-ZrO ₂	19.1	63.5	27.9	1.0	7.5
1.5 K-ZrO ₂	19.0	63.6	26.9	3.9	5.6
1.5 P-ZrO ₂	99.9	11.4	80.6	0.6	7.4
Tetragonal ZrO ₂	59.4	16.3	80.6	0.7	2.4
CeO ₂ ^c	73.0	55.4	7.7	4.6	32.3
Al ₂ O ₃ ^d	100	0.0	99.3	0.0	0.7

Catalytic activities are average for initial 5 h. $W/F = 0.169 \text{ g h cm}^{-3}$.

^a The number of the catalyst name is a content of alkali or phosphorus atoms (mol%).

^b Others include 1,3-butadiene, 2-hydroxytetrahydrofuran, 2-buten-1-ol, 2-butenal, and 1-butanol.

^c Reacted at 425 °C.

^d Reacted at 275 °C, $W/F = 0.113 \text{ g h cm}^{-3}$, the catalytic data was cited from Ref. [1].

ity in the dehydration of 1,4-butanediol over sodium-modified ZrO₂ at 325 °C. The selectivity to 3-buten-1-ol increases with increasing the Na content, and exceeds 70% at Na contents of 1.0–1.5 mol%. The selectivity to THF steeply decreases, and that to γ -butyrolactone (GBL) gradually increases with increasing the Na content. At high Na contents above 1.5 mol%, the selectivity to 3-buten-1-ol gradually decreases as the Na content increases because of increase in the selectivity to γ -butyrolactone, which results from the dehydrogenative cycliza-

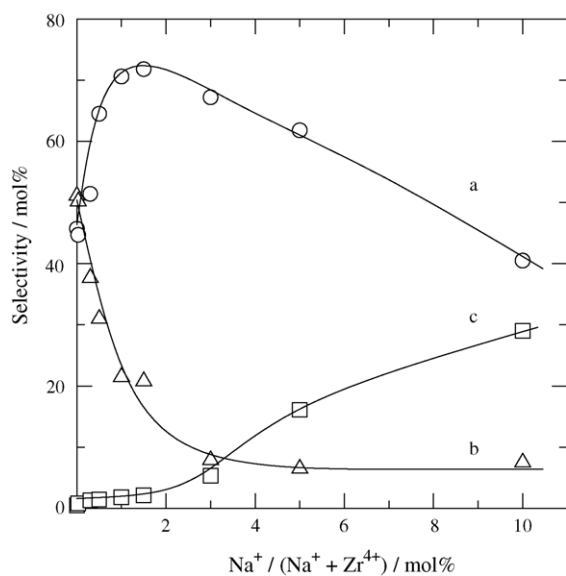
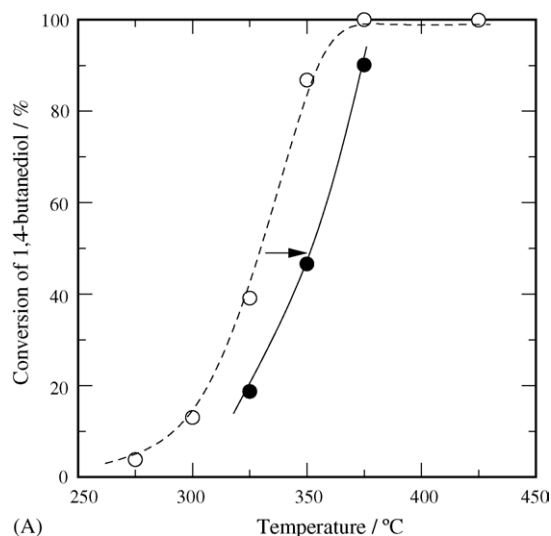
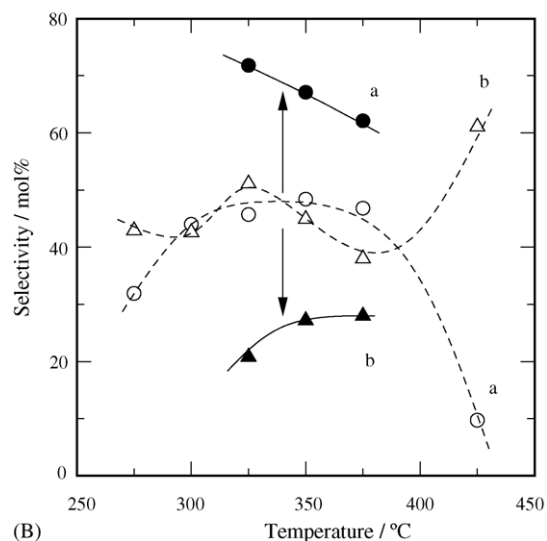


Fig. 1. Relationship between Na content and the selectivity to the products in the dehydration of 1,4-butanediol over sodium-modified ZrO₂ at 325 °C and $W/F = 0.169 \text{ g h cm}^{-3}$. (a) 3-buten-1-ol, (b) THF, (c) γ -butyrolactone (GBL).



(A)



(B)

Fig. 2. Temperature-dependence of catalytic activity of monoclinic and sodium-modified ZrO₂ in the dehydration of 1,4-butanediol at $W/F = 0.169 \text{ g h cm}^{-3}$. (A) Conversion of 1,4-butanediol and (B) selectivity to (a) 3-buten-1-ol and (b) THF over monoclinic ZrO₂ (broken line) and ZrO₂ modified with 1.5 mol% Na (solid lines).

tion of 1,4-butanediol. In addition, Na-ZrO₂ shows the highest selectivity to 3-buten-1-ol among the three alkali-modified ZrO₂.

Fig. 2 shows temperature dependence of catalytic activity of Na-ZrO₂ at Na content of 1.5 mol%, together with pure monoclinic ZrO₂. The average conversion for initial 5 h increases as reaction temperature increases (Fig. 2A). The addition of sodium decreases the conversion of 1,4-butanediol at the same reaction temperature. At temperatures of 325–375 °C, the selectivity to 3-buten-1-ol over the Na-ZrO₂ is higher than that over pure monoclinic ZrO₂, and exceeds 62 mol% (Fig. 2B). On the other hand, the selectivity to THF over Na-ZrO₂ decreases to below 28 mol%.

Fig. 3 depicts change in the composition of reactant and products with contact time in the dehydration of 1,4-butanediol over Na-ZrO₂ at Na content of 1.5 mol%, at 350 °C. The contact

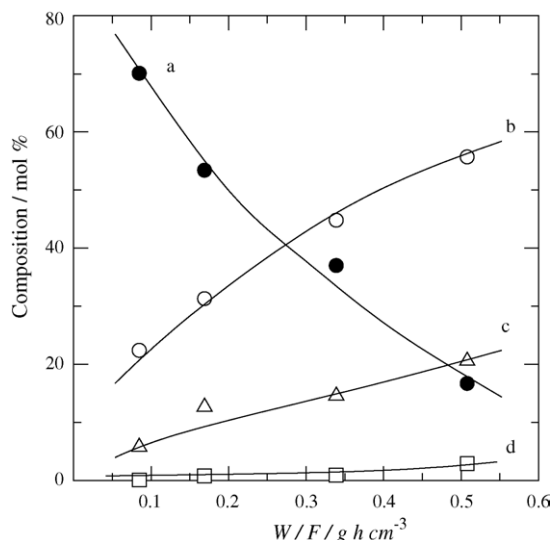


Fig. 3. Change in the composition of reactant and products with contact time in the dehydration of 1,4-butanediol over ZrO_2 modified with 1.5 mol% Na at 350 °C. (a) 1,4-butanediol, (b) 3-buten-1-ol, (c) THF, (d) stepwise products including 1,3-butadiene, 2-buten-1-ol, 2-butenal and 1-butanol.

time, W/F , is defined as a time factor in a flow reactor, where W and F are a catalyst weight and a flow rate of 1,4-butanediol, respectively. The composition of 1,4-butanediol decreases as the contact time increases. The composition of 3-buten-1-ol, i.e. the space-time yield, increases with increasing the contact time. The total yield of by-products including 1,3-butadiene, 2-buten-1-ol, 2-butenal and 1-butanol, which are converted from 3-buten-1-ol, is less than 1.0 mol% at W/F below $0.339 \text{ g h cm}^{-3}$ at 350 °C.

3.2. Characterization of sodium-modified ZrO_2 catalyst

Fig. 4 illustrates TPD profiles of NH_3 and CO_2 adsorbed on the catalysts. In the TPD experiments of adsorbed NH_3 (Fig. 4A), both monoclinic and tetragonal ZrO_2 have desorption peaks at around 300 °C. In the ZrO_2 modified with NaOH, the desorption peak at 300 °C declines gradually with increasing Na content, and disappears at Na content of 1.0 mol%. In addition, no new desorption peaks are observed in the Na- ZrO_2 . The ZrO_2 modified with H_3PO_4 (P- ZrO_2) also has desorption peak at around 300 °C without new desorption peak. These results indicate that modification of ZrO_2 with acidic and basic solutions does not vary the original acid strength of ZrO_2 . Al_2O_3 has desorption peak at ca. 430 °C [25], which is higher than those of the ZrO_2 samples. CeO_2 has no desorption peak in the temperature range.

In the TPD of CO_2 adsorbed on the modified ZrO_2 (Fig. 4B), the CO_2 desorption peaks are obtained at around 120 °C in the catalysts used in this study, and no new desorption peaks are observed. On the other hand, desorption peak is obtained at around 150 °C for CeO_2 catalyst. The results indicate that these catalysts have weak basic sites on the surface, and that CeO_2 has stronger basic sites on its surface than the other catalysts used in this work.

Table 2 summarizes the physical properties of the catalysts used in this work. The monoclinic ZrO_2 without modification

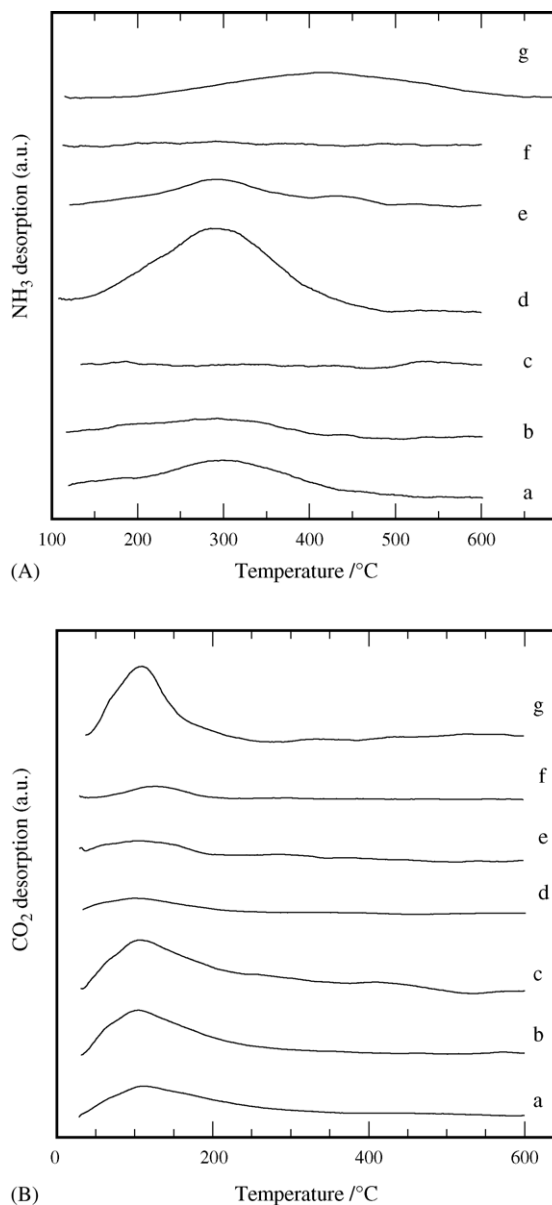


Fig. 4. TPD spectra of (A) NH_3 and (B) CO_2 adsorbed on the catalysts. (a) Monoclinic ZrO_2 , (b) 0.3 Na- ZrO_2 , (c) 1.5 Na- ZrO_2 , (d) 1.5 P- ZrO_2 , (e) tetragonal ZrO_2 , (f) CeO_2 , (g) Al_2O_3 . The NH_3 -TPD profile of Al_2O_3 is cited from Ref. [25].

has both acidic and basic sites, as shown in Fig. 4. Moreover, the basic sites are present ca. three times as much as the acidic sites on the monoclinic ZrO_2 . As the Na content increases, the number of acidic sites steeply decreases and disappears at Na content of 1.0 mol%, while number of basic sites gradually increases (Table 2). Modification of ZrO_2 with H_3PO_4 causes the decrease in the number of basic sites. In addition, modification with NaOH and H_3PO_4 results in a slight change in the original specific surface area of monoclinic ZrO_2 . The tetragonal ZrO_2 also has both acidic and basic sites, where the basic sites are present ca. three times as much as the acidic sites. Al_2O_3 also has much basic sites than acidic sites. Table 2 also lists densities of acidic and basic sites of the samples calculated by dividing the number of sites by specific surface area. The densities of acidic and basic

Table 2
Physical properties of various catalysts

Catalysts ^a	S.A. ^b (m ² g ⁻¹)	Number of acidic sites ^c (μmol g ⁻¹)	Number of basic sites ^d (μmol g ⁻¹)	Density of acidic sites (nm ⁻²)	Density of basic sites (nm ⁻²)
Monoclinic ZrO ₂	99.7	82.1	232	0.496	1.40
0.3 Na-ZrO ₂	94.0	44.7	314	0.286	2.01
0.5 Na-ZrO ₂	97.7	47.2	371	0.291	2.29
1.0 Na-ZrO ₂	96.2	0	343	0	2.17
1.5 Na-ZrO ₂	97.1	0	396	0	2.46
3.0 Na-ZrO ₂	96.2	0	516	0	3.23
5.0 Na-ZrO ₂	94.4	0	671	0	4.28
1.5 P-ZrO ₂	107	142	103	0.802	0.581
Tetragonal ZrO ₂	90.2	47.8	133	0.320	0.888
CeO ₂	20.0	0	50.7	0	1.53
Al ₂ O ₃	205	56.2 ^e	333	0.165	0.978

Catalytic activities are average for initial 5 h. $W/F = 0.169 \text{ g h cm}^{-3}$.

^a Numbers of the name are contents (mol%) of sodium or phosphorus.

^b Specific surface area (m² g⁻¹).

^c Calculated from amount of desorbed NH₃ in the temperature range from 100 to 600 °C.

^d Calculated from amount of desorbed CO₂ in the temperature range from 25 to 600 °C.

^e The datum is cited from Ref. [25].

sites on the unmodified monoclinic ZrO₂ are roughly twice as large as those on the tetragonal one.

Fig. 5 shows the relation between selectivities to the major products and number of acidic and basic sites. The selectivity to THF increases with increasing the number of acidic sites (Fig. 5A). However, the selectivity to 3-buten-1-ol seems to be independent of the acidity. In contrast, the selectivity to γ -butyrolactone increases with increasing the number of basic sites (Fig. 5B), while the selectivity to 3-buten-1-ol shows a maximum.

Fig. 6 illustrates XRD profiles of the ZrO₂ catalysts used in this study. The diffraction peaks of the monoclinic ZrO₂ are observed at $2\theta = 24.3^\circ, 28.4^\circ, 31.6^\circ, 34.5^\circ, 41.0^\circ, 45.3^\circ, 50.1^\circ$ and 55.5° , and those of the tetragonal one are at $2\theta = 30.2^\circ, 35.1^\circ, 50.4^\circ$, and 60.1° . The sodium- and phosphorous-modified ZrO₂ catalysts have the monoclinic structures. The monoclinic structure of ZrO₂ is maintained even after the modification. In addition, no new peaks, which are ascribed to Na₂O, Na₂CO₃, phosphates etc., are observed in the modified ZrO₂ catalysts.

4. Discussion

4.1. Surface properties of ZrO₂

ZrO₂ has been known as a bifunctional catalyst with acidic and basic sites [20,27]. Xu et al. reported that monoclinic ZrO₂ had both acidic and basic sites on its surface in the TPD experiments of adsorbed NH₃ and CO₂ [20]. They found that pre-adsorbed NH₃ enhanced the adsorption of post-adsorbing CO₂ in the case that acidic and basic sites were located closely. On the other hand, this type of interaction was not found on solid acid such as SiO₂-Al₂O₃ or solid base such as MgO. In the present study, both weak acidic and basic sites are present on the monoclinic ZrO₂. This is consistent with their results. It has also been reported that monoclinic ZrO₂ has larger adsorption

capacity of CO₂ than tetragonal ZrO₂ does in the TPD experiment of adsorbed CO₂ [28]. This is also consistent with the present results that monoclinic ZrO₂ is more basic than tetragonal one. Thus, it is obvious that the crystalline structures of ZrO₂ influence the acid-base property.

Cerrato et al. reported that several OH groups were present on the surface of monoclinic ZrO₂ calcined in air even at 600 °C in FTIR spectroscopy [29]. We speculate that the ZrO₂ surface is covered with OH groups, and that the surface OH groups of ZrO₂ are ion-exchanged with Na⁺ to form ONa species by neutralization with NaOH. If a proton of OH groups of ZrO₂ surface is exchanged with sodium cations, all the acidic OH groups would be converted into ONa species at Na content of 0.70 mol%, which is calculated from the number of total acidic sites of monoclinic ZrO₂ (Table 2). Thus, it is reasonable that the acidic sites disappear at Na content of 1.0 mol% in the present work.

In contrast, the number of basic sites increases with the increase in Na content (Table 2). The results indicate that ONa groups, which are formed by ion exchange of the surface OH groups on ZrO₂ with NaOH, adsorb CO₂, namely an ONa group functions as a basic site. Excess sodium cations are agglomerated to form sodium hydroxides or carbonates, which act as basic sites. They would be present as microparticles on the catalyst due to not being detected by XRD.

In the P-ZrO₂, the H₃PO₄ loading (1.5 mol%) is calculated to be 123 μmol g⁻¹, which corresponds to the difference in the basic sites between pure monoclinic and P-ZrO₂. This indicates that the loaded H₃PO₄ neutralizes the surface basic site as a monovalent acid. Therefore, residual basic sites are still present on the P-ZrO₂, which is clarified in the TPD experiment of adsorbed CO₂ (Table 2). Parida and Pattnayak studied on the effect of H₃PO₄ on textural and acidic properties of ZrO₂ [30]. The addition of H₃PO₄ caused a phase transition from monoclinic into tetragonal even at 2.24 wt.% of PO₄³⁻ (2.8 mol%).

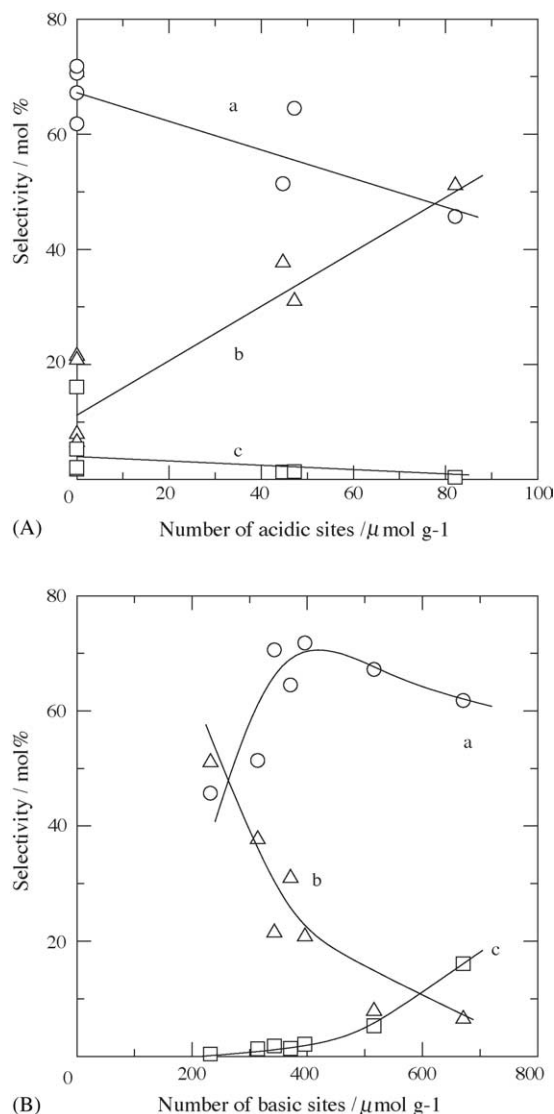


Fig. 5. Relationship between selectivities to (a) 3-buten-1-ol, (b) THF, and (c) γ -butyrolactone and number of (A) acidic and (B) basic sites of sodium-modified ZrO₂.

In our study, however, the phase transition was not observed at 1.5 mol% loading. The addition of PO₄³⁻ with a concentration up to 15.7 wt.% increased the number of acidic sites and the specific surface area [30]. Second components caused the enhancement of specific surface area of ZrO₂ and they strongly influence the crystal structure [31].

4.2. Formation of THF and γ -butyrolactone

It is well known that 1,4-butanediol is selectively dehydrated into THF over strong acid catalysts [1,6,7]. THF is selectively produced in the dehydration of 1,4-butanediol over Al₂O₃ [1], which has strong acidic sites on the surface together with basic sites (Fig. 4). Baba and Ono reported that the formation rate of THF was proportional to the concentration of proton in the liquid-phase dehydrative cyclization of 1,4-butanediol with heteropoly acid [7]. Generally, acidity of protonic acids is weakened

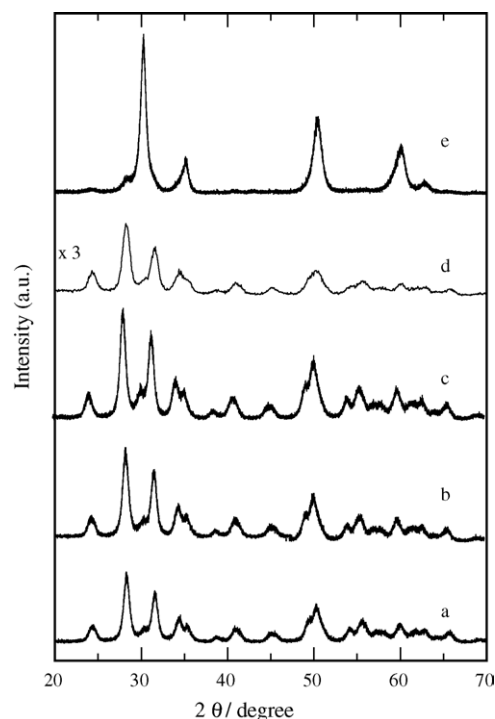


Fig. 6. XRD profiles of the catalysts used in this study. (a) Monoclinic ZrO₂, (b) 1.0 Na-ZrO₂, (c) 10.0 Na-ZrO₂, (d) 1.5 P-ZrO₂, (e) tetragonal ZrO₂.

by solvation with water: the formation rate of THF decreased by hydration of the protons with water [7], and water inhibited the reaction because of strong adsorption of water on active acidic sites of acidic resin [6].

THF is predominantly produced over P-ZrO₂ (Table 1). Large amount of acidic sites with the strength equivalent to the unmodified monoclinic ZrO₂ contributes the selective production of THF. Although weak acidic sites of ZrO₂ are related to the formation of THF from 1,4-butanediol (Fig. 5A), THF is produced even over Na-ZrO₂ without acidic sites, on which NH₃ gas can be adsorbed at 100 °C. In addition, CeO₂ has only weak basic sites on its surface without acidic sites (Fig. 4), which is consistent with the previous study [26]. The density of weak basic sites on CeO₂, 2.54 μmol m⁻², which is calculated by dividing the number of basic sites (50.7 μmol g⁻¹) by its specific surface area (20.0 m² g⁻¹), is in good agreement with 2.1–2.6 μmol m⁻² of CeO₂ reported in the previous study. A small amount of THF is produced in the dehydration of 1,4-butanediol over the non-acidic CeO₂ [1]. In this sense, THF is readily formed even over very weak acidic surface.

Basic sites have an ability to dehydrogenate alcohols to the corresponding carbonyl compounds. It was reported that alkali earth catalysts, such as Rb/Al₂O₃ and Sr/Al₂O₃, catalyzed the dehydrogenation of 2-propanol into propanone, which was well adopted to evaluate the basicity of catalysts [32,33]. 1-Propanol and 2-propanol were dehydrogenated into propanal and propanone, respectively, over Zn–Mica due to a preference for its basicity more than acidity [34]. In the dehydrogenative cyclization of 1,4-butanediol over copper-based catalyst at 240 °C, γ -butyrolactone was selectively produced via two-step dehydrogenation [35]: one is the dehydrogenation of

1,4-butanediol to 4-hydroxybutanal and the other is the dehydrogenation of 2-hydroxytetrahydrofuran, which is the hemiacetal of 4-hydroxybutanal, to γ -butyrolactone. Since the selectivity to γ -butyrolactone increases with increasing the number of basic sites (Fig. 5B), γ -butyrolactone is probably formed through the dehydrogenative cyclization of 1,4-butanediol on basic sites of ZrO_2 .

4.3. Relationship between acid–base property and the selectivity to 3-buten-1-ol

We have already reported that 3-buten-1-ol can be formed from 1,4-butanediol over pure CeO_2 at high temperatures of 400–425 °C [1]. CeO_2 shows specific catalytic activity in some reactions, such as dehydration of 1,3-diols into allylic alcohols [2–4], *ortho*-selective alkylation of phenol with alcohols [26,36,37], and ketonization of alcohol [37,38], aldehyde, ester [39], and carboxylic acid [40]. We explained the catalyses of CeO_2 through redox mechanism [3,4,26,37]. We speculate that 3-buten-1-ol is also formed over pure CeO_2 via redox mechanism, not through acid–base catalysis.

In the review of Tanabe and Yamaguchi [27], acid–base bifunctional catalyses over ZrO_2 are introduced: orientation of acid–base pair sites is vitally important for the bifunctional catalysis. In the dehydration of 2-butanol, ZrO_2 dominantly catalyzes the formation of 1-butene [11]. Over the ZrO_2 , both H^+ of terminal methyl group and OH^- are simultaneously abstracted from 2-butanol to form 1-butene. Both acidic and basic sites on ZrO_2 concertedly play a role of catalysis, which is confirmed by poisoning tests with *n*-butylamine. It is proposed that acidic and basic sites on the catalyst interacted with OH group and β -hydrogen, respectively, to form alkenes [27]. Analogously, we speculate that simultaneous abstraction of β -hydrogen and OH group is necessary for the formation of 3-buten-1-ol in the dehydration of 1,4-butanediol over ZrO_2 without cyclization into THF.

In the present study, the selectivity to 3-buten-1-ol is maximized at the Na content of 1.5 mol% (Fig. 1). The change in the selectivity to 3-buten-1-ol cannot be explained by either monotonical increase in the basic sites or decrease in the acidic sites (Fig. 5). Since the acidic sites disappeared at Na content of 1.0 mol%, the acidic sites did not seem to be concerned with the dehydration. However, much weaker acidic sites, of which strength can be estimated by adsorption of NH_3 at temperatures below 100 °C, could contribute the dehydration as an adsorption site for OH group.

The densities of acidic and basic sites of unmodified monoclinic ZrO_2 are larger than those of tetragonal one (Table 2). This indicates that acidic and basic sites are located closely on the monoclinic ZrO_2 , whereas they are separated on the tetragonal one. The high densities present much more acid–base pair sites on the monoclinic ZrO_2 . Tetragonal ZrO_2 with less acid–base pair sites catalyzes the cyclization of 1,4-butanediol into THF, while monoclinic one with more acid–base pair sites catalyzes the dehydration into 3-buten-1-ol. It is probable that the selectivity in the dehydration of 1,4-butanediol is reflected by the difference in the number of acid–base pair sites.

5. Conclusions

Catalytic activities of sodium-modified monoclinic ZrO_2 for the dehydration of 1,4-butanediol into 3-buten-1-ol were investigated at 325–375 °C. The selectivity to 3-buten-1-ol of the original monoclinic ZrO_2 was enhanced by the modification with sodium hydroxide, whereas the formation of THF was suppressed.

The temperature-programmed desorption (TPD) experiments of adsorbed NH_3 and CO_2 were performed to evaluate the acidity and basicity of catalysts, respectively. It was confirmed that both acidic and basic sites were present on monoclinic ZrO_2 . Modification with sodium hydroxide onto ZrO_2 led to decrease in the acidic sites, whereas led to increase in the basic sites.

In the dehydration of 1,4-butanediol over sodium-modified ZrO_2 at 325 °C, the selectivity to products varied with the amount of sodium hydroxide modified. The selectivity to THF steeply decreased with decreasing acidic sites, whereas that to γ -butyrolactone increased as basic sites increase. In contrast, both acidic and basic sites cooperatively catalyze the dehydration of 1,4-butanediol into 3-buten-1-ol over monoclinic ZrO_2 .

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