# Catalytic reaction of 1,3-butanediol over solid acids

Naoki Ichikawa [a], Satoshi Sato [b,*], Ryoji Takahashi [b], Toshiaki Sodesawa [b]

[a] *Graduate School of Science and Technology, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan*
[b] *Department of Applied Chemistry, Faculty of Engineering, Chiba University, Yayoi, Inage, Chiba 263-8522, Japan*

## Abstract

Catalytic reaction of 1,3-butanediol over solid acids such as $SiO_2$–$Al_2O_3$, $Al_2O_3$, $ZrO_2$ and $TiO_2$ was investigated. The catalytic activities of these acids were in good coincidence with their acid properties: strong acid catalysts, $SiO_2$–$Al_2O_3$ and $Al_2O_3$, catalyzed dehydration of 1,3-butanediol at the reaction temperature below 250 °C, while weak acid catalysts, $ZrO_2$ and $TiO_2$, required the temperature above 325 °C to activate 1,3-butanediol. $SiO_2$–$Al_2O_3$ catalyzed the dehydration of 1,3-butanediol into unsaturated alcohols, and consecutively dehydrated them into 1,3-butadiene. 4-Methyl-1,3-dioxane, which is the acetal compound of 1,3-butanediol and formaldehyde, was obtained with high selectivity over $Al_2O_3$. Several compounds were produced over $TiO_2$ and $ZrO_2$ owing to the side reactions such as dehydrogenation and hydrogenation. The characteristics in the reaction were discussed in connection with other reactions of monoalcohols and of the produced unsaturated alcohols.
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## 1. Introduction

Unsaturated alcohols are important compounds in industrial chemistry because they are used as raw materials and intermediates of pesticides and medicines. Selective hydrogenation of unsaturated carbonyl compounds to unsaturated alcohols have been attempted over heterogeneous catalysts such as Cr-modified Raney-Ni [1], Sn-Pt/Nylon [2], M/zeolite (M = Ru, Pt, Rh) catalysts [3], Co/$Al_2O_3$ [4–6] and supported Au catalyst [7,8].

Recently, we have found that $CeO_2$ has catalytic activity for the selective dehydration of 1,3-diols [9,10] and 1,4-butanediol [11] to unsaturated alcohols. For example, 1,3-butanediol is dehydrated into 3-buten-2-ol and *trans*-2-buten-1-ol at 325 °C with selectivity of 56.9 and 35.5 mol.%, respectively [10], while activation of 1,4-butanediol requires reaction temperatures above 375 °C, and the selectivity to 3-buten-1-ol is at most 68.1 mol.% [11]. In the previous study, the mechanism of the dehydration of 1,3-butanediol over $CeO_2$ (1 1 1) surface was investigated, and we concluded that the oxygen-defect sites on $CeO_2$ (1 1 1) surface are probably the active sites

for the dehydration of 1,3-butanediol to unsaturated alcohols [12,13].

Our research on the dehydration of 1,3-diols has been mainly focused on $CeO_2$ catalyst systems. In this paper, we investigate promising acid catalysts for the dehydration of 1,3-butanediol into unsaturated alcohols. We also discuss effects of acid–base properties of the catalysts on the catalytic activity and selectivity.

## 2. Experimental

We used four metal oxides such as $SiO_2$–$Al_2O_3$, $Al_2O_3$, $ZrO_2$ and rutile-$TiO_2$. $SiO_2$–$Al_2O_3$ (N631-L), $Al_2O_3$ (DC2282) and $ZrO_2$ (RSC-100) were supplied from Nikki Chemical, Dia Catalyst and Daiichi Kigenso Kagaku Kogyo Co. Ltd., respectively. $TiO_2$ was supplied by Catalysis Society of Japan, Japan Reference Catalyst TIO-3. The specific surface area of $SiO_2$–$Al_2O_3$, $Al_2O_3$, $TiO_2$ and $ZrO_2$ were 420, 200, 40 and 100 $m^2\,g^{-1}$, respectively, which were estimated by BET method using $N_2$ isotherm at −196 °C.

Temperature-programmed desorptions (TPD) of $NH_3$ and $CO_2$ were performed to evaluate the acid and base properties, respectively. The numbers of acid and base sites were estimated from the neutralization–titration curves of diluted $H_2SO_4$ and

NaOH solution, respectively. Details of TPD procedure were described elsewhere [14,15].

1,3-Butanediol, 1-butanol and 2-butanol were purchased from Waco Pure Chemical Ind. Ltd., Japan, and unsaturated alcohols such as 3-buten-1-ol, 3-buten-2-ol and 2-buten-1-ol were purchased from Tokyo Kasei Kogyo Co. Ltd., Japan. All the reagents were used without further purification. The catalytic reactions of alcohols were carried out in a conventional fixed-bed down-flow reactor. The catalyst bed was heated in an $N_2$ flow at the desired reaction temperature of 200–375 °C and kept for 1 h as the pretreatment. Then, a reactant was fed into the reactor at a liquid feed rate of $1.7 \, cm^3 \, h^{-1}$ and it was vaporized and brought over the catalyst bed with nitrogen gas at a flow rate of $30 \, cm^3 \, min^{-1}$. An effluent was condensed and collected periodically with ice trap every 1 h. The effluent was analyzed by FID-GC (Shimadzu GC-8A equipped with 30 m length of TC-WAX column). Gaseous products such as 1,3-butadiene and formaldehyde were analyzed by on-line TCD-GC (Shimadzu GC-8A equipped with 6 m length of VZ-7). The products were identified with GC–MS (Shimadzu GCMS-QP5050A).

Selectivity to a product, $S_i$, was calculated with the following equation:

$$S_i = \frac{M_i}{\sum M_i}$$

where $M_i$ is the mole number of a product $i$ in the collected effluent and was calibrated with the carbon number in the product as, $M_i =$ (mole number of a product estimated with GC) × (carbon number in the product).

Conversion of 1,3-butanediol was slightly decreased in the initial period. Thus, the catalytic activity was evaluated by both conversion of 1,3-butanediol and selectivities to products averaged in the initial 5 h.

## 3. Results

Fig. 1 shows $NH_3$- and $CO_2$-TPD profiles of the catalysts, and Table 1 lists their physical properties. The desorption of $NH_3$ was observed over all the catalysts. $SiO_2$–$Al_2O_3$ showed the largest and asymmetric desorption peak of $NH_3$. This asymmetry implies that $SiO_2$–$Al_2O_3$ has acid sites with different strength. We deconvoluted the desorption peak into two peaks with Gaussian fitting, as shown in Fig. 1A. The peaks centered at 279 and
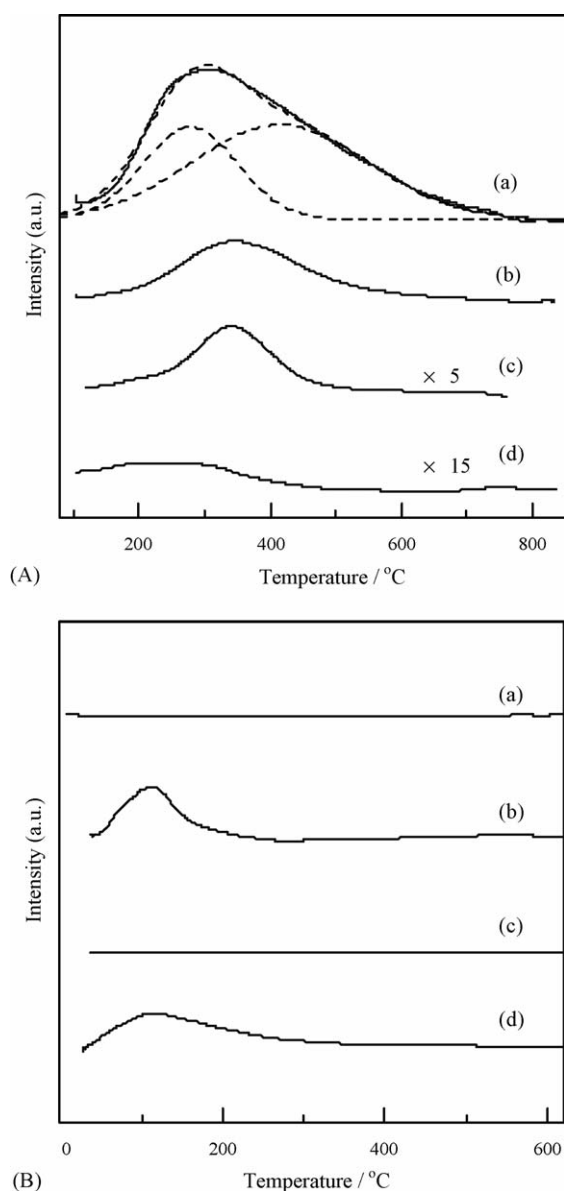


Fig. 1. TPD profiles of (a) $SiO_2$–$Al_2O_3$, (b) $Al_2O_3$, (c) $TiO_2$ and (d) $ZrO_2$. The probe molecules are (A) $NH_3$ and (B) $CO_2$. The dotted lines in 'A' are the deconvolution of the profile of $SiO_2$–$Al_2O_3$ according to Gaussian fitting.

Table 1
Specific surface area and acid and base property of catalysts

| Catalyst | SA[a] ($m^2 \, g^{-1}$) | $NH_3$-desorption | | $CO_2$-desorption | |
|---|---|---|---|---|---|
| | | $T^{[b]}$ (°C) | $A^{[c]}$ ($\mu mol \, g^{-1}$) | $T^{[b]}$ (°C) | $A^{[c]}$ ($\mu mol \, g^{-1}$) |
| $SiO_2$–$Al_2O_3$ | 420 | 279, 414 | 440 | – | 0 |
| $Al_2O_3$ | 200 | 345 | 166 | 113 | 333 |
| $TiO_2$ | 40 | 342 | 30.8 | – | 0 |
| $ZrO_2$ | 100 | 214 | 10.4 | 115 | 232 |

[a] Specific surface area.
[b] Temperature at which the desorption peak centered in the TPD profile.
[c] Number of acid or base sites.

414 °C, respectively. $Al_2O_3$ and $TiO_2$ have symmetric desorption peak of $NH_3$ centered at 345 and 342 °C, respectively, while the amount of acid sites of $Al_2O_3$ is ca. five times larger than that of $TiO_2$. $ZrO_2$ had the weakest and broad desorption peak centered at 214 °C. This suggests that $ZrO_2$ has the weakest acid sites and the amount is the smallest. In the $CO_2$-TPD, we could not confirm the desorption of $CO_2$ from $SiO_2$–$Al_2O_3$ and $TiO_2$, whereas $Al_2O_3$ and $ZrO_2$ have a small desorption peak centered around 110 °C. These results indicate that $SiO_2$–$Al_2O_3$ and $TiO_2$ have no base sites on their surface, and $Al_2O_3$ and $ZrO_2$ have weak base sites together with acid ones. Hence, it was summarized that the sequences of acid and base strength of the catalysts were $SiO_2$–$Al_2O_3 > Al_2O_3 > TiO_2, > ZrO_2$, and $Al_2O_3 > ZrO_2 \gg SiO_2$–$Al_2O_3$, $TiO_2$, respectively.

Fig. 2 shows the activities of the catalysts at different reaction temperatures. Conversion of 1,3-butanediol monotonously increased with increasing the reaction temperature over the acid catalysts. $SiO_2$–$Al_2O_3$ catalyzed the dehydration of 1,3-butanediol at the lowest reaction temperature among the catalysts. $Al_2O_3$, $TiO_2$ and $ZrO_2$ required the temperature around 250, 350 and 350 °C to activate 1,3-butanediol, respectively. Table 2 summarizes the products distribution in the reaction of 1,3-butanediol over the catalysts. In this comparison, the catalysts with different specific surface areas were tested at the same space velocity. When 1.5 g of $TiO_2$ was used as being the same surface area as $SiO_2$–$Al_2O_3$, the conversion of 1,3-butanediol was at most 32% at 325 °C (dotted line in Fig. 2).

3-Buten-1-ol was the major product over $SiO_2$–$Al_2O_3$, $TiO_2$ and $ZrO_2$ at any temperatures. Formaldehyde and 4-methyl-1,3-dioxane, however, were mainly obtained over $Al_2O_3$. With increasing the reaction temperature, the selectivity to 1,3-butadiene, the consecutive dehydration product from unsaturated alcohols, increased while that to unsaturated ethers, the bimolecular dehydration products from unsaturated alcohols, decreased over $SiO_2$–$Al_2O_3$. $TiO_2$ and $ZrO_2$ exhibited similar
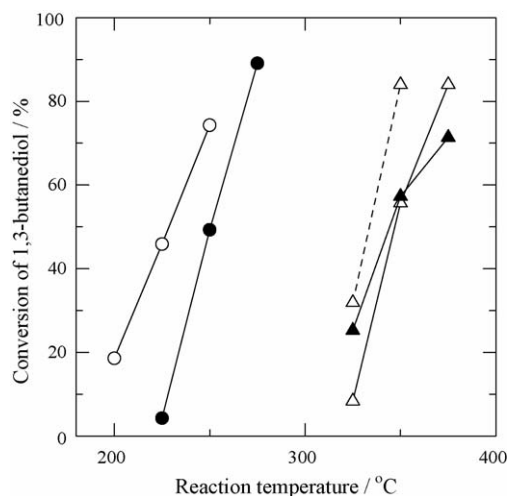


Fig. 2. Relationship between 1,3-butanediol conversion and reaction temperature over several metal-oxide catalysts. $SiO_2$–$Al_2O_3$ (open circle), $Al_2O_3$ (closed circle), $TiO_2$ (open triangle), $ZrO_2$ (closed triangle). Solid line, 0.15 g of catalyst was used; dotted line, 1.5 g of $TiO_2$ was used.

conversion level of 1,3-butanediol at the same reaction temperature. Compounds such as 3-buten-2-one, 2-butenal, 1-butanol and 2-butanol were produced via dehydrogenation and/or hydrogenation and were obtained with relatively large selectivities over $TiO_2$ and $ZrO_2$. Over $ZrO_2$, 3-buten-2-ol is preferably produced compared to the other catalysts, where 3-buten-2-one and butanone are major by-products.

We tested the dehydration of 1-butanol and 2-butanol in order to confirm the difference in reactivity of OH groups of the butanols. Tables 3 and 4 summarize the reaction results of 1- and 2-butanols over $SiO_2$–$Al_2O_3$, $TiO_2$ and $ZrO_2$, respectively. In the reaction of 1-butanol, $SiO_2$–$Al_2O_3$ exhibited the highest activity even though the reaction temperature over $SiO_2$–$Al_2O_3$ was lower than that over $TiO_2$ and $ZrO_2$ by 125 °C. $TiO_2$

Table 2
Reaction of 1,3-butanediol over various catalysts

| Catalyst | Temperature (°C) | Conv. (%) | Selectivity[a] (mol.%) | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Group I | | | | | Group II | | | | Group III | | | Group IV | | | Group V | |
| | | | **1** | **2** | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | **13** | **14** | **15** | **16** | **17** |
| $SiO_2$–$Al_2O_3$ | 200 | 18.6 | 43.8 | 14.2 | 2.1 | 19.6 | 12.1 | 0 | 0 | 0 | 5.5 | 1.3 | 0 | 0 | 1.4 | 0 | 0 | 0 | 0 |
| | 225 | 45.9 | 36.7 | 9.6 | 3.2 | 30.0 | 3.0 | 2.4 | 3.5 | 0 | 6.4 | 2.4 | 0 | 0 | 2.8 | 0 | 0 | 0 | 0 |
| | 250 | 74.3 | 27.7 | 3.2 | 2.9 | 36.0 | 1.2 | 0.3 | 7.7 | 3.8 | 6.6 | 4.1 | 1.5 | 0.3 | 3.5 | 0 | 0.2 | 0.6 | 0.4 |
| $Al_2O_3$ | 225 | 4.7 | 25.8 | 9.2 | 0 | 0 | 0 | 0 | 31.0 | 0 | 28.8 | 0 | 0 | 0 | 0 | 5.2 | 0 | 0 | 0 |
| | 250 | 49.3 | 15.4 | 4.4 | 0 | 0 | 0 | 0.9 | 27.9 | 1.1 | 18.4 | 8.6 | 9.5 | 0 | 2.0 | 6.5 | 0 | 3.1 | 2.2 |
| | 275 | 89.1 | 17.0 | 2.2 | 0 | 0 | 0. | 0.8 | 28.3 | 2.3 | 22.1 | 7.5 | 2.5 | 0 | 0.3 | 5.2 | 0.6 | 7.2 | 4.0 |
| $TiO_2$ | 325 | 8.4 | 27.3 | 19.6 | 4.9 | 0 | 0. | 4.4 | 0 | 0 | 0 | 13.5 | 3.4 | 7.3 | 9.1 | 10.5 | 0 | 0 | 0 |
| | 350 | 55.7 | 20.8 | 10.5 | 2.8 | 0 | 0 | 2.4 | 5.3 | 3.5 | 0 | 18.6 | 1.2 | 9.5 | 11.8 | 8.4 | 0.7 | 3.1 | 1.4 |
| | 375 | 84.0 | 30.2 | 7.3 | 2.1 | 0 | 0 | 2.0 | 11.8 | 4.2 | 0 | 16.0 | 3.7 | 4.1 | 5.3 | 6.6 | 1.9 | 3.0 | 1.8 |
| $ZrO_2$ | 325 | 25.3 | 25.9 | 18.7 | 16.3 | 0 | 0 | 0.6 | 0 | 8.1 | 0 | 14.0 | 5.3 | 2.3 | 1.7 | 0 | 0 | 3.1 | 4.0 |
| | 350 | 57.3 | 18.3 | 14.5 | 12.6 | 3.1 | 0 | 0 | 2.7 | 11.0 | 0 | 11.4 | 9.9 | 5.0 | 2.4 | 0 | 0.8 | 4.7 | 3.6 |
| | 375 | 71.4 | 20.0 | 9.6 | 12.1 | 3.9 | 0 | 0.9 | 0 | 15.4 | 0 | 13.8 | 9.3 | 4.7 | 2.9 | 0 | 1.2 | 2.4 | 3.8 |

Reaction conditions: catalyst weight, 0.150 g; reactant feed rate, 1.7 cm³ h⁻¹; carrier gas, $N_2$ (30 cm³ min⁻¹).

[a] **1**: 3-buten-1-ol, **2**: 2-buten-1-ol, **3**: 3-buten-2-ol, **4**: 1,3-butadiene, **5**: unsaturated ethers, **6**: propanone, **7**: formaldehyde, **8**: methanol, **9**: 4-methyl-1,3-dioxane, **10**: 3-buten-2-one, **11**: butanone, **12**: 2-butanol, **13**: 1-butanol, **14**: 2-butenal, **15**: butanal, **16**: acetaldehyde, **17**: ethanol.

Table 3
Reaction of 1-butanol over $SiO_2$–$Al_2O_3$, $TiO_2$ and $ZrO_2$[a]

| Catalyst | Temperature[b] (°C) | Conv.[c] (%) | Selectivity (mol.%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | 1-Butene | *trans*-2-Butene | *cis*-2-Butene | Butanal | Ether[d] | Ester[e] | Others[f] |
| $SiO_2$–$Al_2O_3$. | 225 | 28.4 | 24.9 | 36.0 | 32.2 | 2.8 | 0.2 | 0.2 | 3.7 |
| $TiO_2$ | 350 | 11.7 | 52.7 | 11.4 | 15.9 | 7.5 | 2.6 | 0.4 | 5.2 |
| $ZrO_2$ | 350 | 3.3 | 59.2 | 0 | 0 | 11.7 | 2.4 | 22.2 | 4.5 |

[a] The reaction conditions are the same as those in Table 2.
[b] Reaction temperature.
[c] Conversion.
[d] Di-*n*-butyl ether.
[e] Butyl butyrate.
[f] Others are unidentified.

Table 4
Reaction of 2-butanol over $SiO_2$–$Al_2O_3$, $TiO_2$ and $ZrO_2$[a]

| Catalyst | Temperature[b] (°C) | Conv.[c] (%) | Selectivity (mol.%) | | | | |
|---|---|---|---|---|---|---|---|
| | | | 1-Butene | *trans*-2-Butene | *cis*-2-Butene | Butanone | Others[d] |
| $SiO_2$–$Al_2O_3$ | 225 | 76.1 | 14.4 | 45.3 | 37.8 | 1.0 | 1.5 |
| $TiO_2$ | 350 | 63.8 | 31.0 | 18.4 | 41.3 | 7.5 | 1.8 |
| $ZrO_2$ | 350 | 39.2 | 70.5 | 7.5 | 8.9 | 10.4 | 2.7 |

[a] The reaction conditions are the same as those in Table 2.
[b] Reaction temperature.
[c] Conversion.
[d] Others are not identified.

showed moderate activity and $ZrO_2$ hardly activated 1-butanol at 350 °C. 2-Butenes were mainly produced over $SiO_2$–$Al_2O_3$, while 1-butene was predominantly obtained over $TiO_2$ and $ZrO_2$. We note that butyl butyrate was produced over $ZrO_2$ with the selectivity of 22.2 mol.%. In the reaction of 2-butanol, the catalytic activity was the same order as the case of 1-butanol, i.e. $SiO_2$–$Al_2O_3 > TiO_2 > ZrO_2$. *cis*-2-Butene was mainly produced over $SiO_2$–$Al_2O_3$ and $TiO_2$, whereas 1-butene was obtained with the largest selectivity over $ZrO_2$. The reactivity of 2-butanol was much higher than 1-butanol over the catalysts.

We also examined the reactivity of unsaturated alcohols over $SiO_2$–$Al_2O_3$ and $TiO_2$. The results over $SiO_2$–$Al_2O_3$ and $TiO_2$ are listed in Tables 5 and 6, respectively. Over $SiO_2$–$Al_2O_3$, 2-buten-1-ol and 3-buten-2-ol were predominantly dehydrated into 1,3-butadiene at the same conversion level (Table 5). On the other hand, 3-buten-1-ol was subject to decomposition to produce propene and formaldehyde with the highest selectivity and the dehydration into 1,3-butadiene did not readily proceed. The reactivity of 3-buten-1-ol was lower than those of 2-buten-1-ol

Table 5
Reaction of unsaturated alcohols over $SiO_2$–$Al_2O_3$ at 250 °C[a]

| Reactant | Conv. (%) | Selectivity[b] (mol.%) |
|---|---|---|
| **1** | 41.5 | **18**[c] (58.0), **4** (12.8), **14** (11.0), **15** (6.9), **8** (5.6) |
| **2** | 76.7 | **4** (92.8), **14** (5.3) |
| **3** | 70.8 | **4** (93.0), **2** (2.6), **6** (2.0) |

[a] The reaction was carried out under following conditions: catalyst weight, 0.300 g; reactant feed rate, 1.7 cm³ h⁻¹; carrier gas, $N_2$ (30 cm³ min⁻¹).
[b] Numbers of the reactants and of the products except **18** are the same as those in Table 2, and numbers in parentheses indicate the selectivity.
[c] Propene.

Table 6
Reaction of unsaturated alcohols over $TiO_2$ at 375 °C[a]

| Reactant | Conv. (%) | Selectivity[b] (mol.%) |
|---|---|---|
| **1** | 38.2 | **4** (50.0), **16** (13.2), **8** (11.4), **14** (8.1), **13** (4.0) |
| **2** | 53.3 | **4** (71.3), **14** (11.9), **8** (3.3) |
| **3** | 70.2 | **4** (70.2), **10** (10.7), **11** (4.0) |

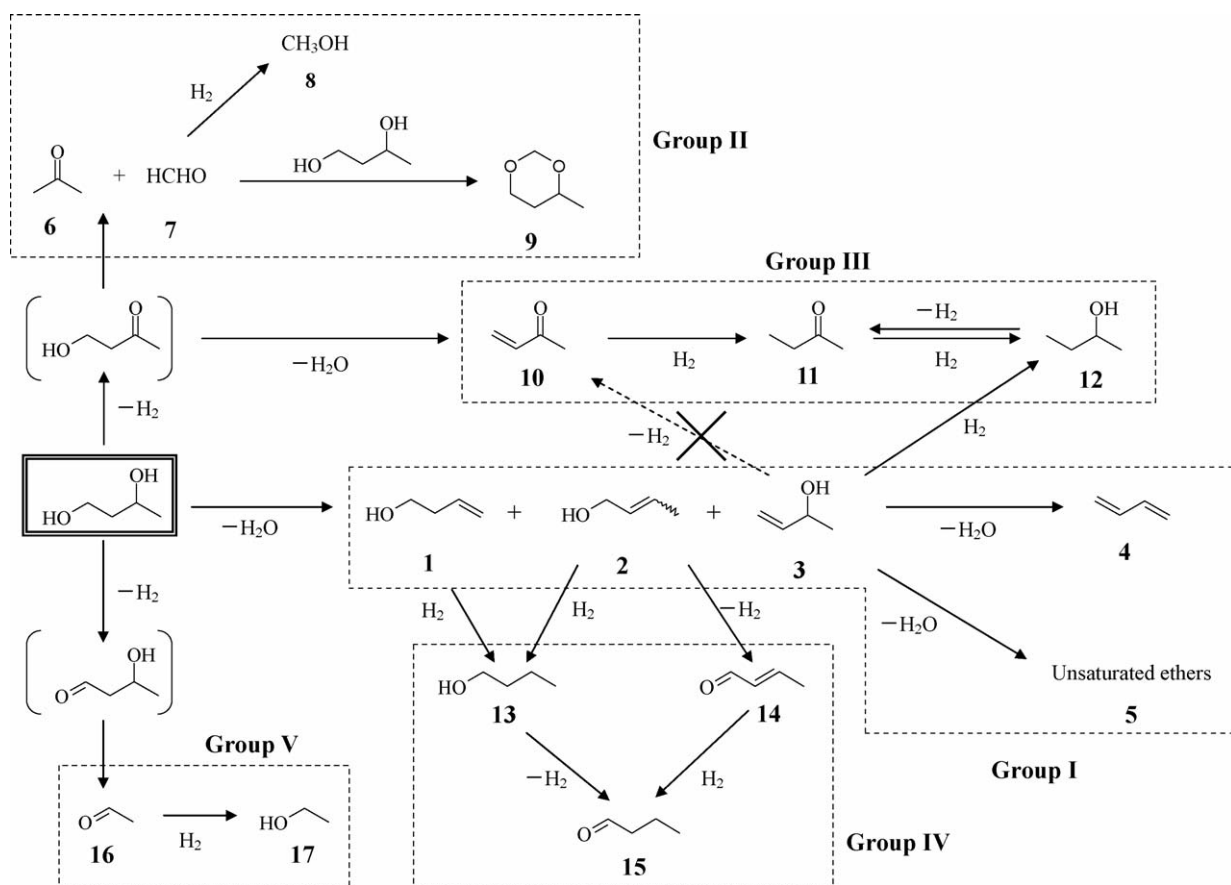[a] The reaction conditions are the same as those in Table 5 except for the temperature.
[b] Numbers of the reactants and of the products are the same as those in Table 2, and numbers in parentheses indicate the selectivity.

and 3-buten-2-ol. In contrast, the reactivity of the unsaturated alcohols over $TiO_2$ was summarized as the following sequence: 3-buten-2-ol > 2-buten-1-ol > 3-buten-1-ol (Table 6). The consecutive dehydration into 1,3-butadiene proceeded for all the unsaturated alcohols over $TiO_2$, while the several side reactions were also promoted. Thus, the products distribution was very complex.

## 4. Discussion

### 4.1. Reaction of monoalcohols over catalysts with different acid–base properties

The reaction of 1- and 2-butanols was carried out over $SiO_2$–$Al_2O_3$, $TiO_2$ and $ZrO_2$ to discuss the reaction mechanism of 1,3-butanediol dehydration (Tables 3 and 4). It should be noted that 2-butanol is more reactive than 1-butanol. This result suggests that the dehydration proceeds via carbocation as the intermediate: a secondary carbocation, which is produced by the elimination of OH group from 2-butanol, is more stable

Scheme 1. Probable reaction pathway from 1,3-butanediol to products over catalysts. Numbers under the products are the same as those in Table 1.

than primary one derived from 1-butanol. Saytzeff products are mainly obtained with acid-catalyzed mechanism [16], and 2-butene, Saytzeff product, was mainly produced from 2-butanol. The products distribution from butanols over acidic SiO$_2$–Al$_2$O$_3$ and TiO$_2$ also supports the acid-catalyzed mechanism. 1-Butene is, however, selectively produced from 2-butanol over ZrO$_2$. It is known that ZrO$_2$ gives Hoffmann products from 2-alcohols [17,18]. We should note that butyl butyrate is produced with a moderate selectivity from 1-butanol over ZrO$_2$. It is reasonable that the reaction from 1-butanol to butyl butyrate proceeds via either Tishchenko reaction of n-butylaldehyde [19] or hemiacetal formation [20–22].

### 4.2. Reaction of 1,3-butanediol over SiO$_2$–Al$_2$O$_3$

In this study, four catalysts with different acid–base properties were employed to investigate the effects of these properties on the reaction of 1,3-butanediol. SiO$_2$–Al$_2$O$_3$ shows the highest activity because it catalyzes the dehydration of 1,3-butanediol at the lowest temperature among the catalysts we tested. Then, the sequence of the catalytic activity can be summarized as follows; SiO$_2$–Al$_2$O$_3$ > Al$_2$O$_3$ ≫ TiO$_2$ ≃ ZrO$_2$ (Fig. 2). This is in good coincidence with the acid property of catalysts: the strongest acid catalyst, SiO$_2$–Al$_2$O$_3$, exhibited the highest activity for the reaction of 1,3-butanediol. These results imply that the dehydration of 1,3-butanediol is catalyzed at acid sites of the catalysts.

We have already reported the dehydration of 1,3-diols over CeO$_2$ catalyst [9,10,12,13] and conclude that the reaction is promoted by radical mechanism [10,12]. Judging from the products distribution, 1,3-butanediol would be activated with different mechanism between acid catalysts and CeO$_2$. 3-Buten-2-ol and trans-2-buten-1-ol are selectively produced over CeO$_2$, while 3-buten-1-ol is preferably obtained over acid SiO$_2$–Al$_2$O$_3$, which is the strong acid catalyst with no base sites on its surface (Fig. 1).

Alcohols are dehydrated to give Saytzeff products over acid catalysts, as mentioned in the previous section [16]. Thus, 2-buten-1-ol should have been produced as the main dehydrated products over acid catalysts in the dehydration of 1,3-butanediol. We elucidated that unsaturated alcohols are consecutively dehydrated to produce 1,3-butadiene over SiO$_2$–Al$_2$O$_3$ (Table 5). The selectivity to 1,3-butadiene increased with increasing the conversion of 1,3-butanediol while those to unsaturated alcohols decreased (Table 2). 1,3-Butadiene could be produced from the unsaturated alcohols over SiO$_2$–Al$_2$O$_3$, while 3-buten-1-ol is less reactive than 2-buten-1-ol and 3-buten-2-ol (Table 5). Thus, 3-buten-1-ol remains in the reaction mixture of 1,3-butanediol (Table 2). The high selectivity to 3-buten-1-ol is probably caused by the faster consumption rate of 2-buten-1-ol than that of 3-buten-1-ol.

In addition, we observed the production of propene in the decomposition of 3-buten-1-ol over SiO$_2$–Al$_2$O$_3$ (Table 5). However, propene was not observed in the reaction of 1,3-

butanediol (Table 2). This difference is probably attributed to the conditions for each reactant: the reaction of unsaturated alcohols was performed at the residence-time twice as long as that of 1,3-butanediol, i.e. using twice amount of catalyst weight, and at high temperature of 250 °C. Such severe conditions may promote the production of propene from 3-buten-1-ol over $SiO_2$–$Al_2O_3$.

### 4.3. Reaction of 1,3-butanediol over other metal oxides

We summarize the probable reaction pathways from 1,3-butanediol to products detected in this work, as shown in Scheme 1. $Al_2O_3$ showed unique catalytic performance in the reaction of 1,3-butanediol: 4-methyl-1,3-dioxane and formaldehyde were obtained with moderate selectivities (Table 2). 4-Methyl-1,3-dioxane can be produced via acetalization of formaldehyde with 1,3-butanediol. Formaldehyde would be produced via the reverse-aldol reaction of 4-hydroxy-2-butanone, which is produced by dehydrogenation of OH group at 3-position in 1,3-butanediol. Then, we face a puzzling question: propanone should be produced by the decomposition of 4-hydroxy-2-butanone. However, the amount of propanone does not make up with that of formaldehyde (Table 2). At this point, we cannot explain the phenomena.

3-Buten-1-ol is the main product from 1,3-butanediol over $TiO_2$, while 2-buten-1-ol is produced with high selectivity and 3-buten-2-ol is rarely produced (Table 2). The lower selectivity to 2-buten-1-ol is not attributed to the consecutive dehydration into 1,3-butadiene because it was not formed over $TiO_2$. In the reaction of 2-butanol over $TiO_2$, *cis*-2-butene was mainly obtained, and the selectivity to 1-buene was higher than that to *trans*-2-butene (Table 4). In the reaction of 1,3-butanediol, however, *cis*-2-buten-1-ol was less selective than *trans*-2-buten-1-ol; the selectivities to *cis*- and *trans*-2-buten-1-ol were 3.2 and 8.0 mol.% at 350 °C, respectively. The formation of *cis*-2-buten-1-ol could be restricted by steric hindrance induced by the OH group at 3-position in 1,3-butanediol, and thus, 3-buten-1-ol would be mainly produced over $TiO_2$.

Although $ZrO_2$ has the weakest acid sites among the catalysts employed in this study, its activity is comparable to that of $TiO_2$ (Fig. 1). Thus, the dehydration of 1,3-butanediol probably does not proceed with the simple acid-catalyzed mechanism over $ZrO_2$. Recently, we have reported the selective dehydration of 1,4-butanediol into 3-buten-1-ol over $ZrO_2$ and concluded that the acid–base property of $ZrO_2$ played a crucial roll in the reaction [23]. It is speculated that 1,3-butanediol is dehydrated in the same mechanism as in the case of 1,4-butanediol. Then, we can emphasize that the acid–base concerted mechanism rather than simple acid catalysis possibly elucidates the high selectivity to 3-buten-2-ol over $ZrO_2$ (Table 1). The primary OH group in 1,3-butanediol can be readily activated in the mechanism because 1,4-butanediol, which has two primary OH groups, is dehydrated into 3-buten-1-ol [23,24]. In the acid-catalyzed dehydration, primary OH group is less reactive, as mentioned in Section 4.1.

Over $TiO_2$ and $ZrO_2$, the products distribution was very complex (Table 2). The complexity is caused by the side reactions, i.e. hydrogenation and dehydrogenation. 3-Buten-2-one is the

major by-product from 1,3-butanediol over $TiO_2$ and $ZrO_2$, and it can be synthesized via two routes: one is the dehydration of 4-hydroxy-2-butanone produced by dehydrogenation of 1,3-butanediol, and another is the dehydrogenation of 3-buten-2-ol. It is deduced that the former route is highly probable because $TiO_2$ rarely catalyzed the dehydration of 1,3-butanediol into 1,3-butadiene (Table 2). Although 3-buten-2-one was produced with the selectivity of 10.7 mol.% in the reaction of 3-buten-2-ol over $TiO_2$ (Table 6), 3-buten-2-ol is readily dehydrated into 1,3-butadiene. We have reported the dehydration of 4-hydroxy-2-butanone over $TiO_2$, and it is dehydrated at the reaction temperature as low as 160 °C [25]. The produced 3-buten-2-one is probably hydrogenated into butanone, and it may be further hydrogenated to produce 2-butanol. 2-Butanol can also be produced by the hydrogenation of 3-buten-2-ol.

Here, we can categorize the products in five groups, as shown in Table 2 and Scheme 1:

Group I: unsaturated alcohols, 1,3-butadiene and unsaturated ethers;
Group II: propanone, formaldehyde, methanol and 4-methyl-1,3-dioxane;
Group III: 3-buten-2-one, butanone and 2-butanol;
Group IV: 1-butanol, 2-butenal and butanal;
Group V: acetaldehyde and ethanol.

Taking the discussion so far into account, we can consider that the products in Groups I–V are formed via the following routes:

Group I: dehydration of 1,3-butanediol;
Group II: decomposition of 4-hydroxy-2-butanone, which is formed via the dehydrogenation of secondary OH group in 1,3-butanediol;
Group III: dehydration of 4-hydroxy-2-butanone;
Group IV: consecutive hydrogenation and dehydrogenation of Group I unsaturated alcohols;
Group V: decomposition of acetaldol, which is produced via the dehydrogenation of primary OH group in 1,3-butanediol.

$SiO_2$–$Al_2O_3$ predominantly produces the Group I products owing to its strong acidity. $Al_2O_3$ preferably produces the Group II products. It is probably caused by its high basicity. $TiO_2$ and $ZrO_2$ mainly form the products in Group I, while moderate formation of the products in Groups II–IV, which implies that they have not only the dehydration ability but also hydrogenation/dehydrogenation ability. Over all the catalysts, the products in Group V are rarely produced, probably due to the low dehydrogenation susceptibility of the primary OH group in 1,3-butanediol.

## 5. Conclusion

Reaction of 1,3-butanediol over several catalysts with different acid–base properties was investigated. The catalytic activity was ruled by its acid strength. The strong acid sites of $SiO_2$–$Al_2O_3$ catalyzed the dehydration of 1,3-butanediol into

unsaturated alcohols, which were further dehydrated into 1,3-butadiene at high conversion level. The weak acidic catalysts, $TiO_2$ and $ZrO_2$, promoted not only the dehydration of 1,3-butanediol but also several side reactions such as hydrogenation and dehydrogenation. Thus, the products distribution was complex over these catalysts. $Al_2O_3$ enhanced the decomposition of 1,3-butanediol into formaldehyde, which reacted with 1,3-butanediol to form an acetal compound, 4-methyl-1,3-dioxane. As the consequence, the acidic catalysts hardly controlled the selectivity to a specific product.

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