Selective Dehydration of 2,3-Butanediol to 3-Buten-2-ol over ZrO₂ Modified with CaO

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Abstract

Vapor-phase catalytic dehydration of 2,3-butanediol (2,3-BDO) was investigated over several metal oxides loaded on well-crystallized monoclinic ZrO₂. In the dehydration of 2,3-BDO, unsaturated alcohol, i.e. 3-buten-2-ol (3B2OL), was preferentially produced together with major by-products such as butanone and 3-hydroxy-2-butanone over ZrO₂-based catalysts. The selectivity to 3B2OL over monoclinic ZrO₂ was greatly enhanced by the alkaline-earth oxides such as CaO, SrO, and BaO. At a CaO loading of 3 wt.% on the monoclinic ZrO₂, a Ca-O-Zr hetero-linkage was formed to generate new basic sites, and the selectivity to 3B2OL exceeded 76% at 350 °C. Poisoning experiments using CO₂ and NH₃ strongly suggest that the formation of 3B2OL from 2,3-BDO proceeds over base-acid concerted sites.

Keywords: Unsaturated alcohol; 3-Buten-2-ol; 2,3-Butanediol; Dehydration; Monoclinic ZrO₂; Supported alkaline-earth oxides; Base-acid concerted sites.

1. Introduction

Unsaturated alcohols such as allylic and homoallylic alcohols are important intermediates for the synthesis of aroma chemicals, medicinal drugs, agricultural chemicals, and polymers [1-5]. We have previously summarized several examples of the production of unsaturated alcohols from glycols [6], i.e. 3B2OL and *trans*-2-buten-1-ol from 1,3-butanediol (1,3-BDO) [7-9], 3-buten-1-ol from 1,4-butanediol (1,4-BDO) [9-11], and 4-penten-1-ol from 1,5-pentanediol [12,13]. 4-Penten-1-ol was preferentially formed from 1,5-pentanediol over monoclinic ZrO_2 (m- ZrO_2) at 325-375°C, and the modification of m- ZrO_2 with lithium cations suppressed the formation of tetrahydropyran and enhanced the selectivity to 4-penten-1-ol [12]. 1,4-BDO was dehydrated into 3-buten-1-ol over m- ZrO_2 at 325-350°C [10]. In the dehydration of 1,4-BDO, m- ZrO_2 modified with sodium cations enhanced the selectivity to 3-buten-1-ol [11], and calcium oxide also improved the 3-buten-1-ol selectivity of tetragonal ZrO_2 [14]. Recently, we have reported the dehydration of 2,3-BDO to produce 3B2OL preferentially over highly crystallized m- ZrO_2 [15].

With the development of fermentation technologies, 2,3-BDO could be obtained from glucose with a high yield and high purity in the cell recycle system of *Escherichia coli* [16-22]. Thus, 2,3-BDO could be a raw material for chemicals such as butanone (MEK), 3B2OL, and 1,3-butadiene, etc. As for the dehydration of 2,3-BDO, some researchers attempted to synthesize 1,3-butadiene directly from 2,3-BDO for the production of rubber during World War II [23,24]. Winfield disclosed the highest yield, which was 62.1% of butadiene from 2,3-BDO over ThO_2 at 500°C [23]. ThO_2 also catalyzed the formation of 3B2OL with a yield of 70.3% in the first step of 2,3-BDO dehydration: 3B2OL could be produced at 350°C firstly, and then converted into 1,3-butadiene for the further dehydration at a high temperature of 500°C. In contrast, Bouns reported that MEK was obtained with a yield of 86% from 2,3-BDO over mineral acids such as bentonite at 225°C, and that 1,3-butadiene was obtained with a yield of about 20% at 700°C [24]. Recently, it has reported that acid catalyzes the dehydration of 2,3-BDO [25,26]: MEK is the main product together with rare formation of 3B2OL and 1,3-butadiene over zeolites [26]. As far as we

know, only ThO_2 is the selective catalyst in the formation of 3B2OL from 2,3-BDO [23]. However, thorium is a toxic radioisotope, so that it would not be used in industrial application.

In this paper, we investigated the dehydration of 2,3-BDO over m- ZrO_2 modified with several basic cations. We have found that CaO modifier efficiently increased the 3B2OL selectivity of well-crystallized m- ZrO_2 . We also characterized the CaO-modified m- ZrO_2 (CaO/ZrO_2) through XRD, FT-IR, CO_2 -TPD, and NH_3 -TPD measurements. We also performed a poisoning experiment using either CO_2 or NH_3 gas to clarify the active sites for the formation of 3B2OL.

2. Experimental

2.1. Catalyst preparation

The support m- ZrO_2 (JRC-ZRO-4) was supplied by the Reference Catalyst Division (former Committee) of Catalyst Society of Japan, as described in [27]. Reference catalysts such as tetragonal ZrO_2 (JRC-ZRO-3) and Al_2O_3 (JRC-ALO-6) were also supplied by the Reference Catalyst Division. Basic modifiers such as $\text{LiOH}\cdot\text{H}_2\text{O}$, NaNO_3 , KNO_3 , $\text{Mg}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Zn}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, and $\text{La}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ were purchased from Wako Pure Chemical Industries, Ltd.

In this study, the support m- ZrO_2 was pre-heated in air at 800 °C for 3 h prior to impregnation of CaO because the calcination is effective in the enhancement of 3B2OL selectivity over pure m- ZrO_2 [15]. Either CaO or other metal oxides was loaded on m- ZrO_2 by using incipient wetness impregnation. Each aqueous solution of either the corresponding nitrate or hydroxide with the prescribed amount of metal was impregnated onto m- ZrO_2 . The resulting samples were dried at 110°C for 12 h, and then calcined in air at a prescribed temperature for 3 h to obtain CaO/ZrO_2 catalysts. As a reference, pure CaO was obtained from $\text{Ca}(\text{NO}_3)_2\cdot 4\text{H}_2\text{O}$ calcined at 800°C for 3 h. Hereafter, CaO/ZrO_2 catalysts are expressed as CaO-X-T, where X is the CaO loading (wt.%), and T is the calcination temperature (°C) after impregnation.

2.2. Catalytic reaction

The dehydration of 2,3-BDO was carried out in a fixed-bed flow reactor under atmospheric pressure of H_2 with a flow rate of $80 \text{ cm}^3 \text{ min}^{-1}$ at 350°C . Prior to the reaction, a catalyst (1.0 g) was preheated in an H_2 flow at 350°C for 1 h. After the catalyst bed had been preheated, 2,3-BDO was fed through the top of the reactor by the contact time $W/F = 84.7 \text{ g}_{\text{cat}} \text{ h mol}^{-1}$, where W and F are the weight of catalyst (g) and the feed rate of 2,3-BDO (mol h^{-1}), respectively. The liquid effluent collected hourly was analyzed by gas chromatography (FID-GC-8A, Shimadzu, Japan) with a 60-m capillary column (DB-WAX: inside diameter, 0.53 mm; liquid-phase thickness, 0.2 μm). The products were identified by gas chromatography with a mass spectrometer (GCMS-QP5050A, Shimadzu, Japan) and a 30-m capillary column (DB-WAX: inside diameter, 0.32 mm; liquid-phase thickness, 0.25 μm). Gaseous products such as 1,3-butadiene were analyzed by on-line gas chromatography (GC-8A, Shimadzu, Japan) with a 6-m packed column (VZ-7: inside diameter, 3 mm). The catalytic activity was evaluated by averaging the conversion and selectivity data in the initial 5 h. Both the conversion of 2,3-BDO and the selectivity to each product were expressed as mol%.

In order to confirm the effects of poisoning on the basic and acidic sites of the catalyst surface during the reaction, the carrier gas was changed to a mixture of either CO_2/H_2 or NH_3/H_2 with the volume ratio of 24/56 in the total flow rate of $80 \text{ cm}^3 \text{ min}^{-1}$.

2.3. Characterization

The specific surface area (SA) of catalysts was calculated by the Brunauer-Emmett-Teller (BET) theory using the N_2 isotherm at -196°C . Temperature-programmed desorption (TPD) of adsorbed CO_2 and NH_3 were measured to estimate the basicity of the catalysts, which were preheated at 500°C under a reduced pressure. The numbers of basic sites and acid sites were estimated from neutralization-titration curves of diluted NaOH and H_2SO_4 solution, respectively, as the

details described in our previous paper [28]. Powder X-ray diffraction (XRD) patterns were recorded on New D8 ADVANCE (Bruker) using Cu K α radiation (λ = 0.154 nm) to detect the crystal structures of the modified ZrO₂. Structural features of CaO/ZrO₂ were characterized by Fourier transform infrared (FT-IR) spectroscopy, i.e. diffuse reflectance infrared Fourier transform (DRIFT) spectrometer with a mercury cadmium telluride detector (JASCO Corp., Japan).

3. Results

3.1. Dehydration of 2,3-BDO over modified m-ZrO₂ catalysts.

Table 1 lists the results of catalytic reactions of 2,3-BDO over various m-ZrO₂ catalysts modified with basic oxides at 350°C. The conversion of 2,3-BDO decreased by loading metal oxides on the support m-ZrO₂, while the selectivity to 3B2OL increased by some metal oxides, compared with the pure m-ZrO₂ calcined at 800°C. Li₂O and La₂O₃ decreased the 3B2OL selectivity. Among the metal oxides we tested, alkaline-earth metal oxides such as MgO, CaO, SrO, and BaO improved the 3B2OL selectivity of m-ZrO₂ together with a moderate 2,3-BDO conversion. The dehydrogenated product, i.e. 3H2BO, also increased with the addition of alkaline-earth metal oxides, while the selectivities to MEK, 2-methylpropanal, and 2-methyl-1-propanol decreased. In particular, the 3B2OL selectivity over CaO/ZrO₂ exceeded 76% at a relatively high 2,3-BDO conversion. Thus, hereafter, the CaO/ZrO₂ catalyst that showed the highest 3B2OL selectivity was selected as the aimed catalyst in the following sections.

3.2. Dehydration of 2,3-BDO over CaO/ZrO₂ catalysts.

Table 2 summarizes the catalytic activities of CaO/ZrO₂ catalysts with different CaO loadings at 350°C. The addition of CaO onto m-ZrO₂ greatly enhanced the selectivity to 3B2OL higher than 70%, whereas the 2,3-BDO conversion significantly decreased with increasing CaO loading. **Table 2** also lists the selectivity to by-products in the reaction. For the dehydrogenated product, i.e. 3H2BO, the selectivity was increased with increase in CaO

loading, while the selectivity to MEK was almost constant at 3-5% over CaO/ZrO₂ catalysts. In addition, the catalytic activity greatly depends upon the calcination temperature over CaO/ZrO₂ with CaO loading of 3 wt.%. It was also confirmed that both the highest 2,3-BDO conversion and the highest 3B2OL selectivity were obtained at a calcination temperature of 800°C.

Figure 1 shows the effect of reaction temperatures on the catalytic dehydration of 2,3-BDO over CaO-3-800 catalyst. With increasing the reaction temperature, the conversion of 2,3-BDO and the selectivity to MEK increased, while the selectivity to 3H2BO decreased. The selectivity to 3B2OL showed a maximum at 350 °C.

Figure 2 depicts the changes in the 2,3-BDO conversion and the selectivity to 3B2OL with contact time (W/F) over CaO-3-800 catalyst at 350 °C. The conversion increased with increasing W/F, and reached 79.8% at 254 g_{cat}h mol⁻¹, while the selectivity to 3B2OL was almost unchanged at different W/F. This result indicates that the excessive side reactions such as the decomposition of 3B2OL rarely proceeds at 350 °C even at a high 2,3-BDO conversion and a long contact time.

3.3. Effect of CO₂ and NH₃ poisoning during the reaction

Judging from the data listed in **Tables 1** and **2**, it is obvious that the supported alkaline-earth metal oxides such as CaO, SrO, and BaO improved the 3B2OL selectivity of pure m-ZrO₂ catalyst. In order to clarify how the acidic and basic functions of the catalysts work during the reaction, we performed poisoning experiment using NH₃ and CO₂ carrier gases. **Figure 3** shows the changes in the catalytic activities in H₂ carrier gas with different poisoning gases, i.e. H₂ carrier gas with 30 vol.% CO₂ or NH₃ over CaO-3-800 catalyst. The 2,3-BDO conversion was significantly reduced in the both CO₂- and NH₃-containing carrier gases. The 3B2OL selectivity was also decreased by CO₂ poisoning, but slightly increased by NH₃ poisoning. It is obvious that the formation of 3B2OL from 2,3-BDO is suppressed in both CO₂- and NH₃-containing carrier gases.

Table 3 summarizes the poisoning effect of CO₂ and NH₃ in the dehydration of

2,3-BDO. Over the pure m-ZrO₂ calcined at 800°C, the 2,3-BDO conversion was slightly reduced by CO₂ poisoning while the 3B2OL selectivity was almost the same as in H₂ flow. However, NH₃ poisoning upgraded the 3B2OL selectivity: the yield of 3B2OL in NH₃ is obviously higher than that in H₂ over pure m-ZrO₂. On the other hand, the 2,3-BDO conversion significantly decreased in both CO₂ and NH₃ over CaO-X-800 catalysts at X= 1 and 3. However, at X= 5, neither CO₂ nor NH₃ gases worked as a poison. In particular, NH₃ gas seems to work as a promoter to increase the 3B2OL selectivity in a similar way to pure m-ZrO₂. At low CaO loadings of X= 1 and 3, the poisoning experiments reveal that both acidic and basic sites on the modified catalyst could cooperatively work as active centers for the formation of 3B2OL.

3.4. Characterization of catalyst samples

Figure 4 illustrates TPD profiles of CO₂ adsorbed on the catalysts. The desorption peak up to 200 °C (assigned as α) was observed on almost all the samples. Over the alkaline-earth metal oxides supported on ZrO₂ (Fig. 4A), a desorption peak appeared at around 350°C (assigned as β), which has also been reported in a mesoporous CaO-ZrO₂ [29]. Figure 4B illustrates CO₂-TPD profiles of CaO-X-800 catalysts. The CaO-3-800 sample had more basic sites β than the other samples. The β peak decreased gradually with increasing CaO loading. At CaO loading of 15 and 30 wt.%, a desorption peak resulted from CaO appeared between 500 and 600 °C (assigned as γ). In Fig. 4C, the β peak was rarely observed and the strong γ peak appeared when the sample was calcined at temperatures lower than 800 °C. At 800 °C, the γ peak disappeared and the β peak appeared. It indicates that calcination temperatures of 800°C are needed for the formation of basic sites β . Table 4 summarizes quantitative data for basicity of CaO-X-T catalysts as well as the specific surface area. Densities of basic sites α and β were calculated from the total amount of basic sites and the specific surface area.

Figure 5 illustrates NH₃-TPD profiles of CaO-X-800 and other reference catalysts. Reference acidic samples have desorption peaks of NH₃: Al₂O₃ had acid sites of 76.8 μ mol

g^{-1} and tetragonal ZrO_2 had ones less than $10 \mu\text{mol g}^{-1}$. They showed the dehydration ability to form MEK and 1,3-butadiene from 2,3-BDO (Table 2). CaO-X-800 , on the other hand, had really few acidic sites on the surface. It can also be observed that the amount of acidic sites even with different strength declined with increasing CaO loading X of CaO -modified m-ZrO_2 .

Figure 6 shows the XRD patterns of CaO-X-T , m-ZrO_2 , and CaO samples. Pure m-ZrO_2 and all the CaO/ZrO_2 samples could be identified as well-crystallized monoclinic phase. In the CaO-X-800 samples ($X=1.5, 3, 5, 10, 15$, and $30 \text{ wt.}\%$), the intensity of the peaks belonging to m-ZrO_2 became weaker with increasing CaO loading when compared with the pure m-ZrO_2 . At CaO loadings of $3 \text{ wt.}\%$ or higher, the diffraction peaks attributed with CaZrO_3 phase were observed at $2\theta = 22.2$ and 45.3 degree [30], which were growing with increasing CaO loading. Although a major diffraction peak of CaZrO_3 should be observed at $2\theta = 31.5$ degree [30], this was hidden by the diffraction peak of m-ZrO_2 . At CaO loadings of $15 \text{ wt.}\%$ or higher, the peaks attributed to CaO phase was also detected at $2\theta = 37.4$ and 54.0 degree [29]. In addition, XRD patterns of the CaO-3-T samples at $T=600, 700$, and 900°C were also measured to compare with that of CaO-3-800 . No CaZrO_3 phase was observed in the samples calcined at low temperatures of 600 and 700°C . In the present work, tetragonal ZrO_2 phase was not detected in the XRD patterns of all the CaO-X-T samples.

Figure 7 shows the DRIFT spectra of the CaO-X-800 catalysts. The broad absorption bands from 447 to 556 cm^{-1} can be identified to be characters of the pure CaO phase and the broad bands from 506 to 760 cm^{-1} to be the Zr-O vibration absorption. With increasing CaO loading, the band confirmed as the vibration absorption of Ca-O-Zr shifted gradually from 506 cm^{-1} to higher wavenumber up to 551 cm^{-1} . The changes are well consistent with the samples of tetragonal ZrO_2 incorporated with Ca cations in the preceding work [14].

4. Discussion

4.1. Confirmation of basic sites β and the new acidic sites over the modified catalysts

In the poisoning experiment of Fig. 3 and Table 3, we can confirm that there are some new basic and acidic sites acting as the active center for the formation of 3B2OL from 2,3-BDO on the surface of CaO-3-800 catalyst. The CO₂-TPD profiles in Fig. 4 indicate new basic sites β appeared on all CaO-X-800 catalysts except CaO-30-800, when compared with the pure m-ZrO₂ and some other modified samples. As discussed in the work of Zhang et al. [14], Ca²⁺ replaced with Zr⁴⁺ of tetragonal ZrO₂ for the new formation of Ca-O-Zr hetero-linkages. Thus, the acidic sites resulted from Zr-O-Zr were removed, and the Ca-O-Zr bond could lead to the uneven distribution of charges to generate new basic and acidic sites. In the present work, Ca-O-Zr hetero-linkages are also confirmed by DRIFT (Fig. 7). Thus, it is possible that the uneven distribution charges of Ca-O-Zr bonds produce the basic sites α and β (Fig. 4). However, the acidic sites of m-ZrO₂ are observed to be neutralized by loading CaO, and weak acidic sites could not be detected in the NH₃-TPD profiles (Fig. 5). In addition, MgO supported on ZrO₂ (MgO/ZrO₂), which shows the highest intensity of the basic sites α but the lowest basic sites β (Fig. 4A), exhibits lower 2,3-BDO conversion, lower 3B2OL selectivity, and higher 3H2BO selectivity than those of CaO-3-800 (Table 1). Both SrO/ZrO₂ and BaO/ZrO₂ with a considerable amount of basic sites β show high 3B2OL selectivity. Thus, it is probable that a basic sited β acts as an effective basic site for the formation of 3B2OL.

In the CaO-3-T samples, calcination temperatures clearly affect the basicity and the catalytic activity (Fig. 4C and Table 2). The CaO-3-T samples need the calcination at a temperature of 800°C or higher to form the basic sites β originated from the new Ca-O-Zr bond together with the disappearance of strong basic sites such as γ peak (around 500-600 °C) observed in the samples at T=600 and 700 °C, which could be originated from CaO dispersed on m-ZrO₂ surface.

4.2. Crystal phases in CaO/ZrO₂ catalysts

The XRD patterns (Fig. 6) indicate that the excess Ca²⁺ aggregates to form CaO phase at high CaO loading over 15 wt.%. In Table 2, both the conversion of 2,3-BDO and the

selectivity to 3B2OL decreased at either a high CaO content or a low calcination temperature. Excess Ca^{2+} also resulted in increase in basic sites α (Table 4) and it aggregated to form CaZrO_3 and CaO (Fig. 7) to reduce the dehydration activities. Therefore, it is reasonable that only by loading a proper content of CaO, the basic sites β as active sites can be induced on the surface of m- ZrO_2 to improve the catalytic activities in the dehydration of 2,3-BDO. In the present study, the formation of tetragonal ZrO_2 phase was not expected because it may preferentially produce butadiene with the competitive by-product MEK rather than 3B2OL, as cited in Table 2. Actually, tetragonal ZrO_2 phase was not detected in the XRD patterns of all the CaO-X-T samples.

4.3. Relationship between acid-base properties and the catalytic activities

In the dehydration of 1,4-BDO, it is reported that the modification of ZrO_2 with an appropriate amount of sodium cations [11] and CaO [14] improved the selectivity to 3-buten-1-ol. We have demonstrated the dehydration of 1,4-BDO to produce 3-buten-1-ol in different carrier gases: both CO_2 and NH_3 act as a poison in the reaction over rare earth oxides such as Er_2O_3 [31]. As we summarized in Fig. 3 and Table 3, both CO_2 and NH_3 act as a poison in the reaction over CaO-1-800 and CaO-3-800 catalysts. The results clearly indicate that both basic and acidic sites of the catalysts play an important role in the dehydration of 2,3-BDO to produce 3B2OL. Judging from the stronger poisoning effect of CO_2 than that of NH_3 , the basic sites on the catalyst play the major role on the formation of 3B2OL, while the acidic sites also support the dehydration of 2,3-BDO. In contrast to the basic sites, we observed few acidic sites through the profiles of NH_3 -TPD of CaO-X-800 (Fig. 5). It is probable that very weak acidic sites, which cannot be detected by NH_3 adsorption, concerted with basic sites could work as active sites for the formation of 3B2OL. Table 3 also suggests that the formation of 3B2OL increased in NH_3 over pure m- ZrO_2 and CaO-5-800. We cannot explain why acidic sites on ZrO_2 work as active sites for the formation of 3B2OL, but NH_3 adsorbed on the catalyst may act as a catalyst. There is another possibility: there may be some acidic sites on the pure m- ZrO_2 to promote the

formation of some by-products more greatly than the formation of 3B2OL from 2,3-BDO, and the acidic sites to catalyze the by-products formation could be poisoned by NH_3 . It is obvious that the basic sites are surely poisoned by CO_2 over CaO-5-800 (Table 3). The major role of the dehydration would be attributed by the basic sites of the abstracting ability of hydrogen of 2,3-BDO in the similar way to the dehydration of 1,4-BDO [31] over Er_2O_3 and tetragonal ZrO_2 -supported CaO [14] as well as the dehydration of 1,3-BDO [32] over Er_2O_3 .

We have to consider the structure of the acid-base sites. As we have discussed in the Section 4.1, the calcination at 800 °C induces the hetero-linkages of Ca-O-Zr as well as the peak β in the CO_2 desorption (Fig. 4). The temperature of peak β is close to the reaction temperature that the catalyst effectively works. We speculate that the new active sites could be generated from the surface Ca-O-Zr hetero-linkages, as we depicted in the Graphical Abstract. It is probable that O^{2-} anion in the Ca-O-Zr hetero-linkage could be the new basic site β , and that the cations of Ca^{2+} and Zr^{4+} would act as acidic sites. This is also discussed in the following section related with the reaction mechanism of Scheme 1.

4.4. Speculative reaction mechanism over CaO/ZrO₂ catalyst

We have calculated the stable adsorption structure of 1,4-BDO on Er_2O_3 catalyst in the dehydration of 1,4-BDO using theoretical calculations [33]. We have demonstrated a probable acid-base concerted mechanism over Er_2O_3 in the formation of 3-buten-1-ol from 1,4-BDO [31,33]. The most reasonable adsorption structure is a tridentate coordination that the position-2 hydrogen atom of 1,4-BDO is placed on the top of an oxygen anion of Er_2O_3 , and that two hydroxyl groups of 1,4-BDO fill two oxygen vacancies of the Er_2O_3 surface. The oxygen anion and the oxygen vacancy can be regarded as a basic and an acidic site, respectively. The estimated reaction mechanism is as follows: firstly a position-2 hydrogen atom is abstracted by an oxygen anion; and consequently the position-1 hydroxyl group of 1,4-BDO is abstracted by a rare earth cation to form π bond between the position-1 and position-2 carbon; and finally unsaturated alcohol is desorbed.

The poisoning experiments in Fig. 3 directly indicate that the basic and acidic sites on the modified catalyst cooperatively work as active sites to produce 3B2OL from 2,3-BDO. In the present study, we have succeeded in introducing the acid-base sites acting as the active sites for the dehydration of 2,3-BDO to the well-crystallized surface of pure m-ZrO₂ through impregnation of CaO. In order to understand how the acid-base sites acting as active center for the formation of 3B2OL from 2,3-BDO, we propose a speculative mechanism described in Scheme 1. The active center in Scheme 1 consists of a basic site (expressed as B) and two acidic sites (expressed as A₁ and A₂). The reaction involves four steps such as adsorption, abstraction, dissociation, and regeneration. In the first step, an oxygen in OH groups of 2,3-BDO is adsorbed on the acidic site A₁ when the reactant 2,3-BDO is passing the catalyst. The other OH is also adsorbed on another acidic site A₂. Finally, the adsorptive interaction between a hydrogen of the methyl group and the basic site B on the catalyst appears to form a tridentate coordination with the largest adsorption energy. In the second step, the hydrogen of methyl group is eliminated by the basic site B to form an anion and followed by elimination of HO⁻ on an acidic site A₁ to form a cation. It is probable that the formation of a pair of C⁺ and C⁻ which could lead to 3B2OL should be produced over a pair of acidic and basic sites. In the third step, the formation of C=C bond occurred by the shortening of C⁺-C⁻ bond and the lengthening of A₁-OH and B-H bonds for the formation of a water molecule. The final step involves the desorption of a water molecule from the acid-base pair sites and the oxygen of OH group desorbs from an acidic site A₂ for the desorption of 3B2OL.

There is another possibility of the adsorption (Scheme 2): an active center consists of an acidic site A and a basic site B to form a bidentate adsorption. Considerable amounts of MEK and 2-methylpropanal are produced over pure m-ZrO₂ with weak basic sites (Table 1). The formation of MEK and 2-methylpropanal can be explained by the acid-catalyzed formation of CH₃CH(OH)C⁺HCH₃ during the dissociation in Scheme 2. It is reasonable that the intermediate CH₃CH(OH)C⁺HCH₃ could be deprotonated to produce MEK, and could lead to 2-methylpropanal via pinacol rearrangement through methyl migration. Actually,

MEK is reported to be a major product in the reaction of 2,3-BDO catalyzed by acidic zeolites [26]. In this case, a basic site would act as an acceptor of H^+ or CH_3^+ cooperatively.

5. Conclusions

Vapor-phase catalytic dehydration of 2,3-BDO was investigated over m-ZrO₂ modified with several metal oxides. In the dehydration of 2,3-BDO, 3B2OL was mainly produced together with major by-products such as butanone and 3-hydroxy-2-butanone over ZrO₂-based catalysts. ZrO₂-supported alkaline-earth metal oxides such as CaO, SrO, and BaO showed a higher selectivity to 3B2OL as well as a higher conversion of 2,3-BDO than other supported metal oxides such as Li₂O, MgO, and La₂O₃.

TPD of adsorbed CO₂ revealed that basic sites with medium strength (named as basic sites β), which probably act as active sites for the formation of 3B2OL from 2,3-BDO, were generated over CaO-, SrO-, and BaO-loaded ZrO₂ after calcination at 800°C or higher. Results of XRD and FT-IR also showed that, with a CaO content of 3 wt.% at calcination temperatures of 800 °C or higher, Ca²⁺ entered into the ZrO₂ to form Ca-O-Zr hetero-linkages and generated basic sites β for the dehydration of 2,3-BDO. It is confirmed that the new basic sites β act as the active sites for the formation of 3B2OL from 2,3-BDO and the acidic sites also work as adsorption sites of 2,3-BDO through CO₂-TPD and the poisoning experiments using NH₃ and CO₂ gas. It is concluded that the dehydration of 2,3-BDO into 3B2OL is promoted by base-acid concerted sites on the surface of the well-crystallized monoclinic ZrO₂ modified with CaO.

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Captions

Scheme 1 Proposed reaction mechanism in the production of 3B2OL from of 2,3-BDO over acid(A)-base(B) concerted active sites.

Scheme 2 Proposed reaction mechanism o in the production of MEK from of 2,3-BDO over acid(A)-base(B) concerted active sites.

Fig. 1. Effects of reaction temperature over CaO-3-800 catalyst. (a) Conversion of 2,3-BDO; (b) Selectivity to 3B2OL; (c) to MEK; (d) to 3H2BO. $W/F=84.7\text{g}_{\text{cat}}\text{h mol}^{-1}$.

Fig. 2. Effects of contact time (W/F) on the catalytic activity of CaO-3-800 at 350°C. (a) Conversion of 2,3-BDO; (b) Selectivity to 3B2OL; (c) to 3H2BO; (d) to MEK.

Fig. 3. Catalytic performance of CaO-3-800 catalyst in different carrier gases.

Solid lines, 2,3-BDO conversion; dotted lines, 3B2OL selectivity. $W/F=84.7\text{g}_{\text{cat}}\text{h mol}^{-1}$.

Total carrier gas flow rate = $80\text{ cm}^3\text{min}^{-1}$; pure H_2 , CO_2 -30vol.%, and NH_3 -30vol.-%- H_2 were used.

Fig. 4. CO_2 -TPD profiles of (A) m- ZrO_2 modified with different metal oxides, (B) CaO-X-800, and (C) CaO-3-T catalysts.

Fig. 5. NH_3 -TPD profiles of CaO-X-800 catalysts.

Fig. 6. XRD patterns of CaO-X-T samples together with pure ZrO_2 and CaO calcined at 800°C.

Fig. 7. DRIFT spectra of CaO-X-800 samples.

Table 1 Catalytic performance of m-ZrO₂ catalysts modified with several metal oxides, MO_n, at 350 °C.

MO _n in catalyst ^a	MO _n content ^a	Conversion ^b (mol%)	Selectivity (mol%) ^b			
			3B2OL	3H2BO	MEK	Others ^c
pure ZrO ₂	0	97.6	43.9	1.7	22.7	31.7 ^e
Li ₂ O	0.073	5.8	40.4	40.7	5.0	13.9
MgO	0.031	41.6	65.9	22.5	4.2	7.4 ^f
MgO	0.068	26.6	65.6	25.1	3.2	6.1
CaO	0.068 ^d	55.2	76.8	13.5	4.5	5.2 ^g
SrO	0.068	55.3	71.0	14.4	3.8	10.8
BaO	0.068	41.9	75.8	11.5	3.8	8.9 ^h
La ₂ O ₃	0.023	47.8	36.5	25.7	9.9	27.9

^a MO_n stands for metal oxides in catalyst; MO_n content is the mole ratio of the metal in metal oxides to Zr in m-ZrO₂. The calcination temperature after impregnation is 800 °C.

^b Catalyst weight = 1.0 g; feed rate of 2,3-BDO = 11.8 mmol h⁻¹; average conversion and selectivity are for initial 0-5 h.

^c Others included butadiene, ethylene, propylene, 2-methylpropanal, 2-methyl-1-propanol, 2,3-butanedione and some unknown products.

^d CaO loading is 3.0 wt.%.

^e Included 8.7 % 2-methylpropanal and 1.6 % 2-methyl-1-propanol.

^f Included 2.7 % 2-methylpropanal and 0.3 % 2-methyl-1-propanol.

^g Included 1.5 % 2-methylpropanal and 0.6 % 2-methyl-1-propanol.

^h Included 1.9 % 2-methylpropanal and 0.8 % 2-methyl-1-propanol.

Table 2 Catalytic performance of CaO/ZrO₂ catalysts calcined at different temperatures after impregnation and with different CaO loadings at 350 °C.

Catalyst (CaO-X-T) ^a	Conversion ^b (mol%)	Selectivity ^b (mol%)				
		3B2OL	3H2BO	MEK	BD	Others ^c
CaO-0-800 (m-ZrO ₂)	97.6	43.9	1.7	22.7	0	31.7
CaO-1-800	81.5	65.8	10.9	5.1	0	18.2
CaO-1.5-800	61.0	67.3	14.7	3.4	0	14.6
CaO-2-800	52.8	69.4	15.7	5.3	0	9.6
CaO-2.5-800	53.7	72.2	15.5	4.8	0	7.5
CaO-3-600	18.5	35.8	45.3	3.9	0	15.0
CaO-3-700	32.1	68.7	20.3	3.3	0	7.7
CaO-3-800	55.2	76.8	13.5	4.5	0	5.2
CaO-3-900	56.1	72.9	14.1	4.6	0	8.4
CaO-3.5-800	55.9	73.5	14.4	4.9	0	7.2
CaO-5-800	34.1	69.9	19.7	4.5	0	5.9
CaO-7-800	32.8	68.2	19.7	4.2	0	7.9
CaO-10-800	35.7	72.1	17.8	5.2	0	4.9
CaO-15-800	30.0	69.4	20.2	5.5	0	4.9
CaO-30-800	16.4	38.3	32.2	8.5	0	21.0
CaO-100-800 (CaO)	3.8	7.7	42.2	40.4	0	9.7
Al ₂ O ₃ ^d	100.0	0.2	1.1	33.1	41.8	23.8
tetragonal ZrO ₂ ^d	93.4	1.7	4.1	34.7	20.1	40.4

^a X is the weight percentage of CaO in the sample and T is the calcination temperature (°C) after impregnation.

^b Catalyst weight = 1.0 g; feed rate of 2,3-BDO = 11.8 mmol h⁻¹; average conversion and selectivity are for initial 0-5 h. BD indicates 1,3-butadiene.

^c Others include butadiene, ethylene, propylene, 2-methylpropanal, 2-methyl-1-propanol, 2,3-butanedione and some unknown products.

^d Data at 325 °C cited from Ref. [15].

Table 3 Catalytic performance of CaO/ZrO₂ catalysts at 350°C under different carrier gases.

Catalyst (CaO-X-T)	2,3-BDO conversion ^a (mol%)		
	in H ₂	in 30% CO ₂	in 30% NH ₃
CaO-0-800 (m-ZrO ₂)	97.6 (43.9)	93.7 (43.4)	89.7 (66.9)
CaO-1-800	81.5 (65.8)	14.1 (50.9)	19.5 (84.1)
CaO-3-800	55.2 (76.8)	21.7 (57.0)	21.0 (80.1)
CaO-5-800	34.1 (69.9)	36.9 (56.0)	38.7 (83.2)

^a Catalyst weight = 1.0 g; feed rate of 2,3-BDO = 11.8 mmol h⁻¹; carrier gas with the total flow rate of 80 cm³ min⁻¹; average conversion and selectivity are for initial 0-5 h. Numbers in parenthesis are the selectivity to 3B2OL.

Table 4 Surface properties of CaO/ZrO₂ catalysts calcined at different temperatures after impregnation and with different CaO loadings.

Catalyst (CaO-X-T)	SA (m ² g ⁻¹)	Basicity ^a (μmol g ⁻¹ _{cat})	Basicity density (μmol m ⁻²)	
			Weak (α) ^b	Medium (β) ^c
CaO-0-800 (m-ZrO ₂)	26.3	44.1	1.3	0.4
CaO-1-800	25.9	104.3	2.6	1.5
CaO-3-800	27.4	211.3	3.2	4.0
CaO-10-800	26.6	147.7	4.3	1.3
CaO-15-800	26.7	158.1	4.2	1.7
CaO-30-800	25.4	16.5	0.7	0.0
CaO-100-800 (CaO)	-	356.2	0.0	0.0
CaO-3-600	22.0	211.3	1.9	0.0
CaO-3-900	30.7	63.7	1.8	0.3

^a Calculated by the method of CO₂-TPD accumulating the amount of CO₂ desorbed up to 800 °C.

^b Calculated by using SA and the amount of CO₂ desorbed up to 200 °C.

^c Calculated by using SA and the amount of CO₂ desorbed from 200 to 450 °C.

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Fig. 2. Effects of contact time (W/F) on the catalytic activity of CaO-3-800 at 350°C. (a) Conversion of 2,3-BDO; (b) Selectivity to 3B2OL; (c) to 3H2BO; (d) to MEK.

Fig. 3. Catalytic performance of CaO-3-800 catalyst in different carrier gases at 350 °C.

Solid lines, 2,3-BDO conversion; Dotted lines, 3B2OL selectivity. $W/F=84.7 \text{ g}_{\text{cat}} \text{ h mol}^{-1}$.

Total carrier gas flow rate = $80 \text{ cm}^3 \text{ min}^{-1}$; pure H₂, CO₂-30vol.%, and NH₃-30vol.-%-H₂ were used.

Fig. 4. CO₂-TPD profiles of (A) m-ZrO₂ modified with different metal oxides, (B) CaO-X-800, and (C) CaO-3-T catalysts.

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Fig. 7. DRIFT spectra of CaO-X-800 samples.

Selective Dehydration of 2,3-Butanediol to 3-Buten-2-ol over ZrO_2 Modified with CaO

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Graphical abstract