Vapor-phase dehydration of C4 unsaturated alcohols to 1,3-butadiene

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Abstract

Vapor-phase dehydration of C4 unsaturated alcohols such as 3-buten-1-ol, 2-buten-1-ol and 3-buten-2-ol were performed to produce 1,3-butadiene over various solid catalysts including ordinary solid acid catalysts such as Al_2O_3 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, and TiO_2 and basic rare earth metal oxides such as Yb_2O_3 and CeO_2 . In the reaction of 3-buten-1-ol, 1,3-butadiene could not be selectively produced because the acid catalysts decomposed 3-buten-1-ol into propylene. In contrast to the acid catalysts, CeO_2 inhibited the decomposition of 3-buten-1-ol and showed a relatively high performance for the formation of 1,3-butadiene. In the dehydration of 2-buten-1-ol and 3-buten-2-ol, however, acid catalysts were effective for the formation of 1,3-butadiene. Among the tested catalysts, commercial $\text{SiO}_2\text{-Al}_2\text{O}_3$ showed a relatively high catalytic performance, although it deactivated rapidly. We prepared a series of $\text{SiO}_2\text{-Al}_2\text{O}_3$ catalysts by depositing SiO_2 species onto Al_2O_3 support, and the $\text{SiO}_2\text{-Al}_2\text{O}_3$ with a SiO_2 content of 10 wt.% showed more stable catalytic activity than the commercial $\text{SiO}_2\text{-Al}_2\text{O}_3$. Furthermore, modification of $\text{SiO}_2\text{-Al}_2\text{O}_3$ with Ag at a loading of 3-5 wt.% was found to be efficient for inhibiting the coke formation and improving the catalytic stability of $\text{SiO}_2\text{-Al}_2\text{O}_3$ in the dehydration of both 2-buten-1-ol and 3-buten-2-ol under hydrogen flow conditions.

Keywords: C4 unsaturated alcohols, 1,3-butadiene, Ag-modified $\text{SiO}_2\text{-Al}_2\text{O}_3$, catalytic deactivation.

1. Introduction

1,3-Butadiene (BD) is an important bulk chemical used for producing rubber and polymers. Currently, BD is primarily produced as a by-product in ethylene plant through the naphtha steam cracking [1-3]. In recent years, the production and the supply of BD are influenced by the unstable price of crude oil as well as the increasing production of shale gas. Thus, alternative routes for producing BD are expected. The conversion of ethanol to BD, which has been attempted at the industrial scale, is the most reported alternative route to replace fossil oils and gases, and *ca.* 80% yield of BD could be achieved in some catalytic processes [2, 3]. The recent developments on the fermentation technology for producing bio-derived ethanol further encourage the investigations for BD production from ethanol. On the other hand, butanediols such as 1,3-butanediol, 1,4-butanediol and 2,3-butanediol are derivable from biomass by either fermentation or catalytic conversion [4-6], and they also have potential as resources for producing biomass-derived BD [3].

Scheme 1 Production of 1,3-butadiene from butanediols via unsaturated alcohols

Scheme 1 shows the production route of BD from butanediols. Butanediols are expected to be converted to BD by two-step dehydration via unsaturated alcohols. However, among the butanediols, 2,3-butanediol is the only one butanediol that can be directly converted into BD in the dehydration over ThO_2 [7], Sc_2O_3 [8] $Na-P/SiO_2$ [9], and CsH_2PO_4/SiO_2 [10]. In addition, the dehydration of butanediols to unsaturated alcohols, as the first step, is also difficult to be selectively

catalyzed by solid acid catalysts: 1,4-butanediol and 2,3-butanediol are primarily converted to tetrahydrofuran and 2-butanone, respectively, over acid catalysts such as Al_2O_3 [11-13]. In the case of 1,3-butanediol, solid acids such as $\text{SiO}_2\text{-Al}_2\text{O}_3$, Al_2O_3 , and TiO_2 produce a wide variety of products including 3-buten-1-ol, formaldehyde, acetaldehyde and acetone [14, 15]. We have conducted a series of works on the vapor-phase dehydration of butanediols, and found that some rare earth metal oxides calcined at high temperatures such as 800 °C were effective for the selective formation of unsaturated alcohols from butanediols [16]. In particular, CeO_2 gave *ca.* 90% total selectivity to 3-buten-2-ol (3B2OL) and 2-buten-1-ol (2B1OL) in the dehydration of 1,3-butanediol at 325 °C [17]; Yb_2O_3 gave 87.6% selectivity to 3-buten-1-ol (3B1OL) in the dehydration of 1,4-butanediol at 375 °C [18]; Sc_2O_3 provided *ca.* 90% selectivity to 3B2OL in the dehydration of 2,3-butanediol at 325 °C [19]. The achievements on the production of unsaturated alcohols from butanediols provide an opportunity for producing BD from butanediols via two-step dehydration. On the other hand, although such a novel route for BD production has been paid much attention [2, 3], detailed studies on the second step, which is selective dehydration of C4 unsaturated alcohols to BD, have not been reported except the preliminary reports [8, 15, 20, 21].

In this study, vapor-phase dehydration of C4 unsaturated alcohols such as 2B1OL, 3B1OL and 3B2OL was studied to produce BD over various solid catalysts. The suitable catalyst system for each reaction was investigated, and the studies for the inhibition of the catalytic deactivation were also conducted.

2. Experimental

2.1 Samples

3B1OL and 2B1OL were purchased from Tokyo Chemical Industries Co., Ltd., Japan, and 2B1OL was a mixture of *cis* and *trans* isomers with a *cis/trans* ratio of *ca.* 1/17. 3B2OL was purchased from Sigma-Aldrich Co., Ltd., Japan. 1-Hexanol, which was used as the internal standard, was purchased from Wako Pure Chemical Industries, Ltd., Japan.

γ -Al₂O₃ (N611N, specific surface area, S_{BET} = 210 m² g⁻¹) and SiO₂-Al₂O₃ (N631L, S_{BET} = 440 m² g⁻¹) with an Al₂O₃ content of *ca.* 15 wt.% were purchased from Nikki Chemical Co., Ltd. Another Al₂O₃ (JRC-ALO-7, S_{BET} = 180 m² g⁻¹) and anatase TiO₂ (JRC-TIO-4, S_{BET} = 50 m² g⁻¹) were supplied by Catalyst Society of Japan. Yb₂O₃ was purchased from Kanto Kagaku Co. Ltd., Japan. Monoclinic ZrO₂ (RSC-HP, S_{BET} = 39 m² g⁻¹) and CeO₂ (HS, S_{BET} = 98 m² g⁻¹) were supplied by Daiichi Kigenso Kagaku Kogyo Co. Ltd, Japan. Yb₂O₃ and CeO₂ were calcined at 800 °C for 3 h before the use as catalysts, and the specific surface areas of Yb₂O₃ and CeO₂ after calcination were 29 and 42 m² g⁻¹, respectively. Tetraethyl orthosilicate, AgNO₃, and Cu(NO₃)₂·3H₂O were purchased from Wako Pure Chemical Industries, Ltd., Japan.

Self-made SiO₂/Al₂O₃ was prepared by an adsorption method described in the related procedure elsewhere [22]. Al₂O₃ (JRC-ALO-7) was used as the support, and an ethanol solution of tetraethyl orthosilicate was used as the precursor of SiO₂. The Al₂O₃ was immersed in the tetraethyl orthosilicate solution at 25 °C for 168 h. After the Al₂O₃ coated with SiO₂ was filtered, the resulted catalysts were dried at 110 °C for 12 h, and then calcined at 500 °C for 3 h. The SiO₂/Al₂O₃ with a SiO₂ loading of 10 wt.% (10SiO₂/Al₂O₃) had a specific surface area of 162 m² g⁻¹. Fig. S1 and S2 show the N₂ isotherm and pore size distribution of 10SiO₂/Al₂O₃, respectively. It is obvious that 10SiO₂/Al₂O₃ is a mesoporous material.

Metal-modified SiO₂/Al₂O₃ catalysts were prepared by an incipient wetness impregnation method using a solution with a prescribed amount of metal nitrate dissolved in distilled water. Self-made 10SiO₂/Al₂O₃ was used as the support. AgNO₃ and Cu(NO₃)₂·3H₂O purchased from Wako Pure Chemical Industries, Ltd., Japan were used as the precursor of the corresponding metal. After the impregnation process, the samples were dried at 110 °C for 12 h, and then calcined for 3 h. The calcination temperature of metal-modified SiO₂/Al₂O₃ catalysts was 500 °C.

Hereafter, the commercially supplied SiO₂-Al₂O₃ (N631L) is named as SiO₂-Al₂O₃-CS. The self-made SiO₂/Al₂O₃ catalysts are named as xSiO₂/Al₂O₃, where x indicates the weight percentage of SiO₂. Metal-modified SiO₂/Al₂O₃ catalysts are denominated as yM-xSiO₂/Al₂O₃, where y indicates the weight percentage of the additive metal; M indicates the species of the additive

metal. For example, 3Ag-10SiO₂/Al₂O₃ indicates 3 wt.% Ag loaded on a self-made SiO₂/Al₂O₃ with a SiO₂ of 10 wt.%.

2.2 Catalytic reaction

The dehydration of unsaturated alcohols was performed in a fixed-bed down-flow glass reactor with an inner diameter of 17 mm at an ambient pressure of N₂. Prior to the reaction, either 0.5 or 0.2 g catalyst was preheated at the reaction temperature for 1 h. After that, an unsaturated alcohol was fed to the reactor at a liquid feed rate of 1.75 cm³ h⁻¹ together with N₂ flow of 30 cm³ min⁻¹. The liquid effluents collected in a trap at 0 °C every hour were analyzed by a FID-GC (GC-2014, Shimadzu, Japan) with a 30-m capillary column of TC-WAX (GL-Science, Japan). The gaseous products were identified by on-line gas chromatography (GC-8A, Shimadzu, Japan) with a 6-m packed column (VZ-7, GL-Science, Japan). A GC-MS (QP5050A, Shimadzu, Japan) was used for the identification of the collected liquid products. 1-Hexanol was used as an internal standard substance. The mass balance could be achieved at a range of 70-99%. The conversion and selectivity were calculated as follows:

$$\text{Conversion (\%)} = \left(1 - \frac{\text{mole of recovered reactant}}{\text{mole of the reactant}}\right) \times 100 \quad (\text{Equation 1})$$

$$\text{Selectivity (\%)} = \frac{\text{mole of carbon in specific product}}{\text{mole of carbon in converted reactant}} \times 100 \quad (\text{Equation 2})$$

2.3 Characterization of catalysts

The specific surface area of the catalysts was measured by the BET method using N₂ isotherm at -196 °C. The temperature-programmed desorption (TPD) of adsorbed NH₃ was measured by neutralization titration using an electric conductivity cell immersed in an aqueous solution of H₂SO₄. The amount of desorbed NH₃, which was bubbled into the solution, was monitored by the change in the conductivity of the solution. A cumulative amount of desorbed NH₃ was obtained as a function of temperature and then differentiated to obtain a TPD profile as an acid strength distribution. The TPD was performed using self-made apparatus with a sample weight of *ca.* 30 mg, a temperature increase of 10 °C min⁻¹, and a heating range from the room temperature to 850

°C. The system image of the experiment for the measurement of NH₃-TPD is shown in Fig. S3, and the details of TPD experiment are described in the supporting information as well as in our previous studies [23, 24]. The thermogravimetry analysis (TG) was conducted using Thermoplus 8120E2 (Rigaku) under the following conditions: sample weight, *ca.* 10 mg; the rate of the temperature increase, 5 °C min⁻¹; heating range, from the room temperature to 900 °C.

3. Results and discussion

3.1. Dehydration of 2B1OL, 3B2OL and 3B1OL over various solid catalysts.

Firstly, some commercial catalysts were tested in the dehydration of 2B1OL, 3B2OL and 3B1OL. The catalysts can be divided to two groups: one group includes the ordinary solid acid catalysts such as Al₂O₃, SiO₂-Al₂O₃-CS, TiO₂ and ZrO₂; the other group includes some rare earth metal oxides such as CeO₂ and Yb₂O₃, which show specifically high catalytic performance for the selective formation of unsaturated alcohols in the dehydration of 1,3-butanediol [17] and 1,4-butanediol [18], respectively. The rare earth metal oxides have weak basicity, which has been confirmed in our previous study [25].

Table 1 shows the reaction results in the dehydration of 2B1OL over various catalysts. The reactions were performed at different temperatures according to the different activity of the catalysts. The catalyst weight and the flow rate of N₂ carrier gas were 0.5 g and 30 cm³ min⁻¹, respectively. Besides BD, butenes, 1-butanol, butanal, and ethers were generated with different selectivities depending on the catalysts. Here, the butenes include 1-butene, cis- and trans-2-butene, but do not include isobutene. The ethers represent the linear unsaturated ethers, which have a formula of C₈H₁₄O, produced by the intermolecular dehydration of 2B1OL. SiO₂-Al₂O₃-CS showed a high activity for the formation of BD, and 97.1% BD selectivity with 99.3% 2B1OL conversion was achieved at 260 °C. Al₂O₃ gave a 2B1OL conversion of 90.3%, while the selectivity to BD was as low as 27.2% because of the formation of ethers and undetected products. TiO₂ and ZrO₂ were also active for the formation of BD from 2B1OL, whereas the selectivities to BD were much lower than SiO₂-Al₂O₃-CS. Yb₂O₃ showed 78.9% selectivity to BD with a relatively low conversion of 42.4%. CeO₂ gave a

high 2B1OL conversion of 93.4%, whereas the selectivity to BD was as low as 21.3% because of the by-production of butanal and undetected products.

Table 2 shows the reaction results in the dehydration of 3B2OL. BD, butenes, 2-butanone, and ethers were the main products. $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ was also effective for the dehydration of 3B2OL to BD, and provided 93.4% selectivity to BD at a 3B2OL conversion of 74.4%. The selectivities to BD were 52.1%, 58.9 and 48.3% over Al_2O_3 , TiO_2 and ZrO_2 , respectively. These were much lower than $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$. Al_2O_3 gave a relatively high selectivity to ethers, and ZrO_2 gave a relatively high selectivity to 2-butanone. Al_2O_3 has been widely used as an effective catalyst for the etherification of alcohols such as methanol to dimethyl ether [26-28], which can explain the fact that Al_2O_3 gave high selectivities to ethers in the dehydration of either 2B1OL or 3B2OL. In contrast to the ordinary acid catalysts, the rare earth metal oxides showed low catalytic activities for the formation of BD from 3B2OL. Yb_2O_3 gave a relatively high selectivity to 2-butanone, while CeO_2 gave the highest selectivity to butenes.

Based on the above reaction results, we found that acid catalysts were effective for the dehydration of 2B1OL and 3B2OL to BD. Compared with Al_2O_3 , TiO_2 and ZrO_2 , $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ was more effective for the dehydration of both 2B1OL and 3B2OL to BD. In Section 3.2, we will give a further study on the dehydration of 2B1OL and 3B2OL to BD over self-made $\text{SiO}_2/\text{Al}_2\text{O}_3$ -based catalysts.

Scheme 2 Products in the dehydration of 3B1OL

Table 3 shows the reaction results in the dehydration of 3B1OL, and Scheme 2 shows the main products. The formation of BD, propylene, formaldehyde, methanol, 1-butanol, butanal, 2B1OL, and ethers were confirmed by GC-MS, while formaldehyde was unable to be detected and quantified by FID-GC. The formation of propylene, methanol, and formaldehyde indicates that C-C cleavage of 3B1OL occurred in all the tested reactions, which is different from the case in the reactions of 3B2OL and 2B1OL. In a similar way, it is known that 3-methyl-1,3-butanediol decomposes to isobutene, formaldehyde and methanol via 3-methyl-3-buten-1-ol [29]. The acid catalysts gave BD selectivities lower than 44% and propylene selectivities higher than 17%, indicating that C-C cleavage of 3B1OL was easily catalyzed by acid catalysts. Among the tested catalysts, SiO₂-Al₂O₃-CS gave the lowest BD selectivity of 12.0% and the highest propylene selectivity of 53.1%. In the case of rare earth metal oxides, Yb₂O₃ gave a propylene selectivity of 25.9% and a BD selectivity of 33.8%, while CeO₂ gave the lowest propylene selectivity of 9.3% and the highest BD selectivity of 54.5%. This result indicates that CeO₂ inhibits the C-C cleavage of 3B1OL and is relatively effective for the formation of BD from 3B1OL.

In the case of acid catalysts, the order of the reactivity of the unsaturated C4 alcohols under the same conditions is 2B1OL > 3B2OL > 3B1OL (Tables 1-3), which means 3B1OL is less reactive over the acids. However, in the case of CeO₂, the reactivity of 3B1OL is similar to that of 2B1OL, and is higher than that of 3B2OL. This result suggests that the catalytic mechanism over acid catalysts and rare earth metal oxides such as CeO₂ is different in the dehydration of unsaturated C4 alcohols. We propose that the different positions of the hydroxyl group and the double bond in 2B1OL, 3B2OL, and 3B1OL lead to different adsorption modes on catalyst surface, which causes the different reactivity and the product distribution. In the dehydration of 1,3-butanediol, CeO₂ with a cubic fluorite structure shows specifically high activity for the formation of 2B1OL and 3B2OL [16]. The specific activity of CeO₂ was supposed to be assigned to the Ce⁴⁺-Ce³⁺ redox nature of CeO₂, which activated the H atom at position 2 of 1,3-butanediol firstly, followed by the dehydration of 1,3-butanediol over CeO₂ through a radical mechanism: an H atom located at position 2 was abstracted first, followed by the elimination of an OH radical at position 1 [16, 20]. The proposed

mechanism was also supported by density functional theory (DFT) and paired interacting orbital (PIO) calculations [30, 31]. Based on the previous findings, we supposed a reaction mechanism for the dehydration of 3B1OL to BD over CeO_2 as shown in Scheme 3. It is reasonable that the dehydration of 1,3-butanediol over CeO_2 also undergoes a radical mechanism, which is quite similar to the dehydration of 1,3-butanediol over CeO_2 above-mentioned.

Scheme 3 Proposed reaction mechanism in the dehydration of 3B1OL over CeO_2

3.2. Catalytic activity of self-made $\text{SiO}_2/\text{Al}_2\text{O}_3$ modified by metals in the dehydration of 2B1OL and 3B2OL

In the dehydration of 2B1OL and 3B2OL, although $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ showed a relatively high activity for 1,3-butadiene formation among the acid catalysts, it deactivated rapidly under low contact time conditions. Deactivation of catalysts is a critical problem in catalytic conversion under continuous flow conditions especially in a practical industrial process. Thus, further studies were conducted in order to develop stable catalysts for the dehydration of 2B1OL and 3B2OL.

Firstly, we prepared a series of $\text{SiO}_2/\text{Al}_2\text{O}_3$ -based catalysts to regulate the acid strength. In contrast to $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ with a low Al_2O_3 content of *ca.* 15 wt.%, the $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts were prepared with low SiO_2 contents. Fig. 1 shows the dependence of the catalytic activity on the SiO_2 content in the dehydration of 2B1OL, and the product distribution in each reaction and the change in the catalytic activity with time on stream are shown in Table S1 and Fig. S4. The conversion of 2B1OL increased with increasing the SiO_2 content, and 100% conversion of 2B1OL was achieved

at SiO₂ contents of 5-10 wt.%. The selectivity to BD increased with increasing the SiO₂ content, and was maximized at 97.5% at a SiO₂ content of 10 wt.%. On the other hand, the selectivity to ethers was higher than 20% over the Al₂O₃ support without SiO₂, whereas it decreased with increasing the SiO₂ content and decreased to 0% at SiO₂ contents higher than 5 wt.%. These results demonstrate that the self-made SiO₂/Al₂O₃ catalysts are effective for the dehydration of 2B1OL to BD, and the suitable SiO₂ content in SiO₂/Al₂O₃ is 10 wt.%.

In order to study the catalytic stability, the dehydration of 2B1OL was performed at a low W/F of 0.14 h (Fig. 2), where W and F are catalyst weight and flow rate of reactant, respectively. Fig. 2 shows the changes in activity of SiO₂-Al₂O₃-CS and 10SiO₂/Al₂O₃ with time on stream at a W/F of 0.14 h. SiO₂-Al₂O₃-CS significantly deactivated with time on stream. In contrast, the activity of 10SiO₂/Al₂O₃ was more stable, while slight decrease in the conversion of 2B1OL was still observed.

In our group, an effective operation for stabilizing the catalytic activity of acid catalysts has been reported [24, 32-35]. For example, vapor-phase aldol condensation of butanal to 2-ethyl-2-hexenal can be catalyzed by TiO₂, whereas TiO₂ deactivates rapidly because of the accumulation of coke on the catalyst surface. We have developed an Ag-modified TiO₂ catalyst, which exhibits stable catalytic activity for the formation of 2-ethyl-2-hexenal from butanal [35]. In a similar way, the loading of Ag onto SiO₂-Al₂O₃, Cu onto Al₂O₃, and Ag onto Al₂O₃ are found to be effective for stabilizing the vapor-phase dehydration of 1,2-propanediol into propanal [24], dehydration of tetrahydrofurfuryl alcohol into 3,4-2H-dihydropyran [33], and cyclodehydration of diethylene glycol to 1,4-dioxane [34], respectively. In these processes, H₂ carrier gas is required for inhibiting the catalytic deactivation. Before the reaction, the loaded metal oxide is reduced to metal, and it removes the product on the catalyst surface together with H₂ to suppress the formation of coke.

In the present study, Ag- and Cu-modified 10SiO₂/Al₂O₃ catalysts were prepared and tested in the dehydration of 2B1OL. Table 4 summarizes the reaction results in the dehydration of 2B1OL over 10SiO₂/Al₂O₃, 3 wt.% Ag- and Cu-modified 10SiO₂/Al₂O₃ in H₂ flow at a W/F of 0.34 h. Compared with 10SiO₂/Al₂O₃, both the conversion and the selectivity to BD were improved by the modification of 10SiO₂/Al₂O₃ with 3 wt.% Ag: the selectivity to BD was 94.1% at conversion of

98.5%. On the other hand, although 3Cu-10SiO₂/Al₂O₃ gave a high conversion of 98.6%, the selectivity to BD was only 0.6%, which was attributed to the production of butenes and 1-butanol with selectivities of 51.8 and 21.3%, respectively. Since Cu is widely used as a hydrogenation catalyst [36, 37], it is reasonable that the loaded Cu metal catalyzes the hydrogenation of 2B1OL to 1-butanol and the hydrogenation of the produced BD to butenes. Thus, the modification of 10SiO₂/Al₂O₃ by Cu was not effective for the dehydration of 2B1OL to BD. The reactions over 10SiO₂/Al₂O₃ and 3Ag-10SiO₂/Al₂O₃ in N₂ flow were also performed in order to study the effect of the reaction atmosphere. Compared with a high conversion of 92.5% and a low BD selectivity of 75.0% over 10SiO₂/Al₂O₃ in H₂ atmosphere (entry 1), a low conversion of 85.9% and a high BD selectivity of 86.7% were obtained in N₂ atmosphere (entry 2), indicating that H₂ took part in the reaction even without the presence of a metal. On the other hand, compared with the reaction results obtained over 3Ag-10SiO₂/Al₂O₃ in an H₂ flow (entry 4), both the conversion and the selectivity to BD were low in N₂ (entry 5), indicating that H₂ could efficiently promote the formation of BD in the presence of Ag.

Table 5 summarizes the reaction results of the dehydration of 2B1OL over Ag-modified 10SiO₂/Al₂O₃ with different Ag loadings. In the reactions with Ag loadings lower than 3%, the selectivity to BD trended to decrease, while the selectivity to undetected products trended to increase. The catalysts with Ag loadings of 3 and 5 wt.% gave both high conversions of 2B1OL and high selectivities to BD, indicating that the suitable loading amount of Ag for BD formation was 3-5 wt.%.

Fig. 2 compares the changes in 2B1OL conversion over SiO₂-Al₂O₃-CS, 10SiO₂/Al₂O₃ and 3Ag-10SiO₂/Al₂O₃. It is obvious that the order of the catalytic stability is 3Ag-10SiO₂/Al₂O₃ > 10SiO₂/Al₂O₃ > SiO₂-Al₂O₃-CS, indicating that the modification of 10SiO₂/Al₂O₃ by Ag is effective for the inhibition of catalytic deactivation in the dehydration of 2B1OL. We further performed the dehydration of 2B1OL over 10SiO₂/Al₂O₃ and 5Ag-10SiO₂/Al₂O₃ with a long run of 10 h. As shown in Fig. 3, the conversion of 2B1OL over 10SiO₂/Al₂O₃ decreased from 97.5 to 76.8% with BD selectivity decreased from 86.9 to 63.3% during 10 h. In contrast, the conversion of 2B1OL over

5Ag-10SiO₂/Al₂O₃ slightly decreased from 99.4 to 96.2% with BD selectivity decreased from 95.0 to 87.1%. The decrease in BD selectivity with time on stream was due to the increase in the formation of undetected products. It seems that the formation of BD favors high conversions. It is proposed that the reactant of unsaturated alcohols would take part in the formation of undetected products especially at low conversions, while there is no evidence.

The dehydration of 3B2OL was also performed over SiO₂-Al₂O₃-CS, 10SiO₂/Al₂O₃, and 5Ag-10SiO₂/Al₂O₃ at a W/F of 0.34 h. Fig. 4 shows the changes in catalytic activity of these catalysts. It is clear that the order of the catalytic stability is 5Ag-10SiO₂/Al₂O₃ > 10SiO₂/Al₂O₃ > SiO₂-Al₂O₃-CS, indicating that 5Ag-10SiO₂/Al₂O₃ is an effective catalyst for the dehydration of 3B2OL to BD. On the other hand, SiO₂-Al₂O₃-CS was stable in the dehydration of 2B1OL within 5 h at a W/F of 0.34 h, whereas it significantly deactivated in the dehydration of 3B2OL at the same W/F (Fig. 4a), indicating that 3B2OL led to more severe catalyst deactivation than 2B1OL.

3.3. Characterization of catalyst samples

In vapor-phase reactions over either acid or base catalysts, it is generally considered that the accumulation of carbonaceous compounds on the catalyst surface results in the catalytic deactivation [35]. In order to evaluate the coke formation, TG analyses of the used SiO₂-Al₂O₃-CS, 10SiO₂/Al₂O₃ and 3Ag-10SiO₂/Al₂O₃ were performed in air. As shown in Fig. 5, a weight loss below 200 °C is considered to be attributed to the desorption of H₂O, and a weight loss can be observed at a temperature range from 200 to 600 °C, which is considered to be caused by the decomposition of coke [34]. The order of the amount of coke in the used catalysts was 3Ag-10SiO₂/Al₂O₃ < 10SiO₂/Al₂O₃ < SiO₂-Al₂O₃-CS, which was reverse to the order of the catalytic stability (Figs. 2-4). This indicates that the formation of coke possibly affects the catalytic deactivation, and the modification of 10SiO₂/Al₂O₃ by Ag is effective for inhibiting the coke formation. However, because there is no significant difference in the amount of coke, different coke component may affect the deactivation behavior.

In order to study the effect of the acidity on the dehydration of 3B2OL and 2B1OL, NH_3 -TPD analyses of fresh $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$, $10\text{SiO}_2/\text{Al}_2\text{O}_3$ and $5\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$ were performed (Fig. 6). The number of acid sites in $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$, $10\text{SiO}_2/\text{Al}_2\text{O}_3$, and $5\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$ was 0.52, 0.20, and 0.18 mmol g^{-1} , respectively. $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ showed two desorption peaks at 283 and 327 $^\circ\text{C}$. $10\text{SiO}_2/\text{Al}_2\text{O}_3$ and $5\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$ showed desorption peaks at 195 and 260 $^\circ\text{C}$, respectively. These results indicate that the order of the averaged acid strength is $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS} > 10\text{SiO}_2/\text{Al}_2\text{O}_3 > 5\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$. In the dehydration of 3B2OL, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ with the strongest acid strength and the largest amount of acid sites gives both the highest initial conversion and the highest initial selectivity to BD (Fig. 4), indicating that the large amount of strong acid sites is effective for BD formation. However, it is generally considered that the catalyst with strong acidity promotes the formation of coke and easily deactivates [38]. Thus, $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ significantly deactivated in the dehydration of 3B2OL (Fig. 4a) and 2B1OL (Fig. 2). It is clear that the loading of Ag on $10\text{SiO}_2/\text{Al}_2\text{O}_3$ reduces the acid strength without significant effect on the total number of acid sites. Similar results have been also obtained in our previous study using different kinds of $\text{SiO}_2\text{-Al}_2\text{O}_3$ [24]. We propose that the additive Ag particles are located on the surface of $10\text{SiO}_2/\text{Al}_2\text{O}_3$, and they poison the strong acid sites on $10\text{SiO}_2/\text{Al}_2\text{O}_3$ to form new active sites for BD formation. The reduced acid strength by the addition of Ag is supposed to contribute to the relatively stable catalytic activity of the Ag-modified $10\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts. The XRD profiles of the reduced Ag-modified $10\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts are shown in Fig. S5. The peaks assigned to Ag metal were observed at Ag loadings higher than 5%, indicating the additive Ag was reduced to metal before the reaction, and worked at a metal state during the reaction. It is possible that Ag also plays another important role for the inhibition of catalytic deactivation, as has been described in our previous studies [24, 32, 34, 35]. It is supposed that H_2 can be cleaved to produce H atoms by Ag metal, and through the spillover effect, the generated H atoms can shift from Ag to $\text{SiO}_2/\text{Al}_2\text{O}_3$ surface to form H^+ . The H^+ on $\text{SiO}_2/\text{Al}_2\text{O}_3$ is proposed to be effective for suppressing the formation of coke and inhibiting the catalytic deactivation, thus, the selectivity to BD is increased. Compared with Cu, Ag has low hydrogenation ability and does not catalyze the hydrogenation of unsaturated alcohols to saturated

alcohols as well as the further hydrogenation of BD to butenes. Therefore, the low hydrogenation ability of Ag is another important factor making the modification of Ag to be effective.

3.4. Future perspective of BD production

The production of BD from biomass-derived ethanol is a well-known process, and many research works have been reported in vapor-phase condensation of ethanol to produce BD [2, 3]. Another possible route for producing BD is proposed via the dehydration of intermediate unsaturated alcohols from renewable butanediols [3]. The butanediols-to-BD process have advantage to give high BD selectivity although the biobutanediol is currently more expensive than bioethanol. Both the two processes suffer from the catalytic deactivation, and the development of stable catalysts and technology for inhibiting the catalytic deactivation would significantly affect the industrial applications of the processes in future.

4. Conclusions

Vapor-phase dehydration of C4 unsaturated alcohols, such as 2B1OL, 3B2OL and 3B1OL, to BD were investigated over various solid catalysts. Acid catalysts were found to be effective for the dehydration of 2B1OL and 3B2OL to BD, and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ showed a relatively high catalytic performance. In the dehydration of 3B1OL, however, acid catalysts promoted the C-C cleavage of 3B1OL to propylene, while rare earth metal oxides such as CeO_2 were effective for the formation of BD from 3B1OL. Compared with the dehydration of 2B1OL and 3B2OL, the dehydration of 3B1OL undergoes different mechanism. The high performance of CeO_2 in the dehydration of 3B1OL into BD is considered to be attributed to its weak basicity as well as the $\text{Ce}^{4+}\text{-Ce}^{3+}$ redox nature of CeO_2 . The dehydration of 2B1OL and 3B2OL was further studied using self-made $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts. The suitable SiO_2 content in $\text{SiO}_2/\text{Al}_2\text{O}_3$ was found to be 10 wt.%, and the 10 $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst showed a better catalytic performance than $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$. In order to inhibit the catalytic deactivation, metal-modified $\text{SiO}_2/\text{Al}_2\text{O}_3$ was prepared and tested. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ modified by Ag with a loading of 3-5 wt.% was found to be efficient for inhibiting the catalytic

deactivation and improving the conversion and the selectivity to BD in the dehydration of 2B1OL and 3B2OL. In the dehydration of 2B1OL over 5Ag-SiO₂/Al₂O₃ the selectivity to BD was 94.6% at conversion of 99.1%.

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Table 1 Dehydration of 2-buten-1-ol over various solid catalysts ^a.

Catalyst	Temp. /°C	Conv. ^b /%	Selectivity/% ^b					
			BD	Butenes ^c	1-Butanol	Butanal	Ethers ^d	Others ^e
SiO ₂ -Al ₂ O ₃ -CS	260	99.3	97.1	2.0	0.2	0.0	0.0	0.7
Al ₂ O ₃	260	90.3	27.2	3.7	4.5	4.3	25.4	34.9
TiO ₂	300	99.4	71.6	4.1	1.7	0.9	1.4	20.3
ZrO ₂	400	78.4	57.0	2.6	5.0	2.0	3.3	30.1
Yb ₂ O ₃	400	42.4	78.9	0.0	2.9	2.2	2.6	13.4
CeO ₂	400	93.4	21.3	2.7	5.3	27.6	3.8	39.3

^a Reaction conditions: N₂ flow rate, 30 cm³ min⁻¹; catalyst weight, 0.5 g. W/F, 0.34 h.

^b Conversion and selectivity are averaged between 1h and 5h.

^c Butenes include 1-butene and 2-butene.

^d Ethers represent the liner unsaturated ethers with a chemical formula of C₈H₁₄O.

^e Others represent undetectable products.

Table 2 Dehydration of 3-buten-2-ol over various solid catalysts ^a.

Catalyst	Temp. /°C	Conv. ^b /%	Selectivity/% ^b				
			BD	Butenes ^c	2-Butanone	Ethers ^d	Others ^e
SiO ₂ -Al ₂ O ₃ -CS	260	74.4	93.4	1.5	0.4	0.6	4.1
Al ₂ O ₃	260	70.2	52.1	1.4	11.1	9.0	28.4
TiO ₂	300	90.0	58.9	8.1	7.1	1.1	24.8
ZrO ₂	400	67.4	48.3	4.7	18.2	3.1	25.7
Yb ₂ O ₃	400	4.3	17.7	3.6	13.4	3.9	62.0
CeO ₂	400	61.7	26.5	28.5	5.9	2.3	26.8

^a Reaction conditions: N₂ flow rate, 30 cm³ min⁻¹; catalyst weight, 0.5 g. W/F, 0.34 h.

^b Conversion and selectivity are averaged between 1h and 5h.

^c Butenes include 1-butene and 2-butene.

^d Ethers represent the liner unsaturated ethers with a chemical formula of C₈H₁₄O.

^e Others represent undetectable products

Table 3 Dehydration of 3-buten-1-ol over various solid catalysts ^a.

Catalyst	Temp. /°C	Conv. ^b /%	Selectivity/% ^b							
			BD	Propylene	Methanol	1-Butanol	Butanal	2B1OL ^c	Ethers ^d	Others ^e
SiO ₂ -Al ₂ O ₃ -CS	260	40.3	12.0	53.1	3.4	0.1	3.9	0.3	12.2	15.0
Al ₂ O ₃	260	32.7	12.0	34.4	7.4	4.5	9.1	1.0	12.7	18.9
TiO ₂	300	34.5	34.6	17.6	3.8	1.5	3.4	0.2	8.0	30.9
ZrO ₂	400	59.0	43.2	23.7	3.6	0.8	1.1	5.1	8.5	14.0
Yb ₂ O ₃	400	46.1	33.8	25.9	4.0	0.1	0.2	20.7	10.0	5.3
CeO ₂	400	90.0	54.5	9.3	0.6	1.4	6.1	3.6	3.6	20.9

^a Reaction conditions: N₂ flow rate, 30 cm³ min⁻¹; catalyst weight, 0.5 g. W/F, 0.34 h.

^b Conversion and selectivity are averaged between 1h and 5h.

^c 2B1OL includes cis and trans isomers.

^d Ethers represent the liner unsaturated ethers with a chemical formula of C₈H₁₄O.

^e Others represent undetectable products

Table 4 Dehydration of 2-buten-1-ol over metal-modified 10SiO₂/Al₂O₃ catalysts ^a.

Catalyst	Conv. ^b /%	Selectivity/% ^b					
		BD	Butenes ^c	1-Butanol	Butanal	Ethers ^d	Others ^e
10SiO ₂ /Al ₂ O ₃	92.5	75.0	1.5	0.5	1.2	1.3	20.5
10SiO ₂ /Al ₂ O ₃ ^f	85.9	86.7	0.9	0.3	0.8	1.1	10.2
3Cu-10SiO ₂ /Al ₂ O ₃	98.6	0.6	51.8	21.3	10.4	0.0	15.9
3Ag-10SiO ₂ /Al ₂ O ₃	98.5	94.1	1.9	0.2	0.3	0.1	3.4
3Ag-10SiO ₂ /Al ₂ O ₃ ^f	93.7	86.5	1.1	0.3	0.0	1.8	10.3

^a Reaction conditions: temperature, 260 °C; H₂ flow rate, 30 cm³ min⁻¹; catalyst weight, 0.2 g. W/F, 0.34 h.

^b Conversion and selectivity are averaged between 1h and 5h.

^c Butenes include 1-butene and 2-butene.

^d Ethers represent the liner unsaturated ethers with a chemical formula of C₈H₁₄O.

^e Others represent undetectable products.

^f The reactions were performed in N₂ flow with a flow rate of 30 cm³ min⁻¹.

Table 5 Dehydration of 2-buten-1-ol over Ag-modified 10SiO₂/Al₂O₃ catalysts with different Ag loadings ^a.

Catalyst	Conv. ^b /%	Selectivity/% ^b					
		BD	Butenes ^c	1-Butanol	Butanal	Ethers ^d	Others ^e
10SiO ₂ /Al ₂ O ₃	92.5	75.0	1.5	0.5	1.2	1.3	20.5
1Ag-10SiO ₂ /Al ₂ O ₃	96.4	91.5	1.5	0.3	0.6	0.3	5.8
3Ag-10SiO ₂ /Al ₂ O ₃	98.5	94.1	1.9	0.2	0.3	0.1	3.5
5Ag-10SiO ₂ /Al ₂ O ₃	99.1	94.6	2.3	0.1	0.1	0.0	2.9
7Ag-10SiO ₂ /Al ₂ O ₃	98.4	91.6	2.8	0.3	0.5	0.3	4.5
10Ag-10SiO ₂ /Al ₂ O ₃	97.3	91.2	2.2	0.3	0.6	0.3	5.4

^a Reaction conditions: temperature, 260 °C; H₂ flow rate, 30 cm³ min⁻¹; catalyst weight, 0.2 g. W/F, 0.34 h.

^b Conversion and selectivity are averaged between 1h and 5h.

^c Butenes include 1-butene and 2-butene.

^d Ethers represent the liner unsaturated ethers with a chemical formula of C₈H₁₄O.

^e Others represent undetectable products.

Figure captions

Fig. 1 Dehydration of 2-buten-1-ol over self-made $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalysts with different SiO_2 contents.

Reaction conditions: temperature, $260\text{ }^\circ\text{C}$; N_2 flow rate, $30\text{ cm}^3\text{ min}^{-1}$; catalyst weight, 0.5 g ; W/F, 0.34 h . The conversions and selectivities were averaged between 1-5 h.

Fig. 2 Changes in the conversion of 2-buten-1-ol with time on stream over $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$,

$10\text{SiO}_2/\text{Al}_2\text{O}_3$ and $3\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$. Reaction conditions: temperature, $260\text{ }^\circ\text{C}$; H_2 flow rate, $30\text{ cm}^3\text{ min}^{-1}$; catalyst weight, 0.2 g ; W/F, 0.14 h .

Fig. 3 Changes in catalytic activity of $10\text{SiO}_2/\text{Al}_2\text{O}_3$ (a) and $5\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$ (b) in the

dehydration of 2-buten-1-ol with time on stream. Reaction conditions: temperature, $260\text{ }^\circ\text{C}$; H_2 flow rate, $30\text{ cm}^3\text{ min}^{-1}$; catalyst weight, 0.2 g ; W/F, 0.14 h .

Fig. 4 Changes in catalytic activity of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$ (a), $10\text{SiO}_2/\text{Al}_2\text{O}_3$ (b), and $5\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$

(c) in the conversion of 3-buten-2-ol with time on stream. Reaction conditions: temperature, $260\text{ }^\circ\text{C}$; flow rate of carrier gas, $30\text{ cm}^3\text{ min}^{-1}$; catalyst weight, 0.5 g ; W/F, 0.34 h .

Fig. 5 TG profiles of the used $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$, $10\text{SiO}_2/\text{Al}_2\text{O}_3$ and $3\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$. Reaction

conditions for the used catalysts: temperature, $260\text{ }^\circ\text{C}$; H_2 flow rate, $30\text{ cm}^3\text{ min}^{-1}$; catalyst weight, 0.2 g ; W/F, 0.14 h .

Fig. 6 NH_3 -TPD profiles of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$, $10\text{SiO}_2/\text{Al}_2\text{O}_3$ and $5\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$.

Fig. 1 Dehydration of 2-buten-1-ol over self-made SiO₂/Al₂O₃ catalysts with different SiO₂ contents. Reaction conditions: temperature, 260 °C; N₂ flow rate, 30 cm³ min⁻¹; catalyst weight, 0.5 g; W/F, 0.34 h. The conversions and selectivities were averaged between 1-5 h.

Fig. 2 Changes in the conversion of 2-buten-1-ol with time on stream over SiO₂-Al₂O₃-CS, 10SiO₂/Al₂O₃ and 3Ag-10SiO₂/Al₂O₃. Reaction conditions: temperature, 260 °C; H₂ flow rate, 30 cm³ min⁻¹; catalyst weight, 0.2 g; W/F, 0.14 h.

Fig. 3 Changes in catalytic activity of 10SiO₂/Al₂O₃ (a) and 5Ag-10SiO₂/Al₂O₃ (b) in the dehydration of 2-buten-1-ol with time on stream.

Reaction conditions: temperature, 260 °C; H₂ flow rate, 30 cm³ min⁻¹; catalyst weight, 0.2 g; W/F, 0.14 h.

Fig. 4 Changes in activity of SiO₂-Al₂O₃-CS (a), 10SiO₂/Al₂O₃ (b), and 5Ag-10SiO₂/Al₂O₃ (c) in the dehydration of 3-buten-2-ol with time on stream. The solid cycle and the open cycle represent the conversion of 3B2OL and the selectivity to BD, respectively.

Reaction conditions: temperature, 260 °C; flow rate of carrier gas, 30 cm³ min⁻¹; catalyst weight, 0.5 g; W/F, 0.34 h.

Fig. 5 TG profiles of the used $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$, $10\text{SiO}_2/\text{Al}_2\text{O}_3$ and $3\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$.

Reaction conditions for the used catalysts: temperature, $260\text{ }^\circ\text{C}$; H_2 flow rate, $30\text{ cm}^3\text{ min}^{-1}$; catalyst weight, 0.2 g . W/F, 0.14 h .

Fig. 6 NH_3 -TPD profiles of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CS}$, $10\text{SiO}_2/\text{Al}_2\text{O}_3$ and $5\text{Ag-}10\text{SiO}_2/\text{Al}_2\text{O}_3$.

Vapor-phase dehydration of C4 unsaturated alcohols to 1,3-butadiene

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Graphic abstract