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# Catalytic Dehydration of 1,4-Butanediol over Mg-Yb Binary Oxides and the Mechanism Study

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Abstract: In this study, Mg-Yb binary oxides were synthesized using different MgO concentrations and investigated for the catalytic dehydration of 1,4-butanediol (BDO) into 3-buten-1-ol (BTO). The physicochemical properties of the catalysts were characterized by N<sub>2</sub> physisorption, X-ray diffraction, Raman spectroscopy, temperatureprogrammed techniques, and diffuse reflectance infrared Fourier transform spectroscopy. The Mg-Yb binary oxides exhibited superior catalytic activity and better BTO selectivity compared with the pristine Yb<sub>2</sub>O<sub>3</sub> or MgO. Structures of Mg-O-Yb were generated in the binary oxides via the interchange of Yb or Mg in the MgO or Yb<sub>2</sub>O<sub>3</sub> crystalline phases. Extra basic and acidic sites were formed over the Mg-Yb binary oxides because of the formation of surface defects and the presence of Mg-O-Yb structures, respectively. The acidic as well as basic sites were observed to influence the catalytic performance: BDO reactivity was enhanced by the more acidic sites, while BTO selectivity was favored by the basic sites. The highest BTO yield of 71.1% was achieved over the Mg7Yb3 catalyst with 90.4% BDO conversion and 78.6% BTO selectivity at 350 °C. The in situ DRIFTS results indicated that BDO was first adsorbed on the catalyst and then reacted with the acidic sites to generate butoxides. The β-H of the surface butoxides was abstracted by the basic oxygen anions to produce aldehyde species, which dissociated to form BTO.

#### Introduction

The ongoing environmental deterioration and fossil resource exhaustion have prompted scientists to explore renewable and green alternative energy sources.<sup>[1,2]</sup> Recently, several processes for the conversion of biomass into valuable oil-based products have increasingly attracted attention, such as hydrogenation of succinic acid and levulinic acid, esterification of glycerol, oxidation or hydrogenation of 2-furaldehyde, and dehydration of polyols.<sup>[3-</sup> <sup>15]</sup> In particular, 1,4-butanediol (BDO), which can be manufactured from not only fossil- and coal-based feedstock, but also biomass resources, is reportedly the most extensive source among all diols. The global BDO market has been projected to reach USD 12.6 billion by 2025, and China with its production capacity of over 55% of the total world's capacity, continues to be the world's highest BDO producer. Furthermore, the increasing BDO production has led to overcapacity and lower market prices in recent years, causing sufficient demand for its utilization.[6]

Similarly, 3-buten-1-ol (BTO), which combines with active hydroxyl groups and double bonds, is frequently used for the synthesis of medicines, agrochemicals, polymers, and additives.<sup>[16-19]</sup> Hence, direct catalytic dehydration of BDO has been proposed not only as one of the most promising methods for BTO production, but also as an essential technology for expanding BDO downstream products.<sup>[20,21]</sup> BDO dehydration forms a complex reaction network that can produce various chemicals including BTO, tetrahydrofuran (THF), γ-butyrolactone (GBL), 1-butanol (BuOH), 2-buten-1-ol (2BT1O), and 1,3butadiene (BDE) as shown in Scheme 1.[16,22,23] Among these, THF is preferentially formed over BTO in the presence of normal dehydration catalysts. The catalysts used for BDO dehydration, such as *t*-ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, generally exhibit strong surface acidity, resulting in the cyclodehydration of BDO into THF, which limits the BTO selectivity to less than 10%.[24] Previously, our group studied BDO dehydration over m-ZrO<sub>2</sub> supported Yb<sub>2</sub>O<sub>3</sub>, and the results showed that the hydroxyl groups of BDO molecules could be adsorbed onto the acidic sites while  $\beta$ -H could be captured by the basic sites, resulting in the formation of BTO.<sup>[22]</sup> Sato et al. also reported that BDO dehydration proceeded with an acid-base concerted mechanism over the Er<sub>2</sub>O<sub>3</sub> catalyst, wherein both BDO conversion and BTO selectivity were markedly suppressed by poisoning the Er<sub>2</sub>O<sub>3</sub> catalyst with either CO<sub>2</sub> or NH<sub>3</sub> carrier gas.<sup>[25]</sup> Therefore, BDO dehydration is highly dependent on the acid-base properties of the catalyst-while the strong acidity of the catalysts facilitates the formation of the byproduct THF, its strong basicity reduces the BDO conversion.<sup>[22]</sup> Thus, a proper acid-base regulation is an effective approach to improving the catalytic performance for BDO dehydration. Therefore, amphoteric oxides have received increasing attention for their use in the dehydration reaction as they contain both acidic and basic sites. Among these, Yb<sub>2</sub>O<sub>3</sub> exhibits higher BTO selectivity (>85%) and is generally regarded as a superior catalyst for BDO dehydration.<sup>[16,25,26]</sup> However, as the conversion of BDO over Yb<sub>2</sub>O<sub>3</sub> is generally very low (<40%), it could not meet the requirements for industrial application, owing to its weak acidity.[16,23,25,26]

Therefore, two main strategies are reportedly used for the regulation of the acid–base properties of the  $Yb_2O_3$  catalyst: obtaining different crystal forms of  $Yb_2O_3$  through the calcination of the  $Yb_2O_3$  precursor at high temperatures, or loading  $Yb_2O_3$  on

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different supports with proper acid–base properties.<sup>[23,26,27]</sup> However, the former strategy significantly reduces the specific surface area of the catalyst, which limits its industrial application. Meanwhile, our previous study showed that the latter strategy can be mainly carried out by acid–base neutralization in *m*-ZrO<sub>2</sub> supported Yb<sub>2</sub>O<sub>3</sub> catalysts; namely, the acidic sites on the support could be covered by the basic sites of Yb<sub>2</sub>O<sub>3</sub>. This considerably changes the surface basicity while controlling the acidity of the catalyst, which significantly limits the regulation range of the surface acid–base properties.<sup>[22]</sup> Thus, manipulation of the acidity of Yb<sub>2</sub>O<sub>3</sub> without lowering the basic property is a promising approach toward the development of BDO dehydration catalysts.



Scheme 1. Reaction network of BDO dehydration.

Previous studies have shown that the preparation of metal composite oxides is also a common strategy to regulate the acid-base properties of the metal oxides.[28,29] For instance, Tanabe et al. prepared 18 binary metal oxides, and observed that the acid amounts and strength of the tested binary oxides, including TiO<sub>2</sub>-MgO and ZnO-MgO, were remarkably higher than those of the mono-composition oxides.<sup>[30]</sup> The generation of extra acidity could be explained by Tanabe's hypothesis, according to which different coordination numbers of the two components in the metal composite oxides cause an imbalanced charge distribution, resulting in the formation of extra acidity.<sup>[28,29,31]</sup> Thus, the addition of MgO to Yb<sub>2</sub>O<sub>3</sub> can enhance the acidity of the Mg-Yb metal composite oxide because the coordination number of O in MgO is different from that in Yb2O3 based on Tanabe's hypothesis. Similarly, the basic properties could also be maintained at a high level, thereby enhancing the catalytic dehydration performance of BDO.

In this study, a series of Mg-Yb binary oxide catalysts were synthesized by a foaming esterification sol-gel method to manipulate their acid-base properties. The texture and surface chemical properties were characterized, and the relationship between their acid-base properties and catalytic performance was subsequently investigated. Furthermore, an acid-base concerted mechanism was proposed based on the results of the *in situ* DRIFTS. These results depicted a roadmap for BDO dehydration, providing a fundamental basis for the rational design of the acid-base catalysts and large-scale implementation of the BDO dehydration reaction.

#### **Results and Discussion**





Figure 1. Effect of reaction temperature on BDO conversion (A) and selectivity of: BTO (B), THF (C), BuOH + GBL (D), and 2BT1O + BDE (E) over Mg-Yb binary oxide catalysts; (F) effect of *W/F* on the catalytic performance of Mg7Yb3 at 350 °C.

The catalytic performance of the Mg-Yb binary oxides was evaluated in the temperature range of 300-425 °C. Prior to the measurements, a blank experiment was conducted to ensure that BDO dehydration did not occur in the absence of a catalyst in all temperature ranges. The temperature dependence of BDO conversion and the selectivity of BTO, THF, BuOH, GBL, 2BT1O, and BDE are displayed in Figure 1. As shown in Figure 1(A), BDO conversion increases with increasing reaction temperature over all catalysts except MgO, over which there was hardly any BDO dehydration reaction.<sup>[24]</sup> Figure 1(B) shows the BTO selectivity versus reaction temperature curve, which exhibits a volcano-like behavior wherein a significant increase in the BTO selectivity is observed as the temperature is increased from 300 to 375 °C. However, when the reaction temperature is increased beyond 375 °C, the BTO selectivity begins to decline. Figure 1(C) displays the relationship between the reaction temperature and THF selectivity, which is observed to rapidly decline as the temperature increases. Similarly, Figure 1(D) shows that the selectivities of BuOH and GBL also decrease as the temperature increases. In contrast, Figure 1(E) shows that the selectivities of 2BT10 and BDE rapidly increase as the reaction temperature is increased beyond 350 °C.

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According to the previous study of our group, dehydration of BDO into BTO is an endothermic reaction, while the formation of THF from BDO is an exothermic reaction.<sup>[22]</sup> These results indicate that during BDO dehydration, higher temperatures favor BTO formation while suppressing THF formation, which is consistent with the results shown in Figure 1(B) and Figure 1(C). Furthermore, the results shown in Figure 1(B) and Figure 1(E) indicate that the isomerization of BTO into 2BT1O or further dehydration of BTO into BDE occurs at a higher reaction temperature, and both reactions result in low BTO selectivity.<sup>[21]</sup> Figure 1(F) shows the effect of *W/F* (where *W* is the weight of the catalyst and *F* is the BDO flow rate) on the catalytic performance of Mg7Yb3 at 350 °C. This ratio (i.e., *W/F*) represents the contact time between the reactant and catalyst—the highest BTO yield of 71.1% was obtained at  $W/F = 0.93 \text{ g}\cdot\text{h}\cdot\text{ml}^{-1}$ .

For a better comparison of the performance of all catalysts, the influence of mass and heat transfer should be eliminated. For this, the Koros-Nowak criterion was employed using the Mg7Yb3 catalyst, and the results are shown in Figure S1. The plot of the BDO conversion vs.  $1/\rho$  (where  $\rho$  is the active space velocity) using a catalyst sample with  $f_w = 0.5$  (where  $f_w$  is defined as the weight fraction of the active material in the catalyst) coincides with the plot when the experiment was repeated using a catalyst sample with  $f_w = 0.6$  at both 325 and 337 °C; this indicates that the Koros-Nowak criterion is satisfied and the effects of mass and heat transfers are excluded when the reaction temperature is lower than 337 °C.<sup>[32,33]</sup> Figure 2(A) shows the BDO conversion at 325 °C, which is observed to be 7.3%, 11.5%, 13.3%, 16.7%, 7.8%, and 0% for Yb<sub>2</sub>O<sub>3</sub>, Mg3Yb7, Mg5Yb5, Mg7Yb3, Mg9Yb1, and MgO, respectively, which forms a volcano curve as a function of the Mg concentration. The catalytic activity of the catalysts is as follows: Mg7Yb3 > Mg5Yb5 > Mg3Yb7 > Mg9Yb1 > Yb<sub>2</sub>O<sub>3</sub> > MgO. Thus, all Mg-Yb catalysts performed better than pristine MgO or Yb<sub>2</sub>O<sub>3</sub>, while the Mg7Yb3 catalyst achieved the highest BDO conversion. The selectivities of BTO, THF, BuOH, 2BT1O, and GBL are shown in Figure 2(B) by controlling the BDO conversion at 10%, at 325 °C over different catalysts. The BTO selectivity over the Mg-Yb binary oxides is observed to increase from 70.5% to 73. 6%, 79.2%, 78.2%, and 82.6% as the Mg content increased from 0% to 30%, 50%, 70%, and 90%, respectively. In contrast, the THF selectivity is initially observed to increase from 12.5% to 18.4% with increasing Mg content, and then decreases to 12.3%, 11.5%, and 9.2% with further increase in the Mg content. Meanwhile The selectivities of BuOH, 2BT1O, and GBL slightly varied with the MgO content. These results indicate that the synergistic effect between Mg and Yb facilitates the catalytic activity for BDO dehydration and BTO selectivity.



Figure 2. BDO conversion at 325  $^\circ C$  (A) and selectivities of BTO, THF, BuOH, 2BT1O, and GBL at 10% isoconversion at 325  $^\circ C$  over different catalysts.

#### Structural and textural characteristics

Characterizations of both structure and surface properties were carried out to study the synergistic effect between Mg and Yb in the binary oxides. The surface area, pore distribution, and pore volume of the different catalysts were determined by N2 physisorption, and the results are displayed in Figure 3. As shown in Figure 3(A), pure MgO and Yb<sub>2</sub>O<sub>3</sub> exhibit type IV isotherms with H3-type hysteresis loops, indicating the presence of slit-shaped pores in the catalysts.<sup>[34,35]</sup> The Mg-Yb binary oxides exhibit type IV isotherms with type H2(b) loops, which are associated with inkbottle-shaped pores.<sup>[34,36]</sup> Figure 3(B) shows the pore distributions, wherein a small pore diameter centered at 2 nm is observed for pure Yb<sub>2</sub>O<sub>3</sub> and MgO. However, the most probable pore size increases from 2 to 5 nm as the MgO content is increased. Table 1 presents the textural properties of all catalysts, and the following observations are made: The surface area increases from 8.6 to 22.9, 39.3, 45.3, and 72.9 m<sup>2</sup>/g, while the total pore volume increases from 0.047 to 0.065, 0.089, 0.118 and 0.265 cm<sup>3</sup>/g, as MgO content increases from 0 to 29.2, 50.3, 69.6, and 89.2 mol%, respectively. The increase in the surface area can be attributed to the insertion of MaO into the Yb<sub>2</sub>O<sub>3</sub> lattice, which restricts the growth of the Yb<sub>2</sub>O<sub>3</sub> nanocrystals.<sup>[37]</sup> Overall, the large specific surface area and unique mesoporous structure would be more favorable for the adsorption and mass transport of the BDO molecules, which are beneficial for a high catalytic performance.



Figure 3.  $N_{\rm 2}$  adsorption isotherms (A) and pore distribution of Mg-Yb mixed oxides (B).

Catalysts	Mg/(Mg+Yb) <sup>[a]</sup>	Surface area <sup>[b]</sup>	$D_{mp}^{[c]}$	$D_{p}^{[d]}$	$V_{p}^{[e]}$			
	(mol%)	(m²/g)	(nm)	(nm)	(cm³/g)			
Yb <sub>2</sub> O <sub>3</sub>	0	8.6	1.9	21.7	0.047			
Mg3Yb7	29.2	22.9	1.9	11.4	0.065			
Mg5Yb5	50.3	39.3	2.4	9.7	0.089			
Mg7Yb3	69.6	45.3	3.1	10.4	0.118			
Mg9Yb1	89.2	72.9	4.6	14.6	0.265			
MgO	100	10.6	1.9	18.5	0.049			

Table 1 Taxtural properties of Ma Vb actaluate

[a] The actual Mg molar ratio was determined by XRF analysis. [b] The specific surface area was determined from the adsorption isotherms using the Brunauer–Emmett–Teller (BET) equation. [c]  $D_{mp}$  represents the most probable pore size, which was determined by the Barrett–Joyner–Halenda (BJH) method. [d]  $D_p$  represents for average pore diameter, which was determined from the desorption isotherms by the BJH method. [e]  $V_p$  represents the total pore

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volume, which was determined from the desorption isotherms by the BJH method at  $\rho/\rho_0$  = 0.99.

The XRD patterns of the Mg-Yb binary oxides and single oxides are shown in Figure 4(A). The diffraction peaks of  $Yb_2O_3$  are well indexed to cubic  $Yb_2O_3$  (PDF card 41-1106) (Ia3(206)) and the peaks at 20.84°, 29.62°, 34.34°, 49.4°, and 58.7° are due to the (211), (222), (400), (440), and (622) planes of  $Yb_2O_3$ , respectively. The strong and sharp reflection peaks suggest that the synthesized catalysts were well crystallized. Meanwhile, the diffraction peaks at 36.94°, 42.92°, and 62.24° were due to the (111), (200), and (220) planes, respectively, of periclase phase (PDF card 45-0946) (cubic Fm-3m(225)), which could be observed in the XRD patterns of MgO.



Figure 4. XRD patterns (A) and Raman spectra (B) of the Mg-Yb mixed oxides.

It is observed that all the peaks attributed to cubic Yb<sub>2</sub>O<sub>3</sub> and cubic MgO in the mixed oxides are broader and less intense than those of pure Yb<sub>2</sub>O<sub>3</sub> and MgO. The broader peaks of the mixed oxides indicate a decrease in the crystal size, while the lower intensity verifies that the addition of MgO would affect the Yb<sub>2</sub>O<sub>3</sub> crystallization and vice versa. The Mg3Yb7 catalyst exhibits characteristic diffraction peaks of Yb<sub>2</sub>O<sub>3</sub>, while those of MgO are not detected. This absence of MgO diffraction peaks suggests that either the Mg ions were incorporated into the Yb<sub>2</sub>O<sub>3</sub> lattice or MgO was highly dispersed on the surface of Yb<sub>2</sub>O<sub>3</sub>, because powder XRD is only sensitive to grain sizes of 4.0 nm or greater. The diffraction peaks of MgO are observed when the Mg content reached 50 mol%. For the Mg9Yb1 catalyst, the intensity of the diffraction peaks of Yb<sub>2</sub>O<sub>3</sub> is much lower while that of MgO is higher than in the Mg7Yb3 catalyst. Moreover, a broad feature that appeared at 25°-40° may be due to the amorphous phases of the pristine oxides or mixed solid solutions. The XRD data of all Mg-Yb catalysts are listed in Table 2, and the following observations are made: The introduction of Mg into the crystal lattice of Yb<sub>2</sub>O<sub>3</sub> slightly shifts the Yb<sub>2</sub>O<sub>3</sub> (222) plane from 29.63° to 29.61°. The d-spacing of (222) also increases from 3.012 to 3.015 Å. A further increase in the Mg content also leads to an expansion in the d-spacing of all catalysts except Mg5Yb5. A similar d-spacing expansion is observed for the MgO (200) plane. These observations are mainly due to the interchange between Mg and Yb in the Yb<sub>2</sub>O<sub>3</sub> and MgO phases, which means that Yb<sub>2</sub>O<sub>3</sub> and MgO are the two major phases present in the Mg-Yb oxides; meanwhile, a part of the added Mg or Yb is present in the crystal lattice of the other oxides. Notably, the peaks in Mg5Yb5 are more intense, and the crystallite sizes of both Yb<sub>2</sub>O<sub>3</sub> and MgO are also larger than those of the other mixed oxides. This is because the driving force for the interchange of both cations is much lower in Mg5Yb5, owing to the same proportion of Mg and Yb, which leads to the higher crystallinity of both MgO and Yb<sub>2</sub>O<sub>3</sub> phases.<sup>[38]</sup> As discussed, the Mg-Yb oxide catalysts exhibit superior catalytic activity compared with the pristine Yb<sub>2</sub>O<sub>3</sub> or MgO, which may be due to the interaction between Mg and Yb.

#### Table 2. Powder XRD data of the Mg-Yb catalysts.

		Yb <sub>2</sub> O <sub>3</sub> (222)	MgO (200)			
Catalysts	2θ (°)	d-spacing <sup>[a]</sup> (Å)	D <sup>[b]</sup> (nm)	2θ (°)	d-spacing (Å)	D (nm)
Yb <sub>2</sub> O <sub>3</sub>	29.63	3.012	13.3	-	-	-
Mg3Yb7	29.61	3.015	6.7	-	-	-
Mg5Yb5	29.67	3.009	9.0	42.66	2.118	9.0
Mg7Yb3	29.61	3.015	8.4	42.77	2.112	8.4
Mg9Yb1	29.51	3.024	5.0	42.73	2.115	8.6
MgO	-	-	-	42.83	2.110	19.6

[a] Interplanar distance (d-spacing) was calculated by assuming that the structures of  $Yb_2O_3$  and MgO are cubic phases according to the XRD data. [b] *D* stands for the average crystallite size, which was calculated from the XRD patterns using the Scherrer equation from the (222) plane of  $Yb_2O_3$  and (200) plane of MgO.

The microstructures of all samples were examined by Raman spectroscopy, as shown in Figure 4(B). It is observed that MgO exhibits a rocksalt structure and therefore shows no first-order Raman effect.<sup>[39]</sup> Furthermore, the figure shows five main bands at 227.4, 312.6, 361.7, 430.3, and 610.5 cm<sup>-1</sup> for Yb<sub>2</sub>O<sub>3</sub>. The C-type Yb<sub>2</sub>O<sub>3</sub> is body-centered cubic with the space group Ia3, Th, Z = 16.<sup>[40]</sup> This structure is related to the fluorite structure with each Yb ion located at the cubic center from which two of the eight nearest-neighbor oxygen atoms in the fluorite structure have been removed.<sup>[40-42]</sup> Thus, the structure contains 32 cations and 48 anions. The irreducible representations for the optical and acoustic modes from the Bhagavantam–Suranarayana method are as follows:

$$\Gamma_{op} = 4A_g(R) + 4E_g(R) + 14F_g(R) + 5A_{2u}(i) + 5E_u(i) + 16F_u(ir)$$
(1)  
$$\Gamma_{ac} = F_u$$
(2)

where (R) stands for the Raman active, (ir) for infrared active, and (i) for inactive modes. Thus, twenty-two Raman lines of the Ag, Eg, and Fg modes and 16 Fu infrared bonds were predicted. [40-44] However, the number of bands observed in the spectra in Figure 4(B) are different from this prediction. This could be due to the high temperature at which the spectra were collected, which could possibly lead to the overlapping of some of the bands. Similar results have also been reported in previous studies: the frequencies above 300 cm<sup>-1</sup> were practically identical for Yb<sub>2</sub>O<sub>3</sub> and isostructural rare earth cubic sesquioxides.  $^{\left[ 41,44,45\right] }$  These bands can be ascribed to the oxygen motions and the deformations of the YbO<sub>6</sub> octahedra.<sup>[46]</sup> As shown in Figure 4(B), the Raman bands of Yb<sub>2</sub>O<sub>3</sub> became much broader and less intense after doping with MgO, which suggests a strong interaction between MgO and Yb<sub>2</sub>O<sub>3</sub> crystallites.<sup>[46]</sup> Meanwhile, compared with pure  $Yb_2O_3,$  the band at 362.0  $\mbox{cm}^{-1}$  for  $Yb_2O_3$  is observed to shift to 361.3, 359.9, and 356.8 cm<sup>-1</sup> as the MgO

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Catalysts	Amount of basic sites <sup>a</sup> (µmol/g)	Amount of acidic sites <sup>a</sup> (µmol/g)	Density of basic sites <sup>b</sup> (nm <sup>-2</sup> )	Density of acidic sites <sup>b</sup> (nm <sup>-2</sup> )	Density ratio of basic/acidic sites	<i>B/L</i> ratio <sup>c</sup>	Density of L acidic sites <sup>d</sup> (nm <sup>-2</sup> )	Density of B acidic sites <sup>e</sup> (nm <sup>-2</sup> )
Yb <sub>2</sub> O <sub>3</sub>	60.9	29.1	4.26	2.04	2.09	-	-	-
Mg3Yb7	125.2	114.4	3.29	3.01	1.09	0.73	1.73	1.27
Mg5Yb5	211.7	55.3	3.24	0.85	3.83	0.50	0.56	0.28
Mg7Yb3	260.5	116.0	3.46	1.54	2.24	0.66	0.93	0.61
Mg9Yb1	407.5	81.4	3.37	0.67	5.01	0.56	0.43	0.24
MgO	353.5	20.4	20.08	1.16	17.34	-	-	-

[a] The amount of basic (or acidic) sites was calculated from the amount of desorbed  $CO_2$  in the temperature range of 100 to 650 °C. [b] The density of basic (or acidic) sites was calculated as the amount of basic (or acidic) sites × Avogadro constant / surface area of the catalyst. [c] The *B/L* ratio was calculated from the intensity of the bands at 1540 cm<sup>-1</sup> and 1444 cm<sup>-1</sup>. [d] The density of L acidic sites was calculated as the density of acidic sites / (*B/L* + 1). [e] The density of B acidic sites was calculated as the density of acidic sites × (*B/L*) / (*B/L* + 1).

concentration is increased from 0 mol% to 29.2, 50.3, and 69.6 mol%, respectively. This redshift was mainly due to the increasing distance between Yb and O. It is generally accepted that the band frequency in the Raman spectrum is directly related to the metal-oxygen distances.<sup>[46]</sup> Assuming that the band with the *Fg*+*Ag* mode is mainly due to the stretching modes, the frequency of a band could be calculated from an empirical force constant using the classical equation:

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \tag{3}$$

where  $\nu$ , k, and  $\mu$  are the frequency, force constant, and reduced mass of the system Yb–O, respectively.<sup>[40,46]</sup> As the Raman shift in Yb<sub>2</sub>O<sub>3</sub> is dependent on the force constants of the Yb–O bond, it could be assumed that the redshift of the *Fg+Ag* mode is mainly due to the weaker force constant of the Yb–O bond, which results from the increasing Yb–O bond length.<sup>[40,42,49]</sup> Combined with the XRD data, these redshifts can be ascribed to the lattice distortion caused by the insertion of the Mg ions into the Yb<sub>2</sub>O<sub>3</sub> crystal lattice, which generate the Mg–O–Yb bonds and further increase the Yb– O bond length. It could also be further assumed that the Mg–O– Yb linkage is also generated in the MgO crystal in the Mg–Yb binary oxides.

#### Surface acid-base properties

The catalytic performance for BDO dehydration was observed to be mainly influenced by the acid-base properties of the catalyst.<sup>[22]</sup> To better understand the synergistic effects of Mg and Yb on catalytic performance, CO<sub>2</sub>- and NH<sub>3</sub>-TPD measurements were performed to determine the surface acidity and basicity of the Mg-Yb oxide catalysts. The CO2-TPD curves for all catalysts are presented in Figure 5(A). Pristine MgO exhibits one broad peak centered at 254 °C with high intensity. The amount of desorbed CO2 and the desorption temperature increases from 353.5 µmol/g and 254 °C for pure MgO to 407.5 µmol/g and 264 °C for the Mg9Yb1 catalyst, respectively. The addition of 29.2 mol% of Yb to MgO not only increases the basic strength but also generates more basic sites. These extra basic sites were mainly a result of the doping of Yb to MgO, which could generate more surface defects and unsaturated oxygen over MgO, because the basic sites of MgO are associated with defects and unsaturated coordinated oxygen.<sup>[38,50,51]</sup> However, a further increase in the Yb content from 50.3 to 89.2 mol% adversely affects the basicity of the catalyst; this decrease is mainly due to the dilution effect of Yb<sub>2</sub>O<sub>3</sub> because there is little CO<sub>2</sub> desorption observed over Yb<sub>2</sub>O<sub>3</sub> alone.

The acidity of Mg-Yb mixed oxide catalysts was evaluated using  $NH_3$ -TPD. As observed in Figure 5(B),  $Yb_2O_3$  exhibits two

desorption peaks of  $NH_3$  centered at 192 and 446 °C, while MgO exhibits two peaks centered at 299 and 543 °C-all peaks are less intense than those of the Mg-Yb mixed oxides. Furthermore, the binary oxides also exhibit two NH<sub>3</sub> desorption peaks at a maximum desorption temperature below 200 °C and above 250 °C. Moreover, the desorption temperature of NH<sub>3</sub> over all Mg–Yb binary oxides at low temperatures is nearly unchanged at approximately 170 °C at different MgO contents. In contrast, at high temperatures, the desorption temperature of NH<sub>3</sub> shifts from 380 to 319, 310, and 320 °C as the MgO content is increased from 30 to 50, 70, and 90 mol%, respectively. The decrease in the acidic strength of the Mg-Yb catalysts is mostly because MgO neutralizes some of the strong acidic sites of Yb<sub>2</sub>O<sub>3</sub>.<sup>[52]</sup> However, the NH<sub>3</sub> uptake over the Mg–Yb catalysts dramatically increased: the total NH<sub>3</sub>-uptake amounts are 114.4, 55.3, 116.0, and 81.4 µmol/g over Mg3Yb7, Mg5Yb5, Mg7Yb3, and Mg9Yb1, respectively. Thus, all the Mg-Yb binary oxides exhibited higher acidity compared to the mono-component oxides. Moreover, the generation of acidic sites over the mixed oxides has also been reported in similar studies.<sup>[52-55]</sup> To further investigate the acidity types of the catalysts, pyridine adsorption analysis was carried out.



Figure 5. CO<sub>2</sub>–TPD (A) and NH<sub>3</sub>–TPD (B) profiles of the Mg-Yb mixed oxides.

The acidic properties of the Mg–Yb binary oxides were evaluated using an *in situ* DRIFTS method following the pyridine adsorption technique: Figure 6 shows that all catalysts exhibited bands at

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1444, 1489, and 1540 cm<sup>-1</sup>. The bands at 1540 and 1444 cm<sup>-1</sup> could be assigned to pyridinium (PyH<sup>+</sup>) and the pyridine coordinatively bonded to Lewis acid sites (PyL), respectively. The band at 1489 cm<sup>-1</sup> could be ascribed to a combination of Lewis and Brønsted acid sites (L+B). As shown in Figure 6, pristine MgO and Yb<sub>2</sub>O<sub>3</sub> exhibited weak bands at 1450 cm<sup>-1</sup>, while hardly any bands assigned to the Brønsted acid sites are observed, indicating the weak Lewis acidity of the MgO and Yb<sub>2</sub>O<sub>3</sub>.<sup>[56-58]</sup> The Lewis acidity of pristine MgO and Yb<sub>2</sub>O<sub>3</sub> mainly originated from the coordinatively unsaturated surface metal cations.[31,51] Meanwhile, the Mg-Yb binary oxides display more intense bands at both 1444 and 1540 cm<sup>-1</sup>, which could be related to the generation of extra acidic sites over the binary oxides. The relative proportion of the Brønsted and Lewis acid sites (B/L ratio) was calculated from the intensity of the bands at 1540 cm<sup>-1</sup> and 1444 cm<sup>-1</sup> to quantify the Brønsted and Lewis acid sites of the mixed Mq-Yb oxides. Assuming that the adsorption sites of pyridine are identical to those of ammonia, the densities of Brønsted and Lewis acid sites were calculated by multiplying the total acid density (measured from NH<sub>3</sub>-TPD) by (B/L) / (B/L + 1) and 1 / (B/L + 1), respectively, as shown in in Table 3.<sup>[59,60]</sup>



Figure 6. In situ DRIFTS spectra of pyridine adsorbed on the Mg–Yb mixed oxides.

From Figure 6 and Table 3, it can be concluded that extra acidity, which includes both Lewis and Brønsted acids, is generated over the binary oxides. This can generally be explained by the excess charges of the binary oxides based on Tanabe's hypothesis. These excess charges were determined by the coordination numbers and valences of the elements in the model structures based on the following two postulates: (i) the coordination number of all the positive elements is maintained even when the two components are mixed; (ii) the coordination number of the negative elements (oxygen) of a major component oxide is retained for all the oxygen in a binary oxide.<sup>[61]</sup> In our case, the results of the XRD and Raman spectroscopy indicated that both MgO and Yb<sub>2</sub>O<sub>3</sub> were formed in the mixed oxides, while some of

In the Mg-O-Yb structures located in the Yb-rich region, the coordination numbers of Yb and Mg were six, which are the same as those in pure Yb<sub>2</sub>O<sub>3</sub> and MgO. In contrast, the coordination number of oxygen was four, which is the same as that in pure Yb<sub>2</sub>O<sub>3</sub>, according to the two postulates from Tanabe's hypothesis. Therefore, in MgO, the two positive charges of Mg<sup>2+</sup> were distributed to six coordinated covalent bonds, i.e., +1/3 of the valence unit was distributed to each bond. Similarly, the two negative charges of O2- were distributed to the four coordinated covalent bonds, i.e., -1/2 of the valence unit was distributed to each bond. The difference in the charge for one Mg-O bond was  $+1/3 - \frac{1}{2} = -1/6$ , and the valence unit of  $-1/6 \times 6 = -1$  was excess for all the bonds. In this case, Brønsted acidity was assumed to appear because one proton was considered to be associated with the six oxygen atoms, which coordinated to Mg to maintain the electrical neutrality. Furthermore, the Lewis acidity would also appear in the Mg-O-Yb structure located in the Mg-rich regions owing to the presence of an excess positive charge according to the above postulates. Therefore, both Lewis and Brønsted acids could be generated over the mixed oxides. Notably, Mg5Yb5 exhibits weaker acidity than the Mg3Yb7 and Mg7Yb3 catalysts, as shown in Figure 6. These results are mainly due to the smaller Mg-O-Yb structure formed in Mg5Yb5, because the XRD results show that the interchange between the Mg and Yb cations in Mg5Yb5 is much lower than the Mg3Yb7 and Mg7Yb3 catalysts. Similarly, the Mg9Yb1 catalyst also exhibits weaker acidity, which is mostly due to the small amount of Yb<sub>2</sub>O<sub>3</sub>, resulting in fewer Mg-O-Yb structures and the strong basic nature of MgO.

# Relationship between acid-base properties and catalytic performance

It is generally accepted that the dehydration of alcohol is most likely influenced by the acidity or basicity of a catalyst. The above discussions indicate that the Mg-Yb binary oxides could generate a Mg-O-Yb structure, which results in extra acidity and basicity of the catalysts. Therefore, the correlation between the catalytic performance and the acid-base properties was investigated to provide a more definitive proof for the dehydration of BDO into BTO. Figure S2(A) and (B) show the plots of the density of single acidic or basic sites versus the BDO reaction rate and BTO selectivity, respectively. However, no clear relationship is observed between the single densities of the acidic or basic sites. Yamamoto et al. investigated BDO dehydration over a series of Na-modified ZrO<sub>2</sub> catalysts and reported that the number of acidic sites on the ZrO<sub>2</sub> rapidly decreased with increasing Na content, while the number of basic sites increased with increasing Na content.<sup>[20]</sup> Furthermore, BTO selectivity was maximized at an appropriate Na content, which was independent of the increase or decrease in the basic sites or acidic sites, respectively.<sup>[20]</sup> Inoue et al. studied the dehydration of BDO over Yb/ZrO2 catalysts and reported that an increase in Yb loading resulted in an increase in the number of basic sites on Yb/ZrO2, which might reduce BDO conversion.<sup>[26]</sup> However, there is no clear relationship between the basicity and BTO selectivity of Yb/ZrO2. Thus, the abovementioned studies showed that the dehydration of BDO into BTO cannot be explained by the number of basic or acidic sites.

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Interestingly, Figure 7(A) and 7(B) show that while considering the acidic and basic sites, the density ratio has a linear relationship with the BDO reaction rate and BTO selectivity, respectively: the specific reaction rate decreases while BTO selectivity increases as this ratio increases. These results suggest that the dehydration of BDO into BTO does not simply occur over single acidic or basic sites-both acidic and basic sites are involved in the BDO dehydration reactions. Similar effects of the acidic and basic site ratio on the catalytic activity were also observed by Espinosa et al. who obtained 5-hydroxymethylfurfural from glucose using Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>-W catalysts.<sup>[62]</sup> Sato et al. reported that both acidic and basic sites on Er<sub>2</sub>O<sub>3</sub> concertedly catalyzed the BDO dehydration reaction, which was confirmed by the poisoning tests using NH<sub>3</sub> and CO<sub>2</sub> as the carrier gas.<sup>[25]</sup> Analogously, BDO dehydration over the Mg-Yb binary oxides followed the mechanism wherein the hydroxyl groups of BDO were adsorbed and activated over the acidic sites, while the basic sites abstracted the  $\beta$ -H of the adsorbed BDO species to produce BTO.<sup>[6,22]</sup> Thus, the BDO reaction rate, which decreased with the increase in the density ratio of the basic and acidic sites, could be understood as more acidic sites are helpful for the adsorption and activation of the BDO molecules. Similarly, the BTO selectivity, which increased with the density ratio of the basic and acidic sites, could also be explained by the more number of basic sites favoring the abstraction of  $\beta$ -H of the adsorbed BDO to form BTO.



**Figure 7.** Relationship between the density ratio of the basic and acidic sites and the BDO dehydration reaction rate (A) or BTO selectivity (B) (The BDO reaction rate was evaluated at 325 °C and W/F = 0.17 g-h-ml<sup>-1</sup> in the kinetic region; the BTO selectivity obtained by controlling the BDO conversion at 10%); (C) relationship between the density of the acidic sites and THF selectivity (THF selectivity was obtained at BDO conversion = 10%).

Figure 7(C) shows the relationship between the density of the acidic sites and THF selectivity; THF and BTO are competitive products of the BDO dehydration reaction. As the density of the acidic sites increases from 0.67 to 0.85, 1.54. and 3.01 nm<sup>-2</sup>, THF selectivity also increases from 9.2% to 11.5%, 12.3%, and 18.4%, respectively. Thus, it is evident that THF formation occurs over

the acidic sites, as also reported by previous studies.<sup>[63,64]</sup> The following mechanism for THF formation has also been proposed: one of the hydroxyl groups of the BDO molecule would be protonated by the acidic sites before the other hydroxyl group attacks the hydronium ion, resulting in the cyclization and elimination of water to THF.<sup>[65]</sup> Therefore, considering that the surface properties of the Mg-Yb binary oxides are more basic than acidic, and that BTO is formed over both acidic and basic sites while THF is generated only over acidic sites, BTO selectivity was enhanced while THF selectivity was suppressed over the Mg-Yb binary oxides.

Although the above results lead to the conclusion that both Lewis and Brønsted acid sites were generated over the Mg-Yb binary oxides, the types of acidic sites that were more active in the BDO dehydration reaction could not be identified. Therefore, the influence of the density ratio of the basic / Lewis acid sites and basic / Brønsted acid sites on the reaction rate of BDO dehydration were investigated, and the results are shown in Figure 8. Based on Table 3, the density ratios of the basic / Lewis acid sites were 2.59, 11.46, 5.64, and 13.96, while those of the basic / Brønsted acid sites were 1.90, 5.75, 3.73, and 7.81 for Mg3Yb7, Mg5Yb5, Mg7Yb3, and Mg9Yb1, respectively, However, compared with the density ratio of the basic/acidic sites in Figure 8(A) and 8(B), no apparent difference between the Lewis acid and Brønsted acid sites is observed in the dehydration reaction. These results indicate that both Lewis and Brønsted acids might contribute similarly to the BDO dehydration reaction.



Figure 8. Relationship between the density ratio of basic / Lewis acid sites (A), basic / Brønsted acid sites (B) and the reaction rate of BDO dehydration. (The BDO dehydration reaction rate was evaluated at 325 °C and  $W/F = 0.17 \text{ g} \cdot \text{h} \cdot \text{m}^{-1}$ .)

#### Stability of the catalysts

From a practical view, the stability of the catalysts is vital for industrial applications. Therefore, the stability of the Mg3Yb7 catalyst was tested at 337 °C and  $W/F = 0.17 \text{ g}\cdot\text{h}\cdot\text{ml}^{-1}$ , where the BDO dehydration reaction was under kinetic regime with reliable BDO conversion. Figure 9 shows the stability of the BDO dehydration reaction over the Mg7Yb3 catalyst under theabovementioned conditions. Initially, the BDO conversion slightly decreases while BTO selectivity slightly increases. However, between 10 to 50 h, both processes are observed to remain nearly unchanged: while BDO conversion fluctuates in the range of 26%–28%, BTO selectivity varies at ca. 84%. These results indicate that Mg7Yb3 exhibits high stability during the catalytic dehydration of BDO. Table 4 compares the BDO dehydration process over various catalysts to evaluate their catalytic performance. The rare earth metal oxides exhibit high

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Catalysts	Temperature	W/F	0	BDO conversion	BTO selectivity	BTO yield	Deference
	(°C) (g	(g∙h∙ml⁻¹)	Carrier gas	jas (%)	(%)	(%)	Releiences
CeO <sub>2</sub>	375	0.046	N <sub>2</sub>	22.0	72.5	16.0	[25]
Yb <sub>2</sub> O <sub>3</sub>	375	0.046	N <sub>2</sub>	33.9	87.6	29.7	[25]
<i>m</i> -ZrO <sub>2</sub>	325	0.407	N <sub>2</sub>	94.4	34.1	32.2	[26]
CaO/ <i>m</i> -ZrO <sub>2</sub>	350	1	N <sub>2</sub>	94.6	68.9	65.2	[23]
Yb <sub>2</sub> O <sub>3</sub> / <i>m</i> -ZrO <sub>2</sub>	325	0.407	N <sub>2</sub>	73.1	85.4	62.4	[26]
Mg7Yb3	350	0.93	N <sub>2</sub>	90.4	78.6	71.1	This study

BTO selectivity, while m-ZrO<sub>2</sub> exhibits high BDO conversion. Therefore, the modification of m-ZrO<sub>2</sub> using rare earth oxides or alkaline earth metal oxides is an effective approach toward enhancing the catalytic performance for BDO dehydration: for instance, CaO/m-ZrO<sub>2</sub> achieves 94.6% BDO conversion with 68.9% BTO selectivity, while Yb<sub>2</sub>O<sub>3</sub>/m-ZrO<sub>2</sub> produces a lower BDO conversion but higher BTO selectivity. Meanwhile, the Mg7Yb3 catalyst prepared in this study exhibited the highest catalytic performance. Considering that Mg7Yb3 also exhibited high stability during the dehydration process, it is believed to have a promising application potential in the BDO dehydration reactions.



Figure 9. Stability of BDO dehydration reaction over Mg7Yb3 at 337 °C and  $W/F = 0.17 \text{ g-h-ml}^{-1}$ .

#### Mechanism study

The above discussions suggest that both acidic and basic sites are involved in BDO dehydration, and also that a higher density ratio of the acidic/basic sites benefited BDO conversion while a higher basic/acidic ratio favored BTO formation. However, the mechanisms by which BDO was adsorbed and reacted over the Mg-Yb catalysts remain ambiguous. Therefore, in situ DRIFTS investigation was performed on the reaction mechanism of BDO dehydration leading to the formation of BTO over the Mg7Yb3 catalyst, which exhibits higher BDO dehydration activity and similar BTO selectivity as that of Mg9Yb1. Figure 10 shows the spectra of Mg7Yb3 with the introduction of BDO at 100 °C, and Table 5 lists all the vibrations and their assignments. As shown in Figure 10, the peaks that emerged above 3500 cm<sup>-1</sup> could be assigned to the H-O stretching vibrations of the adsorbed water contained in the BDO reactant;[66,67] the band at 2983 cm<sup>-1</sup> could be ascribed to the C-H stretching vibration of the molecularly adsorbed BDO;<sup>[6,22]</sup> the band at 1643 cm<sup>-1</sup> could be ascribed to O-H-O scissors bending;<sup>[67]</sup> and the bands at 1428, 1341, and 1220 cm<sup>-1</sup> could be associated with the C-H deformation, wagging, and twisting vibrations of the CH<sub>2</sub> group, respectively.<sup>[68]</sup> At 0.5 min, before any peak of the BDO molecular appears, water is observed to emerge on the surface of the catalyst.<sup>[66,67]</sup> A possible reason for this is that water vapor is typically present in alcohol, which competes with alcohol for adsorption onto the catalysts owing to its higher affinity to the acidic sites than the diol.<sup>[69,70]</sup> At 2 min, the intensity of the O-H stretching vibrations of the adsorbed water increases while the bands of the CH<sub>2</sub> group at 1200–1430 cm<sup>-1</sup> appear.<sup>[68]</sup> The band of the molecularly adsorbed BDO appears at 4 min, which confirms the molecular adsorption of BDO onto the surface of Mg7Yb3, as the BDO was introduced at a low surface temperature.<sup>[6,22]</sup>



Figure 10. In situ DRIFTS of Mg7Yb3 with the introduction of BDO at different times, at 100 °C. ((A) 3900–2900 cm<sup>-1</sup>; (B) 1800–800 cm<sup>-1</sup>).

 
 Table 5. Vibrations and assignments of the IR peaks appearing in the spectra of the Mg7Yb3 catalysts in the *in situ* DRIFTS experiments of BDO dehydration.

Vibrations	Assignment	References
3648	H-O stretching vibrations of adsorbed water	[66,67]
3753	Surface terminal -OH groups	[66]
3100, 3030	C-H asymmetric and symmetric vibrations of the double bond	[22,71,72]
2983	C-H stretching vibrations of molecularly adsorbed BDO	[6,22]
2966, 2923	C-H asymmetric and symmetric vibrations of the CH <sub>2</sub> group	[73,74]
2840, 2720	C-H stretching vibrations of the aldehyde group	[22,75]
1643	O-H bending vibrations	[67]

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1600	C=O stretching vibrations of the aldehyde	[22,75]
1474	C-H deformation vibrations of =CH <sub>2</sub> group	[22,71,72]
1420	C-H deformation vibrations of the CH <sub>2</sub> group	[68]
1341	C-H wagging vibrations of the CH <sub>2</sub> group	[68]
1288	C-H bending vibrations of =CH <sub>2</sub> group	[22,71,72]
1220	twisting vibrations of the CH <sub>2</sub> group	[68]
1024	C-O stretching vibrations of adsorbed butoxides	[73,74]
902, 877	C=C-H wagging vibrations	[22,71,72]



Figure 11. In situ DRIFTS results of Mg7Yb3 with the introduction of BDO at different temperatures. ((A) 3850-3700 cm<sup>-1</sup>; (B) 3200-2700 cm<sup>-1</sup>; (C) 1700-800 cm<sup>-1</sup>).

Figure 11 shows the DRIFTS spectra of Mg7Yb3 under BDO flow at temperatures ranging from 100 to 400 °C. The adsorbed water (a broad band at 1640 cm<sup>-1</sup>) and molecularly adsorbed BDO (at 1428, 1341, and 1220 cm<sup>-1</sup>) are observed at 100 °C. The negative band at 3753 cm<sup>-1</sup> emerges as the surface temperature increases to 200 °C. This band could be assigned to the surface terminal OH groups.[66] Simultaneously, the bands at 2966, 2923, and 1024 cm<sup>-1</sup> could be assigned to the asymmetrical and symmetrical vibrations of the C-H bands and the C-O stretching vibrations of the adsorbed butoxides.<sup>[73,74]</sup> The presence of the negative O-H stretching bands and butoxides bands indicates that BDO reacts with the surface hydroxyl groups to generate surface butoxide species as intermediates. The bands at 2840, 2720, and 1600 cm<sup>-</sup> <sup>1</sup> could be ascribed to the C-H stretching vibrations and C=O

stretching vibrations of the surface aldehyde species. Generally, basic sites could cause the dehydrogenation of alcohols into the corresponding carbonyl compounds.<sup>[20]</sup> In the dehydration of BDO into BTO, the basic sites in the Mg-Yb binary oxides, which are generally composed of O2- anions, could abstract β-H from the adsorbed butoxide species to form aldehyde species, because the O<sup>2-</sup> anions could donate electron pairs to β-H of butoxides. Similar studies were also reported by Sato et al., wherein the basic O2- anions over Er2O3 could abstract the H from alcohol in the dehydration process.<sup>[16,76]</sup> The bands at 3100, 3030, 1474, 1288, 902, and 877 cm<sup>-1</sup> could be assigned to the C-H stretching vibrations, C-H deformation vibrations, C-H bending vibrations, and C=C-H wagging vibrations of the double bonds, which could be associated with the formation of BTO from the aldehyde species.<sup>[22,71,77]</sup> As the surface temperature increases from 200 to 300 °C, the number of surface hydroxyl groups rapidly decrease, while the number of aldehyde species and olefins simultaneously increase. These results indicate that the molecularly adsorbed BDO and butoxides are quickly consumed, while the aldehyde species and BTO are abundantly formed. A further increase in the surface temperature to 400 °C would consume more aldehyde species, resulting in several negative bands at 1600, 2720, and 2840 cm<sup>-1</sup>, which in turn leads to the enhancement of the intensity of the BTO bands. The bands ascribed to THF and BDE are not observed along with the other byproducts in the spectra during the process, which could be attributed to the lower boiling point and surface adsorption amount.



Figure 12. Mechanism of BDO dehydration into BTO over Mg7Yb3 catalyst (the yellow ball represents the metal cation and the red ball represents the oxygen anion).

As already mentioned, both acidic and basic sites are involved in the reaction and influence both BDO reaction rate and BTO selectivity. Figure 12 shows the reaction mechanism of BDO dehydration over the Mg-Yb binary oxides based on the results mentioned earlier: firstly, the BDO is adsorbed on the surface to VIANUS

form molecularly adsorbed BDO, which then reacts with the surface hydroxyl groups (Brønsted acid) or the coordinately unsaturated metal cations (Lewis acid) to generate the butoxides. Notably, in the adsorption of BDO over the Lewis acid sites, the O-H bond of the BDO dissociates to form a surface H and a butoxide. Subsequently, the surface O<sup>2-</sup>, which acts as a basic site, abstracts the  $\beta$ -H of the adsorbed butoxide species to form the aldehyde species. Consequently, BTO is formed from the dissociation of the aldehyde species. The surface OH reacts with the surface H to form H<sub>2</sub>O to complete the catalytic cycle in the last step of the Lewis acid-mediated mechanism. Thus, both acidic and basic sites play a significant role in the catalytic dehydration reactions.

#### Conclusion

In this study, catalytic dehydration of BDO was systematically investigated over Mg-Yb mixed oxides to study the effect of the acid-base properties on the catalytic performance. Compared with the pristine oxides, all the Mg-Yb binary oxides significantly enhanced BDO reactivity and BTO selectivity. Extensive characterization showed that superior BDO reactivity and BTO selectivity were achieved by the generation of extra basic and acidic sites, which could be attributed to the surface defects and Mg-O-Yb linkages generated from the interaction between Mg and Yb. Both acidic and basic sites were observed to influence the catalytic performance during BDO dehydration. The catalytic activity during BDO dehydration was suppressed by the high density ratio of the basic and acidic sites, while BTO selectivity was enhanced by increasing this ratio. At 350 °C and W/F = 0.93g·h·ml<sup>-1</sup>, the BDO yield over the Mg7Yb3 catalyst reached 71.1% with 90.4% BDO conversion and 78.6% BTO selectivity. Furthermore, the in situ DRIFTS results indicated that BDO was first adsorbed on the surface of the catalyst, which then reacted with the acidic sites to generate butoxides. The  $\beta$ -H of the butoxides was further captured by the basic oxygen anions leading to the generation of the aldehyde species, which finally dissociated to form BTO. Thus, these results have not only provided greater insights into the BDO dehydration mechanism, but also presented a wide range of possibilities for the further development of acid-base catalysts for dehydration reactions.

#### **Experimental Section**

#### **Catalyst preparation**

The Mg-Yb composite oxides were prepared via an esterification sol-gel method.<sup>[78]</sup> Typically, 40 mmol of citric acid (>99.5%, Sinopharm Chemical Reagent) was dissolved in 80 mL of deionized water in a 500 mL beaker. Then, 13 mmol of ethylene glycol (>99.5%, Sinopharm Chemical Reagent) was added to obtain a colorless solution. After stirring for 30 min, 20 mmol of mixed metal nitrate, including Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (≥99.0%, Sinopharm Chemical Reagent) and Yb(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (99.99%, Energy Chemical) with different molar ratios, were added sequentially to the solution. After another 30 min of stirring, the beaker was placed in an oven preheated to 200 °C. This stage of the process promotes the esterification reaction because decomposition of citric acid occurs at *ca.* 170 °C.<sup>[78]</sup> Upon removal from the oven after 3 h, the beaker was filled with a highly porous brown foam. This foam was ground and subsequently calcined in air at 150 °C for 1 h, 400 °C for 2 h, and 650 °C for 6 h in a muffle furnace at a heating rate of 1 °C/min to convert the Mg- and Yb-containing organic foam into

#### Catalyst characterization

The X-ray diffraction (XRD) experiments were performed using a Shimadzu XRD-6100 X-ray diffractometer with a Cu K $\alpha$  ( $\lambda$  = 0.15406 nm) radiation source at a generator voltage and current of 40 kV and 40 mA, respectively. Scanning was performed between 10° and 80° (2 $\theta$ ) with a step size of 0.017° at a scan speed of 7°/min to identify the crystal structure of each catalyst. The average crystallite size was estimated using the Scherrer equation. The composition of the catalysts was determined by XRF using a Bruker S8 Tiger X-ray fluorescence spectrometer. The voltage and current of the generator were 50 kV and 80 mA, respectively.

The N<sub>2</sub> physisorption experiments were carried out in a BELSORP-Max at -196 °C. The catalysts were degassed using a BELPREP-vac II at 300 °C for 3 h before measurements. The specific surface area of the catalyst was calculated using the Brunauer–Emmett–Teller (BET) equation, and the pore size distribution was obtained using the desorption branch via the Barrett–Joyner–Halenda (BJH) method.

Raman spectra were acquired using a laser Raman spectrometer at room temperature. The samples were illuminated by a 532 nm Ar ion laser with a resolution of  $0.35 \text{ cm}^{-1}$ , and the power was 100 mW.

The properties of the acidic sites on the catalyst surface were probed by NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD) using a Quantachrome ChemBET Pulsar chemisorption analyzer with a thermal conductivity detector (TCD). Before testing, the catalyst was fixed in a U-shaped quartz tube and pretreated at 650 °C in a 30 mL/min He flow for 60 min. After this pretreatment, the catalyst was cooled to 100 °C, and 5 mol% NH<sub>3</sub>/Ar was passed over the samples at a flow rate of 30 mL/min for 60 min. After purging the catalyst with He flow for another 60 min, NH<sub>3</sub>-TPD was performed by heating the catalyst to 850 °C at 10 °C/min. The desorbed NH<sub>3</sub> was monitored by TCD. The properties of the basic sites were investigated using CO<sub>2</sub>-TPD measurements, which were performed following the same process as that of the NH<sub>3</sub>-TPD, but using CO<sub>2</sub> instead of NH<sub>3</sub> as probe molecules.

Pyridine-adsorbed diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed using a Nicolet iS50 spectrometer equipped with a DiffusIR reflectance accessory, which includes a heat chamber, a sample cell with ZnSe window, and an MCT-A detector. All spectra were collected every 30 s in Kubelka-Munk units and were averaged over 32 scans at 4 cm<sup>-1</sup>. The catalyst was first preheated to 450  $^\circ\!C$  under  $N_2$  flow for ca. 2 h to remove the impurities adsorbed on the surface. The preheated catalyst was then cooled to 50 °C, and pyridine adsorption was conducted after recording the background spectrum. Pyridine adsorption was carried out by bubbling N2 through a liquid pyridine saturator. The pyridine-containing N2 flow was introduced to the sample and saturation with pyridine was performed for 30 min until the spectra remained unchanged. The adsorbed pyridine was then partially desorbed by purging the sample with N2 flow at 150 °C for ca. 30 min to eliminate the influence of the gas phase and physisorbed pyridine. The sample was then cooled to 50 °C before recording the spectra.

Furthermore, the BDO dehydration reaction mechanism over the Mg-Yb mixed oxide catalysts was also studied by *in situ* DRIFTS. The experiment was performed using the aforementioned DRIFTS instrument, and BDO dehydration was studied as a function of temperature from 100 to 400 °C. Prior to the test, a fresh sample was pretreated with 30 mL/min N<sub>2</sub> (99.999 vol%) at 450 °C for 2 h. After cooling to 100 °C, the spectrum of the pure catalyst was recorded as background. The BDO was then fed into the sample cell by bubbling a 30 mL/min N<sub>2</sub> flow through a liquid BDO saturator; this condition was maintained until the spectra were stable. The spectra were collected every 30 s in the Kubelka–Munk units and averaged over 32 scans at 4 cm<sup>-1</sup>. The sample cell was then flushed with N<sub>2</sub> at 100

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°C to obtain spectra without the contribution of the gas-phase and physisorbed BDO, which were used to analyze the surface adspecies during the experiments. The same procedures were carried out at 200, 300, and 400 °C to monitor the change in the adspecies at different temperatures.

#### Catalytic tests

The catalytic activity during the BDO dehydration was evaluated using a tubular stainless fixed-bed reactor (7 mm inner diameter and 700 mm height) at atmospheric pressure. The catalyst bed consisted of a physical mixture of 1 g of catalyst (40 to 60 mesh) and 1 g of inert quartz sand (40 to 60 mesh) in order to minimize the hot spot effect. The catalyst was treated for 2 h under N2 flow at 450 °C before measurement. In a typical process, BDO (>99.0%, Sinopharm Chemical Reagent) was vaporized and mixed with 30 mL/min N2 at 300 °C before flowing into the fixed-bed reactor. The temperature of the catalyst bed was controlled within ±1 °C of the target temperature using thermocouples. The pipes on the reactor were heated to 300 °C with heat tape to prevent the condensation of the gaseous reactant. The products were collected from the outlet that was placed after the condenser and gas-liquid separator. The composition of the liquid products was analyzed by gas chromatography (Fuli 9790II). The outlet gas from the gas-liquid separator was measured using a gas flowmeter and sent to GC-MS (Shimadzu GCMS-QP2010 Plus) to detect the gaseous byproducts. All catalytic data were reported after a 2 h reaction. The BDO dehydration was investigated in the temperature range of 300–425 °C and *W/F* ratio of 0.17–1.23 g·h·ml<sup>-1</sup> (where *W* is the weight of catalyst and F is the BDO flow rate). The carbon balance at the outlet was checked for all the investigated conditions.

The results including BDO conversion, selectivity of the product i, and BTO yield were calculated using the following equation:

BDO conversion (%) = 
$$\frac{\text{moles of BDO consumed}}{\text{moles of BDO in the feed}} \times 100\%$$

Selectivity of *i* (%) =  $\frac{\text{moles of } i \text{ produced}}{\text{moles of BDO consumed}} \times 100\%$ 

BTO yield (%) = BDO conversion × BTO selectivity × 100%

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Mg-Yb binary oxides were synthesized and investigated for the catalytic dehydration of 1,4-butanediol to 3-buten-1-ol. All the Mg-Yb binary oxides performed better than pristine MgO or  $Yb_2O_3$ . Strong interaction between MgO and  $Yb_2O_3$  results in physicochemical properties. Extra basic and acid sites were formed on Mg-Yb binary oxides. 1,4-Butanediol dehydration on Mg-Yb catalyst via an acid-base concerted mechanism.