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In situ DRIFTS for the mechanistic studies of 1,4-butanediol dehydration over Yb/Zr catalysts

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ABSTRACT

To study the effect of acid-base properties of catalysts on 1,4-butanediol (BDO) dehydration to 3-buten-1ol (BTO), Yb/Zr catalysts with different Yb content were synthesized by a wet impregnation method. The texture property, crystalline form and surface properties of the catalysts were characterized by N₂ physisorption, XRD, NH₃-TPD, CO₂-TPD and in situ DRIFTS. The catalytic performance of BDO dehydration was also tested in a fixed-bed reactor. The experimental results showed that the activity of BDO dehydration and the selectivity of by-product tetrahydrofuran (THF) decreased with the increased Yb content, while the selectivity of the main product BTO gradually increased. The yield of BTO maximized at 64.5% when the Yb content reached 15%, which showed the best catalytic performance. Comprehensive analysis of experimental results showed that the activity of BDO dehydration and the selectivity to the by-product THF were manipulated by the acid sites of the catalysts, while BTO selectivity was tuned by both acid and basic sites of the catalysts. A higher density ratio of basic/acid sites favored the BTO formation and inhibited the formation of by-products THF. The in situ DRIFTS study of BDO dehydration over m-ZrO₂ and Yb₂O₃ elucidated that the hydroxyl groups of BDO molecules first interacted with acid sites to form several types of butoxides. Further abstraction of β -H by basic oxygen anion could convert these butoxides into aldehyde species, which finally reacted to form BTO. The DRIFTS results were consistent with the experimental conclusions that the acid sites of the catalysts could interact with hydroxyl groups and basic sites facilitate the β -H abstraction of BDO and thereby enhancing the formation of BTO.

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1. Introduction

3-Buten-1-ol (BTO) is a valuable unsaturated alcohol, which is used as the intermediate for a range of products including medicines, agrochemicals, function polymers and food additives. Due to the presence of its reactive double bond and hydroxyl group, BTO can take part in many kinds of reactions, producing a variety of products, especially pemetrexed disodium, an antifolate antineoplastic agent used as cancer medicine [1–5]. Since the pemetrexed disodium was approved by the U.S. Food and Drug Administration to treat patients with advanced nonsquamous non-small cell lung cance, the demand for BTO is rapidly growing as the global drug market rises [5–7].

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Currently, the processes to produce BTO include formaldehyde addition to propylene, reduction of 3,4-epoxy-1-butene by formic acid and reduction of crotonic acid [8]. However, the use of a cosolvent is questionable from the viewpoint of green chemistry during the formaldehyde addition to propylene. Furthermore, formic acid has a toxic and corrosive nature in the 3,4-epoxy-1-butene reduction process. The reducing agent for crotonic acid reduction is lithium aluminum hydride, which is expensive and hazardous [9]. Such disadvantages limit the appliance of these processes. Therefore, the use of novel technology to minimize the aforementioned problems while achieving high conversion and selectivity is of great technological and economic interest.

1,4-Butanediol (BDO) are compounds containing two hydroxyl groups, which are very important platform chemicals that have been widely employed in various areas, including solvents, fuels, polymers, cosmetics, and pharmaceuticals, with an annual production of more than 1 million tons [10,11]. BDO can be obtained from coal by the Reppe method, which has already been industrialized around the world [12,13]. In addition, production of BDO from







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renewable bioresources by environmentally benign biological processes has also attracted abundant attention [14-18], and the processes have already been commercialized by several companies such as Genomatica [17]. Increase in the BDO production capacity urges the necessity for technology development of downstream products. Hence, direct catalytic dehydration of BDO has been proposed as one of most promising method to produce BTO [19,20]. Scheme 1 shows the scheme of BDO dehydration. It could be seen from the scheme that the BDO dehydration is a very complex reaction network, which could generate various chemicals including BTO, tetrahydrofuran (THF), 1-butanol, 2-buten-1-ol (2BT1O), 1,4-butyrolactone (GBL) and 1,3-butadiene, where THF, as a competitive product, is more preferential to generate than BTO [21–23]. Although vapor-phase selective dehydration of BDO could offer some advantages such as mild reaction conditions, simple experimental procedure and environmental friendliness, the lower activity and selectivity of BDO dehydration is still the main restriction of this technology [24]. Consequently, it is a challenging task to obtain a catalyst that favors BTO production by dehydration of BDO.

The acid-base properties of catalysts show a vital influence on the BDO dehydration [25]. The main methods to manipulate the acid-base properties of the catalysts are to modify the catalysts with different metal oxides. Yamamoto in previous study showed that a complicated reaction network existed in the BDO dehydration [26]. The regulation of catalysts acid-base properties can improve the selectivity of target product BTO and inhibit the byproducts formation [26]. The authors modified the acidity and alkalinity of the catalyst via loading sodium hydroxide on zirconium dioxide, and found that the introduction of Na⁺ can neutralize the acidic hydroxyl groups on the surface of zirconium dioxide to form -ONa species, leading to an increase of the basic sites amount and a decrease of the acid sites amount on the catalyst surface [27]. It could be found that the reduction of acid sites amounts result in a decrease of the selectivity of by-product THF, in association with the catalytic performance, yet the selectivity of the by-product GBL is in proportion to the basic sites amount. The selectivity to BTO was increased firstly and subsequently declined as the Na content increased. These results were attributed to the modification of Na⁺, which resulted in a change in the acid-base properties of the catalyst surface. Sato et al. further changed the strategy of studying the acid-base properties of the catalyst [28]. When ammonia and carbon dioxide were employed to poison the surface acid and basic sites of the Er₂O₃ catalyst, the rate of BTO production was significantly inhibited. The authors therefore proposed that the active sites of BTO are composed of acidic sites and basic sites; however, no quantitative relation between BTO yield and acid-base properties was obtained. It can be concluded from above reports that the acid-base properties of the catalyst have an important influence on the dehydration performance of BDO. However, a quantitative analysis between the acid-base amount and the catalytic performance is still lacking. Furthermore, studies on the mechanisms of dehydration of BDO to BTO have rarely been reported. Sato et al. investigated the mechanism of BDO dehydration over Er₂O₃ with theoretical calculations using density functional theory (DFT) and paired interacting orbitals (PIO) calculations, and claimed that the position-2 hydrogen atom is firstly abstracted by a basic oxygen anion and that the position-1 hydroxyl group is subsequently abstracted by an acidic erbium cation to form BTO and desorbed from the surface [29]. Yet, no direct experiment results could confirm the BDO dehydration mechanism.

In this work, a series of supported catalysts with different Yb loadings were prepared by the wet impregnation method. The acidity and alkalinity of the catalyst surface were regulated by Yb loading, while the crystal shape, pore structure, average pore size, and crystallite size of the catalyst were maintained nearly unchanged, to investigate the effects of acid and basic sites amount on the BDO dehydration and further obtain the quantified relationship between acid-base properties and catalytic performance, and thus lay the foundation for the sensible design and preparation of the reaction catalyst. In addition, the adsorption model and dehydration mechanism of BDO for different catalysts were investigated through *in situ* DRIFTS, which provided theoretical support for the study of the subsequent reaction kinetics and the design of the catalysts.

2. Experimental

2.1. Catalysts preparation

The m-ZrO₂ support was prepared *via* hydrothermal method. In a typical process, urea (>99.0%, Sinopharm Chemical Reagent) and zirconium oxynitrate (>99.5%, Shanghai Macklin Biochemical) were dissolved in deionized water. The concentration of Zr⁴⁺ and urea were 0.4 mol/L and 4 mol/L, respectively. 60 mL zirconium



Scheme 1. Reaction network of BDO dehydration.

oxynitrate and urea solution was transferred into a 100 mL Teflonlined autoclave. Hydrothermal treatment was carried out at 473 K under autogenous pressure for 6 h. The resulting precipitate was recovered by centrifugation, fully washed with deionized water until a neutral pH and finally dried at 383 K overnight. The white powder was then calcined in air at 773 K for 4 h with a heating rate of 1 K/min.

 ZrO_2 -supported Yb₂O₃ catalysts were prepared by wet impregnation method. 3 g ZrO₂ was impregnation for over 12 h with magnetic stirring using 30 mL aqueous solution of Yb(NO₃)₃·5H₂O (99.99%, Energy Chemical). The concentration of Yb³⁺ was varied from molar ratio of Yb/(Yb + Zr) various from 2.5 to 20%. The suspension was dried at 333 K, 10 kPa in a rotary evaporator with 60 r/min and after that in an oven at 383 K overnight. The powder was calcined in air at 773 K for 4 h with a heating rate of 1 K/min. The powder was denoted as *n* Yb/Zr, where "*n*" represented the molar ratio of Yb/(Yb + Zr). The actual loading of Yb was analyzed by X-ray fluorescence (XRF) using a Bruker S8 tiger WDXRF spectrometer.

2.2. Catalysts characterization

X-ray diffraction (XRD) patterns were collected on a Shimadzu XRD-6100 X-ray diffractometer with a Cu K α (λ = 0.15406 nm) radiation source at 40 kV and 30 mA to identify the crystal structure of each catalyst. The 2 θ angles were scanned from 10 to 80° with a step size of 0.02° and scan speed of 7°/min. The average crystallite sizes (*D*) were estimated by the Scherrer equation, D = 0.90 λ/β cos θ , where θ was the diffraction angle and β was the full width at half maxima (FWHM).

Specific surface area was measured at 77 K using a BELSORP-Max instrument. Prior to the measurement, the sample was treated using a BELPREP-vac II at 573 K for 3 h. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method and the pore size distribution was calculated by Barrett–Joyner– Halenda (BJH) method.

Acid sites on the catalyst surfaces were probed by NH_3 temperature programmed desorption using a Quantachrome ChemBET Pulsar chemisorption analyzer with a thermal conductivity detector (TCD). NH_3 -TPD was performed by heating the sample to 823 K with a heating rate of 10 K/min. The desorbed NH_3 was monitored by TCD. Prior to the test, samples (*ca.* 100 mg) were placed in a U-shaped glass tube, purged with He flow (30 mL/min) for 10 min and then heated to 823 K (10 K/min) in He flow (30 mL/ min) and held at this temperature for 60 min before the temperature was lowered to 323 K. After this pretreatment, 5 mol % NH_3/Ar was passed over samples with a flow rate of 30 mL/min for 60 min and then switched back to He flow for 60 min. CO_2 -TPD measurements were performed following the aforementioned process, but using CO_2 instead of NH_3 to probe the basic sites of samples.

In situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) of m-ZrO₂ and Yb₂O₃ were performed on a Nicolet iS50 spectrometer (Thermo Scientific) equipped with a DiffusIR Reflectance Accessory (Pike Technology), which consists of a heat chamber, DRIFT cell with ZnSe window and an MCT-A detector. All spectra were collected in Kubelka-Munk units and were averaged over 32 scans at 4 cm⁻¹ resolution at desired temperature. In a typical process, the powder sample was placed in a DRIFTS cell and set at 1 mm lower than cell surface by using sample press stick. The cell was heated to 723 K in Ar flow (30 mL/min) and held at this temperature for 60 min before the temperature was controlled to desired temperature (373, 473, 573 673 K) under Ar flow. After stabilization of the spectrum, the background spectrum was collected. The BDO molecule was introduced by flowing 30 mL/ min Ar through a room-temperature saturator, and the spectra were began to be recorded every 30 s, simultaneously. Afterward

(spectra will reach steady in about 40 min), the sample was flushed with Ar (30 mL/min) for another 40 min until the spectra reaching steady again. All spectra shown in figure were obtained using difference spectra method.

2.3. Catalytic tests

Reactions were carried out at atmospheric pressure in a tubular stainless fixed-bed reactor of 7 mm inner diameter and 700 mm height. The catalyst bed consisted of a mixture of 1 g of catalyst (40 mesh) and 1 g of inert quartz sand (40 mesh), which was fixed at the center of the reactor with quartz wool. In a typical process, the catalyst was treated for 2 h in a nitrogen flow at 723 K first. The reactant, BDO (>99.0%, Sinopharm Chemical Reagent) was continuously pumped from vessel by a calibrated digital pump (Series II Digital Pump, SSI) to a gasifier (553 K), and then the BDO gas was mixed with 30 mL/min nitrogen as carrier gas in a mixer (573 K) into the fixed bed reactor. The reactor was placed in a temperature-controlled electrically heated furnace and heated to the reaction temperature, which was monitored with thermocouples placed inside the reactor touching the inlet of the catalyst bed. The temperature of the catalyst bed can be controlled to ± 1 K. Reactor effluent gas lines were heated to 573 K with heating tapes to prevent possible condensation. The reactor outlet products were passed through a condenser to the gas-liquid separator and weighed at regular intervals. The condensate was qualified and quantified by off-line gas chromatography (Fuli 9790II) using retention time and internal standard method, respectively. Outlet gas from gas-liquid separator was measured by a gas flow meter. A small portion of gas was subjected to GC-MS (Shimadzu GCMS-QP2010 Plus) to detect the possible gaseous by-products. Essentially, only BDO, BTO, THF, 1-butanol, 2BT1O and GBL were detected in the reactor effluent mixture, and no gaseous byproduct was detected. The results including BDO conversion, BTO selectivity, THF selectivity and BTO yield were calculated using the following equation:

BDO Conversion (%) =	$\frac{\text{moles of BDO consumed}}{\text{moles of BDO in the feed}} \times 1009$	7
BTO Selectivity (%) =	moles of BTO produced \times 100%	

 $\label{eq:THF Selectivity} \text{THF Selectivity (\%)} \ = \ \frac{\text{moles of THF produced}}{\text{moles of BDO consumed}} \times 100\%$

BTO Yield (%) = BDO Conversion \times BTO Selectivity

All of the catalytic data were reported after 2 h reaction. The catalytic performance of BDO dehydration were investigated at temperature range of 573–723 K and W/F of 0.019 g·h·ml⁻¹ over all the catalysts.

3. Results and discussion

3.1. Structural and textural characteristics

Fig. 1 shows the nitrogen adsorption–desorption isotherm and pore size distributions of n Yb/Zr catalysts with different molar ratio of Yb / (Yb + Zr). It can be seen from Fig. 1(a) that all isotherms belong to type IV with H1 hysteresis loops, which is typical for mesopores materials. The gentle slope of the capillary condensation step indicates non-uniformity and disorder of mesopores. The impregnation of Yb on the mesopores m-ZrO₂ resulted in a narrowing of the hysteresis loops and a slight shift of the condensation step toward lower relative pressure, indicating lower pore volume and pore diameter. Indeed, Fig. 1(b) exhibits narrow pore size



Fig. 1. (a) Nitrogen adsorption-desorption isotherm and (b) pore size distributions of *n* Yb/Zr catalysts.

distributions, and the average pore size of *n* Yb/Zr is between 2 and 13 nm, which locates in the mesopore range. BET surface areas and pore diameter from BJH analysis of the materials are summarized in Table 1. As can be seen, the BET surface area of *m*-ZrO₂ was 91.7 m²/g. After loading Yb, the surface area decreased from 91.7 to 89.3, 87.3, 86.8, 81.1, 70.2 and 58.6 m²/g when the *n* (Yb molar ratio) increased from 0% to 2.5%, 5%, 7.5%, 10%, 15% and 20%, respectively. Except for 20 Yb/Zr (58.62 m²/g), impregnation with Yb on the *m*-ZrO₂ resulted in a small decline on the BET surface area. The specific pore volume obviously decreased from 0.27 mL/g to 0.17 mL/g upon impregnation of Yb onto the *m*-ZrO₂ support, while the average pore diameter keeps invariant at 11.3 nm with Yb impregnation. These results suggest that the impregnation of Yb occurred inside the mesopores [30,31].

Fig. 2 shows the XRD patterns of Yb/Zr catalysts as well as pure m-ZrO₂. All of the catalysts show the peaks characteristic of m-ZrO₂ phase at $2\theta = 24.1^{\circ}$, 28.2° , 31.5° , 34.2° , 38.5° , 40.7° , 44.8° , 50.1° , 55.4° , 59.8° and 65.7° (JCPDS card 37-1484). No diffraction pattern which can be attributed to Yb₂O₃ is observed in all samples. Furthermore, the peak intensity of n Yb/Zr catalysts ($2\theta = 24.1^{\circ}$, 28.2° , 31.5°) is weaker than that of the corresponding m-ZrO₂ supports. These observations could suggest that Yb₂O₃ species is

highly dispersed on the surface [31,32]. The average crystallite size was calculated by Scherrer Equation and is shown in Table 1. The crystallite size keeps invariant at 9 nm over *n* Yb/Zr catalysts. It could be concluded that despite the wide variety of chemical composition, the as-prepared catalysts have similar textural properties.

3.2. Effect of Yb loading

Prior to catalytic measurements, a blank experiment was conducted in which only quartz sands were fixed inside the reactor. No BDO was dehydrated among all the temperature range, indicating there was no reaction under investigated conditions.

The effects of mass transfer and heat transfer should be excluded to measure the intrinsic activities of the catalysts. Therefore, the Koros-Nowak criterion test modified by Madon–Boudart [33] has been employed using *m*-ZrO₂ catalyst and the results were plotted in Fig. 3. It can be found from Fig. 3 that the plot of conversion vs. $1/\rho$ (ρ is defined as the active space velocity) [33] using a catalyst sample with $f_w = 0.5$ (f_w is defined as the weight fraction of the active material in the catalyst) [33] coincides with the plot when repeat the experiment using a catalyst sample with $f_w = 1$ at both 598 and 618 K, which indicates that the Koros-Nowak

Table I			
Textual	properties	of Yb/Zr	catalysts

Catalyst	$Yb/(Yb + Zr)^a$ %	$S_{BET} \left(m^2/g \right)^b$	Vp (mL/g) ^c	Dp (nm) ^d	D (nm) ^e
m-ZrO ₂	0	91.7	0.27	11.7	9.2
2.5 Yb/Zr	2.3	89.3	0.25	11.4	9.3
5 Yb/Zr	4.7	87.3	0.24	11.2	9.5
7.5 Yb/Zr	7.3	86.8	0.25	11.4	8.8
10 Yb/Zr	9.9	81.1	0.22	11.0	8.6
15 Yb/Zr	16.8	70.2	0.20	11.5	8.6
20 Yb/Zr	22.3	58.6	0.17	11.6	8.9

^a Actual Yb molar ratio was determined by XRF analysis.

^b Specific surface area was determined from the adsorption isotherms by BET equation.

^c Total pore volume was determined from the desorption isotherms by BJH method at $p/p_0 = 0.99$.

^d Average pore diameter was determined from the desorption isotherms by BJH method.

^e Average crystallite size was calculated from XRD patterns by Scherrer Equation.



Fig. 2. XRD patterns of *n* Yb/Zr catalysts.



Fig. 3. The Koros-Nowak Criterion applied in the study of BDO dehydration at 598 and 618 K in the 1.67–2.08 mL/min flow rate range for m-ZrO₂ catalyst with two different f_w : 0.5 and 1 (as diluted with quartz sand).

criterion is obeyed and the effects of mass transfer and heat transfer are excluded when the reaction temperature was lower than 618 K.

The catalytic performance was evaluated over *n* Yb/Zr catalysts in the range of 578–618 K to investigate the effects of reaction temperature. Fig. 4(a) shows the Arrhenius plot of BDO dehydration. Activation energy of BDO dehydration was calculated based on Arrhenius equation. It can be seen from Fig. 4(a) that the BDO reaction rates over all the catalysts increase as reaction temperature increasing. *m* ZrO₂ shows the highest activation energy (142.7 kJ/mol), and therefore shows the highest dehydration activity while higher temperature benefits larger activation energy based on Arrhenius equation. Fig. 4(b) and (c) show the temperature dependence of BTO and THF selectivity. Obviously, m-ZrO₂ and 2.5 Yb/Zr show the lower BTO selectivity and higher THF selectivity among all the catalysts. The selectivity of BTO and THF keeps nearly unchanged with the increasing reaction temperature over m-ZrO₂ and 2.5 Yb/Zr catalysts. However, the BTO selectivity on other Yb/Zr catalysts increases with the rising reaction temperature while the selectivity of THF decreases along with the increasing temperature. It is noteworthy that the 15 Yb/Zr shows the highest BTO selectivity and lowest THF selectivity.

In order to get the highest yield over n Yb/Zr catalysts, the temperature dependence of BTO yield was investigated at the temperature range from 578 to 723 K in Fig. 4(d). The BTO yield on all the catalysts is increased first to its maximum as reaction temperature rises to 698 K, and then decreases with the reaction temperature further increasing to 723 K. The 15 Yb/Zr catalysts show the highest BTO yield of 64.5% at 698 K compared to other catalysts.

To see the effect of Yb content, the catalytic performance over *n* Yb/Zr catalysts at 618 K and 0.019 g·h·ml⁻¹ are plotted in Fig. 5(a) which are free from mass and heat transfer limitations as indicated by the Koros-Nowak criterion. It can be seen that the mass specific activity (MSA) of BDO decreases from 4.35×10^{-5} to 3.16×10^{-5} , 1.57×10^{-5} mol/(g·s) as Yb loading increases from 0% to 2.5% and 5%, respectively. Further Yb loading ($\geq 7.5\%$) hardly changes the MSA of BDO while it keeps nearly invariant at *ca*. 2.51×10^{-5} mol/(g·s). The BTO selectivity increases rapidly from 23% to 27%, 34%, 36%, 52% and 72% as Yb loading increases from 0% to 2.5%, 7.5%, 10% and 15%, respectively. Further increase of Yb loading to 20% leads to slight reduction of BTO selectivity to 68%. Simultaneously, the selectivity of THF is suppressed from 77% to 19%, where THF is the main by-products of BDO dehydration.

The difference in both BTO and THF selectivity may arise from the different activation energy of BTO and THF formation over nYb/Zr catalysts for parallel reactions. Therefore, further investigation of apparent activation energy is shown in Fig. 5(b). The corresponding Arrhenius plots for n Yb/Zr catalysts are shown in Fig. S1, where the BDO conversion was controlled below 25% and the reaction temperature is controlled below 618 K to obev the Koros-Nowak criterion. The reverse reactions can also be ignored according to Fig. S2 that the values of equilibrium constants of the forward reactions are nearly over 10⁴. It could be seen from the Fig. 5(b) that the activation energy of BTO formation (E_{a-BTO}) are 146.6 kJ/mol, which is more than that of BDO conversion $(E_{a-BDO} = 142.7 \text{ kJ/mol})$ and THF formation $(E_{a-THF} = 142.7 \text{ kJ/mol})$ over *m*-ZrO₂. The E_{a-BDO} decreases from 142.7 to 124.4 kJ/mol and 116.3 kJ/mol as Yb loading increases from 0% to 2.5% and 5%, respectively. Further Yb loading (\geq 7.5%) increases E_{a-BDO} from 116.0 to 131.9 kJ/mol. Meanwhile, E_{a-THF} decreases rapidly from 142.7 to 83.4 kJ/mol as Yb loading increases from 0% to 20%. It can be seen that the Yb loading distinctly reduces E_{a-THF}, while hardly changes the E_{a-BTO}. These results imply that Yb loading can enhance the BTO selectivity and suppress THF selectivity at high temperature, since larger activation energy is more sensitive for higher temperature according to Arrhenius equation.

The texture properties of pure Yb_2O_3 were characterized by N_2 -physisorption and XRD, while the catalytic performance of pure Yb_2O_3 was also examined as can be seen in Fig. S3. As shown in Fig. S3(a), the isotherms of Yb_2O_3 belong to type IV with H3 hysteresis loops, which indicating slit-shaped pores. The BET specific surface area and total pore volume of Yb_2O_3 are $47.8 \text{ m}^2/\text{g}$ and 0.59 mL/g, respectively. Fig. S3(b) exhibits a broad pore size distribution (2.4–95.2 nm) with the average pore diameter of 49.4 nm. Fig. S3(c) shows that the crystalline phase of pure Yb_2O_3 nanoparticles is well consistent with the JCPDS Card (No. 41-1106) for cubic Yb_2O_3 . An average crystalline size of pure Yb_2O_3 nanoparticles calculated by the Scherrer Equation is 8.9 nm. Fig. S3(d) shows



Fig. 4. Arrhenius plot of BDO dehydration (a), temperature dependence of BTO selectivity (b), THF selectivity (c) and BTO yield (d) at different reaction temperature over *n* Yb/ Zr catalysts with *W*/*F* = 0.019 g·h·ml⁻¹.



Fig. 5. (a) Catalytic performance of BDO dehydration at 618 K and (b) activation energy of BDO dehydration, BTO formation and THF formation with different Yb loading.

the Arrhenius plot of BDO dehydration over Yb_2O_3 . The BDO reaction rates increase as reaction temperature increasing and the activation energy of BDO dehydration is 144.8 kJ/mol. Fig. S3(e) shows the BTO selectivity and THF selectivity at reaction temperature range from 578 to 618 K. The BTO selectivity increases while the

THF selectivity decrease with the reaction temperature. Fig. S3(f) shows that the BTO yield over pure Yb_2O_3 increases along with the rising reaction temperature. The MSA of BDO over Yb_2O_3 catalyst is 9.04×10^{-6} mol/(g·s). It could be seen that Yb_2O_3 shows the lowest BDO dehydration activity and higher BTO selectivity, while

m-ZrO₂ shows the highest BDO activity and lowest BTO selectivity. By Yb₂O₃ impregnation on m-ZrO₂, Yb/Zr catalysts show both high BDO activity and BTO selectivity. This synergistic effect of Yb-Zr catalysts maybe results from acid-base properties of the catalysts.

The surface acid-base property is an essential factor of the BDO dehydration performance [21,24]. However, the relation between the acid-base property and BDO dehydration is still ambiguous, especially for BTO formation [34]. Therefore, the acidity and alkalinity of the *n* Yb/Zr catalysts were evaluated from NH₃-TPD and CO₂-TPD measurements.

3.3. Surface acid-base property and relation with catalytic performance

Fig. 6 shows the NH₃-TPD and CO₂-TPD profiles of n Yb/Zr catalysts. The quantified data are shown in Table 2.

NH₃-TPD provides a quantitative measure of ammonia uptake by the catalyst and a qualitative measure of the strength of acid sites. Fig. 6(a) shows the NH₃-TPD profiles of the different catalysts. All NH₃-TPD curves feature a broad peak, starting at *ca.* 373 K, maximizing at ca. 473 K and lasting up to 773 K. It is widely reported that the position and area of the desorption peak are closely related to the strength and amount of acid sites over the catalysts, respectively [31,35,36]. It could be seen from Fig. 6(a) that m-ZrO₂ exhibits three desorption peaks during the temperature range of measurement, which can be attributed to NH₃ species desorbed from weak acid sites, medium acid sites and strong acid sites, respectively [31,36,37]. The three peaks are labeled as α_1 , α_2 and α_3 . As shown in the figure, the peaks representing the strong acid sites (α_3) vanished quickly when Yb loading increased from 0% to 7.5%. The peaks representing the medium acid sites (α_2) shifted from 568 to 527 K when Yb loading increased from 0% to 5%, and eventually disappeared at 7.5% Yb loading. Further increase of the Yb content to 20% gradually shifted the weak acid sites peak (α_1) from 462 to 442 K. As shown in Table 2, a decrease in the

amount of acid sites was also observed from 114.5 to 98.2, 78.7, 75.0, 55.6, 13.9 umol/g and 32.6 umol/g with *n* increased from 0% to 2.5%, 5%, 7.5%, 10%, 15% and 20%, respectively. The density of acid sites also varied from 0.75 to 0.66, 0.54, 0.52, 0.41, 0.12 nm^{-2} and 0.33 nm^{-2} with *n* increasing, respectively. Especially, the 15 Yb/Zr catalysts have both the lowest amount and density of acid sites. The decrease of both the strength and amount of acid sites is mainly ascribed to the Yb species surface coverage, since it is well known that the ytterbium oxide is more basic than being acid [34].

The basic strength and basicity of the catalysts were studied by CO₂-TPD. Fig. 6(b) shows the CO₂-TPD profiles of the different catalysts. The desorption profile shows a broad, structured peak starting at ca. 323 K, maximizing at ca. 373 K and lasting up to ca. 673 K. It can be seen from Fig. 6(b) that m-ZrO₂ exhibits two desorption peaks during the temperature range of measurement, labeled as β_1 and β_2 . These desorption peaks can be attributed to two CO₂ species desorbed from weak basic sites [38–40]. The weak basic sites shifted from 371 (β_1) and 434 (β_2) to 388 (β'_1) and 439 K (β'_2) when the Yb loading increased from 0% to 20%, respectively. As Yb loadings >5%, new basic sites which can be assigned to medium basic sites appeared at 536 K (β_3). As can be seen in Table 2, a decrease in the amount of total basic sites can be observed from 181.8 to 150.2, 146.6, 154.8, 140.2, 159.6 umol/g and 128.6 umol/g when n increased from 0% to 2.5%, 5%, 7.5%, 10%, 15% and 20%, respectively. However, the density of basic sites which was calculated by CO₂-TPD and specific surface area decreased from 1.19 to 1.01 firstly and then increased to 1.07, 1.04, 1.37 and 1.32 when *n* increased from 0% to 2.5%, 5%, 7.5%, 10%, 15% and 20%, respectively. The decreased amount and density of basic sites could probably be due to the neutralization of surface acid sites with addition of ytterbium oxide, since ytterbium oxide is basic. However, further Yb loading could simply increase the strength and density of basic sites.

It is well accepted that both acid and basic sites play important roles in alcohol dehydration [41–44]. Acid-base properties are key



Fig. 6. NH₃-TPD (a) and CO₂-TPD (b) profiles of *n* Yb/Zr catalysts.

Table 2	
Total acidity and basicity of catalysts.	

Catalyst	Total acid sites ^a (umol/g)	Density of acid sites ^b (m^{-2})	Total basic sites ^a (umol/g)	Density of basic sites ^b (m ⁻²)
m-ZrO ₂	114.5	0.75	181.8	1.19
2.5 Yb/Zr	98.2	0.66	150.2	1.01
5 Yb/Zr	78.7	0.54	146.6	1.01
7.5 Yb/Zr	75.0	0.52	154.8	1.07
10 Yb/Zr	55.6	0.41	140.2	1.04
15 Yb/Zr	13.9	0.12	159.6	1.37
20 Yb/Zr	32.6	0.33	128.6	1.32

^a Total acid and basic sites were calculated using area of all the NH₃-TPD desorption peaks and CO₂-TPD desorption peaks, respectively.

^b Density of acid and basic sites was calculated as total acid and basic sites divided by specific surface area of corresponding catalysts, respectively.

parameters in oxide catalysts to determine the selectivity and activity of catalytic reactions [43]. Thus, the relationship between catalytic performance and acid-base density were elucidated by quantitative NH_{3} - and CO_2 -TPD.

It is found that the acid-base properties of the Yb/Zr catalysts have significant influence on the dehydration of BDO. However, no clear relationship was found between the specific acid and basic sites and the catalytic activity. Sato et al. [27] and Zhao et al. [21] described the relationship between acid-base properties and catalytic activity using density of total acid and basic sites. Therefore, the relationship between total acid-base densities and catalytic performance of Yb/Zr catalysts were shown in Fig. 7. The influence of density of acid sites over the MSA of BDO is plotted in Fig. 7(a). It could be seen that the density of acid sites varied from 0.12 to 0.75 nm^{-2} , which shows a positive correlation with the MSA of BDO that increased from 3.03×10^{-5} to $4.36 \times 10^{-5} \text{ mol/(g·s)}$. These results suggest that higher BDO activity can be attributed to the rich acid sites on the surface of the catalysts. As it is known, the dehydration of alcohol readily proceeds over acid sites. The hydroxyl groups can easily adsorb on the acid sites due to the electrophilicity of the acid sites, which could enhance the dehydration conversion of the alcohol. In addition, when the 10% NH₃-N₂ was used as carrier in the BDO dehydration to poison the surface acid sites, the conversion of BDO decreased in the NH₃ flow [21]. This



Fig. 7. (a) Relationship between acid sites density and mass specific activity of BDO at 618 K; (b) Relationship between acid sites density and THF selectivity as BDO conversion = 9.5%; (c) Relationship between ratio of basic and acid sites density and BTO selectivity as BDO conversion = 9.5%.



Fig. 8. DRIFTS of BDO adsorbed on *m*-ZrO₂ at 373 K; (a). 3800–3660 cm⁻¹; (b). 3000–2800 cm⁻¹; (c). 1450–1000 cm⁻¹.

poisoning experiment indicates that acid sites could assure the BDO conversion. Therefore, it can be concluded that acid sites can activate BDO molecules to give higher BDO activity.

The acid-base properties of the Yb/Zr catalysts were shown in Fig. 7(b) and (c). BDO reaction over Yb/Zr catalysts in this study generated BTO, THF, GBL, 2BT1O, or 1,3-butadiene in varying proportions. In such parallel/sequential reactions, selectivity is meaningful only at an equivalent level of BDO conversion, which was set at $9.5 \pm 1\%$ in Fig. 7(b–c). Fig. 7(b) shows the relationship between acid sites and selectivity to the by-product THF. As the density of

acid sites increases from 0.12 to 0.33 nm⁻², the THF selectivity keeps nearly invariant at 24%. Further increase in the density of acid sites from 0.33 to 0.75 nm⁻² could increase the THF selectivity from 24.2% to 74.8%. It is clear that THF selectivity is closely related to density of acid sites of catalysts. THF can be selectively produced by BDO dehydration over acid catalysts, including strong mineral acids, heteropolyacids, zeolites and sulfonic acids [45]. Katari et al. [46] proposed that BDO is dehydrated to THF in two steps: one of the hydroxyl groups of BDO first adsorbs on the acid sites to form hydronium ion and the other terminal hydroxyl group



Fig. 9. DRIFTS of BDO adsorbed on *m*-ZrO₂ at 373, 473, 573 and 673 K; (a). 3800–3660 cm⁻¹; (b). 3050–2800 cm⁻¹; (c). 2800–2600 cm⁻¹; (d). 1350–1000 cm⁻¹.

tends to attack the hydronium ion to form THF. Combined with the relationship between THF selectivity and density of acid sites, it can be confirmed that dehydro-cyclization of BDO to THF takes place on acid sites.

In the present study, the BTO selectivity is improved by Yb loading over m-ZrO₂ (Fig. 5(a)), whereas the density of basic sites decrease at a lower Yb content and increase at a higher Yb content (Table 2). Based on the results from Fig. S4, there is no clear



Fig. 10. Reaction mechanism of BDO dehydration to BTO over *m*-ZrO₂.

relationship between the density of basic sites and the BTO selectivity. Furthermore, Sato et al. [19] have investigated the catalytic performance of BDO over MgO catalysts, and they found that the BDO could hardly react over MgO, which is a typical basic catalyst. Therefore, the BTO formation cannot be explained solely by the basic property of the Yb/Zr catalysts. The relationship between density ratio of basic/acid sites and BTO selectivity is investigated in Fig. 7(c). As the density ratio of basic/acid increased from 1.5 to 4.0, the BTO selectivity increased rapidly from 21.4% to 71.1%. Further increase of this ratio to 11.4 does not affect the BTO selectivity. These results indicate that acid sites also take part in the dehydration process. Tanabe et al. reported that ZrO₂ is an acid-base bifunctional catalyst in which both acid and basic sites on ZrO₂ play a concerted role in catalysis [47]. It is proposed that acid and basic sites interact with hydroxyl group and β -H of alcohol to form alkenes. Analogously, it could be speculated that abstraction of B-H and OH group is necessary for the formation of BTO. Similar research was also reported by both Sato et al. [24,27,29] and Zhang et al. [21] who proposed that BDO dehydration may proceed via an acid-base concerted mechanism.

Furthermore, it could be found that a higher density ratio of basic / acid sites favors BTO formation from Fig. 7(c). As mentioned above, the dehydration of BDO is thermodynamically feasible in two pathways: cyclodehydration to THF and dehydration to BTO. BTO and THF are competitively produced in the dehydration process. Fig. 7 shows that THF can be produced by BDO dehydration over acid sites with much lower activation energy (Fig. 5(b)), while both acid and basic sites are needed to produce BTO with higher activation energy. THF could be easily formed with abundant acid sites. Therefore, Yb loading could cover the acid sites of the *m*-ZrO₂ surface and result in a decrease of density of acid sites, which suppresses the THF formation, and simultaneously enhances the basicity of the catalysts surface, benefiting the β -H abstraction and thereby favoring the BTO formation.

3.4. In situ DRIFTS studies

3.4.1. BDO dehydration over m-ZrO₂

DRIFTS is a recently developed *in situ* technology that collects only diffusely scattered infrared radiation from the sample's rough surface by ellipsoidal mirrors in the spectrometer. By this, the surface compounds of a material can be tracked and characterized to get some valuable surface information. Atakan et al. [48] have investigated the CO₂ hydrogenation mechanism over the Cu-Zr-SBA-15 catalysts by *in situ* DRIFTS. Liu et al. [49] also use DRIFTS to study the reaction pathway for the hydrogenation of 3-nitrostyrene over supported gold nanocatalysts. To delineate the mechanism of BDO dehydration, the in situ DRIFTS studies were carried over *m*-ZrO₂ and Yb₂O₃ catalysts with contrasting acid-base properties. Fig. 8 shows the DRIFTS spectra of m-ZrO₂ in a flow of BDO for 30 min at 373 K. In Fig. 8(a), the negative bands at 3750, 3734 and 3671 cm⁻¹ are assigned to O–H stretching vibrations of the monodentate hydroxyls and bridged hydroxyls groups in defective and regular positions, respectively [50-52]. The band at 3690 cm^{-1} can be assigned to the hydroxyl of adsorbed BDO according to Plyler's research [53]. In Fig. 8(b), the bands at 2964–2860 cm⁻¹ can be assigned to the C-H asymmetrical and symmetrical stretching vibration of α -CH₂ and β -CH₂ of adsorbed species [54], respectively. In Fig. 8(c), the band at 1292 cm⁻¹ is ascribed to C–H bending vibration of CH₂ [55,56] and the bands at 1150 and 1073 cm^{-1} are assigned to v(CO) vibration of monodentate and bridged butoxides, respectively [50,57].

It can be seen from Fig. 8, the bands at 3690 cm^{-1} emerge at the time of 1 min of feeding BDO. At the time of 2 min, the bands at 3750, 3732 and 3671 cm^{-1} in Fig. 8(a) negatively increase rapidly, while 3690, 2964, 2921, 2889, 2858, 1292, 1150 and 1073 cm⁻¹ in Fig. 8(b) and 8(c) increase simultaneously. Additional time to 20 min could intensify the trend until it reaches steady. The negative growth of the bands at 3750, 3732 and 3671 cm⁻¹ means the decrease of surface hydroxyl over *m*-ZrO₂, which was accompanied with increase of 2964, 2921, 2889, 2858, 1292, 1150 and 1073 cm⁻¹ that represents the BDO adsorption. Given that the hydroxyl groups on *m*-ZrO₂ surface generally act as acid sites [58], which could react with alcohol-hydroxyl groups to form water, these results reveal that the surface hydroxyl groups could interact with BDO hydroxyl when BDO molecules adsorb on the *m*-ZrO₂ to form adspecies including monodentate and bridged butoxides.

Fig. 9 shows the DRIFTS spectra of m-ZrO₂ under BDO flow at the temperature ranging from 373 to 673 K, which are divided into (a), (b), (c) and (d) based on the wavenumber, respectively. The short dots in Fig. 9(a) and Fig. 9(d) are the zero-line of each spectrum. As can be seen from Fig. 9, the spectrum of 373 K is the same as the Fig. 8. The surface hydroxyl groups react with BDO hydroxyl to form monodentate and bridged butoxides. It should be pointed out that two weak bands emerge at 2740 and 2704 cm⁻¹ in Fig. 9 (c) at 373 K, which could be ascribed to the C—H stretching vibration of an aldehyde species of H-C____O [59]. Actually, no aldehyde species was detected in the dehydration process. Such behavior could account for the reactive intermediate in the reaction.



Fig. 11. DRIFTS of BDO adsorbed on Yb₂O₃ at 373, 473, 573 and 673 K; (a). 3780–3660 cm⁻¹; (b). 3050–2700 cm⁻¹; (c). 1400–1000 cm⁻¹.

As the surface temperature increases to 473 K, the intensity of 3750 and 3732 cm⁻¹ in Fig. 9(a) shows a negative growth while the band at 3690 cm⁻¹ increases. The intensity of CH₂ stretching vibration in Fig. 9(b) and v(CO) vibration of monodentate and bridged butoxides in Fig. 9(d) increase to its maximum, which results from the increase of the temperature that could enhance the adsorption of BDO molecules. Meanwhile, the intensity of aldehyde species in Fig. 9(c) also increases. As the surface temperature increases to 573 K, the band at 3671 cm⁻¹ in Fig. 9(a) increases. Meanwhile, the bands of aldehyde species at 2740 and

2704 cm⁻¹ in Fig. 9(c) and the bands at 1150 and 1173 cm⁻¹ in Fig. 9(d) decrease at the 573 K. The bands at 3029 and 3006 cm⁻¹ in Fig. 9(b) emerge at temperature of 573 K, which could be assigned to the C-H asymmetrical stretching vibration and symmetrical stretching vibration of $R = CH_2$ from BTO [60,61]. It is worth noting that BDO dehydration actually occurred at 573 K. Therefore, all these results suggest that aldehyde species could deoxygenate to form BTO and simultaneously regenerate surface hydroxyl groups, which results in a decrease of 2740 and 2704 cm⁻¹ and an increase of 3671 cm⁻¹. As the surface temperature



Fig. 12. Reaction mechanism of BDO dehydration to BTO over Yb₂O₃.

increases to 673 K, the BDO conversion reaches 90%. Therefore, most bands disappear except for $R = CH_2$ at 3029 and 3006 cm⁻¹ from BTO and monodentate butoxides at 1150 cm⁻¹.

Notably, the band at 1292 cm^{-1} , which is ascribed to bending vibration of CH₂, decreases as temperature increases from 373 to 673 K. These results imply that part of the C—H bond is broken during the process. Given that the basic sites, possibly composed of surface O²⁻ anions which have an ability to extract hydrogen atom from alcohols [25,28,58], a possible explanation could be proposed that basic sites could interact with the β -H of the adsorbed butoxides, leading to a C-H cleavage of the β -H.

Therefore, the mechanism of BDO dehydration over m-ZrO₂ can be proposed based on the aforementioned results as shown in Fig. 10. The surface hydroxyls of m-ZrO₂ interact with BDO molecules to form two adsorption types of monodentate and bridged butoxides. As the temperature increases, the β -H of butoxides is abstracted to form carbanion, which can be transformed into an aldehyde species. The aldehyde species are unstable and further deoxygenating to BTO, while regenerating the surface hydroxyl groups to complete the catalytic cycle.

It is also important to highlight that the bands at 1150 and 1073 cm⁻¹, which are assigned to monodentate and bridged butoxides, both exist at low temperature at 373 and 473 K. As the surface temperature increases to 673 K, the bridged butoxides vanish while monodentate butoxides still exist. These results could imply that the monodentate butoxides are more stable at the *m*-ZrO₂ surface. No THF bands are found in the spectrum. The possible reason is that THF is volatile at the tested temperature range.

3.4.2. BDO dehydration over Yb₂O₃

Fig. 11 shows the DRIFTS spectra of Yb_2O_3 under BDO flow at the temperature ranging from 373 to 673 K, which are divided into (a), (b) and (c) based on the wavenumber, respectively. The short dots in Fig. 11(d) are the zero-line of each spectrum.

As can be seen from Fig. 11(a), the bands at 3710, 3689 and 3669 cm⁻¹ are ascribed to the different adsorbed alcohol hydroxyl on the Yb₂O₃. The bands at 3029 and 3006 cm⁻¹ in Fig. 11(b) are assigned to the C—H asymmetrical stretching vibration and symmetrical stretching vibration of R = CH₂. The bands at 2961–2892 cm⁻¹ are assigned to the C—H asymmetrical and symmetrical stretching vibration of CH₂ of adspecies. The bands at 2840 and 2730 cm⁻¹ are ascribed to the C—H stretching vibration of H-C⁻⁻⁻⁻O of aldehyde species. In Fig. 11(c), the band at 1324 cm⁻¹ is ascribed to the bending vibration of CH₂. The bands at 1249 and 1219 cm⁻¹ are ascribed to C—C stretching vibration and c—O stretching vibration of γ -butyrolactone (GBL). The bands at 1104, 1061 and 1012 cm⁻¹ are assigned to the different

adsorbed type of butoxides, which can be assigned as I, II and III butoxides.

Fig. 11(a) shows the spectrum of three different types of alcohol hydroxyl at 373 K. As the surface temperature increases, the intensity of both bands at 3710 and 3689 cm⁻¹ increases at 473 K and decreases at 573 and 673 K. which is consistent with the same trend of bands at 2961, 2923, 1061 and 1012 cm⁻¹. Therefore, these two hydroxyl groups could be attributed to types II and III of butoxides. Meanwhile, the intensity of bands at 3669 cm⁻¹ also shows the same tendency as the bands at 1104 cm⁻¹, which indicates that the hydroxyl groups at 3669 cm⁻¹ could be attributed to type I of butoxides. The intensity of these bands increases at 473 K which could be attributed to high temperature that could enhance the BDO adsorption, and the deterioration of these bands could be ascribed to the reaction of BDO. Only type I and III butoxides exist on the surface of the Yb₂O₃ at 673 K, which means that the two types of butoxides are more stable than type II. The bands at 1324 cm⁻¹ decrease while those at 2840 and 2730 cm⁻¹ increase as the BDO is dehydrated, which shows that β -H is abstracted to form aldehyde species in the process. The weak bands at 3029 and 3006 cm⁻¹ indicate the formation of BTO. Besides, the variation of 1246 and 1219 cm⁻¹ shows that GBL is formed at 373 K and desorbed at 673 K.

The mechanism of BDO dehydration over Yb_2O_3 is proposed based on the aforementioned results as shown in Fig. 12. Three types of butoxides are formed on the surface Yb^{3+} , which act as acid sites. The β -H of butoxides is abstracted to form an aldehyde species, which is dehydroxylated to BTO. In summary, the mechanism of BDO dehydration over both *m*-ZrO₂ and Yb_2O_3 includes two steps: interaction of BDO molecules with acid sites to generate butoxides and abstraction of the β -H of butoxides to form aldehyde species, which react further to afford BTO. These results confirm that BDO is dehydrated to BTO *via* an acid-base concerted mechanism, as the acid sites could interact with the hydroxyl groups and the basic sites could abstract the β -H of BDO. These mechanisms are also consistent with the previous study mentioned in Section 3.3.

4. Conclusions

The effects of catalyst acid-base properties on BDO dehydration were systematically investigated over n Yb/Zr catalysts. The surface acid-base properties of the catalysts could be manipulated by the introduction of Yb₂O₃ into m-ZrO₂. Experimental results showed that the activity of BDO dehydration and THF selectivity were influenced by the acid sites of the catalysts. BTO selectivity was controlled by both acid and basic sites of the catalysts and a higher density ratio of basic / acid sites could increase the BTO selectivity. The in situ DRIFTS study of BDO dehydration clarified that the hydroxyl groups of BDO molecules could interact with acid sites to form several types of butoxides. The β -H of butoxides was abstracted subsequently by basic oxygen anion and this converted the butoxides into an aldehyde species. Finally, the aldehyde species reacted to form BTO and completed the catalytic cycle. These results were in line with the experimental results that acid sites could adsorb the BDO molecules and basic sites facilitate the β -H elimination that enhanced the BTO selectivity. The overall results provide deep insight into the dehydration mechanisms and guidance for the rational design of BDO dehydration catalysts.

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Appendix A. Supplementary material

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