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Heterogeneous CaO-ZrO_2 acid–base bifunctional catalysts for vapor-phase selective dehydration of 1,4-butanediol to 3-buten-1-ol

Qian Zhang, Yin Zhang, Haitao Li, Chunguang Gao, Yongxiang Zhao*

School of Chemistry and Chemical Engineering, Engineering Research Center for Fine Chemicals of Ministry of Education, Shanxi University, Taiyuan, 030006, Shanxi, PR China

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ABSTRACT

A series of acid–base bifunctional CaO-ZrO_2 catalysts was prepared simply by the impregnation method and evaluated for the vapour-phase dehydration of 1,4-butanediol (BDO). The effects of CaO content and calcination temperature on the catalytic properties of the CaO-ZrO_2 catalysts were investigated. It was found that the catalyst with 12.5 wt% CaO and at a calcination temperature of 650 °C exhibited favorable catalytic performance and good stability for the selective dehydration of BDO to 3-buten-1-ol (BTO). The maximum BTO selectivity and BDO conversion reached 68.9% and 94.6%, respectively. The formation of by-product, THF, was markedly suppressed. These catalysts were characterized by N_2 physisorption, XRD, FT-IR spectra, NH_3-TPD and CO_2-TPD. The results indicated that the CaO-ZrO_2 catalysts showed higher basicity density and similar acidity density compared to unmodified ZrO_2 due to the formation of Ca–O–Zr Hetero-linkage by CaO introduction. The catalytic performance depended on the coexistence of acidic and basic sites on the surface of catalysts.

1. Introduction

3-Buten-1-ol (BTO) is a valuable intermediate for the synthesis of heterocyclic drugs, such as multidrug resistant compounds, antiproliferative, antiviral and antitumor agents [1–4]. Currently, there are three strategies for the synthesis of BTO: (1) formaldehyde addition to propylene in aqueous solution [5,6], (2) 3,4-epoxy-1-butene reduction by formic acid with a homogeneous catalyst in tetrahydrofuran (THF) solvent [7,8], and (3) vapor-phase selective dehydration of 1,4-butanediol (BDO) over metal oxide catalysts [9–21]. The routes (1) and (2) encounter various disadvantages: the high-temperature and high-pressure reaction conditions, the low BTO yield, the difficulty in separation, utilization of organic solvent and so on. In contrast, the route (3) offers mild reaction conditions, simple experimental procedure, and more importantly, it is environmental friendly. The dehydration of BDO is thermodynamically feasible in two ways (Scheme 1) [10]. One is a cyclodehydration to THF by eliminating a hydroxyl group to form a carbenium cation followed by nucleophilic substitution. The other is dehydration between terminal hydroxyl and adjacent β-H of BDO to form BTO. And the competitive production, THF, is more preferential to generate rather than BTO. Thus, it is great significance to obtain a catalyst that favors BTO production and suppresses THF production.

The catalysts used for BDO selective dehydration can be divided into two types according to the reaction mechanism. One type is redox oxides such as CeO_2 [9–12] and In_2O_3 [13]. The metal ions which have redox properties can interact with terminal hydroxyl or β-H of BDO and produce corresponding radical intermediates. When hydroxyl radical and β-H radical are simultaneously eliminated from one BDO molecule, a BTO molecule is formed. During above process, these intermediates can further generate a series of by-products including 2-butene-1-ol, 1,3-butadiene, butanol, butyraldehyde, and so on.

Another type is solid acid and base catalysts such as Al_2O_3, MgO [14], ZrO_2 [15,16], rare earth oxides [16–20] etc. During reaction process, the acid sites interact with the terminal hydroxyl group of BDO, while the basic sites interact with the β-H [9,20]. The subsequent elimination of water leads to the formation of BTO. This kind of catalyst has more advantages of less side-reaction, higher activity than that of the redox catalysts. Stao and coworkers studied the catalytic performance of ZrO_2 and alkali metal (Li, Na, K) modified ZrO_2 catalyst [15,16]. Among these catalysts, the pure ZrO_2 showed highest BDO conversion, however, it is selectivity for BTO is low. The introduction of alkali metal can improve BTO selectivity greatly, while the conversion of BDO and the yield of BTO decrease sharply. Further studies revealed that the reason for BDO conversion decline resided in the quick reduction of surface acidic sites

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* Corresponding author. Tel.: +86 351 7011587; fax: +86 351 7011688.
E-mail address: yxzhao@sxu.edu.cn (Y. Zhao).

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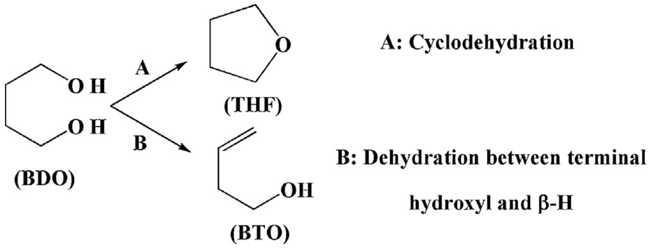

Scheme 1. Reaction scheme of 1,4-butanediol dehydration.

caused by the introduction of alkali metal. The key point for obtaining a high active and selective catalyst for BDO dehydration to BTO is how to prepare an acid–base bifunctional catalyst.

Acid–base bifunctional catalyst is a popular concept quoted from enzyme catalysis reactions that contain two types of active centers of acid and base in catalytic systems [22–27]. These catalysts may act in a cooperative way to provide superior reactivity and selectivity than monofunctional materials. The acid–base bifunctional catalysts can be prepared by the grafting method, the co-condensation method and the formation of an organosilica material [28]. However, there are several problems with these routes due to the use of highly toxic raw materials, high process cost, and complicated synthetic procedures to be disposed of.

Many references suggested that the formation of M_1–O–M_2 hetero-linkages in binary complex oxides can lead to the uneven distribution of charges and subsequently generate new acid sites. Our earlier study has also reported that the formation of Zr–O–Si hetero-linkages generated a large number of acidic sites over ZrO_2–SiO_2 mixed oxide surface [29,30]. Compared with alkali metal promoters, the alkaline–earth metal ions especially for Ca^{2+} can enter into the ZrO_2 crystal lattice (Zr^{4+} ions are substituted by Ca^{2+} ions) to form Ca–O–Zr hetero-linkages easily that is very likely to generate new acidic sites. Herein, we developed a series of CaO-ZrO_2 catalyst and investigated their performance in BDO dehydration. On basis of characterizations, the probable adsorption model of BDO and active centers over the acid–base bifunctional catalysts were also discussed in details.

2. Experimental

2.1. Catalyst preparation

ZrO_2 aerogel support was prepared via heating alcohol–aqueous solutions followed by supercritical fluid drying method that we had reported previously [31]. The support was calcined at 400 °C for 80 min before impregnation. An appropriate amount of calcium nitrate was impregnated to the above-mentioned support, and then the samples were dried at 120 °C over night and calcined at an appropriate temperature for 3 h to obtain the CaO-ZrO_2 catalysts. The catalysts are designated as *X*CZ-*T*, in which *X* stands for CaO content calculated by $X_{CaO} = m_{CaO}/(m_{CaO} + m_{ZrO_2})$ and *T* is the calcination temperature.

2.2. Catalytic reaction

The dehydration of BDO was carried out in a fixed-bed flow reactor. Before the reaction, 2.0 g catalyst (20–40 mesh) was preheated in the N_2 flow at 350 °C for 1 h. At this temperature, the BDO gas was fed into the reactor at a flow rate of 2.0 mL h^{-1} together with a N_2 (carrier gas) flow of 30 mL min^{-1}. In the poisoning experiment, CO_2 or 10%NH_3–N_2 were used as carrier gas. A flow rate was also 30 mL min^{-1}. Liquid effluent was collected periodically and analyzed by gas chromatography (Agilent-7890A) using a 30 m capillary column (AT.OV-1701) and a flame ionization detector (FID). The catalytic performance was evaluated using average of the initial 2–9 h.

2.3. Characterization

N_2 physisorption measurement was performed on a Micromeritics ASAP 2020 instrument at −196 °C. Before the measurement, the samples were degassed at 100 °C for 3 h. The specific surface area was calculated by the BET method.

X-ray powder diffraction (XRD) analysis was performed using a Bruker D8 Advance X-ray diffractometer with a Cu Kα radiation at 40 kV and 40 mA. Scanning was carried out over a 2θ ranging from 20° to 70° in increments of 0.05°.

The FT-IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with a resolution of 4 cm^{-1}, using the KBr diluting technique for the analysis of the samples. The spectra (100 scans) were recorded in the 4000–400 cm^{-1} wavenumber range.

Temperature-programmed desorption (TPD) profiles of NH_3 and CO_2 were measured to estimate the acidity and the basicity of the catalysts, respectively. The samples (100 mg, 40–60 mesh) were pretreated at 500 °C in a flow of helium (99.999%) at a rate of 60 mL min^{-1} for 60 min and saturated with a pure NH_3 or CO_2 flow after cooling to 100 °C. These pretreated samples were purged under helium atmosphere at 100 °C to remove physisorbed NH_3 or CO_2 until the baseline was stable, then these samples were heated from 50 °C to 600 °C at a rate of 10 °C min^{-1} in the helium flow. The amount of NH_3 or CO_2 evolved from the sample was determined by thermal conductivity detector (TCD). The quantitative analysis of the acid/basic amount was based on NH_3/CO_2-TPD profiles and the acid/base density were expressed as the number of NH_3/CO_2 molecules per area of catalyst (NH_3 nm^{-2}, CO_2 nm^{-2}).

3. Results

3.1. Dehydration of BDO over CaO-ZrO_2 catalysts

3.1.1. Effects of CaO content

Distribution of products in the dehydration of BDO over *X*CZ-500 catalysts is listed in Table 1. It is found that the main products are BTO, THF and γ-butyrolactone (GBL). Besides, dozens of by-products are detected by gas chromatography, such as 2-buten-1-ol, 1-butanol, and butanal, however, the selectivity of each by-product is lower than 1%. Thus the main products of BTO, THF and GBL are discussed in this dehydration reaction as references. Over 0CZ-500 (unmodified ZrO_2), the conversion of BDO is nearly to 100%, but THF is dominantly produced (the selectivity is 79.6%). With CaO content lower than 12.5 wt%, the BDO conversion is over 90% and the BTO selectivity increases from 18.1% of unmodified ZrO_2 to 63.8% of ZrO_2 modified with 12.5 wt% CaO. When CaO content further increases, the BDO conversion decreases and the BTO selectivity remains at a high level. For the by-products of THF and GBL, the selectivity is monotonously decreasing and gradually increasing separately with increasing the CaO content.

3.1.2. Effects of calcination temperature

The catalyst with 12.5 wt% CaO was chosen as the typical sample to investigate the effect of calcination temperature on the catalytic performance. The corresponding results are presented in Table 1. From Table 1, the conversion of BDO exceeds 90% over the catalysts calcined at 500–650 °C, and then decreases with a further rise in temperature. Similarly, the selectivity to BTO initially increases slowly, until a maximum (68.9%) is reached at 650 °C, and then a decrease follows. And the maximum yield of BTO is 65.2% when calcination temperature is 650 °C. For this dehydration reaction, the group of S. Sato has systematically done fundamental researches. The obtained maximum yield of BTO is 64.8% over $Sc_{1.5}Yb_{0.5}O_3$ at

Table 1
Specific surface area, acid–base properties, and catalytic performance of CaO-ZrO_2 catalysts with different CaO content and calcined at different temperature.

Catalyst (XCZ-T)[a]	S_{BET} ($m^2 g^{-1}$)	Acidity[b] (μmol g^{-1})	Basicity[b] (μmol g^{-1})	Conversion[c] (%)	Selectivity[c] (%)			
					BTO	THF	GBL	Others[d]
0CZ-500	115	261	263	99.1	18.1	79.6	1.1	1.2
2CZ-500	137	273	348	92.6	23.6	72.1	1.8	2.5
5CZ-500	130	268	404	91.8	36.1	55.3	3.6	5.0
10CZ-500	117	245	448	91.5	57.3	25.8	4.7	12.2
12.5CZ-500	92	248	455	90.5	63.8	13.6	5.9	16.7
15CZ-500	82	203	371	82.7	58.6	15.2	6.9	19.3
20CZ-500	70	138	306	70.9	55.3	16.3	8.1	20.3
30CZ-500	59	106	255	58.8	51.2	18.9	10.3	19.6
12.5CZ-600	85	235	480	92.3	67.6	11.1	6.1	15.2
12.5CZ-650	82	251	486	94.6	68.9	9.8	6.3	15
12.5CZ-700	76	138	235	75.6	49.1	15.6	3.2	32.1
12.5CZ-800	73	85	155	61.3	43.6	21.7	3.0	31.7

[a] X stands for the CaO content and T is the calcination temperature. Catalyst 2.0 g, 350 °C.
[b] Acid and basic values are derived from NH_3-TPD and CO_2-TPD analysis, which are expressed as the mol number of NH_3 or CO_2 molecules per gram of catalyst.
[c] Average conversion and selection are for initial 2–9 h.
[d] Others include 2-buten-1-ol, 1-butanol, butanal, etc.

350 °C [19], suggesting that the CaO-ZrO_2 catalysts have certain practical value for further research. In addition, the selectivity to the competitive products of THF and GBL changes within the range of 9.8% to 21.7% and decreases from about 6% to 3.0% with the calcination temperature.

3.1.3. Stability of 12.5CZ-650 catalyst to BDO dehydration

In view of optimum activity of 12.5CZ-650 catalyst, we evaluate its stability in a long-time test (300 h). The dehydration activity and BTO selectivity are shown in Fig. 1. Observing from Fig. 1, the 12.5CZ-650 catalyst exhibits high performance and good stability within 300 h. The BDO conversion and BTO selectivity maintain a high level for a long time. Only 200 h later, the selectivity to BTO decreases slightly. Meanwhile, the selectivity to the by-products of THF and GBL is limited to low levels (the average selectivity is 9.28% and 5.87%, respectively).

3.2. Characterization of CaO-ZrO_2 catalysts

The BET surface areas (S_{BET}) of the CaO-ZrO_2 catalysts are shown in Table 1. From Table 1, with the introduction of CaO, the S_{BET} of ZrO_2 catalysts modified by low CaO content (10 wt%) is higher than that of the unmodified ZrO_2, while the S_{BET} decreases obviously with the elevated CaO content (from 137 $m^2 g^{-1}$ to 59 $m^2 g^{-1}$) for all the CaO–modified ZrO_2 catalysts. It is probable that the introduction of CaO can improve the anti-sintering ability of the catalyst and inhibit the rapid decrease of surface area caused by the sintering of ZrO_2 from surface diffusion [32–34]. The reason of the fall in the S_{BET} is probable that the excessive CaO begins to aggregate on the ZrO_2 surface. Also in Table 1, the S_{BET} of 12.5CZ-T catalysts decreases from 92 $m^2 g^{-1}$ to 73 $m^2 g^{-1}$ with the calcination temperature increasing from 500 °C to 800 °C.

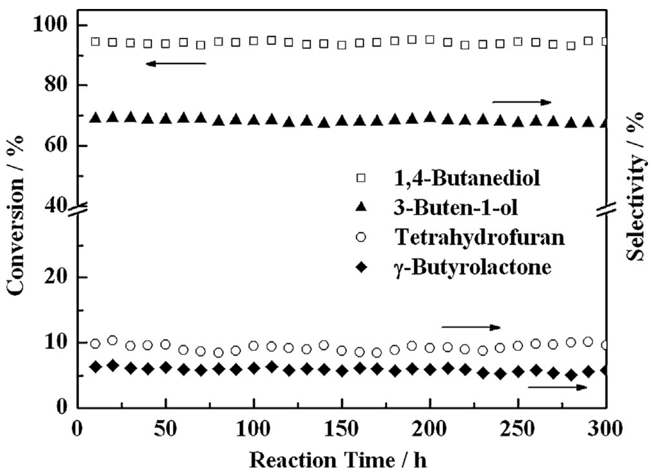

Fig. 1. The long-time test of BDO dehydration over 12.5CZ-650 catalyst (catalyst 2.0 g, 350 °C).

From the XRD patterns of XCZ-500 catalysts shown in Fig. 2a, it is clear that monoclinic and tetragonal phase coexist in ZrO_2,

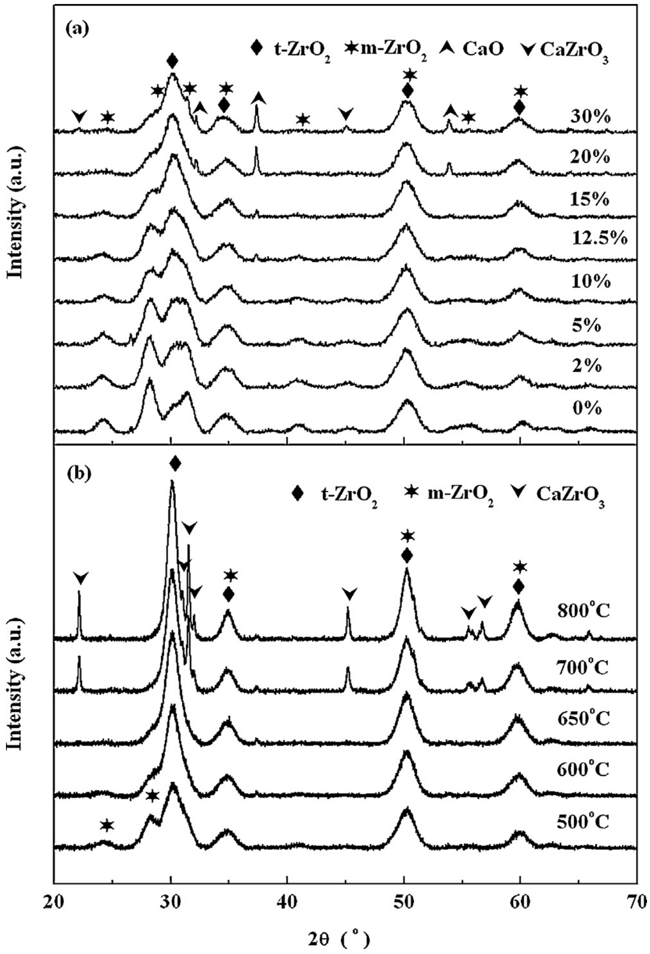

Fig. 2. XRD patterns of CaO-ZrO_2 catalysts with different CaO content (a) and calcined at different temperature (b).

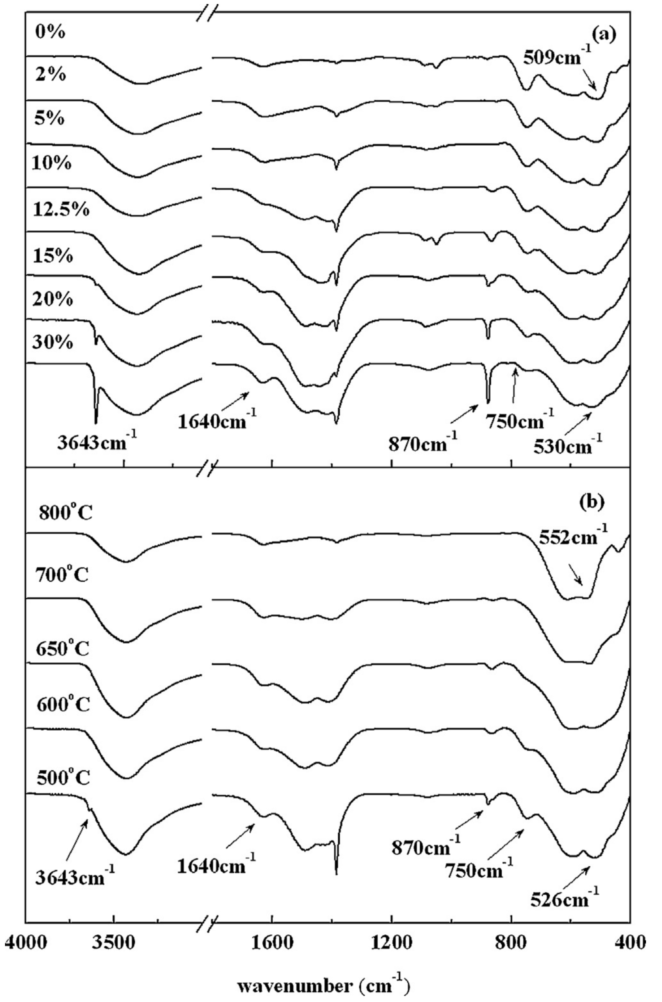

Fig. 3. FT-IR spectra of CaO-ZrO_2 catalysts with different CaO content (a) and calcined at different temperature (b).

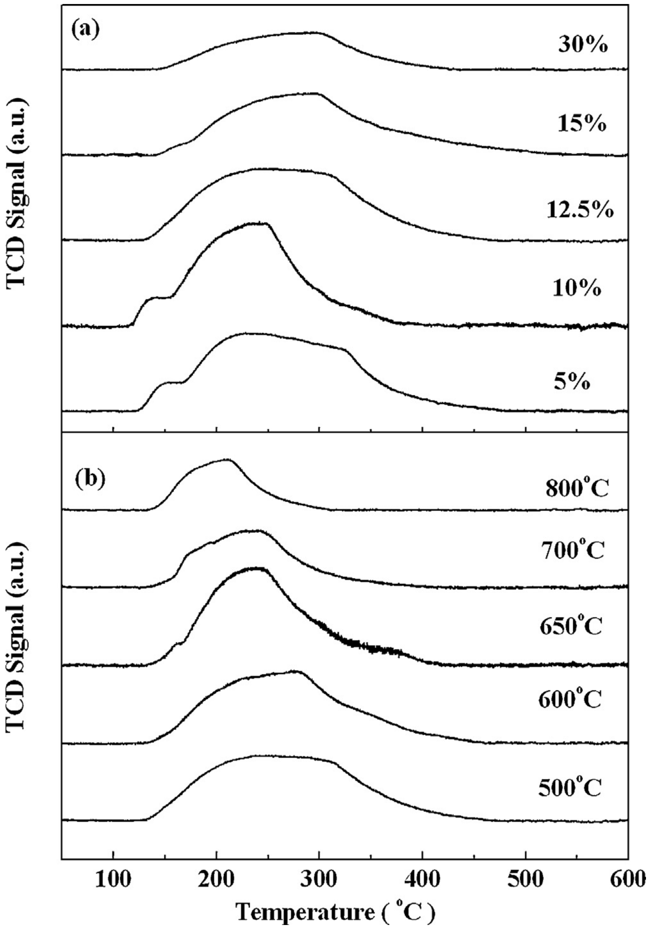

Fig. 4. NH_3-TPD profiles of CaO-ZrO_2 catalysts with different CaO content and at different calcination temperature. (a) NH_3-TPD profiles of *X*CZ-500 (b) NH_3-TPD of 12.5CZ-*T*.

while the monoclinic peaks are less intense and the tetragonal peaks become more intense with the introduction of CaO. This is explained that more Ca^{2+} ions enter into the ZrO_2 crystal lattice (Zr^{4+} ions are substituted by Ca^{2+} ions partly and form Ca–O–Zr hetero-linkages). Moreover, the presence of Ca^{2+} contributes to the stabilization of the tetragonal phase. It can also be seen that the characteristic diffraction peaks of CaO appear and the intensity increase when CaO content is higher than 12.5 wt%. This suggests that the excessive CaO begins to aggregate on the ZrO_2 surface. For 30CZ-500, a characteristic diffraction peak of $CaZrO_3$ is identified. The formation of this new phase indicates that CaO reacted with ZrO_2 and form a new stable Ca species [35]. The XRD patterns of 12.5CZ-*T* catalysts are shown in Fig. 2b. With the increase of calcination temperature, the monoclinic ZrO_2 transforms to tetragonal phase gradually and disappears at 12.5CZ-650. And the diffraction peaks of $CaZrO_3$ are observed as the calcination temperature exceeds 700 °C. This suggests that more Ca–O–Zr hetero-linkages formation can explain the change of ZrO_2 crystal phase and the stable specie of $CaZrO_3$ appears at the higher temperature.

The FT-IR spectra of *X*CZ-500 catalysts are gathered in Fig. 3a. The broad absorption bands at around 509 cm^{-1} and 750 cm^{-1} are attributed to the Zr—O vibration absorption [36,37]. With CaO content increasing, the band at 509 cm^{-1} shifts gradually to a high wavenumber (from 509 cm^{-1} to 530 cm^{-1}). Correspondingly, the intensity of the band at 750 cm^{-1} decreases by degrees. The changes of these broad peaks (509 cm^{-1} and 750 cm^{-1}) are speculated to be caused by two factors. One is that Zr^{4+} ions are substituted by Ca^{2+} ions partly to formed Ca–O–Zr hetero-linkages which weaken the covalency of Zr—O bond. The other is attributed to the phase transition from monoclinic ZrO_2 to tetragonal [36]. The absorption bands at 3643 cm^{-1}, 1640 cm^{-1} and 870 cm^{-1}, assigned to —OH stretching vibrations, —OH bending vibration and vibration of water absorbed on the surface respectively, appear in the high CaO content samples, which is similar with the pure CaO phase. This suggests that free CaO begins to aggregate and form crystal phase [37]. This is consistent with the XRD results obtained above. Fig. 3b shows the FT-IR spectra of 12.5CZ-*T* catalysts. As the calcination temperature rising, the bands of Zr—O (750 cm^{-1}) and —OH (870 $cm^{-1}$and 1640 cm^{-1}) vibration absorption decrease and then disappear, while the absorption band at around 526 cm^{-1} (Zr—O vibration absorption) shifts toward a high wavenumber gradually. These results indicate that the high calcination temperature make more Zr^{4+} ions be substituted by Ca^{2+} ions and form Ca–O–Zr hetero-linkages or stable species $CaZrO_3$.

NH_3-TPD and CO_2-TPD measurements of the CaO-ZrO_2 catalysts were carried out in order to evaluate their acidity and basicity, respectively. Figs. 4 and 5 show the TPD profiles of samples and the quantitative analysis of NH_3 or CO_2 desorbed is listed in Table 1. From Table 1, the total amount of acidic sites is almost same when CaO content $\leq$12.5% or $T \leq 650$ °C. That is to say, the amount of acidic sites changes little with the introduction of CaO. With the further increase in CaO content or calcination temperature, the total amount of acidic sites decreases significantly. Also in Table 1, the

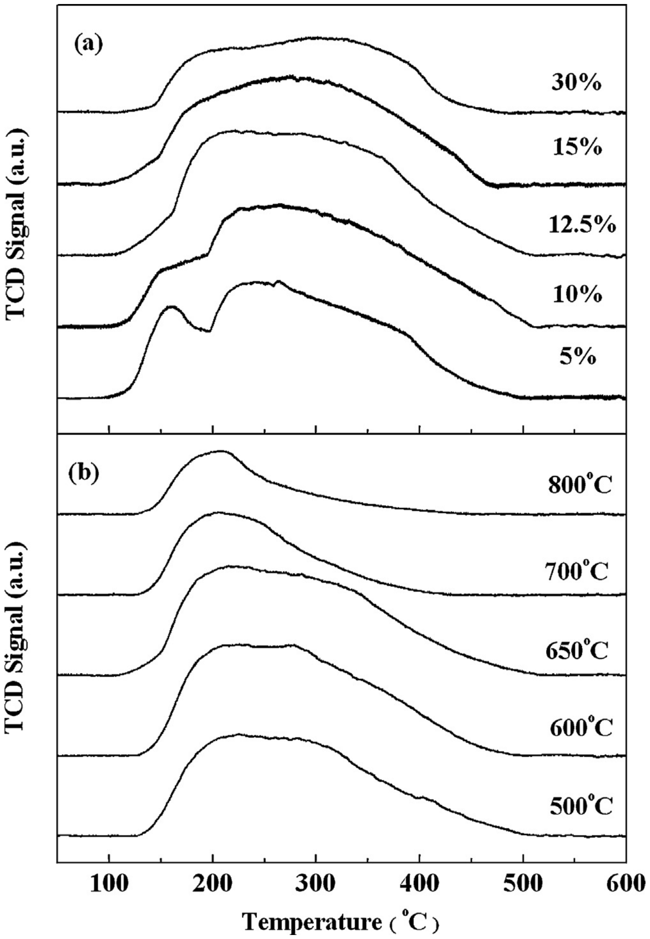

Fig. 5. CO_2-TPD profiles of CaO-ZrO_2 catalysts with different CaO content and at different calcination temperature. CO_2-TPD profiles of *X*CZ-500 (b) CO_2-TPD profiles of 12.5CZ-*T*.

total amount of basic sites increases initially and then a decrease follows with elevated CaO content. Similarly, the amount of basic sites increases gradually as the calcination temperature is lower than 650 °C, and then decreases rapidly at higher temperatures. The maximum amount of acidic sites and basic sites are 273 $\mu mol\,g^{-1}$ and 486 $\mu mol\,g^{-1}$.

4. Discussion

4.1. Correlations between structure and acid–base properties

The formation of M_1—O—M_2 hetero-linkages in binary complex oxides generates the uneven distribution of charges and subsequently generates new acid sites. Our earlier study has also reported that the formation of Zr–O–Si hetero-linkages generated a large number of acidic sites over ZrO_2–SiO_2 mixed oxide surface [29,30]. From XRD and FT-IR results shown above, when being introduced to ZrO_2 catalyst, Ca^{2+} ions enter into the ZrO_2 crystal lattice to form Ca–O–Zr hetero-linkages. This structure leads to the uneven distribution of charges and makes the catalyst generate new acidic sites, that is the reason why the total amount of acidic sites have little change with CaO content lower than 12.5 wt% or calcination temperature lower than 650 °C. However, the amount of acidic sites reduces obviously due to the aggregation of CaO and generation of $CaZrO_3$ at the high CaO content or calcination temperature. This can be interpreted as the aggregation of CaO and the generation of $CaZrO_3$, which is ascertained by XRD and FT-IR results.

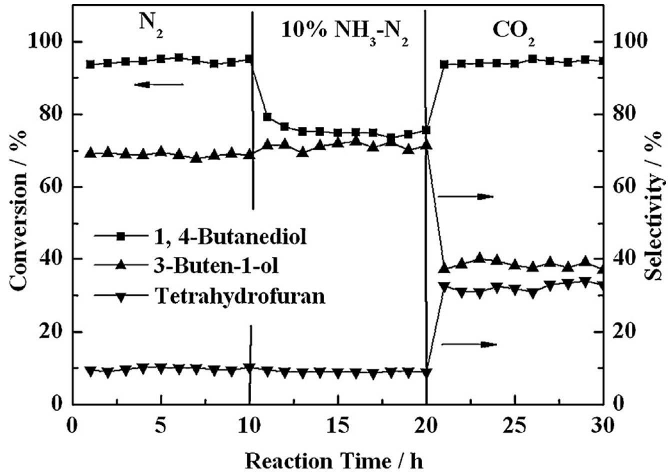

Fig. 6. BDO conversion and selectivity of BDO dehydration over 12.5CZ-650 catalyst in different carrier gases (catalyst 2.0 g, 350 °C).

As an acid–base bifunctional catalyst, introduction of appropriate CaO on the ZrO_2 surface can increase the basic sites, while the excess of CaO or generation of $CaZrO_3$ may decline the amount of basic sites. The amount of basic sites increases gradually as the calcination temperature is lower than 650 °C, and then decreases rapidly at higher temperatures. The results indicate that generation of $CaZrO_3$ may decline the amount of basic sites. In summary, For CaO-ZrO_2 catalyst, Ca^{2+} incorporates into the ZrO_2 crystal lattice to form Ca–O–Zr hetero-linkages, and these offer CaO-ZrO_2 catalysts not only new acidic sites but also higher basicity.

4.2. Relationship between acid–base properties and catalytic activity

To understand the relationship between acid–base properties and catalytic activity, we have demonstrated in the poisoning experiments of 12.5CZ-650 catalyst and the unmodified ZrO_2. The variations of BDO conversion and selectivity to BTO or THF are entirely consistent, so we discuss the results taking the former catalyst for example. Fig. 6 summarizes conversion and selectivity in the dehydration of BDO over 12.5CZ-650 catalyst with different carrier gases. Either 10%NH_3-N_2 or CO_2 instead of N_2 was used as carrier gases. In acidic CO_2 flow instead of N_2, the formation rate of BTO was markedly suppressed and the selectivity of THF, as competitive product, increased correspondingly. The results of comparison experiments on THF selectivity in CO_2 gas without catalyst showed that the BDO conversion was very low and no product was detected. The acidic CO_2 molecules react with the basic sites on the catalyst surface. This clearly indicates that the basic sites play an important role in the formation of BTO. Comparing the poisoning experiments of Er_2O_3 and Yb_2O_3 [9,20,21,38], the conversion of BDO reaches nearly 100% due to the rich acidic sites on unmodified ZrO_2 surface. Thus, the conversion of BDO decreases in basic 10%NH_3–N_2 flow, while the selectivity to BTO has hardly changed due to the constant basic sites. The poisoning experiments indicate that both basic and acidic sites participate in the formation of BTO via the acid–base tridentate coordination mechanism. The results strongly suggest that the acidic and basic sites assure the conversion of BDO and the selectivity to BTO, separately. In addition, a marked competition exists between the products of BTO and THF.

In this study, through activity evaluation and characterization of the catalysts, it is found that the acid–base properties of the CaO-ZrO_2 catalysts have significant influence in the dehydration of BDO. Fig. 7 shows the relationship between acid–base density and catalytic performance. From Fig. 7, the surface acid–base property

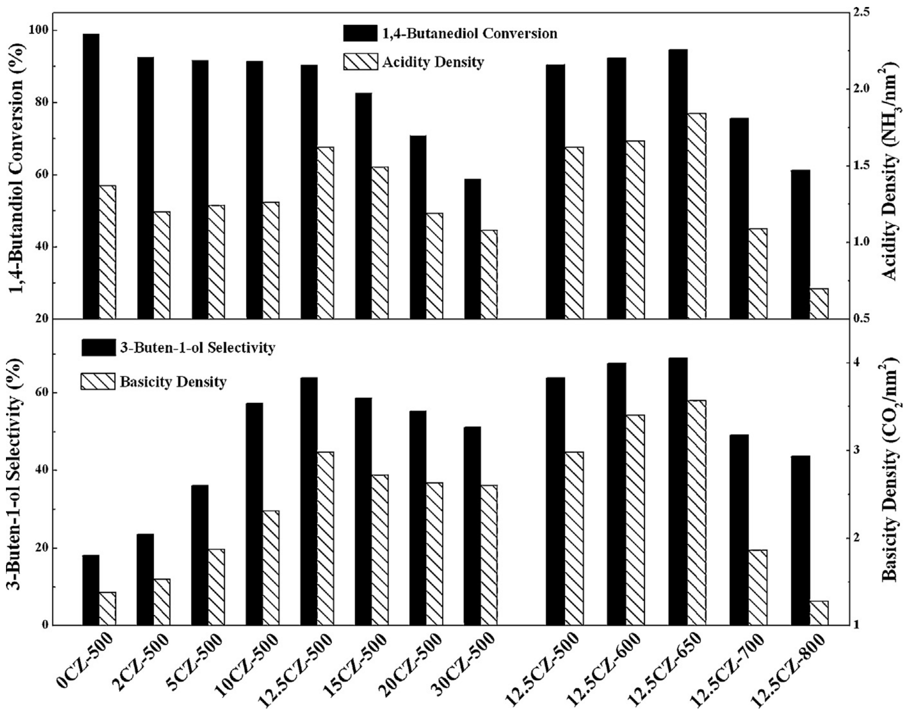

Fig. 7. Relationship between acid–base properties and catalytic performance.

exerted great influence on the catalytic performance and BTO selectivity. The surface acid densities of unmodified ZrO_2, 12.5CZ-500, 12.5CZ-600 and 12.5CZ-650 are 1.37 NH_3/nm^2, 1.62 NH_3/nm^2, 1.66 NH_3/nm^2, and 1.84 NH_3/nm^2, respectively. They exhibited high BDO conversion due to the rich acidic sites on their surface. With the decrease of acid density, BDO conversion decreases accordingly (from 99.1% to 58.8%), thus it is clear that BDO conversion is closely related to acid density of catalysts. Given that acidic sites act as an anchoring site for the OH group to activate BDO [9,20], it follows that more acidic sites can activate more BDO molecules to give higher BDO conversion. Fig. 7 also shows the relationship of BTO selectivity and surface base density of the catalysts. It shows clearly that greater base density led to increase BTO selectivity. The basic sites, probably composed of surface O^{2-} anions [9,20], are thought to interact with the β-H of BDO and thereby contribute to the formation of BTO. 10CZ-500, 12.5CZ-600 and 12.5CZ-650 showed high BTO selectivity, which is attributed to the abundant basic site. The maximum base density was 3.57 CO_2/nm^2 for 12.5CZ-650, and the BTO selectivity reached 68.9%.

In the vapor-phase selective dehydration of BDO, the terminal hydroxyl group and the adjacent β-H of BDO interact with acidic sites and basic sites, respectively, before the terminal hydroxyl group and β-H are eliminated to form BTO [9,20]. This probable adsorption structure was provided by S. Sato group, which is verified in our systems. In detail, every active center forming BTO is composed of two acidic sites and one basic site, while the active center includes acidic sites only for the competitive product of THF. Thus the rich content of acidic and basic sites ensures the excellent performance in BDO dehydration to BTO. In present study, with the addition of CaO to ZrO_2, the amount of basic sites initially increases obviously and then a decrease follows (Table 1). Correspondingly, the same tendency of BTO selectivity and the reverse tendency of THF selectivity are also observed. Analogously, with the increment of the calcination temperature ($T > 650\,^{\circ}C$), the BDO conversion and the BTO selectivity decrease obviously due to the decrease of acid–base active center. It is reasonable that acid–base concerted site is favorable to the dehydration of BDO to BTO and acidic sites can cyclize BDO to THF.

5. Conclusions

In summary, we developed a simple preparation process to synthesize acid–base bifunctional catalyst for the vapor-phase dehydration of BDO to BTO. The catalysts exhibited good stability, high BDO conversion and BTO selectivity. The surface acid–base properties of the catalysts were improved by the introduction of appropriate CaO into ZrO_2. Increased basic sites were accompanied by the generation of new acidic sites due to the formation of Ca–O–Zr hetero-linkages. BTO was formed on acid–base concerted sites of CaO-ZrO_2 catalysts in activating the terminal hydroxyl group and adjacent β-H of BDO. Our present research provides a novel potential way toward adjusting the amount of acidic and basic sites on the modified ZrO_2 catalysts.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2013.06.020.

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