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Article

Vapor-phase selective dehydration of 1,4-butanediol to 3-buten-1-ol over ZrO_2 catalysts modified with alkaline earth metal oxides

ZHANG Qian, ZHANG Yin, LI Haitao, ZHAO Yongxiang*, MA Meng, YU Yu

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

ARTICLE INFO

Article history:

Received 28 November 2012

Accepted 24 January 2013

Published 20 June 2013

Keywords:

1,4-Butanediol

3-Buten-1-ol

Alkaline earth metal oxide

Zirconia

Acid-base concerted site

ABSTRACT

Modified ZrO_2 catalysts were prepared by doping with alkaline earth metal oxides (CaO, SrO, or BaO) in a wet impregnation method. The catalysts were characterized by N_2 physisorption, X-ray diffraction, and temperature-programmed desorption (TPD) with NH_3 and CO_2 . Their catalytic performance in the vapor-phase selective dehydration of 1,4-butanediol (BDO) to 3-buten-1-ol (BTO) was investigated. The results showed that the alkaline earth metal can change the acid–base properties on the catalyst surface and thus affect BDO conversion and BTO product selectivity. For ZrO_2 catalyst modified by CaO, Ca^{2+} entered the ZrO_2 crystal lattice and formed Ca–O–Zr hetero-linkages. These allowed the CaO/ ZrO_2 catalyst to maintain a high acid density and generate a large number of basic sites when compared with unmodified ZrO_2 . In contrast, SrO and BaO reacted with ZrO_2 to generate the corresponding zirconates, which resulted in decreased acid density on the catalyst surface. Of the catalysts tested, CaO/ ZrO_2 showed the best catalytic performance. The highest yield of BTO was 60.5% and was achieved at 350 °C over CaO/ ZrO_2 catalyst. The key point for highly selective dehydration of BDO to BTO resided in the synergistic effect between acid and base sites on the catalyst surface.

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1. Introduction

3-Buten-1-ol (BTO) is a valuable chemical that is widely used in food flavoring, agricultural products, and especially in the medical field [1–4]. Currently, methods used for BTO synthesis include formaldehyde addition to propylene [5,6], reduction of 3,4-epoxy-1-butene by formic acid [7,8], and vapor-phase selective dehydration of 1,4-butanediol (BDO) [9–20]. Among them, the third of these methods, when using a solid oxide as catalyst, offers some advantages that include mild reaction conditions, a simple experimental procedure, and environmental friendliness. However, this approach has two favorable thermodynamic pathways. One is the intramolecular cyclodehydration of BDO to give tetrahydrofuran (THF), which

in this context is a byproduct, while the other is the dehydration of BDO involving the terminal hydroxyl group and a β -H atom on the adjacent carbon atom (shown in Scheme 1) [9]. Thus, it is a challenging task to obtain a catalyst that favors BTO production by dehydration of BDO. To increase BTO yield by this reaction pathway, the general requirement is for the design and preparation of appropriate catalysts with particular attention paid to regulation and control of the structure, texture, and surface properties of the materials.

The catalysts involved in the selective dehydration of BDO are mainly metal oxide catalysts, and are generally of two different types according to the reaction mechanism. One type exerts its catalytic effect according to its redox properties, with examples being CeO_2 [9–11] and In_2O_3 [12]. The redox proper-

* Corresponding author. Tel: +86-351-7011587; Fax: +86-351-7011688; E-mail: yxzhao@sxu.edu.cn

DOI: 10.1016/S1872-2067(12)60525-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 6, June 2013

Scheme 1. 1,4-Butanediol dehydration to tetrahydrofuran and 3-buten-1-ol.

ties of these metal ions are expressed at the catalyst surface, such that they can interact with the terminal hydroxyl group and adjacent β -H of BDO. The hydrogen and hydroxyl free radicals are then eliminated to form a C=C bond, thus producing BTO. Accompanying this catalytic process, the hydrogen free radical or hydroxyl free radical can be eliminated to generate many intermediates, which can further generate a series of byproducts including 2-butene-1-ol, 1,3-butadiene, butyraldehyde, butanol, and so on.

The second main catalyst type is solid acid and base catalysts (e.g., Al_2O_3 , MgO [15], ZrO_2 [16], rare earth oxides [18]), in which both acidic and basic sites are active centers for BDO dehydration. The acid sites interact with the terminal hydroxyl group of BDO, while the basic sites interact with the β -H. The subsequent elimination of water leads to the formation of BTO. The solid acid and base catalysts have advantages over the redox catalysts that include few side reactions, high activity, and high selectivity toward the desired product.

ZrO_2 is well known as a classical catalyst with both acidic and basic sites [21,22], and has used to facilitate BDO dehydration to BTO. Stao and coworkers reported the use of ZrO_2 catalyst for BDO dehydration and investigated the effect of introducing alkali metals (Li, Na, K) on the catalytic performance [15,16,19]. It was found that pure ZrO_2 showed the highest BDO conversion, but gave the lowest BTO selectivity (BTO yield of about 40%). The introduction of alkali metal improved BTO selectivity greatly, while the conversion of BDO and the yield of BTO decreased significantly. From the experimental data, it was found that the acidic sites on the surface of alkali-metal-modified ZrO_2 catalysts were reduced rapidly or disappeared, resulting in a decrease of BDO activation ability.

Many studies have suggested that the formation of $\text{M}_1\text{-O-M}_2$ hetero-linkages in binary complex oxides can lead to an uneven distribution of charge and generate new acidic sites. In our previous study on the preparation and properties of $\text{ZrO}_2\text{-SiO}_2$ complex oxide, we found that the acid properties of complex oxides influence the formation of Zr-O-Si hetero-linkages [23,24]. As a result, the acid properties and catalytic activity are significantly improved. Based on our understanding of the acid-base reaction mechanism and our previous work, we prepared ZrO_2 catalysts doped with alkaline earth metal oxide (CaO, SrO, or BaO) and investigated their catalytic performance in the vapor-phase selective dehydration of BDO to BTO.

2. Experimental

2.1. Catalyst preparation

ZrO_2 aerogel was prepared by heating alcohol-aqueous solutions, followed by supercritical fluid drying as we reported previously [25]. The ZrO_2 aerogel was calcined at 400 °C for 80 min before impregnation. The specific surface area (A_{BET}) of the ZrO_2 aerogel was 185 m^2/g . An appropriate amount of $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$) was added to the ZrO_2 aerogel, which was then dried at 120 °C for 12 h and calcined at 650 °C for 3 h to give the MO/ZrO_2 catalyst. The MO content of catalysts prepared in this way was 10% (w/w).

2.2. Catalytic reaction

Dehydration of BDO was conducted in a fixed-bed flow reactor. Before the reaction, 2.0 g of catalyst (20–40 mesh) was preheated under N_2 flow at 350 °C for 1 h. Then the BDO gas was fed into the reactor at a flow rate of 2.0 ml/h together with N_2 carrier gas at a flow rate of 30 ml/min. 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).

2.3. Characterization

Measurement of N_2 physisorption was performed on a Micromeritics ASAP 2020 instrument at -196 °C. Before the measurement, samples were degassed at 150 °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 $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA. Scanning was carried out over a 2θ range of 20° – 70° in increments of $6^\circ/\text{min}$.

Temperature-programmed desorption (TPD) profiles of NH_3 and CO_2 were measured to estimate the acidity and basicity, respectively, of the catalysts. The samples (100 mg) were pretreated at 500 °C in a flow of helium (99.999%) at a rate of 60 ml/min for 1 h, and then were saturated with 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, after which the samples were heated from 50 to 600 °C at a rate of 10 °C/min under helium flow. The amount of NH_3 or CO_2 evolved from the sample was recorded by a thermal conductivity detector (TCD). The quantitative analysis of the acid/base amount is based on NH_3/CO_2 -TPD profiles. The acid/base densities are expressed as the number of NH_3/CO_2 molecules per area of catalyst (NH_3/nm^2 , CO_2/nm^2).

3. Results and discussion

3.1. Dehydration of 1,4-butanediol over MO/ZrO_2 catalysts

Table 1 lists the distribution of products in the dehydration of 1,4-butanediol over MO/ZrO_2 catalysts. The major products

Table 1Specific surface area, acid-base properties, and catalytic performance of MO/ZrO₂ catalysts.

Catalyst ^a	Conversion ^b (%)	Selectivity ^b (%)		BTO yield (%)	<i>A</i> _{BET} (m ² /g)	Acidity ^c		Basicity ^c	
		BTO	THF			(μmol/g)	(NH ₃ /nm ²)	(μmol/g)	(CO ₂ /nm ²)
ZrO ₂	100	26.9	51.6	26.9	81	338	2.53	154	1.15
CaO/ZrO ₂	92.6	65.4	11.3	60.5	91	295	1.96	496	3.29
SrO/ZrO ₂	84.1	45.1	33.7	37.9	73	127	1.04	211	1.73
BaO/ZrO ₂	74.3	35.9	40.8	26.6	71	72	0.61	164	1.39

^a Catalyst 2.0 g, 350 °C.^b Average conversion and selectivity are for initial 2–9 h.^c Derived from NH₃-TPD/CO₂-TPD analysis, which are expressed as the mol number of NH₃/CO₂ molecules per gram of catalyst (μmol/g) and the number of NH₃/CO₂ molecules per square nanometer of area (NH₃/nm², CO₂/nm²).

were BTO and THF. The use of alkaline earth metal oxides in the catalysts had an obvious influence on BDO dehydration. Over unmodified ZrO₂, the conversion of BDO was 100%. When the catalysts were doped with alkaline earth metal oxides, the BDO conversion decreased in the order of Ca > Sr > Ba (BaO/ZrO₂ the lowest at 74.3%), while the BTO selectivity increased. Among the catalysts used, CaO/ZrO₂ showed the highest selectivity (65.4%) and yield (60.5%) of BTO.

3.2. Characterization of MO/ZrO₂ catalysts

3.2.1. Surface area of MO/ZrO₂ catalysts

Table 1 also lists the *A*_{BET} values of the MO/ZrO₂ catalysts. For unmodified ZrO₂ calcined at 650 °C, *A*_{BET} was 81 m²/g, but this increased to 91 m²/g for CaO/ZrO. It is considered likely that the CaO improved the antisintering ability of the catalyst and thereby inhibited rapid decrease of surface area caused by sintering of ZrO₂ from surface diffusion [26,27]. Unlike the CaO/ZrO₂ catalyst, the *A*_{BET} values of SrO/ZrO₂ (73 m²/g) and BaO/ZrO₂ (71 m²/g) were slightly lower than that of unmodified ZrO₂.

3.2.2. Structure of MO/ZrO₂ catalysts

The XRD patterns of the MO/ZrO₂ catalysts are shown in Fig. 1. The diffraction peak of 2θ = 30.2° was assigned to tetragonal ZrO₂(011) and the peaks at 2θ = 24.1°, 28.2°, and 31.5° were assigned to the (110), (-111), and (111) faces of monoclinic ZrO₂. As shown in Fig. 1, monoclinic ZrO₂ was the dominant phase together with a small amount of tetragonal ZrO₂ in un-

modified ZrO₂, while tetragonal ZrO₂ was the dominant phase in CaO/ZrO₂. The characteristic diffraction peaks of other Ca species (such as CaO and CaZrO₃) were not observed. For SrO/ZrO₂, the tetragonal peaks became more intense, and the intensities were similar to monoclinic ZrO₂. The characteristic diffraction peaks at 2θ = 30.8°, 44.1°, and 54.7° were attributed to SrZrO₃. In contrast to CaO/ZrO₂ and SrO/ZrO₂, the phases of BaO/ZrO₂ showed no significant change with the introduction of BaO, but a diffraction peak for BaZrO₃ was identified at 2θ = 30.2°.

Other researchers have shown that the second catalyst component can enter into the ZrO₂ crystal lattice (Zr⁴⁺ ions are substituted by other ions) to form M–O–Zr hetero-linkages [28–31]. In such cases, an oxygen vacancy is generated around Zr⁴⁺ to maintain electrical neutrality. The oxygen vacancy can reduce the repulsive force between local O²⁻ and create high distortion in the coordination sphere. As a result, the presence of the M ion contributes to the stabilization of the tetragonal phase. According to the XRD results, Ca²⁺ was incorporated into the ZrO₂ crystal lattice in the form of Ca–O–Zr hetero-linkages in the CaO/ZrO₂ catalyst. A small amount of Sr²⁺ entered into the ZrO₂ crystal lattice for SrO/ZrO₂, while Ba²⁺ could not enter. Excess SrO and BaO can react with ZrO₂ to form the corresponding zirconate. The differences between the three catalysts are thought to be caused by two factors: one is that Sr²⁺ and Ba²⁺ have difficulty in substituting for Zr⁴⁺ because of their large ions radii [32], while the other is the high basicities of SrO and BaO, which react readily with ZrO₂ to form SrZrO₃ and BaZrO₃.

3.2.3. Surface acidity and basicity of MO/ZrO₂ catalysts

The surface acidities of MO/ZrO₂ catalysts were studied by NH₃-TPD measurement and the profiles are shown in Fig. 2. The quantitative analysis of NH₃ desorbed from the catalysts is listed in Table 1. As shown in Fig. 2, a broad NH₃ desorption peak appeared at 100–450 °C. This was attributed to the intrinsic weakly acidic sites (100–250 °C) and medium-acidity sites (250–450 °C) on the unmodified ZrO₂ catalyst surface. For CaO/ZrO₂ catalyst, the number of acidic sites was similar to that of ZrO₂, while the number of intrinsic weakly acidic sites increased slightly over that of ZrO₂. After considering these results in light of the XRD data, it was concluded that the Ca²⁺ ions enter into the ZrO₂ crystal lattice to form Ca–O–Zr hetero-linkages. These linkages lead to an uneven distribution of charge and generate new acid sites that cover the loss of acid

Fig. 1. XRD patterns of MO/ZrO₂ catalysts.

Fig. 2. NH_3 -TPD profiles of MO/ZrO_2 catalysts.

sites caused by the introduction of CaO. As SrO and BaO were introduced, the total number of acidic sites decreased significantly due to the formation of zirconate, which can be ascertained from the XRD data.

Figure 3 illustrates the CO_2 -TPD profiles of MO/ZrO_2 catalysts in the desorption temperature range of 100–600 °C. A broad CO_2 desorption peak range spans the range of 100 to 500 °C. For unmodified ZrO_2 catalyst, a significant low-temperature desorption peak ranged from 120 to 180 °C, and this was assigned to the weakly basic sites on the ZrO_2 surface. With modification by alkaline earth metal oxides, the total number and distribution of basic sites of the MO/ZrO_2 samples changed significantly. The total count of basic sites, especially medium-basicity sites, increased markedly with the introduction of CaO, while the total basic count and intensity increased slightly for SrO/ZrO_2 and BaO/ZrO_2 . For CaO/ZrO_2 , the formation of Ca–O–Zr hetero-linkages and the high dispersion of Ca through the CaO/ZrO_2 sample were considered to cause the change in basicity. In contrast, SrO and BaO can react with ZrO_2 to form SrZrO_3 and BaZrO_3 , which leads to a decrease in the number of basic sites.

3.3. Relationship between acid-base properties and catalytic activity

The acid-base density of MO/ZrO_2 catalysts are shown in Table 1. As seen in Table 1, the surface acid–base property exerted great influence on the catalytic performance and BTO selectivity. The surface acid density of unmodified ZrO_2 catalyst was 2.53 NH_3/nm^2 , and that of CaO/ZrO_2 , SrO/ZrO_2 , and BaO/ZrO_2 were 1.96, 1.04, and 0.61 NH_3/nm^2 , respectively. With the decrease of acid density, BDO conversion decreased accordingly (from 100% to 74.3%). Thus, it is clear that BDO conversion is closely related to the acid density of the catalyst. Given that acidic sites act as an anchoring site for the OH group to activate BDO [19,20], it follows that more acidic sites can activate more BDO molecules to give higher BDO conversion. Table 1 also shows the relationship of BTO selectivity and surface base density of the catalysts. It shows clearly that greater base density led to increased BTO selectivity. The maximum base density was 3.29 CO_2/nm^2 for CaO/ZrO_2 , and the BTO

Fig. 3. CO_2 -TPD profiles of MO/ZrO_2 catalysts.

selectivity reached 65.4%. The basic sites are thought to interact with the β -H of BDO and thereby contribute to the formation of BTO.

In the vapor-phase selective dehydration of BDO, every reaction center for the formation of BTO is made up of two acidic sites and one basic site that act synergistically [19,20]. 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. 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. The rich content of acidic and basic sites leads to excellent performance in BDO dehydration to BTO.

4. Conclusions

The introduction of alkaline earth metal oxide to ZrO_2 had a marked influence on the acid–base properties of the material and its catalytic activity in dehydration of BDO to BTO. Due to the appropriate ionic radius and basicity, Ca^{2+} ions enter the ZrO_2 crystal lattice to form Ca–O–Zr hetero-linkages, which not only improve the surface acid density but also react with ZrO_2 to generate new acid sites. In contrast, SrO and BaO react with ZrO_2 to form zirconate, leading to a decrease in the number of acidic sites. The rich content of acid–base bifunctional reaction centers on the CaO/ZrO_2 surface is favorable for the formation of BTO, leading to decreased yield of byproducts like THF and increased yield of BTO.

References

- [1] Negishi E, Tan Z, Ling B, Novak T. *Proc Natl Acad Sci USA*, 2004, 101: 5782
- [2] Magnin-Lachaux M, Tan Z, Liang B, Negishi E. *Org Lett*, 2004, 6: 1425
- [3] Csuk R, Kern A. *Tetrahedron*, 1999, 55: 8409
- [4] Min T, Yi B X, Zhang P, Liu J, Zhang C, Zhou H P. *Med Chem Res*, 2009, 18: 495
- [5] Brace N O. *J Am Chem Soc*, 1955, 77: 4666
- [6] Mueller H, Pfalz F, Overwien H, Pommer H. US Patent 3 574 773. 1971

Graphical Abstract

Chin. J. Catal., 2013, 34: 1159–1166 doi: 10.1016/S1872-2067(12)60525-7

Vapor-phase selective dehydration of 1,4-butanediol to 3-buten-1-ol over ZrO_2 catalysts modified with alkaline earth metal oxides

ZHANG Qian, ZHANG Yin, LI Haitao, ZHAO Yongxiang*, MA Meng, YU Yu
Shanxi University

Modified ZrO_2 catalysts doped with alkaline earth metal oxides exhibit excellent catalytic performance in the vapor-phase selective dehydration of 1,4-butanediol to 3-buten-1-ol. The high catalytic activity is attributed to the rich content of acid-base bifunctional reaction centers.

- [7] Tsuji J, Shimizu I, Minami I. *Chem Lett*, 1984, 13: 1017
- [8] McCombs C A. US Patent 6 103 943. 2000
- [9] He Y Y, Li Q B, Wang Y Z, Zhao Y X. *Chin J Catal* (贺永艺, 李奇彪, 王永钊, 赵永祥. 催化学报), 2010, 31: 619
- [10] Sato S, Takahashi R, Sodesawa T, Honda N, Shimizu H. *Catal Commun*, 2003, 4: 77
- [11] Igarashi A, Ichikawa N, Sato S, Takahashi R, Sodesawa T. *Appl Catal A*, 2006, 300: 50
- [12] Takahashi R, Yamada I, Iwata A, Kurahashi N, Yoshida S, Sato S. *Appl Catal A*, 2010, 383: 134
- [13] Sato F, Sato S. *Catal Commun*, 2012, 27: 129
- [14] Sato F, Okazaki H, Sato S. *Appl Catal A*, 2012, 419-420: 41
- [15] Sato S, Takahashi R, Sodesawa T, Yamamoto N. *Catal Commun*, 2004, 5: 397
- [16] Yamamoto N, Sato S, Takahashi R, Inui K. *Catal Commun*, 2005, 6: 480
- [17] Igarashi A, Sato S, Takahashi R, Sodesawa T, Kobune M. *Catal Commun*, 2007, 8: 807
- [18] Inoue H, Sato S, Takahashi R, Izawa Y, Ohno H, Takahashi K. *Appl Catal A*, 2009, 352: 66
- [19] Yamamoto N, Sato S, Takahashi R, Inui K. *J Mol Catal A*, 2006, 243: 52
- [20] Sato S, Takahashi R, Kobune M, Inoue H, Izawa Y, Ohno H, Takahashi K. *Appl Catal A*, 2009, 356: 64
- [21] Wei Y D, Zhang S G, Li G S, Yin S F, Au C T. *Chin J Catal* (韦玉丹, 张树国, 李贵生, 尹双凤, 区泽棠. 催化学报), 2011, 32: 891
- [22] Tanabe K, Yamaguchi T. *Catal Today*, 1994, 20: 185
- [23] Zhang Y, Pan L, Gao C G, Wang Y Z, Zhao Y X. *J Sol-Gel Sci Technol*, 2010, 56: 27
- [24] Zhang Y, Pan L, Gao C G, Zhao Y X. *J Sol-Gel Sci Technol*, 2011, 58: 572
- [25] Wu Z G, Zhao Y X, Xu L P, Liu D S. *J Non-Cryst Solids*, 2003, 330: 274
- [26] Bellido J D A, De Souza J E, M'Peko J C, Assaf E M. *Appl Catal A*, 2009, 358: 215
- [27] Zhu Q, Liang L P, Jia Z Q, Gao C G, Zhao Y X. *Acta Phys-Chim Sin* (朱晴, 梁丽萍, 贾志奇, 高春光, 赵永祥. 物理化学学报), 2011, 27: 491
- [28] Yin Y S, Chen S G, Liu Y C. The Doping Stability and Growth Kinetic of Zirconia Ceramic. Beijing: Chem Ind Press (尹衍升, 陈守刚, 刘英才. 氧化锆陶瓷的掺杂稳定及生长动力学. 北京: 化学工业出版社), 2004. 8
- [29] Lu X Y, Liang K M, Gu S R, Fang H S, Zheng Y K, Liu P. *J Chin Ceram Soc* (路新瀛, 梁开明, 顾守仁, 方鸿生, 郑燕康, 刘鹏. 硅酸盐学报), 1996, 24: 670
- [30] Wang H, Liu S G, Zhang W Y, Zhao N, Wei W, Sun Y H. *Acta Chim Sin* (王慧, 刘水刚, 张文郁, 赵宁, 魏伟, 孙予罕. 化学学报), 2006, 64: 2409
- [31] Liu S G, Zhang X L, Li J P, Zhao N, Wei W, Sun Y H. *Petrochem Technol* (刘水刚, 张学兰, 李军平, 赵宁, 魏伟, 孙予罕. 石油化工), 2008, 37: 226
- [32] Zhu Y X, Zhuang W, Jiang D E, Xie Y C. *Chin J Catal* (朱月香, 庄伟, 江德恩, 谢有畅. 催化学报), 2000, 21: 52

碱土金属氧化物改性 ZrO_2 催化1,4-丁二醇选择性脱水合成3-丁烯-1-醇

张 骞, 张 因, 李海涛, 赵永祥*, 马 萌, 郁 宇

山西大学化学化工学院精细化学品教育部工程研究中心, 山西太原030006

摘要: 采用浸渍法制备了碱土金属氧化物 CaO 、 SrO 或 BaO 改性的 ZrO_2 酸碱双功能催化剂, 借助X射线衍射、低温 N_2 物理吸附、 NH_3 和 CO_2 程序升温脱附等手段表征了催化剂的结构、织构以及表面酸碱性质, 并考察了其催化1,4-丁二醇选择性脱水合成3-丁烯-1-醇的反应性能。结果表明, 碱土金属氧化物的引入显著调变了催化剂表面的酸性和碱性中心, 进而对1,4-丁二醇转化率和3-丁烯-1-醇选择性产生重要影响。其中, CaO 改性的 ZrO_2 样品中形成了大量的 Ca-O-Zr 结构, 在 ZrO_2 表面形成大量碱性位点的同时, 保持了较高的酸密度; 而 SrO 和 BaO 改性的样品中生成了相应的锆酸盐, ZrO_2 表面的酸密度呈现不同程度的下降。因此, CaO/ZrO_2 催化剂表现出最优的催化活性和3-丁烯-1-醇选择性, 350 °C时, 3-丁烯-1-醇收率最高, 达60.5%。催化剂表面的酸碱协同作用是选择性合成3-丁烯-1-醇的关键因素。

关键词: 1,4-丁二醇; 3-丁烯-1-醇; 碱土金属氧化物; 氧化锆; 酸碱双功能催化剂

收稿日期: 2012-11-28. 接受日期: 2013-01-24. 出版日期: 2013-06-20.

*通讯联系人. 电话: (0351)7011587; 传真: (0351)7011688; 电子信箱: yxzhao@sxu.edu.cn

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1. 前言

3-丁烯-1-醇(BTO)是一种附加值极高的精细化学品,广泛应用于食用香精,农化产品,尤其是医药领域^[1~4]。目前,合成BTO的方法有丙烯甲醛加成法^[5,6],3,4-环氧-1-丁烯还原法^[7,8]以及1,4-丁二醇(BDO)气相脱水法^[9~20]。其中,BDO脱水法采用固体氧化物为催化剂,具有反应条件温和、环境友好以及产物易分离等优点。该反应在热力学上可向两个方向进行(见图式1):(1)BDO分子内环化脱水生成四氢呋喃(THF);(2)BDO分子端羟基与相邻碳原子的 β -H脱水合成BTO^[9]。如何调控催化剂的种类、结构、织构及表面性质等,以实现BDO高选择性的脱水合成BTO,是该领域目前面临的重要难题。

在BDO气相脱水反应中,涉及的催化剂主要为金属氧化物催化剂,按反应机理可分为两类。一类是氧化还原型催化剂,如 CeO_2 ^[9~11]和 In_2O_3 ^[12]。这类催化剂表面具有氧化还原性能的金属离子,分别与BDO分子中的 β -H以及端羟基相互作用,脱去H自由基和端羟基自由基,进而形成 $\text{C}=\text{C}$,生成BTO;但也会生成仅脱除H自由基或羟基自由基的中间体,最终生成2-丁烯-1-醇、1,3-丁二烯、丁醛、丁醇等一系列副产物。第二类催化剂为固体酸碱氧化物催化剂,如 Al_2O_3 , MgO ^[15], ZrO_2 ^[16]及其它稀土氧化物^[18]。这类催化剂表面的酸性位和碱性位分别与BDO分子中的端羟基和 β -H相互作用,在脱除水分子的同时形成 $\text{C}=\text{C}$,生成BTO。比较而言,酸碱氧化物催化剂具有副反应少,目标产物选择性高的优点。

ZrO_2 表面同时具有酸性位和碱性位^[21,22],在催化BDO气相脱水合成BTO反应中表现出潜在的应用价值。Stao及其合作者将 ZrO_2 应用于催化BDO气相脱水反应中,并考察了碱金属Li, Na, K的引入对 ZrO_2 催化剂性能的影响^[15,16,19]。结果表明, ZrO_2 催化剂的活性最高,但BTO选择性最低,其收率约40%;碱金属的引入可提高BTO选择性,而BDO转化率却急剧降低,目标产物BTO收率也随之减少。这是由于经碱金属改性后的 ZrO_2 表面酸性中心锐减甚至消失所致。

研究表明,当二元氧化物中形成 $\text{M}_1\text{-O-M}_2$ 结构时,可在其表面形成不平衡电荷位点,进而产生新的酸性中心。本课题组在研究 $\text{ZrO}_2\text{-SiO}_2$ 复合氧化物的制备及性质时发现,复合氧化物表面的酸性质与其中 Zr-O-Si 结构的形成有重要关系^[23,24]。因此本文考察了碱土金属氧化物CaO, SrO, BaO改性的 ZrO_2 催化剂上BDO脱水合成

BTO反应性能,以制备出同时具有丰富酸碱中心,高活性、高选择性的BDO脱水合成BTO催化剂。

2. 实验部分

2.1. 催化剂的制备

ZrO_2 气凝胶采用醇水溶液加热法结合乙醇超临界干燥技术制备^[25],经400 °C预处理80 min后用作催化剂载体, ($A_{\text{BET}} = 185 \text{ m}^2/\text{g}$)。再等体积浸渍于计量比的 $\text{M}(\text{NO}_3)_2$ ($\text{M} = \text{Ca}, \text{Sr}, \text{Ba}$)水溶液中,于120 °C干燥12 h, 650 °C焙烧3 h制得催化剂,记为 MO/ZrO_2 ,各样品中MO含量均为 $\omega = 10\%$ 。

2.2. 催化剂的评价

BDO气相脱水反应在自制的固定床反应器中进行,催化剂(20~40目)用量为2.0 g。反应前在350 °C的 N_2 气氛中预处理1 h。BDO经液体微量计量泵(2.0 ml/h)打入汽化炉,汽化后用 N_2 (30 ml/min)带入反应管,通过催化剂床层反应后,冷凝得到产物。产物分析采用Agilent-7890A型气相色谱仪, AT.OV-1701毛细管柱(0.25 mm $\times$ 30 m), FID检测器,内标法定量。

2.3. 催化剂的表征

催化剂的比表面积测定在Micromeritics ASAP 2020型自动物理吸附仪上进行,样品先于150 °C下高真空脱气预处理5 h,然后在-196 °C下进行 N_2 吸附测定,由BET方程计算比表面积。

X射线衍射(XRD)表征在Bruker D8 Advance型X射线衍射仪上进行,使用Cu靶, K_α 辐射,管电压40 kV,管电流40 mA,扫描范围 $2\theta = 20^\circ \sim 70^\circ$,扫描速率 $6^\circ/\text{min}$ 。

催化剂样品的酸碱性质采用 NH_3 程序升温脱附($\text{NH}_3\text{-TPD}$)和 CO_2 程序升温脱附($\text{CO}_2\text{-TPD}$)表征。将100 mg样品(40~60目)置于石英管中,以He(99.999%)为载气(60 ml/min),以15 °C/min的速率升温至500 °C处理60 min,降温至100 °C,用脉冲法注入 NH_3 或 CO_2 吸附至饱和,待基线平稳后以10 °C/min的速率升温至600 °C, TCD记录 NH_3 或 CO_2 脱附曲线。样品总酸量和总碱量根据TPD曲线的积分峰面积求得,表示为单位质量样品 NH_3 或 CO_2 的吸附量,进一步结合比表面积分别得到样品的酸密度值和碱密度值,表示为单位面积吸附的 NH_3 或 CO_2 分子数。

3. 结果与讨论

3.1. 催化剂评价结果

表1为各样品催化BDO气相脱水的反应结果。该系

列催化剂上BDO的主要脱水产物为BTO和THF. 由表可见, ZrO_2 上BDO转化率为100%; 当引入碱土金属氧化物后, 催化剂活性均有所下降, 其中 BaO/ZrO_2 催化剂的最低, BDO转化率为74.3%; 但BTO选择性则有所升高. 其中 CaO/ZrO_2 催化剂上BTO选择性最高, 具有最优的BDO选择脱水合成BTO催化性能, BTO收率可达60.5%.

3.2. 催化剂表征结果

3.2.1. 催化剂的比表面积

表1列出了各 MO/ZrO_2 催化剂的比表面积. 可以看出, 经650 °C焙烧后未改性 ZrO_2 催化剂的比表面积为81 m^2/g ; CaO 的引入使得样品的比表面积增至91 m^2/g , 这可能是 CaO 的引入提高了样品的抗烧结性能, 降低了由 ZrO_2 颗粒表面扩散引起的烧结作用所致^[26,27]. SrO 和 BaO 的修饰则使样品的比表面积分别略降至73 m^2/g 和71 m^2/g .

3.2.2. 催化剂的物相结构

图1为各 MO/ZrO_2 催化剂的XRD谱. 由图可知, 未改性 ZrO_2 样品主要以单斜相($2\theta = 24.1^\circ, 28.2^\circ$ 和 31.5°)存在, 同时含有极微量的四方晶相($2\theta = 30.2^\circ$). 经 CaO 改性后的样品中 ZrO_2 以四方相为主. 且未观察到其它Ca物种(如 CaO , CaZrO_3)的特征衍射峰. SrO/ZrO_2 样品中的四方相 ZrO_2 衍射峰较未改性的有所增强, 其强度与单斜相 ZrO_2 衍射峰相近; 此外, 在 $2\theta = 30.8^\circ, 44.1^\circ, 54.7^\circ$ 处呈现 SrZrO_3 特征衍射峰. BaO 的引入未对 ZrO_2 晶型产生明显影响, 但出现尖锐的 BaZrO_3 特征衍射峰($2\theta = 30.2^\circ$).

研究表明, 当 ZrO_2 中引入合适的第二组分时, 其将取代 Zr^{4+} 的位置, 形成 M-O-Zr 结构^[28-31]. 此时, 为了保持材料的电中性, 会在 Zr^{4+} 周围形成氧空位从而降低了局部氧氧之间的排斥力, 使配位层产生较大的畸变, 起到稳定四方相 ZrO_2 的作用. 结合XRD结果可推测, 在 CaO/ZrO_2 催化剂中, Ca^{2+} 比较容易进入 ZrO_2 晶格结构替换 Zr^{4+} , 形成 Ca-O-Zr 结构, 以高分散形态存在于样品中; 对于 SrO/ZrO_2 样品, 只有少量 Sr^{2+} 进入 ZrO_2 的晶格结构. Ba^{2+} 未进入 ZrO_2 的晶格结构. 未进入晶格结构中的 SrO 及 BaO 与 ZrO_2 反应生成了相应的锆酸盐. 这是由于 Sr^{2+} 与 Ba^{2+} 的离子半径较大, 未能进入 ZrO_2 晶格结构所致^[32]; 另一方面, SrO 和 BaO 的碱性较强, 易与 ZrO_2 发生反应, 生成相应的锆酸盐物相.

3.2.3. 催化剂的表面酸碱性质

图2为各 MO/ZrO_2 催化剂的 NH_3 -TPD谱; 由曲线积分所得的单位质量催化剂酸量列于表1. 由图可见, 未改性 ZrO_2 样品在100~450 °C出现明显的 NH_3 脱附峰, 其表

面酸中心强度分布范围较宽, 以弱酸(100~250 °C)和中强酸(250~450 °C)为主; 经 CaO 改性后催化剂表面酸量基本不变, 甚至其表面弱酸性位略有增加. 结合XRD结果可知, Ca^{2+} 进入了 ZrO_2 晶格, 形成 Ca-O-Zr 结构, 导致了电荷的分布不均, 产生了新的酸性位点, 弥补了 ZrO_2 表面由于 CaO 引入导致的酸性位点损失. 而 SrO 和 BaO 则分别与 ZrO_2 发生反应生成了相应的锆酸盐, 使样品表面总酸量和酸强度均明显降低.

图3为各 MO/ZrO_2 催化剂的 CO_2 -TPD谱. 由图可见, 各样品在100~500 °C均存在 CO_2 脱附峰. 未经改性的 ZrO_2 样品上出现明显的低温脱附峰(120~180 °C), 表明其表面呈弱碱性. CaO 的引入使样品的碱量, 特别是中强碱性位显著增加. SrO/ZrO_2 和 BaO/ZrO_2 的总碱量和碱强度也略有提高. 这主要是由于在 CaO/ZrO_2 样品中, 形成了 Ca-O-Zr 结构, Ca物种以高分散形式存在于样品中; 而碱性相对较强的 SrO , BaO 与 ZrO_2 发生了相互作用分别生成了 SrZrO_3 和 BaZrO_3 , 因而其表面碱量明显少于 CaO/ZrO_2 样品.

3.3. 催化剂表面酸碱性质与反应活性的关系

表1给出了各催化剂样品表面酸密度和碱密度. 可以看出, 未改性 ZrO_2 的表面酸密度为2.53 NH_3/nm^2 ; 经 CaO , SrO 和 BaO 改性后分别降至1.96, 1.04和0.61 NH_3/nm^2 . 相应地, BDO转化率也由100%逐渐下降至74.3%. 可见, 样品活性与其酸密度大小密切相关. BDO分子通过两个端羟基与酸性位点相互作用被锚定在催化剂表面^[19,20], 丰富的表面酸位会吸附活化更多的BDO分子, 因而活性较高. 由表1可知, 催化剂表面碱密度越大, BTO选择性越高. 其中表面碱密度最高的是 CaO/ZrO_2 , 为3.29 CO_2/nm^2 , 其BTO选择性达到65.4%. 催化剂表面的碱性位点可活化BDO分子中的 $\beta\text{-H}$, 有助于BTO的生成.

在BDO气相脱水合成BTO的反应中, 催化生成BTO的活性中心可能由两个酸性位点和一个碱性位点构成, 是一种酸碱协同催化中心^[19,20]. BDO分子中的羟基被酸性位点吸附, 而分子中的 $\beta\text{-H}$ 则被碱性位点所吸附活化, 与相邻的端羟基同时消去, 脱水生成目标产物BTO. 碱土金属氧化物 CaO 的引入, 在 ZrO_2 样品中形成 Ca-O-Zr 结构, Ca物种以高分散形式存在于催化剂中; 在显著增加碱性位点的同时, 较好地保持了 ZrO_2 表面的酸性位点, 使其同时具有丰富的酸性和碱性中心, 大幅提高了BTO的选择性, 同时抑制了副产物THF的生成, 表现出优异的BDO选择脱水合成BTO催化性能.

4. 结论

碱土金属氧化物的引入对 ZrO_2 表面酸碱性质及催化BDO脱水性能有重要影响. 受离子半径和碱性强度影响, Ca^{2+} 能够进入 ZrO_2 晶格替换其中的 Zr^{4+} , 形成Ca-O-Zr结构, 不仅大幅提高了 ZrO_2 的表面碱密度, 也较

好地保持了 ZrO_2 表面的酸性位点; 而SrO和BaO分别与 ZrO_2 发生反应生成了相应的锆酸盐, 使样品表面酸密度明显降低. 同时具有丰富酸碱位点的CaO/ ZrO_2 样品表面产生了更多有利于BTO生成的酸碱协同活性中心, 从而抑制THF的生成, 显著提高BTO的最终产率.