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# Sol-gel synthesis of ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts for the transformation of bioethanol and acetaldehyde into 1,3-butadiene

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**ABSTRACT:** A series of ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts synthesized by sol-gel method were investigated for the 1,3-butadiene formation from bioethanol and acetaldehyde. The influence of ZrO<sub>2</sub> content and reaction conditions on catalytic performance were studied. The catalysts were characterized by N<sub>2</sub> adsorption–desorption analysis, Temperature-programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD), IR spectroscopy of adsorbed pyridine (Py-IR), Fourier Transform Infrared Resonance (FTIR), X-ray diffraction (XRD) and Transmission Electron Microscope (TEM). These characterization results indicated that suitable intensity of acid sites, especially Lewis acid, are very crucial to obtain an active catalyst. The catalysts showed significantly higher selectivity for C4 chemicals, and 2wt% ZrO<sub>2</sub> content reached the highest selectivity to BD (69.7%), at space velocity (WHSV) of 1.8h<sup>-1</sup>.

Keywords: 1,3-Butadiene, Ethanol, Acetaldehyde, ZrO<sub>2</sub>-SiO<sub>2</sub>, Sol-gel

# 1. INTRODUCTION

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1,3-Butadiene (BD) is an important chemical product in petrochemical industry. As one of the most important basic organic chemical materials, it is widely used in producing synthetic rubber such as acrylonitrile butadiene styrene (ABS), acrylonitrile butadiene (NBR) and styrene-butadiene (SBR).<sup>1</sup> Recently, BD has received more attention owing to the rapid economic growth of developing countries.<sup>2</sup>

Nowadays, approximately 95% of BD is predominantly produced by isolation from naphtha steam cracker fractions generated during ethylene production.<sup>3, 4</sup> However, the recent trends in lightening of the feedstock for steam cracking, as a result of the recent shale gas boom, threaten BD production and are expected to significantly affect its price.<sup>5</sup> Moreover, aware of the gradually decreasing resources of non-renewable oil and the deterioration of the environment, it is crucial to develop alternative technologies for BD production from renewable, non-petroleum resources such as bioethanol.<sup>2</sup> This is not a new process, as the catalytic conversion of ethanol into BD was ever used industrially during the world war two when oil extraction was extraordinarily expensive. With the advancement of bioethanol industry and the increasingly large volumes of bioethanol production, bioethanol again, gradually becomes a promising feedstock in the formation of BD.<sup>6</sup>

Since the early 1990s, two processes have been reported for the synthesis of BD from ethanol, that is, one-step process and two-step process.<sup>7</sup> The direct conversion of ethanol to BD was called one-step process and first discovered by Sergey Lebedev using a variety of mixed metal oxide catalysts, typically  $MgO/SiO_2^{8-12}$  or

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ZnO/Al<sub>2</sub>O<sub>3</sub><sup>13-15,16</sup> While much earlier in the USA, a two-step process has been implemented by Ostromyslensky<sup>17</sup> in which partial ethanol (EtOH) dehydrogenation to acetaldehyde  $(AA)^{18, 19}$  as the first step, followed by the transformation of the mixture of ethanol and acetaldehyde into BD.<sup>20</sup> The mechanism of BD formation from ethanol or the mixture of ethanol and acetaldehyde is very complicated and is still a subject of debate. However, the following five steps are applicative to both one-step and two-step processes and commonly accepted by most researchers<sup>2, 12, 20-22</sup>: (1) acetaldehyde formation from ethanol; (2) aldol condensation of acetaldehyde to acetaldol; (3) dehydration of acetaldol to crotonaldehyde; (4) Meerwein–Ponndorf– Verley reaction between crotonaldehyde and ethanol to obtain crotyl alcohol and acetaldehyde; and (5) dehydration of crotyl alcohol to BD. The ideal catalyst for this process thus should be active for both dehydration and dehydrogenation reactions.

Although it remains undecided whether the two-step process should be preferred over the one-step process, some available bibliographic data showed that for some catalysts the added acetaldehyde in the feed improved the selectivity of BD.<sup>16</sup> However, after several papers published in the 1940s, few catalyst studies of two-step process has been reported.<sup>2</sup> As early as 1947, tantalum, zirconium or niobium oxide promoted silica were used to study the two-step process of BD formation.<sup>23</sup> At 325-350°C and a space velocity of 0.4-0.6 h<sup>-1</sup>, 2wt% Ta<sub>2</sub>O<sub>5</sub> content reached the highest selectivity to BD (67%); 1.6wt% ZrO<sub>2</sub> on the SiO<sub>2</sub> showed a BD selectivity of 59% under comparable reaction conditions. Later on, Corson et al<sup>24</sup> screened many metallic and non-metallic oxides and concluded that catalysts like tantala-silica and

zirconia-silica exhibited excellent catalytic activity in the two-step process. Jones et al<sup>25</sup> reported the utility of a variety of silica impregnated bi- and trimetallic catalysts for the conversion of ethanol into BD; Zr : Zn system impregnated on silica was supposed as the most promising catalyst and the highest BD selectivity to be 67.4% was found. Commonly, the structure of the catalysts may have an influence on the catalytic performance.<sup>26, 27</sup> Chae et al<sup>2</sup> focused their study on the structure of ordered mesoporous silica supports. Along with research thorough, zirconia was later reported as a successful replacement for tantalum oxide.<sup>28</sup> Although many recent researchers<sup>1, 5, 29-33</sup> focused on the one-step process by using MgO/SiO<sub>2</sub> as their catalysts, the two-step process with ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts is still a fascinating subject worthy of study.

In this study, ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts prepared via sol-gel method were characterized and their catalytic performances for the formation of BD from bioethanol and acetaldehyde were investigated. The effects of pore structures and surface acidity on the catalytic activity were studied. The ZrO<sub>2</sub> contents and experimental conditions, such as the reaction temperature, the molar ratio of ethanol to acetaldehyde and the WHSV were optimized. Different characterization means were performed to determine the influences of acid sites and surface structure on the catalytic process.

## 2. EXPERIMENTS

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# 2.1. Catalyst preparation

A series of ZrO<sub>2</sub>-SiO<sub>2</sub> with different ZrO<sub>2</sub> contents up to 8.4wt% were prepared by

the sol-gel method. Briefly, zirconium oxynitrate (Alladin Industrial Corporation, AR), and tetraethyl orthosilicate (TEOS, Tianjin-guangfu Corporation, AR) were used as the precursors and ethanol as the co-solvent. The appropriate amounts of zirconium oxynitrate were dissolved in the solvent, deionized water. The solution was heated to 30°C under stirring to thoroughly mix the components, then ethanol (40mL), nitric acid (80mL, 2M) and tetraethyl orthosilicate were added in the solution in sequence. After 24 hours' standing, the solution was then dried for 6 hours at 110°C and subsequently calcined in a muffle furnance for 6 hours at 650°C<sup>34</sup> (ramping rate, 5°C/min).

#### 2.2. Catalyst testing

The catalytic conversion of ethanol (99wt%) and acetaldehyde (99wt%, 97wt%) to BD was carried out in a fixed bed quartz reactor. The reaction was performed at 320-410°C and atmospheric pressure after pretreating the catalysts in nitrogen (50 ml/min) at reaction temperature for 1 hour. The mixed solution of ethanol and acetaldehyde with a molar ratio of 0.5-4.5 was introduced into a vaporizer (120°C) by a metering pump. The dry gas was analyzed online by Agilent 7890A equipped with a Carbon-PLOT column (30 m, 0.535 mm, 3  $\mu$ m) and Thermal Conductivity Detector (TCD), while liquid product was collected by a cold trap and also analyzed by Agilent 7890A equipped with a HP-INNowax (30 m, 0.32 mm) and Thermal Conductivity Detector (TCD).

In this study, total conversions and BD selectivities were calculated by the

following equations, which were confirmed by the previous literature  $^2$ .

 $Total \text{ conversion} = \frac{(Total \text{ C moles} - (C \text{ mole}_{unreacted \text{ EtOH}} + C \text{ mole}_{unreacted \text{ AA}}))}{Total \text{ C moles}} \times 100$ 

BD selectivity= $\frac{C \text{ mole}_{BD \text{ in products}}}{Total C \text{ moles in products except for EtOH and AA} \times 100$ 

EtOH, ethanol; AA, acetaldehyde; BD, 1,3-butadiene.

#### 2.3. Characterization

Nitrogen adsorption-desorption isotherms were obtained at -198°C using a Micromeritics Tristar 3000 instrument. Before the measurement, all samples were pretreated at 200°C for 12 h. The Brunauer-Emmett-Teller (BET) method was used to calculate the surface areas.

The strength of acid sites was determined by NH<sub>3</sub>-TPD using a Micromeritic Autochem II 2920. Sample was first pre-treated at 200°C for two hours under a helium (99.999%) flow rate of 50 mL/min. Subsequently, by exposing the sample under the flow of ammonia (Argon 99% Ammonia 1%) at rate of 20 mL/min for one and a half hours at 70°C, the absorption process was completed. After the baseline was stable at 70°C, the temperature was then ramped to 800°C (15°C/min) in helium at rate of 50mL/min. All the results were recorded by Thermal Conductivity Detector (TCD).

Thermo Scientific Nicolet 560 FTIR spectrometer with 64 scans at 4cm<sup>-1</sup> resolution was used to determine the type of acid of the samples. The samples were pre-treated at 200°C under the vacuum of 10<sup>-3</sup> Pa for two hours. When the samples were cooled to room temperature, IR background spectra were recorded. Before flushing with

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nitrogen to remove physisorbed pyridine, the sample was exposed to pyridine vapor at room temperature for 30 min. Pyridine absorbed spectras were recorded at 200°C. High purity nitrogen flowed constantly during the experiment.

The infrared spectra was obtained using a Nicolet 560 spectrometer with a scanning range between 4000  $\sim$  400 cm<sup>-1</sup> and at a resolution of 4 cm<sup>-1</sup>. The samples were prepared with the addition of KBr at the weight proportion of 99%.

X-ray diffraction analysis was obtained using a Rigaku D/Max 2500 type X-ray powder diffractometer with Cu K $\alpha$  radiation operating at 40 kV and 150 mA. The scan range was  $2^{\theta}$ = 5 to 90° with a speed of 5°/s.

Transmission electron microscopy figures were obtained using a Tecnai G2 F20 operated at 200 kV. The samples were prepared on the porous copper grids by dispersing in ethanol.

# **3. RESULTS AND DISCUSSION**

#### 3.1. Catalyst characterization

As shown in Figure 1, all the N<sub>2</sub> adsorption-desorption isotherms for different ZrO<sub>2</sub> contents exhibited type IV isotherms with H1 hysteresis loop as defined by IUPAC.<sup>35</sup> This indicates that all the catalysts have mesoporous structures. In addition, the total adsorption volume decrease gradually with the increasing of ZrO<sub>2</sub> loading. Mostly, it is because that more ZrO<sub>2</sub> loading led to the smaller pore volumes. BET surface areas measured by N<sub>2</sub> sorption for different ZrO<sub>2</sub> contents (1.4wt%, 2.0wt%, 2.8wt%, 5.6wt%, 8.4wt%) are 743m<sup>2</sup>/g, 606m<sup>2</sup>/g, 589m<sup>2</sup>/g, 568m<sup>2</sup>/g, 528m<sup>2</sup>/g, respectively.

The sol-gel synthesized catalysts have relatively high surface areas. XRD patterns of these catalysts only showed the characteristic peaks of  $SiO_2(2\theta=23^\circ)$  (Figure 2). No ZrO<sub>2</sub> diffraction was detected, suggesting the highly dispersed nature of ZrO<sub>2</sub>.



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**Fig.1.** N<sub>2</sub> adsorption-desorption isotherms of ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts with different ZrO<sub>2</sub> contents



Fig.2. XRD patterns of ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts with different ZrO<sub>2</sub> contents (a) 0%; (b) 1.4%; (c) 2.0%; (d) 2.8%; (e) 5.6%; (f) 8.4%

NH<sub>3</sub>-TPD was performed to further investigate the acidic properties of the catalysts (Figure 3). In low temperature range, all samples showed a broad peak from

100 to 170°C conforming the existence of weak acid sites. When the temperature exceeds 170°C, no obvious peaks were observed, indicating the mere existence of weak acid sites on the surface. Figure 3 also shows that with the increasing of  $ZrO_2$ loading, the strength of weak acid increased obviously to the high temperature, contributing to the enhancement of total number of acid sites in Table 1. The enhanced strength of these samples indicates that the addition of ZrO<sub>2</sub> contributed to forming the new weak sites on the surface of the samples<sup>36</sup>. Py-IR was also used to compare the change of the type of acidity. Both Brønsted acid sites (1545cm<sup>-1</sup>) and Lewis acid sites (1445cm<sup>-1</sup>, 1595cm<sup>-1</sup>) were observed (Figure 4). The peak located at 1445 cm<sup>-1</sup> belongs to pyridine adsorbed on Lewis acid sites which has a slight shift comparing to the 1450 cm<sup>-1</sup>. According to former research the peak at 1450 cm<sup>-1</sup> could suffer some shift when the size or charge of the cation constituting the acid site changes.<sup>37</sup> 1595 cm<sup>-1</sup> also attributes to pyridine adsorbed on Lewis acid sites but corresponds to a different vibration mode. When the ZrO<sub>2</sub> content increased from 1.4 to 8.4wt%, the surface Brønsted acid sites almost had no change, but the Lewis acid sites increased significantly. Combined with the NH3-TPD results, it indicated that the addition of  $ZrO_2$  can only increase the intensity of Lewis acid. As shown in Figure 4, at 1445 cm<sup>-1</sup> and 1595 cm<sup>-1</sup>, the characteristic peak areas of lower ZrO<sub>2</sub> contents (1.4wt% and 2.0wt%) were much smaller than 5.6wt% and 8.4wt%, whereas Table 1 clearly showed that as the ZrO<sub>2</sub> content increases, the growth of the acid sites number was steady. This probably because the molecular volume of pyridine is bigger than NH<sub>3</sub>, and pyridine can't enter into the internal surface and holes of ZrO<sub>2</sub>-SiO<sub>2</sub>

catalysts sufficiently. So the result of Py-IR mostly reflected the external surface type of acidity. With the  $ZrO_2$  content from 2.0 to 5.6wt%, the adsorption of  $ZrO_2$  on the internal surface was saturated, while the external surface appeared more  $ZrO_2$ , which can be detected by Py-IR easily.



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**Fig.3.** NH<sub>3</sub>-TPD profiles of ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts with different ZrO<sub>2</sub> contents (a) 0%; (b) 1.4%; (c) 2.0%; (d) 2.8%; (e) 5.6%; (f) 8.4%



Fig.4. Py-IR spectra of  $ZrO_2$ -SiO<sub>2</sub> catalysts with different  $ZrO_2$  contents (a) 1.4%; (b) 2.0%; (c) 5.6%; (d) 8.4%

Table 1 The amounts of weak acidic sites of ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts with different

$ZrO_2$ content	Number of Acid Sites (mmol/g)					
(we /0)						
0	0.10					
1.4	0.11					
2.0	0.13					
2.8	0.12					
5.6	0.15					
8.4	0.17					

ZrO <sub>2</sub>	contents
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FTIR spectra method was used to explore the existence of typical group between ZrO<sub>2</sub> and SiO<sub>2</sub>. Figure 5 exhibited the infrared spectrum of ZrO<sub>2</sub>-SiO<sub>2</sub> and pure SiO<sub>2</sub>. Both of ZrO<sub>2</sub>-SiO<sub>2</sub> and pure SiO<sub>2</sub> showed a strong band noticed at 1080 cm<sup>-1</sup> accompanied with a shoulder at 1220 cm<sup>-1</sup>. These belong to the typical asymmetric stretching vibrations of Si-O-Si.<sup>38,39</sup> Two other bands at 800 cm<sup>-1</sup> and 460 cm<sup>-1</sup> are due to symmetric stretching and bending vibrations of Si-O-Si bonds, respectively.<sup>39,40</sup> The band at 1630 cm<sup>-1</sup> indicates the existence of the physisorbed molecular water on the surface of the catalyst.<sup>41</sup> The frequency at around 960 cm<sup>-1</sup> appears different in two samples which contributes to the stretching vibration of Si-O-Zr groups if the bands observed at higher frequencies. As to the pure SiO<sub>2</sub>, 960 cm<sup>-1</sup> is due to the Si-O- groups.<sup>42</sup> These results indicated that those ZrO<sub>2</sub>-SiO<sub>2</sub> samples didn't mingle mechanically, whereas had some interactions and finished the ethanol and acetaldehyde to BD process cooperatively.



Fig. 5. Infrared spectrum of the samples (a) 2% ZrO<sub>2</sub>-SiO<sub>2</sub>; (b) SiO<sub>2</sub>

As demonstrated in Figure 6, the leafy shape of  $SiO_2$  is shown in (a). The agglomeration of the particles can also be seen in the same image, but in a small amount. However in (b), clots are obvious as the black cloudy sites in the image shown and there is no trace of crystal structure of  $ZrO_2$  which elucidates that  $ZrO_2$  is at its amorphous state or the crystal particles are so small that can't be seen. That is to say, the  $ZrO_2$  is well dispersed on the SiO<sub>2</sub> support, which is in good agreement with the results of XRD.





Fig. 6. Transmission electron microscopy (TEM) pictures of (a) SiO<sub>2</sub>, (b) 2% ZrO<sub>2</sub>-SiO<sub>2</sub> (100nm), (c) ZrO<sub>2</sub><sup>34</sup>, (d) 2% ZrO<sub>2</sub>-SiO<sub>2</sub> (5nm)

## 3.2. Catalyst testing

As Zr has different acidic and basic properities<sup>43</sup>, varying the ZrO<sub>2</sub> content was hypothesized to have an effect on the delicate acid-base balance and at the same time determined the optimal content for BD yield. The influence of different ZrO<sub>2</sub> contents on catalytic performance was studied using sol-gel method with five ZrO<sub>2</sub> contents: 1.4wt%, 2.0wt%, 2.8wt%, 5.6wt% and 8.4wt%. These samples may not show distinct differences in morphology, but they emerged high variability in catalytic activity. For these catalysts, activity and selectivity are reported in Figure 7, providing the first data of catalyst performance. As the ZrO<sub>2</sub> content increased, dehydration activity (i.e., ethylene and diethyl ether selectivity) increased and the increasing dehydration activity matched well with the increased weak acid sites. This was evidenced by the aforementioned NH<sub>3</sub>-TPD and IR-Py results, and presumably the increased dehydration activity was only affected by Lewis acid sites. As the secondary product of acetaldehyde<sup>28</sup>, BD mostly reflected the dehydrogenation activity. Actually, the

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dehydrogenation is a competitive process compared to its dehydration.<sup>44</sup> Thus dehydration of ethanol to ethylene and diethyl ether should be avoided to attain high BD yields.<sup>16</sup> However, the catalysts for BD formation should be active for both dehydration and dehydrogenation.<sup>7</sup> Then, the dehydrogenation and dehydration components should be present in an optimal ratio. In this article, as the  $ZrO_2$  content increased, the selectivity of BD was increased at first and then decreased remarkably. 2wt% ZrO<sub>2</sub> content reached the highest selectivity to BD. Presumably, this ZrO<sub>2</sub> content balanced the dehydrogenation and dehydration processes. What's more, the work by Jones et al. has confirmed that a degree of acidity in the support is critical as several steps in the mechanism are acid catalyzed and Zr(IV) is Lewis acidic, which is believed to enhance the activity.<sup>25</sup> Ordomaky et al. also suggested that Lewis acid sites play important role in the aldol condensation of acetaldehyde.<sup>45</sup> It suggested that the acidity of catalysts could be beneficial to the transforming of acetaldehyde into BD, but high selectivity of BD required a suitable acid sites rather than as much as possible.



Fig.7. Effect of  $ZrO_2$  content on 1,3-butadiene and other main products selectivity over  $ZrO_2$ -SiO<sub>2</sub> catalysts

(Conditions: 0.5g catalyst, The ethanol-to-acetaldehyde feed ratio: 2.5:1, WHSV=1.8g EtOH/g cat  $h^{-1}$ , T=350°C. Note: Other minor products included propylene, ethyl acetate, 1-butanol and C<sub>6</sub>+. Selectivity to all minor products were<10% ).

Interestingly, despite the varied  $ZrO_2$  content, the sum of BD selectivity and butene selectivity was always very high. This result indicated that  $ZrO_2$ -SiO<sub>2</sub> catalysts were beneficial to the generation of C<sub>4</sub>s. A balance of acidic and basic sites were present on  $ZrO_2$ -SiO<sub>2</sub> catalysts which, upon further optimization of reaction conditions, could be used for the BD formation.<sup>28</sup>

The effects of the different parameters, such as the reaction temperature, the molar ratio of ethanol to acetaldehyde and the WHSV on the selectivity of BD and butene were studied (See Figure 8).

In order to determine the effect of temperature, the reaction was conducted at temperature from 290 to  $410^{\circ}$ C. The optimum ZrO<sub>2</sub> content obtained in the previous section were used here. As Figure 8 (a) shows, the total conversion of ethanol and

acetaldehyde appeared to increase apparently with an increase in the temperature. At 320°C, the selectivity of BD reached a top value and butene was low enough. Therefore, in our experiment, 320°C was chosen as the optimum temperature for this system.

Generally speaking, the change of WHSV mostly led to a great difference of the conversion. This law was consistent with our experiment. As showed in Figure 8 (b), despite the increase of WHSV, the selectivity of BD and butene had little change, while the total conversion had a decreasing trend. The maximum BD selectivity was achieved at 1.8, which was then chosen as the optimum WHSV.

The effect of ethanol-to-acetaldehyde molar ratio on the selectivity of BD and butene was determined using ratios of 0.5 to 4.5. All other conditions were those obtained in the previous sections. As Figure 8 (c) shows, the molar ratio made the greatest influence on the selectivity. With the increase of ethanol-to-acetaldehyde molar ratio, the selectivity of BD appeared to increase too. The highest BD selectivity was obtained at 3.5, then dropped slightly at 4.5. But, the change of butene selectivity exhibited a completely opposite situation. Therefore, the feed ratio was very important to the selectivity of BD. Too much or too little didn't do benefit to the conversion to BD. The molar ratio of 3.5:1 was the optimum condition.



**Fig.8.** Effect of temperature (a); WHSV (b) and ethanol/acetaldehyde molar ratio (c) on the total conversion and the selectivity of butadiene and butene over 2wt% ZrO<sub>2</sub> content catalysts

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Table 2 shows the total conversion of ethanol and acetaldehyde, the selectivity of main products and unidentified compounds on  $ZrO_2$ -SiO<sub>2</sub> catalysts at appropriate conditions. Through the optimization of reaction conditions, these catalysts indeed demonstrated high activity to BD. The relatively high conversion and BD selectivity were closely associated with the high surface area (about 606m<sup>2</sup>/g), which offers a good dispersion of active sites (zirconium oxide). What's more, as discussed in Section 3.1, it is supposed that the acid-base properties and the synergistic effects of  $ZrO_2$  and SiO<sub>2</sub> played a more important role in the process of ethanol and acetaldehyde to BD.

# Table 2 Catalytic performance of 2wt% ZrO<sub>2</sub> supported SiO<sub>2</sub> catalysts in 1,3-BD

Catalyst	E:A <sup>a</sup>	E/A	Carbon se	Carbon selectivity (C mol%)									
		$con.(\%)^b$	Ethylene	Propylen	e Butene	1,3 <b>-</b> BD	Ether	AA	Ethyl	l Butanol	Others*		
									aceta	te			
ZrO <sub>2</sub> -SiO <sub>2</sub> <sup>c</sup>	3.5:1	42.2	14.2	0.9	1.0	65.8	9.2	_	5.2	0.9	3.6		
$ZrO_2$ - $SiO_2^d$	3.5:1	45.4	16.0	2.0	0.9	69.7	8.2	—	0.8	0.5	2.2		
$ZrO_2$ - $SiO_2^d$	4.5:0	30.2	85.8	0	0	0.7	8.4	5.0	0	0	0		
<sup>a</sup> The ethanol	-to-acet	aldehyde	feed ratio.	<sup>b</sup> The total	conversion	of ethanol	and	acetalde	ehyde.	<sup>c</sup> The concen	tration of		

production at 320°C, WHSV=1.8 h<sup>-1</sup> at 3h.

<sup>a</sup>The ethanol-to-acetaldehyde feed ratio. <sup>b</sup>The total conversion of ethanol and acetaldehyde. <sup>c</sup>The concentration of acetaldehyde was 99%. <sup>d</sup> The concentration of acetaldehyde was 97%.

\*Unidentified compounds mainly consisting of heavier compounds in GC chromatography.

In an attempt to further improve the catalytic data, the influence of the concentration of acetaldehyde were studied. Both 99% and 97% purities of acetaldehyde were used as feed after mixing with appropriate amount of ethanol. 97% purity showed a higher activity both in the total conversion of ethanol and acetaldehyde and in the selectivity of BD. In addition, the amounts of the unidentified

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compounds and some side products, such as ethyl and butanol got a certain degree reduction too. However, due to the unidentified impurities of 97% purity acetaldehyde, this phenomenon can't be easily explained up to now. Presumably, the impurities contained some intermediate products in the ethanol to BD process, which had the same active effect with the addition of acetaldehyde in the feed.

Strangely enough, when no acetaldehyde was added to the feed there was a dramatic decrease in the selectivity towards BD compared to the mixed feed of ethanol and acetaldehyde, see entry 2 and entry 3 of Table 2. Without the addition, the catalyst mainly played the role of dehydration. This is implying that with the added acetaldehyde, ethanol is being preferentially reacted in the aldol condensation.<sup>25</sup> It is supposed that the ZrO<sub>2</sub>-SiO<sub>2</sub> catalysts have weak ability in dehydrogenation, but benefit aldol condensation with rather high handling capacity. The addition of acetaldehyde is very necessary, otherwise we should enhance the dehydrogenation ability of ethanol with other methods.

# 4. CONCLUSION

A series of  $ZrO_2$ -SiO<sub>2</sub> catalysts were prepared by sol-gel method in the process of 1,3-butadiene formation from ethanol and acetaldehyde. The catalysts exhibited a high dispersion of  $ZrO_2$  and obtained high activity. The highest 1,3-butadiene selectivity of 69.7% was obtained under the optimal conditions:  $320^{\circ}C$ , 2wt%  $ZrO_2$  content, 3.5:1 molar ratio of ethanol-to-acetaldehyde and a WHSV of  $1.8h^{-1}$ . Furthermore, the influence of the acidity and surface structure of the catalysts was

studied in order to illustrate the reason of high selectivity for 1,3-butadiene. The sol-gel synthesized catalysts showed suitable weak acid sites. Moreover, concluded from Py-IR, Lewis acid is a crucial element in the formation of BD. Both XRD and TEM confirmed that  $ZrO_2$  was highly dispersed in the amorphous silica.

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The sol-gel synthesized catalysts showed significantly higher selectivity for 1,3-butadiene (69.7%) , at a high WHSV of  $1.8h^{-1}\!.$ 

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