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1,3-Butadiene Production from Bioethanol and Acetaldehyde over Zirconium Oxide Supported on Series Silica Catalysts

**Meixiang Gao**[1,2] · **Minhua Zhang**[1,2] · **Haoxi Jiang**[1,2]

Abstract

In this paper a series of zirconium oxide supported on silica composite oxides were studied as catalysts for the production of 1,3-butadiene from bioethanol and acetaldehyde. The highest selectivity observed was 91.43%. Different silica materials with varied pore diameters in the range of 3.6–11.6 nm and the service life of the catalyst have been initially investigated. The catalysts were characterized by a nitrogen adsorption analysis, X-ray diffraction, scanning electron micrography and ^{29}Si solid-state NMR spectroscopy. The catalytic results show that the pore sizes are important factors determining the activity when catalyst contains a subtle balance of the acid and base.

Graphical Abstract
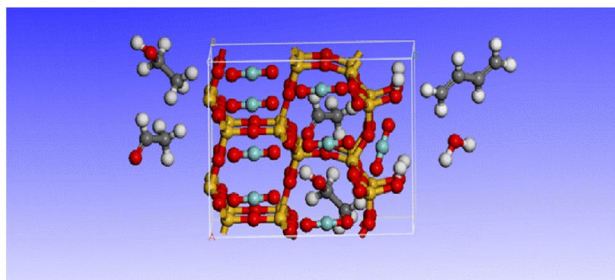
Keywords Bioethanol · Acetaldehyde · 1,3-Butadiene · ZrO$_2$ supported on silica materials · Surface properties

1 Introduction

A main challenge facing the bulk chemical industry in the twenty-first century is the sustainability of its supply chains. It has been advocated that future high-value bio-based chemicals need to be produced from bio-refineries in addition to the lower-value biofuels [1]. One of the most abundant sustainable and practicable raw materials is bioethanol, produced from biomass [2, 3]. There are many applications for the conversion of bioethanol into commodity chemicals [4]. In this paper we report a systematic study of ZrO$_2$ supported on series silica catalysts for the bioethanol conversion into 1,3-butadiene (BD).

BD is an important building block in the chemical industry and generally used as a material for synthetic polymers and rubbers [5]. While BD is currently obtained as by-product of ethylene production in the process of hydrocarbon steam cracking [6]. So there is a desire to produce BD from a sustainable source, bioethanol. This is by no means a new technology, during the first decades of the twentieth century, two processes were developed for the synthesis of BD from ethanol, that is, the Ostromisslenski [7] and Lebedev [8] processes.

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Different classes of catalysts have been adopted in this process [9–11]. As early as 1947, transition metal oxides supported on silica were used in the two-step process of BD formation. Highest BD selectivities 67 and 59% were obtained on Ta_2O_5/SiO_2 and ZrO_2/SiO_2, respectively [12]. Later on, Corson et al. [13] have studied more than 350 oxides as catalysts on BD formation from ethanol and concluded that Ta_2O_5–SiO_2 and ZrO_2–SiO_2 exhibited preferable catalytic activity in the two-step process. Jones et al. [14] have concluded that Zr–Zn/SiO_2 was supposed as the most promising catalyst with the highest BD selectivity 67.4%. Chae et al. [15] have tested a series of ordered mesoporous silica supported tantalum oxide samples as catalysts for conversion ethanol and acetaldehyde to BD and their research have found that pore structure has an influence on the reaction activity. Along with research thorough, we can draw a conclusion that ingenious combination of ZrO_2 and SiO_2 can meet the demand of ethanol and acetaldehyde to BD reaction and the activity of catalysts would improve further through tailoring other factors, which is a meaningful task.

In this study, a variety of ZrO_2 supported on SiO_2 catalysts were synthesized. Moreover, the effect of the physical structure and properties of the catalysts on the performance of BD formation from bioethanol and acetaldehyde reaction was examined. In this case, we used NanoSiO$_2$, SBA-15, MCM-41 as silicon source. This is the first study to apply series silica as a support in Zr-containing catalysts.

2 Experimental

2.1 Preparation of Catalysts

All of the silica-supported 2 wt% ZrO_2 catalysts were obtained by incipient wetness impregnation of silica series with zirconium oxynitrate solutions. After impregnation all samples were treated by ultrasounding for 2 h. Then, all samples were dried at 393 K and calcined at 923 K for 6 h (ramping rate, 5° C/min) in a flow of dry air.

2.2 Catalyst Characterization

Nitrogen adsorption isotherms were measured at 77 K on a Micromeritics Tristar 3000 volumetric adsorption analyzer. Powder X-ray diffraction patterns were recorded on a Rigaku Multiplex instrument using Cu-K radiation operated at 40 kV and 150 mA. Scanning electron micrograph images were obtained with a Philips XL-30S FEG scanning electron microscope. ^{29}Si MAS NMR spectra were recorded on a Bruker AMX300 spectrometer.

2.3 Catalytic Test

The production of BD from ethanol and acetaldehyde was performed in a fixed bed reactor system. A mixture of ethanol and acetaldehyde with ethanol to acetaldehyde volume ratio of 3.5 was fed into the catalytic reactor by a flow pump [16]. The catalyst was loaded in the middle of the quartz tube. Before the reaction, the catalyst was pretreated to the reaction temperature with an N_2 flow as the carrier gas. The reaction was then performed with a weight hourly space velocity (WHSV) of 1.8 h^{-1} at 593 K. Products were detected online by Agilent 7890A. In this study, total conversions and BD selectivities were calculated by the following equations.

Total conversion

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

BD selectivity

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

3 Results and Discussion

3.1 Properties of Silica Materials Supported ZrO$_2$ Catalysts

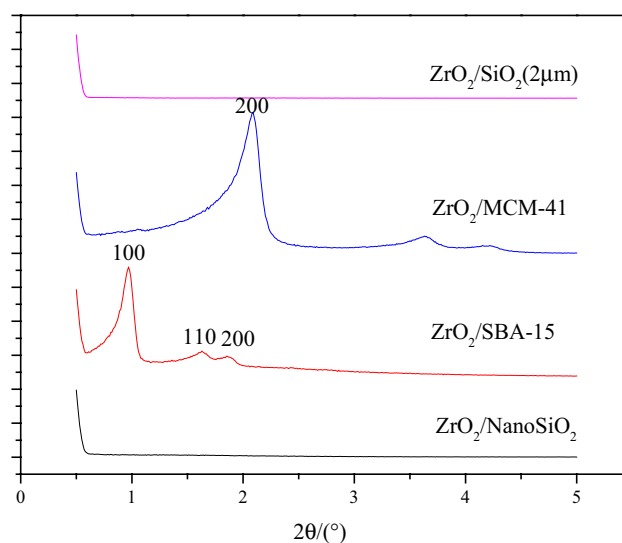Figure 1 shows low-angle XRD patterns of silica materials supported 2 wt% zirconium oxide catalysts. Both the

Fig. 1 Low angle XRD patterns of 2 wt% ZrO_2 supported NanoSiO$_2$, SBA-15, MCM-41 and SiO$_2$ (2 μm) catalysts

ZrO$_2$/NanoSiO$_2$ and ZrO$_2$/SiO$_2$ (2 μm) catalysts exhibit patterns typical for amorphous materials without ordered mesoporous structure. There are three distinct peaks shown for ZrO$_2$/SBA-15. These can be indexed as (1 0 0), (1 1 0) and (2 0 0). The low angle XRD patterns of ZrO$_2$/MCM-41 show one major (100) reflection and two minor reflections corresponding to the (110) and (220) planes, pointing to a highly ordered hexagonal pore structure.

The structural properties of the catalysts are summarized in Table 1. Series of the silica support with zirconium

**Table 1** Structural properties of supports and catalysts

Preparation method	BET surface area (m^2/g)	Average pore diameter (Å)
NanoSiO$_2$	152	90.6
ZrO$_2$/NanoSiO$_2$	131	116.2
SBA-15	610	61.7
ZrO$_2$/SBA-15	573	61.7
MCM-41	664	35.9
ZrO$_2$/MCM-41	612	35.9
SiO$_2$ (2 μm)	510	49.7
ZrO$_2$/SiO$_2$ (2 μm)	477	59.8

results in decreasing of the surface area of the samples. This decrease may occur due to the formation of highly dispersed zirconium species. These species occupy a part of the internal and external surface of series silica particles. However, the average pore sizes of samples increase except ZrO$_2$/SBA-15 and ZrO$_2$/MCM-41 catalysts. These data increase in turn ZrO$_2$/MCM-41, ZrO$_2$/SiO$_2$ (2 μm), ZrO$_2$/SBA-15 and ZrO$_2$/NanoSiO$_2$. Most interesting, the BD selectivity also increases in this turn. The reasons maybe large pore makes both the reagent and product move freely in and out of the catalysts. These results indicate that the pore sizes are important factors determining the activity when catalyst contains a subtle balance of the acid and base, which is in good agreement with other recent studies [14, 15].

SEM images of series ZrO$_2$/SiO$_2$ samples are displayed in Fig. 2. ZrO$_2$/NanoSiO$_2$ shows relatively uniform particles shown in Fig. 2a. Figure 2b shows ZrO$_2$/SBA-15, showing a hexagonal rod-like SBA-15 morphology. However, the ZrO$_2$/MCM-41 and ZrO$_2$/SiO$_2$ (2 μm) samples show randomly amorphous particles and small sphere-like primary particles with particle diameters of around 2 μm, respectively (Fig. 2c and d).

Figure 3 displays the ^{29}Si MAS NMR spectra for ZrO$_2$ supported on silica materials. All of the ZrO$_2$ supported

Fig. 2 SEM images of **a** ZrO$_2$/NanoSiO$_2$, **b** ZrO$_2$/SBA-15, **c** ZrO$_2$/MCM-41, and **d** ZrO$_2$/SiO$_2$ (2 μm) catalysts
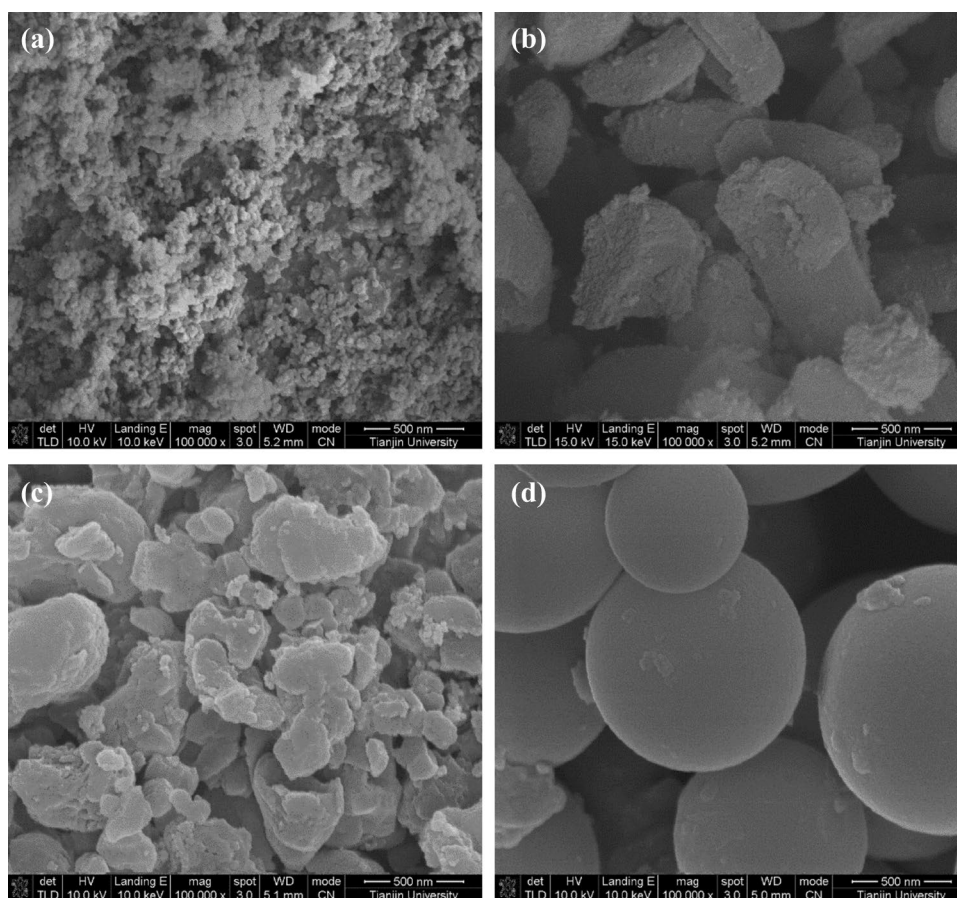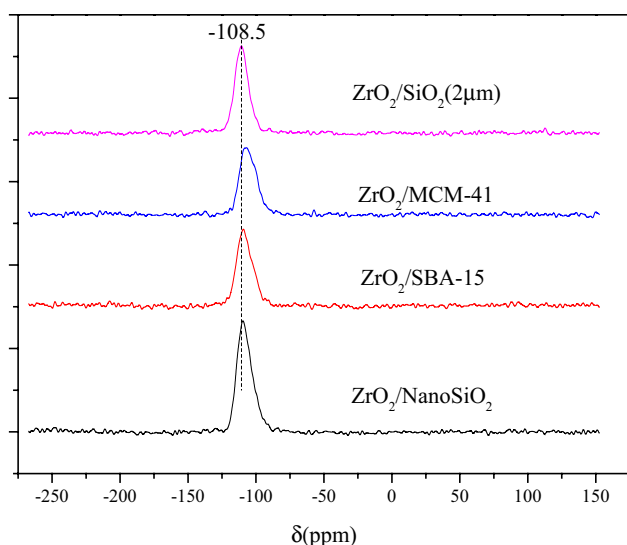
Fig. 3 ^{29}Si MAS NMR spectra of Zr-containing catalysts

silica catalysts show resonances in the range of -108.5 ppm which are attributed to Q4 (Si (4Si)) species. Besides, for ZrO_2/MCM-41 a shoulder at -100 ppm points to the presence of Q3 (Si (OH, 3Si)) defects [17]. This means that the interactions between Zr and Si are weak in the ZrO_2/SiO_2 materials.

3.2 Catalytic Test for BD Production from Ethanol and Acetaldehyde

Table 2 shows catalytic performance of 2 wt% ZrO_2 supported SiO_2 catalysts in BD production at 593 K. Obviously, ZrO_2/NanoSiO$_2$ exhibited the best performance with the 91.43% BD selectivity. As discussed in the part of structural properties of the catalysts, BD yield increases in the turn of ZrO_2/MCM-41, ZrO_2/SiO_2 (2 μm), ZrO_2/SBA-15 and ZrO_2/NanoSiO$_2$, which is the same as pore sizes order of increasing. Thus, the higher total conversion and BD selectivity were associated with its larger pore sizes. It is supposed

that pore sizes are important factors determining the activity when catalyst contains a subtle balance of the acid and base.

In our previous work [16], it was reported the ZrO_2–SiO_2 catalyst sample synthesized by sol–gel method contained the same ZrO_2 content of 2 wt%, reaching the lower selectivity of 1,3-butaidene (69.7%), and the main difference between them is the average pore size of the catalyst. Jones et al. [14] and Chae et al. [15] also reported that the larger pore size of catalysts was a favorable factor to enhance the 1,3-buta-diene selectivity. It could be supposed that the pore sizes parameter would become the important determining factors to improve the catalytic activity, when the catalyst surface contained appropriate active sites.

Finally, the catalytic durability was also preliminarily explored as shown in Fig. 4, which shows the longevity of ZrO_2/NanoSiO$_2$ catalyst. ZrO_2/NanoSiO$_2$ catalyst developed in this work has relatively longer catalyst life. In other words, besides initial BD selectivity and conversion, the long-term stability of catalytic performance of ZrO_2/NanoSiO$_2$ was
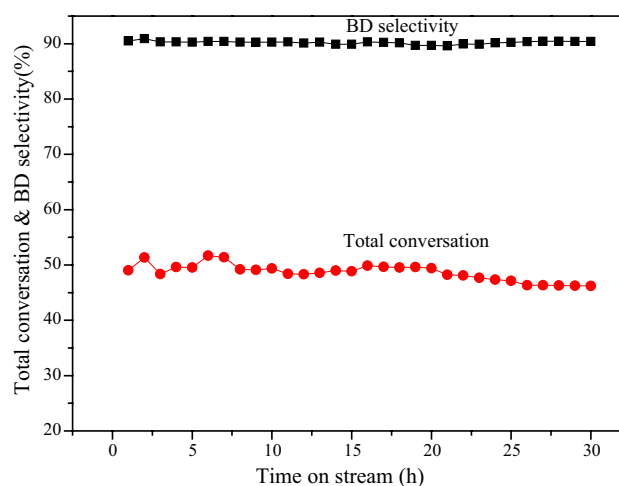

Fig. 4 Ethanol/acetaldehyde total conversion and BD selectivity in the on stream time of 30 h, 2 wt% ZrO_2/Nano-SiO_2 catalyst samples in BD production at 593 K, WHSV = 1.8 h^{-1}

Table 2 Catalytic performance of 2 wt% ZrO_2 supported SiO_2 catalysts in BD production at 593 K, WHSV = 1.8 h^{-1} at 12 h

Catalyst	E:A[a]	E/A Con. (%)[b]	Carbon selectivity (C mol%)							
			BD	Ethylene	Ether	Ethyl acetate	Propylene	Butene	Butanol	Others[c]
ZrO_2/NanoSiO$_2$	3.5:1	52.39	91.43	2.26	3.00	0.51	0.48	0	0.73	1.60
ZrO_2/SBA-15	3.5:1	53.20	88.57	0.77	1.75	1.66	4.90	0.10	1.96	0,30
ZrO_2/MCM-41	3.5:1	53.68	34.85	16.9	41.03	0	0	4.01	2.38	0.80
ZrO_2–SiO_2	3.5:1	5.33	64.09	0.34	8.42	3.04	0	0	14.62	11.26

[a]The ethanol-to-acetaldehyde feed ratio

[b]The total conversion of ethanol and acetaldehyde

[c]Others mainly consisting of heavier compounds in GC chromatography

also obtained. This may due to its larger pore size which enhances the resistance to coke formation.

4 Conclusions

A series of catalysts based on ZrO_2–SiO_2 have been prepared, characterized and tested for the formation of BD from ethanol and acetaldehyde. The most promising catalyst investigated is ZrO_2/NanoSiO$_2$ with the highest selectivity achieved being 91.43% and the total conversion obtained being 52.39%. The investigation also indicates that the pore sizes are more important factors determining the activity when catalyst contains a subtle balance of the acid and base. These effects of the pore size could be explained by the better accessibility of the reactants and products and the better coke tolerance of the catalysts.

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