Zr-Modified ZnO for the Selective Oxidation of Cinnamaldehyde to Benzaldehyde

Pengju Du 1, Tongming Su 1, Xuan Luo 1, Xinling Xie 1, Zuzeng Qin 1,* and Hongbing Ji 1,2

1 School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China
2 School of Chemistry, Sun Yat-sen University, Guangzhou 510275, China
* Correspondence: qinzuzeng@gxu.edu.cn; Tel.: +86-771-323-3718

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Abstract: ZnO and Zr-modified ZnO were prepared using a precipitation method and used for the selective oxidation of cinnamaldehyde to benzaldehyde in the present study. The results showed that physicochemical properties of ZnO were significantly affected by the calcination temperature, and calcination of ZnO at 400 °C demonstrated the optimum catalytic activity for the selective oxidation of cinnamaldehyde to benzaldehyde. With 0.01 g ZnO calcined at 400 °C for 2 h as a catalyst, 8.0 g ethanol and 2.0 g cinnamaldehyde reacted at an oxygen pressure of 1.0 MPa and 70 °C for 60 min, resulting in benzaldehyde selectivity of 69.2% and cinnamaldehyde conversion of 16.1%. Zr was the optimal modifier for ZnO: when Zr-modified ZnO was used as the catalyst, benzaldehyde selectivity reached 86.2%, and cinnamaldehyde conversion was 17.6%. The X-ray diffractometer and N2 adsorption–desorption characterization indicated that doping with Zr could reduce the crystallite size of ZnO (101) and increase the specific surface area of the catalyst, which provided more active sites for the reaction. X-ray photoelectron spectrometer results showed that Zr-doping could exchange the electrons with ZnO and reduce the electron density in the outer layer of Zn, which would further affect benzaldehyde selectivity. The results of CO2 temperature-programmed desorption showed that Zr-modification enhanced the alkalinity of the catalyst surface, which caused the Zr–ZnO catalyst to exhibit higher catalytic activity.

Keywords: ZnO; cinnamaldehyde; oxidation; benzaldehyde; Zr-modified

1. Introduction

Benzaldehyde is the second most frequently used perfume in the world and is widely used in foods, beverages, medicines, and cosmetics [1–3]. With the increasing demand for benzaldehyde, research regarding the production of benzaldehyde has gained increasing attention from researchers globally [4–8]. In industry, benzaldehyde is obtained by the gas phase oxidation of toluene and air or oxygen on V2O5, WO3, or MnO2 catalysts; by the chlorination of toluene to benzyl chloride under light irradiation, and subsequent hydrolyzation and oxidation; by the chlorination of toluene to dichloromethylbenzene and then hydrolyzation; and by the ozonation of styrene.

On the other hand, natural benzaldehyde is mainly obtained by using amygdalin from bitter almond as the raw material, and the combined process of enzymatic hydrolysis, steam distillation, and caustic washing; 40% of the amount sold on the international market is obtained by this method, with the remaining 60% provided by the biotransformation of microorganisms or natural cinnamon oil conversion. The alkaline hydrolysis of cinnamon oil (whose main component is cinnamaldehyde) is a simple, easily controlled, and environmentally friendly method, and does not require a large amount of equipment; this method has gained increasing attention. In addition, natural benzaldehyde has also been prepared by an emulsifier alkaline hydrolysis method [9,10], β-cyclodextrin catalysis [11,12], and biomimetic catalysis [13]. However, these methods are homogeneous processes, and isolating the
products from the alkaline solution is not only difficult, but also increases the production cost and affects the purity of the benzaldehyde.

In the present study, noble metal catalysts were also used in a benzaldehyde preparation process [14,15]. Although the use of noble metals significantly increases the cost of the catalytic reaction, few reports to date have investigated the combination of oxygen and transition metal oxide catalysts in the catalytic oxidation of cinnamaldehyde. Transition metal oxide is a very common catalyst, exhibiting a good catalytic activity and a lower price [16,17], and has been widely used in the fields of pollutant degradation, air purification, and heterogeneous catalytic processes [18,19]. Compared with TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CuO, and other transition metal oxides, ZnO exhibits higher chemical stability, better biological compatibility, and a larger specific surface area, which shows the potential for use in the catalytic oxidation of cinnamaldehyde to benzaldehyde. Furthermore, some metals or metal oxides, such as Fe [20], Cu [21–23], Ce [24], Ag [25], Al [26], SnO$_2$ [27], and NiO [28,29], have been used to modify or promote ZnO, which significantly increased the catalytic oxidation activity of ZnO. Therefore, ZnO and metal-modified ZnO exhibit the potential for the selective oxidation of cinnamaldehyde to benzaldehyde.

Based on previous studies of the catalytic ozonation of cinnamaldehyde [30,31], in the present work, ZnO and a transition metal-modified ZnO catalyst were prepared and used to catalyze cinnamaldehyde to benzaldehyde, using O$_2$ as an oxidant. The effects of the metal modification on the catalyst structure and activity of ZnO were analyzed by combining various characterization methods and experimental results. The mechanism of the catalytic reaction was studied by gas chromatography (GC), and gas chromatography-mass spectrometry (GC-MS).

2. Results and Discussion

2.1. Catalytic Oxidation of Cinnamaldehyde

The oxidations of cinnamaldehyde to benzaldehyde by catalyzing ZnO, TiO$_2$, CuO, Al$_2$O$_3$, and Fe$_2$O$_3$, and with no catalytic oxidation, are shown in Figure 1A. According to Figure 1A, in the case of no catalytic oxidation, the conversion of cinnamaldehyde and the selectivity of benzaldehyde were 15.6%, and 4.3%, respectively. After adding the catalysts (Fe$_2$O$_3$, CuO, TiO$_2$, Al$_2$O$_3$, and ZnO), the conversion increased to 9.6%, 43.9%, 48.1%, 59.9%, and 16.1%, respectively. At the same time, the benzaldehyde selectivity increased to 12.7%, 10.8%, 25.7%, 22.3%, and 69.2%, respectively. The selectivity order of the catalysts was CuO < Fe$_2$O$_3$ < Al$_2$O$_3$ < TiO$_2$ < ZnO. Therefore, in the following study, ZnO, with the optimal benzaldehyde selectivity, was selected as the catalyst for the selective oxidation of cinnamaldehyde to benzaldehyde.

![Figure 1](image.png)

**Figure 1.** The catalytic oxidation of cinnamaldehyde on metal oxides (A) and transition metal modified ZnO (B). Reaction conditions: 0.01 g ZnO (or other catalysts) calcined at 400 °C for 2 h as a catalyst, 8.0 g ethanol and 2.0 g cinnamaldehyde reacted at an oxygen pressure of 1.0 MPa and 70 °C for 60 min.
Figure 1B shows the catalytic activities of Zr–ZnO, La–ZnO, Ce–ZnO, Co–ZnO, and ZnO catalysts with a 1.0% doping amount of Zr, La, Ce, and Co, respectively. After Zr modification, benzaldehyde selectivity reached the peak selectivity of 86.2% after a 1.0-h reaction, compared to 69.2% benzaldehyde selectivity of ZnO; when ZnO modified by La, Ce, and Co were used as catalysts, cinnamaldehyde conversion was maintained at about 16–17% for the five catalysts, and benzaldehyde selectivity increased to 72.6%, 75.2%, and 80.4%, respectively. Therefore, in the following study, Zr-modified ZnO was further studied.

2.2. Surface Acidity and Surface Alkali

The CO2 temperature programmed desorption (CO2-TPD) profiles of ZnO, La–ZnO, Ce–ZnO, Co–ZnO, and Zr–ZnO are exhibited in Figure 2, and these samples basic strengths are listed in Table 1. In summary, a higher basicity of the adsorption center corresponded to a higher temperature CO2 desorption peak [31]; and the weak, medium, and strong base sites had CO2 desorption peaks at 100–300 °C, 350–550 °C, and >600 °C, respectively [32]. Two obvious CO2 desorption peaks were shown on all samples’ curves, at about 440 °C and 640 °C, which were the medium and the strong base sites, respectively.

![Figure 2. CO2-TPD profiles for transition metal-modified ZnO.](image)

| Catalyst   | Basic Strength * (µmol g⁻¹) | Medium (350–550 °C) | Strong (>600 °C) | Total |
|------------|------------------------------|----------------------|------------------|-------|
| ZnO        | 558                          | 103                  | 637              |
| La–ZnO     | 563                          | 112                  | 660              |
| Ce–ZnO     | 582                          | 123                  | 685              |
| Co–ZnO     | 621                          | 127                  | 704              |
| Zr–ZnO     | 637                          | 134                  | 765              |

* The basic strength was obtained by using an external standard method.

According to the basic strength of transition metal-modified ZnO in Table 1, the total basicity sites of ZnO, La–ZnO, Ce–ZnO, Co–ZnO, and Zr–ZnO were 637, 704, 685, 660, and 765 µmol·g⁻¹, respectively, and the total basicity order was Zr–ZnO > Co–ZnO > Ce–ZnO > La–ZnO > ZnO. The order was identical to the increasing order of benzaldehyde selectivity, proving there was a positive correlation in the catalyst basic strength and its oxidation activity. In these catalysts, Zr–ZnO had the highest benzaldehyde selectivity of 86.2%.

2.3. XRD Analysis

X-ray diffraction (XRD) was used to characterize the crystallinity and composition of ZnO, Zr–ZnO, La–ZnO, Co–ZnO, and Ce–ZnO (both doping amounts were 1.0%) calcined at 400 °C (see Figure 3).
From Figure 3, five ZnO diffraction peaks at 2θ = 31.7°, 37.4°, 34.4°, 36.2°, and 47.5° (Powder diffraction file (PDF) card NO. 36–1451) [33] were found in all samples. However, there were no obvious diffraction peaks of the transition metals of Zr, La, Co, or Ce in the patterns, which could be because the doping amount was outside of the detection range of the instrument, or because Zr, La, Co, or Ce were distributed in the ZnO catalyst in an amorphous state [34,35]. Calculated by the Scherrer equation [36], the crystallite sizes of the ZnO (101) of the Zr–ZnO, Co–ZnO, Ce–ZnO, La–ZnO, and ZnO were 166.2, 178.4, 185.1, 209.3, and 220.8 nm, respectively. A smaller crystallite size indicated lower crystallinity [37,38], and the data of the crystallite size of Zr–ZnO indicated an increase in pore volume and specific surface area, which would be more favorable to the reaction [39].

![Figure 3. XRD patterns of ZnO catalyst modified by transition metal.](image)

2.4. N$_2$ Adsorption–Desorption Analysis

The surface area, pore size distribution and the textural properties of the ZnO catalyst modified by transition metal were obtained using N$_2$ adsorption–desorption and are shown in Figure 4. According to Figure 4A, the isotherms matched Type III isotherms on the basis of the International Union of Pure and Applied Chemistry (IUPAC) classification [40]. The adsorption capacity of N$_2$ was proportional to the relative pressure in the range of $P/P^o = 0–0.7$, which was the low-pressure region. This phenomenon indicated that the adsorption of N$_2$ on the ZnO surface changed from single layer to multilayer [41]. In the high-pressure region ($P/P^o = 0.7–1.0$), an H3 type hysteresis loop was produced by capillary condensation [42], indicating slit-shaped pores (Figure 4A). From Figure 4B, the pore sizes of the five samples were 50–100 nm, and the pore size of Zr–ZnO was the smallest.

![Figure 4. N$_2$ adsorption–desorption isotherm (A) and pore size distribution (B) of ZnO catalyst modified by transition metal.](image)

The specific surface area, average pore size, and pore volume of ZnO modified by transition metal were calculated using the isothermal adsorption–desorption data and are shown in Table 2. The Brunauer–Emmett–Teller (BET) surface areas of Zr–ZnO, Co–ZnO, Ce–ZnO, La–ZnO, and ZnO were...
6.231, 5.831, 5.423, 4.651, and 4.023 m²·g⁻¹, respectively. The same change in pore volume was also found. These results indicate that modification of the transition metals, Zr, Co, Ce, and La, can increase the specific surface area and pore volume of the catalyst. Notably, the surface area of Zr–ZnO was the largest. For industrial applications of the catalyst, increased specific surface area and pore volume indicate more active sites, which are conducive to the catalytic oxidation of cinnamaldehyde [43] and explain why Zr has optimal catalytic activity.

Table 2. Textural properties of ZnO catalyst modified by transition metal.

| Catalysts | BET Surface Area (m²·g⁻¹) | Average Pore Diameter (nm) | Pore Volume (cm³·g⁻¹) |
|------------|-----------------------------|---------------------------|------------------------|
| ZnO        | 4.023                       | 29.6                      | 0.362                  |
| La-ZnO     | 4.651                       | 28.5                      | 0.442                  |
| Ce-ZnO     | 5.423                       | 26.3                      | 0.541                  |
| Co-ZnO     | 5.831                       | 22.1                      | 0.632                  |
| Zr-ZnO     | 6.231                       | 20.4                      | 0.724                  |

2.5. XPS Analysis

X-ray photoelectron spectrum (XPS) analysis was carried out to identify the chemical states of the surface elements of pure ZnO and Zr–ZnO; the results are shown in Figure 5 and Table 3.

Figure 5. XPS profile of Zn 2p (A), O 1s (B), and Zr 3d (C) in the ZnO and Zr–ZnO catalysts.

In ZnO, the peaks centered at approximately 1020.79 and 1043.86 eV correspond to Zn 2p 3/2 and Zn 2p 1/2 [44], respectively. For the Zn 2p spectrum of Zr–ZnO, the peaks centered at 1020.95 and 1044.04 eV are attributed to Zn 2p3/2 and Zn 2p1/2, respectively, indicating that Zn existed in the form of Zn²⁺ on the surface of the catalyst. In ZnO and Zr–ZnO, the peaks centered at approximately 529.60 and 531.18 eV correspond to O 1s, which corresponded to the O 1s characteristic peaks in the band of Zn–O–Zn and the oxygen in the hydroxyl group on the catalysts surface, respectively [45]. In the O 1s spectrum of Zr–ZnO, there was a third peak, centered at 530.25 eV, which corresponded to the O 1s characteristic peaks in the band of O–Zr–O [46]. In the Zr 3d spectrum, the peaks centered at 181.80 and 184.20 eV were attributed to Zr 3d⁵/₂ and Zr 3d₃/₂, respectively, indicating that Zr existed in ZnO in the form of Zr⁴⁺ [47].

From the above data, there were 0.02 and 0.01 eV blueshifts at 529.62 and 531.19 eV of O 1s in the spectra of Zr–ZnO in comparison with pure ZnO. There were also 0.16 and 0.18 eV blueshifts of Zr–ZnO relative to the Zn 2p characteristic peaks of pure ZnO. These results indicate that Zr can exchange electrons with ZnO and reduce the electron density of the Zn outer layer, resulting in minor changes in the chemical state of ZnO, thereby resulting in a blueshift of the binding energy of Zn elements [48], and thus affecting the catalytic performance of selective oxidation of cinnamaldehyde to benzaldehyde. Therefore, the Zr–ZnO catalyst exhibited high activity in the catalytic oxidation of cinnamaldehyde.
Table 3. The electron binding energy (BE) of the ZnO and Zr–ZnO catalysts.

| XPS Spectra | Element        | BE (eV)  |
|-------------|----------------|----------|
|             | O 1s           | ZnO 529.60 | Zr-ZnO 529.62 |
|             | O 2s           | ZnO 531.18 | Zr-ZnO 530.25 |
|             | O 3s           | ZnO 531.19 | Zr-ZnO 531.19 |
| Zn 2p       | Zn Zn Zn 5p 3/2 | ZnO 1020.79 | Zr-ZnO 1020.95 |
| Zr 3d       | Zr Zr 3d 3/2   | ZnO 1043.86 | Zr-ZnO 1044.04 |

2.6. Deactivation and Regeneration of Zr–ZnO

Stability is one of the most important features of a solid catalyst in the catalytic process. In the present study, the Zr–ZnO catalyst was treated with several different recovery methods after a catalytic oxidation round, including: (A) filtration and washing with methanol and ethanol several times to remove the adsorbed material from the Zr–ZnO catalyst surface, and desiccation at 110 °C for 12 h; (B) desiccation at 110 °C for 12 h and calcination at 400 °C for 2 h only; (C) no treatment. The catalytic stability of Zr–ZnO in cinnamaldehyde oxidation regenerated by the different methods is shown in Figure 6.

In Figure 6A, cinnamaldehyde conversion decreased slightly from 16.2% to 11.5% after the first five cycles, indicating that the Zr–ZnO catalyst still had good activity for cinnamaldehyde conversion; however, benzaldehyde selectivity decreased significantly, by almost 16.9%, from 69.2% to 52.3%. Using method B (Figure 6B), both conversion and selectivity was stable in the first five cycles, indicating that calcination was able to maintain the catalytic activity. Finally, after directly using catalysts without any treatment (Figure 6C), benzaldehyde selectivity decreased from 69.2% to 48.5%, representing a nearly 20.7% decrease of benzaldehyde selectivity, indicating that without treatment the catalytic activity decreased rapidly. However, for the Zr–ZnO used in four cycles and treated by method C, activity increased to almost that of the fresh catalyst level after high-temperature calcination (at 400 °C for 2 h). Interestingly, the used catalyst showed a pale-yellow color before the treatment, which indicated that the adsorption of an organic substance was the major reason for the deactivation of the catalyst.

![Figure 6](image-url)

**Figure 6.** Recyclability data of the Zr–ZnO catalyst for cinnamaldehyde oxidation ((A) filtration, washing, and desiccation; (B) desiccation and calcination; (C) no treatment). Reaction conditions: 0.01 g Zr–ZnO, 8.0 g ethanol and 2.0 g cinnamaldehyde reacted at an oxygen pressure of 1.0 MPa and 70 °C for 60 min.

Thermal analysis, i.e., thermal gravity- differential thermal gravity (TG-DTG) and FT-IR were used to investigate the reason for the decease of benzaldehyde selectivity. After the fourth cycle, the Zr–ZnO catalyst was washed with methanol and ethanol, followed by analysis. The used and fresh Zr–ZnO catalyst data are compared in Figures 7 and S2.
which is a double bond type- and location-dependent process \[47\]. In the present study, cinnamaldehyde (VII), also yields benzoin ethyl ether and triethyl orthoformate (process G). However, ethyl benzoate is a trans-styrene aldehyde in which the aldehyde group with the electron-withdrawing electron is on the C=C double bonds \[55,56\], therefore, according to the above discussion, the mechanism of the cinnamaldehyde oxidation as proposed is shown in Figure 8.

Firstly, the cinnamaldehyde is adsorbed on the Zr–ZnO catalyst surface, and, at the same time, the oxygen attacks the C=C bond to yield the unstable oxide (II) (process A), which rapidly decomposes to produce the carbonyl compound (III, IV) and carbonyl oxide (VI, V) (shown as process B) \[57\]. If no participating solvents exist, the carbonyl compounds (III) and (IV) [or carbonyl oxide (V) and (VI)] can recombine and form the 1, 2-trioxolanes (VII) (process C). Decomposition of the oxide, 1, 2-trioxolanes (VII), also yields benzoic acid, ethyl benzoate, and benzoin ethyl ether. Ethyl benzoate or benzoic acid, respectively, which were absorbed on the Zr–ZnO surface \[50–52\]. Compared with the FT-IR spectra of the fresh and used Zr–ZnO, these substances might have covered some of the catalyst’s active sites and caused a selectivity reduction.

Moreover, Figure S2 shows three weight loss stages at 179, 212, and 249 °C for the used Zr–ZnO catalyst, which corresponded to the decomposition of benzaldehyde, ethyl benzoate, and benzoic acid, respectively. Overall, this proved that some organic components covered the surface of Zr–ZnO catalysts after four cycles, which could explain the decrease of the ZnO catalyst activity.

2.7. Proposed Reaction Mechanisms

To investigate the reaction mechanism, the reaction products were analyzed by GC-MS and GC, and results of the intermediate species are shown in Table S1. The intermediate species included benzaldehyde, ethyl benzoate, benzoic acid, and triethyl orthoformate, as well as benzoin ethyl ether. In the present process, the catalytic oxidation of cinnamaldehyde would be in a pathway of oxygen–olefin reaction in the liquid phase \[53,54\]. Radical production from oxygen–olefin reactions is either a slower independent process or due to a very small yield of radicals “leaking” from the oxidation process. In general, unsaturated oil oxidation causes the formation of significant amounts of other products, which is a double bond type- and location-dependent process \[47\]. In the present study, cinnamaldehyde is a trans-styrene aldehyde in which the aldehyde group with the electron-withdrawing electron is on the C=C double bonds \[55,56\], therefore, according to the above discussion, the mechanism of the cinnamaldehyde oxidation as proposed is shown in Figure 8.

Figure 7. FT-IR of calcined treated Zr–ZnO (a), and Zr–ZnO before use (b) and after being used five times (c).

After four cycles, the surface groups on the Zr–ZnO catalyst exhibited significant change, as shown in Figure 7: water was found on the Zr–ZnO surface due to the 3700–3050 cm⁻¹ broad peak and the 1650 cm⁻¹ peak \[49\]. The peaks at 3000–2750 cm⁻¹, 1250–1000 cm⁻¹, and 800–600 cm⁻¹ were assigned to the function groups –CH, –CH₂, –C=O, –C–O, and –C=O, of cinnamaldehyde, benzaldehyde or ethyl benzoate, respectively, which were absorbed on the Zr–ZnO surface \[50–52\]. Compared with the FT-IR spectra of the fresh and used Zr–ZnO, these substances might have covered some of the catalyst’s active sites and caused a selectivity reduction.

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which is not surprising as the O\(_2\) also oxidized the aldehydes to carboxylic acids [58]. Furthermore, with the increase of the reaction time, benzoic acid can be oxidized by the excess benzaldehyde (process F).

![Chemical Mechanism Diagram](Image)

**Figure 8.** Suggested oxidation mechanism of cinnamaldehyde with O\(_2\).

### 3. Materials and Methods

#### 3.1. Catalyst Preparation

The ZnO catalysts were prepared via a precipitation method. Typically, 1.2 mol·L\(^{-1}\) Na\(_2\)CO\(_3\) water solution was added drop by drop to a 200 mL 0.4 mol·L\(^{-1}\) Zn(NO\(_3\))\(_2\) water solution at 200 rpm until the solution pH value reached 9 and a white precipitate was obtained. After filtration, the precipitate was dried at 90 °C for 12 h and calcined at 400 °C for 2 h to have ZnO. Fe\(_2\)O\(_3\), Al\(_2\)O\(_3\), and CuO were prepared by a similar method.

Modification treatment: nitrates of transition metals were used as raw material. Five different nitrates were weighed according to 0.5%, 1%, and 2% of the mole amount of each transition metal element of Zn and then added into the prepared 0.40 mol·L\(^{-1}\) Zn(NO\(_3\))\(_2\) solution. The catalysts were Zr–ZnO, Co–ZnO, Ce–ZnO, and La–ZnO.

#### 3.2. Characterization of the Catalysts

X-ray diffraction (XRD) analysis was carried on a D8 Advance X-ray diffractometer (Bruker Karlsruhe, Germany). A NOVA 2200e physical adsorption instrument (Quantachrome Corp., Boynton Beach, USA) was used in N\(_2\) adsorption–desorption. The Brunauer–Emmett–Teller (BET) and Barret–Joyner–Halenda (BJH) methods were used to calculate the specific surface areas and the pore size distributions. A Thermo ESCALAB 250X multifunction imaging electron spectrometer (Thermo Fisher Scientific, Waltham, USA) was used to obtain the X-ray photoelectron spectrum (XPS) of catalysts, using the Al K\(_\alpha\) ray as the X-ray source. Thermal analysis (TG-DTA) was performed using an STA-449-F5 thermal analyzer (Netzsch Co. Ltd., Deutschland, Germany). Fourier transform infrared (FT-IR) spectra were measured on a Nexus 470 Fourier transform spectrometer (Thermo Nicolet, Waltham, USA).
3.3. Catalytic Oxidation of Cinnamaldehyde

The catalytic oxidation of cinnamaldehyde to benzaldehyde was reacted in a high-pressure tank reactor, as shown in Figure S1. During the ZnO-catalyzed oxidation cinnamaldehyde experiments, 2.00 g cinnamaldehyde and 8.00 g ethanol were mixed together in the reactor (40 mm diameter, 75 mm tube length), and 0.01 g ZnO was added. The gas atmosphere in the reactor was replaced with oxygen 7 times; subsequently, the oxygen pressure was adjusted to 1.0 MPa, and the cinnamaldehyde mixture was maintained at 70 °C. When using other catalysts, the reaction conditions were the same as for using ZnO as the catalyst. After the reaction, the products were quantitatively analyzed by GC Smart (GC-2018) gas chromatography (Shimadzu Corporation, Suzhou, China), using dichlorobenzene as the internal standard. To identify the composition of the products, a GC7820-MS GC-MS (Agilent Technologies, Santa Clara, USA) was used.

4. Conclusions

ZnO and metal-modified ZnO were prepared and the catalytic oxidation of cinnamaldehyde on ZnO-based catalysts was studied in this paper. Zr–ZnO calcined at 400 °C for 2 h appeared to exhibit better structural and textural properties for cinnamaldehyde oxidation. Under optimal reaction conditions, namely, 0.01 g Zr–ZnO catalyst, oxygen pressure of 1.0 MPa, and reaction at 70 °C for 1.0 h, cinnamaldehyde conversion and benzaldehyde yield reached 17.6% and 86.2%, respectively. The catalyst characterization results indicated that: doping with Zr could reduce the grain size of ZnO and increase the specific surface area of the catalyst, which provided more active sites for the reaction; Zr-doping could exchange electrons with ZnO and reduce the electron density in the outer layer of Zn, which would further affect benzaldehyde selectivity; and Zr-modified ZnO enhanced the alkalinity of the catalyst surface, which caused the Zr–ZnO catalyst to exhibit higher catalytic activity. Compared with other research, the present study provided higher benzaldehyde selectivity under significantly milder conditions.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/9/716/s1, Figure S1: Schematic diagram of the reaction equipment, Figure S2: TG-DTG curves of Zr-ZnO catalyst after being fourth used, Table S1: Intermediates detected during catalytic oxidation of cinnamaldehyde.

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