A Novel High-Activity Zn-Co Catalyst for Acetylene Acetoxylation

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Abstract: In this paper, $Zn(OAc)_2/AC$ and Zn-Co/AC catalysts were prepared and applied in an acetylene acetoxylation reaction. Compared with monometallic $Zn(OAc)_2/AC$ catalyst, which is widely applied in industry, the Zn-Co catalysts exhibited excellent catalytic performance. Transmission electron microscopy results displayed that the addition of cobalt improved the dispersity of zinc acetate particles and inhibited catalyst sintering on the catalyst surface. X-ray photoelectron spectra suggested that the Co additive changed the electron density of zinc acetate probably because of the interaction between Zn and Co species. Temperature programmed desorption analysis demonstrated Co additive strengthened the adsorption of acetic acid and weakened the adsorption of acetylene.

Keywords: acetylene acetoxylation; $Zn(OAc)_2$ catalyst; cobalt

1. Introduction

Vinyl acetate monomer (VAM) production is one of the 50 largest among chemical raw materials in the world, mainly used in the production of polyvinyl acetate, polyvinyl alcohol, acetal resin, etc. [1–3]. It has been widely used in coatings, synthetic fibers, leather processing, soil improvement and other fields. Nowadays, the ethylene method and the acetylene method are the two routes used in the synthesis of vinyl acetate in industry [4,5].The reaction equation of the ethylene method is [5]:

$$C_2H_4 + CH_3COOH + 0.5O_2 \overset{Pd/Au}{\rightarrow} CH_2CHCOOCH_3 + H_2O \tag{1}$$
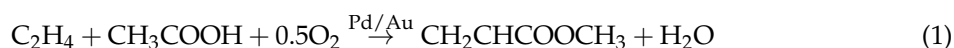
The acetylene method is characterized by the reaction of C_2H_2 with HAc via an acetylene acetoxylation reaction [4]:

$$C_2H_2 + CH_3COOH \overset{Zn/AC}{\rightarrow} CH_2CHCOOCH_3 \tag{2}$$

The increasing shortage of petroleum resources and the instability of oil prices make the acetylene method more economical in China where coal resources are abundant [6]. The catalyst ($Zn(OAc)_2/AC$) for acetylene acetoxylation has a number of shortcomings, such as poor mechanical strength, quickly decreasing activity, low production capacity, short catalyst life, and so on. In order to realize high efficiency production of vinyl acetate, it is very necessary to develop a new catalyst with high activity, high strength and a long life.

In the early years, zinc acetate catalysts had been studied in depth for the acetylene acetoxylation reaction. Researchers carried out much research on the reaction mechanism and kinetics of acetylene acetoxylation [7–11]. Miyazawa et al. [12] investigated multi-metallic oxidesas an active ingredient of the catalyst. The above catalyst showed a higher activity than the monometallic $Zn(OAc)_2$/AC catalysts at 250 °C; the feed HAc–C_2H_2 molar ratio was one; C_2H_2 hourly space velocity (GHSV) = 1700 h^{-1}; and it could still maintain the basic initial activity after 100 h^{-1}. However, those catalysts failed to achieve industrialization because of the tough reaction conditions. Zinc acetate is considered to be the best catalyst active ingredient when taking into account product quality and environmental and economic factors.

The nature of the catalyst carrier has an important impact on the catalytic activity [13]. Russian scientists [14–16] studied the relationship between the optimal load of active ingredient and the carrier after oxidation treatment, which was one of the main factors that affected the catalytic activity. Hou et al. [17] developed a novel catalyst, which used activated carbon after oxidation treatment as the support. Hou et al. thought that the reason for the promotion of catalyst was the increase in the number of oxygenated functional groups in the carrier. Yan et al. [18] chose porous carbon spheres (PSC) instead of AC as the carrier of zinc acetate, because the PSC carrier has an excellent abrasive resistance, special pore structure and large specific surface area. The yield of synthetic vinyl acetate exceeded 1000 g mol^{-1} h^{-1}. Dai et al. [19] developed a new high performance catalyst by using nitrogen-doped activated carbon as the catalyst carrier. The activity of the modified catalyst was greatly improved under the same conditions.

Co was selected as a promoter in bimetallic Zn-Co catalyst for the thermal decomposition of hexamethylene-1,6-dicarbamate to hexamethylene-1,6-diisocyanate, which had a positive effect on the acidic sites, thus improving the catalytic performance [20]. The Zn-Co catalyst also exhibited a good performance for the selective catalytic reduction of NO_X by methane because the interaction between Zn and Co largely inhibited the combustion of methane and increased its utilization [21]. Therefore, we selected Co as the secondary metal to prepare a new type of bimetallic Zn-Co/AC catalyst and to evaluate the catalytic activity and stability of all catalysts in a fixed bed reactor.

2. Results and Discussion

2.1. Catalytic Performance

The catalytic activity of Zn-Co/AC catalysts was assessed for acetylene acetoxylation under a reaction condition (reaction temperature = 220 °C, C_2H_2 hourly space velocity (GHSV) = 500 h^{-1}, feed molar ratio C_2H_2(g)/CH_3COOH(g) = 3). As shown in Figure 1, $Co(OAc)_2$/AC has a small amount of catalytic activity. The monometallic $Zn(OAc)_2$ catalyst showed a starting HAc conversion of 1.26%, which increased to 19.9% after 5 h. It was worth noting that $Zn(OAc)_2$/AC had a low initial conversion. After adding the Co additive, the Zn1Co0.1/AC catalyst gave a better initial activity than $Zn(OAc)_2$/AC, and its CH_3COOH conversion reached 25.3% after 5 h. With the increase of Co loading, the performance of the Zn-Co/AC catalysts increased little by little. The Zn1Co0.3/AC exhibited the highest catalytic activity; its CH_3COOH conversion reached 30.0%. However, further addition of Co loading decreased the catalytic activity. The HAc conversion of Zn1Co0.5/AC catalyst was 25.5% after 5 h. The addition of Co to the $Zn(OAc)_2$/AC can improve the catalytic performance with a proper Zn/Co molar ratio.
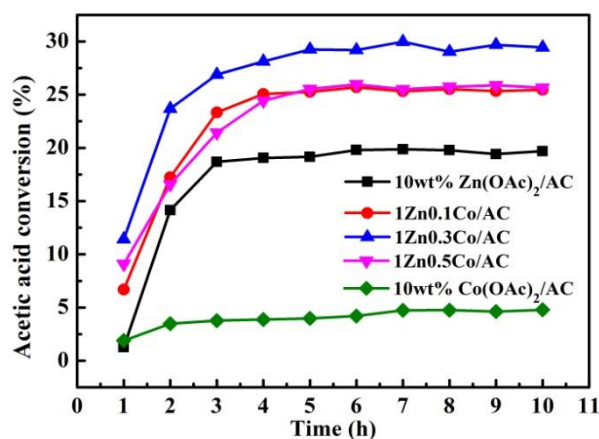
Figure 1. Conversion of HAc on the Zn-Co catalysts.

2.2. Catalyst Texture Properties

Table 1 lists the pore structure information of the fresh catalysts. After loading $Co(OAc)_2$ and $Zn(OAc)_2$, the BET surface area and total pore volume decreased because these components filled a part of the pores in the support. When the amount of $Co(OAc)_2$ was gradually increased, BET surface area and total pore volume decreased more obviously. Specifically, the BET surface area and total pore volumes of Zn-Co/AC decreased from 774.9–473.1 m^2/g and 0.41–0.25 m^2/g after modification as the Co species increased. This phenomenon indirectly indicated the successful preparation of Zn-Co catalysts. The TEM elemental mapping images of Zn and Zn1Co0.3 catalysts also confirmed this (Figure 2).

Table 1. The textural information of the catalysts.

Samples	S_{BET} ($m^2 \cdot g^{-1}$)	V ($cm^3 \cdot g^{-1}$)	D (nm)
AC	1134.4	0.61	2.16
$Zn(OAc)_2$/AC	929.9	0.50	2.17
Zn1Co0.1/AC	774.9	0.41	2.12
Zn1Co0.3/AC	690.4	0.37	2.12
Zn1Co0.5/AC	570.5	0.31	2.12
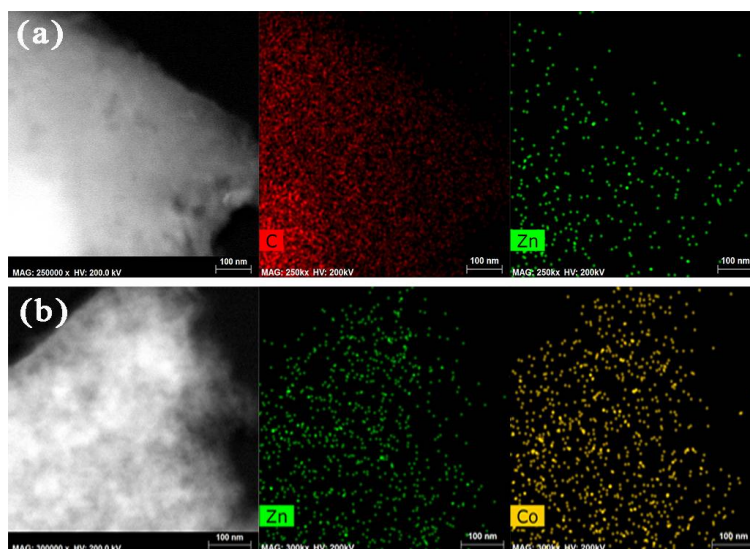
Figure 2. TEM-mapping images of fresh catalysts: $Zn(OAc)_2$/AC (**a**) and Zn1Co0.3/AC (**b**).

2.3. Effect of Co on the Zinc Catalyst before the Reaction

Temperature-programmed desorption experiments of the catalysts were carried out to investigate the adsorption of reactants [22]. In Figure 3a, the desorption temperature of acetylene is located at approximately 473 °C for $Zn(OAc)_2/AC$. For the bimetallic Zn1Co0.3/AC catalyst, the peak position of acetylene is 460 °C. There is a notable decline in the acetylene desorption area. That is to say, the C_2H_2 on the Zn1Co0.3/AC catalysts can be desorbed easily, and the Co additive can weaken the C_2H_2 adsorption on the Zn1Co0.3/AC catalyst. In Figure 3b, the acetic acid desorption temperatures of Zn1Co0.3/AC and $Zn(OAc)_2/AC$ are about 198 °C, 334 °C and 198 °C, 304 °C. Meanwhile, Zn1Co0.3/AC has a larger desorption peak area than that of the $Zn(OAc)_2/AC$ catalyst. Our previous work shows that the excessive acetylene adsorption is one of the important reasons for catalyst deactivation [19]. The TPD results suggested that the addition of Co weakened the adsorption of C_2H_2, but greatly enhanced the adsorption of HAc, thereby enhancing the catalytic performance of the catalysts.
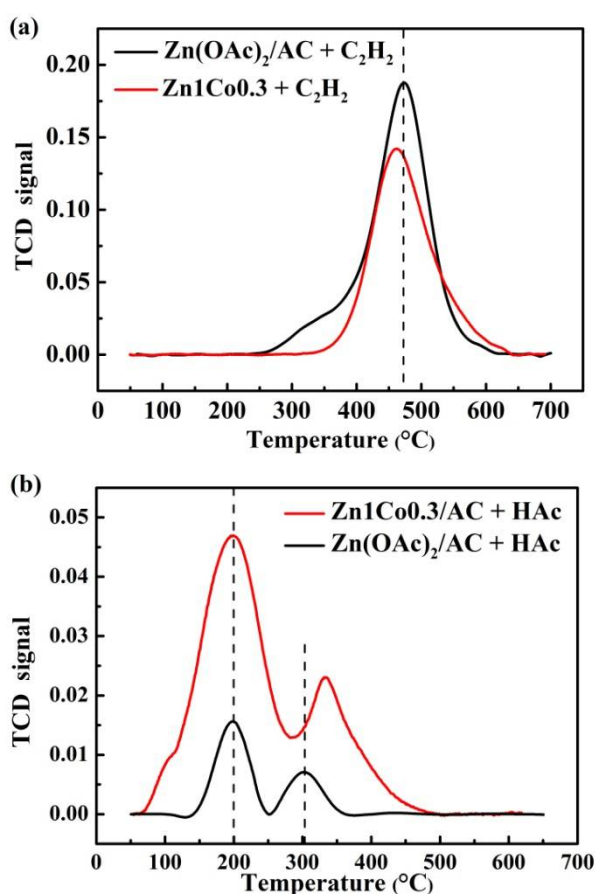

Figure 3. Temperature-programmed desorption profiles of fresh Zn1Co0.3/AC and $Zn(OAc)_2/AC$ with C_2H_2 (**a**) and HAc (**b**).

To further study the interaction between Zn and Co, the chemical composition of the catalysts was investigated by XPS. In Figure 4a, the C 1s, O 1s and Zn 2p signals can be seen from the XPS spectrum of the $Zn(OAc)_2/AC$ and Zn1Co0.3/AC catalysts, proving the existence of C, O and Zn. Moreover, a Co 2p signal was observed from the Zn1Co0.3/AC catalyst, indicating that the Co additives were successfully doped into the Zn catalyst. Figure 4b shows the XPS spectra of Zn 2p for the catalysts. We can clearly see that the peak positions of Zn 2p3/2 and 2p1/2 in the Zn/AC catalyst at 1022.3 eV and 1045.3 eV are in agreement with zinc acetate [23]. When Co is incorporated into the $Zn(OAc)_2/AC$, the binding energies of Zn 2p3/2 and 2p1/2 shift from 1022.3 eV, 1045.3 eV to 1021.8 eV, 1044.9 eV.

To further explore the effect of Co additive, the Co 2p peaks of the fresh Zn1Co0.3/AC were obtained. In Figure 4c, the XPS spectra of Co 2p provide two main peaks. The Co 2p3/2 and 2p1/2 peaks were located around 781.2 eV and 796.6 eV. However, compared with the standard binding energies of Co 2p3/2 (779.6 eV) and 2p1/2 (796.0 eV) [24], this shifted to a higher binding energy. The observed shift from Zn 2p and Co 2p strongly demonstrated that the electron density of the $Zn(OAc)_2$ active center was enhanced, while that of the $Co(OAc)_2$ was weakened [25]. Figure 4d shows the XPS spectra of O 1s for the catalysts. The binding energy of O 1s was 532.0 eV for the Zn/AC catalyst, which is close to the standard reference value of oxygen group in zinc acetate [23]. There was also a noticeable shift in the O 1s binding energy after adding $Co(OAc)_2$, indicating that the collaborative effect between Zn and Co changed the electronic properties of the oxygen groups. The surface of the catalyst can significantly tune the interactions between the catalyst surface and the reactants, changing the adsorption of the reactant [26]. As a result, an improved catalytic performance was obtained.
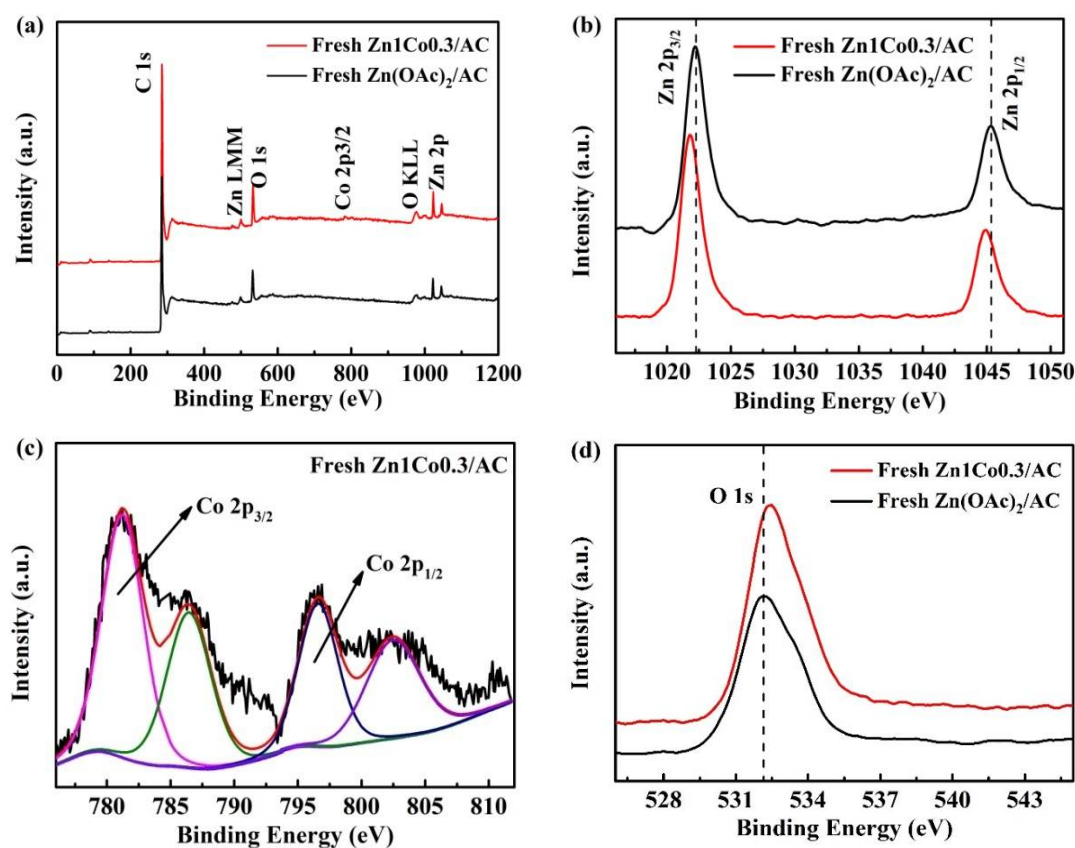

Figure 4. XPS spectra of fresh Zn1Co0.3/AC and $Zn(OAc)_2$/AC catalysts: (**a**) wide XPS survey spectra; (**b**) XPS spectrum of the Zn 2p region; (**c**) XPS spectrum of the Co 2p region for Zn1Co0.3/AC catalyst; (**d**) XPSspectrum of theO 1s region.

2.4. Catalytic Stability of the Zn-Co Catalysts

The stability of the catalyst is one of the most important aspects of its performance evaluation. Therefore, we tested its stability at the same reaction conditions. The Zn1Co0.3/AC showed a high initial conversion, and acetic acid conversion reached a maximum value of 30.0% within 5 h (Figure 5). After 120 h of reaction, the HAc conversion of Zn1Co0.3/AC was still 22.1%, while the Zn/AC catalyst decreased gradually to 11.9%. This result suggested that the bimetallic Zn1Co0.3/AC catalyst could maintain high catalytic activity for 120 h.
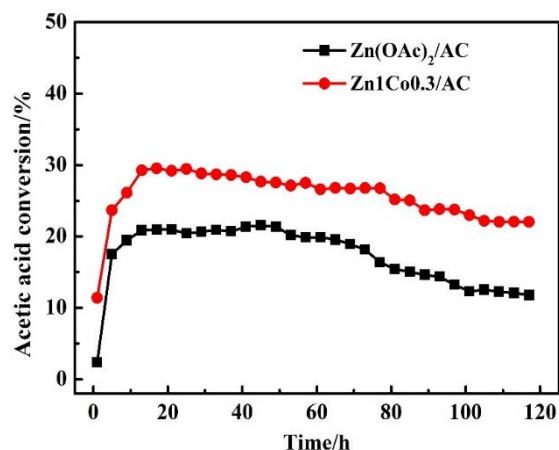
Figure 5. Stability evaluation of the Zn1Co0.3/AC and Zn(OAc)$_2$/AC catalysts.

2.5. Effect of Co on the Zinc Catalyst during the Reaction

The TEM images of fresh and used catalysts are shown in Figure 6, and as the images show, the fresh Zn(OAc)$_2$/AC and Zn1Co0.3/AC catalysts have average particle sizes around 2.6 ± 0.1 nm and 2.4 ± 0.1 nm, respectively. After 120 h of reaction, the average particle sizes had grown to about 4.9 ± 0.1 nm and 3.6 ± 0.1 nm (Figure 6b,d). This indicated that the addition of Co could separate the Zn particles to a certain extent, resulting in increased particle dispersity. Thus, the growth of the catalyst particles was suppressed during acetylene acetoxylation.
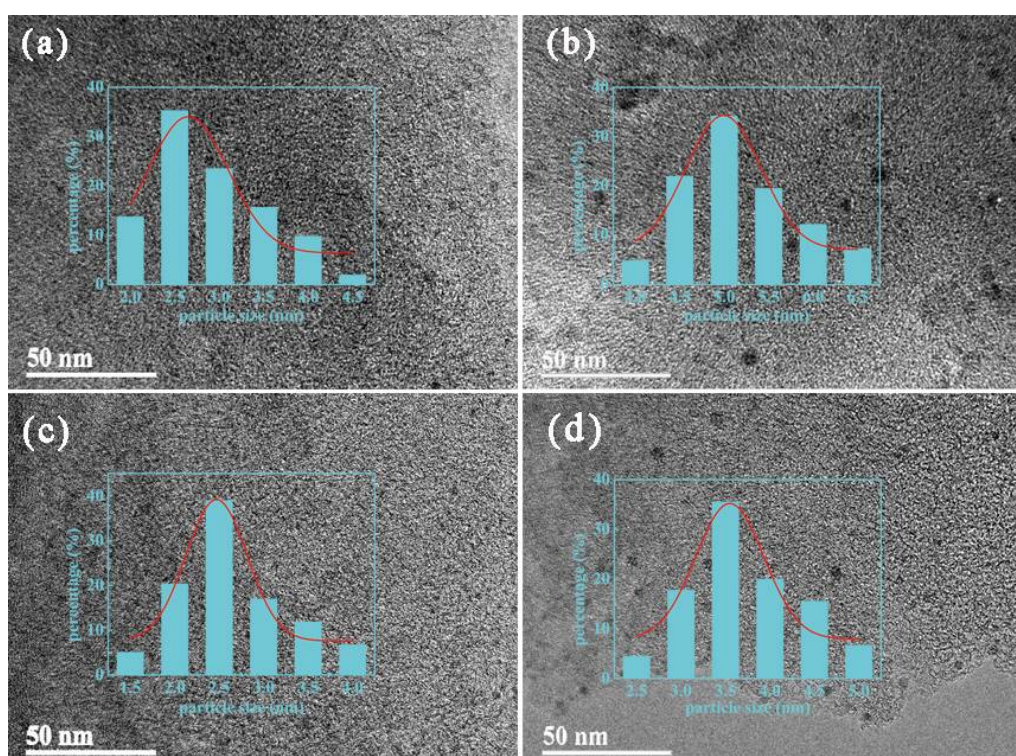

Figure 6. TEM images of fresh and used catalysts for Zn/AC (**a**,**b**) and Zn1Co0.3/AC (**c**,**d**).

Figure 7 shows the TGA analysis used to study the amount of carbon deposition of the catalysts. The amount of carbon deposition for the Zn(OAc)$_2$/AC catalyst was 23.8%, which was counted by calculating the weight loss of the catalyst between 275 and 448 °C before and after acetylene

acetoxylation [27]. The amount of coke deposition for Zn1Co0.3/AC catalyst in the range of 275–416 °C was 13.7%. It is obvious that Zn1Co0.3/AC had a significant anti-carbon deposition capacity. It was ascribed to the Co additive contributing to the diffusion and transfer of the reaction and product.
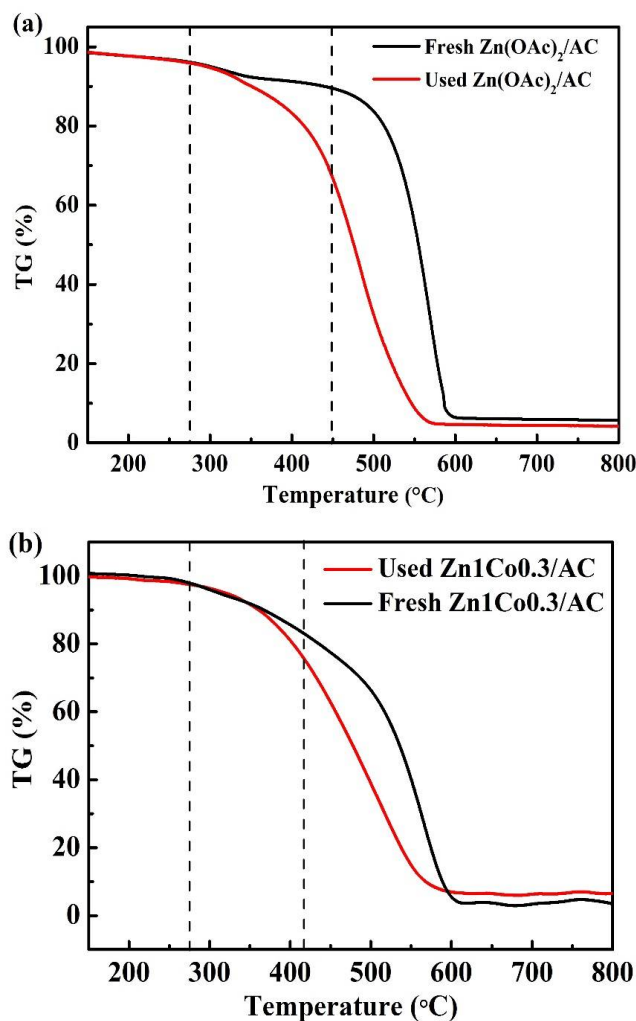

Figure 7. TG curves of fresh and used $Zn(OAc)_2$/AC (**a**) and Zn1Co0.3/AC (**b**) catalysts.

3. Materials and Methods

3.1. Materials

AC (pH = 6–8, coconut carbon); $Zn(OAc)_2 \cdot 2H_2O$ (99.8%, Aldrich, Saint Louis, MO, USA); $Co(OAc)_2 \cdot 4H_2O$ (99.8%, Aldrich); C_2H_2 (gas, 99%); CH_3COOH (acetic acid liquid, 99%).

3.2. Catalysts Preparation

Activated carbon was cleaned with ultrapure water and dried at 120 °C. We used the incipient wetness impregnation method to prepare bimetallic Zn-Co/AC catalysts. A certain amount of $Zn(OAc)_2 \cdot 2H_2O$ and $Co(OAc)_2 \cdot 4H_2O$ was dissolved in 3 mL ultrapure water, and then 2 g activated carbon was impregnated in the solution and stirred for 24 h at 25 °C. The mixture was dried at 80 °C for 10 h. The amount of zinc acetate in these catalysts was fixed at 10 wt %. The Zn-Co/AC catalysts were named as Zn1Co0.1/AC, Zn1Co0.3/AC and Zn1Co0.5/AC with different Zn/Co molar ratios. The same method was also used to prepare $Zn(OAc)_2$/AC and $Co(OAc)_2$/AC. The loading of active component was also 10 wt %.

3.3. Catalysts Characterization

Pore structure information was gathered by a Micromeritics ASAP 2460 apparatus (Micromeritics Instrument Ltd., Norcross, GA, USA),degassing for 4 h at 250 °C, then analyzed with liquid nitrogen adsorption at −196 °C. XPS characterizations were conducted under an ultrahigh vacuum using a Kratos AXIS Ultra DLD spectrometer (Kratos, Manchester, UK). Temperature-programmed desorption measurements were carried out using a Micromeritic Chemisorb 2720 apparatus (Micromeritics Instrument Ltd., Norcross, GA, USA) equipped with a TCD detector. The catalysts were pretreated at the reaction temperature (220 °C) for 10 h under acetylene and acetic acid atmosphere, respectively. Then, the sample was heated at the rate of 10 °C/min from 25–850 °C to collect the data. TEM spectrograms were collected with a JEOL 2011 microscope (FEI, Hillsboro, OR, USA) operated at 200 kV. Samples were prepared by dispersing the catalyst powder in high-purity ethanol, then allowing a drop of the suspension to evaporate on a holey carbon film supported by a copper TEM grid. Thermogravimetric analysis (TGA) was carried out on a Netzsch STA-449 F3 Jupiter (NETZSCH STA 449F3 Jupiter1, Netzsch, Selb, Germany) analyzer in a nitrogen atmosphere. The temperature was increased from50–850 °C at a heating rate of 10 °C min^{-1}.

3.4. Catalysts Activity and Stability

The catalytic performance evaluation for acetylene acetoxylation was carried out in a stainless steel micro-reactor (i.d. of 10 mm). A small amount of catalyst was filled in a reactor. The flow of acetylene and acetic acid was controlled by a mass flowmeter and peristaltic pump. Acetic acid was mixed with acetylene gas entering the reactor after being vaporized by a preheat oven. The gas hourly space velocity (C_2H_2) was 500 h^{-1} and a reaction temperature 220 °C. The reaction products were analyzed by gas chromatography (GC-9A). The temperature of the reactor and preheat oven were regulated by a CKW-1100 temperature controller produced by (Beijing, China). The catalysts were characterized by TEM, BET, XPS and TPD techniques.

Theconversion of HAc (X_A) and the selectivity to VAc (S_{VAc}) were calculated as follows:

$$X_A = \frac{\Phi_{A1} - \Phi_{A2}}{\Phi_{A1}} \times 100\% \tag{3}$$

$$S_{VAc} = \frac{\Phi_{VAc}}{(1 - \Phi_{VAc})} \times 100\% \tag{4}$$

In the equations, Φ_{A1} is the mass fraction of C_2H_2 in the raw gas, Φ_{A2} is the mass fraction of remaining C_2H_2 and Φ_{VAc} is the mass fraction of VAc.

Table 2 shows the calculation of carbon balances after the catalytic tests [28]. The mass of C fed into the reactor was calculated as the total amount of reactant fed during the reaction time. The mass of C at the reactor outlet was calculated as the sum of the mass of C for the amount of carbon deposit obtained by TG, all the products in the liquid phase and the acetylene gas were obtained by chromatographic analysis. The conclusion from Table 2 was that the carbon balance values were higher than 90% for the Zn1Co0.3/AC and Zn(OAc)$_2$/AC catalysts; Co additive improved the carbon balance caused by the reduction of carbon deposition.

Table 2. Calculation of carbon balance.

Catalyst	C$_{Feed}$ [a] in the Reactor (g)	C$_{Outlet}$ [b] in the Gas Phase (g)	C$_{Outlet}$ [c] in the Liquid Phase (g)	C$_{Outlet}$ [d] in the Solid Phase (g)	Carbon Balance (%)
Zn1Ni0.05/AC	348.22	252.15	73.14	0.210	93.5
Zn(OAc)$_2$/AC	348.22	269.54	46.34	0.421	90.8

[a] The mass of carbon fed into the reactor. [b] The mass of carbon outlet in the gas phase. [c] The mass of carbon outlet in the liquid phase. [d] The mass of carbon outlet in the solid phase.

4. Conclusions

Highly active Zn-Co/AC catalysts were prepared and investigated for the acetylene acetoxylation reaction. The Zn1Co0.3/AC catalyst exhibited excellent catalytic performance with an acetic acid conversion of 30.0%. Co additive inhibited the sintering of zinc acetate particles and weakened coke deposition in the catalysts during the reaction. The strong interactions between zinc and cobalt components modulated the adsorption of HAc and C_2H_2, consequently improving the catalytic performance of the catalysts.

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Conflicts of Interest: The authors declare no conflict of interest.

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