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EDTA-Assisted Impregnation of Zn-Based Catalysts for the Preparation of High-Performance and Low Loss Catalysts in Acetylene Acetoxylation

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Abstract: Impregnation of activated carbon (AC) with Zinc acetate in the presence of ethylene diamine tetraacetic acid (EDTA). Introducing EDTA effectively improves the dispersion of Zn in the catalyst and enhances the adsorption capacity of acetic acid due to the interaction between EDTA and Zn, resulting in an effective increase in the conversion of acetic acid from 50% to 65%. At the same time, as EDTA itself can have a chelating effect with Zn, the introduction can play a certain restraining effect on Zn, thus achieving the effect of inhibiting Zn loss. Even after 180 h of reaction, the Zn loss was very low and the acetate conversion did not decrease at all, and the reason for the inhibition of catalyst deactivation by EDTA was explored. This provides a novel way for developing high-performance and stable catalysts in the acetylation reaction of acetylene.

Keywords: Vinyl Acetate; EDTA; High-Performance Catalyst; Acetylene Acetoxylation; Inhibition of Zn Loss

1. Introduction

Vinyl acetate is an essential chemical feedstock for which global demand has been steadily increasing in recent years. The calcium carbide-acetylene process for the production of vinyl acetate is a common employed method when coal is an abundant resource [1, 2]. Activated carbon (AC) is commonly used industrially to load zinc acetate ($Zn(OAc)_2$) as a catalyst for vinyl acetate production; however, these catalysts typically suffer from low conversion and rapid deactivation because the active zinc component is easily lost as the reaction proceeds [3].

To address these issues, many studies have explored the use of carriers and catalyst modifications. Highly active metal oxide catalysts were prepared by Miyazawa et al. [4], such as V_2O_5–ZnO, Fe_2O_3–ZnO, $16ZnO{\cdot}32Fe_2O_3{\cdot}V_2O_5$, and $24ZnO_8{\cdot}Cr_2O_3{\cdot}V_2O_5$, but they failed to achieve better results than the standard zinc acetate on AC. Yan et al. [5] prepared a zinc acetate-loaded porous carbon sphere catalyst by carbonizing suspension polymerised poly (vinylidene chloride) spheres, resulting in acetic acid conversion up to 22.6%. Currently, $Zn(OAc)_2$/AC remains the most economical and environmentally friendly catalyst available for vinyl acetate production. Therefore, much work has been performed on modifications to improve the $Zn(OAc)_2$/AC system. Xu et al. [6] prepared zinc acetate on nitrogen-doped AC (N-AC) as a highly active catalyst. Zhu et al. prepared catalysts with high catalytic activity using boron-doped AC. He et al. [7, 8] used Ni and Co as additives to modify the $Zn(OAc)_2$/AC catalyst and achieved high activity. These studies successfully solved low activity problem of $Zn(OAc)_2$/AC catalysts, but catalyst stability needs further study. The main causes of catalyst deactivation are carbon accumulation and Zn loss; of which, Zn loss is an irreversible deactivation that needs to be addressed urgently.

Ethylene Diamine Tetraacetic Acid (EDTA) is a common chelating agent that can form stable chelates with many metal ions. To enhance the dispersion of metal ion on a carrier, studies that used EDTA to chelate metal ions before introducing them onto the carrier found the resulting catalysts exhibited less metal loss [9-12]. Interestingly, the inrtoduction of EDTA always improved the catalyst activity, regardless of the reaction [13,14]. Intriguingly, AC Villagran–Olivares et al. showed that EDTA/Ni loaded catalysts displayed excellent

activity, low carbon deposition rates and low activity loss in the ethanol steam reforming reaction [15].

In this paper, we prepared and thoroughly characterized $Zn(OAc)_2$/AC catalysts prepared through EDTA-assisted impregnation to reduce the loss of Zn through chelation to EDTA. The effect of EDTA addition ratio during $Zn(OAc)_2$/AC catalyst preparation on the acetylation reaction was studied.

2. Experiments

2.1 Raw Materials

AC was obtained from Fujian SenSen-Carbon. $Zn(OAc)_2$–$2H_2O$ (99.8%) was obtained from Aldrich (Saint Louis, MO, USA). Nitric Acid (69%) and EDTA (99.5) was obtained from Aladin Chemicals. Nitric Acid Acetylene gas (99.99%) and glacial acetic acid (99.8%) were obtained from Tianjin Beilian.

2.2 Catalyst Preparation

AC solution was prepared in Beaker A. AC (2 g) was properly added to 0.1 M nitric acid and deionized water (20 mL) to keep the PH of the solution below 5.65 (less than the PH_{zpc} of AC). Zinc acetate solution was prepared in Beaker B. $Zn(OAc)_2 \cdot 2H_2O$ (2 g) was dissolved in deionized water (20 mL). EDTA solution was prepared in Beaker C. EDTA (0.01 g, 0.02 g, 0.04 g, 0.08 g, 0.16 g, or 0.32 g) was dissolved in deionized water (10 mL, One or two drops of ammonia may be added to accelerate dissolution). The solution in Beaker C was slowly dropped into Beaker B and stirred for 30 min. The combined Beaker B and C solution was then poured into Beaker A, sonicated for 10 min (to degas air trapped inside the AC), and stirred at 80 °C and 250 r/min for 12 h. the solids were collected by filtration and dried in a blast oven to obtain the desired catalysts. The obtained catalysts synthesized with 0.01 g, 0.02 g, 0.04 g, 0.08 g, 0.16 g, and 0.32 g of EDTA were labeled 0.5%EDTA-Zn/AC, 1%EDTA-Zn/AC, 2%EDTA-Zn/AC, 4%EDTA-Zn/AC, 8%EDTA-Zn/AC, and 16%EDTA-Zn/AC, respectively.

2.3 Determination of PH_{zpc} for AC

The batch equilibration method described below was used to measure the PH_{zpc} (zpc: zero point of charge) value of the AC carrier. Disperse AC (0.2 g) in 0.1 mol/L KNO_3 solution (100 mL) and stir vigorously for 10 min. Prepared the eight solutions mentioned above and adjust the initial PH ($PH_{initial}$) of each solution was adjusted to 2, 3, 4, 5, 6, 7, 8 and 9 using HNO_3 and NaOH, respectively. After 12 hours of solution equilibrium, measure the final PH value of the solution (PH_{final}). Draw a chart using the PH value (the difference between the initial PH value, $PH_{initial}$, and the final PH value, PH_{final}), as shown in Figure 1. The point at which ΔPH is 0 was determined to be the PH_{zpc} of AC (5.6).

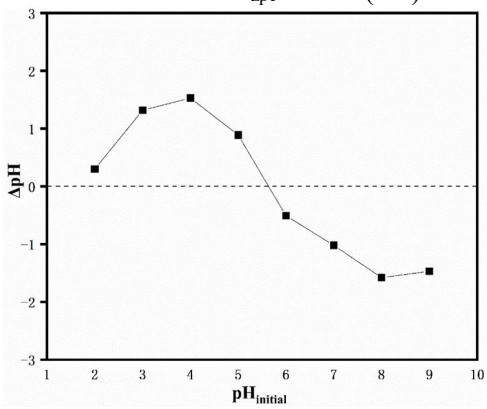

Figure 1. Plotting ΔPH as a Function of $PH_{initial}$

2.4 Determination of Zn Content by Titration

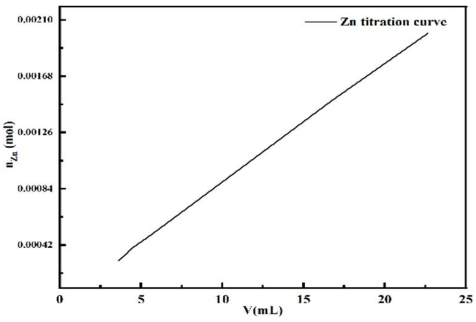

Figure 2. Standard Titration Curve for Zn

Take 3, 4, 5, 10, 15, 20 mL of 0.01 mol/L Zn standard solution in a beaker, add a few drops of HAc-NaAc buffer solution to maintain the PH at 5~6, followed by 4~5 drops of dimethoate orange, and finally titrate with the configured EDTA solution until the solution changes from burgundy to bright yellow, recording the volume of EDTA solution consumed as $V_{initial}$ and V_{final}, respectively. The volumes of EDTA solution consumed (V_{final}-$V_{initial}$) were recorded as V_1, V_2, V_3, V_4, V_5, V_6. As shown in Figure 2, a standard titration curve can be plotted using Zn standard solution volume and the EDTA consumed volume.

$$n_{Zn} = 9E^{-5}V_{EDTA} - 6E^{-6} \quad (1)$$

The equation for the titration curve of Zn was also fitted (Equation 1), allowing a simple and accurate calculation of the concentration of Zn in solution based on the volume of EDTA consumed for the titration. The same method can be used to titrate the washed EDTA-AC.

Weigh mg (1-1.5 g) of catalyst (precise to 0.0001g) that has been dried at 80 ºC for 24 h in an oven at 80 ºC in a quartz crucible, add about 2 mL of sulphuric acid to macerate the sample, evaporate on an alcohol lamp until the white fumes disappear, cool, then add 2 mL of sulphuric acid and treat again under the same conditions, allow the sulphuric acid to evaporate, cauterise in a muffle furnace at 700 ºC until completely free of black particles. Then filter the solution into a 250 mL conical flask, transfer to a 100 mL quantitative flask, and allow to settle. Then pipette 25 mL into a beaker, slowly add 3-4 drops of ammonia, then add 5 mL of HAc-NaAc buffer solution to maintain PH at 5-6, followed by 5-6 drops of dimethoate orange indicator, and finally titrate with EDTA solution until the solution changes from burgundy to bright yellow, record the volume of EDTA used V_{EDTA}, repeat the titration 3 times and take the average value. The percentage of active $Zn(OAc)_2$ in the catalyst, ω, can be calculated by taking the data obtained from Equation (1) into Equation (2).

$$\omega = \frac{4 \times n_{Zn} \times M_{Zn}}{m} \times 100\% \quad (2)$$

2.5 Characterization

Temperature-programmed desorption (TPD, Micromertics, AUTOCHEM II 2920, USA) was performed by heating the catalyst from 40 ºC to 800 ºC at a rate of 10 ºC /min under an atmosphere of N_2. Transmission electron microscopy (TEM) images and high-resolution transmission electron microscopy images were tested using a JEM-2100 (JEOL, Japan) instrument and a Tecnai G2 F30 S-TWIN (FEI, USA) instrument, respectively. Nitrogen adsorption-desorption isotherms were performed on a Micrometrics ASAP 2460 instrument (Micrometrics Instrument Corporation, USA). Specific surface areas were calculated using the Brunauer Emmett Teller (BET) method, while total pore volumes and average pore sizes were calculated using the Barrett Joyner Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Fisher Scientific ESCALAB 250Xi apparatus. Elemental analysis was carried out by inductively coupled plasma (ICP) optical emission spectroscopy on a Thermo Fisher Scientific ICAP 6000 series of spectrometer. Thermogravimetric (TG) analysis was performed on a NETZSCH STA449F5 Jupiter instrument, where the test conditions were to raise the test temperature from room temperature to 850 ºC at a rate of 10 ºC/min in an air atmosphere.

2.6 Catalytic Test

The activity and lifetime of the catalyst were evaluated using a fixed-bed reactor. Catalyst (2.4 mL) was placed in the fixed-bed reactor. During the heating process to 220 ºC, nitrogen gas was passed through the reactor for 0.5 h to purge the system. Subsequently, acetic acid vapor at 150 ºC was introduced into the reactor for 0.5 h. Finally, the nitrogen gas was shut off, and acetylene was introduced with samples being taken every hour. The flow rate of acetylene was 20 mL/min, and the feed ratio of acetylene to acetic acid was 3:1. The samples were analyzed using a gas chromatogram PH (GC-2014C, Shimadzu, Japan). Please refer to Figure 3 for an activity testing process diagram.

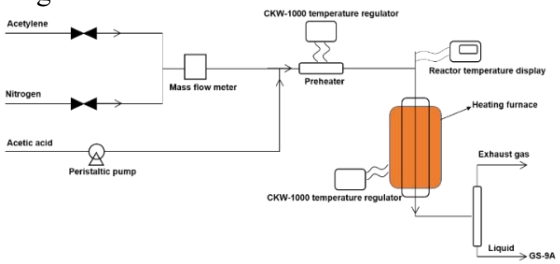

Figure 3. Activity Testing Process Diagram

3. Results and Discussion

3.1 Catalyst Activity and Zn Loss Test

The activity of the catalytic converters prepared with different ratios of EDTA was evaluated, and the results are shown in Figure 4a. The catalyst activity showed a trend of increasing and then decreasing performance as the proportion of EDTA increased, and the highest catalyst activity (65%) was achieved at 2% EDTA. We then subjected the catalysts to 48 h of activity and measured the Zn loss for both the 2%EDTA-Zn/AC and Zn/AC

catalysts. The Zn content in the catalysts was determined using both ICP and ligand titration methods to increase the accuracy of Zn content determination. As can be seen from Table 1, the difference between the Zn contents determined by the two methods was not significant. Therefore, the titraton method was employed in this paper to calculate the loss of Zn before and after the catalyst was deployed.

As seen in Figure 4b, the acetic acid conversion of 2%EDTA-Zn/AC was maintained at about 65%, while the activity of Zn/AC was about 50%. The Zn loss of Zn/AC was 24.56% after 48 h of activity, while the Zn loss of 2%EDTA-Zn/AC was only 3.26% after 48 h of activity.

Table 1. Zn content of Fresh and Used Catalysts

Catalyst	Zn/AC		2%EDTA-Zn/AC	
	Fresh	Used (48 h)	Fresh	Used (48 h)
Titration method	16.86	12.80	15.05	14.56
ICP method	16.42	12.51	15.59	14.75

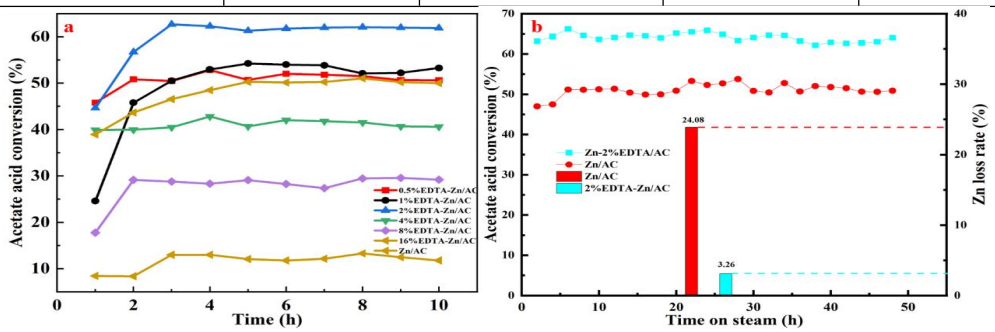

Figure 4. Catalyst activity Tests with Different EDTA Ratios (a) and Comparison of Activity and Zn Loss Rates for Zn/AC and 2%EDTA-Zn/AC (b)

3.2 Effect of EDTA on Catalyst

In AC supported catalyst preparation, the chemical interaction between the support and the materials present in the impregnant is highly dependent on the support's zero-point charge. The AC modified by adding HNO_3 to reduce the PH below the PH_{zpc} 5.6 (HNO_3-AC) and the AC without HNO_3 treatment (AC) were compared. Firstly, the same mass of EDTA was loaded on HNO_3-AC and AC, respectively, dried, and then washed with appropriate amounts of deionized water. The water wash was collected and the EDTA content in the solution was titrated with a Zn standard solution (see the reference for the specific test method used) (Table 2). As can be seen, only minor amounts of EDTA were washed off the AC after modification with HNO_3, indicating that more EDTA was adsorbed on the AC, and the binding of EDTA and AC was enhanced due to the HNO_3 treatment. The same experiment was done with Zn acetate instead of EDTA, and more Zn acetate loss occurred compared to EDTA. Thus, there was a greater binding force between EDTA and AC compared to Zn and AC.

The prepared catalysts were tested for N_2 low temperature adsorption and desorption, and various physicochemical parameters were measured (Table 3). EDTA did not greatly affect the catalysts' BET specific surface areas. BET specific surface area was maintained between 20 and 40 m^2/g and not significantly different from those of Zn/AC. Likewise, EDTA did not greatly affect the pore size and pore capacity.

Table 2. The Loss Rate of EDTA and Zn

Support	AC	HNO_3-AC
EDTA loss rate (%)	45.6	17.8
Zn loss rate (%)	56.8	45.2

All catalysts displayed similar type IV adsorption and desorption curves (Figure 5) with H1 back hysteresis loops, indicating that the catalysts were all mesoporous materials. Thus, EDTA did not cause changes to the pore structure of the catalysts and the improvement in catalyst performance was unrelated to their physicochemical properties. Immediately afterwards, we carried out Zn content tests on catalysts prepared using with different proportions of EDTA (Table 4). As the proportion of added EDTA increased, the Zn content of the catalyst gradually decreased. Significantly less Zn content was observed when EDTA content was greater than 4%. The lower Zn loading explains the observed reduction in catalyst activity for samples

prepared with higher EDTA content.

Table 3. Physicochemical Properties of the Prepared Catalysts

Sample	BET Surface (m^2/g)	Pore Volume (cm^3/g)	Pore Diameter (nm)
Zn/AC	23.58	0.037	1.57
0.5%EDTA-Zn/AC	25.78	0.041	1.55
1%EDTA-Zn/AC	41.10	0.044	1.63
2%EDTA-Zn/AC	22.39	0.039	1.55
4%EDTA-Zn/AC	36.07	0.043	1.75
8%EDTA-Zn/AC	29.04	0.037	1.56
16%EDTA-Zn/AC	27.37	0.033	1.58
Zn/AC-Used (180 h)	35.78	0.043	1.54

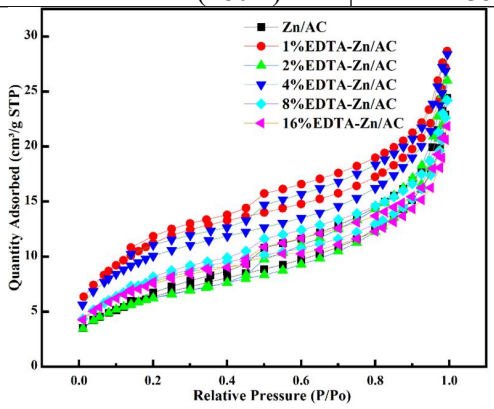

Figure 5. Adsorption and Desorption Curves for Different EDTA Ratios of Catalyst

Table 4. Zn Content of Each Catalyst Determined Using the Ligand Titration Method

Sample	ω_{Zn} (%)
Zn/AC	16.86
0.5%EDTA-Zn/AC	16.24
1%EDTA-Zn/AC	15.81
2%EDTA-Zn/AC	15.05
4%EDTA-Zn/AC	13.32
8%EDTA-Zn/AC	12.33
16%EDTA-Zn/AC	8.54
Zn/AC (after 180 h activity)	8.18
2%EDTA-Zn/AC (after 180 h activity)	13.97

The catalysts were then characterized by TEM (Figure 6). In Figure 6, a large amount of Zn in Zn/AC agglomerated to form larger particles. This locally biased loading of Zn makes less of the Zn available for contact with the reaction gas. On the contrary, the introduction of ETDA resulted in a more homogeneous dispersion of Zn on the carrier without agglomeration into large particles, which allowed more Zn to come into full contact with the reaction gas, resulting in higher catalytic activity. Figure 7a shows the Zn 2p XPS plots of the catalysts with different EDTA loadings. Compared to Zn/AC, the binding energies of Zn 1/2p and Zn 3/2p shifted from 1045.78 eV and 1022.68 eV to 1045.28 eV and 1022.18 eV for 2% EDTA-Zn/AC, respectively, indicating that the introduction of EDTA shifted the binding energies of Zn 2p to the lower field and increased the electron cloud density outside Zn. Electron transfer between Zn and EDTA occurs, and this transfer affects the adsorption properties of the catalyst active site on acetic acid and acetylene. After the addition of EDTA, the Zn content on the catalyst surface was higher, which may be due to the chelation of EDTA with Zn, making the molecule larger, so that more Zn was deposited in the outer layer, which is conducive to speeding up the rate of the reaction, and at the same time, the N element on the surface of the catalyst also increased significantly. This result can also be seen in the Figure N 1s XPS spectra, which is due to the introduction of the N element in the EDTA molecule to the catalyst. And according to previous studies, these changes due to this reaction.

To clarify how the electron transfer induced by the introduction of EDTA affected the adsorption of acetic acid and acetylene by the catalyst, we performed TPD analysis of Zn/AC and 2%EDTA-Zn/AC based on the desorption temperature corresponding to the highest adsorption intensity. The peak areas indicate the adsorption of acetylene and acetic acid, and the horizontal coordinates indicate the desorption temperatures of acetylene and acetic acid. As can be seen in Figure 7d, for the 2%EDTA-Zn/AC catalyst, the adsorption of acetylene was weak compared to the Zn/Ac catalyst, and the desorption peak area also significantly decreased with the desorption temperature decrease. Contrastingly, the acetic acid resolution peak area increased significantly and the resolution temperature also increased (Figure 7c), indicating that the

introduction of EDTA could significantly enhance the adsorption capacity of the catalyst for acetic acid. Enhancing the adsorption of acetic acid and weakening the adsorption of acetylene are known factors for improving catalyst activity [6,7]. We also tested the adsorption properties of Zn/AC versus 2% EDTA-Zn/AC on the reaction product vinyl acetate. Based on the analysis of the TPD results in Figure 7b, it was revealed that the peak area of 2%EDTA-Zn/AC is much smaller than those of Zn/AC, while the desorption of vinyl acetate starts at 260 °C, whereas in Zn/AC, the desorption temperature is 27 °C. This indicates that the catalyst adsorption capacity on the product vinyl acetate also changed after the addition of EDTA, which was able to reduce the adsorption of vinyl acetate by the catalyst and desorbed more easily, thus effectively increasing the acetic acid conversion and improving the catalytic activity.

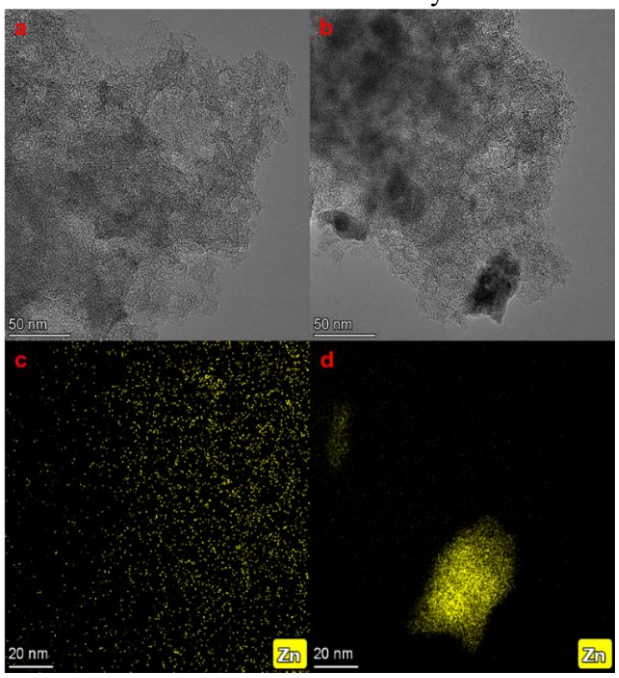

Figure 6. TEM-Mapping Images of Catalysts: (a)(c)2%EDTA-Zn/AC; (b)(d) Zn/AC

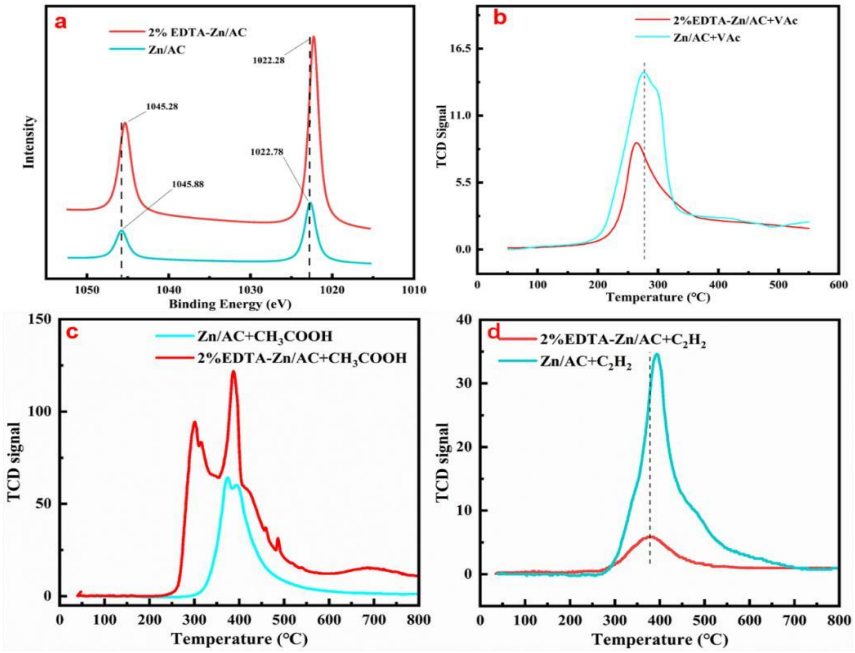

Figure 7. (a) High Resolution XPS Spectra of Zn 2p for Zn/AC and 2%EDTA-Zn/AC. (b-c) TPD Results of Zn/AC and 2%EDTA-Zn/AC with Vinyl Acetate (VAc), CH_3COOH and C_2H_2, Respectively

3.3 Catalyst Stability Studies

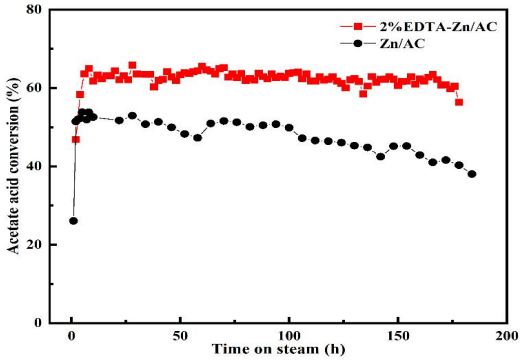

Figure 8. Stability Testing of Zn/AC and 2%EDTA-Zn/AC

We carried out preliminary studies on the stability of 2%EDTA-Zn/AC and Zn/AC catalysts under identical conditions, the results are shown in Figure 8. Both catalysts reached their maximum activity and stabilized after 5 h of reaction time (Zn/AC up to about 52% and 2%EDTA-Zn/AC up to 65%). Zn/AC started to decline after 60 h of reaction and the acetic acid conversion dropped to 40% after 180 h of reaction. For 2%EDTA-Zn/AC conversion of acetic acid remained near 65% after 180 h, with essentially no decline in performance. ICP measurements (Table 4) show a significant loss in Zn content for Zn/AC. After 180 h of reaction, the Zn loss rate of the 2% EDTA-Zn/AC catalyst was only 1/8 of that of the Zn loss rate of the Zn/AC catalyst without added EDTA. It was clear from the results that introducing of EDTA largely inhibited the active component Zn on the catalyst.

FTIR spectroscopic studies were performed that all samples at 450–600 cm^{-1} corresponded to the Zn–O bond (Figure 9b). Curiously, the catalysts after EDTA introduction resulted in an absorption peak at 650 cm^{-1}, possibly due to a shift in the Zn–O absorption band after binding of the carboxyl O on EDTA to Zn [16]. 2%EDTA-Zn/AC demonstrated two clear absorption peaks near 1400 cm^{-1} and 1600 cm^{-1}. Interestingly Zn/AC only has the one absorption peak near 1600 cm^{-1}. Corresponding to the contribution of the carboxylic acid group bound to the metal were the bands detected between 1700 cm^{-1} and 1200 cm^{-1} [17,18]. This illustrates that the absorption band near 1400 cm^{-1} can be attributed to coordination between the carboxyl group on EDTA and Zn. Thus, the absorption band near 1600 cm^{-1} can be attributed to acetate. Furthermore, no other absorption bands were observed above 1630 cm^{-1}, which indicated that there were no uncoordinated carboxyl groups [17,19,20] and that all carboxyl groups were coordinated to Zn. After the catalyst was deployed for 48 h, little change was observed by FTIR. The peak near 1500 cm^{-1} was still present, indicating that Zn was still bound to EDTA after the reaction. We then carried out TG tests for Zn/AC and 2%EDTA-Zn/AC. Figure 9a shows the significant mass loss in 2%EDTA-Zn/AC from 179 °C to 256 °C compared to Zn/AC. This was attributed to the partial decomposition of EDTA. This shows that after the reaction, there is still some EDTA on the catalyst that has not decomposed and that this EDTA fraction has a role in the inhibition of Zn loss. Meanwhile, there is no obvious mass loss of accumulated carbon from the TG plot, which is one of the reasons why the catalyst activity did not decrease, and the same result we can also get from the BET data in Table 3, which shows that the BET surface area of the catalyst does not vary significantly before and after the reaction.

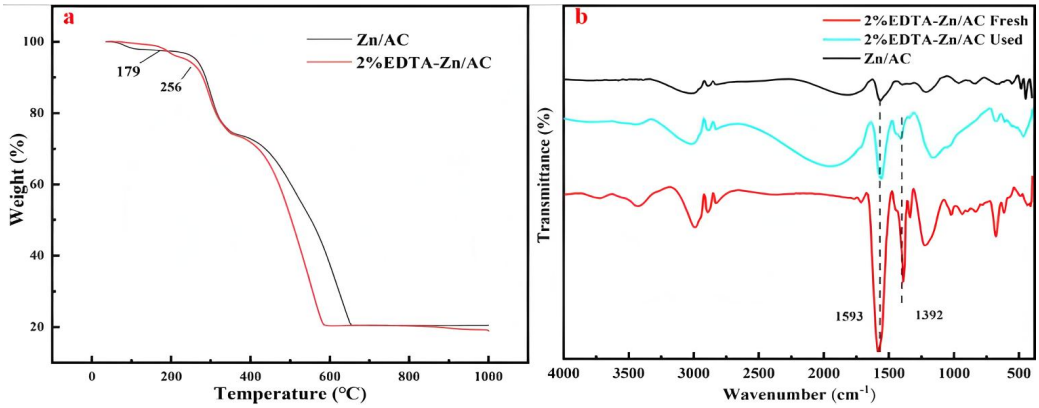

Figure 9. TG Curve of Zn/AC and 2%EDTA-Zn/AC on N_2 (a) and FTIR Spectra of Zn/AC, 2%EDTA-Zn/AC Fresh and 2%EDTA-Zn/AC Used (180h) (b)

4. Conclusions

In this study, $Zn(OAc)_2$ was impregnated on AC by adding EDTA. Optimization studies found 2 wt% loading with EDTA to be optimal. For the optimized catalyst (2%EDTA-Zn/AC), the activity increased from 52% to 65% and the loss rate of Zn from 51.48% to 7.17% (180 h). Physical characterization methods (FTIR, TG and XPS) confirmed that EDTA was indeed introduced into the catalyst and affected the chemical environment around Zn. The adsorption between EDTA and AC was experimentally demonstrated to be stronger than that between Zn and AC, and that the adsorption between EDTA and AC was further enhanced by adjusting the PH to be below the PH_{ZPC}. TEM and TPD characterization showed that the introduction of EDTA effectively improved Zn dispersion on AC. The 2%EDTA-Zn/AC catalyst displayed enhanced acetic acid adsorption and inhibited acetylene adsorption, thus increasing catalyst activity. There was no significant decrease in catalyst activity even after 180 h of continuous deployment. The introduction of EDTA can largely inhibit the loss of the active component Zn, while the carbon accumulation on the catalyst is not obvious, greatly improving the catalyst stability.

Acknowledgements

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