Academic Education Publishing House

Industry Science and Engineering Vol. 1 No. 11, 2024

A High-Performance in Situ Core–Shell Catalyst for the Acetoxylation of Acetylene

Dashun Lu[1], Peng Ren[1], Hao Jiang[1], Yilei Feng[1], Zongyuan Wang[1], Xugen Wang[1,*], Bin Dai[2,*]

[1]School of Chemistry and Chemical Engineering, Shihezi University, Shihezi, Xinjiang, China

[2]School of Chemistry and Chemical Engineering, Xinjiang University, Wulumuqi, Xinjiang, China

**Corresponding Author.*

Abstract: Core–shell catalysts with selective coatings were synthesized using an in situ generation method followed by a carbonization process. These catalysts were successfully applied to acetylene acetoxylation. The results demonstrated that the core–shell-structured catalysts had excellent catalytic activity and stability with a shell layer thickness of 30–50 nm. They achieved an initial acetic acid (CH_3COOH) conversion rate of up to 69%, maintained a conversion rate above 60% after 250 h of reaction. The Zn loss rate was only 0.10% with the ZnO–AC@10%tea polyphenols (TP)–650°C catalyst, whereas it reached 0.25% with the ZnO–AC–650°C catalyst. Compared to catalysts without added TP, those with a core–shell structure exhibited better catalytic activity and stability. This improvement is attributed to the core–shell structure's crucial role in reducing Zn component loss. The vinyl acetate (VAc) selectivity of all catalysts remained above 90%.

Keywords: Suit Core–Shell; Acetylene Acetoxylation; Loss Rate; Activity and Stability; Zn Component Loss.

1. Introduction

Vinyl acetate (VAc) is an important organic chemical raw material used in the production of polyvinyl acetate (PVAc), polyvinyl alcohol (PVA), and ethylene–vinyl acetate resin (EVA). Its downstream products have extensive applications in coating materials, photovoltaics, foaming agents and the automotive industry[1]. The global industrial synthesis of VAc primarily involves the C2H4 method and the C2H2 method. Given China's energy structure, characterized by "rich coal, poor oil, and limited gas," the C2H2 method is used for synthesizing VAc in this study. While zinc acetate (Zn(OAc)2)/activated carbon (AC) is commonly used in industrial applications, it faces issues such as low activity and short lifespan. Researchers have performed in-depth studies from various perspectives to address these challenges. Wu et al.[2] modified AC with hydrogen cyanide to enhance the adsorption strength of CH3COOH and C2H2, thereby improving catalytic activity. Zhu et al.[3] used B-doped AC to change the electron cloud density around Zn, reducing the reaction barrier and increasing the CH3COOH conversion rate from 50% to 63.5%. He et al.[4] used Co as a catalyst promoter to increase electron cloud density around Zn to enhance the adsorption of CH3COOH, leading to a considerable improvement in catalytic activity. Zhang et al.[5] prepared mesoporous carbon material CMK-3 from sucrose and SBA-15 through pyrolysis and acid washing. The deactivation kinetics of the Zn/CMK-3 catalyst were investigated, revealing that Zn component loss was the primary cause of catalyst deactivation in the acetylene acetylation reaction. Consequently, there is an urgent need to design a new, efficient catalyst to minimize the loss of the active component and enhance catalyst stability.

It has been reported that strengthening the interaction between the support and the active component is crucial for reducing the loss of the active component[6]. Currently, many methods such as complexing agents, atomic layer deposition (ALD), metal–organic frameworks (MOFs), and core–shell structure materials have been adopted in academic research to reduce the loss of active components. In this study, we selected the core–shell structure strategy to effectively minimize the loss of active components. Catalysts with a core–shell structure benefit from both physical shielding and chemical coordination mechanisms, which help reduce

active component loss and enhance catalyst stability[7]. Xu et al.[8] found that Zn(OAc)2, produced from ZnO as a precursor after activation with CH3COOH, exhibited superior initial catalytic activity. Consequently, ZnO was selected as the core for the core–shell structure. Tea polyphenols (TP) were chosen for the shell material owing to their phenolic hydroxyl groups, which have a strong complexing ability. This allows TP to effectively minimize active component loss and adhere to the particle surface through self-polymerization, providing a physical shielding effect[9]. Moreover, the TP molecular structure also contains carbonyl functional groups, which can lower the energy barrier of the reaction[10].

In this study, the ZnO–AC precursor was selectively coated with TP using an in situ polymerization method. The TP coating was then carbonized to produce the ZnO–AC@10%TP–650°C catalyst. The composition and chemical bonding of the ZnO–AC@10%TP–650°C catalyst were analyzed using Fourier-transform infrared (FT–IR) spectroscopy, powder X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Additionally, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed to characterize the catalyst's morphology and microstructure. The adsorption capacities of the catalysts for CH3COOH and C2H2, as well as the desorption capacity for VAc, were analyzed using programmed temperature desorption. The Zn content in the catalyst was measured by inductively coupled plasma atomic emission spectroscopy (ICP–OES). Additionally, the activity and stability of the catalysts were evaluated in a fixed-bed microreactor. The catalyst preparation pr°Cess and catalytic reaction mechanism are illustrated in Figure 1.

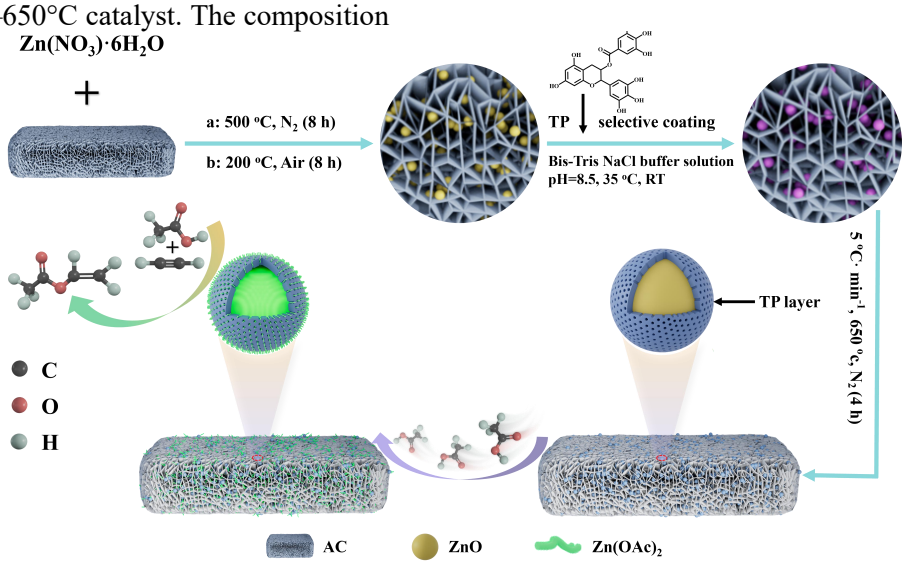

Figure 1. Diagrams Illustrating the Main Preparation Pr°Cess Routes and Catalytic Reaction Mechanisms

2. Experimental Section

2.1 Materials

Neutral c°Conut shell AC from Fujian Sensen Activated Carbon Co., Ltd. was used as the carrier. The materials used in this study include Zn(NO3)2·6H2O (Tianjin Guangfu, 98.00%), ZnO (Tianjin Shenao, 99.00%), CH3COOH (Tianjin Beilian, 99.80%), VAc (Shanghai McLean, 98.00%), N2 and C2H2 (Shihezi Hongsheng, 99.99%), TP (Tianjin Beilian, 98.00%), NaCl (Tianjin Shengao, 99.50%), and bis(2-hydroxyethyl) iminotris(hydroxymethyl)methane (Bis–Tris) (C8H19NO5), provided by Sigma-Aldrich.

2.2 Preparation of the ZnO–AC Precursor

First, 8.0 g of AC and a 100-mL solution containing 12.0 g of Zn(NO3)2·6H2O (used as a precursor for synthesizing nano-ZnO particles) were stirred at room temperature for 24 h and then dried at 80°C to obtain Zn/AC. Dried Zn/AC was subsequently heated in a test tube to 500°C at a rate of 5 °C·min−1 in an N2 atmosphere for 8 h to ensure complete conversion of Zn(NO3)2 to ZnO. The material was then heated to 200°C under air at a rate of

1 °C·min−1 in an electric furnace for 8 h to ensure sufficient oxidation of the ZnO surface. The sample was denoted as ZnO–AC[11].

2.3 Preparation of the ZnO–AC@10%TP–650°C Catalyst

A total of 4.0 g of the ZnO–AC catalyst was dispersed at 35°C in 200 mL of a Bis–Tris buffer solution (0.1 M Bis–Tris and 0.6 M NaCl) containing TP (2.0 mg·mL−1, pH 8.5) for a reaction period of 24 h[9]. Then, the precipitate was centrifuged, washed with deionized water, and dried at 80°C for 10 h. To carbonize the TP coating and stabilize the structure, dried ZnO–AC@ 10%TP was heated to 650°C at a rate of 5 °C·min−1 under nitrogen for 4 h. The resulting catalyst is denoted as ZnO–AC@ mTP–T, where "m" is the mass ratio of TP to ZnO–AC, and "T" is the carbonization temperature.

2.4 Characterization of Catalysts

FT–IR spectra were obtained using a Bruker Vertex 70V spectrometer in a wavenumber range of 4,000–350 cm−1. XRD pattens were collected with a Bruker D8 ADVANCE using Cu Kα radiation, operating at 10 mA tube current and 40 kV tube voltage over a 5°–80° angular range. XPS spectra for Zn 2p, O 1s and C 1s in the catalyst were recorded with a Thermo Fisher K-Alpha spectrometer. The microstructure of the catalyst was examined using a Hitachi SU8010 while HRTEM images were acquired with an FEI Tecnai G2 F30 instrument. The adsorption capacity and strength of the catalyst for CH3COOH, C2H2, and VAc were measured using an AMI-300Lite temperature-programmed desorption (TPD) apparatus. Metallic element measurements were performed using Agilent ICP–OES 730 from Agilent Technologies.

2.5 Evaluation of Gas–Solid Catalytic Performance

The catalyst was evaluated in a fixed-bed microreactor. A 0.9-g (1.5 mL) sample of the catalyst was placed into the reactor tube, and the operation steps were as follows. The N2 valve was opened, and the flow rate was adjusted to 12.5 mL/min. Then, the heating switch of the heating thermostat (T = 220°C) and the heating zone (T = 150°C) were turned on. The reactor device was heated for 30 min, and once the temperature reached the activation temperature (200°C), the peristaltic pump was turned on to activate the catalyst with 0.1 mL/min of CH3COOH for 40 min, allowing ZnO to fully react and form Zn(OAc)2. The N2 valve was closed, and the C2H2 valve was opened, with a volumetric space velocity (GHSV) of 500 h−1 for C2H2 (12.5 mL/min) and a CH3COOH flow rate of 0.01 mL/min. The reaction temperature were 220°C, and the feed molar ratio of C2H2 and CH3COOH was 3:1. Samples were analyzed by gas chromatography (Shimadzu, GC-2014C).

3. Results and Discussion

3.1 Influence of Carbon Shell Precursors on Catalytic Activity

Previous studies have shown that ZnO can be converted to Zn(OAc)2 after activation with CH3COOH. Therefore, ZnO–AC was selected as the core material for the core–shell structure design. In this study, five oxygen-containing precursors were chosen to construct the core–shell structure, including RF, CFR, PGNR, TA and TP.

The impact of precursors on catalytic activity was analyzed (Figure 2b-c). The CH3COOH conversion for RF, CFR, PGNR, TP and TA-coated ZnO–AC was only 48%, 65%, 59, 69% and 64, after 10 h of reaction, respectively, with the selectivity of VAc consistently remaining above 90%. It was observed that the activity of glucose-coated ZnO–AC catalysts decreased rapidly. Consequently, selecting materials with spatial site resistance containing benzene rings and strong coordination from phenolic hydroxyl groups can improve catalyst performance. The CH3COOH conversion for CFR-coated ZnO–AC was only 48%, primarily owing to the coordination of –OH groups in resorcinol with Zn, which occupies some of the active centers, and the high spatial site resistance of cetyltrimethylammonium bromide. In contrast, both 1,2-benzenediol and pyrogallol form tetra-coordinated structures with Zn atoms. The excess phenolic hydroxyl groups in pyrogallol adsorb CH3COOH and C2H2, thereby enhancing the reaction. The impact of chain length on catalytic activity was evaluated by examining organics with varying numbers of pyrogallol groups. Choosing a larger TA molecule reduces CH3COOH conversion because it contains more 1,2-

benzenediol groups, which occupy the active centers and increase spatial site-blocking effects owing to the larger molecular weight. In contrast, selecting a TP molecule with a moderate chain length results in less spatial site-blocking compared to TA. Additionally, the TP molecule contains a carbonyl group, which lowers the energy barrier and catalyzes the reaction[5]. Therefore, TP with a moderate chain length and pyrogallol groups was chosen as the shell layer material (Figure 2a).

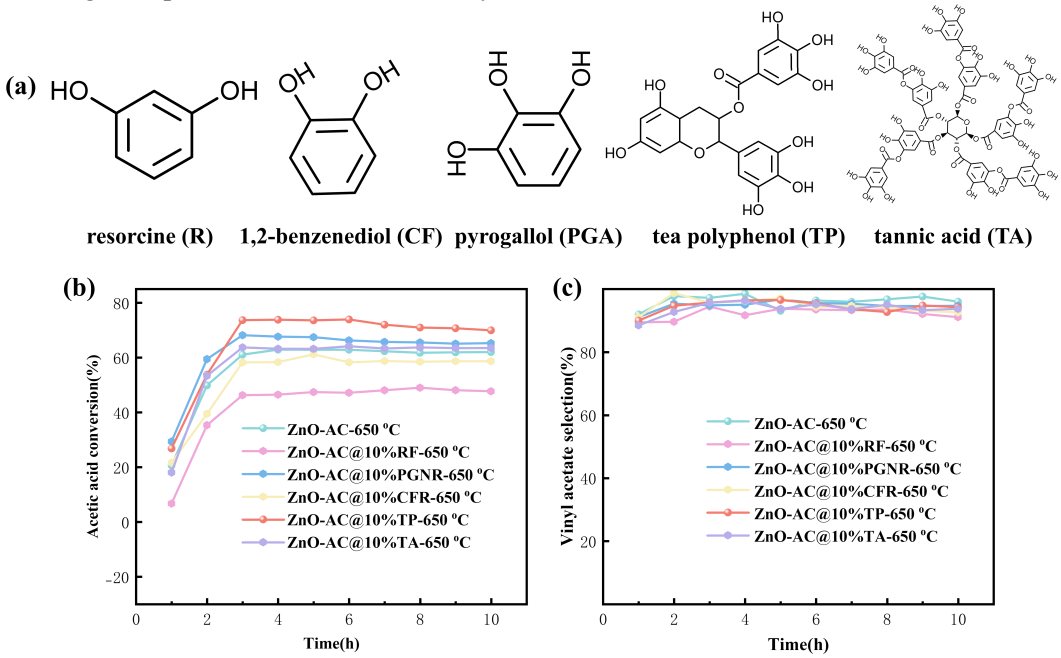

Figure 2. Performance Diagram of the Catalytic Activity of ZnO–AC Coated with Various Materials: (a) Molecular Structure Formula of Various Materials; (b) CH3COOH Conversion Rate; (c) VAc Selectivity

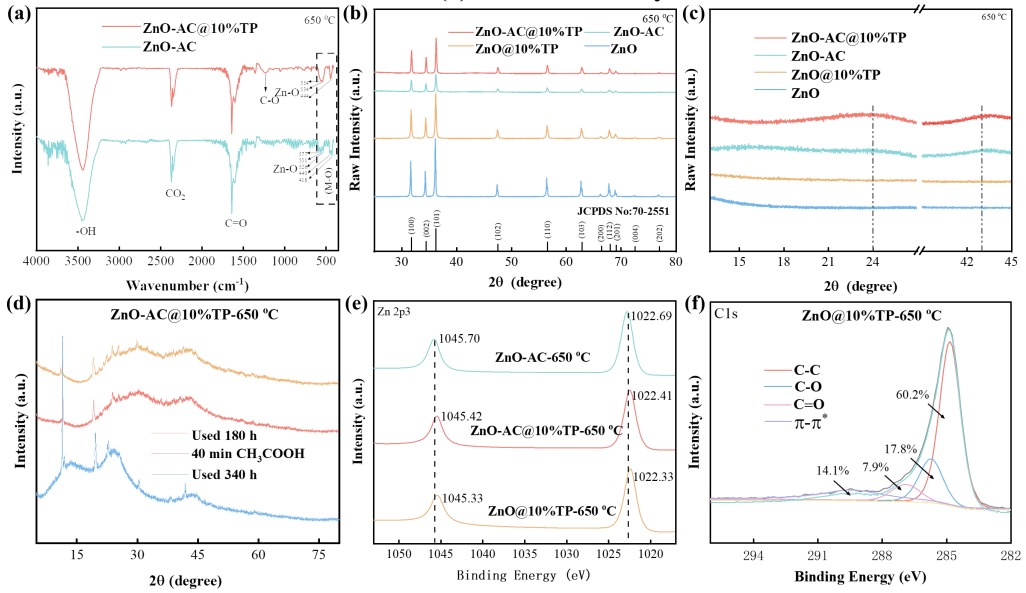

Figure 3. (a) FT–IR Spectra; (b–d) Powder XRD Patterns; (e–f) XPS Survey Spectra for Zn 2p and C 1s of the Catalysts

3.2 Morphology and Structure

Basd the above results, TP is the best precursor for carbon shell, therefore, ZnO–AC@ 10%TP–650°C, ZnO@ 10%TP–650°C, AC@ 10%TP–650°C, ZnO–AC–650°C, and AC were prepared for the research. The structure and morphology of the above catalysts were characterized. FT–IR spectra shows a peak at 1,221 cm−1 was observed (Figure 3a), corresponding to the stretching vibration of C–O in polyol. This result confirms the selective

coating of TP on the surface of ZnO–AC. The peaks that observed at 554, 534, and 444 cm−1 is assigned to Zn–O absorption, confirming the presence of ZnO species. The XRD results revealed characteristic peaks at 2θ = 31.78°, 34.42°, 36.26°, 47.54°, 56.61°, 62.86°, 66.39°, 67.96°, 69.10°, 72.56°, and 76.98°, corresponding to ZnO (JCPDS NO. 70-2551) (Figure 3b). Additionally, the XRD pattern displayed two distinct peaks at 24° and 43°, corresponding to the (002) and (100) planes of the amorphous carbon (Figure 3c). No diffraction peaks related to amorphous carbon were observed in the ZnO and ZnO@ 10%TP–650°C catalysts. However, amorphous carbon was clearly present in the ZnO–AC–650°C and ZnO–AC@ 10%TP–650°C catalysts, confirming the successful introduction of AC. To verify the formation of Zn(OAc)2, the catalyst was activated for 40 min (0.1 mL·min−1) and then analyzed by XRD. The results showed that the original ZnO was completely converted to Zn(OAc)2 after 40 min of activation[8]. The catalyst was characterized by XRD after 180 and 250 h of reaction. No characteristic peaks of ZnO were observed, indicating that the active component remained Zn(OAc)2 after activation (Figure 3d).

Finally, the interactions between TP and ZnO/ZnO–AC catalysts were analyzed using XPS spectra. The binding energies of the Zn 2p1/2 and Zn 2p3/2 peaks for the ZnO@10%TP–650°C catalyst was 1045.33 and 1022.33 eV, respectively. In comparison, the binding energies for the Zn 2p1/2 and Zn 2p3/2 peaks in the ZnO–AC–650°C and ZnO–AC@ 10%TP–650°C catalysts were 1045.42 and 1045.70 eV and 1022.41 and 1022.69 eV, respectively. The increase in binding energy observed with the addition of TP indicates a higher electron density in the outer layer of Zn, as seen in the ZnO@ 10%TP–650°C catalyst. This electron transfer enhances the catalyst's ability to desorb CH3COOH (Figure 3e)[12]. The binding energy peaks at 284.0–285.1 eV are attributed to graphitic carbon (C–C). The C–O bonds, found in alcohol, phenol, or ether groups, appear at 285.3–286.3 eV. Carbonyl or quinone groups (C=O) are represented by binding energies in the range of 286.8–288.1 eV, while the aromatic ring π–π* transitions produce characteristic spectral peaks at 290.2–291.1 eV. All these groups belong to the TP-coated surfaces (Figure 3f).

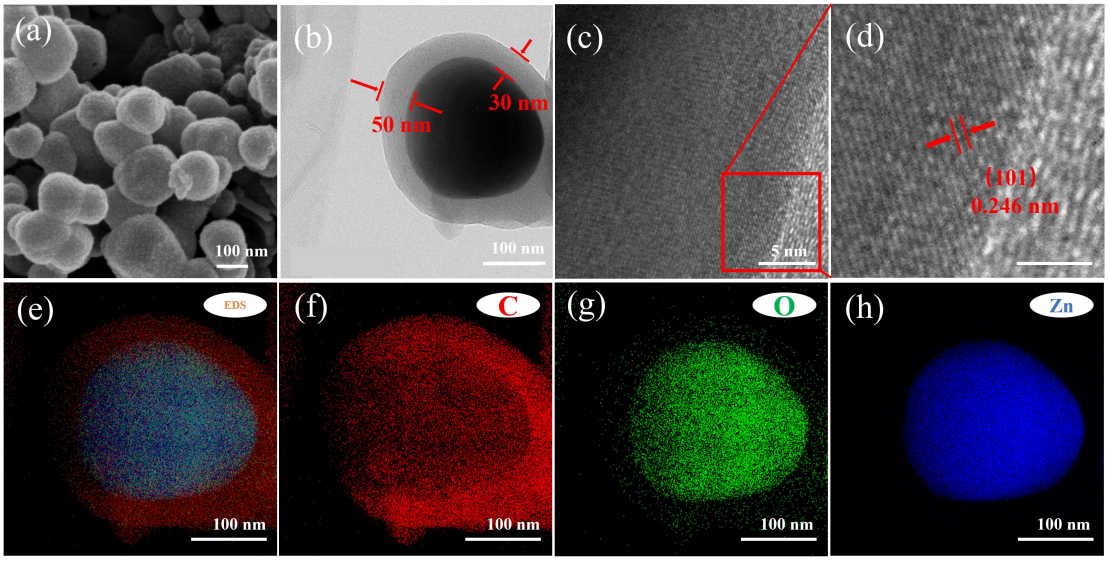

Figure 4. (a) SEM; (b, c) HRTEM; (e-h) TEM Mapping Images the ZnO–AC@10%TP–650°C Catalyst

The coated spherical ZnO nanoparticles were clearly visible at a resolution of 100 nm (Figure 4a). The shell layer thickness of spherical ZnO nanoparticles is 30–50 nm, as observed by TEM (Figure 4b). A lattice spacing of 0.246 nm, corresponding to the (101) crystal plane of ZnO, was identified at a high resolution of 5 nm, confirming the presence of ZnO and aligning with XRD results (Figure 3b). Additionally, high-angle annular dark field imaging clearly shows that ZnO is fully coated with TP. TEM mapping distribution reveals that Zn and O elements are predominantly concentrated at the center of the

image, while carbon elements are located on the outer surface (Figure 4e–h). The characterization confirmed that ZnO was selectively coated with TP, forming a core–shell-structured catalyst. After activation with CH3COOH, the zinc element is distributed either on the carrier or on the surface of the shell layer.

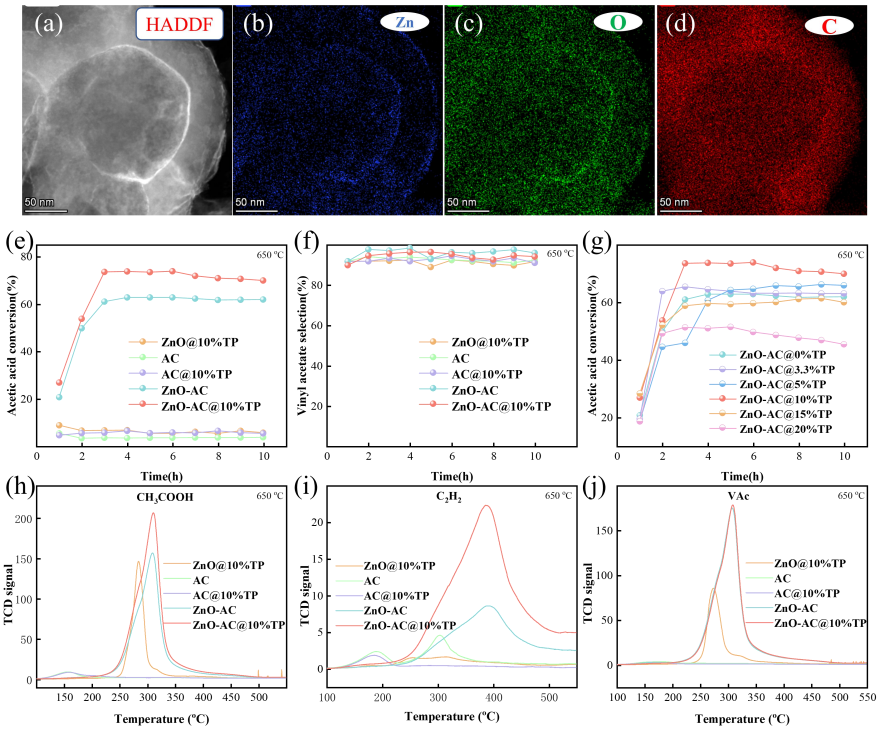

Figure 5. (a–d) TEM-Mapping Images of the ZnO–AC–650°C Catalyst after Activation with CH3COOH; (b, c) Catalytic Performance of ZnO–AC@10%TP–650°C, ZnO@10%TP–650°C, AC@10%TP–650°C, ZnO–AC and AC;(c) Catalytic Performance of ZnO–AC@0-20%TP–650°C; (h) TPD Desorption Spectrum of CH3COOH; (i) TPD Desorption Spectrum of C2H2; (j) TPD Desorption Spectrum of VAc.

Table 1. Desorption Temperature of CH3COOH, C2H2, and VAc on Catalysts

Sample	CH_3COOH (°C)	C_2H_2 (°C)	VAc (°C)
ZnO@10%TP–650°C	284.41	304.27	273.92
AC	157.51	189.76	177.92
AC@10%TP–650°C	158.42	185.21	166.24
ZnO–AC–650°C	309.42	391.71	307.51
ZnO–AC@10%TP–650°C	310.73	387.32	308.63

3.3 Catalytic Performance

Five distinct types of catalytic activity tests were performed (Figure 5a). For the acetylenic acetoxylation reaction, performed at 220°C, the temperature is considerably lower than the Taman temperature of zinc oxide but falls in the Taman temperature range for zinc acetate. This confirms the in situ generation of Zn(OAc)2 (Figures. 5a–d)[8]. This is consistent with the XRD analysis (Figure 3d). The ZnO@ 10%TP–650 °C and AC@ 10%TP–650°C catalysts showed very low activity. The poor performance of the ZnO@ 10%TP–650°C catalyst was attributed to insufficient carbon content, while the AC@ 10%TP–650°C catalyst's low activity was primarily due to the absence of active components. This low activity may be attributed to the catalysts' weak adsorption capacity for CH3COOH and C2H2. The experimental results indicate that catalysts containing ZnO demonstrated a better ability to adsorb CH3COOH.

Among them, the ZnO–AC catalyst coated with TP showed the highest adsorption capacity for CH3COOH (Figure 5h). The desorption temperatures of the ZnO–AC–650°C and ZnO–AC@ 10%TP–650°C catalysts were 309.4°C and 310.7°C, respectively. Therefore, the addition of TP had minimal effect on the desorption of

CH3COOH (Table 1). Previous theoretical studies have indicated that the adsorption capacity of C2H2 plays a considerable role in controlling the reaction rate[13]. Therefore, enhancing the adsorption capacity of C2H2 can effectively improve the catalytic reaction. It was observed that the ZnO–AC@ 10%TP–650°C catalyst had the highest C2H2 adsorption (Figure 5i). Additionally, we noted that the addition of TP had minimal effect on both the desorption temperature and adsorption capacity of VAc, suggesting that the catalytic reaction was not considerably impeded (Figure 5j).

In summary, the simultaneous presence of ZnO and AC results in better adsorption capacities for C2H2 and CH3COOH, leading to enhanced catalytic activity. The addition of TP considerably improved the adsorption capacities of CH3COOH and C2H2 while having minimal impact on the desorption ability of VAc, thereby promoting catalytic reactions. Consequently, the ZnO–AC@ 10%TP–650°C catalyst exhibited higher catalytic activity in acetylene acetylation. The conversion rate of CH3COOH reached 69% after 10 h of reaction, with the selectivity of VAc consistently remaining above 90% (Figure 5e-f).

3.4 Stability Test and Analysis of Zn Component Loss in the ZnO–AC@ 10%TP–650°C Catalyst

The performance evaluation was carried out on the catalyst without TP for 48 h and with TP for 250 h (Figure 6a). The results demonstrated that the core–shell-structured catalysts exhibited good catalytic activity and stability, with an initial CH3COOH conversion rate of up to 69%, a conversion rate above 60% after 250 h, with the selectivity of VAc consistently remaining above 90%. Characterization results showed that the Zn loss rates for catalysts with and without TP were 36.34% and 11.82%, respectively, while the corresponding loss rates were 0.10% and 0.25% (Figure 6b). This indicates that the core–shell catalyst can effectively reduce the loss of Zn components.

Although the loss of Zn components was effectively reduced, it still remained. Therefore, it was necessary to investigate the causes of this loss of active components. SEM analysis at a resolution of 1 μm showed that the overall structure of the catalyst's shell layer remained well-maintained after 250 h of reaction, confirming that the major loss of active components was not due to damage to the core–shell structure (Figure 6c). However, damage to the shell surface structure observed in HAADF images was attributed to the loss of Zn (Figure 6d). TEM mapping revealed that the Zn element was transferred from the interior to the surface of the shell, further confirming that the catalytic reaction occurs on the shell's surface (Figure 6e-f). This indicates that the core–shell structure plays a crucial role in reducing the Zn loss rate, which can be attributed to the strong complexation of phenolic hydroxyl groups on the shell surface (Figures 3f and 4g).

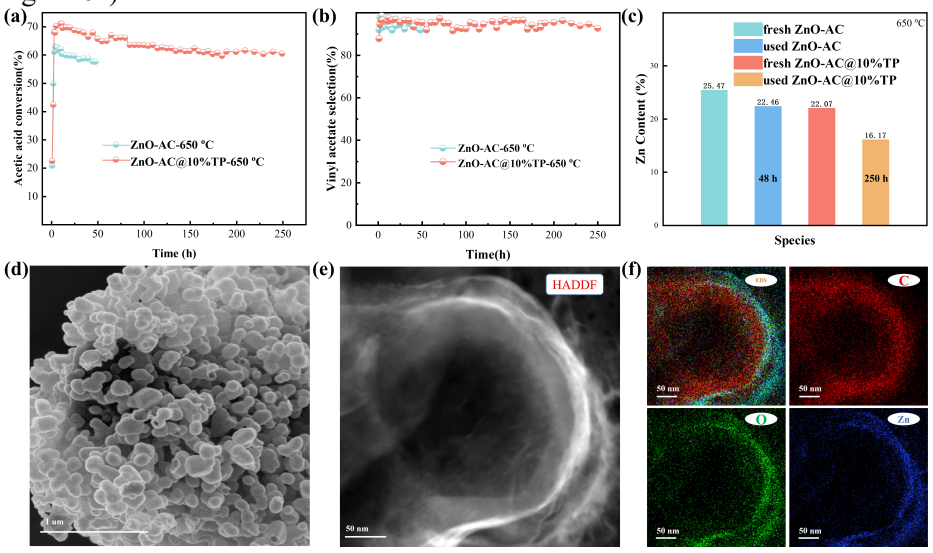

Figure 6. Performance Evaluation of Catalysts:(a) CH3COOH Conversion Rate; (b) VAc Selectivity; (c) ICP Analysis of Catalysts; ZnO–AC@10%TP–650°C Catalysts; (d) SEM Images, (e) HAADF Image, and (f) TEM Mapping Images

4. Conclusion

This study addresses the issue of catalyst deactivation caused by the easy loss of active components in the acetylene acetylation reaction. A core–shell-structured catalyst was designed using the in situ generation method. It was demonstrated that the core–shell-structured catalysts exhibited excellent catalytic activity and stability, with a shell layer thickness of 30–50 nm. The initial CH3COOH conversion rate reached 69%, remained above 60% after 250 h of reaction. The core–shell-structured catalyst effectively reduced the loss of Zn components and considerably enhanced both the activity and stability of the catalyst. It was observed that the shell structure remained intact after 250 h of reaction, demonstrating the material's potential for various applications.

Acknowledgments

We greatly acknowledge the financial support from the National Natural Science Foundation of China (KZ0195), the Major Science and Technology Project of Xinjiang Bingtuan (2017AA007 and 2020AA004), and Tianshan Talent Innovation Team Project and Tianchi Talent Program of Xinjiang.

References

[1] Chen Y, Huang Y, Huang Y, et al. A crosslinked waterborne poly(vinyl acetate) for greenhouse gas fixation with improved elastomeric properties, shape-memory ability, and recyclability. Journal of Environmental Chemical Engineering, 2023, 11 (6): 111170.

[2] Wu X, He P, Wang X, et al. Zinc acetate supported on N-doped activated carbon as catalysts for acetylene acetoxylation. Chemical Engineering Journal, 2017, 309: 172-177.

[3] Zhu F, Zhu M, Kang L. B-doped activated carbon as a support for a high-performance Zn-based catalyst in acetylene acetoxylation. Green Energy & Environment, 2022, 7 (2): 221-228.

[4] He P, Huang L, Wu X, et al. A novel high-activity Zn-Co catalyst for acetylene acetoxylation. Catalysts, 2018, 8 (6).

[5] Zhang Y, Wang Q, Zhu M, et al. The catalytic recycle and deactivation kinetics of Zn/CMK-3 catalyst for acetylene acetoxylation. Molecular Catalysis, 2023, 549: 113502.

[6] Chen Z, Zhao F, Zhang H, et al. Effects of trifluoromethanesulfonic acid ligand on the Zinc-based catalysts for the acetylene hydration. Chinese Chemical Letters, 2023, 34 (6): 107963.

[7] Jiang Y, Zhou X, E Y, et al. Designing molybdenum disulfide/nickel silicide@ sodalite zeolite structure as a high performance core-shell catalyst for methanol oxidation. International Journal of Hydrogen Energy, 2023, 48 (39): 14717-14729.

[8] Xu Z, Zhang X, Li M, et al. A highly active in situ Zn(CH3COO)2-NC catalyst for the acetoxylation of acetylene. Industrial & Engineering Chemistry Research, 2022, 61 (3): 1313-1321.

[9] Tang D, Chen S, Liu X, et al. Controlled reactivity of metastable n-Al@ Bi(IO3)3 by employment of tea polyphenols as an interfacial layer. Chemical Engineering Journal, 2020, 381: 122747.

[10] Dong X, Wang Y, Yu Y, et al. Density Functional Theory Investigation on the Synthesis Mechanism of Vinyl Acetate from Acetylene and Acetic Acid Catalyzed by Ordered Mesoporous Carbon-Supported Zinc Acetate. Industrial & Engineering Chemistry Research, 2018, 57 (22): 7363-7373.

[11] Nordin S N M, Abdullah A H, Zainal Z. Morphologies of nanostuctured ZnO prepared by matrix-assisted method and its effects on photocatalytic activity. Asian Journal of Chemistry, 2013, 25 (18): 10230-10232.

[12] Li M, Xu Z, Chen Y, et al. MOFs-derived Zn-based catalysts in acetylene acetoxylation. Nanomaterials, 2021, 12 (1): 98.

[13] Zhu F, Li J, Zhu M, et al. Effect of oxygen-containing group on the catalytic performance of Zn/C catalyst for acetylene acetoxylation. Nanomaterials, 2021, 11 (5): 1174.