

Article

High-Entropy NiCoZnVCrO_x Oxides Serve as Oxygen Carriers for NO Reduction

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Abstract

Flue gas denitrification represents an environmentally friendly and economically viable strategy for alleviating energy crises and advancing carbon neutrality goals. Although traditional selective catalytic reduction (SCR) catalysts demonstrate excellent denitrification efficiency and catalytic stability, they still face significant challenges, including high cost and ammonia slip. In this study, the high-entropy oxide (HEO) NiCoZnVCrO_x was synthesized via the sol–gel method and evaluated for the reduction of NO to N₂. The effects of varying reaction conditions on the NO reduction performance of this material were systematically investigated alongside the underlying reaction mechanism. The results reveal that the reduced oxygen carrier (OC) achieves optimal performance at an oxidation temperature of 800 °C, oxidizing gas flow rate of 200 mL/min and reduction time of 60 min, yielding the highest NO conversion and N₂ selectivity while simultaneously minimizing NO₂ selectivity. The reaction mechanism was further elucidated through a series of characterization techniques, including DRIFTS. Overall, this HEO demonstrates significant potential as a candidate OC for flue gas denitrification.

Keywords: chemical looping combustion; oxygen carrier; high-entropy oxides; NO reduction

1. Introduction

Nitrogen oxides (NO_x) emitted during fossil fuel combustion are widely recognized as a primary contributor to air pollution. Beyond their direct toxicity, NO_x also play a significant role in the formation of photochemical smog, acid rain and ozone depletion, collectively exacerbating global climate change [1]. In response to the growing concern over rising NO_x emissions, increasingly stringent government regulations have intensified research efforts and heightened global focus on the development of effective NO_x removal technologies [2–4].

In a study of NO removal using HEO, Su et al. [5] prepared a MOF-derived HEO, HEO-350 (Fe/Co/Ni/Cu/Mn), and applied it to the HC-SCR reaction, achieving NO conversion exceeding 89.5% at 225–275 °C, with a peak conversion of 93.2% at 250 °C. Shahid et al. [6] prepared a layered double hydroxide (LDH)-derived HEO catalyst (MnCoCuFeCe-LDO) via a coprecipitation method and applied it to the low-temperature C₃H₆-SCR reaction. The results indicate that this catalyst exhibits excellent low-temperature catalytic activity over a wide temperature range of 150–300 °C; the synergistic effects of multiple elements significantly enhance the redox capability of the catalyst and surface acidity, thereby promoting the efficient conversion of NO. Zhang et al. [7] employed a dual strategy of “high-entropy exclusion” and “element substitution” to prepare a series of high-entropy



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hematite oxide catalysts based on six metals (Mn, Fe, Co, Ni, and Cr) and Al for the low-temperature NH_3 -SCR reaction. Among the prepared OCs, the HEP-no-Al exhibited the highest catalytic activity, with the valence states of B-site elements playing a key role in enhancing catalytic performance. Upon further substitution of Cr at the B site with Mo (HEP-Mo), the catalyst achieved NO conversion of 100% at 180 °C, coupled with excellent N_2 selectivity, demonstrating excellent low-temperature denitrification performance. Niu et al. [8] systematically reviewed the critical role of oxygen vacancies in NH_3 -SCR catalysts. Oxygen vacancies not only serve as preferential adsorption sites for NO and NH_3 but also maintain the catalytic cycle by promoting the regeneration of surface active oxygen, thereby achieving high NO_x conversion in the low-temperature regime.

Chemical looping combustion (CLC) is considered one of the most promising carbon capture technologies. It employs an indirect combustion scheme comprising an OC, an air reactor and a fuel reactor. The OC facilitates oxygen transfer from the air reactor to the fuel reactor, thereby avoiding the co-combustion of air and fuel [9]. The large-scale implementation of CLC technology is critically dependent on the efficient utilization of the OC [10]. The OC design constitutes the technological core of CLC, which fundamentally determines the system's efficiency, productivity and selectivity [11]. Therefore, developing an OC with high reactivity, low breakage and wear, low agglomeration tendency, low cost and high stability in redox cycle is crucial for the successful industrial application of CLC technology [12]. Compared to conventional SCR systems, OCs combine catalytic and oxygen transfer functions. Certain systems exhibit enhanced resistance to poisoning and sintering, enable regeneration cycles, offer extended service life, and can be coupled with chemical looping processes. This results in more compact systems, reduced investment and energy consumption for standalone denitrification units, and lower long-term operating costs. It is noteworthy that there are currently few reports on the specific application of HEO in chemical looping denitrification. This study aims to introduce HEO into chemical looping denitrification systems with the objective of developing a novel OC that combines high activity with a long service life, providing a new material foundation and theoretical basis for chemical looping denitrification technology.

In this study, NiCoZnVCrO_x was synthesized via the sol-gel method and employed as an OC. The effects of varying reaction conditions on the NO reduction activity of the reduced OC were systematically examined, alongside an assessment of its oxidation resistance. By integrating multiple characterization techniques, the reaction mechanism was comprehensively analyzed, ultimately achieving the efficient utilization of HEO for NO reduction.

2. Results

2.1. Denitrification Performance

2.1.1. Effect of Oxidation Temperature of Reduced OC

In Figure 1, NO conversion increases progressively with rising temperature from 600 °C to 800 °C, reaching its peak at 800 °C. This indicates that the reaction between the reduced OC and NO approaches completion at this temperature, resulting in highly efficient denitrification. As the temperature further increases from 800 °C to 900 °C, NO conversion no longer increases but instead slightly decreases, stabilizing at approximately 97%, while N_2 selectivity is maintained at 100% throughout the entire temperature range, suggesting that the denitrification performance of the system reaches a plateau.

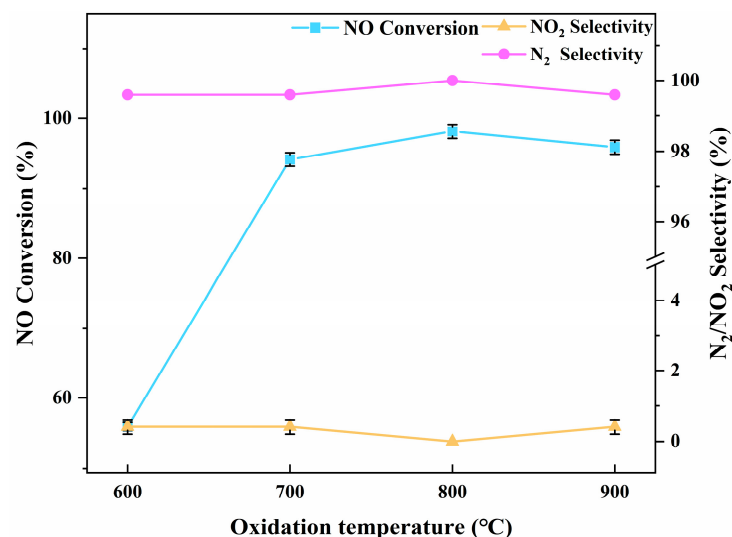


Figure 1. Effect of oxidation temperature on the reactivity of reducing NO.

Within the reaction temperature range of 600–900 °C, NO₂ selectivity remains negligibly low, fluctuating between 0% and 1.1%. With the increase in oxidation temperature, the reactivity of the reduced OC follows a trend of initial enhancement followed by a slight decline. Therefore, 800 °C is identified as the optimal oxidation temperature, at which the chemical looping combustion between the reduced OC and NO is effectively optimized.

2.1.2. Effect of Gas Flow Rate

Figure 2 shows the denitrification performance of the reduced OC at different gas flow rates. The studies by Song [13] and Wojciech Jerzak [14] indicate that within a certain range, the lower the NO flow rate, the higher the NO conversion; conversely, the higher the NO flow rate, the lower the NO conversion. Low flow rates are mainly controlled by external diffusion, and increasing the gas flow rate can eliminate the effect of external diffusion. An appropriate gas flow rate can enhance the interaction between the reduced OC and NO, thereby improving the reaction activity. The N₂ selectivity remains at 100% at all three gas flow rates. Therefore, when the flow rate is selected as 200 mL/min, the NO conversion and NO₂ selectivity reach the optimal level.

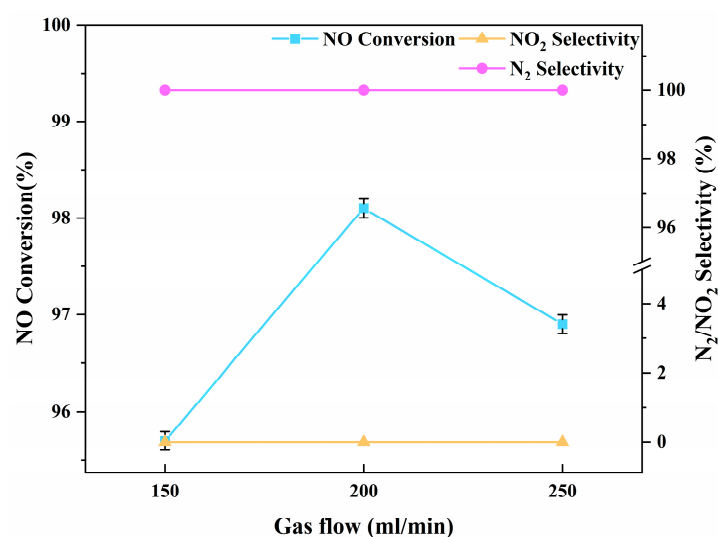


Figure 2. Effect of gas flow rate on the reactivity of reducing NO.

2.1.3. Effect of OC Reduction Time

Figure 3 illustrates the effect of CH_4 reduction time on the reaction performance of the reduced OC in reducing NO. As the reduction time increases, the reduction degree of NiCoZnVCrO_x continuously increases. When the reduction time increases from 60 min to 70 min, the difference in NO conversion and NO_2 selectivity is not significant, and the N_2 selectivity remains at 100%, indicating that at 60 min, NiCoZnVCrO_x is substantially reduced by CH_4 . The depth of OC reduction directly influences the oxidation state of the metal elements, the concentration of oxygen vacancies and the subsequent reaction performance of reducing NO.

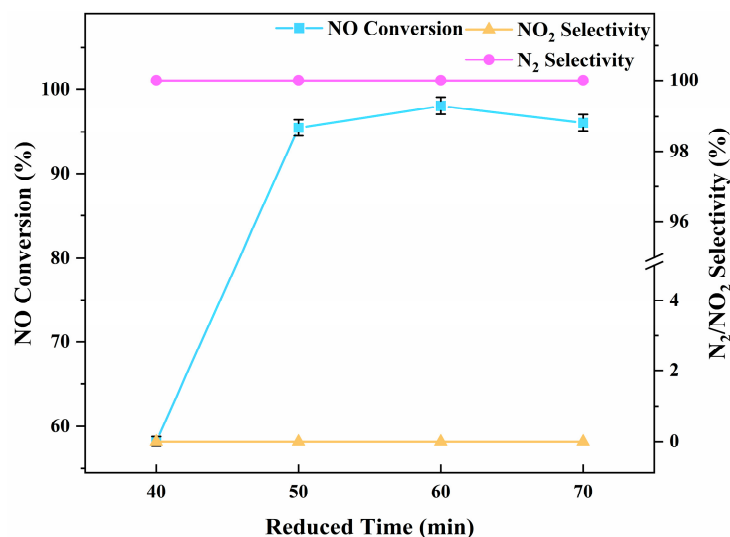


Figure 3. Effect of reduction time on the reactivity of reducing NO.

2.1.4. Effect of Oxygen Concentration

Figure 4 illustrates the effect of O_2 concentration variation during oxidation on the NO reduction performance of the reduced OC, with NO concentration maintained at 170 ppm. The interaction between the reduced OC and NO is significantly weakened when O_2 is introduced during oxidation, and higher O_2 concentrations are unfavorable for enhancing NO conversion. At an O_2 concentration of 1%, the NO conversion decreased by 53.8% compared to the condition without O_2 addition. At an O_2 concentration of 2%, the NO conversion decreased by 27.6% compared to the condition with 1% O_2 addition. At 3% O_2 , the NO conversion decreased by 8.8% compared to the 2% O_2 addition. These results indicate that oxygen presence during NO reduction significantly reduces the NO conversion, while the NO_2 selectivity consistently remains at 0%, and the N_2 selectivity remains at 100%.

The experiments in this study were conducted without the addition of external water, which differs from application scenarios. The current data cannot be directly extrapolated to oxygen-rich and humid application scenarios. Due to limitations in the experimental conditions, the authors did not conduct an in-depth study of the antioxidant properties of the OC under conditions of higher oxygen concentrations and the coexistence of NO, O_2 and H_2O .

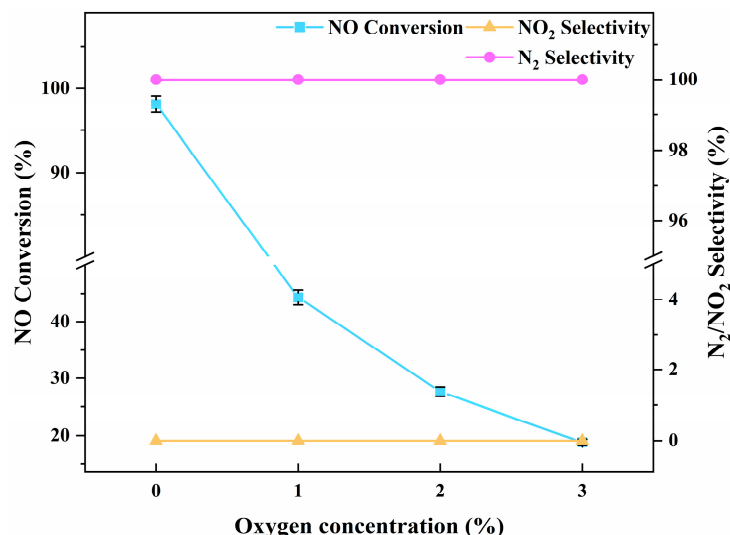


Figure 4. Effect of oxygen concentration on the reactivity of reducing NO.

2.1.5. Effect of Carbon Monoxide Concentration

Figure 5 illustrates the effect of varying CO concentration on NO reduction performance, with NO and O₂ concentrations maintained at 170 ppm and 1%, respectively. Compared to the CO-free condition, the introduction of CO markedly enhances NO conversion. This is attributed to O₂ readily reacting with CO, consuming a significant amount of O₂ and thereby enhancing the reducing power of the reduced OC species. Moreover, increasing CO concentration from 0% to 1% raised NO conversion from 44.3% to 57.9%. Further increasing CO concentration from 1% to 1.5% increased NO conversion from 57.9% to 63.7%. At CO concentration of 2%, the NO conversion reached 91.4%. In the presence of CO, the NO conversion significantly increased compared to the NO + O₂ system alone, exhibiting a proportional relationship with rising CO concentration. Notably, the added CO concentration had no effect on the NO₂ selectivity, which remained consistently at 0%, while the N₂ selectivity remained at 100%.

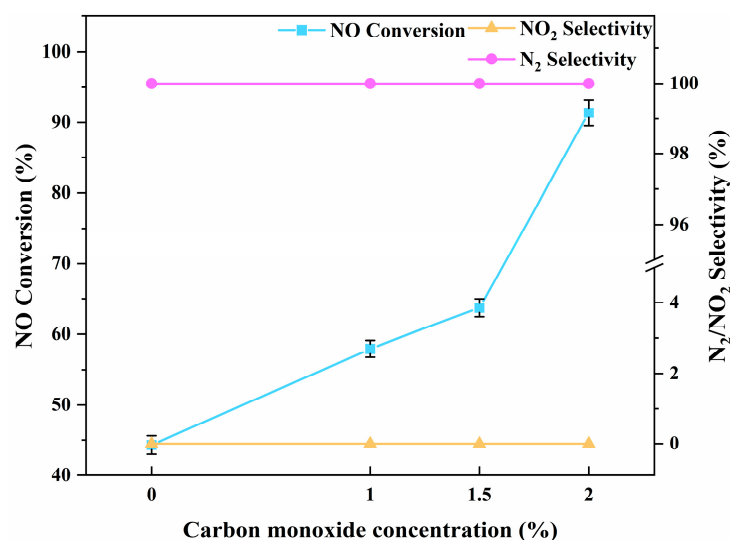


Figure 5. Effect of carbon monoxide concentration on the reactivity of reducing NO.

2.1.6. Ten Redox Cycles Experiments of NiCoZnVCrO_x

Under conditions of 3% CH₄ atmosphere during the reduction phase and 200 ppm NO atmosphere during the oxidation phase, the denitrification performance over ten redox cycles is shown in Figure 6. The highest NO conversion, N₂ selectivity and lowest NO₂

selectivity reached 98.1%, 100% and 0%, respectively. Throughout ten redox cycles, the NO₂ selectivity and N₂ selectivity remained consistently close to 0% and 100%. These results demonstrate that NiCoZnVCrO_x not only exhibits outstanding cyclic reactivity but also sustains consistently high product selectivity over extended periods of operation, effectively suppressing the formation of harmful byproducts such as NO₂, thereby unambiguously validating its excellent stability and practical application potential as an OC for CLC.

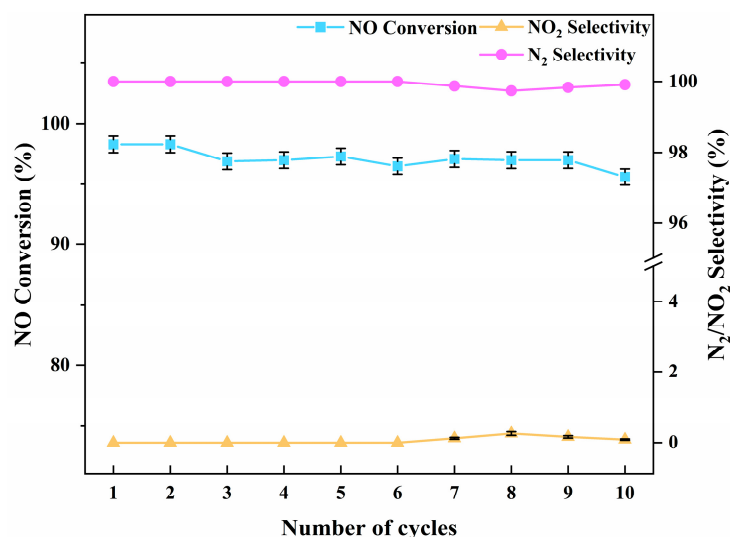


Figure 6. Effect of ten redox cycles on the reactivity of reducing NO.

The XRD patterns results indicate that after the fresh OC was reduced with CH₄ and then oxidized with NO, the NiCoZnVCrO_x phase was restored, demonstrating that this phase transformation process exhibits good reversibility. After ten redox cycles, the XRD patterns of the OC closely matched those of the fresh OC, with no formation of any impurity phases and the crystal structure remaining intact, proving that the OC possesses excellent cycling stability.

The XPS spectra show that lattice oxygen (Peak I) remains the dominant peak after cycling, while the proportion of defect oxygen (Peak II) increases to a limited extent. This indicates that lattice oxygen is effectively replenished periodically during the cycling process, and the moderate increase in oxygen vacancies helps promote the adsorption and activation of NO on the surface. The Co 2p spectrum shows that the positions of the main Co 2p^{3/2} peak and the satellite peak are highly consistent before and after cycling, indicating that the valence state of the Co active sites is fully reversible during redox cycling; Co can be precisely restored to Co²⁺ after oxidation by NO and re-embedded into the spinel lattice. The Cr 2p spectrum further confirms that there were no significant changes in the position or shape of the Cr³⁺ peak, indicating that the Cr₂O₃ framework maintained structural stability throughout the entire cycling process and continued to anchor the Co active sites. The above XPS results are corroborated by the XRD patterns, collectively indicating that the excellent cycling stability of the NiCoZnVCrO_x stems from the high reversibility of its spinel structure.

Due to limitations in experimental conditions, the authors conducted only ten redox cycles. Given that high-temperature operation inevitably leads to carbon deposition from methane cracking, future work should investigate a greater number of redox cycles to fully evaluate long-term stability. This study provides only a preliminary investigation of the cycle performance.

2.2. Characterization of OC

2.2.1. XRD Analysis

The fresh diffraction pattern of NiCoZnVCrO_x fully corresponds to the cubic spinel structure of CoCr_2O_4 . As shown in Figure 7, the diffraction peaks at $2\theta = 18.4^\circ, 30.3^\circ, 35.7^\circ, 37.4^\circ, 43.4^\circ, 53.8^\circ, 57.4^\circ, 63.1^\circ$ and 74.6° correspond to the (111), (220), (311), (222), (400), (422), (511), (440) and (533) crystal planes of CoCr_2O_4 . Furthermore, the absence of diffraction peaks of impurities indicates high product purity [15].

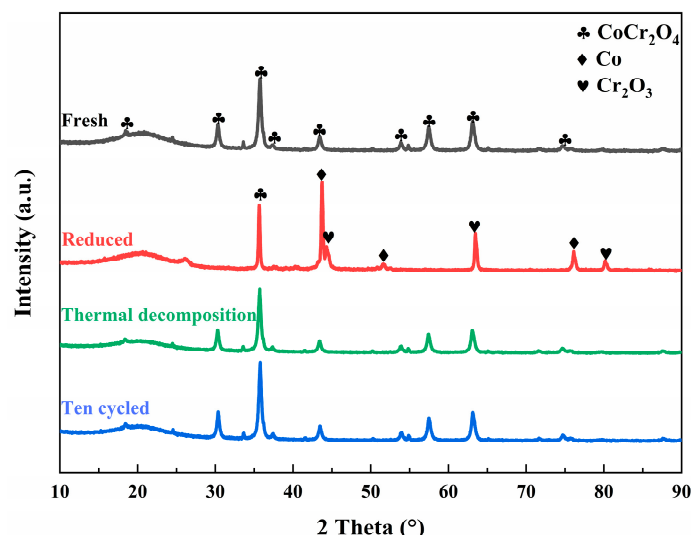


Figure 7. XRD patterns of fresh NiCoZnVCrO_x , after reduction, after thermal decomposition and after ten redox cycles.

The NiCoZnVCrO_x prepared in this study was analyzed by XRD, revealing it to be a single-phase oxide with CoCr_2O_4 as the main phase. This indicates that the OC is a single-phase HEO. Duan et al. [16] confirmed via high-resolution transmission electron microscopy (HRTEM) and selected-area electron diffraction (SAED) that NiCoZnVCrO_x is a HEO with a single-phase spinel structure. The study noted that the lattice spacing of 0.481 nm corresponds to the (111) crystal plane, consistent with the standard CoCr_2O_4 card.

After reduction of NiCoZnVCrO_x by CH_4 , metal Co and Cr_2O_3 appeared with a small amount of CoCr_2O_4 remaining. This indicates that NiCoZnVCrO_x undergoes deep reduction but cannot be completely reduced. After ten redox cycles, NiCoZnVCrO_x exhibits varying degrees of peak intensity reduction in its XRD patterns. The experimental results confirm that the cyclic stability of NiCoZnVCrO_x diminishes with the increase in cycle number. Notably, to eliminate the influence of the pyrolyzed OC on the initial reduction process, XRD characterization was performed on the OC pyrolyzed at 800°C . Figure 7 reveals that the crystalline phases of fresh and the pyrolyzed OC remain virtually unchanged, attributed to the decomposition temperature of CoCr_2O_4 exceeding 1000°C [17]. Subsequent discussions will disregard the effects of OC pyrolysis.

2.2.2. H_2 -TPR and NO-TPD Analysis

The H_2 -TPR spectrum of NiCoZnVCrO_x is shown in Figure 8a, exhibiting four reduction peaks at 365°C , 479°C , 690°C and 853°C . As reported in the literature [18,19], the central peak at 690°C is attributed to the reduction of Co^{2+} to metallic cobalt. The formation of the elemental Co phase, as detected in the XRD patterns (Figure 7) presented, directly confirms from an experimental perspective that this peak corresponds to the reduction of Co^{2+} , while the peak in the 800 – 900°C range is attributed to the formation of Cr_2O_3 . Since the main phase of the OC is CoCr_2O_4 , from the perspective of metal ion ratios, this study

attributes the primary reduction behavior of the OC at 800 °C to the conversion of CoCr_2O_4 to Cr_2O_3 . This attribution is directly supported by the XRD characterization results; the XRD patterns of the reduced OC simultaneously detect both metal Co and Cr_2O_3 phases, which is fully consistent with the aforementioned reduction mechanism.

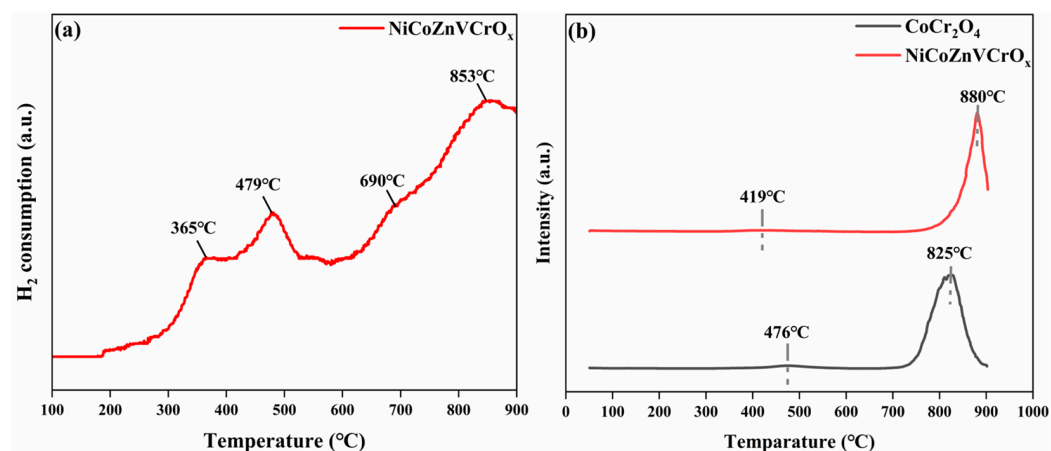


Figure 8. (a) The H_2 -TPR spectrum of NiCoZnVCrO_x and (b) the NO-TPD spectra of NiCoZnVCrO_x and CoCr_2O_4 .

However, there is no consensus on the assignment of the reduction stages exhibiting peaks around 365 °C and 479 °C. Chen et al. [20] suggested that the peak around 365 °C might result from simple chemical adsorption of hydrogen on coordinatively unsaturated Cr^{3+} , while Sloczynski et al. [21] and Wang et al. [22] attributed the hydrogen consumption peak to the reduction of surface chromium ions. Based on the results reported by Grzybowska et al. [23], the reduction peaks at 365 °C and 479 °C are tentatively attributed to the formation of surface Cr^{3+} and the chemical adsorption of hydrogen, respectively.

The adsorption and activation characteristics of NO on the reduced OC directly influence its denitrification reaction activity. In Figure 8b, the NO-TPD spectrum exhibits two desorption peaks, corresponding to medium-temperature desorption at 150–600 °C and high-temperature desorption above 600 °C, representing adsorption sites with different binding strengths on the OC surface (moderately strong and strongly bound sites). Performance is influenced not only by temperature but also by the amount of NO adsorbed. In the pentavalent HEO, the coexistence of five metal cations within the same crystal lattice provides a greater variety and larger number of active surface sites, resulting in a significantly stronger NO capture capacity compared to the binary CoCr_2O_4 . This OC exhibits small particle size, exposing more surface active sites. Concurrently, its superior reducibility and higher oxygen vacancy content further enhance NO adsorption energy. Consequently, the reduced OC demonstrates outstanding NO adsorption/desorption performance, which is a key factor in its enhanced denitrification capability.

2.2.3. MS Analysis

The gases produced by reacting the reduced OC with NO, with $\text{NO} + \text{O}_2$ under optimal reaction conditions were collected in gas collection bags. These gases were then transferred to a gas chromatograph–mass spectrometer for qualitative analysis of their components.

In Figure 9a,b, the signal intensity of N_2 increased and remained consistently high, while the signal intensities of NO, N_2O and NO_2 remained unchanged. The results indicate that the reduced OC reacts with NO and $\text{NO} + \text{O}_2$ to produce exclusively N_2 as the gas product, without generating impurity gases such as NO, N_2O , or NO_2 . This demonstrates an extremely high N_2 selectivity.

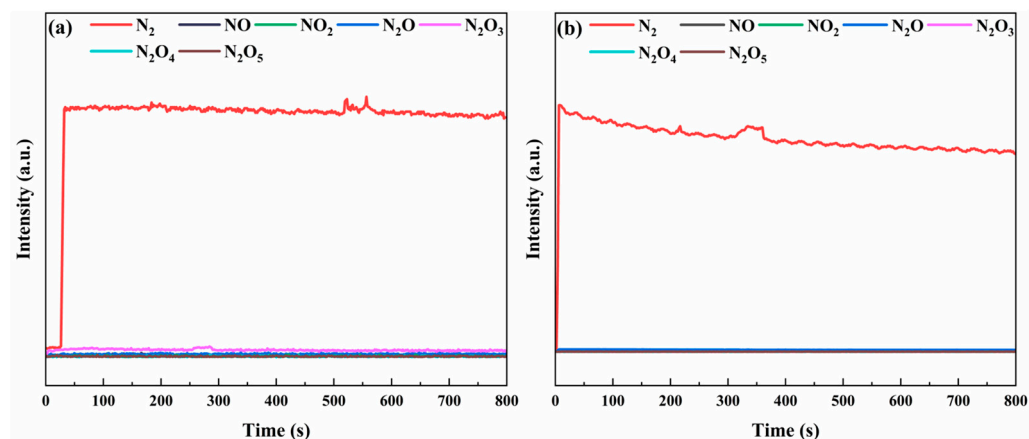


Figure 9. The mass spectrometry of reduced OC reacting with (a) NO and (b) NO + O₂.

2.2.4. Raman Analysis

The Raman spectra of fresh NiCoZnVCrO_x and after one and ten redox cycles are shown in Figure 10. Fresh NiCoZnVCrO_x exhibits six bands at 177 cm^{−1}, 421 cm^{−1}, 501 cm^{−1}, 532 cm^{−1}, 659 cm^{−1} and 773 cm^{−1}.

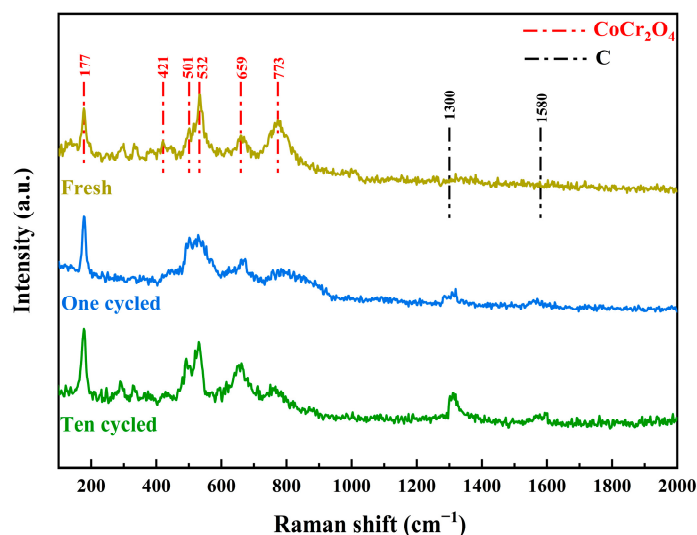


Figure 10. The Raman spectra of fresh NiCoZnVCrO_x, after one and ten redox cycles.

Generally, spinel-type CoCr₂O₄ exhibits five Raman-active phonon modes: A_{1g}, E_g and three F_{2g} modes [15]. Among these, the band at 773 cm^{−1} corresponds to the A_{1g} mode. This peak corresponds to the symmetric stretching vibration between the metal cation and oxygen at the tetrahedral site (A site), primarily arising from the vibrational contribution of the Co²⁺-O bond at the tetrahedral site. The A_{1g} mode is highly sensitive to the occupation state of the cation at the A site and is the most characteristic peak in the spinel structure [24]. The band at 421 cm^{−1} corresponds to the E_g mode. This refers to the bending vibration of the metal–oxygen bond at the octahedral site (B site), which primarily reflects the vibrational characteristics of the Cr²⁺-O bond at the octahedral site and is directly related to the occupancy of the B site by Cr³⁺ [25]. The bands at 177 cm^{−1}, 501 cm^{−1} and 659 cm^{−1} correspond to the F_{2g} modes. These correspond to the mixed translational–vibrational modes in the spinel structure. Specifically, the F_{2g} mode at 659 cm^{−1} is primarily attributed to the asymmetric stretching vibration of the Cr³⁺-O bond in the octahedral site; the mode at 501 cm^{−1} is attributed to the coupling vibration between the Co-O and Cr-O

bonds; and the mode at 177 cm^{-1} corresponds to the translational vibration of metal cations in the lattice [24].

Notably, the origin of the band at 532 cm^{-1} remains unclear. Chen [20] proposed that it may represent a Raman-active mode arising from cation disorder induced by translational symmetry breaking.

Additionally, the peaks corresponding to NiCoZnVCrO_x exhibited weakening and shifting after ten redox cycles yet remained fundamentally consistent, indicating strong cycling stability of this OC. Changes in the carbon peaks at 1300 cm^{-1} and 1580 cm^{-1} suggest carbon deposition on the NiCoZnVCrO_x surface following ten redox cycles, attributed to high-temperature methane cracking [26].

2.2.5. FTIR Analysis

The chemical structure of the prepared OC was analyzed using FTIR. The FTIR spectra of NiCoZnVCrO_x are shown in Figure 11. Two absorption peaks appearing at 507 cm^{-1} and 630 cm^{-1} represent the stretching vibrations of metal–oxygen bonds. These spectral bands confirm that chromium and cobalt occupy oxygen-surrounded sites within the spinel structure, arising from stretching vibrations at tetrahedral and octahedral positions. The properties of the NiCoZnVCrO_x structure primarily depend on the cation distribution at the octahedral sites. The minor peak at 947 cm^{-1} can be attributed to the stretching vibration of the cobalt–oxygen bond in the spinel structure [27]. Additionally, the peaks at 1635 cm^{-1} and 3435 cm^{-1} confirm the presence of hydroxyl (OH) groups [28].

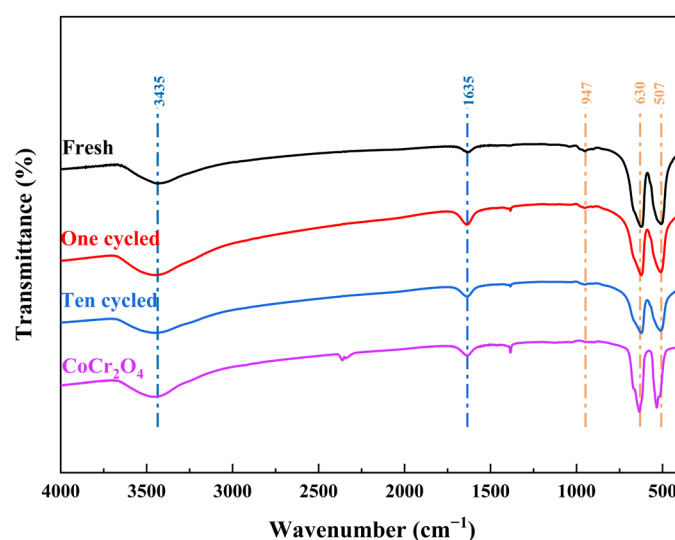


Figure 11. The FTIR spectra of CoCr_2O_4 and fresh NiCoZnVCrO_x , after one and ten redox cycles.

Actual crystals deviate from the ideal CoCr_2O_4 crystal structure due to the presence of multiple cations, each possessing distinct ionic radii. To accommodate cations with larger ionic radii, oxygen atoms undergo displacement from their ideal positions [29,30].

2.2.6. DRIFTS Analysis

As depicted in Figure 12, characteristic NO absorption peaks appear at 1370 cm^{-1} and 1255 cm^{-1} . An infrared absorption peak attributable to the bidentate nitrate anion appears at 1370 cm^{-1} , while a new absorption peak attributable to the bidentate nitrite anion is observed near 1255 cm^{-1} [31].

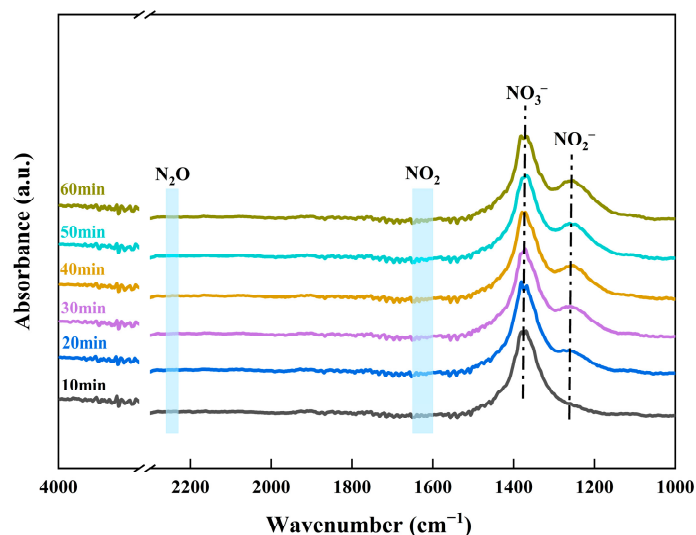


Figure 12. The DRIFTS spectrum of NiCoZnVCrO_x.

The reduced OC exhibits strong adsorption and activation capabilities toward NO molecules. Nitrate ions pre-deposited on the OC surface are reduced to nitrite ions by reductive sites (oxygen vacancies, low-valent metals), demonstrating the strong reductive nature of the OC surface. The generated nitrite ions can be further reduced into more reactive species. Two independently dissociated NO* species directly combine to form N₂ [32].

Notably, no infrared absorption peak characteristic of NO₂ was observed in the 1600 cm^{−1} to 1650 cm^{−1} range; similarly, no infrared absorption peak characteristic of N₂O was detected in the 2230 cm^{−1} to 2260 cm^{−1} range. In summary, the reduced OC complex does not produce gases such as NO₂ and N₂O during the reduction of NO, indicating a high selectivity for N₂.

2.2.7. SEM Analysis

As revealed in Figure 13(a1,a2), the surface of the freshly prepared NiCoZnVCrO_x exhibits a uniform particle distribution with small particle sizes and good overall dispersion. The boundaries between particles are well-defined, and no significant agglomeration is observed, indicating that the sol-gel preparation method effectively suppresses the excessive growth of the initial particles. After ten redox cycles, the surface microstructure of NiCoZnVCrO_x is depicted in Figure 13(b1,b2), where the octahedral structure characteristic of CoCr₂O₄ spinel can be observed. After ten redox cycles, the microstructure of the NiCoZnVCrO_x surface underwent significant changes. Compared to the fresh OC, the particle size increased markedly, and the particles exhibited a polyhedral morphology, which is consistent with the grain growth behavior of spinel-type oxides under high-temperature cycling conditions. Furthermore, varying degrees of sintering and agglomeration occurred between the particles. Particle agglomeration reduces the effective specific surface area and decreases the accessibility of active sites, thereby affecting the overall reactivity of the OC. This constitutes one of the primary factors contributing to the progressive deterioration in reactivity following multiple redox cycles.

The SEM-EDS (Figure 14) mapping reveals that the elements O, Cr and Co were homogeneously distributed on the surfaces of both the fresh and cycled OCs, with no evidence of significant elemental segregation or phase separation. This uniform distribution indicates high consistency in both composition and structure of the synthesized material, ensuring stable performance across different regions. This is particularly crucial for chemical looping

denitrification applications as uniform component distribution significantly enhances the material's overall performance and stability.

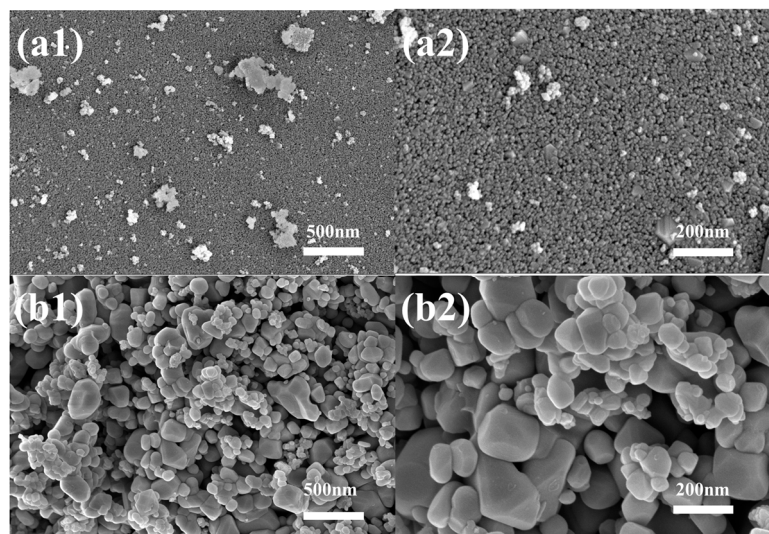


Figure 13. The SEM micrographs of (a1,a2) fresh NiCoZnVCrO_x and (b1,b2) after ten redox cycles.

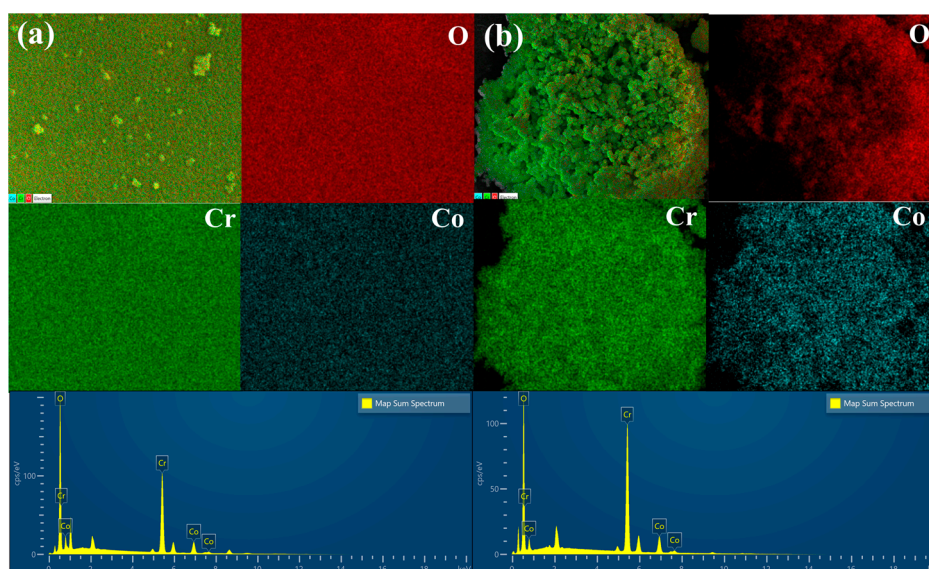


Figure 14. The SEM-EDS elemental mapping of (a) fresh NiCoZnVCrO_x and (b) after ten redox cycles.

Due to experimental constraints, the study was limited to only ten redox cycles on the OC. Nevertheless, the structural evolution of the OC with prolonged high-temperature operation warrants further discussion. Under prolonged cycling conditions at 800 °C for NO-to-N₂ reduction, the OC may face the following structural degradation issues: (1) Risk of phase separation: Phase precipitation may occur in prolonged reducing atmospheres, leading to uneven distribution of active sites. (2) Cation segregation: Polyvalent elements may enrich on the surface, altering the composition of active sites. (3) Irreversible changes in oxygen vacancies: A prolonged cycle experiment may cause the concentration of oxygen defects to deviate from the initial value. (4) Grain coarsening: Although the high-entropy effect can suppress sintering to some extent, prolonged high-temperature cycling experiments will inevitably lead to sintering, thereby reducing the specific surface area.

2.2.8. XPS Analysis

The XPS spectra of fresh NiCoZnVCrO_x and after ten redox cycles are shown in Figure 15. The O 1s spectrum of fresh NiCoZnVCrO_x consists primarily of three peaks: OI at 529.9 eV corresponding to lattice oxygen, OII at 531.3 eV corresponding to surface oxygen defects, and OIII at 532.5 eV attributed to surface-adsorbed oxygen [33,34].

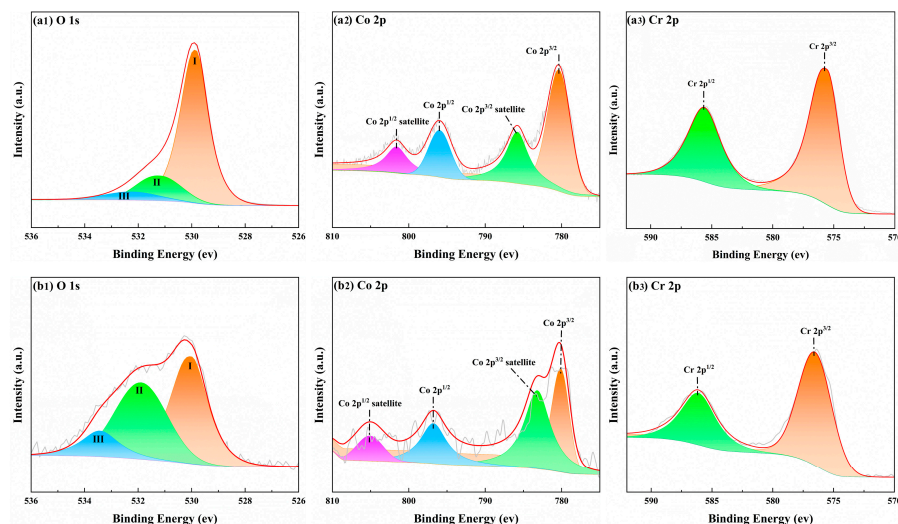


Figure 15. The XPS spectra of (a1–a3) fresh NiCoZnVCrO_x and (b1–b3) after ten redox cycles.

Table 1 shows the relative O1s content of NiCoZnVCrO_x after ten redox cycles compared to the fresh OC. After ten redox cycles, the area of OI decreased by 33.14% compared to the fresh oxygen-loaded OC, while the area of OII increased by 1.58 times relative to the fresh OC, and the area of OIII increased by 7.33% compared to the fresh OC. Importantly, the ratio of integrated areas between the O_{Lat} (lattice oxygen) and O_{Ads} (adsorbed oxygen) peaks (O_{Lat}/O_{Ads}) reflects the proportion of these two oxygen states. In this context, a lower O_{Lat}/O_{Ads} ratio indicates higher oxygen vacancy concentration [35–38]. It is evident that after ten redox cycles, the O_{Lat}/O_{Ads} ratio of the OC decreased significantly more than that of the fresh OC. The OC did not undergo complete oxidative regeneration; instead, a small amount of surface-adsorbed oxygen increased but accounted for a minor proportion, while a large number of oxygen vacancies formed. This indicates that lattice oxygen can be converted into oxygen vacancies on the surface, which helps regulate the surface chemistry and electronic structure, thereby enhancing its reactivity.

Table 1. The relative O 1s content of fresh NiCoZnVCrO_x and after ten redox cycles.

OC	OI/%	OII/%	OIII/%	O _{Lat} /O _{Ads}
Fresh	79.16	16.33	4.51	3.80
After ten redox cycles	46.02	42.13	11.85	0.85

Figure 15 shows the energy level spectra of Co 2p and Cr 2p. The characteristic peaks at 780.1 eV and 795.7 eV correspond to the Co 2p^{3/2} and Co 2p^{1/2} spin orbitals of Co²⁺, respectively, while the two weak peaks at 786.2 eV and 802.5 eV correspond to satellite peaks of Co 2p^{3/2} and Co 2p^{1/2}, respectively. The strong peaks at 576.1 eV and 586.0 eV represent the Cr 2p^{3/2} and Cr 2p^{1/2} spin orbitals, indicating that chromium exists in the +3 oxidation state [39]. Both cobalt and chromium maintain their +2 and +3 oxidation states before and after ten redox cycles. These results indicate that the primary phase of the fresh OC is high-purity CoCr₂O₄. After ten redox cycles, the OC can still be oxidatively

regenerated into CoCr_2O_4 , maintaining the stability of the cyclic reaction. This conclusion is consistent with the findings from XRD analysis.

3. Materials and Methods

3.1. OC Preparation

Nickel acetate tetrahydrate, cobalt acetate tetrahydrate, zinc acetate, oxovanadium oxalate, chromium acetate, and citric acid were dissolved in deionized water at a molar ratio of 0.04:0.48:0.36:0.12:2:4.5 to obtain a homogeneous solution. The mixture was then heated and stirred at 80 °C until gelation occurred. The gel was subsequently transferred to a drying oven at 120 °C until the OC was completely dry. The dried gel was calcined at 800 °C for 8 h in an air atmosphere to obtain the OC. Finally, the naturally cooled OC was ground and designated NiCoZnVCrO_x . Additionally, CoCr_2O_4 was prepared by the same method. Detailed information on the reagents used for preparing the OC is shown in Table 2.

Table 2. Detailed information on the reagents.

Molecular Formula	Molecular Weight	Reagent Manufacturer
$\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	248.843	Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China)
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	249.082	Shanghai Macklin Biochemical Co., Ltd.
$(\text{CH}_3\text{COO})_2\text{Zn}$	183.48	Shanghai Macklin Biochemical Co., Ltd.
$\text{VOC}_2\text{O}_4 \cdot 5\text{H}_2\text{O}$	245.02	Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China)
$(\text{CH}_3\text{COO})_3\text{Cr}$	229.128	Shanghai Aladdin Biochemical Technology Co., Ltd.
$\text{C}_6\text{H}_8\text{O}_7$	192.12	Shanghai Aladdin Biochemical Technology Co., Ltd.

3.2. OC Characterization

XRD patterns were recorded using an X-ray diffractometer (MiniFlex 600 X-ray, Rigaku Corporation, Akishima, Japan): $\text{Cu-K}\alpha$, generator settings: 40 kV, 100 mA, with a scanning speed of 5°/min. The crystalline phases of different OCs were observed within the 2 θ range of 10° to 90°.

H_2 -TPR employs the PCA-1200 chemical adsorption analyzer (Beijing Builder Electronic Technology Co., Ltd., Beijing, China). First, 30 mg of the OC was loaded into a quartz tube and placed in the instrument. The system was purged with nitrogen at 200 °C for 1 h, then cooled to room temperature before 10% hydrogen gas was introduced. Once the hydrogen concentration stabilized, the preset heating program was initiated, and the signal intensity was measured from 100 °C to 900 °C via the thermal conductivity detector (TCD).

NO-TPD and H_2 -TPR employed the same instrumentation. A total of 30 mg of the unreduced OC (40 mesh particles) was placed into a U-tube and connected to the apparatus. Then, 10% H_2 and heat to 800 °C were introduced for one hour of reduction. After cooling to 200 °C, the H_2 was replaced with Ar (30 mL/min) and maintained for one hour to desorb physically adsorbed gases from the OC surface. Subsequently, the system was cooled to 50 °C, then switched to 200 ppmNO (30 mL/min) for adsorption for 1 h. After switching back to Ar for 30 min purging, the OC was heated at 10 °C/min after signal stabilization, and desorption peaks were recorded within the 50 °C to 900 °C temperature range.

MS testing was performed using a gas mass spectrometer. Gases generated during the optimal performance reaction were collected using gas collection bags and manually introduced into the gas chromatograph–mass spectrometer for gas component detection. The collected images represent qualitative measurements of gas components and do not provide quantitative measurements of individual gas components.

Raman spectra were acquired using a Raman imaging spectrometer (Thermo Fisher DXR™3xi, Waltham, MA, USA) equipped with a 532 nm argon ion laser, mounted on a multi-magnification microscope. The laser power was set to 3.0 mW, and the frequency range was set from 100 cm^{-1} to 2000 cm^{-1} . Raman spectroscopy was employed to analyze the composition of the OC and the carbon deposition.

Chemical bonds or functional groups in the OC were detected using a German VERTEX 70 Fourier Transform Infrared Spectrometer (FTIR and DRIFTS, Bruker, Billerica, MA, USA). The FTIR spectral detection range is 4000 cm^{-1} to 400 cm^{-1} . The DRIFTS test conditions were as follows: The OC was tested at $800\text{ }^{\circ}\text{C}$ and in atmospheric pressure, with a flow rate of 30 mL/min of a 200 ppm NO/Ar mixture. The DRIFTS spectral detection range is 4000 cm^{-1} to 1000 cm^{-1} , with a scanning resolution of 4 cm^{-1} .

The microstructure of particles on the surface of the OC was observed using a Zeiss Gemini SEM 300 high-resolution scanning electron microscope (SEM, Jena, Germany) after fresh and ten redox cycles.

The surface elemental composition and valence states of different OCs were determined using XPS (K-Alpha XPS, Thermo Fisher Scientific, Waltham, MA, USA) with a calibration method based on $\text{Al-K}\alpha$ radiation (1486.6 eV , $6\text{ mA} \times 12\text{ kV}$) and the surface contaminant C 1s peak (284.8 eV).

3.3. OC Test

The OC reaction performance experiments were primarily conducted in a GSL-1100X tube furnace. The experimental setup and procedure are shown in Figure 16. The system comprised a mass flow controller (D07-19B, Beijing Sevenstar Electronics Co., Ltd., Beijing, China), tube furnace (GSL-1100X, Hefei Kejing Materials Technology Co., Ltd., Hefei China), gas filter, flue gas analyzer (Gasboard-3100, Cubic Instruments Ltd., Wuhan, China) and computer. The reduction and oxidation of the OC were performed within the tube furnace under experimental conditions detailed in Table 3. The cyclic experimental procedure was as follows: (1) 200 mg of NiCoZnVCrO_x was positioned within a quartz tube. (2) Ar was introduced to reduce the oxygen concentration to 0% . (3) The temperature was programmed to reach the target temperature. Upon reaching the target temperature, CH_4 was introduced into the reactor to reduce NiCoZnVCrO_x . Gas composition changes were monitored in real time using the flue gas analyzer, and the data were recorded by the computer. (4) After reduction, the gas supply was switched to Ar to purge residual gases. Following purging, NO was introduced into the reactor to promote oxidation of the reduced OC. Gas composition changes were monitored with the flue gas analyzer, and the data were recorded. (5) After completing the redox cycle reaction of NiCoZnVCrO_x , the procedure was terminated. Once the reactor had cooled to room temperature, the OC was collected for characterization.

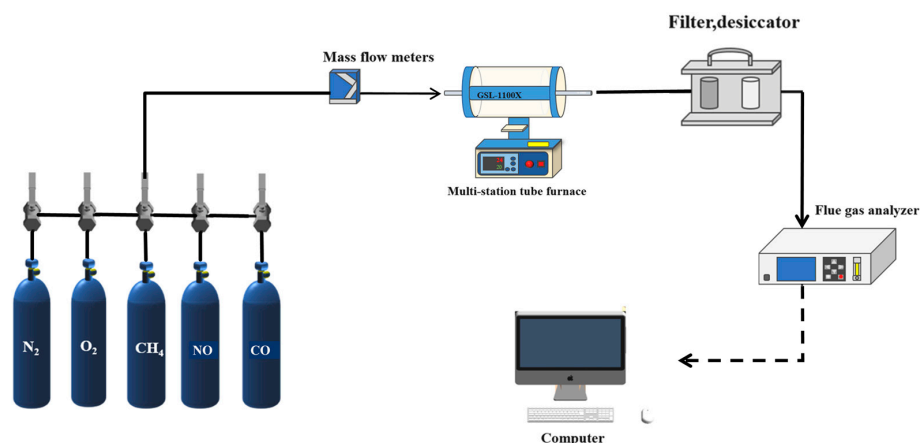


Figure 16. Experimental system diagram.

Table 3. Experimental conditions.

Experimental Groups	Oxidation Temperature of OC (°C)	Gas Flow (mL/min)	Reducing Time of OC (min)	The Reaction Atmosphere of OC in the Oxidation Stage
The reaction temperature in the oxidation stage	600, 700, 800, 900	200	60	200 ppm NO/Ar
Gas flow of NO	800	150, 200, 250	60	200 ppm NO/Ar
Reducing time of OC	800	200	40, 50, 60, 70	200 ppm NO/Ar
O ₂ concentration	800	200	60	170 ppm NO/Ar + 1% O ₂ /Ar, 170 ppm NO/Ar + 2% O ₂ /Ar, 170 ppm NO/Ar + 3% O ₂ /Ar
CO concentration	800	200	60	170 ppm NO/Ar + 1% O ₂ /Ar + 1% CO/Ar, 170 ppm NO/Ar + 1% O ₂ /Ar + 1.5% CO/Ar, 170 ppm NO/Ar + 1% O ₂ /Ar + 2% CO/Ar
Ten redox cycles of OC	800	200	60	200 ppm NO/Ar

The collected gas data is stored in the gas analyzer and can be retrieved and analyzed using Formulas (1)–(3). The redox performance of NiCoZnVCrO_x is determined by NO conversion, NO₂ selectivity and N₂ selectivity. In this study, X_{NO} (NO conversion), S_{NO₂} (NO₂ selectivity) and S_{N₂} (N₂ selectivity) are calculated using the following formulas:

$$X_{\text{NO}} = \frac{C_{\text{NO},\text{in}} - C_{\text{NO},\text{out}}}{C_{\text{NO},\text{in}}} \times 100\% \quad (1)$$

$$S_{\text{NO}_2} = \frac{C_{\text{NO}_2,\text{out}} - C_{\text{NO}_2,\text{in}}}{C_{\text{NO},\text{in}} - C_{\text{NO},\text{out}}} \times 100\% \quad (2)$$

$$S_{\text{N}_2} = (1 - S_{\text{NO}_2}) \times 100\% \quad (3)$$

In the formula, C_{NO,in} and C_{NO,out} represent the cumulative concentrations of NO at the reaction inlet and outlet, respectively; C_{NO₂,in} and C_{NO₂,out} represent the cumulative concentrations of NO₂ at the reaction inlet and outlet, respectively. The computational mean values represent the experimental data, and error curves characterize the data distribution, where the height of the error curve corresponds to the positive or negative standard deviation. Since the flue gas analyzer used in this study can only measure NO_x and cannot directly measure N₂, if no impurity gases such as N₂O are produced, then (S_{NO₂} + S_{N₂}) = 100%. The calculated average of experiments represents data, and uses an error bar to characterize data distribution, where the error bar height is a positive or negative standard deviation.

4. Conclusions

This study clearly demonstrates the feasibility of NO reduction using NiCoZnVCrO_x within a CLC framework.

- (1) In the presence of NO and O₂, the existence of O₂ oxidizes the reduced OC, thereby suppressing its NO reduction performance. In an atmosphere containing 170 ppm NO and 1% O₂, the NO conversion, N₂ selectivity and NO₂ selectivity were 44.3%, 100% and 0%, respectively.
- (2) In the presence of NO, O₂, and CO, CO preferentially consumes a substantial portion of O₂ to form CO₂. By reinforcing the reductive character of the reduced OC, its NO reduction performance is improved. In an atmosphere of 170 ppm NO, 1% O₂ and 2% CO, the NO conversion, N₂ selectivity and NO₂ selectivity were 91.4%, 100% and 0%, respectively.

- (3) Under conditions of 3% CH₄ atmosphere during the OC reduction phase and 200 ppm NO atmosphere during the oxidation phase, NiCoZnVCrO_x underwent ten redox cycles at 800 °C. On the surface of the material, an abundance of oxygen vacancies was generated, enhancing the oxygen storage and release capacity. However, factors such as carbon deposition on the OC and sintering and agglomeration led to a decrease in cycle stability.
- (4) DRIFTS elucidated the mechanistic pathway for NO reduction to N₂: nitrate ions are reduced to nitrite ions, which are further reduced to NO* species. Two NO* molecules dissociate to form N* species that combine to produce N₂.

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