Soot Combustion over Cu–Co Spinel Catalysts: The Intrinsic Effects of Precursors on Catalytic Activity

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Abstract: In this work, a series of CuCoO$_4$-x (x = N, A and C) catalysts were synthesized using different metal salt precursors by urea hydrothermal method for catalytic soot combustion. The effect of CuCoO$_4$-x catalysts on soot conversion and CO$_2$ selectivity in both loose and tight contact mode was investigated. The CuCoO$_4$-N catalyst exhibited outstanding catalytic activity with the characteristic temperatures (T$_{10}$, T$_{50}$ and T$_{90}$) of 451 °C, 520 °C and 558 °C, respectively, while the CO$_2$ selectivity reached 98.8% during the reaction. With the addition of NO, the soot combustion was further accelerated over all catalysts. Compared with the loose contact mode, the soot conversion was improved in the tight contact mode. The CuCoO$_4$-N catalysts showed better textural properties compared to the CuCoO$_4$-A and CuCoO$_4$-C, such as higher specific surface areas and pore volumes. The XRD results confirmed that the formation of a CuCoO$_4$ crystal phase in all catalysts. However, the CuO crystal phase only presented in CuCoO$_4$-N and CuCoO$_4$-A. The relative contents of Cu$^{2+}$, Co$^{3+}$ and O$_{ads}$ on the surface of CuCoO$_4$-x (x = N, A and C) catalysts were analyzed by XPS. The CuCoO$_4$-N catalyst displayed the highest relative content of Cu$^{2+}$, Co$^{3+}$ and O$_{ads}$. The activity of catalytic soot combustion showed a good correlation with the order of the relative contents of Cu$^{2+}$, Co$^{3+}$ and O$_{ads}$. Additionally, the CuCoO$_4$-N catalyst exhibited lower reduction temperature compared to the CuCoO$_4$-A and CuCoO$_4$-C. The cycle tests clarified that the copper–cobalt spinel catalyst obtained good stability. In addition, based on the Mars–van Krevelen mechanism, the process of catalytic soot combustion was described combined with the electron transfer process and the role of oxygen species over CuCoO$_4$ spinel catalysts.

Keywords: soot combustion; spinel catalyst; precursor; transition metal oxides; catalytic activity

1. Introduction

Soot particles are emitted from incomplete combustion of hydrocarbon fuels in diesel engines [1]. Mitigating soot particle emissions from diesel engines has raised much attention due to the negative impact of soot particles on human health and environmental protection [2,3]. A diesel particulate filter (DPF) is the most effective after-treatment technology for soot particles from diesel engines. However, a common issue of pore blockage over DPFs after a period of use should be addressed [4]. One of the most effective measures to improve soot oxidation is to coat the DPF with catalysts and form a catalyzed DPF (CDPF) [5]. CDPFs with highly active catalysts can accelerate soot oxidation and lower the ignition temperatures.

Various catalysts have been proposed and optimized to accelerate the catalytic soot combustion, while Pt-based catalysts have shown superb soot oxidation performance under practical conditions [6,7]. However, due to the high cost of noble metals, transition metal-based catalysts have been intensively studied for catalytic soot oxidation more recently [8]. Copper–cobalt catalysts play an important role as substitutes for noble metals in the field of catalytic soot combustion due to their outstanding redox properties and thermal stability [9].
Zhang et al. reported that a spinel-type CuCo$_2$O$_4$ catalyst showed a lower T$_{50}$ temperature (574 °C) of catalytic soot combustion than that of Co$_3$O$_4$ catalysts (580 °C) due to its higher relative content of Co$^{3+}$ species [10]. Jampaiah et al. found that a CuCo-MnO$_2$ catalyst exhibited a lower T$_{90}$ temperature (485 °C) of catalytic soot combustion than that of NiCo-MnO$_2$ catalysts (513 °C) under the loose contact mode due to more oxygen vacancies and active sites on the catalyst surfaces [11]. Zhang et al. tested the stability of CuCo$_2$O$_4$ spinel catalysts in four consecutive soot combustion cycles and found that the values of T$_{50}$ for catalytic soot combustion increased from 539 °C to 544 °C, 547 °C and 549 °C, respectively [12].

Recently, the effect of metal salt precursor on the textural and redox properties of catalysts was found to play a key role in catalytic activity and product selectivity [13]. Yang et al. found that the catalytic activity of selective acetylene hydrogenation at 50 °C over the Pd/Al$_2$O$_3$ catalyst using acetate as the Pd precursor reached 78.6%, which was 31.1% higher than that using chloride precursors since Cl residuals existed in the form of PdCl$_2$-$^4$, resulting in the decrease of the electron density of Pd atoms [14]. Wang et al. reported that the n-hexadecane conversion over Pt/ZSM-22 catalysts with Pt(NH$_3$)$_2$Cl$_2$ precursors was ~9.1% higher compared to that over catalysts using (Pt(NO$_3$)$_2$ and H$_2$PtCl$_6$ as the precursors due to the higher platinum dispersion [15]. Yun et al. found that the Ni/Al$_2$O$_3$ catalyst using acetate salt precursors achieved the highest activity (85.6%) in the steam reforming of acetic acid at 450 °C, while the catalytic activity of the catalyst prepared from chloride salts was only 38.7% [16]. These results indicated that the role of precursors should be preferentially considered during the designing and preparation of heterogeneous catalysts.

In this work, copper–cobalt spinel oxides were prepared with a urea hydrothermal method using different copper and cobalt precursors (nitrate, chloride and acetate). The physicochemical properties of these catalysts were characterized by N$_2$ adsorption–desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), temperature-programed reduction of H$_2$ (H$_2$-TPR) and temperature-programed desorption of O$_2$ (O$_2$-TPD). The catalytic activity of soot combustion was investigated by temperature-programed oxidation (TPO) experiments under various reaction conditions.

2. Experimental Study
2.1. Catalyst Preparation

In this work, a series of CuCo$_2$O$_4$-x catalysts was synthesized by urea hydrothermal methods with different precursors, where x represented the types of copper and cobalt precursors, e.g., the nitrates (N), acetate (A) and chloride (C), respectively. All chemicals used were of analytical reagent grade and purchased from Macklin Co., Ltd. (Shanghai, China). Taking CuCo$_2$O$_4$-N as an example, 0.02 mol Cu(NO$_3$)$_2$·3H$_2$O, 0.04 mol Co(NO$_3$)$_3$·6H$_2$O and 0.06 mol CH$_3$N$_2$O were dissolved in 100 mL of deionized water and stirred for 1 h at room temperature. Afterwards, the mixed solution was transferred to a polytetrafluoroethylene-lined high pressure reactor placed in a thermostat at 150 °C for hydrothermal reaction. After 12 h, the resulting solution was filtered to obtain a precipitate. The precipitate was then washed three times with deionized water and dried in an oven at 110 °C overnight. Finally, the precipitate was calcined in a muffle furnace at 700 °C for 6 h and sieved to 40–60 meshes. The prepared catalysts were denoted as CuCo$_2$O$_4$-N, CuCo$_2$O$_4$-A and CuCo$_2$O$_4$-C, respectively.
2.2. Catalyst Characterizations

N$_2$ adsorption–desorption analysis was conducted at 77 K to determine the specific surface area, pore size distribution and average pore diameter of the catalysts using TriStar II 3020 (Micromeritics, Norcross, GA, USA). The specific surface areas were calculated using the Brunauer–Emmett–Teller (BET) method. Total pore volume and pore size distribution were calculated via the Barrett–Joyne–Halenda (BJH) method at the relative pressure of $p/p_0 = 0.99$. The crystal structure of catalysts was observed by X-ray diffraction (XRD) using a diffractometer system (D-Max 2000, Rigaku, Tokyo, Japan) with Cu-K$_\alpha$ radiation operating at 40 kV and 30 mA. All catalysts were scanned in the range of 10$^\circ$ to 80$^\circ$ with a step size of 0.02$^\circ$. A scanning electron microscopy (SEM) instrument (JSM-7001F, JEOL, Tokyo, Japan) was used to observe the surface morphology of catalysts at an accelerating voltage of 10 kV. The X-ray photoelectron spectra (XPS) were measured with Thermo Escalab 250Xi equipment with monochromatic Al-K$_\alpha$ X-ray radiation at 150 W. All binding energies were calibrated using the C 1s photoelectron peak at 284.8 eV. The redox properties of all catalysts were analyzed using the temperature-programed reduction of the H$_2$ (H$_2$-TPR) apparatus (Autochem II 2920, Micromeritics, Norcross, GA, USA). To remove impurities, 16 mg catalysts were pretreated at 250 $^\circ$C for 1 h and cooled down to room temperature before each test. Then, the catalysts were heated from room temperature to 800 $^\circ$C at a heating rate of 10 $^\circ$C·min$^{-1}$ in a 30 mL·min$^{-1}$ feeding gas flow (10 vol.% H$_2$/Ar). The amount of H$_2$ consumption was calculated based on the H$_2$-TPR profiles. The profiles of the temperature-programed desorption of O$_2$ (O$_2$-TPD) were performed using the same apparatus as that for H$_2$-TPR. Before the measurement, 200 mg of catalysts were pretreated in an He stream at 200 $^\circ$C for 1 h and cooled down to room temperature. Then, the adsorption of O$_2$ was conducted at 70 $^\circ$C for 1 h in a gas mixture of 3 vol.% O$_2$/He (30 mL·min$^{-1}$). Subsequently, the sample was purged by a flowing pure He stream to remove excessive and weakly adsorbed O$_2$. Finally, the sample was heated to 800 $^\circ$C with a heating rate of 10 $^\circ$C·min$^{-1}$ in a pure He flow (30 mL·min$^{-1}$), and the desorption profile was recorded.

2.3. Experimental System

Figure 1 shows a schematic diagram of the experimental setup. The catalytic activity of the CuCo$_2$O$_4$-$x$ ($x = N$, C and A) catalysts was evaluated by temperature-programed oxidation (TPO) experiments. Printex-U (Degussa, with the size of 20–30 nm) was used as the model soot in this study. For each test, 180 mg of catalyst powder was mixed with 20 mg of soot in loose (mixing with a spatula for 5 min) or tight (grinding in an agate mortar for 5 min) contact mode. Then, the resulting soot–catalyst mixtures (200 mg) were mixed with 400 mg of inert silica (40–60 meshes) for another 5 min to avoid the formation of hot spots during the reaction. The experimental procedure was as follows: Firstly, the mixture of catalyst and inert silica after reaction was collected from the quartz tube and then placed in an agate mortar. Secondly, 20 mg of soot was mixed with the obtained mixture of the catalyst and inert silica. Finally, the above obtained mixture of soot, catalyst and inert silica was filled back into the quartz tube for next catalytic soot combustion reaction cycle. The reaction temperature was increased from 50 $^\circ$C to 700 $^\circ$C at a heating rate of 5 $^\circ$C·min$^{-1}$.

All gas streams from the gas cylinders were regulated by mass flow controllers (Sevenstars D07-B, Beijing, China). The mixed gases (10 vol.% O$_2$ with balanced N$_2$) were fed into the reactor at the flow rate of 200 mL·min$^{-1}$ during the TPO experiment. In addition, 1000 ppm NO was added into the feeding gas to investigate the effect of NO on catalytic soot combustion when necessary. The outlet concentrations of CO and CO$_2$ were monitored online using an infrared (IR) gas analyzer (GXH-3010/3011AE, Huayun, Beijing, China) with the accuracy of $\pm$3%. The temperatures at which 10%, 50% and 90% of the soot was oxidized (denoted as $T_{10}$, $T_{50}$ and $T_{90}$, respectively) were recorded as indicators of the
catalytic activity. Soot conversion (denoted as \( \alpha \)) and CO\(_2\) selectivity (denoted as \( S_{CO_2}\)) were calculated by integrating the CO and CO\(_2\) concentration curves with time as follows:

\[
\alpha (\%) = \frac{\int_0^t ([CO_2]_{out} + [CO]_{out}) dt}{M} \times 100% 
\]

\[
S_{CO_2}(\%) = \frac{\int_0^t [CO]_{out} dt}{\int_0^t ([CO_2]_{out} + [CO]_{out}) dt} \times 100% 
\]

where \([CO_2]_{out}\) and \([CO]_{out}\) are the real-time concentrations of CO and CO\(_2\) at the reactor outlet, respectively, and \(M\) is the weight of the initially packed soot.

Figure 1. Schematic diagram of the experimental setup.

3. Results and Discussion

3.1. Textural Properties of the Catalysts

The specific surface area (\(S_{BET}\)), pore volume and pore size of CuCo\(_2\)O\(_4\)-x (x = N, A and C) catalysts are obtained with a N\(_2\) adsorption–desorption experiment (Table 1). The CuCo\(_2\)O\(_4\)-N catalyst shows the largest specific surface area of 2.1 m\(^2\)·g\(^{-1}\), followed by CuCo\(_2\)O\(_4\)-A (2.0 m\(^2\)·g\(^{-1}\)) and CuCo\(_2\)O\(_4\)-C (1.2 m\(^2\)·g\(^{-1}\)). The pore volumes of CuCo\(_2\)O\(_4\)-N, CuCo\(_2\)O\(_4\)-A and CuCo\(_2\)O\(_4\)-C catalysts are 4.5 mm\(^3\)·g\(^{-1}\), 4.3 mm\(^3\)·g\(^{-1}\) and 2.5 mm\(^3\)·g\(^{-1}\), respectively. The specific surface area and pore volume of the CuCo\(_2\)O\(_4\) catalyst prepared with nitrate and acetate metal salt show no significant differences, while the specific surface area and pore volume of CuCo\(_2\)O\(_4\)-C catalyst dramatically decreases. Yu et al. also reported the formation of hydrochloric acid from chloride salts during calcination, which may inhibit the formation of developed pore systems and negatively affect the specific surface area [16]. Compared with conventional metal oxides and supported catalysts, the specific surface area, pore volume and average pore size of the prepared Cu–Co spinel catalysts are rather low. The results could be ascribed to the formation of the well-crystallized spinel structure under high calcination temperature (700 °C) [12,17].

Figure 2 shows the XRD patterns of the CuCo\(_2\)O\(_4\)-x (x = N, A and C) catalysts. Sharp and intense diffraction peaks of copper–cobalt spinel phases are observed for all samples, suggesting the formation of well-crystallized structures at high calcination temperature of 700 °C. The diffraction peaks observed at 19.1°, 31.4°, 36.9°, 45.1°, 56.0°, 59.6°, 68.9° and 77.5° are attributed to tetragonal spinel crystalline of CuCo\(_2\)O\(_4\) (JCPDS No. 01-1155) [18]. Meanwhile, metal oxide CuO phase (JCPDS No. 80-0076) is observed at 35.6°, 48.6° and 61.7° over CuCo\(_2\)O\(_4\)-N and CuCo\(_2\)O\(_4\)-A catalysts [19]. No distinct CuO phase is found on the CuCo\(_2\)O\(_4\)-C catalyst. Based on the characteristic peak of CuCo\(_2\)O\(_4\) (311) crystal face,
the crystal size of the CuCo$_2$O$_2$-$x$ catalysts were calculated using the Scherrer equation (Table 1). The crystal size of the CuCo$_2$O$_2$-N catalyst (38.0 nm) is slightly smaller than that of CuCo$_2$O$_2$-A and CuCo$_2$O$_2$-C catalysts. Wen et al. also found that the Cl$^-$ coordination anion was an important contributor to the formation of larger clusters of CuCo$_2$O$_4$ [20].

Table 1. Textural properties of the CuCo$_2$O$_2$-$x$ ($x = N$, A and C) catalysts.

| Catalysts     | $S_{BET}$ (m$^2$ g$^{-1}$) | Pore Volume (mm$^3$ g$^{-1}$) | Average Pore Diameter (nm) | Average Crystal Size (nm) $^*$ |
|---------------|-----------------------------|-------------------------------|-----------------------------|--------------------------------|
| CuCo$_2$O$_2$-N | 2.1                         | 4.5                           | 8.3                         | 38.0                           |
| CuCo$_2$O$_2$-A | 2.0                         | 4.2                           | 8.6                         | 38.3                           |
| CuCo$_2$O$_2$-C | 1.2                         | 2.5                           | 8.5                         | 38.8                           |

$^*$ Calculated by the Scherrer equation, based on the characteristic peak of CuCo$_2$O$_4$ (3 1 1) crystal face located at the 2θ of 36.8°.

Figure 2. XRD patterns of the CuCo$_2$O$_2$-$x$ ($x = N$, A and C) catalysts.

Figure 3 shows the representative SEM images of the CuCo$_2$O$_2$-$x$ ($x = N$, A and C) catalysts. The CuCo$_2$O$_2$-N catalyst exhibits a sheetlike morphology with tiny spherical particles on its surface. The stacking of spherical particles and its sheetlike morphologies promote the formation of porous structures (Figure 3a). The phenomenon of particle agglomeration is exhibited over the CuCo$_2$O$_2$-A and CuCo$_2$O$_2$-C catalyst (Figure 3c,e). As shown in Figure 3b, the spherical particles are dispersed on the sheetlike morphology and formed a dendritic structure. However, tiny spherical particles are hardly generated on the surfaces of the CuCo$_2$O$_2$-A and CuCo$_2$O$_2$-C catalysts (Figure 3d,f), while the agglomeration of bulk particles might have resulted in the blockage of the pore systems. These tiny spherical particles can improve the contact between the catalyst and soot particles, which can facilitate the utilization of the catalyst active sites for catalytic soot combustion. The particle sizes of CuCo$_2$O$_2$-A and CuCo$_2$O$_2$-C catalysts increased obviously compared to the CuCo$_2$O$_2$-N catalysts.
3.2. Redox Properties of the Catalysts

The Co 2p spectra of the CuCoO$_4$-x (x = N, A and C) catalysts are shown in Figure 4a. The peaks of Co 2p$_{3/2}$ and Co 2p$_{1/2}$ are observed in the range of 776.0–784.0 eV and 792.0–800.0 eV, respectively [21]. The peaks between 784.0–792.0 eV and 800.0–808.0 eV are attributed to the satellite peaks of Co$^{2+}$ [22,23]. The Co$^{3+}$ and Co$^{2+}$ signals are obtained after the deconvolution of the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ spectra. The peaks centered at 779.7 eV and 794.8 eV correspond to the Co$^{3+}$ species, while the peaks located at 780.8 eV and 796.4 eV belong to the Co$^{2+}$ species [24]. The Cu 2p spectra of all catalysts are also given in Figure 4b. The peaks observed at 932.6 eV belong to the reduced Cu species (Cu$^+$ or Cu$^0$), while the prominent signals at 934.6 eV are ascribed to the Cu$^{2+}$ species [25]. Additionally, the satellite peaks between 937.0 eV to 946.0 eV also confirm the existence of divalent Cu species [19]. Figure 4c shows the Cu LMM Auger spectra of all CuCoO$_4$ catalysts. The peaks at the kinetic energy of 912.6 eV correspond to the Cu$^+$ species, while the peaks at 917.8 eV are attributed to the Cu$^{2+}$ species [26]. However, Cu$^0$ species are not observed on the Cu LMM Auger spectrum. These results suggest that the reduced copper species on the surfaces of CuCoO$_4$-x (x = N, A and C) catalysts mainly exists as Cu$^+$. The de-convoluted XPS signals of O 1s are shown in Figure 4d. Two types of oxygen species present on the surface of the CuCoO$_4$ catalysts. The peaks around 529.8 eV correspond to the lattice oxygen species (O$_{\text{latt}}$), while the peaks around 531.4 eV are attributed to the adsorbed oxygen species (O$_{\text{ads}}$) [27].

The relative contents of Cu$^{2+}$ and Co$^{3+}$ on the surface of CuCoO$_4$-x catalysts are given in Table 2. The highest relative content of Co$^{3+}$/Co$_{\text{total}}$ (38.4%) is obtained over the CuCoO$_4$-N catalyst, followed by CuCoO$_4$-A (35.1%) and CuCoO$_4$-C (33.8%). Moreover, the highest relative content of Cu$^{2+}$/Cu$_{\text{total}}$ is also achieved over the CuCoO$_4$-N catalyst (51.7%), followed by CuCoO$_4$-A (48.2%) and CuCoO$_4$-C (47.8%). The highest relative content of O$_{\text{ads}}$/(O$_{\text{ads}}$ + O$_{\text{latt}}$) (46.8%) is found over the CuCoO$_4$-N catalyst, followed by CuCoO$_4$-A (37.2%) and CuCoO$_4$-C (36.5%) (Table 2). The adsorbed oxygen species were more chemically active than lattice oxygen in catalytic soot combustion, indicating a better soot conversion performance over the CuCoO$_4$-N catalyst with more O$_{\text{ads}}$ species [28].

Figure 3. SEM images of the CuCoO$_4$-N (a,b), CuCoO$_4$-A (c,d) and CuCoO$_4$-C (e,f) catalysts.
Table 2. Redox properties of the CuCoO$_2$-$\chi$ ($\chi = N$, A and C) catalysts.

| Catalysts     | Co$^{3+}$/Co$_{\text{total}}$ (%) | Cu$^{2+}$/Cu$_{\text{total}}$ (%) | O$_{\text{ads}}$/(O$_{\text{ads}} + $O$_{\text{latt}}$) | H$_2$ Consumption (mmol·g$^{-1}$) | O$_2$ Uptake (µmol·g$^{-1}$) |
|---------------|----------------------------------|----------------------------------|---------------------------------|---------------------------------|-----------------------------|
| CuCoO$_2$-N   | 38.4                             | 51.7                             | 46.8                            | 13.4                            | 41.2                        |
| CuCoO$_2$-A   | 35.1                             | 48.2                             | 37.2                            | 13.6                            | 27.1                        |
| CuCoO$_2$-C   | 33.8                             | 47.8                             | 36.5                            | 14.5                            | 25.6                        |

For the CuCoO$_2$-N catalyst, two reduction peaks are observed (Figure 5). The first reduction peak in the range of 150–200 °C is attributed to the reduction of aggregated CuO, while the second peak between 200 °C and 250 °C can be ascribed to the reduction of Cu–Co mixed oxides [29]. The CuCoO$_2$-A catalyst exhibits shoulder peaks at 200–300 °C, the first reduction peak (244 °C) corresponds to the reduction of Cu–Co mixed oxides, and the latter reduction peak at 278 °C represents the reduction of Co$^{3+}$ to Co$^{2+}$ [30]. The CuCoO$_2$-C catalyst also shows two major peaks between 250 °C and 350 °C. The weak reduction peak at 299 °C is ascribed to the reduction of Co$^{3+}$ to Co$^{2+}$, while the reduction peak at 331 °C represents the reduction of Co$^{2+}$ to Co$^{0+}$ [31]. These results suggest that CuCoO$_2$-N catalyst has better reducibility at relatively low temperatures. The amount of H$_2$ consumption was in the order of CuCoO$_2$-C > CuCoO$_2$-A > CuCoO$_2$-N. Although the CuCoO$_2$-C catalysts show the higher H$_2$ consumption (14.5 mmol·g$^{-1}$), the H$_2$ consumption of the CuCoO$_2$-N catalyst is likely mainly concentrated in the low temperature range (150–250 °C). Therefore, the distribution of oxygen species was further investigated.
The CuCo$_4$O$_{4-x}$ catalysts showed an extra oxygen desorption peak in the temperature range of 50 °C to 550 °C compared to the CuCo$_4$O$_4$ catalysts. This indicates that the catalysts had better oxygen mobility [36]. Similarly, Li et al. also reported that the CuCo$_4$O$_4$ and NiCo$_2$O$_4$ catalysts showed an extra oxygen desorption peak in the temperature range of 200 °C to 250 °C compared to the ZnCo$_2$O$_4$. The catalytic performance of CuCo$_4$O$_4$ and NiCo$_2$O$_4$ catalysts were found to be far superior to that of ZnCo$_2$O$_4$ in toluene combustion [7].

Figure 5. H$_2$-TPR profiles of the CuCo$_2$O$_4$-x (x = N, A and C) catalysts.

Figure 6 shows the O$_2$-TPD profiles of the CuCo$_2$O$_4$-x (x = N, A and C) catalysts. The oxygen desorption peaks below 500 °C belong to adsorbed oxygen species (e.g., O$_2$, O$_2^-$ and O$,\text{ labeled as } \alpha$-O$_2$) [32], while the oxygen desorption peaks between 600 °C and 850 °C belong to the lattice oxygen species (O$^{2-}$, labeled as $\beta$-O$_2$) [33]. Figure 6b shows the enlarged O$_2$-TPD profiles in the temperature range of 50 °C to 550 °C. The oxygen desorption peaks within 50–300 °C and 300–500 °C correspond to the physically adsorbed oxygen ($\alpha_1$-O$_2$) and chemically adsorbed oxygen ($\alpha_2$-O$_2$) species, respectively [34,35]. Generally, the adsorption of oxygen followed the procedure of O$_2$→O$_2^-$→O$^-$→O$^{2-}$ [27].

The CuCo$_2$O$_4$-N catalyst shows an extra oxygen desorption peak in the temperature range of 200 °C to 250 °C compared to the CuCo$_2$O$_4$-A and CuCo$_2$O$_4$-C. The extra oxygen desorption peak could be attributed to physically adsorbed oxygen ($\alpha_1$-O$_2$), indicating that the catalysts had better oxygen mobility [36].

Figure 6a shows the O$_2$-TPD profiles of the CuCo$_2$O$_4$-x (x = N, A and C) catalysts. The oxygen desorption peaks below 500 °C belong to adsorbed oxygen species (e.g., O$_2$, O$_2^-$ and O$,\text{ labeled as } \alpha$-O$_2$) [32], while the oxygen desorption peaks between 600 °C and 850 °C belong to the lattice oxygen species (O$^{2-}$, labeled as $\beta$-O$_2$) [33]. Figure 6b shows the enlarged O$_2$-TPD profiles in the temperature range of 50 °C to 550 °C. The oxygen desorption peaks within 50–300 °C and 300–500 °C correspond to the physically adsorbed oxygen ($\alpha_1$-O$_2$) and chemically adsorbed oxygen ($\alpha_2$-O$_2$) species, respectively [34,35]. Generally, the adsorption of oxygen followed the procedure of O$_2$→O$_2^-$→O$^-$→O$^{2-}$ [27].

The CuCo$_2$O$_4$-N catalyst shows an extra oxygen desorption peak in the temperature range of 200 °C to 250 °C compared to the CuCo$_2$O$_4$-A and CuCo$_2$O$_4$-C. The extra oxygen desorption peak could be attributed to physically adsorbed oxygen ($\alpha_1$-O$_2$), indicating that the catalysts had better oxygen mobility [36]. Similarly, Li et al. also reported that the CuCo$_2$O$_4$ and NiCo$_2$O$_4$ catalysts showed an extra oxygen desorption peak in the temperature range of 200 °C to 250 °C compared to the ZnCo$_2$O$_4$. The catalytic performance of CuCo$_2$O$_4$ and NiCo$_2$O$_4$ catalysts were found to be far superior to that of ZnCo$_2$O$_4$ in toluene combustion [7]. The desorption amount of $\alpha_1$-O$_2$ and $\alpha_2$-O$_2$ species were calculated according to the desorption peaks in the O$_2$-TPD profiles. As shown in Table 2, the amount of O$_2$ desorption was in the order of CuCo$_2$O$_4$-N (41.2 μmol·g$^{-1}$) > CuCo$_2$O$_4$-A (27.1 μmol·g$^{-1}$) > CuCo$_2$O$_4$-C (25.6 μmol·g$^{-1}$), which confirms the existence of more adsorbed oxygen species over the CuCo$_2$O$_4$-N catalyst.
3.3. Activity of CuCo$_2$O$_{4-x}$ for Soot Conversion

3.3.1. Soot Conversion in O$_2$/N$_2$

The catalytic activity of CuCo$_2$O$_{4-x}$ (x = N, A and C) catalysts for soot combustion were studied using a TPO experiment under the loose contact mode. Firstly, the soot conversion was investigated under the carrier gases of 10 vol.% O$_2$ balanced with N$_2$. The characteristic temperatures ($T_{10}$, $T_{50}$ and $T_{90}$) of soot conversion are 530 °C, 586 °C and 614 °C, respectively in the absence of a catalyst, which is much higher than those in the presence of the CuCo$_2$O$_4$ catalysts (Figure 7 and Table 3). The catalysts prepared with different metal salt precursors exhibit different catalytic activity in the soot conversion. Among them, the CuCo$_2$O$_4$-N catalyst achieves the highest soot conversion, while the values of $T_{10}$, $T_{50}$ and $T_{90}$ are 451 °C, 520 °C and 558 °C, respectively. The $T_{50}$ values for the CuCo$_2$O$_{4-x}$ (x = N, A and C) catalysts followed the order of CuCo$_2$O$_4$-N (520 °C) < CuCo$_2$O$_4$-A (539 °C) < CuCo$_2$O$_4$-C (550 °C) < no catalysts (586 °C). The CO$_2$ selectivity is also improved remarkably from 81.8% over the CuCo$_2$O$_4$-C to almost 100% over the CuCo$_2$O$_4$-N catalysts.

The CuCo$_2$O$_4$-N and CuCo$_2$O$_4$-A catalysts exhibit larger specific surface area and pore volume compared to the CuCo$_2$O$_4$-C catalyst. It is widely recognized that a larger specific surface area could facilitate the contact between gaseous reactants (e.g., O$_2$, NO and NO$_2$) and the catalyst [37,38]. SEM images further confirmed the generation of more developed pore structure systems of the CuCo$_2$O$_4$-N catalyst compared to the CuCo$_2$O$_4$-A and CuCo$_2$O$_4$-C catalysts. Fang et al. reported that a perovskite-type macro/mesoporous La$_{1-x}$K$_x$FeO$_{3-δ}$ catalysts with large specific surface area and pore volume could improve the utilization of catalytic sites in the soot combustion reaction [39]. Furthermore, the presence of an appropriate amount of single metal oxide CuO on the CuCo$_2$O$_4$ surface could contribute to the crystal lattice distortion of the spinel phase and promote the formation of a defect structure, thereby improving the catalytic activity of the soot combustion reaction [40].

![Figure 7](image-url)  

**Figure 7.** Soot conversion over the CuCo$_2$O$_{4-x}$ (x = N, A and C) catalysts under loose contact mode under the carrier gas of 10 vol.% O$_2$ with balanced N$_2$.

**Table 3.** Catalytic activity of the CuCo$_2$O$_{4-x}$ (x = N, A and C) catalysts for soot combustion under loose contact mode in 10 vol.% O$_2$ with balanced N$_2$.

| Catalysts  | $T_{10}$ (°C) | $T_{50}$ (°C) | $T_{90}$ (°C) | $S_{CO_2}$ (%) |
|------------|---------------|---------------|---------------|---------------|
| CuCo$_2$O$_4$-N | 451           | 520           | 558           | 98.8          |
| CuCo$_2$O$_4$-A | 496           | 539           | 569           | 95.0          |
| CuCo$_2$O$_4$-C | 504           | 550           | 594           | 81.8          |
| No catalysts | 530           | 586           | 615           | 58.7          |
The redox properties of CuCo$_2$O$_4$-x catalysts played a crucial role in catalytic soot combustion. The higher relative content of Co$^{3+}$/Co$_{\text{total}}$ (38.4%) and Cu$^{2+}$/Cu$_{\text{total}}$ (51.7%) obtained over CuCo$_2$O$_4$-N catalysts were much higher compared to the CuCo$_2$O$_4$-A (35.1% and 48.2%) and CuCo$_2$O$_4$-C (33.8% and 47.8%), respectively. Spinel-type CuCo$_2$O$_4$ catalysts possessed outstanding redox properties since the synergistic effects between Co$^{3+}$ and Cu$^{2+}$ species could enhance the adsorption-activation properties of oxygen species for soot conversion [41]. Abundant Co$^{3+}$ species would increase the anionic defects on catalyst surfaces, leading to the formation of more oxygen vacancies [42]. Zhang et al. reported that the presence of Cu$^{2+}$ species induced structural defects on cobalt oxide and weakened the Co-O bonds, which could facilitate the activation of oxygen and improve the reducibility of CuCo$_2$O$_4$ [43]. In addition, the CuCo$_2$O$_4$-N catalysts showed the highest relative content of O$_{\text{ads}}$/(O$_{\text{ads}}$ + O$_{\text{latt}}$) (46.8%) compared to the CuCo$_2$O$_4$-A (37.2%) and CuCo$_2$O$_4$-C (36.5%). The O$_{\text{ads}}$ species possessed better mobility than O$_{\text{latt}}$ species and could participate in catalytic soot combustion via the contact points between catalyst pellets and soot particulates [35].

The lower reduction peaks temperature proved that the CuCo$_2$O$_4$-N catalysts (173 °C) has excellent low temperature reduction performances compared to the CuCo$_2$O$_4$-A (184 °C) and CuCo$_2$O$_4$-C (247 °C). The total H$_2$ consumption amount of the CuCo$_2$O$_4$-N catalysts (13.4 mmol·g$^{-1}$) was slightly lower than that of CuCo$_2$O$_4$-A (13.6 mmol·g$^{-1}$) and CuCo$_2$O$_4$-C (14.5 mmol·g$^{-1}$). The CuCo$_2$O$_4$-N catalyst possessed more adsorbed oxygen species (41.2 μmol·g$^{-1}$) compared to the CuCo$_2$O$_4$-A (27.1 μmol·g$^{-1}$) and CuCo$_2$O$_4$-C (25.6 μmol·g$^{-1}$). It was suggested that the CuCo$_2$O$_4$-N catalysts could release more adsorbed oxygen species below 500 °C [44]. Compared with lattice oxygen species, adsorbed oxygen species were more important in soot conversion due to their better oxygen mobility [45]. He et al. also reported that the adsorbed oxygen species released at low temperatures were more important than lattice oxygen species since the lattice oxygen species could be activated and released only at high temperatures [35]. Lower reduction temperature and abundant adsorbed oxygen species may be crucial factors for soot conversion over the CuCo$_2$O$_4$-N catalyst at lower temperature.

### 3.3.2. Soot Conversion in NO/O$_2$/N$_2$

NO is one of the main components in diesel engine exhaust and has a great effect on soot conversion. Therefore, soot conversion was investigated over the CuCo$_2$O$_4$-x (x = N, A and C) catalysts in the presence of 1000 ppm NO (Figure 8 and Table 4). The addition of NO resulted in lower T$_{10}$, T$_{50}$ and T$_{90}$ values regardless of the presence of a catalyst. The T$_{50}$ values for the CuCo$_2$O$_4$-x (x = N, A and C) catalysts also follow the order of CuCo$_2$O$_4$-N (414 °C) < CuCo$_2$O$_4$-A (458 °C) < CuCo$_2$O$_4$-C (485 °C) < no catalysts (575 °C).

![Figure 8](image-url)

*Figure 8. Soot conversion of the CuCo$_2$O$_4$-x (x = N, A and C) catalysts under the loose contact mode with 1000 ppm NO.*
Table 4. Catalytic activity of the CuCo$_2$O$_4$-$x$ ($x$ = N, A and C) catalysts for soot combustion under the loose contact mode with 1000 ppm NO.

| Catalysts     | $T_{10}$ (°C) | $T_{50}$ (°C) | $T_{90}$ (°C) | $S_{CO_2}$ (%) |
|---------------|---------------|---------------|---------------|---------------|
| CuCo$_2$O$_4$-N | 349           | 414           | 482           | 96.6          |
| CuCo$_2$O$_4$-A | 381           | 458           | 494           | 94.3          |
| CuCo$_2$O$_4$-C | 392           | 485           | 534           | 79.7          |
| No catalysts  | 496           | 575           | 615           | 43.6          |

Using CuCo$_2$O$_4$-N as an example, the $T_{50}$ value decreases from 520 °C to 414 °C with NO addition, while the CO$_2$ selectivity also decreases from 98.8% to 96.6%. NO could be oxidized with O$_2$ to form NO$_2$ in gas phase (Reaction (3)) [46]. NO could be also adsorbed on the surface of CuCo$_2$O$_4$-N catalyst and then oxidized by the active oxygen to form NO$_2$ species, while could promote the formation of surface oxygen vacancies (Reaction (4)). NO$_2$ is a stronger oxidant and participate in catalytic soot combustion as a mobile gaseous oxidant [46]. Possible pathways for the reaction of NO$_2$ with soot are shown in Reaction (5) [47]. NO$_2$ could attack the soot on the surface, resulting in the generation of CO and NO, while CO was eventually oxidized by O$_2$ to CO$_2$, with NO again participating in the NO$_x$-assisted catalytic soot combustion [37]. However, the slight decrease in CO$_2$ selectivity could be attributed to the rapid oxidation of soot by NO$_2$, resulting in the incomplete oxidation of soot to CO [48].

\[
2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2 \quad (3)
\]

\[
\text{NO} + \text{O}^* \rightarrow \text{NO}_2 + \text{O}_v \quad (4)
\]

\[
\text{NO}_2 + \text{C(Soot)} \rightarrow \text{CO} + \text{NO} \quad (5)
\]

where O* represents the active oxygen species, O$_v$ represents the surface oxygen vacancy and C(Soot) represents the soot particulate.

3.3.3. Effect of the Contact Mode

The contact mode between the catalyst and soot could greatly affect the activity of soot conversion [41]. The soot conversion and CO$_2$ selectivity were investigated under both loose and tight contact modes over the CuCo$_2$O$_4$-N catalyst (Figure 9 and Table 5). Under the tight contact mode, soot conversion is accelerated at lower temperatures regardless of the presence of NO compared to the loose contact mode, while the CO$_2$ selectivity reaches up to 100%. The increase of catalyst–soot contact points in the tight contact mode could contribute to better utilization of active sites on the catalyst surface compared to the loose contact mode [4,27]. Machida et al. found that the utilization/transfer of lattice oxygen species was more efficient under the tight contact mode. Besides, the case of “O$_2$ slip” may be decreased in the tight contact mode, which increases the utilization of the released oxygen species to the soot combustion [49].

Table 5. Catalytic activity of the CuCo$_2$O$_4$-N catalysts for soot combustion under the loose and tight contact modes.

| Contact Mode          | $T_{10}$ (°C) | $T_{50}$ (°C) | $T_{90}$ (°C) | $S_{CO_2}$ (%) |
|-----------------------|---------------|---------------|---------------|---------------|
| Loose contact         | 451           | 520           | 558           | 98.8          |
| Loose contact + NO    | 349           | 414           | 482           | 96.6          |
| Tight contact         | 385           | 428           | 499           | 100           |
| Tight contact + NO    | 339           | 394           | 448           | 100           |
3.3.4. Stability Test

The stability test of CuCo$_2$O$_4$-N catalysts was conducted for four consecutive cycles of soot combustion. As shown in Figure 10, the characteristic temperatures ($T_{10}$, $T_{50}$ and $T_{90}$) increased slightly with the increase in the number of cycles of soot combustion. For examples, the values of $T_{50}$ for catalytic soot combustion for each cycle are 520 °C, 524 °C, 526 °C and 528 °C, respectively. Figure 11 shows the deconvoluted XPS spectra of O 1s for the CuCo$_2$O$_4$-N catalyst after four consecutive cycles of soot combustion. The relative content of $O_{ads}/(O_{ads} + O_{latt})$ of CuCo$_2$O$_4$-N catalyst decreases from 46.8% to 40.6% (Table 6). The slight decrease in soot catalytic activity may be due to the minor attenuation of the relative content of $O_{ads}/(O_{ads} + O_{latt})$. Chen et al. also reported the catalytic soot performance of Ag/Co$_3$O$_4$ and found that the decrease in adsorbed oxygen species was an important reason for the decrease of catalytic soot combustion [50].

![Figure 9. Soot conversion over the CuCo$_2$O$_4$-N catalyst under the loose and tight contact modes.](image)

![Figure 10. Stability of CuCo$_2$O$_4$-N catalyst in cycle tests for soot combustion.](image)

| Catalysts                  | $O_{ads}/(O_{ads} + O_{latt})$ (%) |
|----------------------------|-----------------------------------|
| CuCo$_2$O$_4$-N (fresh)    | 46.8                              |
| CuCo$_2$O$_4$-N (used)     | 40.6                              |

Table 6. XPS parameters of CuCo$_2$O$_4$-N catalyst before and after reaction.
4. Reaction Mechanisms for Catalytic Soot Combustion

The potential reaction pathways of catalytic soot combustion over CuCo$_2$O$_4$ were discussed. The excellent catalytic soot combustion of the copper–cobalt spinel catalyst performance depended on the redox properties of the catalysts [41]. The interactions between Cu and Co species in the CuCo$_2$O$_4$ catalyst played a crucial role in the redox reactions. Previous studies showed that the redox pairs of Cu$^{2+}$/Cu$^+$ and Co$^{3+}$/Co$^{2+}$ were involved in the electron transfer process from Co$^{3+}$ to Cu$^{2+}$ within the Cu$^{2+}$–O–Co$^{3+}$ connections in the copper–cobalt spinel catalysts [31,51]. The Cu$^{2+}$–O–Co$^{3+}$ connections could bridge the oxygen transfer within the structure and reduce the redox potential of the Cu species, which ensures the improvement of reducibility for both Cu and Co oxides in the Cu–Co catalysts (Reaction (6)), facilitating the NO$_x$-assisted mechanism in the soot combustion reaction [46].

\[
\text{Cu}^{2+}/\text{Cu}^+ + \frac{2e^-}{\text{O}_2^-}/\text{O}^- \rightarrow \text{Co}^{3+}/\text{Co}^{2+} \tag{6}
\]

Catalytic soot combustion over the copper–cobalt spinel catalyst followed the Mars–van Krevelen (MvK) mechanism, in which the abundance of active oxygen species directly determined the performance of catalytic soot combustion [5]. At the beginning of soot conversion, plenty of active oxygen species on the catalyst surface would come into contact with the soot, resulting in soot combustion at a relatively low temperature and the subsequent formation of oxygen vacancies (O$_x$) (Reaction (7)) [49]. As the reaction proceeded, the consumed reactive oxygen species could be replenished in two ways. Firstly, the reduction of high-valence Cu$^{2+}$ and Co$^{3+}$ to low-valence Cu$^+$ and Co$^{2+}$ released the oxygen species and formed oxygen vacancies, making the surface of the catalyst ready for the oxygen species adsorption from the gas phase (O$_{\text{gass}}$) and accelerating the conversion of the gas phase oxygen species to the adsorbed oxygen species (Reactions (8) and (9)) [7]. The relative content of adsorbed oxygen species of the used CuCo$_2$O$_4$-N catalysts (40.6%) was significantly decreased compared to the fresh CuCo$_2$O$_4$-N catalysts (46.8%), and the activity of soot conversion was also decreased. The adsorbed oxygen species played a crucial role in catalytic soot combustion, which could be transformed to active oxygen species such as O$_2$, O$_2^-$ and O$^-$ (Reactions (10)–(12)) [52]. Moreover, some lattice oxygen species took over the oxygen vacancies and were transferred into adsorbed oxygen species. The adsorbed oxygen species were spilled over to the soot particle surface and further contributed to the soot combustion reaction [35]. All these active oxygen species could directly participate in catalytic soot combustion reaction via the contact points between catalysts and soot particulates to form CO and CO$_2$ [37]. In addition, the released active oxygen species for the conversion of NO oxidation of NO$_2$ [42]. Moreover, the Cu$^+$ and Co$^{2+}$ species were reoxidized to Cu$^{2+}$ and Co$^{3+}$ due to the replenishment of oxygen vacancies.
and participation in catalytic soot combustion (Reaction (13)), and a portion of the gaseous NO molecules were also converted to NO$_2$ (Reaction (4)) [53]. Hence, the facilitated electron transfer process and abundant adsorbed oxygen species endowed the copper–cobalt spinel catalysts with outstanding soot oxidation activity.

\[
\begin{align*}
\text{C(Soot)} + O^* & \rightarrow \text{CO}_x + O_v \quad (7) \\
\text{Cu}^{2+} + \text{Co}^{3+} & \rightarrow \text{Cu}^{+} + \text{Co}^{+} + \text{O}_{\text{ads}} + O_v \quad (8) \\
\text{O}_{2(\text{gas})} + O_v & \rightarrow \text{O}_{\text{ads}} \quad (9) \\
\text{O}_{\text{ads}} + e^- & \rightarrow \text{O}^- \quad (10) \\
\text{O}^2_- & + e^- \rightarrow \text{O}^2^- \quad (11) \\
\text{Cu}^{+} + \text{Co}^{2+} + O_v & \rightarrow \text{Cu}^{2+} + \text{Co}^{3+} + 2e^- \quad (13)
\end{align*}
\]

5. Conclusions

To obtain a fundamental understanding on the catalytic soot combustion performance of the CuCo$_2$O$_4$ catalysts prepared with different metal salt precursors, the relationships between the textural and redox properties of the catalysts and soot conversion were investigated.

1. The tetragonal spinel crystals of CuCo$_2$O$_4$ were formed for all catalysts, while the single-metal oxide CuO species was formed only on the CuCo$_2$O$_4$-N and CuCo$_2$O$_4$-A catalysts. The CuCo$_2$O$_4$-N catalysts exhibited a higher specific surface area and well-developed pore structure.

2. The type of metal precursors could also profoundly affect the redox properties on CuCo$_2$O$_4$ spinel catalysts. The higher relative content of Co$^{3+}$ (38.4%), Cu$^{2+}$ (51.7%) and O$_{\text{ads}}$ (46.8%) species were obtained over the CuCo$_2$O$_4$-N catalysts. Meanwhile, CuCo$_2$O$_4$-N catalysts (173 °C) showed a lower reduction temperature over CuCo$_2$O$_4$-A (184 °C) and CuCo$_2$O$_4$-C (247 °C). The highest amount of surface adsorbed oxygen species (41.2 µmol·g$^{-1}$) was achieved over the CuCo$_2$O$_4$-N catalysts.

3. The highest soot conversion activity and CO$_2$ selectivity were obtained over the CuCo$_2$O$_4$-N catalysts regardless of the soot combustion conditions. The effects of the contact mode (loose and tight) and NO addition on soot conversion were also investigated. A good correlation between soot conversion and the textural and redox properties of the catalysts were observed. The reaction mechanisms and pathways of the CuCo$_2$O$_4$ for catalytic soot combustion were also established.

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