Designing Highly Efficient \( \text{Cu}_2\text{O}\text{-CuO} \) Heterojunction CO Oxidation Catalysts: The Roles of the Support Type and \( \text{Cu}_2\text{O}\text{-CuO} \) Interface Effect

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1. Introduction

With the acceleration of economic globalization, power plants, cement plants, automobile exhaust emissions [1,2], biomass combustion [3], and other sources of fuel produce large quantities of CO due to the incomplete combustion [4–8]. It is reported that when the CO content in the air is larger than 0.1%, it will cause poisoning in humans [9], which further results in nausea, dizziness, loss of consciousness, headache, and even fatal accidents [10]. As well known, CO is a colorless, odorless, and asphyxiating toxic gas, and a flammable and explosive air pollutant, which greatly threatens the health of humans and the safety of the living environment. There are various methods of CO removal reported in the literature, such as the physisorption, CO methanation [11], and catalytic oxidation [12]. Among these strategies, catalytic oxidation is regarded as one of the most efficient techniques for the elimination of CO [13,14]. Additionally, CO oxidation is widely investigated as an interesting probe reaction for other oxidation processes.

Currently, CO oxidation catalysts based on precious metals and transition metal oxides have attracted extensive research interest. Although the noble metal-based catalysts exhibit excellent low-temperature catalytic activity, their high cost and rarity limit their industrial
applications. In comparison, metal oxide-based catalysts are much lower cost than the noble metal-based catalysts, which is more favorable for industrial applications [15–17]. For the transition metal oxides, Cu$_2$O-based materials have been widely used as CO oxidation catalysts because of their high activity at low temperature [18]. These not only have the advantages of low cost, low toxicity, and easy synthesis process, but also have excellent redox performance. Therefore, they are considered to be the potential functionalized catalysts for CO oxidation. In recent years, the heterojunction of Cu$_2$O with semiconductors, such as TiO$_2$ [19], CeO$_2$ [20], WO$_3$ [21], BiVO$_4$ [22], among others, has become a research focus [23]. Shi et al. found that CuO can provide lattice oxygen for the CO oxidation reaction, and then regenerate the oxygen atoms on the Cu$_2$O surface through decomposition of O$_2$ [7]. Both Cu$_2$O and CuO are stable, abundant, low-cost, and environmentally friendly p-type semiconductors with direct band gaps of 2.2 and 1.2 eV, respectively. Copper oxides (Cu$_2$O and CuO) have become important catalysts for photocatalytic degradation of organic pollutants due to their high light absorption coefficients [24,25]. The Cu$_2$O and CuO composite structure has a synergetic effect on the low-temperature oxidation of CO. To be specific, Cu$_2$O and CuO can provide active sites for the oxygen dissociation and CO oxidation, respectively, and the atomic-scale distance between Cu$_2$O and CuO would be conducive to rapid migration of oxygen adsorption atoms on Cu$_2$O-CuO [26]. Therefore, CuOx-based catalysts are potential candidates for the replacement of noble metal CO oxidation.

The CuOx-based catalysts supported on different supports have significant effects on CO oxidation. They can be divided into two categories depending on the reducibility of the support. As for the inert supports, generally a non-reducible oxide (Al$_2$O$_3$, SiO$_2$, MgO, etc.), they mainly play the roles of dispersing and stabilizing active species. As for the reducible active supports, such as transition metal oxides (CeO$_2$, CoO$_x$, TiO$_2$, etc.), they interact with metals and promote the reaction. Additionally, they are also partially involved in the reaction and contribute to the reaction activity. Specifically, CeO$_2$ can form structurally stable and chemically active interfacial interactions with active components due to its unique oxygen storage and release capacity, which significantly improves the performance of the catalyst. Kong et al. [27] reported that the CeO$_2$ catalyst could realize the efficient and stable removal of VOCs due to its high carbon deposition resistance. The ZSM-5 molecular sieve is one of the most important catalytic materials, which has been widely investigated as a support, catalyst, etc., in various fields [28–30]. Pang et al. [31] reported that the Ce-doped Cu/ZSM-5 catalyst greatly improved the catalytic performance, hydrothermal stability, and SO$_2$ toxicity resistance in NH$_3$-SCR selective catalytic reduction of NO. As for the Fe$_2$O$_3$, it has various advantages of good stability, low-cost, good oxygen carrier, and environmental friendliness. Zhao et al. [32] developed a Au/γ-Fe$_2$O$_3$ catalyst with commercial γ-Fe$_2$O$_3$ as the support, which exhibited 20 times higher activity for CO oxidation than the Au/α-Fe$_2$O$_3$ catalyst due to the higher redox property of Au/γ-Fe$_2$O$_3$. Additionally, the manganese oxide (MnOx), as an excellent catalyst support, has been attracting increasingly more attention due to its low price and environmentally harmless features. Mo et al. [33] prepared the CeO$_2$/MnO$_2$ catalyst with high efficiency for toluene degradation. Therefore, in order to further enhance the catalytic activity of CO oxidation at low temperature, it is of great significance to search for an optimal catalytic support for the CO oxidation catalyst.

In this work, a series of oxides, such as α-MnO$_2$ nanotube, CeO$_2$ nanosphere, ZSM-5, and commercial Fe$_2$O$_3$, were investigated as the supports for Cu$_2$O-based CO oxidation catalysts. The optimal support was screened among these oxides by comparing their CO oxidation performance. The supports and catalysts were systematically characterized by X-ray powder diffraction (XRD), N$_2$ physisorption, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), H$_2$ temperature-programmed reduction (H$_2$-TPR), among others. Additionally, the effect of the Cu$_2$O-CuO heterojunction on CO oxidation performance was also studied in depth.
2. Experimental

2.1. Preparation of the Supports

The detailed preparation process of the \( \alpha \)-MnO\(_2\), CeO\(_2\), and ZSM-5 supports are given in Supplemental Materials S1.

2.2. Preparation of the Catalysts

2.2.1. Preparation of Cu\(_2\)O/S Supported Catalysts

A series of the Cu\(_2\)O/S (S = \( \alpha \)-MnO\(_2\), CeO\(_2\), ZSM-5, and Fe\(_2\)O\(_3\)) supported catalyst was prepared by the liquid-phase-reduction deposition–precipitation synthesis strategy. The specific process for Cu\(_2\)O/S supported catalysts preparation is described in detail in Supplemental Materials S1.

2.2.2. Preparation of Cu\(_2\)O-CuO Heterojunction Catalysts

The Cu\(_2\)O-CuO/\( \alpha \)-MnO\(_2\) heterojunction catalysts with various Cu\(^+\)/Cu\(^{2+}\) ratios were synthesized. The Cu\(_2\)O-CuO/\( \alpha \)-MnO\(_2\) heterojunction catalyst obtained was designated as Cu\(_2\)O-CuO/\( \alpha \)-MnO\(_2\)-T, in which “T” denotes the targeted calcination temperature. Further details related to preparation are shown in Supplemental Materials S1.

2.3. Catalyst Characterizations

A series of characterization analyses were carried out on the supports and corresponding catalysts. Further details related to the equipment information, the operational details, and the determination parameters are summarized in Supplemental Materials S2.

2.4. Catalytic Activity Measurements

The catalytic performance of catalyst for CO oxidation was evaluated in a fixed-bed reactor. The productions were detected online by gas chromatography. Further information on the specific reactor and evaluation of catalyst is summarized Supplemental Materials S3.

3. Results and Discussions

3.1. Catalytic Property toward CO Oxidation

3.1.1. Effect of the Support Type on the Catalytic Activity of CO Oxidation

The catalytic activity of CO oxidation on Cu\(_2\)O/S (S = \( \alpha \)-MnO\(_2\), CeO\(_2\), ZSM-5, Fe\(_2\)O\(_3\)) catalysts with different supports was evaluated to investigate the influence of the support type on the catalytic activity of the CO oxidation. Figure 1 shows that the trend of the CO conversions was increasing with the increase in reaction temperature until 100% CO conversion was finally reached. Additionally, it was also interesting to observe that the catalytic activities of the Cu\(_2\)O-based catalysts supported on ZSM-5 and Fe\(_2\)O\(_3\) were much lower than those of Cu\(_2\)O/\( \alpha \)-MnO\(_2\) and Cu\(_2\)O/CeO\(_2\) catalysts. The presence of the \( \alpha \)-MnO\(_2\) and CeO\(_2\) supports could greatly improve the catalytic activities of the Cu\(_2\)O-based catalyst, which might be due to the excellent oxygen storage and release capacities of the \( \alpha \)-MnO\(_2\) and CeO\(_2\) supports. This indicates that the properties of the supports had great effect on the catalytic performance of the Cu\(_2\)O-based catalysts. It is worth noting that the Cu\(_2\)O/\( \alpha \)-MnO\(_2\) catalyst exhibited the best CO oxidation activity among the Cu\(_2\)O-based catalysts investigated. Therefore, \( \alpha \)-MnO\(_2\) was considered as the promising candidate among the investigated supports.

3.1.2. Effect of Cu\(_2\)O-CuO Heterojunction on the Catalytic Activity of CO Oxidation

As shown in Figure 2, detailed evaluations of the catalytic performance for CO oxidation on the Cu\(_2\)O/\( \alpha \)-MnO\(_2\), Cu\(_2\)O-CuO/\( \alpha \)-MnO\(_2\)-T, and CuO/\( \alpha \)-MnO\(_2\)-500 catalysts were also conducted. Figure 2 indicates that the CO conversion on these catalysts increased with the increase in the reaction temperature until reaching 100%. In addition, all the investigated catalysts performed CO oxidation well, and 100% CO conversion could be achieved below 120 °C. However, their reaction temperatures of 10% (\( T_{10} \)), 50% (\( T_{50} \)) and 100% (\( T_{100} \)) CO conversion were quite different. This might be due to the difference in
Cu$_2$O-CuO heterojunction composition between the CuO and Cu$_2$O. Thus, the presence of the Cu$_2$O-CuO heterojunction in Cu$_2$O-CuO/α-MnO$_2$-T catalyst could greatly decrease the ignition temperature (T$_{10}$) of the catalyst. Specifically, the Cu$_2$O-CuO/α-MnO$_2$-T catalysts performed at lower ignition temperatures (even to the room temperature) than the pure Cu$_2$O/α-MnO$_2$ (73 °C) and CuO/α-MnO$_2$-500 (48 °C). Furthermore, the T$_{50}$ and T$_{100}$ of the Cu$_2$O-CuO/α-MnO$_2$-T heterojunction catalysts were lower than those of the pure Cu$_2$O/α-MnO$_2$ and CuO/α-MnO$_2$-500 catalysts. The phenomenon indicated that the Cu$_2$O-CuO heterojunction of Cu$_2$O-CuO/α-MnO$_2$-T catalysts greatly contributed to enhanced CO oxidation activity at low temperature, which was on account of the synergistic effect of the Cu$_2$O-CuO heterojunction [7,34]. The synergistic effect of Cu$^+$ and Cu$^{2+}$ was mainly derived from the atomic scale distance between Cu$_2$O and CuO, which was conducive to the rapid migration of adsorbed oxygen on the Cu$_2$O-CuO surface. In addition, it is noteworthy that the Cu$_2$O-CuO/α-MnO$_2$-260 catalyst with the lowest T$_{10}$, T$_{50}$, and T$_{100}$ showed the highest reactivity among the Cu$_2$O-CuO/α-MnO$_2$-T catalysts investigated. Therefore, the reaction temperature required for the CO catalytic oxidation was greatly reduced and the efficient removal of CO could be realized at low temperature when assisted with the combined effect of the Cu$_2$O-CuO heterojunction.

3.1.3. Kinetic Study

The kinetic study of CO oxidation was carried out over the Cu$_2$O/α-MnO$_2$, Cu$_2$O-CuO/α-MnO$_2$-T, and CuO/α-MnO$_2$-500 catalysts to investigate the Cu$_2$O-CuO heterojunction on the catalytic performance. The Arrhenius curves are shown in Figure 3, and the specific value of the apparent activation energies are listed in Table 1. It is noteworthy that the apparent activation energies of the Cu$_2$O-CuO/α-MnO$_2$-T heterojunction catalysts were in the range from 41.9 to 62.2 kJ·mol$^{-1}$, which were greatly lower compared with the pure Cu$_2$O/α-MnO$_2$ (83.4 kJ·mol$^{-1}$) and CuO/α-MnO$_2$-500 (64.0 kJ·mol$^{-1}$) catalysts. These results indicate that the synergistic effect of the Cu$_2$O-CuO heterojunction can greatly increase the speed of the activation process of O$_2$. Specifically, the Cu$_2$O-CuO/α-MnO$_2$-T catalyst reduced the activation energy of the CO oxidation process. At the same time, the apparent activation energy of Cu$_2$O-CuO/α-MnO$_2$-260 was the lowest among the Cu$_2$O-CuO/α-MnO$_2$-T catalysts. These results suggest that the Cu$_2$O-CuO-T catalyst with the appropriate Cu$^+$/Cu$^{2+}$ ratio dramatically reduced the activation energy owing to the improvement of the O$_2$ activation ability. The two rate-determining steps of the Cu$_2$O-CuO/α-MnO$_2$-260 °C catalysts were close to the optimal dynamic equilibrium ratio. Therefore, the Cu$_2$O-CuO heterojunction structure displays great advantages in improving the CO oxidation activity at low temperature by reducing the apparent activation energy. In addition, it is noteworthy that the apparent activation energy of the Cu$_2$O/α-MnO$_2$-500 (64.0 kJ·mol$^{-1}$) catalyst was also much lower than that of the Cu$_2$O/α-MnO$_2$-260 (83.4 kJ·mol$^{-1}$) catalyst. This proved that the CuO-MnO$_2$ interface provided the new reactive site for the CO catalytic oxidation, which was consistent with the study reported in [34]. The Cu$_2$O-CuO/α-MnO$_2$-T heterojunction catalysts performed excellent CO oxidation activity at low temperature through the comprehensive effects of the Cu$_2$O-CuO heterojunction.

3.1.4. Long-Term Stability Test

The Cu$_2$O/α-MnO$_2$, Cu$_2$O-CuO/α-MnO$_2$-260 and CuO/α-MnO$_2$-500 catalysts were selected as representative catalysts for the CO oxidation stability test at 90 °C for 12 h under certain conditions. Their stability test results are displayed in Figure 4. It can be observed that these three catalysts showed excellent stability throughout the whole 12 h, with no signs of deactivation. Additionally, the Cu$_2$O-CuO/α-MnO$_2$-260 catalyst showed a higher conversion rate than the Cu$_2$O/α-MnO$_2$ and CuO/α-MnO$_2$-500 catalysts in the catalytic stability test due to the presence of the Cu$_2$O-CuO heterojunction. Similarly, the CuO/α-MnO$_2$-500 catalyst showed higher conversion than the Cu$_2$O/α-MnO$_2$ catalyst. These results indicate that the Cu$_2$O-CuO/α-MnO$_2$-T heterojunction catalyst exhibited...
not only excellent low-temperature activity, but good stability owing to the synergistic interaction of CuO-CuO heterojunction.

Figure 1. The curves of CO conversion versus reaction temperature over the as-prepared CuO/S (S = ZSM-5, CeO2, α-MnO2, and Fe2O3) catalysts; reaction conditions: CO/O2/N2 = 1/20/79, GHSV = 12,000 mL g⁻¹ h⁻¹, 1 atm.

Figure 2. The curves of the CO conversion versus reaction temperature over the as-prepared Cu2O/α-MnO2, Cu2O-CuO/α-MnO2-T, and CuO/α-MnO2-500 catalysts; reaction conditions: CO/O2/N2 = 1/20/79, GHSV = 12,000 mL g⁻¹ h⁻¹, 1 atm.
Figure 3. Arrhenius plots for the CO oxidation reaction rate over the as-prepared Cu2O/α-MnO2, Cu2O-CuO/α-MnO2-T, and CuO/α-MnO2-500 catalysts.

Table 1. Apparent activation energy data of the as-prepared Cu2O/α-MnO2, Cu2O-CuO/α-MnO2-T, and CuO/α-MnO2-500 catalysts.

| Samples                  | Ea (kJ/mol) |
|--------------------------|-------------|
| Cu2O/α-MnO2              | 83.4        |
| Cu2O-CuO/α-MnO2-240      | 62.2        |
| Cu2O-CuO/α-MnO2-260      | 41.9        |
| Cu2O-CuO/α-MnO2-280      | 59.2        |
| CuO/α-MnO2-500           | 64.0        |

Figure 4. Results of 12 h long-term stability tests over the as-prepared Cu2O/α-MnO2, Cu2O-CuO/α-MnO2-T, and CuO/α-MnO2-500 catalysts; reaction conditions: CO/O2/N2 = 1/20/79, GHSV = 12,000 mL g⁻¹ h⁻¹, 1 atm.
3.2. Characterization of the Catalysts
3.2.1. XRD Analysis

Figure S1 displays the XRD patterns of the as-prepared Cu2O/S (S = α-MnO2, CeO2, ZSM-5, Fe2O3) catalysts with 15% Cu2O loading amount. As shown in Figure S1, the diffraction peaks of Cu2O/S catalysts were mainly situated at 2θ = 36.6°, 42.5°, 61.7°, and 73.7°, which could be ascribed to the (111), (200), (220), and (311) of Cu2O phase (PDF-#05-0667). However, the intensities of the Cu2O peaks on these catalysts were quite different. Specifically, the intensities of the Cu2O peaks on the Cu2O/α-MnO2 and Cu2O/CeO2 catalysts were much weaker than that on the Cu2O/ZSM-5 and Cu2O/Fe2O3 catalysts, suggesting the high dispersion of the Cu2O species. This indicated that the properties of the support could greatly affect the dispersion of Cu2O, which was further conducive to the improvement of the catalytic activity of CO oxidation. In addition, the diffraction peaks of the supports could be observed over these Cu2O-based catalysts, which were attributed to the crystalline ZSM-5 (PDF-#-47-0715), Fe2O3 (PDF-#-99-0060), CeO2 (PDF-#-34-0394), and α-MnO2 (PDF-#-78-0428) phases.

Figure 5a shows the XRD patterns of the Cu2O/α-MnO2, Cu2O-CuO/α-MnO2-T, and CuO/α-MnO2-500 catalysts. The diffraction peaks of the Cu2O/α-MnO2 catalyst were mainly situated at 2θ = 36.6°, 42.5°, 61.7°, and 73.7°, which could be due to the (111), (200), (220), and (311) of the Cu2O phase (PDF-#-90-0041), respectively. The diffraction peaks of the Cu2O/α-MnO2-500 catalyst were located at 2θ = 35.7° and 38.8°, which might be due to the (−111) and (111) of the CuO phase (PDF-#-01-1117), respectively. However, as for the Cu2O-CuO/α-MnO2-T catalyst, the characteristic diffraction peaks of Cu2O, CuO, and α-MnO2 could also be found at the same time in their XRD patterns. The results indicate that the supported CuO had been transformed into the Cu2O-CuO heterojunction with a different proportion of Cu2+/Cu3+. Specifically, the intensity of the CuO diffraction peaks increased with the increase in the calcination temperature. This suggests that the ratio of CuO in the Cu2O-CuO/α-MnO2-T catalyst increased with the increase in the calcination temperature from 240 to 280 °C. The brown Cu2O/α-MnO2 catalyst, abundant with the Cu2O phase, was eventually oxidized into the CuO/α-MnO2-500 black powder when the calcination temperature further increased to 500 °C. As a result, the XRD patterns of the CuO/α-MnO2-500 catalyst only displayed the characteristic diffraction peaks of CuO and α-MnO2 phases. This indicates that Cu2O was completely transformed into CuO after the calcination at 500 °C for 1 h. Based on this analysis, it can be concluded that the Cu2O-CuO/α-MnO2 heterojunction catalysts with different Cu2+/Cu3+ ratios can be obtained by adjusting the calcination temperature. The appropriate Cu2+/Cu3+ ratio heterojunction could greatly improve the catalytic activity of catalysts based on the catalytic results given in Figure 2.

![Figure 5](image_url)

Figure 5. X-ray diffraction patterns of the as-prepared (a) Cu2O/α-MnO2, Cu2O-CuO/α-MnO2-T, and CuO/α-MnO2-500 catalysts and (b) the XRD patterns of each catalyst after long-term stability tests (SP-).
Figure 5b shows the XRD patterns of the spent (SP-) \( \text{Cu}_2\text{O}/\alpha\text{-MnO}_2 \), \( \text{Cu}_2\text{O-CuO}/\alpha\text{-MnO}_2\)-260, and \( \text{CuO}/\alpha\text{-MnO}_2\)-500 catalysts after 12 h long-term stability tests. Meanwhile, the XRD patterns of their corresponding fresh catalysts are also presented for comparison. As shown in Figure 5b, this pattern represents the fresh catalyst, and the pattern below represents the spent catalyst (SP-) after the stability test. The characteristic diffraction peaks of \( \text{Cu}_2\text{O} \) (PDF#-90-0041), \( \text{CuO} \) (PDF#-72-1982), and \( \alpha\text{-MnO}_2 \) (PDF#-78-0428) can still be obviously observed on the spent catalysts, especially on the SP-\( \text{Cu}_2\text{O-CuO}/\alpha\text{-MnO}_2\)-260 heterojunction catalyst. Therefore, the XRD results confirmed that the \( \text{Cu}_2\text{O-CuO} \) heterojunction existed in the \( \text{Cu}_2\text{O-CuO}/\alpha\text{-MnO}_2\)-260 catalyst after the 12 h long-term stability test of CO oxidation. This implies that the oxygen activation cycle during the CO oxidation on the \( \text{Cu}_2\text{O-CuO}/\alpha\text{-MnO}_2\)-260 heterojunction catalyst was sustainable owing to the thermal stability of the \( \text{Cu}_2\text{O-CuO} \) heterojunction. At the same time, the characteristic peaks of \( \alpha\text{-MnO}_2 \) were also perfectly retained. These results illustrate the important roles of the \( \text{Cu}_2\text{O-CuO} \) heterojunction interface when constructing stable and efficient CO oxidation catalysts.

3.2.2. TG Analysis

The thermal stability and the phase transformation process of the \( \text{Cu}_2\text{O}/\alpha\text{-MnO}_2 \) catalyst were studied by thermogravimetric analysis (TG) in air atmosphere. The weight decreased slowly in the range 30–200 °C, as shown in Figure 6. This might be caused by the removal of the water of physisorption and water of crystallization, together with the removal of trace organic reagent. However, when the temperature further rose to 511 °C, the weight began to drop sharply. The weight loss was equivalent to the loss of oxygen in the lattice of MnO\(_2\), leading to the formation of Mn\(_2\)O\(_3\). Furthermore, when the temperature further increased to 769 °C, the weight again dropped sharply. This indicates that the Mn\(_2\)O\(_3\) once again lost part of the lattice oxygen, leading to the formation of Mn\(_3\)O\(_4\). These results are consistent with precursory literature reports [35–37]. It is worth noting that the mass loss of the catalyst (10.61%) was less than the theoretical value (12.26%) during the conversion of \( \alpha\text{-MnO}_2 \) to Mn\(_3\)O\(_4\). The reason for the actual mass reduction being less than the theoretical mass reduction was that the transformation of the loaded \( \text{Cu}_2\text{O} \) to \( \text{CuO} \) increased the weight.

![Figure 6](image_url)

Figure 6. (a) TG result and (b) the DTG result for the \( \text{Cu}_2\text{O}/\alpha\text{-MnO}_2 \) in air atmosphere.

3.2.3. N\(_2\) Physisorption Analysis

The structural characteristics of the \( \text{Cu}_2\text{O}/\alpha\text{-MnO}_2 \), \( \text{Cu}_2\text{O-CuO}/\alpha\text{-MnO}_2\)-T, and \( \text{CuO}/\alpha\text{-MnO}_2\)-500 catalysts were investigated by \( \text{N}_2 \) physisorption characterization. Their \( \text{N}_2 \) adsorption–desorption isotherms and pore size distributions of catalysts are shown in Figure 7. It can be observed in Figure 7a that all the catalysts were characterized by the type
IV isotherm and H₄ hysteresis loops. This also indicates that the Cu₂O-CuO/α-MnO₂-T and CuO/α-MnO₂-500 catalysts still had mesoporous structures similar to Cu₂O/α-MnO₂ after calcination at different temperatures, thus exhibiting the excellent thermal stability. Typically, the H₄-shaped hysteresis loops indicate the existence of narrow wedge-shaped mesopores. Additionally, the mesopores might originate from the hollow α-MnO₂ nanotube in the catalyst support, the sintering of catalysts in calcination process, and the rupture of internal mesopores. As shown in Figure 7b, the average pore size of the Cu₂O-CuO/α-MnO₂-T and CuO/α-MnO₂-500 catalysts was similar or larger than the original Cu₂O/α-MnO₂ catalyst. This suggested that their mesoporous structures were not severely damaged by the thermal aggregation and phase transformation during the calcination process at different temperature. The nanotube hollow microsphere catalyst exhibited excellent thermal stability. In addition, the specific data of the structural properties of these catalysts are listed in Table 2. The results show that the specific surface areas, average pore diameters, and pore volumes of the Cu₂O-CuO/α-MnO₂-T catalysts were very similar to those of the pristine Cu₂O/α-MnO₂ catalyst. This again confirms the excellent thermal performance stability of these catalysts. The slight reduction in the specific surface area might be due to the sintering of Cu₂O in the process of the calcination. It would further affect the surface morphology of the catalyst-supported nanotube hollow spheres by creating internal pores and surface defects. In contrast, the specific surface area of the CuO/α-MnO₂-500 catalyst was relatively smaller, which might be caused by the complete oxidation of the surface Cu₂O species and the closure and/or blockage of the hollow pores due to the long-term high temperature calcination.

![Figure 7](image-url) (a) N₂ adsorption–desorption isotherms and (b) pore size distribution curves of the as-prepared Cu₂O/α-MnO₂, Cu₂O-CuO/α-MnO₂-T, and CuO/α-MnO₂-500 catalysts.

| Samples                  | Specific Surface Area (m²/g) | Pore Volume (cm³/g) | Average Pore Diameter (nm) | Isotherm Type |
|--------------------------|------------------------------|---------------------|-----------------------------|---------------|
| Cu₂O/α-MnO₂              | 43.64                        | 0.051               | 3.05                        | IV H₄         |
| Cu₂O-CuO/α-MnO₂-240      | 28.33                        | 0.048               | 3.06                        | IV H₄         |
| Cu₂O-CuO/α-MnO₂-260      | 28.82                        | 0.047               | 3.06                        | IV H₄         |
| Cu₂O-CuO/α-MnO₂-280      | 26.37                        | 0.045               | 3.06                        | IV H₄         |
| CuO/α-MnO₂-500           | 10.49                        | 0.045               | 3.06                        | IV H₄         |

3.2.4. SEM and TEM Analyses

The TEM and SEM photos of the support α-MnO₂ nanotube are shown in Figure S2a,b. Figure 8 shows the SEM images of the as-prepared Cu₂O/S (S = α-MnO₂, CeO₂, ZSM-
5, Fe$_2$O$_3$) catalysts with 15% Cu$_2$O loading amount. As shown in Figure 8a,b, the as-synthesized Cu$_2$O/ZSM-5 catalyst exhibits regular cuboid shape with the a-axis (205 nm), b-axis (100 nm), and c-axis (1054 nm). In contrast, Cu$_2$O/Fe$_2$O$_3$ catalyst supported on the commercial Fe$_2$O$_3$, shown in Figure 8c,d, resulted in an irregular morphology in the particle state, which might not be conducive to the dispersion of the Cu$_2$O active sites. In addition, it is interesting to find in Figure 8e,f that the as-prepared Cu$_2$O/CeO$_2$ catalyst exhibited spherical nanoparticles with uniform size distribution about 130 nm. At the same time, it can be observed in Figure 8g,h that the Cu$_2$O/α-MnO$_2$ catalyst presented the morphology of hollow spheres, which were assembled by hollow nanotubes.

Figure 8. SEM images of the as-prepared (a,b) Cu$_2$O/ZSM-5, (c,d) Cu$_2$O/Fe$_2$O$_3$, (e,f) Cu$_2$O/CeO$_2$, and (g,h) Cu$_2$O/α-MnO$_2$ catalysts.
Figure 9 depicts the SEM images of the hollow Cu$_2$O/α-MnO$_2$ catalyst calcined at different temperatures. Further, the spatial distribution of the Cu and Mn elements in the catalysts were investigated by the EDS-mapping technique. The Cu$_2$O/α-MnO$_2$, Cu$_2$O-CuO/α-MnO$_2$-260, and CuO/α-MnO$_2$-500 catalysts are chosen as the representative samples. As can be observed in Figure 9a,b, the Cu$_2$O/α-MnO$_2$ hollow microspheres catalyst with the average size of 5.01 µm exhibits the Cu$_2$O nanoparticles supported on the surface of hollow nanotube. With the increase in calcination temperature, the surface of the Cu$_2$O-CuO/α-MnO$_2$-260 (Figure 9c,d) and CuO/α-MnO$_2$-500 (Figure 9e,f) catalysts became coarse, and the morphology of hollow microsphere was less pronounced compared with the Cu$_2$O/α-MnO$_2$. This was because the Cu$_2$O was gradually oxidized into CuO in the process of the calcination at different temperatures. In addition, the average particle size of the Cu$_2$O-CuO/α-MnO$_2$-260 (4.71 µm) and CuO/α-MnO$_2$-500 (5.09 µm) hollow microspheres did not show significant thermal shrinkage and aggregation in the process of the calcination, and the morphology of hollow microspheres had been successfully maintained.

Figure 9. SEM images of the as-prepared catalysts: (a,b) Cu$_2$O/α-MnO$_2$, (c,d) Cu$_2$O-CuO/α-MnO$_2$-260, and (e,f) CuO/α-MnO$_2$-500.
3.2.5. FTIR Analysis

To investigate the phase transition process from Cu$_2$O to CuO in the calcination process, FTIR analysis of Cu$_2$O/α-MnO$_2$, Cu$_2$O-CuO/α-MnO$_2$-T, and CuO/α-MnO$_2$-500 catalysts in the range 400–4000 cm$^{-1}$ was performed. As shown in Figure 10, it is noteworthy that the samples show infrared transmittance peaks at 598 and 468 cm$^{-1}$, which are attributed to the stretching vibration of the Cu$^{(1)}$-O and Cu$^{(2)}$-O bond, respectively [38]. In addition, the coexistence of stretching vibration peaks at 598 and 468 cm$^{-1}$ indicate the existence of the Cu$_2$O-CuO heterojunction. When the calcination temperature increased to 240 °C or other higher temperature, the characteristic stretching vibration peak of Cu(2)-O bond gradually appeared at 468 cm$^{-1}$, while the Cu(1)-O stretching vibration at 598 cm$^{-1}$ progressively weakened due to the complete oxidation of Cu$_2$O to CuO until it finally disappeared at 500 °C. This further verifies the change in crystal structure and valence state of Cu species in the calcination process in air atmosphere. Meanwhile, it can be found that the catalyst also provided strong infrared transmission peaks at 720 and 523 cm$^{-1}$, which are attributed to the stretching vibration of O-Mn-O and layered manganese oxide, respectively [39–42]. As for the transmittance peaks around 3423 and 1637 cm$^{-1}$, they are attributed to the stretching and flexural oscillations of the O-H groups caused by the physiosorbed water [43,44]. Therefore, the results of FTIR characterization further confirm the oxidation process of the Cu$_2$O supported on the surface of α-MnO$_2$ nanotube and the formation of Cu$_2$O-CuO heterojunction in the process of the calcination.

![Figure 10. FTIR characterization for the as-prepared Cu$_2$O/α-MnO$_2$, Cu$_2$O-CuO/α-MnO$_2$-T, and CuO/α-MnO$_2$-500 catalysts.](image)

3.2.6. XPS Analysis

XPS analysis was performed on the Cu$_2$O/S (S = ZSM-5, CeO$_2$, α-MnO$_2$, and Fe$_2$O$_3$) catalysts to further investigate the states of valence, surface chemical coordination, and composition. The results of Cu 2p and O 1s spectra are shown in Figure 11. Specifically, the pristine Cu$_2$O/α-MnO$_2$, Cu$_2$O/Fe$_2$O$_3$, Cu$_2$O/CeO$_2$, and Cu$_2$O/ZSM-5 catalysts showed the 2p$_{3/2}$ peak of Cu$^+$ at 931.38 eV (Figure 11a). This indicates the presence of the Cu$_2$O species on the support surface. As shown in Figure 11b, the O 1s main peak of the catalyst...
was around 529.36–529.46 eV, and the shoulder peak was around 530.76–530.96 eV. To be specific, the peaks of 529.36–529.46 eV and 530.76–530.96 eV could be attributed to surface adsorbed oxygen (O\textsubscript{ads}) and lattice oxygen (O\textsubscript{latt}), respectively [45]. However, the location of the main peak and shoulder peak of Cu\textsubscript{2}O/ZSM-5 catalyst differed greatly from the catalysts above. The shoulder peak at 530.58 eV should be attributed to the \(O\) species of Si-OH on the surface of SiO\textsubscript{2} support, rather than the surface-adsorbed oxygen (O\textsubscript{ads}) [46,47]. In general, the number of the O\textsubscript{ads} mainly depends on the number of oxygen vacancies at the surface. The reason is that the O\textsubscript{ads} could only be absorbed on the oxygen vacancies. Thus, the O\textsubscript{ads}/(O\textsubscript{latt} + O\textsubscript{ads}) ratio became the valid parameter to analyze the content of the surface oxygen vacancy. Table 3 shows that the O 1s shoulder peak area ratio (O\textsubscript{ads}/(O\textsubscript{latt} + O\textsubscript{ads})) of the Cu\textsubscript{2}O/CeO\textsubscript{2}, Cu\textsubscript{2}O/Fe\textsubscript{2}O\textsubscript{3}, Cu\textsubscript{2}O/ZSM-5, and Cu\textsubscript{2}O/\(\alpha\)-MnO\textsubscript{2} catalysts were 31.8%, 46.67%, 37.46%, and 21.26%, respectively. Although the (O\textsubscript{ads}/(O\textsubscript{latt} + O\textsubscript{ads})) ratio of Cu\textsubscript{2}O/\(\alpha\)-MnO\textsubscript{2} catalyst is somewhat lower compared with other supported Cu\textsubscript{2}O catalysts, the Cu\textsubscript{2}O/\(\alpha\)-MnO\textsubscript{2} catalyst exhibits excellent catalytic performance. This suggests that the ratio of O 1s shoulder peak area has a close relationship with the type of support.

![Image](image_url)

**Figure 11.** (a) Cu 2p and (b) O 1s XPS spectra of the as-prepared Cu\textsubscript{2}O/S (S = ZSM-5, CeO\textsubscript{2}, \(\alpha\)-MnO\textsubscript{2}, and Fe\textsubscript{2}O\textsubscript{3}) catalysts.

**Table 3.** O 1s peak area of the as-prepared Cu\textsubscript{2}O/S (S = ZSM-5, CeO\textsubscript{2}, \(\alpha\)-MnO\textsubscript{2}, and Fe\textsubscript{2}O\textsubscript{3}) Cu\textsubscript{2}O/\(\alpha\)-MnO\textsubscript{2}, Cu\textsubscript{2}O-CuO/\(\alpha\)-MnO\textsubscript{2}-T and CuO/\(\alpha\)-MnO\textsubscript{2}-500 catalysts.

| Samples         | O 1s Main Peak Area | O 1s Shoulder Peak Area | O 1s Shoulder Peak Area Ratio \(\times\) (%) |
|-----------------|---------------------|-------------------------|-------------------------------------------|
| Cu\textsubscript{2}O/CeO\textsubscript{2} | 283,829.4           | 122,367.2               | 41.80                                     |
| Cu\textsubscript{2}O/Fe\textsubscript{2}O\textsubscript{3} | 173,370.0           | 157,701.6               | 46.67                                     |
| Cu\textsubscript{2}O/ZSM-5       | 653,388.9           | 391,390.7               | 37.46                                     |
| Cu\textsubscript{2}O/\(\alpha\)-MnO\textsubscript{2} | 223,908.2           | 60,458.9                | 28.45                                     |
| Cu\textsubscript{2}O-CuO/\(\alpha\)-MnO\textsubscript{2}-240 | 227,943.7           | 88,607.3                | 38.36                                     |
| Cu\textsubscript{2}O-CuO/\(\alpha\)-MnO\textsubscript{2}-260 | 222,799             | 123,070.9               | 35.58                                     |
| Cu\textsubscript{2}O-CuO/\(\alpha\)-MnO\textsubscript{2}-280 | 227,844.3           | 119,566.3               | 34.42                                     |
| CuO/\(\alpha\)-MnO\textsubscript{2}-500 | 249,089.8           | 98,654.84               | 28.45                                     |

*The O 1s shoulder peak area ratio represents the ratio of O\textsubscript{ads}/(O\textsubscript{latt} + O\textsubscript{ads}).*

The XPS results of Cu 2p, O 1s, and Mn 2p over Cu\textsubscript{2}O/\(\alpha\)-MnO\textsubscript{2}, Cu\textsubscript{2}O-CuO/\(\alpha\)-MnO\textsubscript{2}-T, and CuO/\(\alpha\)-MnO\textsubscript{2}-500 catalysts are shown in Figure 12. Generally, there are two main peaks around 933.08–933.82 eV and 952.68–952.88 eV observed over these catalysts (Figure 12a), which can be attributed to the Cu 2p\textsubscript{3/2} and Cu 2p\textsubscript{1/2} peaks, respectively [48]. Interestingly, the Cu 2p\textsubscript{3/2} peak was accompanied by an oscillating satellite peak from
944.78 to 945.28 eV. It was previously reported that the satellite peaks are generated by the transfer of electrons from the ligand orbital to the 3d orbital of Cu\cite{49,50}. This indicates that the Cu\textsuperscript{2+} exists in the divalent form with the 3d\textsuperscript{9} structure, rather than the Cu\textsuperscript{+} or Cu\textsuperscript{0} species with the 3d\textsuperscript{10}-filled energy level. It was reported that the CO oxidation activity of the Cu\textsubscript{2}O-CuO heterojunction catalyst is largely dependent on the surface of Cu\textsuperscript{+}/Cu\textsuperscript{2+} ratio \cite{26}. The Cu\textsuperscript{2+}/Cu\textsuperscript{1+} relative percentages can be estimated by the peak-fitted areas of their corresponding XPS peaks. As shown in Table 4, the relative percentages of different oxidation states in the Cu\textsubscript{2}O/\textalpha-MnO\textsubscript{2}, Cu\textsubscript{2}O-CuO/\textalpha-MnO\textsubscript{2}-240, Cu\textsubscript{2}O-CuO/\textalpha-MnO\textsubscript{2}-260, Cu\textsubscript{2}O-CuO/\textalpha-MnO\textsubscript{2}-280, and CuO/\textalpha-MnO\textsubscript{2}-500 catalysts were 0, 6.30, 9.64, 9.99, and \infty, respectively. These results indicate that the calcination temperature greatly affects the relative percentages of different oxidation states over the catalyst surface. Meanwhile, the XPS results also reveal the formation of the Cu\textsubscript{2}O-CuO heterojunction structure on the surface of the Cu\textsubscript{2}O-CuO-T catalyst, which is consistent with the FTIR and XRD characterization results.

![Figure 12](image-url)
Table 4. Cu 2p peak area of the as-prepared Cu2O/S (S = α-MnO2, CeO2, SBA-ZSM-5, Fe2O3), Cu2O/α-MnO2, CuO-CuO/α-MnO2-T, and CuO/α-MnO2-500 catalysts.

| Samples                  | Cu2O Peak Area | CuO Peak Area | Satellite Peak Area | Cu2O Peak Area Percentage (%) | CuO Peak Area Percentage (%) | Cu2+/Cu+ Relative Ratio |
|--------------------------|----------------|---------------|---------------------|-------------------------------|-------------------------------|--------------------------|
| Cu2O/CeO2               | 58,985.93      | 0             | 0                   | 100.0                         | 0                             | 0                        |
| Cu2O/Fe2O3              | 23,117.54      | 0             | 0                   | 100.0                         | 0                             | 0                        |
| Cu2O/ZSM-5              | 15,803.46      | 0             | 0                   | 100.0                         | 0                             | 0                        |
| Cu2O/α-MnO2             | 28,836.83      | 0             | 0                   | 100.0                         | 0                             | 0                        |
| Cu2O-CuO/α-MnO2-240     | 8059.77        | 16,647.28     | 33,992.70           | 13.7                          | 86.3                         | 6.30                     |
| Cu2O-CuO/α-MnO2-260     | 8803.58        | 36,178.22     | 49,118.25           | 9.4                           | 90.6                         | 9.64                     |
| Cu2O-CuO/α-MnO2-280     | 7076.77        | 16,647.28     | 54,040.24           | 9.1                           | 90.9                         | 9.99                     |
| CuO/α-MnO2-500          | 0              | 55,346.21     | 96,344.52           | 0.0                           | 100.0                        | ∞                        |

Figure 12a indicates that in the O 1s spectra of the catalysts studied, each catalyst showed a main peak centered at 529.40 eV and a shoulder peak around 531.12 eV. The results in 3 show that the O_ads/(O_latt + O_ads) ratio of the Cu2O-CuO/α-MnO2-T heterojunction catalyst was higher than that of Cu2O/α-MnO2. CuO/α-MnO2-500 was also found to have a relatively high acromion area ratio O_ads/(O_latt + O_ads), possibly due to the large amount of additional oxygen species provided by the CuO-MnO2 interface effect [34]. Among Cu2O-CuO/T heterojunction catalysts, Cu2O-CuO-260 catalyst possessed the highest proportion of shoulder peak area. According to previous report [51], the surface oxygen vacancies could enhance the redox properties of catalysts, which would be beneficial to the improvement of the performance of catalysts. The two binding energy peaks around 642.7 and 654.0 eV could be speculated to be a two-step reduction process with MnO as the final state, namely MnO→Mn3O4→MnO [34,44,55].

3.2.7. H2-TPR Analysis

To investigate the reduction, the Cu2O/S (S = ZSM-5, CeO2, α-MnO2, and Fe2O3), Cu2O/α-MnO2, CuO-CuO/α-MnO2-T, and CuO/α-MnO2-500 catalysts were performed H2-TPR analysis. The H2-TPR curves of the ZSM-5, CeO2, α-MnO2, and Fe2O3 supports are shown in Supplemental Materials S4. As can be observed, ZSM-5 zeolite had no obvious reduction peak, which might be due to the inert support. Additionally, it could be interesting to find that the Fe2O3 support exhibited a small reduction peak at 532 °C and a wide non-termination peak at 745 °C. According to the literature [54], the Fe2O3 support experiences the reduction from Fe2O3 to FeO and from FeO to Fe. The reduction of CeO2 support might be due to the existence of Ce4+/Ce3+ redox pairs. In addition, α-MnO2 showed two reduction peaks at 432 and 579 °C. The reduction process of α-MnO2 samples could be speculated to be a two-step reduction process with MnO as the final state, namely MnO2→Mn3O4→MnO [34,44,55].

As for the H2-TPR curves of Cu2O/S catalysts supported on different oxides, shown in Figure 13a, they reveal two or three reduction peaks in the range 30–800 °C. This indicates that the reduction of Cu2O species at different temperatures was related to the different metal–support interaction. Specifically, the Cu2O/ZSM-5 catalyst showed a large reduction peak and a shoulder peak near 296 and 420 °C, respectively, which could correspond to the interaction strength of the Cu2O and ZSM-5 with different intensities. The Cu2O/Fe2O3 catalyst showed three reduction peaks, which might correspond to the interaction strength of Cu2O and Fe2O3 with different intensities, and the reduction peak of Fe2O3 support. The Cu2O/CeO2 catalyst showed two reduction peaks, and the peak at 258 °C might be the common reduction peak of Cu2O and CeO2 species. It is worth noting that the reduction peak intensity of the Cu2O/α-MnO2 catalyst was the largest among these four catalysts. Therefore, the nature of the support had an important influence on the reduction property of the catalyst and the metal–support interaction.
The $\text{H}_2$ reduction profiles of the Cu$_2$O/\(\alpha\)-MnO$_2$, Cu$_2$O-CuO/\(\alpha\)-MnO$_2$-T, and CuO/\(\alpha\)-MnO$_2$-500 catalysts are shown in Figure 13b. These catalysts had three reduction peaks: 156–290, 337–385, and 442–487 °C. Generally, their $\text{H}_2$-TPR curves are analogous in the shape, with a large reduction peak at 442–487 °C (\(\gamma\)-type), a big shoulder peak at 337–385 °C (\(\beta\)-type), and a small shoulder peak at 156–290 °C (\(\alpha\)-type). Additionally, it is noteworthy that the reduction peak area of the CuO/\(\alpha\)-MnO$_2$-500 catalyst was somewhat larger than that of the Cu$_2$O/\(\alpha\)-MnO$_2$ catalyst. The main reason for this was that the reduction process of the CuO consisted of two reduction stages, which contained the reduction processes from Cu$^{2+}$ to Cu$^+$ and then from Cu$^+$ to Cu$^0$. Therefore, compared with the reduction of Cu$_2$O/\(\alpha\)-MnO$_2$, the reduction of the Cu$_2$O-CuO/\(\alpha\)-MnO$_2$ heterojunction and CuO/\(\alpha\)-MnO$_2$ catalysts required more $\text{H}_2$ reductant, resulting in the larger $\text{H}_2$ consumption. Furthermore, it is interesting to find that the initial reduction temperature of Cu$_2$O-CuO/\(\alpha\)-MnO$_2$-T heterojunction catalysts gradually shifted to the lower temperature with the increase in the calcination temperature. This suggests that the presence of the Cu$_2$O-CuO heterojunction had an important influence on the reduction property of the catalysts.

4. Conclusions

In summary, a series of Cu$_2$O/S (S = \(\alpha\)-MnO$_2$, CeO$_2$, ZSM-5, Fe$_2$O$_3$) catalysts were prepared by the liquid-phase reduction deposition–precipitation strategy and used for CO oxidation. It was found that the Cu$_2$O/\(\alpha\)-MnO$_2$ catalyst performed the optimum low-temperature activity of CO oxidation. Furthermore, the influence of the Cu$_2$O-CuO heterojunction structure on the catalytic activity of CO oxidation was also carefully investigated. It was found that Cu$_2$O-CuO/\(\alpha\)-MnO$_2$-260 with the Cu$_2$O/total Cu proportion of 9.4% exhibited the highest catalytic activity. The presence of the Cu$_2$O-CuO heterojunction greatly increased the content of the surface oxygen vacancy. This further enhanced the activation ability of oxygen, and finally improved the low temperature COoxidation property. Kinetic study showed that the Cu$^+/$/Cu$^{2+}$ proportion of the Cu$_2$O-CuO heterojunction and redox property of the Cu$_2$O-CuO/\(\alpha\)-MnO$_2$-T catalyst significantly reduced the apparent activation energy of CO oxidation. As a result, the catalytic activity of CO oxidation at low temperature was greatly improved. In addition, there are few reports on Cu$_2$O-CuO heterojunction catalysts supported on MnO$_2$ for CO oxidation. Although researchers have prepared CuOx-type catalysts with MnO$_2$ as the support by some methods, its catalytic CO oxidation performance is not ideal. In conclusion, the Cu$_2$O-CuO/\(\alpha\)-MnO$_2$-T hetero-
junction catalysts with adjustable Cu$^{+}$/Cu$^{2+}$ ratios are expected to be promising catalyst candidates for CO oxidation in future applications.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12173020/s1, S1. Experimental; S2. Catalyst Characterizations; S3. Catalytic Activity Measurements; Figure S1: X-ray diffraction patterns of the as-prepared Cu$_2$O/S (S = ZSM-5, CeO$_2$, α-MnO$_2$ and commercial Fe$_2$O$_3$) catalysts; Figure S2: SEM (a,b) and TEM (c,d) image of the as-prepared α-MnO$_2$ supports; Figure S3: H$_2$-TPR profiles of the as-prepared ZSM-5, CeO$_2$, α-MnO$_2$ and Fe$_2$O$_3$ supports. References [56–58] are cited in the supplementary materials.

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**Data Availability Statement:** The data supporting the findings of this study are available by reasonable request to leileixu88@gmail.com.

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