

Article

Highly Active CuO/KCC–1 Catalysts for Low-Temperature CO Oxidation

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Abstract: Copper catalysts have been extensively studied for CO oxidation at low temperatures. Previous findings on the stability of such catalysts, on the other hand, revealed that they deactivated badly under extreme circumstances. Therefore, in this work, a series of KCC–1-supported copper oxide catalysts were successfully prepared by impregnation method, of which 5% CuO/KCC–1 exhibited the best activity: CO could be completely converted at 120 °C. The 5% CuO/KCC–1 catalyst exhibited better thermal stability, which is mainly attributed to the large specific surface area of KCC–1 that facilitates the high dispersion of CuO species, and because the dendritic layered walls can lengthen the movement distances from particle-to-particle, thus helping to slow down the tendency of active components to sinter. In addition, the 5% CuO/KCC–1 has abundant mesoporous and surface active oxygen species, which are beneficial to the mass transfer and promote the adsorption of CO and the decomposition of Cu⁺–CO species, thus improving the CO oxidation performance of the catalyst.

Keywords: air pollution control; CuO; dendritic mesoporous silica; CO oxidation; sintering resistance



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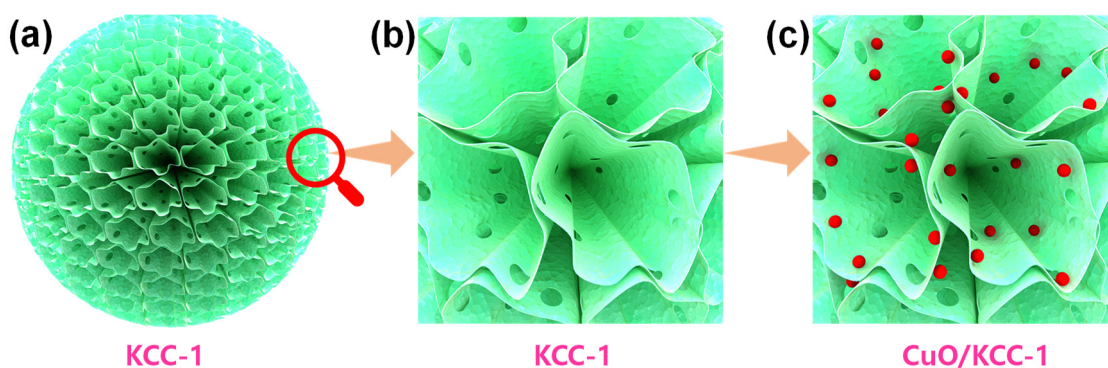
1. Introduction

Colorless, odorless, and tasteless carbon monoxide (CO) is a kind of toxic gas generated by the low combustion efficiency of the fuels from different sources of fuel combustion, such as vehicle exhaust emissions, cement plants, electricity plants, biomass combustion, etc. [1–4]. Catalytic oxidation is considered to be one of the most promising methods for CO elimination, especially at low temperature [5–8]. Recently, the catalytic oxidation of CO has been favored by many researchers due to its wide application in fields, such as indoor air purification, automobile exhaust purification, and providing pure hydrogen to automotive proton exchange membrane fuel cells [3]. Various catalytic systems have been explored as catalysts for the oxidation of CO, including noble metals, transition metals, and rare earth oxides. [9–11]. Noble metal catalysts, such as Au/ZnO [12], Pt/MnO_x [13], and Pd/CeO₂ [14], usually exhibit outstanding low-temperature CO oxidation performance, however, the inherent rarity and high cost restrict their widespread application. Therefore, more attention has been paid to the use of transition metal oxide catalysts, especially copper (Cu)-based catalysts, due to their excellent activity comparable to that of noble metals [15].

However, one of the most fundamental hurdles to overcome in catalytic reactions is sintering, both for precious metals and non-noble metals catalysts [16,17]. In order to retard the sintering of nanoparticles (NPs), some strategies were proposed [18]: (i) steric confinement of NPs by carbon nanotubes or other one-dimensional metal oxides [19,20];

(ii) embedding NPs in a silica matrix or porous shell [21,22]; (iii) restriction of NPs to channels of mesoporous materials, e.g., SBA-15 [23,24], MCM-41 [25]; (iv) stable anchoring of NP to the catalyst surface by a strong metal-support interaction [26,27]. In fact, this sort of confinement can significantly reduce sintering of the active NP's component, resulting in increased catalytic stability. However, traditional confinement strategies, particularly porous or core-shell structures, may hinder the transport of reactants to some extent or sacrifice a fraction of the active sites [28], which is detrimental to the catalytic reaction. Better strategies to stabilize active metal or metal oxide NPs are needed.

In recent years, dendritic mesoporous silica zeolite (such as KCC-1) has been attracting attention as a support with good sintering resistance [29,30]. In particular, Basset and his colleagues synthesized high surface area fibrous mesoporous silica nanospheres with a wide open-mouth spherical morphology [31], consisting of dendritic silica layers presented in three dimensions. The existence of dendritic silica layers with mesoporous channels makes this type of material highly accessible to active sites. In addition, the dendritic layered walls have open-mouth spherical morphology that can lengthen the movement distances from particle-to-particle, thus helping to slow down the tendency of active components to sinter. Peng et al. [18] also found that Ni/KCC-1 catalysts showed satisfying coking and sintering resistance in the dry reforming of a methane reaction due to the special structure of KCC-1. In this work, we used KCC-1 as a support for copper oxide nanoparticles and found that the synthesized catalyst was very effective in CO oxidation due to the mesopore-rich structure with a large specific surface, which facilitates mass transfer and the high dispersion of CuO, as well as the redox performance of the catalyst. Furthermore, the surface spatial confinement effect of KCC-1 support can significantly improve the thermal stability of the catalyst as displayed in Scheme 1.



Scheme 1. Diagram of the surface spatial confinement strategy ((a,b): KCC-1; (c): CuO/KCC-1, red spheres: CuO NPs).

2. Experimental Procedure

2.1. Preparation of Catalysts

All of the reagents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Beijing, China) and utilized without any further purification. KCC-1 support was prepared according to the literature [31]. Typically, 60 mL of cyclohexane (99.5%), 3 mL of n-pentanol (99.5%), and 5.0000 g of tetraethyl orthosilicate (TEOS, 99%, 18.92 mmol) were mixed at room temperature to obtain liquid A; 2.0000 g of cetyltrimethylammonium bromide (CTAB, $\geq 99\%$, 5.48 mmol) and 1.2000 g of urea (99%, 19.98 mmol) were dissolved in 60 mL of deionized water to obtain liquid B; liquid B was poured into liquid A slowly and the resulting solution mixed well; then, the mixture was transferred into a stainless steel autoclave, sealed, and maintained at 120 °C for 6 h with constant stirring; after cooled to room temperature, the precipitation was collected by filtering and washing with acetone (99.5%) and ethanol (99.5%); then, the final precipitation was dried at 80 °C overnight and calcined in a muffle furnace at 550 °C for 6 h to remove the template agent (the heating rate was

2 °C min^{−1}); finally, the white powder of mesoporous molecular sieve material KCC-1 was obtained.

CuO/KCC-1 catalysts with different CuO loadings were prepared by an incipient wetness method using the synthesized KCC-1 support. The 0.5000 g of KCC-1 supports were impregnated in a solution containing 10 mL of ethylene glycol (99.5%) and proper amounts of Cu(NO₃)₂·6H₂O (≥99%). Then, the resulting solid-liquid mixture was dried in a vacuum oven at 80 °C until the solvent was completely evaporated; then, the resulting solid was calcined in a tube furnace at 550 °C under N₂ atmosphere for 4 h; finally, the gas was switched to air and maintained at 550 °C for 2 h. The attained catalysts were named as x% CuO/KCC-1-EG, where x% represents the CuO loading in mass fraction. Moreover, the effect of impregnating solution on the catalytic performance was also investigated: we replaced ethylene glycol with deionized water or ethanol, and the other conditions were the same as above; the obtained catalysts were named as x% CuO/KCC-1-H₂O or x% CuO/KCC-1-EtOH, where x% represents the CuO loading in mass fraction.

For comparison, the pristine CuO that without three-dimensional spatial structure was prepared by a homogeneous precipitation method. In a typical process, appropriate amount of Cu(NO₃)₂·6H₂O (≥99%) was first dissolved in deionized water (the Cu²⁺ concentration was 0.1 mol L^{−1}), after 30 min of stirring, ammonia solution (Sinopharm, 25~28 wt.%) was added drop by drop to the above solution until the pH was about 10. The above mixture was stirred at room temperature for 3 h. At last, the precipitation was filtered and washed, dried, and calcined using the same calcination procedures as above.

2.2. Characterization of Catalysts

The detailed characterization of catalysts, including XRD, Nitrogen adsorption-desorption, H₂-TPR, SEM, TEM, and in situ DRIFTS are displayed in the Supplementary Materials.

2.3. Catalytic and Kinetic Tests

The CO catalytic oxidation activity of the prepared samples were measured in a fixed-bed quartz flow reactor with 100 mg of catalyst (60~80 mesh). The feed gases were composed of 1% CO, 21% O₂, and balanced by high purity N₂. The total flow rate was 30 mL·min^{−1} and the WHSV (weight hourly space velocity) was 18,000 mL g_{cat.}^{−1}·h^{−1}. The reactants and products were analyzed on-line on a GC9310 gas chromatograph equipped with a TDX-01 column and a TCD. The conversion of CO (*X*_{CO}) was calculated using Equation (1)

$$X_{\text{CO}} = \left(1 - \frac{S_{\text{CO-outlet}}}{S_{\text{CO-inlet}}} \right) \times 100\% \quad (1)$$

where *S*_{CO-outlet} and *S*_{CO-inlet} are the CO concentrations in the outlet and inlet gas streams, respectively, corresponding to the CO inlet and outlet peak areas, as determined by the gas chromatograph responses using the external standard method. Carbon balance was close to 100%.

We can calculate the normalized reaction rate (*r*) and apparent activation energy (*E*_a) of the reaction by performing CO catalytic oxidation reactions at different temperatures to obtain the CO conversion according to Equations (2)–(4) [32]

$$r = \frac{X_{\text{CO}} F_{\text{CO}}}{m_{\text{cat.}}} \quad (2)$$

$$r = -\frac{F_{\text{CO}}}{m_{\text{cat.}}} \times \ln(1 - X_{\text{CO}}) \quad (3)$$

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (4)$$

where *F*_{NO_x} is the gas flow rate (in mol s^{−1}) of CO; *m*_{cat.} is the mass of the catalyst (in g); *A* is the pre-exponential factor; *T* is the reaction temperature (in K); *R* is the gas constant (in kJ mol^{−1} K^{−1}). Generally, the reaction orders in the equations were set as first and zero for

CO and O₂, respectively. The E_a can be calculated from the Arrhenius plots of the reaction rate coefficient.

Differential reaction mode was used to study the reaction kinetics of certain sample catalysts (with CO conversion below 10%). The catalyst was diluted to 200 mg with quartz sand (of the same size) and evaluated under the same conditions as the catalytic test above, with the exception that the gas flow rate was increased to 120 mL min^{−1}, and the absence of mass and heat transfer limitations ensured the reaction was in the kinetic region. Weisz–Prater criteria (C_{WP}) for internal diffusion and Mears' criterion (C_M) for exterior diffusion were used to verify the lack of mass transport resistances according to Equations (5) and (6) [33–36]

$$C_M = \frac{r\rho_b R_p^n}{k_c C_{Ab}} < 0.15 \quad (5)$$

$$C_{WP} = \frac{r_{obs}\rho_c R_p^2}{D_{eff} C_{As}} < 1 \quad (6)$$

where r_{obs} is the observed reaction rate (in mol kg_{cat}^{−1}·s^{−1}, $r_{obs} \approx r$); n is the reaction order (the reaction orders in the equations were set as first and zero for CO and O₂, respectively); R_p is the catalyst particle radius (1.1×10^{-4} m); ρ_c is the solid catalyst density (in kg m^{−3}); ρ_b is the bulk density of catalyst bed (in kg m^{−3}, $\rho_b \approx \rho_c$); D_{eff} is the effective diffusivity (8.9×10^{-6} m² s^{−1}); C_{As} is the gas concentration of CO at the external surface of the catalyst (in mol m^{−3}); C_{Ab} is the bulk gas concentration of CO (in mol m^{−3}, $C_{Ab} \approx C_{As}$); k_c is the external mass transfer coefficient (0.1 m s^{−1}).

3. Results and Discussion

3.1. SEM and TEM Results Analysis

To understand the microscopic morphology of the catalysts, the as-prepared KCC–1 support and CuO/KCC–1 series catalysts were characterized by SEM, and the SEM images of the catalysts are shown in Figure 1. We can see that, for the KCC–1 support, the morphology is that of flower-like fibrous microspheres with an average spherical diameter of approximately 500 nm. This structure allows KCC–1 to maintain good thermal stability and an effective surface spatial confinement effect. The morphology did not change significantly when KCC–1 was loaded with a small amount of CuO (as shown in Figure 1b–d), but the morphology of the catalyst was disrupted when the loading of CuO was excessive (as shown in Figure 1e). When the impregnating solution was changed from ethylene glycol to deionized water, the morphology of the catalyst did not change significantly (as shown in Figure 1f).

The micro morphology of CuO/KCC–1 series catalysts and CuO was further studied, and the as-prepared samples were characterized by TEM and EDX-Mapping technologies. As shown in Figure 2a, the TEM image of CuO shows that it is composed of bulk nanoparticles. From Figure 2b–d, we can clearly see the dendritic skeleton structure of KCC–1 spreading from the center to the periphery, which is an important factor for the good stability of the support structure. The interweaving between dendritic fibers forms a pore-rich structure, which is beneficial to the high dispersion of CuO nanoparticles. In addition, it can be seen from the TEM image that after the CuO nanoparticles were confined in KCC–1 support, no large metal particles are seen on the surface of the KCC–1, which indicates that the CuO nanoparticles are highly dispersed on the surface of the KCC–1 supports. As shown in Figure 2e–h, the high-angle annular dark field image and EDX-Mapping images of 5% CuO/KCC–1–EG show that the CuO nanoparticles are uniformly distributed and highly dispersed.

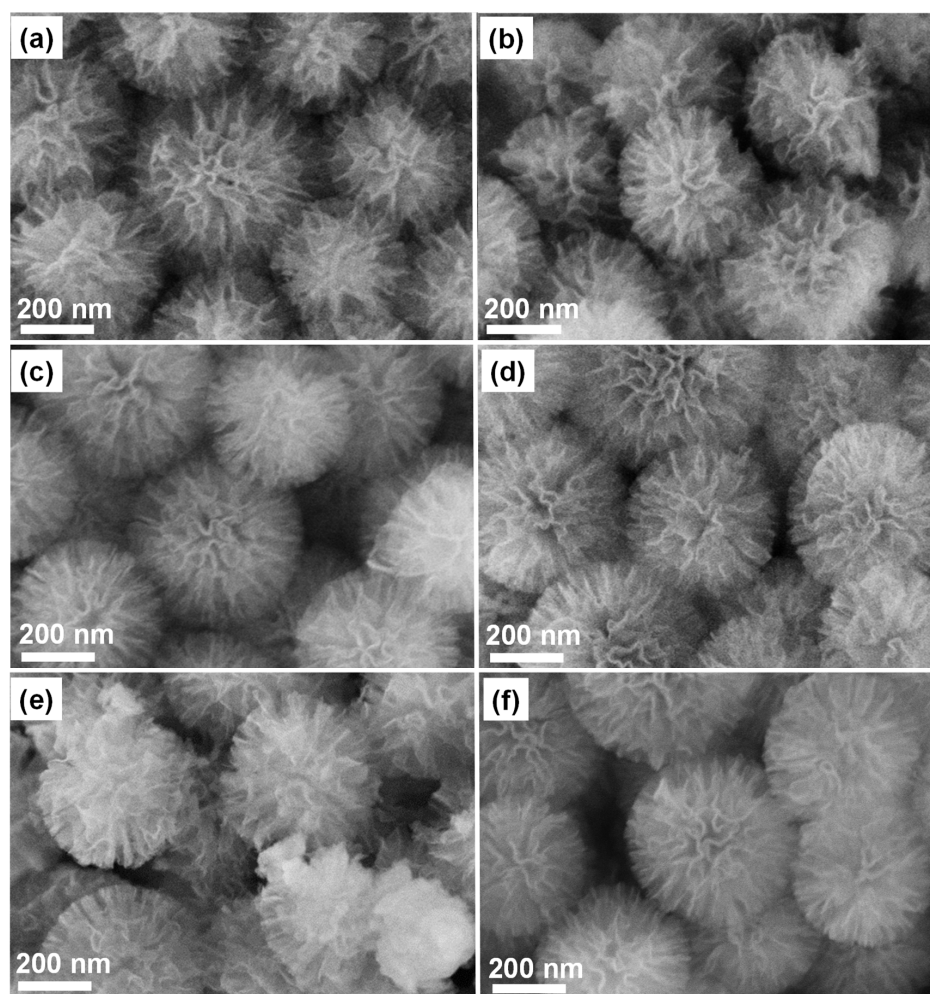


Figure 1. The SEM images of the catalysts ((a) KCC-1; (b) 1% CuO/KCC-1-EG; (c) 3% CuO/KCC-1-EG; (d) 5% CuO/KCC-1-EG; (e) 7% CuO/KCC-1-EG; (f) 5% CuO/KCC-1-H₂O).

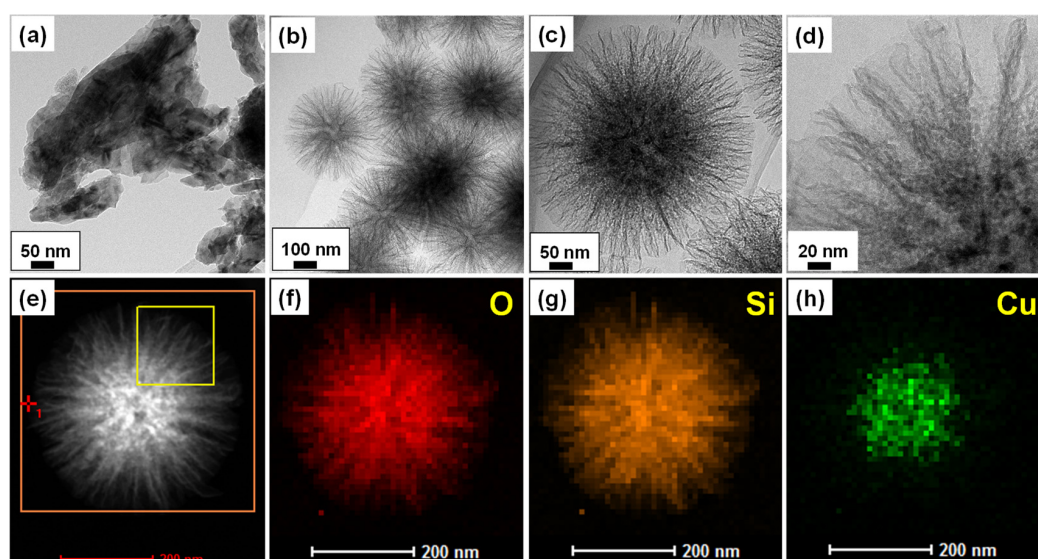


Figure 2. The TEM images of the catalysts ((a) CuO; (b–d) 5% CuO/KCC-1-EG); (e) High-angle annular dark field image of 5% CuO/KCC-1-EG; (f–h) EDX Mappings of 5% CuO/KCC-1-EG).

3.2. CO Oxidation Performance, Kinetic and Thermal Stability

The CO oxidation activity of the CuO/KCC-1 series catalysts were tested, as shown in Figure 3a, from which it can be seen that the dendritic mesoporous molecular sieve KCC-1 composed of SiO₂ showed almost no CO catalytic oxidation activity. When the KCC-1 was loaded with a small amount of CuO, the CO catalytic oxidation activity of the catalyst increased and reached an optimum level when the CuO loading reached 5%, with a complete conversion of CO at 120 °C. The CuO loading should not be too high and the activity of the catalyst decreased when the CuO loading reached 7%, with a complete conversion of CO at 160 °C. Pristine CuO exhibited barely satisfactory CO catalytic oxidation activity, and CO could be completely reacted when the reaction temperature reached 280 °C. By comparing the CuO/KCC-1-EG series catalysts with different CuO contents, it was found that 1% CuO/KCC-1-EG has the lowest catalytic activity, and the CO catalytic oxidation activity of the catalysts was boosted and then decreased with the increasing CuO content. The possible reason for this is that KCC-1, which has a high specific surface area and abundant mesoporous pores, has no catalytic activity, but CuO nanoparticles have a certain CO catalytic oxidation activity. The CuO nanoparticles were highly dispersed on the surface of KCC-1 and in the pore channels, making the catalyst exhibit excellent catalytic performance; as the CuO content increased, the number of active components also increased, thus enhancing the catalytic activity; however, as the CuO content increased further, the CuO nanoparticles covered the surface of the KCC-1, blocking part of the molecular sieve catalyst pore channels, leading to a decrease in the specific surface area and pore volume of the samples, which ultimately led to a decrease in the catalytic oxidation activity of the catalysts. In addition, the influence of the impregnating solution on the catalytic performance of the catalysts was investigated, as presented in Figure 3b, and the results showed that the choice of impregnating solution significantly affected the catalytic performance of the catalysts. For 5% CuO/KCC-1-EtOH and 5% CuO/KCC-1-H₂O catalysts, the temperature for complete CO conversion were 220 and 260 °C, respectively. The order of preference is: ethylene glycol > ethanol > deionized water. When ethylene glycol is used as the impregnating solution, it is beneficial to the high dispersion of CuO on the surface of the KCC-1 supports.

In order to test the intrinsic activity of the catalyst and the activation energy of catalytic reaction, high weight hourly space velocity and low conversion (72,000 mL g_{cat}⁻¹ h⁻¹, CO conversion were less than 10%) and catalysts doped with quartz sand were used to eliminate the effects of mass and heat transfer. The kinetic calculation (Mear and Weisz-Prater's criterion) was used to determine whether the effects of internal and external diffusion were excluded, and the calculation results are displayed in Table 1. The $C_M < 0.15$ and $C_{WP} < 1$, therefore, the internal and external diffusion effects and heat transfer effect on the catalysts during the kinetic experiment could be neglected; the activities tested were the intrinsic activity of the catalysts. The Arrhenius curve obtained from the kinetic test of the catalyst is shown in Figure 3c, and the activation energies of the reactions were calculated. The result is $E_a(1\% \text{ CuO/KCC-1-EG}) \approx E_a(\text{CuO}) > E_a(7\% \text{ CuO/KCC-1-EG}) > E_a(5\% \text{ CuO/KCC-1-EG})$. When 5% CuO/KCC-1-EG was used as the catalyst for the reaction, the catalytic reaction had the lowest activation energy, which was 31 kJ mol⁻¹. The kinetic test results showed that 5% CuO/KCC-1-EG could reduce the energy barrier of the catalytic reaction and promoted the catalytic reaction, which was consistent with its optimal CO catalytic oxidation performance. To test the thermal stability of the catalyst, the as-prepared CuO and 5% CuO/KCC-1-EG catalysts were calcined at 700 °C for 3 h in air atmosphere, and then their CO catalytic oxidation performances were tested. As shown in Figure 3d, the activity of 5% CuO/KCC-1-EG decreased slightly after high-temperature calcination, the temperature of CO complete conversion increased slightly to 140 °C; although the temperature of CO complete conversion increased slightly to 300 °C over the CuO catalyst, the T₅₀ (the temperature when CO conversion reached 50%) increased obviously from 195 to 240 °C. The thermal stability results show that 5% CuO/KCC-1-EG had better thermal stability, which is mainly due to the large specific

surface area of KCC-1 support, which is beneficial to the high dispersion of CuO species. In addition, the dendritic layered walls have open-mouth spherical morphology that can lengthen the movement distances from particle-to-particle, thus helping to slow down the tendency of active components to sinter.

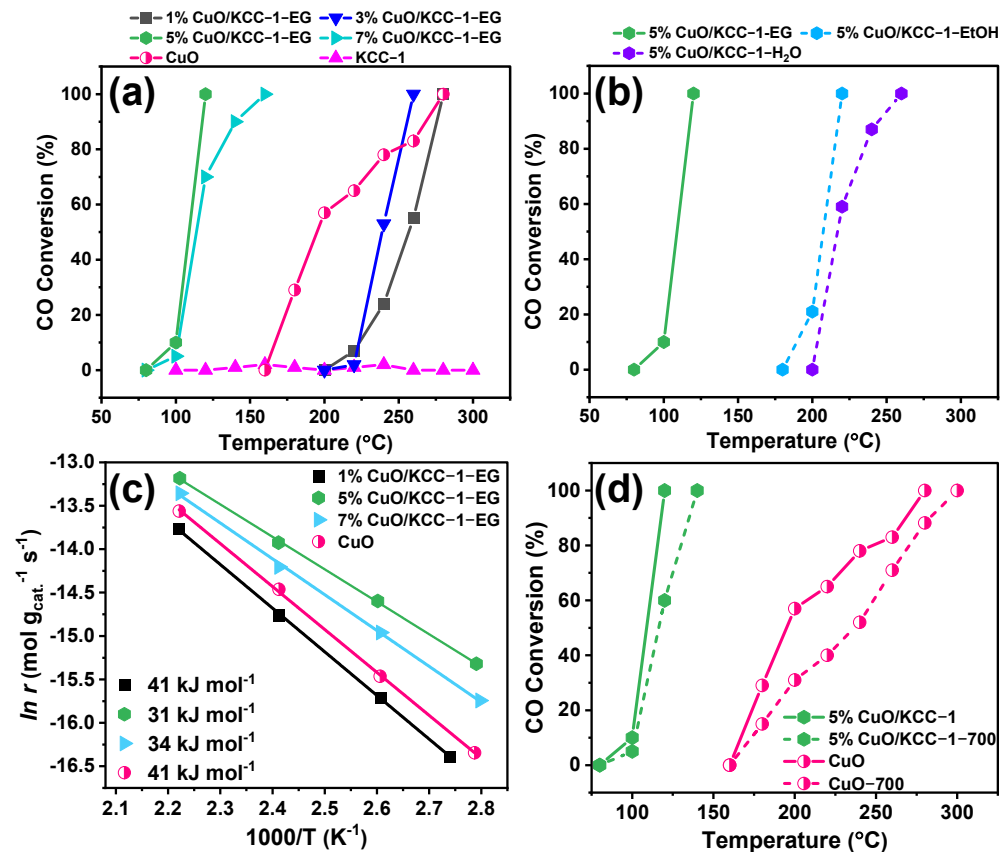


Figure 3. (a) Light-off curves of CO conversion for CO oxidation reaction; (b) Effect of impregnating solution on catalyst performance; (c) Arrhenius curves of CO catalytic oxidation over various catalysts; (d) The thermal stability curves of catalysts.

Table 1. The C_{WP} and C_M over the various catalysts in CO oxidation performance.

Catalysts	ρ_b	r	C_{Ab}	T_m^a	C_M	C_{WP}
1% CuO/KCC-1	1882	7.6×10^{-5}	0.423	365	3.38×10^{-4}	3.80×10^{-4}
5% CuO/KCC-1	1897	2.2×10^{-4}	0.391	358	1.09×10^{-3}	1.22×10^{-3}
7% CuO/KCC-1	1926	1.4×10^{-4}	0.403	358	6.97×10^{-4}	7.84×10^{-4}
CuO	6114	7.5×10^{-5}	0.412	365	1.12×10^{-3}	1.26×10^{-3}

^a: T_m were the maximum temperatures during CO oxidation kinetic measurements (in K).

3.3. XRD Results Analysis

The XRD spectrum of the CuO/KCC-1 series catalysts are shown in Figure 4. It can be seen that a broad diffraction peak appears at a 2θ value at 22.58° , which corresponded to the characteristic diffraction peak of the amorphous SiO₂ of the mesoporous molecular sieve KCC-1 [18]. The pure CuO sample shows a characteristic diffraction peak typical of CuO with a strong peak intensity, indicating a high degree of crystallinity of CuO. For the CuO/KCC-1-EG catalysts impregnated by ethylene glycol, the characteristic diffraction peaks of CuO species were not detected even though the loading of CuO was as high as 7%, indicating that the CuO species were highly dispersed on the surface of KCC-1,

which is consistent with their SEM and TEM results. When the impregnating solution was changed to deionized water, faint characteristic peaks of CuO species could be detected. The above XRD results show that the CuO nanoparticles were highly dispersed on the KCC-1 support and the use of ethylene glycol as the impregnating solution was more favorable to the high dispersion of Cu species on KCC-1 than deionized water.

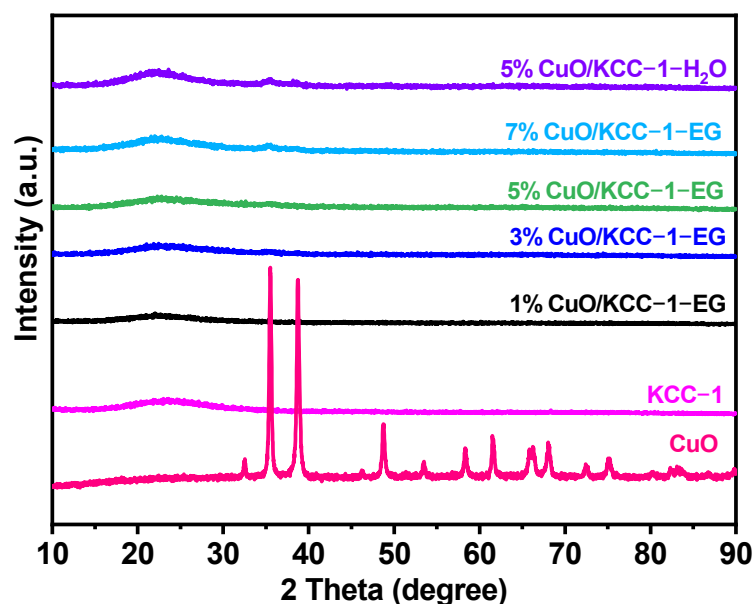


Figure 4. The XRD patterns of the catalysts.

3.4. N₂ Adsorption/Desorption Results Analysis

The N₂ adsorption and desorption isotherms, as well as the pore size distribution curves of CuO/KCC-1 series catalysts, are shown in Figure 5a,b, respectively. Table 2 shows the quantitative data. It can be seen from Figure 5a that the adsorption–desorption isotherms curve of CuO/KCC-1 catalysts showed typical type IV isotherms with a hysteresis loop of type H1 in the p/p_0 between 0.4 and 1.0, which is caused by the capillary condensation phenomenon of the mesoporous structure, indicating that the catalysts have mesoporous structure [18]. As shown in Figure 5b, narrow and strong peaks at 3.5 nm and fluctuations over a range of 10 to 50 nm are observed on the pore size distribution curve of the CuO/KCC-1 catalysts due to the narrow inside channels and broader outside channels. Although the CuO sample also has a pore structure, its pore diameter is basically zero, which shows that its pores are formed by the accumulation of a large number of CuO particles and not its own inherent pore structure, which can also be confirmed by the TEM image of CuO. It can be seen from Table 2 that the specific surface area of pristine CuO is the smallest, only 10 m² g^{−1}, and the pore volume is only 0.006 cm³ g^{−1}. The KCC-1 support shows high specific surface area (638 m² g^{−1}) and the largest pore volume (1.68 cm³ g^{−1}). As the loading of CuO increases, the specific surface area and pore volume of the catalyst show a decreasing trend. This is mainly because CuO nanoparticles block part of the pores. Nevertheless, when the ethylene glycol is used as the impregnating solution, the specific surface area of CuO/KCC-1 series samples is still higher than 300 m² g^{−1}, which provides abundant reaction place for the catalytic reaction. When the impregnating solution was changed from ethylene glycol to deionized water, the specific surface area of the catalyst was significantly reduced, which indicated that the type of impregnating liquid would affect the physical structure of the catalyst. Using deionized water as the impregnating liquid is not beneficial to the high dispersion of CuO, which is consistent with the XRD results.

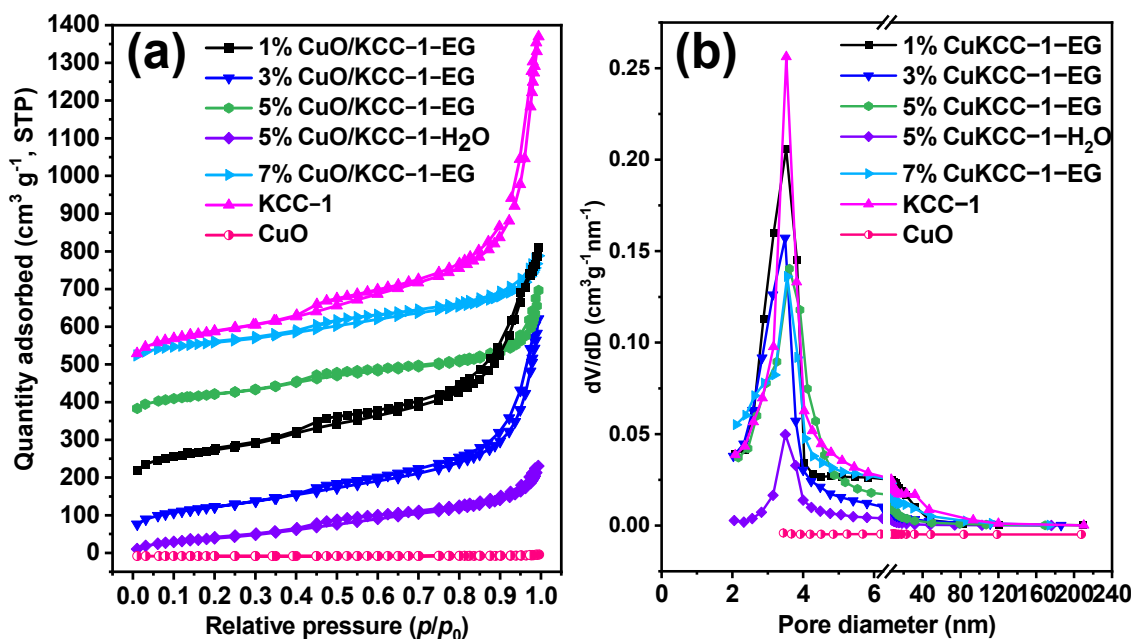


Figure 5. (a) N_2 adsorption–desorption isotherms and (b) pore size distributions of the catalysts.

Table 2. The textual properties of $Mn_{0.50}Co_{0.49}V_{0.01}$ and various catalysts.

Samples	Surface Area ($m^2 g^{-1}$)	Pore Volume ($cm^3 g^{-1}$)	Pore Size (nm)
7%Cu/KCC-1-EG	309	0.76	3.5
5%Cu/KCC-1-EG	345	0.95	3.5
5%Cu/KCC-1- H_2O	264	0.87	3.4
3%Cu/KCC-1-EG	388	0.97	3.5
1%Cu/KCC-1-EG	457	1.21	3.5
KCC-1	638	1.45	3.5
CuO	10	0.006	7.0

3.5. H_2 -TPR Result Analysis

Figure 6 depicts the H_2 -TPR curve of the CuO/KCC-1 catalysts. Pure CuO displays a noticeable reduction peak with a peak temperature of 324 °C, which is related to the reduction of CuO to Cu [37]. The 1% CuO/KCC-1-EG has no obvious reduction peak. The reduction peak temperature of 3% CuO/KCC-1-EG is 231 °C, which is not much different from the reduction peak temperature of 5% CuO/KCC-1. When the Cu loading amount reaches 7%, the reduction peak temperature of Cu species shifts to a higher temperature, which is 237 °C. The intertwined abundant pores are beneficial to the transmission and diffusion of substances, and are beneficial to promoting the migration of active oxygen species and, thus, improving the reduction properties of the catalyst. This is the important factor for the improvement of the CO catalytic oxidation performance. In addition, it can be seen that when the impregnating solution was changed from ethylene glycol to deionized water, the reduction peak temperature of the catalyst shifted to the higher temperature, which indicates the decreased reduction property, and that it is consistent with the weaker CO catalytic performance over the 5% CuO/KCC-1- H_2O catalyst.

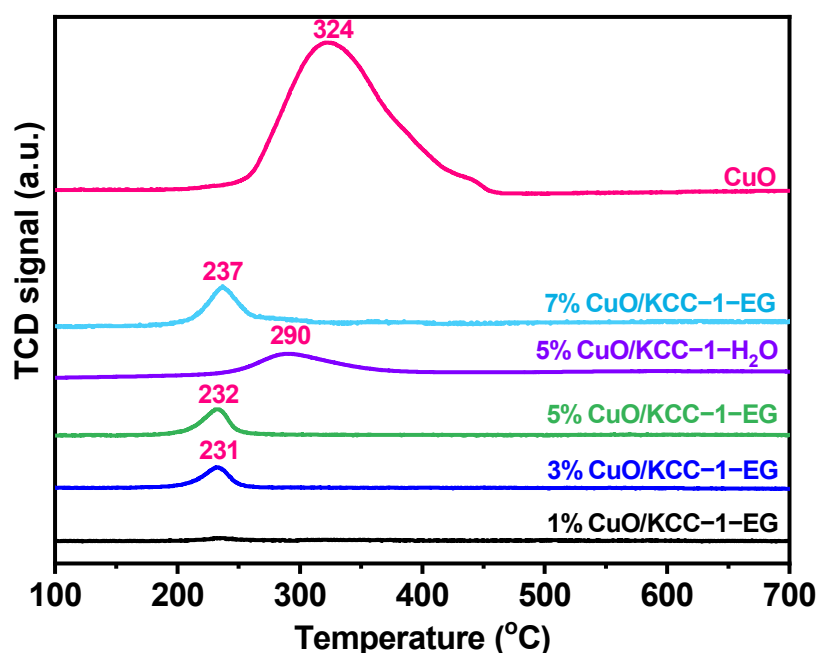


Figure 6. The H₂-TPR curves of the catalysts.

3.6. XPS Result Analysis

Because the catalytic reaction occurs on the catalyst's surface, it is critical to investigate the surface element composition and valence. The XPS spectra of 5% CuO/KCC-1-EG, 5% CuO/KCC-1-H₂O, and CuO catalysts are shown in Figure 7, and the surface atom concentrations' results are shown in Table 3. For the XPS spectrum of O 1s (Figure 7a–c), the peaks located at 530.9 ~ 531.0 eV are ascribed to the surface chemically adsorbed oxygen species; the peaks located at 529.1 ~ 530.3 eV are assigned to the lattice oxygen species [38–41]. It can be seen from the quantitative results in Table 3 that the 5% CuO/KCC-1-EG has the largest surface adsorption oxygen species ratio, followed by the 5% CuO/KCC-1-H₂O, and CuO has the smallest surface adsorption oxygen species ratio. As we all know, the adsorbed oxygen on the surface has stronger mobility than the lattice oxygen and can promote the catalytic oxidation of CO, which is consistent with the H₂-TPR results and catalytic performance. Figure 7d is the spectrum of the Cu 2p orbital of the catalysts. The peak intensity of CuO is significantly higher than that of 5% CuO/KCC-1-EG and 5% CuO/KCC-1-H₂O, which confirms the high dispersion of Cu species on KCC-1 from the side, and this is in accordance with the results of XRD, SEM, and TEM.

3.7. In Situ DRIFTS Results Analysis

In this section, in situ DRIFTS measurements for as-synthesized 5% CuO/KCC-1-EG and CuO were performed at 100 °C to better understand the CO adsorption behavior. As shown in Figure 8a,b, the bands located at 2119~2127 cm⁻¹ and 2162~2172 cm⁻¹ were observed in both catalysts when exposed in a CO atmosphere, which were attributed to the CO adsorption on Cu⁺ (Cu⁺-CO) species and gaseous CO species [4], respectively. The intensity of the adsorption peak over the 5% CuO/KCC-1-EG was higher than that of CuO, which indicates that 5% CuO/KCC-1-EG is more beneficial to the adsorption of CO. The bands located at 2336~2363 were ascribed to gaseous CO₂ [4,42], suggesting the incoming CO reduced the surface species of oxides. After being treated with CO for an hour, the catalysts were purged with N₂ for 30 min. As presented in Figure 8c,d, the band corresponding to gaseous CO₂ disappeared and the band ascribed to Cu⁺-CO still existed over the CuO catalyst, the peak intensity decreased with the time of the O₂ treatment, but the peak intensity was still high when exposed in an O₂ atmosphere for an hour. However, for the 5% CuO/KCC-1-EG catalyst (Figure 8d), two big bands appeared when the gas was shifted to O₂ for only 1 min: gaseous CO₂ and Cu⁺-CO species emerged

simultaneously, and the intensity declined sharply and almost completely disappeared when treated with O₂ for an hour. The above results indicate that 5% CuO/KCC-1-EG was more beneficial to the adsorption of CO and the decomposition of Cu⁺-CO species: this may be an important reason for its better catalytic activity than that of CuO.

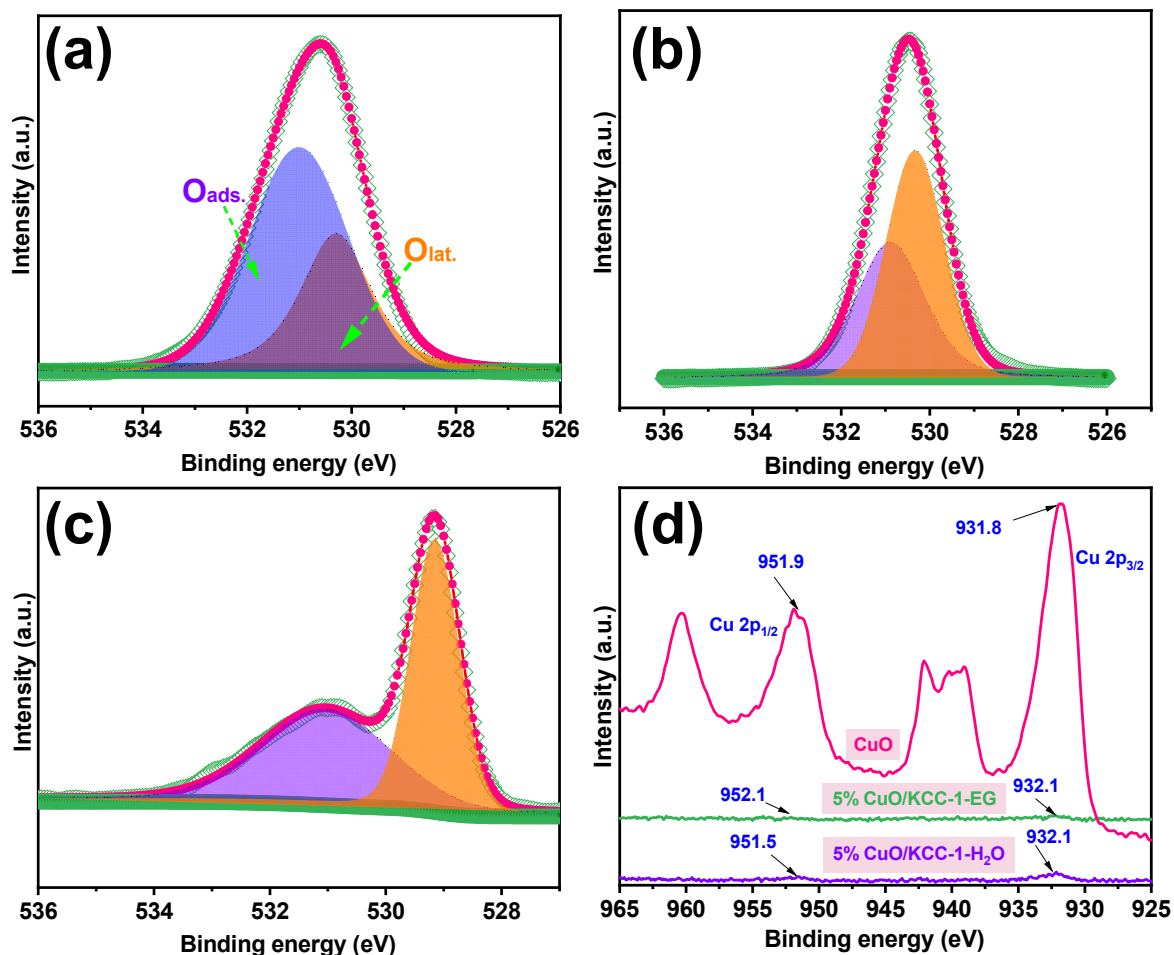


Figure 7. The O 1s XPS patterns (a) 5% CuO/KCC-1-EG; (b) CuO; (c) 5% CuO/KCC-1-H₂O; (d) Cu 2p XPS patterns) of the catalysts.

Table 3. Surface atom concentrations of the catalysts.

Samples	Cu 2p Binding Energy (eV)		ΔE (eV)	O 1s Binding Energy (eV)		O_{ads}/O_{lat}
	2p _{1/2}	2p _{3/2}		O _{ads}	O _{lat}	
5% Cu/KCC-1-EG	952.1	932.1	20.0	531.0	530.3	1.7
5% Cu/KCC-1-H ₂ O	951.5	932.1	19.4	531.0	529.1	0.9
CuO	951.9	931.8	20.1	530.9	530.3	0.7

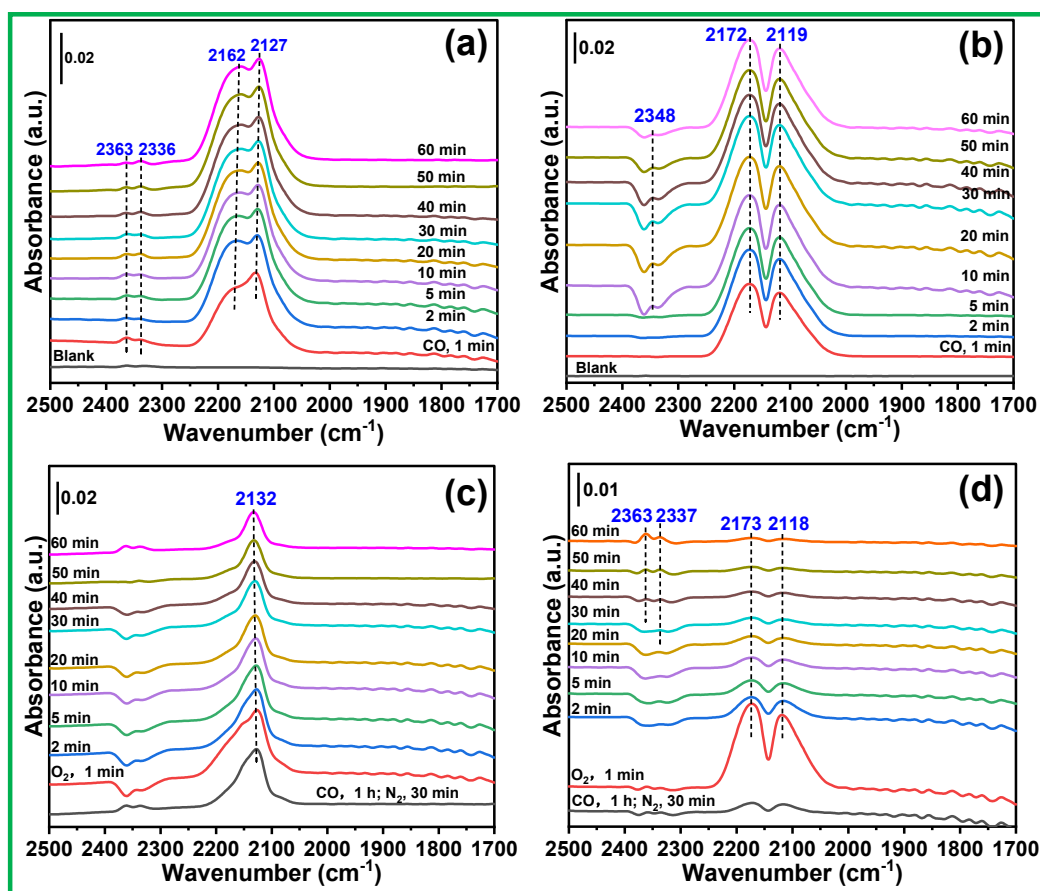


Figure 8. In situ DRIFT spectra of the (a) CuO and (b) 5% CuO/KCC-1-EG catalysts under an atmosphere of 1000 ppm of CO/N₂ (30 mL min^{−1}) at 100 °C; in situ DRIFT spectra of the transient reactions at 100 °C between 5% O₂/N₂ (30 mL min^{−1}) and pre-adsorbed CO/N₂ species over the (c) CuO and (d) 5% CuO/KCC-1-EG catalysts recorded as a function of time.

4. Conclusions

In this work, a series of CuO/KCC-1 catalysts with varying CuO loadings were successfully prepared via the impregnation method and applied to the CO catalytic oxidation reaction. The catalyst showed good catalytic performance, of which 5% CuO/KCC-1-EG exhibited the best activity: CO could be completely converted at 120 °C. Compared with the pristine CuO catalyst, the 5% CuO/KCC-1-EG exhibited better activity and thermal stability, which is mainly attributed to the large specific surface area of KCC-1 that facilitates the high dispersion of CuO species and because the dendritic layered walls can lengthen the movement distances from particle-to-particle, thus helping to slow down the tendency of active components to sinter. In addition, the KCC-1 has abundant mesoporous and surface active oxygen species, which is beneficial to the mass transfer and promotes the adsorption of CO and the decomposition of Cu⁺-CO species, thus improving the CO oxidation performance of the catalyst.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr10010145/s1>. The detailed characterization of catalysts, including XRD, Nitrogen adsorption-desorption, H₂-TPR, SEM, TEM, and in situ DRIFTS are displayed in the Supplementary Materials.

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