

Study on catalytic combustion performance of CO over Sn-modified CuCeO_x catalysts under high humidity conditions

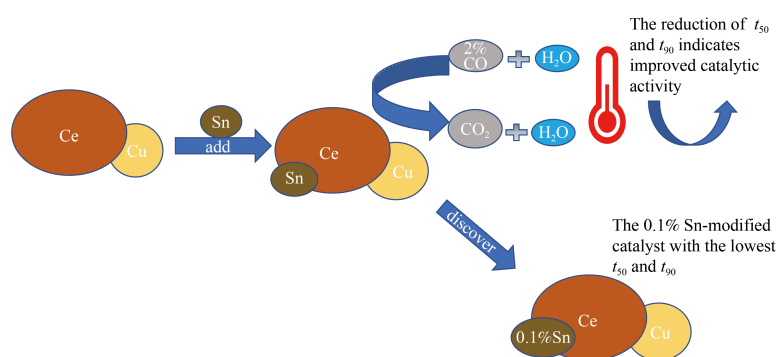
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Abstract: Low-temperature CO oxidation technology has been widely applied in the field of environmental pollution control, yet challenges remain in CO purification under high-moisture environments. In this study, a series of CuCeO_x -Sn catalysts supported on CeO_2 were prepared via the excess impregnation method, and their catalytic performance in the low-temperature catalytic combustion of

CO was systematically evaluated. The results indicate that $\text{CuCeO}_x\text{-Sn}_{0.1}$ (with a Sn loading of 0.1%) exhibits the optimal low-temperature catalytic activity, with the lowest t_{50} and t_{90} values. The temperature for 90% CO conversion (t_{50} and t_{90}) decreases progressively with increasing Sn loading up to 0.1%. Beyond this threshold, further Sn loading does not lead to a significant reduction in t_{90} ; in fact, t_{90} slightly increases compared to that observed at 0.1% Sn. Furthermore, this catalyst maintains stability during water-on/water-off switching tests, demonstrating excellent water resistance. Through characterization techniques including XPS, O_2 -TPD, CO-TPD and CO-TPSR, it is revealed that the introduction of Sn effectively increases the concentration of surface oxygen vacancies and promotes the activation and migration of surface adsorbed oxygen and lattice oxygen.

Key words: Cu-Ce; Sn modification; excess impregnation method; H_2O resistance; CO catalytic oxidation



Carbon monoxide (CO) is a common and highly hazardous pollutant that poses significant threats to human health due to its flammability and explosive properties^[1–2]. Excessive emissions of CO can also indirectly exacerbate global warming and deplete the ozone layer^[3]. Although CO is colorless, odorless, and non-irritating, it can bind with human hemoglobin, reducing the oxygen-carrying capacity and leading to hypoxia or even fatal shock^[3]. Data from the Global Burden of Disease Study (GBD 2021) showed that the global number of deaths from accidental CO poisoning was approximately 28900^[4]. CO poisoning is a common

incident in confined spaces such as ships, coal mines, submarines, and underwater channel work areas. However, the removal of CO still faces challenges due to factors such as complex atmospheric composition and high humidity in these environments. Therefore, there is an urgent need to research and develop CO purification technologies suitable for high-humidity conditions. CO purification technologies mainly include physical adsorption^[5], catalytic oxidation, photocatalysis and others. Among these, catalytic oxidation is widely used in the environmental removal of CO due to its high cost-effectiveness. Therefore, it is crucial to design

Received: 2025-12-05; Revised: 2026-01-08

Foundation items: Supported by Key Scientific and Technological Project of Henan Province (252102321085, 252102320372) and the Key Scientific Research Projects of Colleges and Universities in Henan Province (26A150017, 25B480002) and the Natural Science Foundation of Henan (242300421620) and the Fundamental Research Funds for the Universities of Henan Province (NSFRF240504, NSFRF240707).

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DOI: 10.1016/S1872-5813(26)60689-5 CSTR: 32157.14.2097-213X.2026.JFCT.0047 Associated Data DOI: 10.57760/sciencedb.j00124.00422

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CO removal catalysts with high activity and high cost-performance ratio. Many scholars have found that supported noble metal catalysts (such as Au^[6-7], Pd^[8-10], Pt^[11], Ru) exhibit high catalytic activity, but they generally suffer from the problems of easy deactivation and low economic efficiency. Transition metal catalysts, especially cerium-based metal oxides, have become important catalysts in CO purification technologies due to their high cost-effectiveness and good stability^[12-14].

In the past few decades, ceria has been widely used in catalysts for CO oxidation due to its unique high oxygen storage capacity (OSC) and high oxygen mobility. The catalytic combustion performance of copper-doped ceria catalysts is particularly remarkable. Lee et al.^[15] found that the bimetallic oxide catalyst constructed by introducing copper into ceria enhanced the interaction between copper and ceria, enriched the surface defects of ceria, and improved its oxidation capacity. Furthermore, methods such as oxide loading and non-metallic atom doping can alter the local chemical environment of the catalyst surface or interface, thereby improving its catalytic oxidation performance and stability for CO^[16-17]. For example, the addition of promoters such as cobalt, tin and iron to CuCeO_x catalysts can affect the specific surface area, particle size, and active site distribution of the catalyst, thereby effectively improving the low-temperature activity of CO oxidation catalysts. Li et al.^[18] found that due to the n-type semiconductor characteristics of SnO₂, doping Sn into Cu-based catalysts can enhance the electron transfer capacity of the catalysts. In addition, SnO₂ can effectively inhibit the adsorption of water molecules on the catalyst surface, thereby improving the catalytic stability of the catalyst^[19]. Owing to the complex properties of polymetallic oxides, although it has been proven that Sn doping can alter the properties of catalysts, its specific role in the CO oxidation reaction process remains unclear. However, the development of characterization techniques, specifically high-resolution imaging of transmission electron microscopy (TEM) and high spatial resolution of X-ray photoelectron spectroscopy (XPS), has made this possible, which is of great significance for deeply understanding the structure-performance relationships, intrinsic nature of active sites and catalytic reaction mechanisms of catalysts, as well as exploring strategies for further enhancing catalytic efficiency.

To improve the water resistance of CuCeO_x catalysts for CO catalytic oxidation reaction and investigate the regulatory mechanism of Sn doping on their redox ability and electron transfer capacity, a series of Sn-doped CuCeO_x catalysts with different Sn contents were prepared by the excess impregnation method in this study, aiming to improve their catalytic oxidation performance and moisture resistance. A series of systematic characterization techniques including XRD, BET, TEM, H₂-TPR, XPS, O₂-TPD, CO-TPD and CO-TPSR were employed to clarify the mechanism by which Sn doping regulates the structure, electronic properties, and surface reaction behaviors of

CuCeO_x catalysts, thereby providing a theoretical basis for understanding its influence mechanism on the catalytic oxidation activity, selectivity, and long-term stability of CO over CuCeO_x catalysts under humid conditions. This study also offers technical support for the design of high-performance Cu-based catalysts with water and poisoning resistance, and further lays a foundation for optimizing the process of low-temperature catalytic oxidation for CO removal.

1 Experimental

1.1 Preparation of catalysts

A certain amount of Ce(NO₃)₂·6H₂O was placed in a crucible and spread evenly, and then the crucible was put into a muffle furnace. The temperature was raised from room temperature to 350 °C at a heating rate of 2 °C/min and maintained at this temperature for 2 h. The obtained pale yellow solid powder was denoted as CeO₂.

Based on 2 g of CeO₂, the corresponding mass of copper nitrate (Cu(NO₃)₂·3H₂O) was calculated and weighed according to the mass fractions of Cu relative to CeO₂ (1%, 4%, 6%, 8%, 10% respectively). The weighed copper nitrate was dissolved in deionized water to prepare a 2 mL solution, followed by ultrasonic treatment for 5 min to achieve uniform dispersion. Subsequently, 2 g of CeO₂ was placed in a mortar, and the above solution was added dropwise with a dropper at 5 min intervals. Meanwhile, thorough grinding was performed to ensure uniform mixing, and this operation was repeated until the entire solution was added dropwise. The resulting mixture was placed in a drying oven at 100 °C for overnight drying, and finally transferred to a muffle furnace. The temperature was increased to 400 °C at a heating rate of 5 °C/min and calcined at this temperature for 6 h, thus preparing the CuCeO_x catalysts.

Using the optimized CuCeO_x catalyst as the precursor, the Sn component was introduced *via* the excess impregnation-grinding method. 2 g of CeO₂ was subjected to dropwise grinding impregnation with a mixed solution of Cu(NO₃)₂ and Sn(NO₃)₄ at a specific concentration. The impregnation method was consistent with the above-mentioned method: the above solution was added dropwise with a dropper at 5 min intervals, and thorough grinding was performed simultaneously to ensure uniform mixing, and this operation was repeated until the entire solution was added dropwise. The resulting mixture was placed in a drying oven at 100 °C for overnight drying, and finally transferred to a muffle furnace. The temperature was raised to 400 °C at a heating rate of 5 °C/min and calcined at this temperature for 6 h, thus preparing the CuCeO_x-Sn catalysts. By adjusting the loading amount of Sn, a series of samples were prepared and named CuCeO_x, CuCeO_x-Sn_{0.05}, CuCeO_x-Sn_{0.1}, CuCeO_x-Sn_{0.2} and CuCeO_x-Sn_{0.5} according to the mass fractions of Sn relative to CuCeO_x (0, 5%, 10%, 20%, 50%), respectively.

1.2 Characterization methods

X-ray diffraction (XRD) was employed to characterize the crystal phases of the catalysts, with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) used, operating at a voltage of 40 kV and a current of 40 mA. The 2θ scanning range was set from 10° to 90° with a scanning rate of $10^\circ/\text{min}$. N $_2$ physisorption was performed on a Micromeritics ASAP-2020 M instrument at -196°C . The samples were degassed under vacuum at 150°C for 2 h prior to the test. The specific surface area (S_{BET}) and pore size distribution were calculated by the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) desorption method, respectively. The surface elements and chemical states of the catalysts were characterized by X-ray photoelectron spectroscopy (XPS) on a Thermo Scientific K-Alpha electron spectrometer, which was equipped with an Al K α radiation source ($h\nu = 1486.6 \text{ eV}$) operating at a working voltage of 12 kV. All binding energies were calibrated with the standard C 1s peak (284 eV) as the reference.

The reduction performance of the catalysts was characterized by hydrogen temperature-programmed reduction (H $_2$ -TPR) using a Micromeritics AutoChem II chemisorption analyzer. Approximately 0.5 g of the catalyst sample was accurately weighed and placed in a quartz U-shaped reaction tube, and its position was fixed with quartz wool. Prior to the start of the test, the catalyst was first pretreated at 150°C for 30 min under an Ar atmosphere (flow rate: 40 mL/min) to completely remove physically adsorbed impurities on the surface. Subsequently, in an atmosphere of 5% H $_2$ /95% Ar mixed gas (flow rate: 40 mL/min), the sample was heated programmatically from 50 to 800°C at a heating rate of $10^\circ\text{C}/\text{min}$. A thermal conductivity detector (TCD) was used to monitor the hydrogen consumption signal in real time during the experiment, and pure CuO was employed as a reference sample to calibrate the detection signal.

CO temperature-programmed desorption (CO-TPD) experiments were conducted using an AutoChem II 2920 chemisorption analyzer to investigate the effect of Sn loading amount on the CO adsorption capacity of the catalysts. The specific procedures are as follows: 0.5 g of the sample was placed in a quartz reactor, pretreated in a He atmosphere at 300°C for 2 h first, and then exposed to a 10% CO/90% He mixed gas with a flow rate of 30 mL/min for adsorption at room temperature for 1 h. Subsequently, the system temperature was raised to 50°C , and physically adsorbed CO molecules were removed by purging with a pure He gas flow of 30 mL/min for 30 min. Finally, the CO-TPD test was carried out by heating the system programmatically from 50 to 700°C at a heating rate of $10^\circ\text{C}/\text{min}$ under a pure He atmosphere with a flow rate of 30 mL/min. Oxygen temperature-programmed desorption (O $_2$ -TPD) measurements were performed to investigate the effect of Sn loading amount on the oxygen properties of the catalysts. The experimental procedure was basically the same as that for CO-TPD, except that the catalyst treated under an inert atmosphere was saturated by adsorption in 3% O $_2$ /97% He with a flow rate of 30 mL/min prior to the

O $_2$ -TPD experiment.

Temperature-programmed surface reaction (CO-TPSR) experiments were conducted to investigate the surface reaction activity of the CuCeO $_x$ -Sn catalysts. During the experiment, 0.5 g of the sample was first held at 350°C in an inert He atmosphere for approximately 1 h to remove impurities adsorbed on the catalyst surface. Subsequently, the system was cooled to room temperature, and a 10% CO/90% He mixed gas was introduced for 30 min of adsorption at this temperature. After that, the gas was switched to He for purging to remove physically adsorbed CO molecules on the catalyst surface. Finally, the temperature was raised programmatically to 800°C at a rate of $10^\circ\text{C}/\text{min}$ in a 3% O $_2$ /97% He atmosphere, and a mass spectrometer was used to monitor the changes in product signals in the tail gas in real time (O $_2$: $m/z = 32$, CO $_2$: $m/z = 44$).

1.3 Performance evaluation

1.3.1 Evaluation of CO oxidation activity in a fixed-bed reactor

The catalytic reaction setup used in this experiment is shown in Figure 1. The CO oxidation activity of the catalysts was evaluated in a fixed-bed reactor in this experiment. 0.2 g of the 40–60 mesh catalyst was loaded into the middle of the reaction tube, and both ends were fixed with quartz wool. Under atmospheric pressure, 80 mL/min of air and 20 mL/min of a 20% CO/80% N $_2$ mixed gas were introduced into the reaction system, maintaining the volume fraction of CO in the reaction atmosphere in the range of 1%–4%, with a weight hourly space velocity (WHSV) of 30000 mL/(g·h). The regulation of different water contents was achieved by the following method: the reaction mixed gas was passed through a bubble column to introduce water vapor, and the temperature of the bubble column was precisely controlled by a water bath, thereby adjusting the water content in the atmosphere. The reaction temperature was raised programmatically from room temperature at a rate of $2^\circ\text{C}/\text{min}$, and held isothermally for 30 min for every 10°C increase to ensure the reaction reached a steady state. The CO $_2$ concentration in the outlet gas was monitored in real time using a CO $_2$ sensor, and the CO conversion rate (x_{CO}) was calculated according to the following formula (1)^[20–21]:

$$x_{\text{CO}} = \frac{(n_{\text{CO},\text{in}} - n_{\text{CO},\text{out}})}{n_{\text{CO},\text{in}}} \times 100\% \quad (1)$$

In the above formula, $n_{\text{CO},\text{in}}$ represents the CO content in the inlet mixed gas, and $n_{\text{CO},\text{out}}$ denotes the CO content in the outlet mixed gas.

$$r_{\text{CO}} = \frac{x_{\text{CO}} \times F_{\text{in}} \times C_{\text{CO}} \times 60}{22400} \quad (2)$$

The formula for calculating the CO reaction rate in this experiment is given by Equation (2), where r_{CO} (mol/h) represents the CO reaction rate, x_{CO} denotes the CO conversion, and F_{in} (mL/min) stands for the inlet gas flow rate and C_{CO} is the CO concentration in the gas.

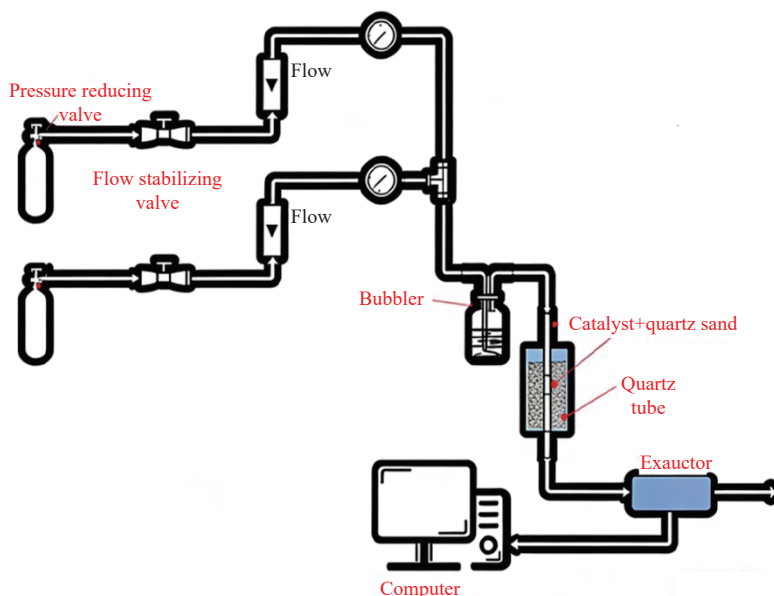


Fig. 1 Schematic diagram of the catalytic reaction apparatus

1.3.2 Long-term stability and water tolerance test

A stability test was performed using 0.2 g of catalyst under a total flow rate of 100 mL/min (reaction conditions: 0.1 MPa, 2% CO in the reaction atmosphere, 30000 mL/(g·h)). Initially, CO catalytic oxidation was carried out under dry conditions by heating the catalyst at a ramp rate of 2 °C/min and holding for 30 min at each 10 °C increment until CO conversion no longer increased with temperature, indicating that the reaction had essentially reached completion. The temperature was then maintained constant for 5 h to assess initial steady-state performance. Subsequently, water vapor was introduced into the feed gas, adjusting the moisture content to 3.8% H₂O. The same stepwise temperature-ramping procedure was repeated until CO conversion reached a plateau and the outlet CO concentration stabilized. The system was then kept at this temperature for an additional 5 h to evaluate catalyst stability under humid conditions. Finally, the water vapor supply was stopped, and the reaction temperature was gradually decreased until the CO conversion stabilized again. The catalyst was maintained at this temperature for a further 5 h to examine its activity recovery after water removal. Throughout the test, CO conversion was monitored continuously to comprehensively assess the long-term stability and water tolerance of the catalyst.

2 Results and discussion

2.1 Catalyst performance testing

In this study, the reaction temperatures corresponding to 50% and 90% CO conversion rates (t_{50} and t_{90}) in the CO catalytic combustion reaction were used as the main evaluation indicators for catalytic oxidation activity.

To investigate the influence of copper loading on

catalytic performance, a series of CuCeO_x catalysts with varying Cu contents were systematically evaluated under identical reaction atmosphere and space velocity conditions. As shown in Figure S1, both the t_{50} and t_{90} for CO catalytic oxidation decreased with increasing Cu loading, indicating that higher Cu content effectively enhances the low-temperature activity of the catalyst. However, when the Cu loading exceeded 6%, the downward trend in t_{50} and t_{90} leveled off, and the values slightly increased compared to those of the sample with 6% Cu. Therefore, an optimal Cu loading of 6% was identified for the CO oxidation reaction, under which the catalyst exhibited the best low-temperature catalytic performance.

Given that an appropriate amount of promoter can improve the water resistance of Cu-based catalysts, different contents of Sn were introduced into the CuCeO_x catalyst in the experiment, and its catalytic performance was evaluated in a mixed reaction atmosphere containing water vapor. As shown in Figure 2(a) and 2(b), the CO conversion rate showed no significant change when the reaction temperature was below 50 °C, indicating that catalysts with different Sn loadings exhibited no significant catalytic activity for CO combustion in this temperature range. When the temperature exceeded 50 °C, the CO conversion rate increased rapidly with the rise in temperature. Notably, as the Sn loading increased from 0 to 0.5%, t_{50} and t_{90} exhibited a typical “inverted volcano-shaped” variation trend (Figure 2(a)), reaching the minimum values at a Sn loading of 0.1%, which indicates that the catalyst achieved the optimal CO catalytic combustion activity under this condition. From the perspective of reaction rate, the catalytic combustion reaction rate was significantly increased after the introduction of Sn compared with the catalyst without Sn doping; Furthermore, at the same reaction rate, the catalyst with 0.1% Sn loading required the lowest reaction temperature, which further confirms that it exhibits excellent CO catalytic combustion performance

under low-temperature conditions. Within a certain loading range, the catalyst performance was significantly improved with the increase in Sn content; however, when the Sn loading exceeded 0.1%, the performance improvement tended to level off, and t_{50} and t_{90} even increased slightly. In practical industrial applications and motor vehicle exhaust treatment, the CO catalytic combustion reaction is often carried out in a water-containing atmosphere, and the presence of water vapor can significantly inhibit the CO oxidation performance of Cu-based catalysts. Specifically, H₂O molecules can undergo competitive adsorption at active sites, hindering the adsorption and activation of CO. To investigate the effect of water vapor on catalytic performance, the CuCeO_x-Sn_{0.1} catalyst with the optimal activity was selected in this study, and experiments were conducted by introducing different contents of water vapor into the feed gas, with the results shown in Figure 3(a) and 3(b). With the increase in water vapor content, the CO catalytic combustion activity was significantly inhibited, and t_{50} and t_{90} showed an overall upward trend, which confirms the negative effect of water vapor. Notably, the catalyst maintained a low t_{90} (below 140 °C) at different water vapor contents, indicating that it possesses good water resistance. From the perspective of the change in reaction rate (Figure 2(d)), the increase in water vapor content led to a gradual decrease in the catalytic reaction rate, which further verifies its inhibitory effect on the activity. In

addition, the optimal catalyst in this study was compared in terms of performance with typical catalysts reported in the literature^[22] (Table S1). The data show that the temperatures for 50% conversion (t_{50}) and 90% conversion (t_{90}) of the catalyst in this study are lower than the values reported in the literature under both water vapor-containing and dry reaction conditions, demonstrating more excellent low-temperature catalytic activity.

The catalytic performance at different space velocities to identify the general trend was evaluated. As shown in the Figure S2, the catalytic performance varied with space velocity: the t_{90} value first decreased and then increased with increasing space velocity. Therefore, 30000 mL/(g·h) was chosen as it corresponds to a relatively low t_{90} .

To evaluate the stability of the CuCeO_x-Sn_{0.1} catalyst under water-containing conditions, a stability test was conducted in a water vapor atmosphere (Figure 4). The results show that: under water-free conditions, the CO conversion rate reached 90% when the temperature rose to 80 °C and remained stable for 8 h; subsequently, 3.8% H₂O was introduced, and t_{90} increased slightly, but the catalyst still maintained stable performance for the subsequent 8 h at the same reaction temperature; Finally, after the water vapor was removed, t_{90} recovered to the initial level and remained stable for the subsequent 8 h, which indicates that the catalyst can maintain stability under the switching of water-containing and water-free environments.

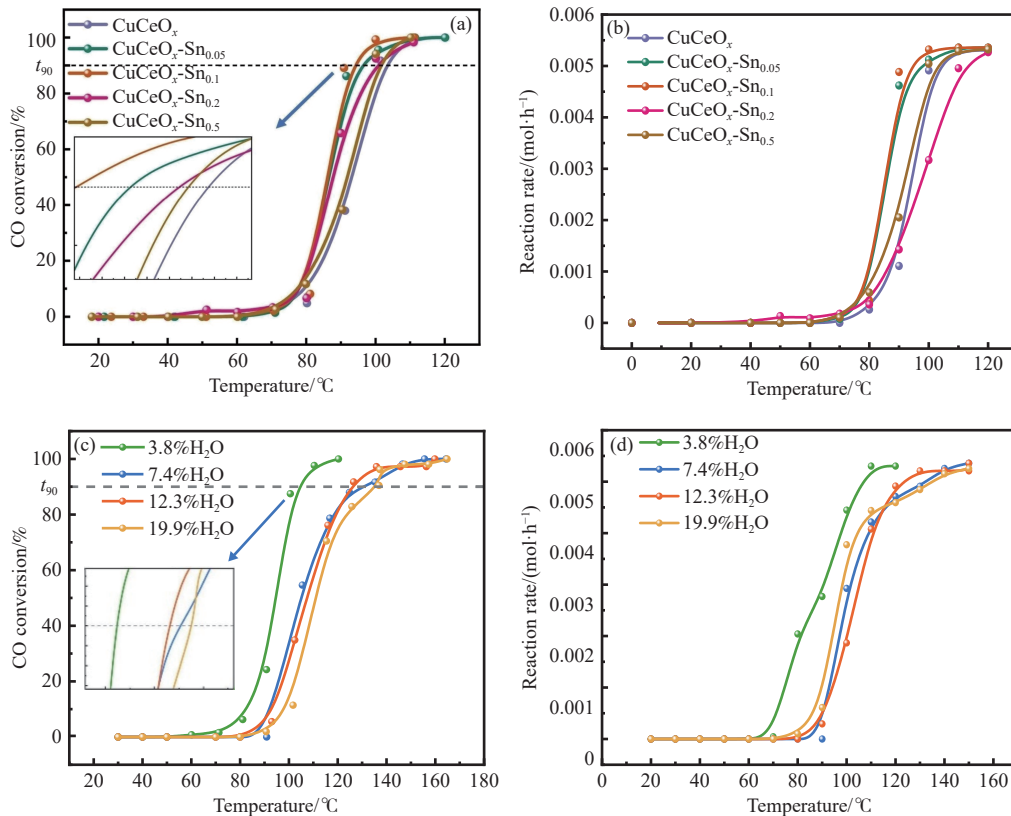


Fig. 2 Catalytic performance of CuCeO_x-Sn catalysts for CO oxidation; (a) CO conversion under 3.8% water vapor content; (b) Reaction rate under 3.8% water vapor content (reaction conditions: 0.1 MPa, 2% CO in the reaction atmosphere, 30000 mL/(g·h)); Catalytic performance of CuCeO_x-Sn_{0.1} catalyst for CO oxidation under different water vapor contents; (c) CO conversion, (d) Reaction rate (reaction conditions: 0.1 MPa, 2% CO in the reaction atmosphere, 30000 mL/(g·h))

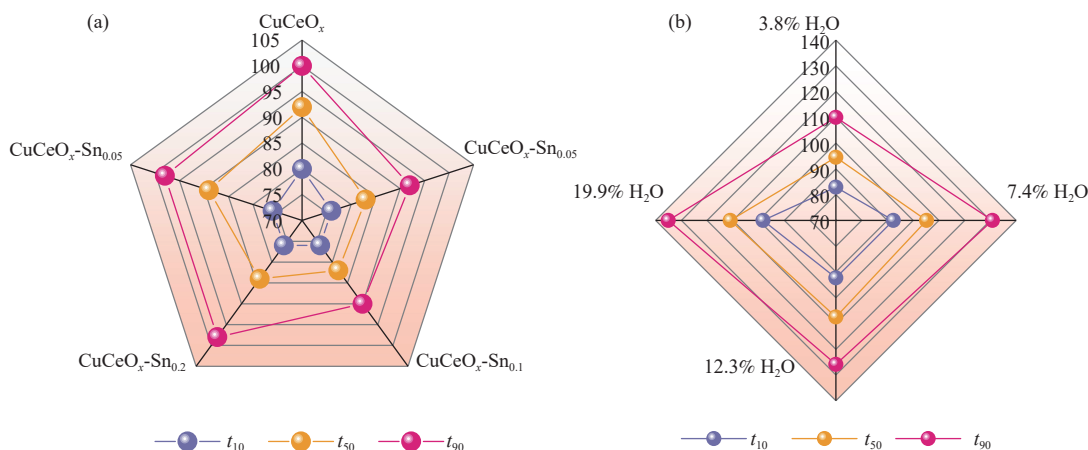


Fig. 3 (a) Variation of t_{10} , t_{50} and t_{90} temperatures for CuCeO_x-Sn catalysts under 3.8% water vapor content; (b) Variation of t_{10} , t_{50} and t_{90} temperatures for CuCeO_x-Sn_{0.1} catalysts under different water vapor contents

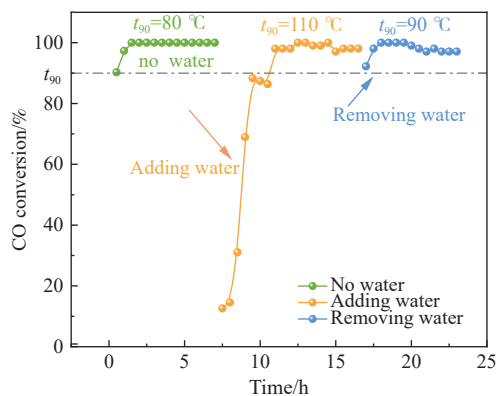


Fig. 4 Stability test of CuCeO_x-Sn_{0.1} catalyst under water-on and water-off environment switching
Reaction conditions: 0.1 MPa, 2% CO in the reaction atmosphere, 30000 mL/(g·h).

2.2 Study on the structure-activity relationship between catalyst performance and structure

2.2.1 Analysis of pore channel characteristics

As can be observed from Figure S3, the adsorption isotherms of all samples exhibit a typical Type IV isotherm with a Type H3 hysteresis loop. This can be attributed to capillary condensation occurring inside the slit-shaped porous structure formed by the aggregation of oxide particles. The different gaps in the hysteresis loop are due to the changes in the pore structure of the catalyst^[9]. As shown in Table S2, the doping of Sn increases the specific surface area and pore volume of the CuCeO_x catalyst. With the increase in Sn content, the specific surface area of the catalyst increases from 61.6 to 80.0 m²/g, and the pore volume increases from 0.0295 to 0.0399 cm³/g. Among these catalysts, the CuCeO_x-Sn_{0.1} catalyst exhibits a uniform pore size distribution and the largest pore volume, indicating that the CuCeO_x-Sn_{0.1} catalyst has a similar particle size and excellent pore structure. As can be seen from Table S1, the pore size of the CuCeO_x catalyst is

mainly concentrated in the range of 2–15 nm, which further confirms the existence of a mesoporous structure (2–50 nm), and this is mostly attributed to the agglomerated pores of secondary particles.

The pore size in metal oxide catalysts mainly depends on the size of secondary particles and the interaction force between oxides. A large specific surface area and excellent pore structure can significantly increase the number of active sites and promote the mass transfer of reactants^[23]. Therefore, the CuCeO_x-Sn_{0.1} catalyst with a large specific surface area and uniform pore size distribution after Sn doping exhibits more excellent CO catalytic combustion performance. The reasons why the CuCeO_x-Sn_{0.1} catalyst achieves the lowest t_{50} and t_{90} in the performance evaluation test shown in Figure 2(a) are elaborated from the perspective of pore channel characteristics.

2.2.2 Analysis of crystal structure and reducibility

To investigate the effect of Sn doping on the crystal structure of CeCuO_x, XRD characterization was performed on the catalysts, and the results are shown in Figure 5(a). The XRD patterns show that all samples exhibit the characteristic diffraction structure of cubic CeO₂. The diffraction peaks appearing at $2\theta = 14.3^\circ$, 29.5° , 34.7° , 47.7° and 57.4° correspond to the (111), (222), (400), (511) and (531) crystal planes of CeO₂, respectively. In addition, characterization analyses were performed on the catalyst samples before and after the reaction under different water content treatment conditions (Figure S4). The results show that the positions and relative intensities of the diffraction peaks of all samples remain basically unchanged, indicating that the crystal structure of the catalyst does not change during the reaction, which confirms its excellent stability. Notably, the introduction of Sn significantly enhances the diffraction peak intensity of the CuCeO_x catalyst, indicating that Sn doping promotes the formation of metal oxide crystal phases and the improvement of crystallinity. The doping of Sn also enhances the activity of oxygen species on the catalyst surface, which can be further verified by the

results of the H_2 -TPR test (Figure 5(b)). Reported literature indicates that the initial reduction temperature of pure CeO_2 is approximately 350 °C, and thus the reduction peaks below 350 °C are mainly associated with the reduction of CuO species^[24]. Depending on the differences in coordination environment and valence state, the Cu species in the catalyst exhibit diverse reduction behaviors. Two distinct reduction peaks can be observed in the $CuCeO_x$ sample: among them, the strong reduction peak at approximately 239 °C corresponds to the reduction of bulk CuO particles. After the introduction of Sn, the reduction behavior of the catalyst changes significantly. Based on the comparison of the peak areas of each reduction peak, the reducibility of the catalysts can be ranked as follows:

$CuCeO_x-Sn_{0.1} > CuCeO_x-Sn_{0.2} > CuCeO_x-Sn_{0.5} > CuCeO_x-Sn_{0.05} > CuCeO_x$. When the Sn content is 0.1%, the $CuCeO_x-Sn_{0.1}$ catalyst not only exhibits a lower initial reduction temperature (approximately 129 °C) but also has a larger reduction peak area, indicating that the reactivity of oxygen species on its surface is enhanced. In addition, compared with Sn-undeficient $CuCeO_x$, its reduction temperature is shifted forward by approximately 30 °C, which confirms that Sn doping effectively improves the reducibility of the catalyst and promotes the migration of electrons inside the catalyst. The optimal reducibility exhibited by $CuCeO_x-Sn_{0.1}$ is closely related to its enhanced electron transfer capacity, which provides an important foundation for its high activity in the CO catalytic combustion reaction.

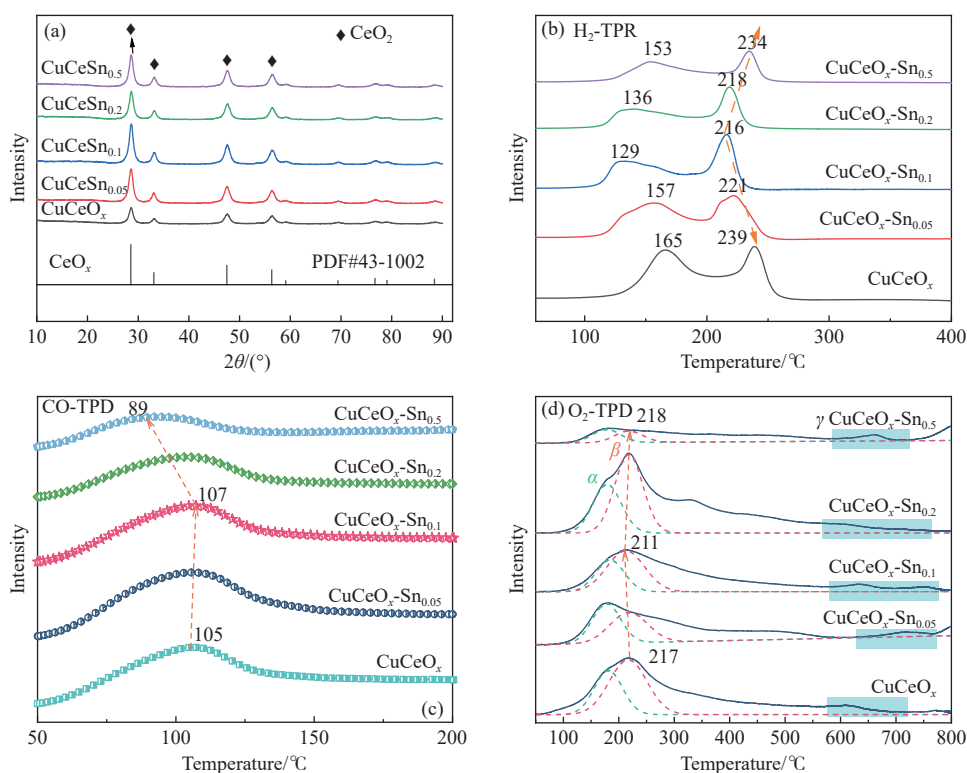


Fig. 5 (a) XRD patterns, (b) H_2 -TPR profiles, (c) CO-TPD profiles and (d) O_2 -TPD profiles of $CuCeO_x-Sn$ catalysts

2.2.3 Effect of chemisorption and desorption behaviors of reactant molecules (CO and O_2) on catalytic performance

To clarify the effect of Sn content on the CO and O_2 adsorption-desorption behaviors of $CuCeO_x-Sn_x$ catalysts, CO-TPD and O_2 -TPD were conducted and the relevant results are shown in Figure 5(c). CO molecules are first adsorbed and activated on the catalyst surface, then react with active surface oxygen or lattice oxygen to form CO_2 , and the consumed oxygen sites are replenished and regenerated by gaseous O_2 ^[25]. Therefore, the CO adsorption capacity of the catalyst has an important influence on its overall catalytic performance. A typical CO desorption peak appears at approximately 100 °C for all catalysts, which corresponds to the weak chemisorption process of CO.

Compared with the $CuCeO_x$ catalyst without Sn addition, the peak temperature of the CO desorption peak shows a “volcano-type” variation trend after the introduction of Sn, and reaches the maximum value when the Sn content is 0.1% ($CuCeO_x-Sn_{0.1}$). This phenomenon indicates that the introduction of an appropriate amount of Sn enhances the desorption strength of CO on the catalyst surface, which helps to promote the sufficient reaction between CO and surface oxygen species, thereby improving its activity in the CO catalytic combustion reaction. As shown in Figure 5(d), the O_2 -TPD method was used to analyze the activation and migration capacity of oxygen species in the catalyst. According to the differences in desorption temperature, the O_2 -TPD curves can usually be divided into three regions: the α region (< 200 °C) corresponds to the desorption of surface chemisorbed oxygen, the β region (200–550 °C) is attributed to surface lattice oxygen, and the γ region

(> 550 °C) reflects the release behavior of bulk lattice oxygen^[26]. The bulk lattice oxygen desorption peak of the unmodified CuCeO_x catalyst is at 707 °C, while the introduction of Sn significantly enhances the dissociation tendency of surface and bulk lattice oxygen. This phenomenon can be attributed to the fact that Sn doping weakens the bonding interaction between Ce and Cu atoms, thereby reducing the stability of lattice oxygen and promoting its migration. Compared with other catalysts, CuCeO_x-Sn_{0.1} exhibits the optimal oxygen activation performance: the temperatures of its α and β desorption peaks are the lowest, indicating that surface adsorbed oxygen and surface lattice oxygen are more prone to desorption and participation in the reaction. This characteristic directly contributes to the highest reaction activity of CuCeO_x-Sn_{0.1} in CO catalytic combustion.

2.2.4 Microstructure analysis

To further investigate the microstructure of CuCeO_x,

TEM characterization was conducted. As shown in Figure 6(a1) and (b1), clear lattice fringes can be observed, corresponding to the characteristic crystal planes of CuO and CeO₂, respectively, with the measured lattice spacings of approximately 0.27 nm (CuO) and 0.31 nm (CeO₂). Moreover, CuO and CeO₂ are in an inter-doped state, which indicates the presence of CuO and its close contact with CeO₂, and this result verifies the analysis results of XRD and H₂-TPR. After diffraction analysis was performed on the (a1) and (b1) images, the corresponding diffraction patterns (a3) and (b3) were obtained. Among them, the positions of the characteristic diffraction peaks of CuO and CeO₂ are completely consistent with the lattice spacing results measured in the aforementioned (a1) and (b1) images. In addition, the results of elemental distribution characterization show that the Cu and Ce elements are uniformly distributed in the catalyst. Combined with the XRD analysis results, this phenomenon indicates that Cu species are highly dispersed on the surface of the CeO₂ support.

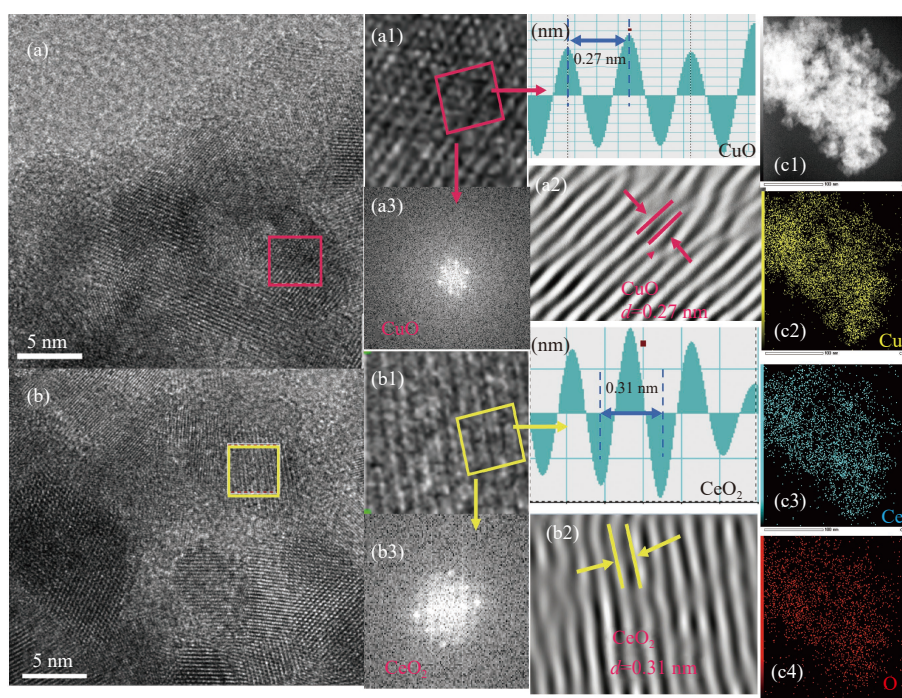


Fig. 6 TEM images of CuCeO_x catalysts

2.2.5 Analysis of elemental composition and chemical valence states

As shown in Figure 7 below, the surface composition, chemical states and oxygen species of the CuCeO_x-Sn_x catalysts were analyzed by XPS. The surface elemental composition of the catalysts obtained from the fitting calculation of XPS curves is summarized. As shown in Figure 7(c), the Cu 2p XPS spectra of all catalysts exhibit two characteristic peaks, and the peaks at 930.6–937.5 and 949.2–957.9 eV are attributed to Cu²⁺^[27–28]. The oxidation

state of Sn was analyzed by fitting the Sn 3d spectra (Figure 7 (d)). The Sn 3d spectra of the prepared catalysts can be fitted into two peaks located at the binding energies of 495 and 487 eV^[29]. Table 1 lists the surface contents of Sn²⁺ and Sn⁴⁺, among which the CuCeO_x-Sn_{0.1} catalyst has the highest Sn⁴⁺/(Sn²⁺ + Sn⁴⁺) ratio. The O 1s XPS spectrum shows three distinct peaks corresponding to surface lattice oxygen O_L (529.7 eV), surface chemisorbed oxygen O_S (530.9 eV) and hydroxyl oxygen O_H (532.1 eV). Compared with the CuCeO_x catalyst, the CuCeO_x-Sn_{0.1} catalyst exhibits higher contents of O_S (44.8%) and O_H (11%), which is consistent with the result of the lower

desorption peak temperature of surface adsorbed oxygen in the O₂-TPD curves. In addition, the O_s/O_L ratio of 1.01 is significantly higher than that of other catalysts, indicating that it has a higher content of surface active oxygen, which indirectly proves the presence of more oxygen vacancies on the catalyst surface. The deconvolution of the Ce 3*d* XPS spectra of the five catalysts yields eight peaks.

The *u* peaks are attributed to the characteristic peaks of Ce³⁺, while the *v* peaks are assigned to the characteristic

peaks of Ce⁴⁺, indicating that Ce³⁺ and Ce⁴⁺ coexist in the catalysts. As shown by the Ce³⁺/(Ce³⁺+Ce⁴⁺) ratio in Table 1, the CuCeO_x-Sn_{0.1} catalyst contains a higher content of Ce³⁺ species. This further confirms the presence of more oxygen vacancies in CuCeO_x-Sn_{0.1}. In summary, abundant oxygen species, excellent electron transfer capacity, and more CO adsorption sites are the main reasons for the outstanding activity and stability of the CuCeO_x-Sn_{0.1} catalyst in a high-humidity environment.

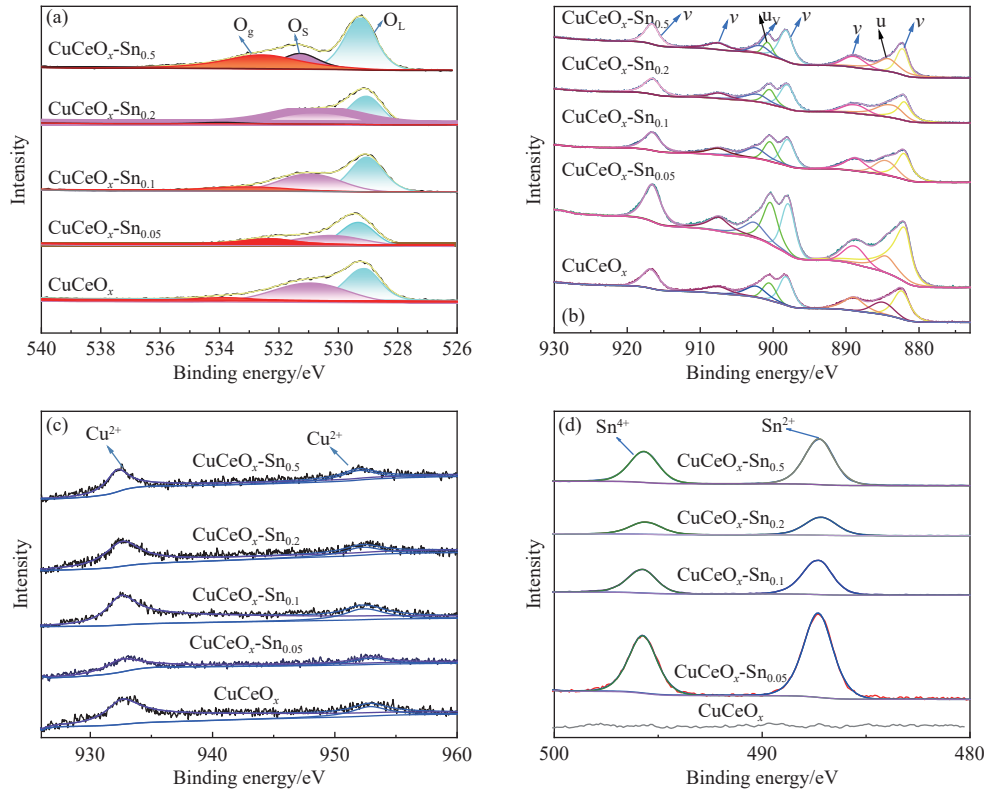


Fig. 7 XPS spectra of CuCeO_x-Sn catalysts: (a) O 1s, (b) Ce 3*d*, (c) Cu 2*p* and (d) Sn 3*d*

Table 1 Surface composition of CuCeO_x-Sn catalysts

Sample	Ce			Sn			O			
	Ce ³⁺	Ce ⁴⁺	Ce ³⁺ /(Ce ³⁺ +Ce ⁴⁺)	Sn ²⁺	Sn ⁴⁺	Sn ⁴⁺ /(Sn ²⁺ +Sn ⁴⁺)	O _L	O _s	O _γ	O _s /O _L
CuCeO _x	0.205	0.795	0.205	—	—	—	0.465	0.431	0.104	0.93
CuCeO _x -Sn _{0.05}	0.23	0.77	0.23	0.397	0.603	0.603	0.436	0.404	0.193	0.92
CuCeO _x -Sn _{0.1}	0.253	0.747	0.253	0.391	0.609	0.609	0.442	0.448	0.11	1.01
CuCeO _x -Sn _{0.02}	0.239	0.761	0.239	0.410	0.590	0.590	0.376	0.31	0.314	0.82
CuCeO _x -Sn _{0.5}	0.11	0.89	0.11	0.398	0.602	0.602	0.524	0.20	0.276	0.38

2.2.6 Study on the dynamic evolution of CO catalytic combustion reaction pathways on catalyst surfaces by CO-TPSR

To investigate the influence of surface active oxygen species on the CO catalytic combustion surface reaction over the CuCeO_x-Sn catalysts, CO-TPSR characterization analysis was carried out, and the results are shown in Figure 8.

All catalysts start to generate CO₂ at around 100 °C (Figure 8(a)), indicating that the CO oxidation reaction has occurred in this temperature range. Among them, the CuCeO_x-Sn_{0.1} catalyst exhibits the lowest CO₂ generation peak temperature (approximately 185 °C), which is about 15–20 °C lower than that of other catalysts, directly indicating that it has the optimal low-temperature CO oxidation performance. Combined with the analysis results of XPS and O₂-TPD, the CuCeO_x-Sn_{0.1} catalyst has the

highest ratio of surface adsorbed oxygen (O_s) to lattice oxygen (O_l) (0.442), indicating that the introduction of Sn promotes the generation of surface active oxygen species. Meanwhile, the $Ce^{3+}/(Ce^{3+}+Ce^{4+})$ ratio increases to 25.3%, which further confirms the formation of more oxygen vacancies and provides favorable conditions for oxygen activation. The above characterization results are highly consistent with the phenomena observed in the O_2 -TPD analysis, and the desorption peaks all shift towards lower temperatures, indicating that the migration capacities of both surface chemisorbed oxygen and surface lattice oxygen are significantly enhanced. From the O_2 consumption curves (Figure 8(b)), the $CuCeO_x-Sn_{0.1}$ catalyst shows a distinct O_2 consumption peak at 135 °C. The lower O_2 consumption

temperature indicates that the catalyst can achieve the adsorption-activation-conversion cycle of gas-phase oxygen under mild conditions, providing a sufficient source of active oxygen for the continuous CO oxidation reaction. The systematic characterization results of XRD, BET, TEM, H_2 -TPR, XPS, O_2 -TPD, CO-TPD and CO-TPSR mentioned above jointly reveal the intrinsic reasons for the excellent performance of the $CuCeO_x-Sn_{0.1}$ catalyst. The introduction of Sn effectively increases the concentration of surface oxygen vacancies, promotes the activation and migration of oxygen species, and the rapid cycling and continuous replenishment of surface active oxygen species enable the catalyst to maintain stable CO oxidation activity even in a water-containing atmosphere.

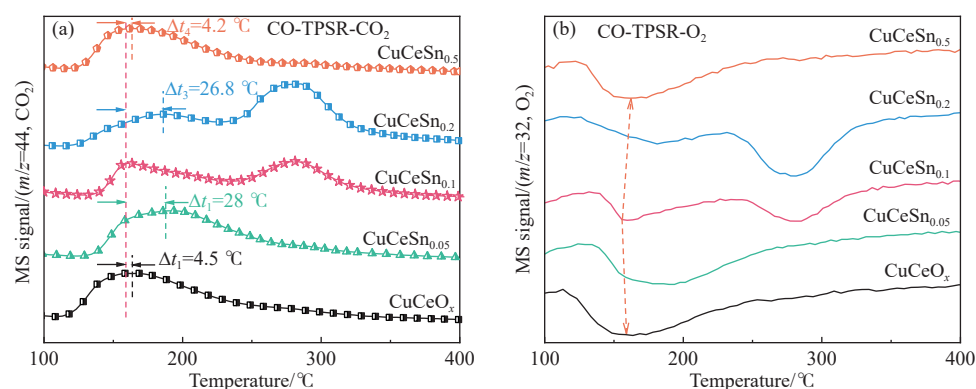


Fig. 8 CO-TPSR profiles of $CuCeO_x-Sn$ catalysts: (a) Effect of temperature on CO_2 formation; (b) Effect of temperature on O_2 consumption

3 Conclusions

In this work, $CuCeO_x-Sn$ catalysts were prepared *via* incipient wetness impregnation using CeO_2 as the support and evaluated for low-temperature CO catalytic combustion. With Sn loading increasing from 0 to 0.5%, the t_{50} and t_{90} followed an inverted volcano trend, reaching minima at 0.1% Sn loading, corresponding to optimal catalytic activity. Elevated water vapor content inhibited CO oxidation, yet all catalysts retained a low t_{90} (< 140 °C) with stable performance under alternating humid/dry atmospheres, demonstrating good water resistance. XPS, O_2 -TPD, CO-TPD and CO-TPSR characterizations revealed that appropriate Sn doping increased surface oxygen vacancy concentrations, promoted oxygen species activation and migration, and enhanced CO desorption strength. This facilitated sufficient reaction between CO and surface oxygen species, enabling rapid cycling and replenishment of active oxygen species. Consequently, the optimized $CuCeO_x-Sn_{0.1}$ catalyst exhibited superior performance and water tolerance, providing a novel strategy for CO catalytic oxidation under high-humidity, low-temperature conditions.

Declaration of Competing Interest

The authors declare no conflict of interest.

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Sn 修饰 CuCeO_x 催化剂的高湿 CO 催化燃烧性能研究

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摘 要: 低温一氧化碳氧化技术已广泛应用于环境污染治理领域, 但高湿环境下的 CO 净化仍面临挑战。本研究通过过量浸渍法制备了一系列 CeO₂ 负载的 CuCeO_x-Sn 催化剂, 评价了其在 CO 低温催化燃烧中的性能。结果表明, Sn 负载量为 0.1% 的 CuCeO_x-Sn_{0.1} 表现出最优低温催化活性, t_{50} 和 t_{90} 值最低; 当 Sn 负载量增至 0.1% 时, CO 转化率达 90% 对应的温度 (t_{50} 、 t_{90}) 逐步降低; 超过该阈值后, 继续增加 Sn 负载量不会显著降低 t_{90} , 甚至相比 0.1% Sn 时略有升高。该催化剂在有/无水蒸气切换评价中保持稳定, 展现出优异的耐水性。通过 XPS、O₂-TPD、CO-TPD 及 CO-TPSR 等表征手段发现, Sn 的引入有效提升了表面氧空位浓度, 促进了表面吸附氧与晶格氧的活化和迁移。

关键词: Cu-Ce; Sn 修饰; 过量浸渍法; 抗水性; CO 催化氧化

中图分类号: O643

文献标识码: A

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