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Article

Tuning SnO₂ surface with CuO for soot particulate combustion: The effect of monolayer dispersion capacity on reaction performance

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ABSTRACT

With the objective to investigate the structure-reactivity relationship of CuO/SnO₂ and eventually design more applicable catalysts for soot combustion, catalysts with different CuO loadings have been prepared by impregnation method. By using X-ray diffraction and X-ray photoelectron spectroscopy extrapolation methods, it is disclosed that CuO disperses finely on the SnO₂ support to form a monolayer with a capacity of 2.09 mmol 100 m⁻², which equals 4.8 wt% CuO loading. When the CuO loading is below the capacity, it is in a sub-monolayer state. However, when the loading is above the capacity, CuO micro-crystallites will be formed that coexist with the CuO monolayer. The soot combustion activity of the catalyst increases with the CuO loading until it reaches the monolayer dispersion capacity. A further increase in the CuO loading has no evident influence on the activity. Raman results have testified that with the addition of CuO onto the SnO₂ support, a surface-active oxygen species can be formed, the amount of which also increases significantly with the increase in the CuO loading until it reaches the monolayer dispersion capacity. Increasing the CuO loading further has no evident impact on the amount of surface oxygen. Therefore, an apparent monolayer dispersion threshold effect is observed for soot combustion over CuO/SnO₂ catalysts. It is concluded that the amount of surface-active oxygen sites is the major factor determining the activity of the catalyst.

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1. Introduction

In recent decades, the number of cars powered by diesel engines has significantly increased owing to their good dynamic performance [1,2]. However, the soot particulate emitted from diesel engines is one of the most hazardous pollutants that can

cause severe environmental and health problems [3–5]. To eliminate soot particle pollution, filtering it with a DPF trap followed by catalytic oxidation is an efficient current strategy [6]. To meet the increasingly stringent emission regulations, it is still a major challenge to develop highly active and stable catalysts for soot particulate combustion, especially a catalyst

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that can match the low exhaust temperature of diesel engines.

In the late 1970s, Xie et al. [7–9] found that a metal oxide can spontaneously disperse onto the surfaces of different supports to form a monolayer or sub-monolayer, which is a thermodynamically favored process that has been termed by them as “monolayer dispersion”. A “close-packed model” has been proposed by them for calculating the ideal and maximum monolayer dispersion capacities of supported metal oxides on different supports. Moreover, X-ray diffraction (XRD), Raman, and X-ray photoelectron spectroscopy (XPS) extrapolation methods have been developed by them to quantify the real monolayer dispersion capacities of different supported systems. It is revealed that in most cases, the real monolayer dispersion capacity of a supported system is lower than the ideal value calculated by the “close-packed model” owing to the interaction between the supported component and the support [9]. Chen et al. [10–13] studied the dispersion of CuO and MoO₃ on various supports such as Al₂O₃, TiO₂, CeO₂, and CeO₂-Al₂O₃ etc. and found the same phenomenon. However, an “incorporation model” was proposed by them to explain the phenomenon. By using different supports, Wachs et al. [14–16] explored the dispersion behaviors of supported MoO₃ and V₂O₅ and discovered a strong interaction between the supports and the supported metal oxides. On the basis of their work, the surface oxide-support interaction theory was proposed. In spite of the different terminologies used, all the researchers have found that when a metal oxide is loaded onto a support, the monolayer dispersion phenomenon is commonly observed, and the monolayer capacity can be quantified by different methods. Furthermore, when a supported system is used as a catalyst for a certain reaction, a monolayer dispersion threshold effect is generally observed. In more detail, a catalyst with a monolayer dispersed active component generally shows some special reaction performance, such as the highest activity and selectivity [14]. Nowadays, monolayer dispersion has been well accepted and has become an important theory in the design of highly functional catalytic materials.

Numerous studies have proved that CuO is very active towards many catalytic oxidation reactions [17–23]. For instance, the famous Hopcalite catalyst, which typically consists of 30%–40% copper oxide and 60%–70% manganese oxide, displays superior activity for CO oxidation at room temperature and has been practically used [17,18]. For CO oxidation on CuO, Boronin et al. [19] found that O[−] species is responsible for its superior CO oxidation activity. Kakuta et al. [20] found that when starting from stoichiometric CuO, the valency of the surface copper cycles as per $\text{Cu}^{2+} \rightleftharpoons \text{Cu}^0$ during the reaction process, which might determine the reaction rate. In contrast, Tikhov et al. [21] revealed that Cu⁺ clusters at the outlets of surface defects, which are paths for quick oxygen migration from the CuO bulk, are active sites that account for the CO oxidation activity. Through DFT calculation, Sun et al. [22] investigated the adsorption and dissociation of molecular O₂ on CuO (111) surface. It was disclosed that both the surface species O₂^{2−} and O₂[−] can be effectively formed as active oxygen sites.

Our earlier work also demonstrated that mesoporous copper-tin solid solutions prepared through coprecipitation [24] or

hydrothermal method with KIT-6 as the hard template [25] show superior activity towards CO oxidation, owing to the formation of a large amount of surface-active oxygen species, high surface areas, and porous structures. Moreover, by using a colloidal crystal templating method, a 3DOM structured copper-tin solid solution catalyst can be obtained, which exhibits very good soot combustion activity because the coexistence of meso- and macro-pores favors the contact of soot particles with the surface-active oxygen species [26]. Therefore, in the work that continued, the structure-reactivity relationship of pure CuO for soot oxidation was particularly investigated [27]. It was discovered that for CuO prepared by using different copper precursors and precipitants, four kinds of active sites with varied activities were present on the surface, but in different amounts. However, only the two kinds of active sites that are reducible by soot particulates below 500 °C contribute to soot oxidation. The mobility and abundance of surface oxygen are critical factors that control the soot oxidation activity of pure CuO catalysts.

However, bare CuO generally has low surface areas and physical stability, which restrict its feasibility as a catalyst for most of the exothermic processes such as soot combustion, where it experiences deactivation [27]. SnO₂ is a typical n-type semiconductor that has a high melting point of 1630 °C [28]. Many earlier studies, including those of our group, have proved that it has not only abundant surface-deficient oxygen species, but also good physical stability [29]. Therefore, SnO₂ could be an appropriate support for many active components in the preparation of catalysts for reactions that require good stability more than a high intrinsic activity, e.g., some strong exothermic processes such as soot and VOC combustion. However, its properties as a catalyst support have been rarely investigated. With the objective to understand the interfacial interaction between CuO and SnO₂, and eventually realize more applicable catalysts for real soot combustion processes, in this study, a series of CuO/SnO₂ catalysts have been prepared and used for soot oxidation based on the monolayer dispersion theory. An evident monolayer dispersion threshold effect has been observed, and the catalysts with CuO loadings not below the monolayer dispersion capacity show the best activity towards soot oxidation. By using different characterization methods, the reasons for the observed activity have been elucidated in this work.

2. Experimental

2.1. Catalyst preparation

All the CuO/SnO₂ catalysts were prepared by the traditional impregnation method with a Cu(NO₃)₂ (Sinopharm Chemical Reagent Corporation, China) solution (0.58 M) acting as the precursor. In detail, a certain amount of CVD SnO₂ (Shanghai Zaiyi New Material Co., Ltd., China) was added into the Cu(NO₃)₂ solution under constant stirring in a water bath at 80 °C for 3 h. After evaporating the solvent water, the solids obtained were dried at 110 °C overnight for approximately 12 h and then calcined at 550 °C in air atmosphere for 4 h, before

being heated to the target temperature at the rate of 2 °C min⁻¹. Afterwards, the samples were cooled to room temperature to obtain the final CuO/SnO₂ samples, which are labeled as 1% CuO/SnO₂, 3% CuO/SnO₂, 5% CuO/SnO₂, 7% CuO/SnO₂, 9% CuO/SnO₂, 11% CuO/SnO₂, 13% CuO/SnO₂, and 15% CuO/SnO₂, according to their CuO loadings.

2.2. Catalyst characterization

The powder XRD patterns of the samples were recorded on a Bruker AXS D8Focus diffractometer operating at 40 kV and 30 mA with a copper target and $K\alpha$ radiation. The scans were collected over the 2θ range 20° to 80° in steps of 2° min⁻¹.

XPS tests were carried out on a PerkinElmer PHI1600 system by using a single Mg-K X-ray source operating at 300 W and 15 kV. The spectra were obtained at ambient temperature and ultrahigh vacuum. The binding energies were calibrated by using the C 1s peak of a standard graphite sample (at 284.8 eV) as the reference.

N₂ adsorption-desorption experiments of the samples were performed at -196 °C on an ASAP2020 instrument. The specific surface areas of the catalysts were calculated by using the Brunauer-Emmett-Teller (BET) method in the relative pressure (P/P_0) range 0.05–0.25. The pore size distributions of the samples were calculated through the Barrett-Joyner-Halenda method. Furthermore, the pore sizes were obtained from the peak positions of the distribution curves. The total pore volume was calculated at the relative pressure of $P/P_0 = 0.99$.

Raman spectra of the catalysts were recorded on a Renishaw inVia Raman spectrometer equipped with an argon laser excitation source (532 nm) and a Renishaw RenCam CCD detector. The scanned Raman shift range varied from 200 to 1100 cm⁻¹.

Transmission electron microscopy (TEM) images were recorded on a TecnaiTM F30 transmission electron microscope. STEM mapping images of some typical catalysts were also obtained by using the TecnaiTM F30 instrument that was equipped with an Oxford EDX detector operating at 300 keV.

H₂ temperature-programmed reduction (H₂-TPR) experiments were also carried out by using a FINESORB 3010C instrument. In general, 0.05 g of the catalysts was used for the tests. Before the experiments, the catalysts were pretreated in high-purity air that flowed at 120 °C for 30 min to remove any possible surface impurities. After purging with ultrahigh purity argon that flowed at room temperature for 30 min, the temperature was then increased from room temperature to 800 °C, with the ramp rate being 10 °C min⁻¹, in 30 mL min⁻¹ 10% H₂/Ar gas mixture flow. A thermal conductivity detector (TCD) was employed to monitor the H₂ uptake. To quantify the amount of H₂ consumed, a 99.99% CuO sample was used as the calibration standard.

Temperature-programmed oxygen desorption (O₂-TPD) measurements were performed on a DAS-7000 multiple adsorption instrument that was equipped with a TCD detector. Typically, 0.05 g of the sample was placed in a quartz reactor, which was pretreated in 30 mL min⁻¹ ultrahigh purity argon flow at 300 °C for 60 min. Afterwards, the sample was cooled to

50 °C and saturated in a 10% O₂+Ar flow at the rate of 30 mL min⁻¹, which was followed by flushing in 30 mL min⁻¹ ultrahigh purity argon flow for 60 min to remove any physically adsorbed O₂. The TPD experiments were then carried out from 50 to 700 °C at the heating rate of 10 °C min⁻¹ in 30 mL min⁻¹ ultrahigh purity argon flow.

Soot temperature-programmed reduction (soot-TPR) experiments were conducted by using a TP-5076 multiple adsorption instrument (Xian-quan, China). Typically, 55 mg of the sample, which was prepared by uniform mixing of 5 mg soot with 50 mg catalyst powder, was placed in a quartz reactor. Prior to the test, it was treated in ultrahigh purity argon flow for 60 min at 120 °C to remove any physically adsorbed impurities. Afterwards, soot-TPR was carried out from 50 to 800 °C at the heating rate of 10 °C min⁻¹ in 30 mL min⁻¹ ultrahigh purity argon flow. A TCD was employed to monitor the formation of CO₂.

2.3. Activity evaluation

Temperature-programmed oxidation (TPO) was used to evaluate the soot combustion activities of the catalysts. To determine the activity of a catalyst under tight contact condition, typically, 5 mg of soot (Printex-U, diameter 25 nm, purchased from Degussa) was mixed with 50 mg of catalyst powder and ground for 10 min. Before loading into a microreactor with an inner diameter of 6 mm, the mixture was diluted by adding 100 mg of inert silica to ensure a soot/catalyst/silica weight ratio of 1/10/20 to avoid the formation of hot spots during the activity test. A K-type thermocouple was used to accurately monitor the temperature of the catalyst bed, with the thermocouple head point touching the catalyst. To examine the reaction behaviors of the catalysts, all data were collected by increasing the temperature from 120 to 800 °C at the rate of 10 °C min⁻¹. The volume composition of the feed gas was 10% O₂, with the balance being high-purity argon; the flow rate was 30 mL min⁻¹. To accurately quantify the amount of O₂ consumed, prior to entering the TCD, the CO₂ formed was removed thoroughly by using a soda-lime trap.

3. Results and discussion

3.1. XRD analysis of the catalysts

XRD was used to determine the phase compositions of the CuO/SnO₂ samples, and the patterns are shown in Fig. 1(A). For the pure SnO₂ support, tetragonal rutile SnO₂ is the only crystalline phase detected, as evidenced by the three typical diffraction peaks: (110) = 26.79°, (101) = 34.12°, and (211) = 52.10° [JCPDS no. 41-1445]. For pure CuO, monoclinic CuO is the only detected crystalline phase, as indicated by the three typical sharp peaks: (11-1) = 35.68°, (111) = 38.95°, and (20-2) = 49.04° [27,30]. For all the CuO/SnO₂ samples with different loadings, the rutile SnO₂ phase is obviously detected with very similar peak intensities, proving that the addition of different amounts of CuO has no evident impact on the crystallinity of the SnO₂ support. Interestingly, when the CuO loading is below

Fig. 1. XRD analysis of CuO/SnO₂ catalysts with different CuO loadings. (A) XRD patterns, and (B) the correlation line for quantifying the monolayer dispersion capacity of CuO on SnO₂.

5%, no diffraction peak related to it can be observed, which indicates that CuO is dispersed finely on the support surface and is nearly amorphous. However, when the CuO loading is above 5%, the monoclinic CuO phase starts to appear, the intensity of which increases with the increase in the CuO loading.

According to earlier studies, for a metal oxide dispersed on a support, there exists a monolayer dispersion capacity [9]. When the loading is not higher than this capacity, a sub-monolayer or monolayer of the supported metal oxide will be formed. On the other hand, when the loading is above this

capacity, the excess supported metal oxide will start forming micro-crystallites, the average size of which increases with loading until the size reaches 5 nm and can be detected by XRD. Therefore, to determine the monolayer capacity accurately, the XRD extrapolation method was developed previously by Xie et al. [9,31]. Based on this method, the monolayer dispersion capacity of CuO on SnO₂ support was correlated and quantified, as shown in Fig. 1(B). In detail, the intensity of the CuO (11-1) peak of each sample was measured and divided by the intensity of the SnO₂ (110) peak to obtain a series of $I_{\text{CuO}}/I_{\text{SnO}_2}$ ratios, which are then plotted against the CuO loading to obtain a correlation line. The line intersects the x-axis at a point, as displayed in Fig. 1(B). The CuO loading corresponding to this point is considered as the monolayer dispersion capacity of CuO on SnO₂ support, which is 2.09 mmol 100 m⁻² SnO₂ surface. Upon conversion, this monolayer dispersion capacity equals 4.8 wt% loading.

3.2. XPS analysis of the catalysts

XPS technique was employed to evaluate the surface properties of some typical CuO/SnO₂ samples (Fig. 2). Fig. 2(A) presents the XPS spectra of the SnO₂ support, which displays two Sn 3d peaks at 487.2 and 495.6 eV that are assigned to Sn 3d_{5/2} and 3d_{3/2} in that order [31]. In contrast, CuO reveals two typical Cu 2p peaks at 934.2 and 953.0 eV, as displayed in Fig. 2(B), which are assigned to Cu 2p_{3/2} and 2p_{1/2} in that order [32]. In all the CuO/SnO₂ samples, the two typical SnO₂ and CuO peaks can also be observed, but with some slight shifts. In comparison with the binding energies of pure CuO and SnO₂, the binding energy of CuO in the CuO/SnO₂ samples increases, but that of SnO₂ decreases, which indicates that the CuO present on the surface interacts with the SnO₂ support and donates electrons to it.

With the increase in the CuO loading, the intensity of the Sn 3d peak decreases, whereas that of the Cu 2p peak increases, as observed in Fig. 2(A) and 2(B). Therefore, to further confirm the monolayer dispersion capacity of CuO on SnO₂ support that was determined by XRD, the XPS extrapolation method was also used to measure the capacity [9]. In detail, the intensity of the Cu 2p_{1/2} peak is divided by that of the Sn 3d_{5/2} peak for each sample to obtain a series of $I_{\text{Sn}3d}/I_{\text{Cu}2p}$, which are then plotted against the CuO loadings of the samples. As exhibited in Fig. 2(C), two linearly correlated lines with different slopes are

Fig. 2. XPS analysis of CuO/SnO₂ catalysts with different CuO loadings. (A) Sn 3d; (B) Cu 2p; (C) the monolayer dispersion capacity of CuO on SnO₂ support, as quantified by XPS extrapolation.

Fig. 3. N_2 adsorption-desorption study of CuO/SnO_2 catalysts with different CuO loadings. (A) isotherms; (B) pore size distribution profiles.

obtained, which intersect each other at the point corresponding to $2.02 \text{ mmol } 100 \text{ m}^{-2} \text{ SnO}_2$. According to previous studies [9], the CuO loading corresponding to this point corresponds to the monolayer dispersion capacity of CuO on SnO_2 . Within the experimental error range, this value is the same as that of $2.09 \text{ mmol } 100 \text{ m}^{-2} \text{ SnO}_2$, which is the monolayer dispersion capacity obtained by the XRD extrapolation method.

In brief, the results obtained by using the XRD and XPS extrapolation methods are highly consistent with each other, testifying that CuO exhibits a monolayer dispersion capacity of around $2.09 \text{ mmol } 100 \text{ m}^{-2}$ on SnO_2 support, which equals $4.8 \text{ wt\%}$ CuO loading. Above this capacity, the excess CuO starts to form CuO micro-crystallites, the average grain sizes of which increase until they are detectable by XRD.

3.3. N_2 adsorption-desorption measurements of the catalysts

The texture properties of the catalysts were evaluated through N_2 adsorption-desorption experiments, and the results are shown in Fig. 3. It is noted here that with the increase in the CuO loading, the surface areas of the CuO/SnO_2 samples decrease slightly, as observed in Table 1. For all the samples containing the SnO_2 support, Fig. 3(A) indicates that a type IV

isotherm and an H3-type hysteresis loop in the relative pressure (P/P_0) range 0.8–1.0 are observed. Fig. 3(B) reveals that the pore size distribution profiles of the samples are similar upon changing the CuO loading, proving that CuO is dispersed finely on the SnO_2 support, without any evident impact on its texture properties.

3.4. TEM, HR-TEM, and STEM mapping studies of the catalysts

As quantified by the XRD and XPS extrapolation methods, the monolayer dispersion capacity of CuO on SnO_2 support is $2.09 \text{ mmol } 100 \text{ m}^{-2}$, which equals a CuO loading of 4.8% . Therefore, to investigate the changes in the surface properties of the CuO/SnO_2 samples by altering the CuO loading, three typical catalysts with CuO loadings below (1%), close to (5%), and above (9%) the monolayer dispersion capacity were analyzed by TEM. Fig. 4(A, C, and E) reveals that all the three samples are composed of irregular spherical particles, indicating that the change in the CuO loading has no evident impact on the morphology.

Interestingly, the HR-TEM image of $1\% \text{ CuO/SnO}_2$ in Fig. 4(B) shows only the (101) and (110) diffraction planes of the SnO_2 support. None of the CuO diffraction peaks are observed, which testify the fact that below the monolayer capacity, CuO is present on the surface in an amorphous state. However, in Fig. 4(D) and (F), which display the HR-TEM images of $5\% \text{ CuO/SnO}_2$ and $9\% \text{ CuO/SnO}_2$, besides the diffraction planes of SnO_2 , the Cu (11-1) plane of crystalline CuO is obviously detected, with the planar distance being 0.260 nm . This demonstrates that when the CuO loading is above the monolayer dispersion capacity, the excess CuO forms micro-crystallites on top of the CuO monolayer.

To obtain more direct information on the CuO dispersion, the three typical samples were further studied by STEM mapping, and the images are exhibited in Fig. 5. For $1\% \text{ CuO/SnO}_2$, elemental copper is distributed highly homogeneously along with elemental tin and oxygen, suggesting that it is dispersed very finely on the SnO_2 support surface. However, in the mapping images of $5\% \text{ CuO/SnO}_2$, some local CuO aggregation is

Table 1

Physicochemical properties of CuO/SnO_2 catalysts with different CuO loadings.

Sample	Average crystallite size ^a (nm)	Surface area ^b ($\text{m}^2 \text{ g}^{-1}$)
SnO_2	13.3	32
$1\% \text{ CuO/SnO}_2$	13.6	31
$3\% \text{ CuO/SnO}_2$	12.8	32
$5\% \text{ CuO/SnO}_2$	13.4	30
$7\% \text{ CuO/SnO}_2$	13.7	31
$9\% \text{ CuO/SnO}_2$	12.9	27
$11\% \text{ CuO/SnO}_2$	13.7	28
$13\% \text{ CuO/SnO}_2$	13.3	26
$15\% \text{ CuO/SnO}_2$	13.3	27

^a Calculated by Scherrer's equation for the (110) peak.

^b Calculated by the BET method.

Fig. 4. TEM and HR-TEM images of CuO/SnO₂ catalysts. (A, B) 1%; (C, D) 5%; (E, F) 9%.

Fig. 5. STEM mapping images of 1% CuO/SnO₂, 5% CuO/SnO₂, and 9% CuO/SnO₂ catalysts.

evidently observed, as indicated by the randomly bright copper mapping spot, which is not accompanied by any elemental tin. This indicates that some excess CuO has already formed in the

micro-crystallites. In contrast, in the images of 9% CuO/SnO₂, owing to the formation of a much larger amount of CuO micro-crystallites, the copper mapping signal becomes completely bright, with some of the copper species not being accompanied by elemental tin.

In summary, both the HR-TEM and STEM mapping results reveal that when the CuO loading is below the monolayer dispersion capacity, CuO is present in an amorphous monolayer dispersed state on the support surface. On the other hand, if the CuO loading is above the capacity, crystalline CuO particles will then be formed. These microscopy results provide direct evidence that confirm what was observed through XRD and XPS.

3.5. Raman characterization of the catalysts

The surface properties of the CuO/SnO₂ samples were further analyzed by Raman spectroscopy in the shift range 200–1100 cm⁻¹, and the results are displayed in Fig. 6. For comparison purpose, the Raman spectra of pure CuO and SnO₂ support were also collected. Monoclinic CuO displays three typical Raman bands, which are A_g at 275 cm⁻¹ and B_g at 320 and 605 cm⁻¹ [27,33]. The CVD SnO₂ support used in this study exhibits tetragonal rutile structure, which belongs to the D144h space group. According to group theory, its active Raman modes are B_{1g}, E_g, A_{1g}, and B_{2g}, and theoretically four first-order Raman peaks should be observed [34]. However, as shown in Fig. 6, only three Raman peaks at 478, 636, and 780 cm⁻¹, corresponding to the E_g, A_{1g}, and B_{2g} vibration modes, respectively, are detected.

For the CuO/SnO₂ samples, when the CuO loading is below 5%, the three typical Raman peaks of rutile SnO₂ are still evidently observed, but their intensities decrease with the increase in the CuO loading. In addition, the A_{1g} and B_{2g} bands shift to lower values gradually, which suggest interaction between CuO and SnO₂ support. In comparison, when the CuO loading is above the monolayer dispersion capacity and reaches 7%, it seems that the E_g band of rutile SnO₂ shifts to 498 cm⁻¹, while the A_{1g} and B_{2g} bands shift further to lower values. More interestingly, two new Raman peaks at about 541 cm⁻¹ (A₁) and 684 cm⁻¹ (A₂) are also observed in the spectra of the CuO/SnO₂

Fig. 6. Raman spectra of CuO/SnO₂ catalysts with different CuO loadings.

samples. According to the literature [34–36], the former peak is ascribed to the interface or surface phonon modes, and corresponds to surface defects such as oxygen vacancies and lattice disorder. The latter peak is believed to correspond to the IR-active A2uLO modes. It is apparent that the difference in the CuO loading has altered the surface properties of the SnO₂ support. Particularly, for the sample with CuO loading close to the monolayer dispersion capacity, an abrupt change in the surface property can be observed. The presence of this turning point indicates that the interactions of monolayer CuO and crystalline CuO with SnO₂ support are different, which testify to the presence of a threshold effect on the surface composition. Indeed, the Raman results are highly consistent with the XRD and XPS results, proving that CuO exhibits a monolayer dispersion capacity of 2.09 mmol 100 m⁻², which equals a CuO loading of around 4.8%.

3.6. Evaluation of the soot combustion activity

Soot combustion was used to investigate the reaction performances of the CuO/SnO₂ catalysts, with the TPO profiles depicted in Fig. 7. For easy comparison, the T_i , T_p , and ΔT_{i-p} , which are the combustion ignition temperature, peak temperature, and the gap between the two temperatures, respectively, are listed in Table 2. For the thermal combustion of pure soot without any catalyst, the T_i and T_p are 530 and 630 °C, respectively, and the ΔT_{i-p} is as wide as 100 °C. With the incorporation of CVD SnO₂ as the catalyst, the T_i and T_p drop slightly to 525 and 605 °C, respectively, and the ΔT_{i-p} becomes 20 °C narrower, indicating that the presence of SnO₂ accelerates the combustion process. Interestingly, with the addition of even 1% CuO, the T_i and T_p drop significantly to 505 and 560 °C, respectively, and the ΔT_{i-p} becomes 55 °C, which strongly suggest that the presence of dispersed surface CuO has a tremendous influence on the activity. By increasing the CuO loading to 5%, which is close to the monolayer loading of 4.8%, the T_i and T_p drop further to 465 and 515 °C, respectively, and the ΔT_{i-p} becomes 50 °C. However, upon further increasing the CuO loading to 7% or higher, no significant impact on the reaction performance of the catalyst is observed. Starting from 5% CuO/SnO₂, the sample

Table 2

Soot combustion on CuO/SnO₂ catalysts with different CuO loadings.

Catalyst	T_i (°C)	T_p (°C)	ΔT_{i-p} (°C)
Blank	530	630	100
SnO ₂	525	605	80
1% CuO/SnO ₂	505	560	55
3% CuO/SnO ₂	480	525	45
5% CuO/SnO ₂	465	515	50
7% CuO/SnO ₂	470	515	45
9% CuO/SnO ₂	470	515	45
11% CuO/SnO ₂	470	515	45
13% CuO/SnO ₂	470	515	45
15% CuO/SnO ₂	470	515	45

with a loading close to the monolayer dispersion capacity, all the catalysts with higher CuO loadings exhibit nearly the same activity relative to each other, which proves that beyond the monolayer capacity, increasing the CuO loading does not have a beneficial effect on the soot combustion activity. Apparently, this substantiates the fact that the CuO monolayer on SnO₂ support plays a crucial role in determining the reactivity of the catalyst. In addition, the presence of the turning point suggests a strong threshold effect for the CuO/SnO₂ catalysts for the soot combustion activity.

Soot combustion over CuO/SnO₂ catalysts should follow the Mars-van Krevlen mechanism, which involves the consumption and regeneration of surface-active oxygen species [36]. With the addition of CuO, active surface oxygen species is formed, as evidenced by the Raman results, which is possibly related to the formation of Cu–O–Sn interface bonds. Many earlier studies have demonstrated that for supported metal oxide systems, surface interface bonds can be effectively generated, and that the interfacial oxygen species are active and selective towards many oxidation reactions [37,38]. In this study, although the Cu–O–Sn interface bonds were not directly observed, the Raman results in Fig. 6 prove the interaction between CuO and SnO₂ support, which induces the formation of surface-active oxygen species. In the following sections, more experimental details will be provided to support this theory.

Below the monolayer dispersion capacity, CuO keeps the SnO₂ support surface covered, thus producing more Cu–O–Sn interface bonds and improving the activity continuously. On the other hand, above the monolayer dispersion capacity, the excess CuO starts to form micro-crystallites, which remain on top of the CuO monolayer. Since crystalline CuO itself is very active towards oxidation reactions [19,20,27,39], the activities of the catalysts with CuO loadings above the monolayer capacity are not degraded by the formation of CuO crystallites, but rather retained without any evident change.

The stability of a soot combustion catalyst determines its potential for application. Therefore, the typical 5% CuO/SnO₂ catalyst was subjected to five continuous TPO tests. As illustrated in Fig. 8, no temperature increase is observed after five cycles, which indicates that the catalyst displays stable reaction performance and has potential for application in some real exhaust post-treatment processes.

Fig. 7. Soot combustion over CuO/SnO₂ catalysts with different CuO loadings.

Fig. 8. Stability test of 5% CuO/SnO₂ for soot combustion over five continuous TPO cycles.

3.7. H₂-TPR studies of the catalysts

H₂-TPR experiments were performed to evaluate the redox properties of the CuO/SnO₂ catalysts, and the profiles are presented in Fig. 9. Pure SnO₂ shows a major reduction peak at 660 °C, which is assigned to the reduction of bulk SnO₂ to metallic tin [24,40]; this is also verified by the quantification results shown in Table 3. For all the CuO/SnO₂ samples, besides the major reduction peak of SnO₂, a group of low-temperature reduction peaks assigned to CuO reduction are observed [27], which is confirmed by the quantified O/Cu atomic ratios listed in Table 3. For the reduction of bare CuO, two peaks are typically observed in the range 200 to 400 °C, which are attributed to the stepwise reduction of CuO to Cu₂O and eventually to metallic copper [24]. It is apparent that in all the CuO/SnO₂ samples, the reduction of CuO shifts to a significantly lower temperature region (below 300 °C), due to the fine dispersion of CuO on the support surface. As demonstrated earlier, when a metal oxide disperses finely on a support surface, its reduction will become thermodynamically favorable [9,11]. However, even in the sub-monolayer or monolayer dispersed state, two peaks corresponding to the two typical reduction steps of CuO

Fig. 9. H₂-TPR profiles of CuO/SnO₂ catalysts with different CuO loadings.

Table 3

Quantified H₂-TPR results of CuO/SnO₂ catalysts with different CuO loadings.

Catalyst	H ₂ uptake amount below 300 °C (mmol g ⁻¹ CuO)	O/Cu atomic ratio	H ₂ uptake amount above 300 °C (mmol g ⁻¹ SnO ₂)	O/Sn atomic ratio
SnO ₂	0	0	13.3	2.0
1% CuO/SnO ₂	12.7	1.0	13.2	2.0
3% CuO/SnO ₂	12.9	1.0	13.3	2.0
5% CuO/SnO ₂	13.5	1.1	13.2	2.0
7% CuO/SnO ₂	13.7	1.1	13.3	2.0
9% CuO/SnO ₂	14.0	1.1	13.3	2.0
11% CuO/SnO ₂	13.7	1.1	13.2	2.0
13% CuO/SnO ₂	13.4	1.1	13.3	2.0
15% CuO/SnO ₂	13.3	1.1	13.1	2.0

can still be clearly observed. With the increase in the CuO loading, the second peak around 200 °C becomes gradually larger, which confirms the formation of crystalline CuO.

What is interesting here is the shift in the SnO₂ reduction peak with the addition of CuO. Below the monolayer dispersion capacity, with the increase in the CuO loading up to 5%, the SnO₂ reduction peak temperature drops from 660 to 625 °C. However, further increasing the CuO loading to 15% results in the reduction peak temperature remaining at 625 °C. This trend is highly consistent with the reaction performances of the catalysts. Therefore, it is believed that in the presence of gas-phase oxygen, the lattice oxygen of SnO₂ could also be involved in the soot combustion process.

3.8. O₂-TPD and XPS studies on the oxygen properties of the catalysts

To further understand the oxygen properties of the CuO/SnO₂ samples, O₂-TPD experiments were performed, with the results shown in Fig. 10. For all the samples, two oxygen desorption peaks are observed around 110 and 580 °C. For the convenience of discussion, the desorption peak around 110 °C is named α peak, whereas the desorption peak around 580 °C is named β peak. The α peak is assigned to the desorption of loosely bonded surface oxygens, whereas the β peak is assigned

Fig. 10. O₂-TPD profiles of CuO/SnO₂ catalysts with different CuO loadings.

Table 4
Quantified O₂-TPD results of catalysts with different CuO loadings.

Catalyst	Relative oxygen amount of the α peak (a.u.)	Relative oxygen amount of the β peak (a.u.)	Total (a.u.)
SnO ₂	10	41	51
1% CuO/SnO ₂	50	35	85
3% CuO/SnO ₂	53	31	84
5% CuO/SnO ₂	58	32	90
7% CuO/SnO ₂	55	30	85
9% CuO/SnO ₂	53	37	90
11% CuO/SnO ₂	46	33	79

to the desorption of mobile surface lattice oxygens [41]. For clarity of information, the integrated areas of the two peaks of each sample have been quantified and included in Table 4. With the addition of CuO, the amount of loosely bonded surface oxygen increases significantly, proving again the generation of surface-active oxygen species due to the interaction between the dispersed CuO and the SnO₂ support, which is evidenced by the Raman results. Although pure SnO₂ contains a slightly larger amount of surface lattice oxygen than the CuO/SnO₂ samples, its peak is much wider in comparison with the β peak of the CuO/SnO₂ catalysts, indicating the surface lattice oxygen of pure SnO₂ is kinetically much less active than that of CuO/SnO₂. Furthermore, with the increase in the CuO loading from 1% to 7%, the β peak temperature decreases, indicating that when the CuO loading is close to the monolayer dispersion capacity, the most active surface lattice oxygen species can be formed. Upon further increasing the CuO loading, the β peak temperature increases slightly due to the formation of surface CuO micro-crystallites. It is noted that the total oxygen desorption amounts of the CuO/SnO₂ catalysts are obviously higher than that of pure SnO₂ support. Indeed, the presence of highly abundant and reactive surface oxygen species on CuO/SnO₂ could account for its much-improved soot combustion activity in comparison with that of pure SnO₂.

To verify what is observed through O₂-TPD experiments, some of the typical CuO/SnO₂ samples were also analyzed by XPS, with attention particularly paid to the surface oxygen property. As shown in Fig. 11, doublet O 1s peaks are observed for all the samples, suggesting the presence of two types of oxygen species with different chemical environments on the catalyst surfaces. According to the literature [42], the peak around 530.6 eV is assigned to the surface lattice oxygen species, and the peak around 531.9 eV can be ascribed to the loosely bounded surface oxygen species. For clarity, the per-

Fig. 11. XPS analysis of the O 1s peaks of CuO/SnO₂ catalysts with different CuO loadings. (A) O 1s spectra; (B) T_i , T_p versus ($O_{\text{ads}}/(O_{\text{ads}} + O_{\text{latt}})$) percentages.

centages of the surface loosely bounded oxygen species, $O_{\text{ads}}/(O_{\text{ads}} + O_{\text{latt}})$, are quantified and listed in Table 5. With the addition of 1% CuO, the percentage increases from 22.9% to 28.1%, testifying again that the interaction between the surface sub-monolayer CuO and the SnO₂ support creates more abundant surface-active oxygen species. With the increase in the CuO loading to 5%, the percentage improves to 35.9%. However, further improving the CuO loading has little influence on the percentages of the loosely bounded surface oxygen species, which is in good accordance with the changes in the soot combustion activities of the catalysts.

To determine the relationship between the soot combustion activity and the amount of loosely bounded surface-active oxygen species, the T_i and T_p for soot combustion over the CuO/SnO₂ samples are plotted against their $O_{\text{ads}}/(O_{\text{ads}} + O_{\text{latt}})$

Table 5
Quantified XPS results of catalysts with different CuO loadings.

Catalyst	O_{ads}		O_{latt}		$O_{\text{ads}}/(O_{\text{ads}} + O_{\text{latt}})$ (%)
	B.E. (eV)	Amount (a.u.)	B.E. (eV)	Amount (a.u.)	
SnO ₂	532.3	24	531.1	81	22.9
1% CuO/SnO ₂	532.0	39	530.6	100	28.1
3% CuO/SnO ₂	531.8	48	530.6	98	32.9
5% CuO/SnO ₂	531.9	51	530.6	91	35.9
7% CuO/SnO ₂	531.7	52	530.6	93	35.8
9% CuO/SnO ₂	531.7	48	530.5	86	35.8

percentages in Fig. 11(B). Interestingly, below 5% CuO loading, with the increase in the $O_{\text{ads}}/(O_{\text{ads}} + O_{\text{latt}})$ percentages, both the T_i and T_p of the catalysts follow the same trend in that they decrease. When the CuO loading is above 5% and the $O_{\text{ads}}/(O_{\text{ads}} + O_{\text{latt}})$ percentages of all the samples become constant, the T_i and T_p of the catalysts also remain unchanged. Therefore, it is rational to propose that the amount of the loosely bounded surface oxygen sites might play a critical role in determining the soot combustion activities of the catalysts.

3.9. Soot-TPR studies of the catalysts

To examine more directly the interaction of soot particles with the surface-active sites of the CuO/SnO₂ catalysts, they were subjected to soot-TPR tests, and the results are displayed in Fig. 12 and Table 6. The pure SnO₂ support without CuO displays two soot reduction peaks at 200 and 370 °C, testifying the presence of two kinds of surface sites that can react with soot particulates [36]. With the addition of CuO, both the reduction peaks become larger (Table 6), and the high-temperature peak shifts downward to 340 °C, suggesting the formation of a large amount of highly active surface oxygen species due to the interaction between the dispersed surface CuO and the SnO₂ support. Our previous results have demonstrated that for bare CuO prepared by using different copper precursors and precipitants, four types of oxygen sites that can react with soot particles are present [27]. However, by dispersing CuO onto SnO₂ support, even with the formation of CuO micro-crystallites above the monolayer dispersion capacity, only two kinds of

surface-active oxygen sites are observed in the lower-temperature region, as evidenced by the soot-TPR profiles of the CuO/SnO₂ catalysts. Apparently, owing to the interaction between CuO and SnO₂, the property of the active sites has been changed. In brief, the soot-TPR results are in agreement with the Raman, O₂-TPD, and XPS results, indicating that by dispersing CuO onto SnO₂ support, more abundant and active oxygen species can be formed that benefits the soot combustion activities of the catalysts.

4. Conclusions

With the objective to design and prepare more applicable catalysts for soot combustion, a series of CuO/SnO₂ catalysts with different CuO loadings have been prepared by impregnation method to investigate the structure-reactivity relationship, which was also characterized by different means.

(1) By using XRD and XPS extrapolation methods, it was discovered that CuO disperses finely on the SnO₂ support surface to form a monolayer with a capacity of 2.09 mmol 100 m⁻², which equals to 4.8 wt% CuO loading. As testified by HR-TEM, STEM mapping, and H₂-TPR results, when the CuO loading is below the monolayer dispersion capacity, CuO is present in a sub-monolayer amorphous state. On the other hand, when the loading is above the monolayer dispersion capacity, CuO micro-crystallites are formed, which coexist with the CuO monolayer.

(2) The soot combustion activity of the catalyst increases with CuO loading until it reaches the monolayer dispersion capacity. Further increase in the CuO loading has no evident influence on the activity. Therefore, an apparent monolayer dispersion threshold effect is observed for soot combustion over CuO/SnO₂ catalysts.

(3) Raman results have testified that with the addition of CuO onto SnO₂ support, surface-active oxygen sites can be formed. O₂-TPD and XPS results have proved that the amount of the surface oxygen species increases significantly with the increase in the CuO loading until it reaches the monolayer capacity. Further increase in the CuO loading has no evident impact on this amount. This is highly consistent with the activities of the catalysts. Therefore, the amount of surface-active oxygen sites is believed to be the main factor influencing the activities of the catalysts.

Acknowledgments

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Fig. 12. Soot-TPR profiles of catalysts with different CuO loadings.

Table 6
Quantitative results of the measurement of soot-TPR profiles.

Catalyst	Amount of CO ₂ formed (a.u.)
SnO ₂	140
1% CuO/SnO ₂	218
3% CuO/SnO ₂	238
5% CuO/SnO ₂	261
7% CuO/SnO ₂	305
9% CuO/SnO ₂	323
11% CuO/SnO ₂	335

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Graphical Abstract

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Tuning SnO₂ surface with CuO for soot particulate combustion: The effect of monolayer dispersion capacity on reaction performance

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The amount of surface active oxygen sites is the major factor to control the activity of CuO/SnO₂ catalysts for soot combustion. An evident monolayer dispersion threshold effect is observed for the reaction performance.

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CuO调配SnO₂表面用于碳烟颗粒燃烧：单层分散阈值效应对催化性能的影响

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摘要: 柴油发动机由于具有良好的动力和经济性等优势而得到广泛的应用, 但排放的尾气中碳烟颗粒物(PM)却给人类健康和环境带来了严重的危害。目前PM污染的治理引起了广大科研工作者的关注。催化燃烧成为PM污染消除技术中最有效的方法。

金属氧化物负载到载体上时, 通常会出现单层分散现象, 其单层分散容量可以通过XRD, XPS和Raman等外推法测定。此外, 当负载体系用作某种反应的催化剂时, 往往会表现出单层分散阈值效应, 即阈值附近的催化剂通常具有较高的活性和选择性等。目前单层分散理论已被广泛接受, 成为设计高性能催化材料的重要指导思想。

在过去八年本课题组将SnO₂基催化材料用于多种环保和能源反应, 并系统地探究了其催化性能。结果表明, SnO₂含有丰富的表面活泼氧和晶格氧, 且热稳定性高, 是一种优良的催化剂载体。基于单层分散理论, 为获得更实用的PM燃烧催化剂, 我们利用浸渍法设计制备了系列不同CuO负载量的CuO/SnO₂催化剂, 并使用XRD, XPS, Raman, TEM, STEM-mapping, H₂-TPR, soot-TPR和O₂-TPD等手段深入研究了其构效关系。利用XRD和XPS外推法测得的CuO高度分散在SnO₂载体表面, 其单层分散阈值为2.09 mmol 100 m⁻², 即相当于4.8% CuO负载量。低于该负载量时, CuO以亚单层分散态存在; 而高于该负载量时, 形成的CuO微晶和单层分散态的CuO共存。在单层分散阈值之前, 催化剂的碳烟燃烧活性随CuO负载量的升高而上升; 进一步提高CuO负载量对其活性无明显的影响。Raman结果表明, 在单层分散阈值之前, CuO负载到SnO₂载体上可有效形成表面活泼氧中心, 且其含量随CuO负载量升高而增加; 进一步提高CuO负载量则对其含量无明显改变。因此, CuO/SnO₂催化剂用于碳烟颗粒燃烧具有明显的阈值效应。以上结果表明, 表面活泼氧中心含量是决定该催化剂活性的主要因素。

关键词: 氧化锡负载的氧化铜; 碳烟颗粒燃烧; 单层分散; XRD和XPS外推法; 阈值效应

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