available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article

Stable CuO/La₂Sn₂O₇ catalysts for soot combustion: Study on the monolayer dispersion behavior of CuO over a La₂Sn₂O₇ pyrochlore support

Xiaohui Feng, Rui Liu, Xianglan Xu, Yunyan Tong, Shijing Zhang, Jiacheng He, Junwei Xu, Xiuzhong Fang, Xiang Wang*

Key Laboratory of Jiangxi Province for Environment and Energy Catalysis, College of Chemistry, Nanchang University, Nanchang 330031, Jiangxi, China

ARTICLE INFO

Article history:

Received 11 May 2020

Accepted 20 June 2020

Published 5 March 2021

Keywords:

CuO/La₂Sn₂O₇ catalyst

Soot combustion

DFT calculations

Preferential interaction

Monolayer dispersion on pyrochlore support

Active O₂⁻ and O₂²⁻ sites

ABSTRACT

To understand the dispersion behavior of metal oxides on composite oxide supports and with the expectation of developing more feasible catalysts for soot oxidation, CuO/La₂Sn₂O₇ samples containing varied CuO loadings were fabricated and characterized by different techniques and density functional theory calculations. In these catalysts, a spontaneous dispersion of CuO on the La₂Sn₂O₇ pyrochlore support formed, having a monolayer dispersion capacity of 1.90 mmol CuO/100 m² La₂Sn₂O₇ surface. When loaded below this capacity, CuO exists in a sub-monolayer or monolayer state. X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and Bader charge and density of states analyses indicate that there are strong interactions between the sub-monolayer/monolayer CuO and the La₂Sn₂O₇ support, mainly through the donation of electrons from Cu to Sn at the B-sites of the structure. In contrast, Cu has negligible interactions with La at the A-sites. This suggests that, in composite oxide supports containing multiple metals, the supported metal oxide interacts preferentially with one kind of metal cation in the support. The Raman, *in situ* diffuse reflectance infrared Fourier transform spectroscopy, and XPS results confirmed the formation of both O₂⁻ and O₂²⁻ as the active sites on the surfaces of the CuO/La₂Sn₂O₇ catalysts, and the concentration of these active species determines the soot combustion activity. The number of active oxygen anions increased with increase in CuO loading until the monolayer dispersion capacity was reached. Above the monolayer dispersion capacity, micro-sized CuO crystallites formed, and these had a negative effect on the generation of active surface oxygen sites. In summary, a highly active catalyst can be prepared by covering the surface of the La₂Sn₂O₇ support with a CuO monolayer.

© 2021, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Compared with gasoline engines, diesel engines have generally higher fuel efficiencies and lower costs [1,2]. However, the soot particulate matter (PM) released from diesel engines has a

severe impact on the environment and human health [3–5]. Trapping the soot PM in the exhaust using a diesel particulate filter (DPF) honeycomb, which is usually coated with an oxidation catalyst, has been shown to be an effective way to reduce pollution and has been applied in vehicles [6–8]. Presently,

* Corresponding author. Tel: +86-15979149877; E-mail: xwang23@ncu.edu.cn

This work was supported by the National Natural Science Foundation of China (21962009, 21567016, 21666020), the National Key Research and Development Program of China (2016YFC0209302), the Natural Science Foundation of Jiangxi Province (20181ACB20005, 20171BAB213013, 20181BAB203017), the Key Laboratory Foundation of Jiangxi Province for Environment and Energy Catalysis (20181BCD40004).

DOI: 10.1016/S1872-2067(20)63657-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 42, No. 3, March 2021

noble metals are most commonly used catalysts for soot oxidation, but their wide application is restricted by their limited availability and high cost. Therefore, the development of low cost and efficient catalysts is highly desirable. To date, catalysts based on alkaline metal oxides [9,10], transition metal oxides [4,7,11], Ce-Zr solid solutions [12,13], perovskite oxides [14,15], and pyrochlore oxides [16,17] have been studied. Nevertheless, achieving a feasible soot combustion catalyst without using noble metals remains a challenge [18].

CuO-based materials are active catalysts used for many oxidation processes because of the highly reactive Cu–O bonds [19,20]. A typical example is the famous Hopcalite catalyst, which is composed of CuO and manganese oxides, and catalyzes complete CO oxidation at room temperature [21]. Over the past few years, CuO supported on materials such as Al₂O₃ [22], CeO₂ [23], perovskites [24], Ce-Zr-O solid solutions [25], and ZrO₂-TiO₂ composite oxides [26] have been investigated as soot combustion catalysts, and considerable catalytic activity has been observed. Meng et al. [27] prepared monolithic lawn-like pure CuO nanorod arrays for soot combustion and found that the catalysts display higher activity than typical CuO nanoparticles. To understand the structure–reactivity relationship of CuO for soot combustion, we previously prepared a series of CuO samples using various Cu precursors and precipitants [28], and we found that the redox properties, morphology, and texture significantly affect the soot oxidation activity. For example, a CuO sample synthesized with a Cu(NO₃)₂ precursor and Na₂CO₃ precipitant showed the best soot oxidation performance of all the tested samples, mainly because of the formation of abundant active surface superoxide (O₂^{•−}) and peroxide (O₂^{2−}) anions. However, pure CuO suffers from low thermal stability, which hinders its practical use. To obtain more applicable catalysts, CuO was supported on a stable SnO₂ support [29]. Although the catalytic stability of CuO can be improved by using a support (as in CuO/SnO₂), the catalytic activity is decreased. Therefore, more appropriate supports are required to obtain practical CuO-based catalysts.

A₂B₂O₇ pyrochlore compounds are important functional materials that have been applied in gas sensors [30], ferroelectric materials [31], and catalysts [32,33]. In particular, these compounds possess excellent thermal stability and excellent oxygen anion conductivity, which are vital features of redox catalysts for exothermic processes [34,35]. Moreover, in the unit cell of pyrochlore compounds, eight inherent 8a oxygen vacancies are present, which results in excellent lattice oxygen mobility, especially when the radii of the A- and B-site ions are similar [35,36]. As a consequence, active O₂^{•−} and O₂^{2−} anions at the surface are generated, which is favorable for many redox reactions, as demonstrated in our previous publications [35,37]. In particular, we have shown that supporting Pd onto a high-surface-area La₂Sn₂O₇ pyrochlore results in catalysts with better activities than those of Pd/Al₂O₃ and Pd/SnO₂ [38]. Therefore, pyrochlore compounds with suitable chemical compositions and surface areas might be good candidates as supports for CuO for use as soot combustion catalysts.

Monolayer dispersion is an important theory established by Xie and co-workers [39] in the late 1970s, and it is particularly

useful in the design of supported metal oxide catalysts for various reactions. Xie and co-workers [29,39] discovered that metal oxides can spontaneously disperse onto the surface of many supports to generate a monolayer or sub-monolayer, and the monolayer capacity can be quantified by extrapolation of data obtained from X-ray diffractometry (XRD), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) measurements. For many reactions, an evident monolayer dispersion threshold effect is observed. That is, a catalyst containing the active components at the monolayer dispersion capacity limit often exhibits the best activity and selectivity [29,39]. As pointed out by Wachs et al. [40,41], in the monolayer dispersion state, interfacial oxygen bonds (M–O–S) between the supported metal oxides and supports are generated, and these species show unique catalytic activity for many reactions. Over the past decades, although metal oxide dispersions on individual component supports, such as Al₂O₃, SiO₂, ZrO₂, and TiO₂, have been extensively explored, the use of composite oxides to support active components to prepare catalysts has been investigated little.

Inspired by these previous investigations and aiming to obtain more applicable soot combustion catalysts, we used a La₂Sn₂O₇ pyrochlore compound as the support for CuO to prepare a series of soot combustion catalysts. In addition, to understand the dispersion behavior of the supported metal oxide on the composite oxide support, the interfacial interaction between CuO and the La₂Sn₂O₇ support was thoroughly investigated by various characterization techniques and density functional theory (DFT) calculations. We found that there is a significant monolayer threshold effect. Moreover, the supported CuO preferentially interacts with the B-site Sn cations in the support instead of the A-site La cations. We found that the CuO/La₂Sn₂O₇ catalyst with a CuO loading close to the monolayer dispersion capacity showed the best performance for soot oxidation of all samples because of the formation of a high quantity of electrophilic oxygen sites at the catalyst surface.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of La₂Sn₂O₇ pyrochlore support

A La₂Sn₂O₇ pyrochlore support was prepared using a hydrothermal method. The chemical reagents used in the preparation were analytical grade to ensure the purity of the obtained samples. First, 0.5 mol L^{−1} aqueous La(NO₃)₃ and Na₂SnO₃ solutions were prepared separately. Then, the two solutions were mixed together in equal volumes (150 mL) in a Teflon liner with 500-mL capacity. On mixing, a white sodium stannate precipitate was formed. On adding nitric acid solution (30%) dropwise, the precipitate was dissolved, yielding a transparent solution. With constant stirring, the pH of the mixture was adjusted to 9 with an ammonia aqueous solution (25%–28%). Subsequently, the Teflon liner was sealed in a stainless-steel autoclave and heated at 200 °C for 24 h. After filtration and complete washing with distilled deionized (DDI) water until the filtrate had a total dissolved solids (TDS) con-

tent of less than 20 ppm, the prepared solid product was dried at 110 °C overnight. Finally, the dried solid was calcined at 550 °C in air for 4 h at a heating rate of 2 °C min⁻¹. This solid was used as the support for CuO to prepare the CuO/La₂Sn₂O₇ catalysts. N₂ sorption analysis indicates that the La₂Sn₂O₇ pyrochlore support has a specific surface area of 17.5 m² g⁻¹ (Table 1).

2.1.2. Preparation of CuO/La₂Sn₂O₇ catalysts

The CuO/La₂Sn₂O₇ catalysts with different CuO contents were synthesized by a traditional impregnation method. Cu(NO₃)₂ was dissolved in 1 mL DDI water. To this aqueous solution, 2 g La₂Sn₂O₇ powder was added with constant stirring at room temperature for additional 2 h. Then, the wet solids were transferred to a 80 °C water bath with constant stirring until the excess water had evaporated completely. The resulting solids were further dried overnight at 110 °C and calcined for 4 h at 550 °C in air at a heating rate of 1 °C min⁻¹ to obtain the final catalysts, which are denoted by their CuO loadings. The actual CuO loadings of the catalysts were verified by inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements (Table 1).

2.2. Catalyst characterization and activity evaluation

To understand the dispersion behavior of CuO on the La₂Sn₂O₇ support, the interaction between these components, and any subsequent influence on the activity of the CuO/La₂Sn₂O₇ catalysts for soot oxidation, the structural properties of the catalysts were investigated using XRD, XPS, high-resolution transmission electron microscopy (HRTEM), ICP-OES, Raman spectroscopy, N₂ adsorption-desorption isotherms, H₂-temperature programmed reduction (TPR), O₂-temperature programmed desorption (TPD), soot-TPR, and *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). Moreover, the electron transfer between CuO and the La₂Sn₂O₇ and the density of states (DOS) of the atoms were calculated by DFT using the Vienna Ab Initio Simulation Package (VASP) code. In addition, temperature programmed oxidation (TPO) was employed to evaluate the activity of the catalysts under tight contact conditions. The catalyst synthesis

methods, equipment, experimental conditions, and operating procedures are described in detail in the Supplementary Material.

3. Results and discussion

3.1. N₂ sorption results

The textural features of the CuO/La₂Sn₂O₇ catalysts with different CuO loadings were analyzed by N₂ sorption. Fig. S1(a) shows that the catalysts, together with the La₂Sn₂O₇ support, exhibit type-IV isotherms and H3-type hysteresis loops. This indicates that the CuO/La₂Sn₂O₇ catalysts possess a mesoporous structure, which is due to the accumulation of holes in the sample particles. Fig. S1(b) shows that the CuO/La₂Sn₂O₇ catalysts have pore size distribution profiles similar to that of La₂Sn₂O₇, implying that adding CuO has no significant influence on the textural properties of the support. As listed in Table 1, with increase in CuO loading, both the surface areas and mesopore volumes of the CuO/La₂Sn₂O₇ samples decreased gradually. However, the average pore sizes increased slightly with increase in CuO loading. This indicates that some of the initial smaller pores of the La₂Sn₂O₇ support were blocked by the dispersed CuO species; however, the changes in textural properties are not the determining factors in soot oxidation performance, as explained in more detail in the following sections.

3.2. XRD measurements

XRD measurements were used to identify the bulk compositions of the CuO/La₂Sn₂O₇ samples. As shown in Fig. 1(a), the pure La₂Sn₂O₇ support comprises a cubic pyrochlore phase, as shown by the three strong peaks at (222) = 29.06°, (440) = 48.16°, and (622) = 57.18° (JCPDS NO. 00-013-0082). For pure CuO, monoclinic CuO was the only observed phase, as indicated by the three sharp peaks at (11-1) = 35.68°, (111) = 38.95°, and (20-2) = 49.04° (JCPDS NO. 00-048-1548) [42]. For all CuO/La₂Sn₂O₇ samples, cubic La₂Sn₂O₇ pyrochlore is the predominant phase, as indicated by the evident diffraction peaks corresponding to La₂Sn₂O₇. In fact, when the CuO content was below 4%, no XRD peaks related to CuO were observed, implying that CuO is highly dispersed over the La₂Sn₂O₇ support. However, when the CuO loading exceeded 4%, a peak corresponding to CuO [(11-1) = 35.68°] appeared, and the intensity of this peak increased with the increase in CuO loading.

On the basis of former studies, the metal oxide dispersed on the support always had a monolayer dispersion capacity, which can be quantified by the extrapolation of XRD data [39]. Therefore, the monolayer dispersion capacity of CuO on the La₂Sn₂O₇ support was correlated and quantified, as shown in Fig. 1(b). In detail, the CuO (11-1) peak intensity (*I*_{CuO}) of each sample was measured and divided by the La₂Sn₂O₇ (222) peak intensity (*I*_{La₂Sn₂O₇}), thus yielding a series of *I*_{CuO}/*I*_{La₂Sn₂O₇} ratios, which were then plotted against the actual CuO loadings of the samples measured by ICP-OES (Table 1). A linear fit of these data was obtained, and the x-axis intercept of 1.90 mmol/100 m² La₂Sn₂O₇ surface is the monolayer dispersion capacity of CuO

Table 1
Textural properties measured by N₂ sorption.

Sample	CuO loading ^a (wt%)	Surface area ^b (m ² g ⁻¹)	Average pore size ^c (nm)	Average pore volume ^c (cm ³ g ⁻¹)
La ₂ Sn ₂ O ₇	—	17.5	10.2	0.057
1% CuO/La ₂ Sn ₂ O ₇	0.9	16.5	10.4	0.049
2% CuO/La ₂ Sn ₂ O ₇	1.9	15.9	10.3	0.042
3% CuO/La ₂ Sn ₂ O ₇	2.9	15.5	10.4	0.039
4% CuO/La ₂ Sn ₂ O ₇	4.0	15.1	10.6	0.037
5% CuO/La ₂ Sn ₂ O ₇	4.9	14.9	11.1	0.034
6% CuO/La ₂ Sn ₂ O ₇	6.0	14.7	11.5	0.031
7% CuO/La ₂ Sn ₂ O ₇	7.1	10.1	11.4	0.031
8% CuO/La ₂ Sn ₂ O ₇	8.1	9.6	11.7	0.030
9% CuO/La ₂ Sn ₂ O ₇	9.1	7.6	12.9	0.030

^a Measured by ICP-OES.

^b Calculated by Brunauer-Emmett-Teller (BET) analysis.

^c Calculated by Barrett-Joyner-Halenda (BJH) analysis.

Fig. 1. (a) XRD patterns of the CuO/La₂Sn₂O₇ catalysts; (b) CuO monolayer dispersion capacity on the La₂Sn₂O₇ support.

on the La₂Sn₂O₇ support. By conversion, this capacity is equal to 4.3 wt% CuO loading on the support. Thus, similar to single component supports, a monolayer dispersion was also observed on the La₂Sn₂O₇ pyrochlore compound support.

3.3. XPS and HRTEM analysis

XPS was used to identify the surface species in the CuO/La₂Sn₂O₇ catalysts. Fig. 2(a) shows the Cu XPS scan, which contains two Cu 2p peaks at around 953.1 and 933.4 eV, which are assignable to Cu 2p_{1/2} and Cu 2p_{3/2}, respectively, of CuO [43,44]. Fig. 2(b) shows the Sn XPS scan, which contains two Sn 3d peaks at around 494.6 and 486.3 eV, which are assignable to Sn 3d_{3/2} and Sn 3d_{5/2} of Sn⁴⁺ in the La₂Sn₂O₇ support [45,46]. In contrast, as shown in Fig. 2(c), the La in the support yielded both doublet La 3d_{3/2} peaks at 855 and 851.6 eV and La 3d_{5/2} peaks at 838.2 and 834.1 eV, and these are assignable to La³⁺ cations [47,48].

Interestingly, when the CuO content did not exceed 4.3% (i.e., the monolayer dispersion capacity measured by XRD), the binding energies of the Cu 2p peaks increased with increase in the amount of CuO but the binding energies of the Sn 3d peaks decreased. In contrast, the binding energies of the La 3d peak remained constant. This strongly indicates that there is an intimate interaction between CuO and the La₂Sn₂O₇ support when CuO is in a sub-monolayer or monolayer state on the support [49]. Furthermore, the interaction occurs mainly through the partial donation of electrons from Cu to Sn cations in the B-sites, possibly via the formation of Cu–O–Sn interfacial bonds [29]. In contrast, Cu cations have a negligible interaction with the La cations at the A-sites.

When the CuO content was greater than 4%, increasing the CuO amount had no effect on the binding energies of the Sn 3d and Cu 2p peaks. This result indicates that above the monolayer dispersion capacity, the excess CuO is present on top of the formed CuO monolayer and has no close interaction with the La₂Sn₂O₇ support. This indicates that the dispersion of CuO on La₂Sn₂O₇ is present as a monolayer. Therefore, XPS extrapolation was used to determine the monolayer dispersion capacity

of CuO on the La₂Sn₂O₇ support [39]. In detail, for each sample, the Cu 2p_{3/2} peak intensity (I_{Cu2p}) was divided by the Sn 3d_{5/2} peak intensity (I_{Sn3d}), and, following a previously reported method [29,39], these values were then plotted versus the actual CuO content of each sample, as measured by ICP-OES. As shown in Fig. 2(d), two linear fits were obtained, and the value at the crossover point (turning point) corresponds to 1.94 mmol CuO/100 m² La₂Sn₂O₇ surface, which is the monolayer dispersion capacity of CuO on La₂Sn₂O₇. Within experimental error, this is consistent with the value obtained by XRD extrapolation (1.90 mmol/100 m²), verifying that, on the La₂Sn₂O₇ support with a surface area of 17.5 m² g⁻¹, only 4.3 wt% CuO can be supported as a CuO monolayer. Above this loading, the excess CuO begins to accumulate into micro-sized CuO crystallites, which are detectable by XRD when the crystallite size reaches 3 nm [39].

Our former work indicates that CuO has a monolayer dispersion capacity of 2.02 mmol/100 m² SnO₂ surface (quantified by XPS extrapolation) [29], which is similar to the value (1.94 mmol/100 m² La₂Sn₂O₇ surface) obtained in this study. This is additional evidence that Cu interacts preferentially with the Sn in the support. Apparently, when using a composite compound as the support, the supported metal oxide interacts preferentially with one of the metal cations.

To understand the CuO distribution on the La₂Sn₂O₇ support more intuitively, several catalysts were analyzed by HRTEM. Figs. 3(a) and 3(b) show HRTEM images of the 1% and 4% CuO/La₂Sn₂O₇ catalysts, which show only the La₂Sn₂O₇ (222) diffraction planes of the La₂Sn₂O₇ support, and no CuO diffraction peaks are observed. This result indicates that CuO is dispersed on the support as an amorphous sub-monolayer or monolayer state when its content does not exceed the monolayer capacity. In contrast, in the HRTEM images of the 5% and 7% CuO/La₂Sn₂O₇ catalysts, in addition to the La₂Sn₂O₇ (222) diffraction plane, the CuO (11-1) diffraction plane with a *d*-spacing of 0.260 nm, corresponding to crystalline CuO, can be clearly seen. Obviously, when the CuO content exceeds the monolayer dispersion capacity, micro-sized CuO crystallites start to form on top of the initially formed CuO monolayer. In

Fig. 2. XPS spectra of the CuO/ $\text{La}_2\text{Sn}_2\text{O}_7$ catalysts: (a) Cu 2p, (b) Sn 3d, and (c) La 3d. (d) CuO monolayer dispersion capacity on $\text{La}_2\text{Sn}_2\text{O}_7$ support.

brief, the HRTEM results are consistent with the XRD and XPS results, indicating that a monolayer dispersion is formed in the CuO/ $\text{La}_2\text{Sn}_2\text{O}_7$ system.

3.4. Activity evaluation

The soot oxidation activity over the catalysts was evaluated, and the results are shown in Fig. 4(a). The ignition temperature (T_i), highest combustion rate temperature (T_p), complete combustion temperature (T_c), difference between T_i and T_p (ΔT_{i-p}), and the CO_2 selectivity are also listed Table 2. Without a catalyst, T_i , T_p , T_c , and ΔT_{i-p} were 530, 640, 690, and 110 °C, respectively, whereas, with the $\text{La}_2\text{Sn}_2\text{O}_7$ support alone as the catalyst, T_i , T_p , and T_c were reduced by around 100 °C, indicating that $\text{La}_2\text{Sn}_2\text{O}_7$ itself can accelerate the combustion rates.

With the addition of 1%–4% CuO onto the $\text{La}_2\text{Sn}_2\text{O}_7$ support, the soot oxidation activity of the resulting catalysts increased obviously, as shown by the gradually reduced T_i , T_p , T_c , and ΔT_{i-p} values. The 4% CuO/ $\text{La}_2\text{Sn}_2\text{O}_7$ sample, which possesses a CuO content close to the dispersion capacity of 4.3%, demonstrates the highest activity of all the prepared catalysts.

Fig. 3. HRTEM images of the CuO/ $\text{La}_2\text{Sn}_2\text{O}_7$ catalysts. (a) 1% CuO/ $\text{La}_2\text{Sn}_2\text{O}_7$; (b) 4% CuO/ $\text{La}_2\text{Sn}_2\text{O}_7$; (c) 5% CuO/ $\text{La}_2\text{Sn}_2\text{O}_7$; (d) 7% CuO/ $\text{La}_2\text{Sn}_2\text{O}_7$.

Fig. 4. Soot combustion activity on the CuO/La₂Sn₂O₇ catalysts under tight contact conditions. TPO profiles (a) and stability tests (b) of 4% CuO/La₂Sn₂O₇ over five continuous TPO cycles.

Above 4% CuO loading, further increasing the CuO loading had a marginal effect on the combustion activity, as shown by the nearly constant T_i , T_p , T_c , and ΔT_{i-p} values. This result strongly implies that the part of the CuO forming a sub-monolayer or monolayer on the La₂Sn₂O₇ support has a strong interaction with the support and plays a critical role in the activity of the catalysts. Above the monolayer dispersion capacity, the excess CuO begins to form as micro-sized crystallites on the catalyst surface, and these are less active than the highly dispersed interfacial CuO species.

Our former study revealed that pure crystalline CuO without any support is also active for soot oxidation but suffers from low stability [28]. To solve this problem, SnO₂ synthesized by chemical vapor deposition (CVD) has been used as the support for CuO. This support increases the stability of the prepared CuO/SnO₂ catalysts significantly but decreases the activity [29]. However, compared with the most active 5% CuO/SnO₂ catalyst, the most active 4% CuO/La₂Sn₂O₇ catalyst in this study exhibits much higher activity, as shown by the obviously decreased T_i and T_p values at around 70 °C. This strongly indicates that, although La₂Sn₂O₇ has a lower surface area than the CVD SnO₂ (32 m² g⁻¹), it is a better support for CuO. Notably, on both

supports, the monolayer dispersion capacity affects the activity. For the 5% CuO/SnO₂ catalyst, the CuO monolayer has an intimate interaction with the SnO₂ support, possibly via Cu–O–Sn interfacial bonds [40]. Thus, it is reasonable to presume that the CuO monolayer might have a stronger interaction with La₂Sn₂O₇, as indicated by the significant shift in the binding energies of Cu and Sn in opposite directions, which is not observed in the CuO/SnO₂ catalysts [29]. Indeed, this might be caused by the co-presence of La and Sn cations in the La₂Sn₂O₇ support.

In particular, the thermal oxidation of soot without a catalyst resulted in a low CO₂ selectivity of 68%, and is further increased to 89% by the incorporation of the La₂Sn₂O₇ support. For the CuO/La₂Sn₂O₇ catalysts, the CO₂ selectivity was further improved above 90%. For the most active 4% CuO/La₂Sn₂O₇ catalyst, the selectivity reached 97%, indicating that the soot particles were almost completely oxidized.

Because soot combustion is a strongly exothermic process, the thermal stability of a catalyst is important and determines its applications. Therefore, five consecutive TPO activity tests were performed on the most active 4% CuO/La₂Sn₂O₇ catalyst to evaluate its practical applicability. As shown in Fig. 4(b), during the five runs, T_i , T_p , T_c , and ΔT_{i-p} remained nearly constant, which indicates that the catalyst has good thermal resistance, stable catalytic performance, and potential for soot elimination from diesel exhaust.

In summary, the results strongly indicate that the presence of a monolayer dispersion threshold effect on the soot oxidation activity of the CuO/La₂Sn₂O₇ system. In addition, the catalyst surface active sites, such as O₂⁻ and O₂²⁻ anions, could play a critical role in the reaction. Finally, the catalysts demonstrate stable performance for the target reaction.

3.5. Raman spectroscopy measurements

Raman spectroscopy is an effective technique to distinguish the phase structures of A₂B₂O₇ compounds [35,50]. The

Table 2

Soot combustion activity on the CuO/La₂Sn₂O₇ catalysts.

Sample	T_i (°C)	T_p (°C)	T_c (°C)	ΔT_{i-p} (°C)	S_{CO_2} (%)
Soot	530	640	690	110	68
La ₂ Sn ₂ O ₇	425	525	600	100	89
1% CuO/La ₂ Sn ₂ O ₇	420	515	590	95	92
2% CuO/La ₂ Sn ₂ O ₇	420	500	580	80	93
3% CuO/La ₂ Sn ₂ O ₇	400	490	565	90	94
4% CuO/La ₂ Sn ₂ O ₇	395	460	535	65	97
5% CuO/La ₂ Sn ₂ O ₇	395	470	540	75	96
6% CuO/La ₂ Sn ₂ O ₇	400	470	545	70	96
7% CuO/La ₂ Sn ₂ O ₇	400	475	550	75	95
8% CuO/La ₂ Sn ₂ O ₇	405	475	550	70	95
9% CuO/La ₂ Sn ₂ O ₇	405	480	555	75	95

well-ordered $A_2B_2O_7$ cubic pyrochlore phase belongs to a $Fd-3m$ space group, and, on the basis of group theory, there are six Raman active modes distributed as $A_{1g} + E_g + 4F_{2g}$ [34,51,52]. As shown in Fig. 5(a), all six typical Raman bands are clearly observed for the $La_2Sn_2O_7$ support, proving that a well-ordered pyrochlore phase is present in the bulk [34]. For comparison, the Raman spectra of the pure CuO sample was also collected, and the spectrum exhibits three typical Raman bands belonging to monoclinic CuO: 274 cm^{-1} for A_g and 322 and 608 cm^{-1} for B_g [28,53]. The Raman bands of CuO are much weaker than those of the $La_2Sn_2O_7$ support, which could be the reason why the characteristic Raman peaks of CuO are not observed in the spectra of the CuO/ $La_2Sn_2O_7$ catalysts with different CuO loadings.

Interestingly, even with the dispersion of a small amount of CuO on the $La_2Sn_2O_7$ support, the Raman peaks of the pyrochlore phase broadened, accompanied by the disappearance of two F_{2g} peaks at 335 and 525 cm^{-1} , as shown by the spectrum of the sample containing 1% CuO. Below the monolayer dispersion capacity, on increasing the CuO content, the Raman peaks of the pyrochlore support continued to shift to lower wavenumbers, and their intensities continuously decreased. This is probably caused by the increase of the coverage of the $La_2Sn_2O_7$ surface by the highly dispersed CuO until the monolayer dispersion capacity is reached. Moreover, these results also indicate that there is a strong interaction between the sub-monolayer/monolayer CuO and the $La_2Sn_2O_7$ support [54,55]. In contrast, when the CuO content was higher than the monolayer dispersion capacity (i.e., > 4.3%), the positions of the three typical Raman peaks of $La_2Sn_2O_7$ remained nearly constant, indicating that the excess CuO was located over the initially formed CuO monolayer as micro-sized crystallites, thus having a much weaker interaction with the support. Consequently, the monolayer dispersion threshold effect was also observed in the Raman spectra, which is consistent with the results of the XRD, XPS, and HRTEM measurements.

In addition, as shown in Fig. 5(b), superoxide (O_2^-) species

were observed on the surfaces of both the $La_2Sn_2O_7$ support and CuO/ $La_2Sn_2O_7$ catalysts, as indicated by the Raman band at 1050 cm^{-1} [35]. As discussed above, the $La_2Sn_2O_7$ support with a pyrochlore structure possesses intrinsic 8a oxygen vacancies, which can facilitate the creation of surface active oxygen anions/sites [35]. The addition of CuO on the surface obviously enhances the formation of the active oxygen anions, especially when CuO is in the sub-monolayer and monolayer states, as shown by the experimental evidence in the following sections.

3.6. H_2 -TPR, O_2 -TPD, and soot-TPR studies

H_2 -TPR experiments were conducted to identify the redox characteristics of the samples, and the corresponding profiles are shown in Fig. 6. Pure CuO shows an asymmetric peak at around 270 $^{\circ}C$ arising from the reduction of CuO to Cu_2O and, subsequently, to Cu^0 [28]. The $La_2Sn_2O_7$ support displays a small peak around 645 $^{\circ}C$, which is ascribed to the reduction of the residual amount of SnO_2 to metallic Sn. Our previous study has demonstrated that, for the synthesis of $A_2B_2O_7$ compounds with Sn cations as the B-site, a residual amount of free SnO_2 is always formed, even if the A-site precursor is in excess because of the incomplete reaction limited by equilibrium [38]. Because of the H_2 spillover effect on the formed metallic Cu, the reduction of this free SnO_2 occurs at lower temperatures in all CuO/ $La_2Sn_2O_7$ samples.

For all the CuO/ $La_2Sn_2O_7$ samples, a low-temperature peak attributed to CuO reduction was observed, as also validated by the quantitative O/Cu molar ratio in Table S1. On increasing the CuO loading, the CuO reduction peak gradually shifted to higher temperatures, accompanied by an increase in the integrated areas, which shows that CuO agglomerates slowly into micro-sized crystallites. The micro-sized CuO crystallites on the $La_2Sn_2O_7$ support show slightly higher reduction temperatures than the bulk CuO, reflecting the interaction between CuO and the support.

To elucidate the characteristics of the oxygen species,

Fig. 5. Raman spectra of the CuO/ $La_2Sn_2O_7$ catalysts. (a) From 150 to 800 cm^{-1} ; (b) in an enlarged region from 800 to 1300 cm^{-1} .

Fig. 6. H_2 -TPR profiles of the $CuO/La_2Sn_2O_7$ catalysts.

O_2 -TPD measurements were used to analyze the $CuO/La_2Sn_2O_7$ catalysts. As shown in Fig. 7(a), multiple oxygen desorption peaks were detected in the TPD profiles of all catalysts, indicating the presence of oxygen species in different chemical environments. Here, the peaks are classified into three groups according to their observed temperatures. The peak below 400 °C is defined as the α peak and could correspond to loosely bound surface oxygen sites [29,35]. Because the profile of the pure $La_2Sn_2O_7$ support also contains this desorption peak, the corresponding oxygen species are believed to be induced by the intrinsic 8a oxygen vacancies in the pyrochlore $La_2Sn_2O_7$ structure [35].

The peak at 400–600 °C is defined as the β peak. Because this desorption peak is not observed in the pure $La_2Sn_2O_7$ support, it is related to the existence of the surface CuO component. On the basis of the catalyst structure analyzed above, there is a high possibility that this peak could be related to the interfacial oxygen species formed at the dispersed CuO and $La_2Sn_2O_7$ interface. The quantification results in Table 3 show that the quantity of the oxygen species increased with increase in CuO content until 4%. However, further increasing the CuO

loading above the monolayer dispersion capacity reduced the amount of these oxygen species slightly.

The peaks above 600 °C are defined as the γ group and can be attributed to the removal of some facile surface lattice oxygen species [35]. Notably, the profile of $La_2Sn_2O_7$ pyrochlore alone also contains this peak, indicating that some of its surface lattice oxygen species can be desorbed at high temperatures. With the addition of CuO up to 4%, which is close to the monolayer capacity, the peaks become significantly larger, indicating that, in these samples, this desorption peak arises from the breakage of the $Cu-O$ bonds in the micro-sized CuO crystallites. Thus, the soot oxidation results shown in Fig. 4 and listed in Table 2 reveal that the activity of the catalysts remains nearly constant above the monolayer dispersion capacity; hence, these oxygen species contribute only marginally to the reaction performance.

Indeed, the quantification results in Table 3 reveal a correlation between the catalytic activity and the total amount of oxygen desorption determined from the α and β peaks, indicating that the oxygen species desorbed below 600 °C mainly account for the soot oxidation activity. The most active catalyst (4% $CuO/La_2Sn_2O_7$) in this study contains the largest quantity of total desorbed active oxygen species in this temperature region.

To determine the reactivity between soot particles and the active oxygen sites directly, soot-TPR experiments were carried out using the $CuO/La_2Sn_2O_7$ samples without gas phase O_2 . As shown in Fig. 7(b), multiple soot reduction peaks were obtained, and these can be divided into the α and β groups. The peak below 440 °C is defined as the α group, which is attributed to the active oxygen species on the catalyst that make the main contribution to soot oxidation. Table 3 shows that the pure $La_2Sn_2O_7$ support also contains a small amount of α oxygen species, and the addition of CuO improves the amount of α oxygen species significantly. With increase in the CuO loading up to 4%, the α oxygen species reaches a maximum, which is consistent with the soot TPO activity.

The peaks above 440 °C are defined as the β group. When the CuO loading was greater than 4%, two soot reduction peaks

Fig. 7. O_2 -TPD (a) and soot-TPR (b) profiles of the $CuO/La_2Sn_2O_7$ catalysts.

Table 3Quantified O_2 -TPD and soot-TPR results for the $CuO/La_2Sn_2O_7$ catalysts.

Samples	O_2 -TPD			Soot-TPR
	Oxygen from α peak ($\mu\text{mol g}^{-1}$)	Oxygen from β peak ($\mu\text{mol g}^{-1}$)	Active oxygen ($\mu\text{mol g}^{-1}$)	Oxygen uptake from α peak (a.u.)
$La_2Sn_2O_7$	3.56	—	3.56	12.3
1% $CuO/La_2Sn_2O_7$	4.27	11.41	15.68	25.2
3% $CuO/La_2Sn_2O_7$	4.70	15.51	20.21	38.5
4% $CuO/La_2Sn_2O_7$	5.70	35.21	40.91	100.0
5% $CuO/La_2Sn_2O_7$	7.98	29.14	37.12	82.9
7% $CuO/La_2Sn_2O_7$	5.56	27.47	33.03	78.4
9% $CuO/La_2Sn_2O_7$	6.13	25.24	31.37	72.4

were clearly observed, and these are obviously related to the formed CuO crystallites. Our former studies have demonstrated that four kinds of surface oxygen species reactive to soot particles are always present on pure crystalline CuO samples prepared in different ways [28]. However, the two kinds of sites reactive to soot particles above 500 °C make a negligible contribution to soot oxidation. Thus, it is reasonable to believe that the oxygen species related to the β peaks have little effect on the activity. Indeed, this explains why increasing the CuO loading above the monolayer dispersion capacity does not enhance the activity of the $CuO/La_2Sn_2O_7$ catalysts.

In summary, both the O_2 -TPD and soot-TPR measurements confirm that the monolayer dispersion threshold affects the activity. The interaction between sub-monolayer/monolayer CuO with the $La_2Sn_2O_7$ support can create active interfacial oxygen species, which reach a maximum at the monolayer dispersion capacity, generating a catalyst with the best reaction performance for soot combustion.

3.7. *In situ* DRIFTS studies

In situ DRIFTS experiments were carried out to identify the oxygen sites generated on the catalyst surface with 4% $CuO/La_2Sn_2O_7$, the best catalyst in this study. The sample was treated first at 400 °C in a 30 mL min^{-1} 99.99% Ar flow for 1 h to eliminate any surface pollutants, and the gas flow was then changed to a 10% O_2 /Ar flow without changing the temperature. In Fig. 8(a), two bands at 1083 and 1058 cm^{-1} can be observed, and these can be assigned to surface O_2^- anions [35]. In addition, another band at 867 cm^{-1} can also be seen, and this is attributable to O_2^{2-} anions on the catalyst surface [37].

After 30 min, when the bands became stable, the catalyst was immediately exposed to a 30 mL min^{-1} 10% H_2 /Ar flow at 400 °C. As shown in Fig. 8(b), the intensity of all bands decreased gradually with increase in time, and the bands nearly disappeared after 20 min, proving that the O_2^- anions are reactive to and reducible by H_2 . Following this step, the catalyst was re-exposed to the 10% O_2 /Ar feed at 400 °C. As shown in Fig. 8(c), after 8 min, the IR bands corresponding to surface O_2^- and O_2^{2-} anions were fully restored. Thus, the *in situ* DRIFTS measurements provide strong evidence that the 4% $CuO/La_2Sn_2O_7$ catalyst is covered by a CuO monolayer and both active surface O_2^- and O_2^{2-} sites were generated, which are favorable for soot combustion.

3.8. XPS studies

XPS measurements of the catalysts were carried out to explore the surface oxygen properties. Hence, the O 1s spectra were deconvoluted and fitted, as shown in Fig. 9. The asymmetric peak shapes suggest that various oxygen anions in different chemical environments are present on the surfaces of the catalysts. As shown by the Raman and *in situ* DRIFTS results, both active O_2^- and O_2^{2-} were generated on the $CuO/La_2Sn_2O_7$ catalysts. Therefore, the O 1s spectra were fitted to three peak components corresponding to O_2^- (532.6–532.9 eV), O_2^{2-} (531.4–531.6 eV), and O^{2-} (529.7–529.9 eV) [56,57].

The relative amount of the surface oxygen anions together with the corresponding binding energies are listed in Table 4. Furthermore, the $(O_2^- + O_2^{2-})/O^{2-}$ ratios of the samples, which indicate the reactivity of the catalysts, are also listed in the table. Again, a threshold effect is clear. In detail, when the CuO

Fig. 8. *In situ* DRIFTS spectra showing the effects on the surface oxygen sites on 4% $CuO/La_2Sn_2O_7$ at 400 °C after pretreatment at 400 °C in an Ar feed for 1 h. (a) In a 10% O_2 /Ar feed; (b) in a 10% H_2 /Ar feed; (c) after re-exposure to the 10% O_2 /Ar feed.

Fig. 9. XPS O 1s spectra of the CuO/La₂Sn₂O₇ catalysts.

loading is lower than 4.3%, i.e., the monolayer dispersion capacity, the $(O_2^- + O_2^{2-})/O_2^-$ ratio increases with increase in CuO content and reaches maximum in 4% CuO/La₂Sn₂O₇. However, further increasing the amount of CuO above the monolayer dispersion capacity results in a slight reduction in the $(O_2^- + O_2^{2-})/O_2^-$ ratio because of the generation of CuO crystallites on top of the CuO monolayer. This result indicates that crystalline CuO is not favorable for the production of active electrophilic oxygen anions/sites.

To summarize the relationship between the reactivity and the concentrations of surface active oxygen sites/species distinguished by various techniques, T_p values for different catalysts were plotted against the $(O_2^- + O_2^{2-})/O_2^-$ XPS ratios, as well as the active oxygen quantities obtained by O₂-TPD and soot-TPR measurements (Fig. 10). In this figure, good and consistent correlations can be seen, and samples having more surface active oxygen anions/sites usually exhibit better soot combustion activity. Therefore, the quantity of surface O₂⁻ and O₂²⁻ determines the soot combustion activity of the CuO/La₂Sn₂O₇ catalysts [57,58]. In addition, Fig. 10 clearly shows the threshold effect on the activity, demonstrating that the most active catalyst can be designed by covering the surface of the La₂Sn₂O₇ support with a dispersion of CuO at the monolayer limit. As a result, 4% CuO/La₂Sn₂O₇, the sample possessing a CuO content close to the monolayer dispersion capacity, exhibits the best reaction performance among all the catalysts.

Fig. 10. Relationships between soot oxidation activity (T_p) and the amount of active oxygen identified by XPS, O₂-TPD, and soot-TPR measurements.

3.9. Bader charge and density of state analyses

In the XRD and HRTEM results, the (222) crystal plane of the cubic La₂Sn₂O₇ pyrochlore support was preferentially observed. Therefore, the (222) facet was selected as the model for use in DFT calculations of the CuO monolayer on the support surface. The calculations were performed in VASP. Bader charge calculations were performed on the optimized adsorption model, as shown in Fig. 11(a). A Cu atom was placed on the model surface, and it was found that this Cu atom loses 0.123 electrons. Simultaneously, La, Sn, and O gain 0.02, 0.095, and 0.008 electrons, respectively. Apparently, the supported Cu atom donates its electrons mainly to Sn in the La₂Sn₂O₇ support, which is consistent with the XPS results. Therefore, it is reasonable to conclude that a significant interaction is present between Cu and the support in the sub-monolayer/monolayer dispersion state, which predominantly occurs through the interaction of Cu with Sn, possibly by forming interfacial Cu–O–Sn bonds.

Fig. 11(b) shows the DOS close to the Fermi level for the CuO/La₂Sn₂O₇ system based on the optimized adsorption model shown in Fig. 11(a). It can be seen that the valence bands are mainly dominated by the O 2p orbitals [59] with relatively lower contributions from the Sn and Cu 3d orbitals. Interestingly, the orbitals of the La atom make no contribution to the valence bands. This strongly indicates that Cu interacts intimately with Sn on the surface of the La₂Sn₂O₇ pyrochlore sup-

Table 4
Quantified XPS O 1s results for the CuO/La₂Sn₂O₇ catalysts.

Sample	O 1s binding energy and relative amount (%)			$(O_2^- + O_2^{2-})/O_2^-$ ratio
	O ₂ ⁻	O ₂ ²⁻	O ₂ ⁻	
1% CuO/La ₂ Sn ₂ O ₇	532.8/7.6	531.5/43.5	529.8/48.9	1.05
3% CuO/La ₂ Sn ₂ O ₇	532.9/19.7	531.6/40.4	529.8/39.9	1.50
4% CuO/La ₂ Sn ₂ O ₇	532.7/16.2	531.5/54.4	529.7/29.4	2.40
5% CuO/La ₂ Sn ₂ O ₇	532.6/18.6	531.5/49.9	529.9/31.5	2.17
7% CuO/La ₂ Sn ₂ O ₇	532.8/21.3	531.4/46.2	529.7/32.5	2.08
9% CuO/La ₂ Sn ₂ O ₇	532.7/13.3	531.4/53.8	529.8/32.9	2.04

Fig. 11. Optimized configuration of the CuO/La₂Sn₂O₇ surface. (a) Electron transfer; (b) projected DOS distribution.

port, which is consistent with the XPS and Bader charge analysis. In brief, when CuO is supported over the pyrochlore support to generate a sub-monolayer or monolayer, strong interactions between CuO and the support occur. As a consequence, electron transfer and orbital hybridization between Cu, Sn and O atoms occurs, possibly generating Cu–O–Sn interface bonds and resulting in a monolayer dispersion threshold effect and activity enhancement of the catalyst.

4. Conclusions

To understand the dispersion behavior of a metal oxide on a composite oxide support and with the aim of developing catalysts for soot oxidation, CuO/La₂Sn₂O₇ catalysts with different CuO loadings were prepared on the basis of monolayer dispersion theory. Using various characterization techniques and DFT calculations, the surface and bulk structure properties of the samples were thoroughly explored.

(1) As for single component metal oxide supports, a spontaneous monolayer dispersion of CuO on the La₂Sn₂O₇ pyrochlore compound support was also achieved. By using XRD and XPS extrapolation methods, the monolayer dispersion capacity of CuO on the support was determined to be 1.90 mmol/100 m² La₂Sn₂O₇ surface. Below this capacity, CuO exists as a sub-monolayer or monolayer state. Above this capacity, CuO crystallites start to form over the initially formed CuO monolayer.

(2) XPS, Raman, Bader charge, and DOS analyses indicate that there are strong interactions between the sub-monolayer/monolayer state CuO and the La₂Sn₂O₇ support, mainly through the donation of electrons from Cu to Sn at the B-sites of the structure. In contrast, Cu has negligible interaction with La at the A-site. This suggests that the supported metal oxide preferentially interacts with one kind of metal cation in the composite oxide support.

(3) Raman spectroscopy, *in situ* DRIFTS, and XPS measurements confirmed the formation of both O₂⁻ and O₂²⁻ as the active sites on the surface of CuO/La₂Sn₂O₇ catalysts, whose amount determines the soot combustion activity of the catalysts. The quantity of active oxygen anions was increased by increasing the CuO loading until the monolayer dispersion capacity was reached. At loadings above the capacity, micro-sized CuO crystallites form, and these have negative effects on the generation of active surface oxygen sites.

(4) The most active CuO/La₂Sn₂O₇ catalyst was achieved by covering the surface of the La₂Sn₂O₇ support with a CuO monolayer.

References

- [1] M. Cortés-Reyes, C. Herrera, M. Á. Larrubia, L. J. Alemany, *Appl. Catal. B*, **2016**, 193, 110–120.
- [2] R. Kimura, J. Wakabayashi, S. P. Elangovan, M. Ogura, T. Okubo, *J. Am. Chem. Soc.*, **2008**, 130, 12844–12845.
- [3] Y. F. Yu, J. L. Ren, D. S. Liu, M. Meng, *ACS Catal.*, **2014**, 4, 934–941.
- [4] A. Bueno-López, *Appl. Catal. B*, **2014**, 146, 1–11.
- [5] A. M. Hernandez-Gimenez, D. L. Castello, A. Bueno-Lopez, *Chem. Pap.*, **2014**, 68, 1154–1168.
- [6] M. Piumetti, S. Bensaid, N. Russo, D. Fino, *Appl. Catal. B*, **2015**, 165, 742–751.
- [7] X. Wu, F. Lin, H. Xu, D. Weng, *Appl. Catal. B*, **2010**, 96, 101–109.
- [8] T. Andana, M. Piumetti, S. Bensaid, L. Veyre, C. Thieuleux, N. Russo, D. Fino, E. A. Quadrelli, R. Pirone, *Appl. Catal. B*, **2017**, 209, 295–310.
- [9] R. Matarrese, L. Castoldi, L. Lietti, P. Forzatti, *Catal. Today*, **2008**, 136, 11–17.
- [10] G. Pecchi, B. Cabrera, A. Buljan, E. J. Delgado, A. L. Gordon, R. Jimenez, *J. Alloys Compd.*, **2013**, 551, 255–261.
- [11] S. Putla, M. H. Amin, B. M. Reddy, A. Nafady, K. A. Al Farhan, S. K. Bhargava, *ACS Appl. Mater. Interfaces*, **2015**, 7, 16525–16535.
- [12] J. Liu, Z. Zhao, C. Xu, J. Liu, *Chin. J. Catal.*, **2019**, 40, 1438–1487.
- [13] Y. Wei, J. Liu, Z. Zhao, G. Jiang, A. Duan, H. He, X. Wang, *Chin. J.*

- Catal.*, **2010**, 31, 283–288.
- [14] J. Zheng, J. Liu, Z. Zhao, J. Xu, A. Duan, G. Jiang, *Catal. Today*, **2012**, 191, 146–153.
- [15] L. Tang, Z. Zhao, K. Li, X. Yu, Y. Wei, J. Liu, Y. Peng, Y. Li, Y. Chen, *Catal. Today*, **2020**, 339, 159–173.
- [16] L. J. Ai, Z. P. Wang, C. C. Cui, W. Liu, L. G. Wang, *Materials*, **2018**, 11, 16.
- [17] Z. Wang, H. Zhu, L. Ai, X. Liu, M. Lv, L. Wang, Z. Ma, Z. Zhang, *J. Colloid Interface Sci.*, **2016**, 478, 209–216.
- [18] I. Atribak, A. Bueno-Lopez, A. Garcia-Garcia, *Top. Catal.*, **2009**, 52, 2088.
- [19] K. Nagase, Y. Zheng, Y. Kodama, J. Kakuta, *J. Catal.*, **1999**, 187, 123–130.
- [20] G. G. Jernigan, G. A. Somorjai, *J. Catal.*, **1994**, 147, 567–577.
- [21] A. B. Lamb, W. C. Bray, J. C. W. Frazer, *J. Ind. Eng. Chem.*, **1920**, 12, 213–221.
- [22] C.-C. Chien, T.-J. Huang, *Ind. Eng. Chem. Res.*, **1995**, 34, 1952–1959.
- [23] K. Nakagawa, T. Ohshima, Y. Tezuka, M. Katayama, M. Katoh, S. Sugiyama, *Catal. Today*, **2015**, 246, 67–71.
- [24] F. E. López-Suárez, A. Bueno-López, M. J. Illán-Gómez, J. Trawczynski, *Appl. Catal. A*, **2014**, 485, 214–221.
- [25] B. M. Reddy, K. N. Rao, *Catal. Commun.*, **2009**, 10, 1350–1353.
- [26] G. Zhang, H. Chen, Y. Gong, Z. Shu, D. He, Y. Zhu, X. Zhou, X. Fan, H. Zhang, J. Shi, *Catal. Commun.*, **2013**, 35, 105–109.
- [27] Y. Yu, M. Meng, F. Dai, *Nanoscale*, **2013**, 5, 904–909.
- [28] J. Shen, C. Rao, Z. Fu, X. Feng, J. Liu, X. Fan, H. Peng, X. Xu, C. Tan, X. Wang, *Appl. Surf. Sci.*, **2018**, 453, 204–213.
- [29] J. Shen, X. Feng, R. Liu, X. Xu, C. Rao, J. Liu, X. Fang, C. Tan, Y. Xie, X. Wang, *Chin. J. Catal.*, **2019**, 40, 905–916.
- [30] F. Zhong, L. Shi, J. Zhao, G. Cai, Y. Zheng, Y. Xiao, J. Long, *Ceram. Int.*, **2017**, 43, 11799–11806.
- [31] D. Liang, H. Liu, N. Liu, L. Ling, Y. Han, L. Zhang, C. Zhang, *Ceram. Int.*, **2016**, 42, 4562–4566.
- [32] J. Xu, R. Xi, X. Xu, Y. Zhang, X. Feng, X. Fang, X. Wang, *J. Rare Earths*, **2020**. doi: 10.1016/j.jre.2020.01.002.
- [33] L. J. Ai, Z. P. Wang, Y. B. Gao, C. C. Cui, B. Q. Wang, W. Liu, L. G. Wang, *J. Mater. Sci.*, **2019**, 54, 4495–4510.
- [34] J. Zhang, D. Wang, L. Lai, X. Fang, J. Xu, X. Xu, X. Zhang, J. Liu, H. Peng, X. Wang, *Catal. Today*, **2019**, 327, 168–176.
- [35] J. W. Xu, Y. Zhang, X. L. Xu, X. Z. Fang, R. Xi, Y. M. Liu, R. Y. Zheng, X. Wang, *ACS Catal.*, **2019**, 9, 4030–4045.
- [36] X. Zhang, X. Fang, X. Feng, X. Li, W. Liu, X. Xu, N. Zhang, Z. Gao, X. Wang, W. Zhou, *Catal. Sci. Technol.*, **2017**, 7, 2729–2743.
- [37] Y. Zhang, J. Xu, X. Xu, R. Xi, Y. Liu, X. Fang, X. Wang, *Catal. Today*, **2019**.
- [38] J. S. Tian, H. G. Peng, X. L. Xu, W. M. Liu, Y. H. Ma, X. Wang, X. J. Yang, *Catal. Sci. Technol.*, **2015**, 5, 2270–2281.
- [39] Y.-C. Xie, Y.-Q. Tang, *Adv. Catal.*, **1990**, 37, 1–43.
- [40] G. Deo, I. E. Wachs, *J. Catal.*, **1994**, 146, 323–334.
- [41] B. M. Weckhuysen, I. E. Wachs, R. A. Schoonheydt, *Chem. Rev.*, **1996**, 96, 3327–3350.
- [42] J. Song, L. Xu, C. Y. Zhou, R. Q. Xing, Q. L. Dai, D. L. Liu, H. W. Song, *ACS Appl. Mater. Interfaces*, **2013**, 5, 12928–12934.
- [43] S. Masudy-Panah, R. Siavash Moakhar, C. S. Chua, A. Kushwaha, G. K. Dalapati, *ACS Appl. Mater. Interfaces*, **2017**, 9, 27596–27606.
- [44] X. Y. Bi, K. L. Yang, *Langmuir*, **2007**, 23, 11067–11073.
- [45] W. Luc, C. Collins, S. W. Wang, H. L. Xin, K. He, Y. J. Kang, F. Jiao, *J. Am. Chem. Soc.*, **2017**, 139, 1885–1893.
- [46] S. Yim, T. Kim, B. Yoo, H. Xu, Y. Youn, S. Han, J. K. Jeong, *ACS Appl. Mater. Interfaces*, **2019**, 11, 47025–47036.
- [47] W. Grunert, U. Sauerlandt, R. Schlögl, H. G. Karge, *J. Phys. Chem.*, **1993**, 97, 1413–1419.
- [48] J. Y. Zhang, G. Q. Zhu, S. P. Li, F. Rao, H. Qadeer-Ul, J. Z. Gao, Y. Huang, M. Hojamberdiev, *ACS Appl. Mater. Interfaces*, **2019**, 11, 37822–37832.
- [49] J. Liang, Z. Zhang, K. Wu, Y. Shi, W. Pu, M. Yang, Y. Wu, *Fuel Process. Technol.*, **2019**, 188, 153–163.
- [50] B. P. Mandal, P. S. R. Krishna, A. K. Tyagi, *J. Solid State Chem.*, **2010**,

Graphical Abstract

Chin. J. Catal., 2021, 42: 396–408 doi: 10.1016/S1872-2067(20)63657-9

Stable CuO/La₂Sn₂O₇ catalysts for soot combustion: Study on the monolayer dispersion behavior of CuO over a La₂Sn₂O₇ pyrochlore support

Xiaohui Feng, Rui Liu, Xianglan Xu, Yunyan Tong, Shijing Zhang, Jiacheng He, Junwei Xu, Xiuzhong Fang, Xiang Wang*
Nanchang University

Active surface O₂²⁻ and O₂⁻ sites determine the soot combustion activity on CuO/La₂Sn₂O₇. The best catalyst can be obtained by covering La₂Sn₂O₇ surface with a CuO monolayer.

- 183, 41–45.
- [51] M. T. Vandenborre, E. Husson, J. P. Chatry, D. Michel, *J. Raman Spectrosc.*, **1983**, 14, 63–71.
- [52] L. G. Kong, I. Karatchevtseva, M. G. Blackford, N. Scales, G. Triani, *J. Am. Ceram. Soc.*, **2013**, 96, 2994–3000.
- [53] L. Debbichi, M. C. Marco de Lucas, J. F. Pierson, P. Kruger, *J. Phys. Chem. C*, **2012**, 116, 10232–10237.
- [54] V. Kumar, R. Sharma, S. Kumar, M. Kaur, J. D. Sharma, *Ceram. Int.*, **2019**, 45, 20386–20395.
- [55] A. López Cámara, V. Cortés Corberán, A. Martínez-Arias, L. Barrio, R. Si, J. C. Hanson, J. A. Rodriguez, *Catal. Today*, **2020**, 339, 24–31.
- [56] C. Cao, L. Xing, Y. Yang, Y. Tian, T. Ding, J. Zhang, T. Hu, L. Zheng, X. Li, *Appl. Catal. B*, **2017**, 218, 32–45.
- [57] P. Yao, J. He, X. Jiang, Y. Jiao, J. Wang, Y. Chen, *J. Energy Inst.*, **2020**, 93, 774–783.
- [58] J. Xiong, X. Mei, J. Liu, Y. Wei, Z. Zhao, Z. Xie, J. Li, *Appl. Catal. B*, **2019**, 251, 247–260.
- [59] C. G. Liu, Y. H. Li, Y. D. Li, L. Y. Dong, J. Wen, D. Y. Yang, Q. L. Wei, P. Yang, *J. Nucl. Mater.*, **2018**, 500, 72–80.

构建稳定的CuO/La₂Sn₂O₇催化剂用于碳烟颗粒燃烧: CuO在La₂Sn₂O₇烧绿石复合氧化物载体上的单层分散行为

冯小辉, 刘 瑞, 徐香兰, 佟云艳, 张诗婧, 何佳城, 徐骏伟, 方修忠, 王 翔*

南昌大学化学学院, 江西省环境与能源催化重点实验室, 江西南昌330031

摘要: 柴油车尾气排放的碳烟颗粒造成了日益严重的环境污染。目前催化燃烧是消除碳烟颗粒污染的有效技术。针对金属氧化物负载体系, 20世纪70年代末谢有畅教授等人提出了单层分散理论, 是指导设计高效负载催化剂的一个重要思想, 已被科研工作者们普遍接受。当负载催化剂体系用于某个特定反应时, 通常会表现出单层分散阈值效应, 即负载的活性组含量为单层分散阈值时, 催化剂往往具有最好的活性和选择性。

为探究金属氧化物在复合氧化物载体上的分散行为, 并期望研制出性能优良的碳烟颗粒消除催化剂, 本文制备了系列不同负载量的CuO/La₂Sn₂O₇催化剂, 并把实验表征技术和DFT计算方法相结合, 对其构效关系进行了研究。结果表明, CuO可自发分散在La₂Sn₂O₇烧绿石载体, 其单层分散容量为1.90 mmol CuO/100 m² La₂Sn₂O₇。CuO负载量不高于该容量时, 以亚单层或单层分散状态存在。XPS、Raman、Bader电荷和DOS分析证明, 亚单层/单层CuO中的Cu²⁺离子可把其电荷选择性地传递给La₂Sn₂O₇烧绿石载体结构中B位的Sn⁴⁺离子, 因而与载体产生强相互作用。反之, Cu²⁺离子与载体结构中A位的La³⁺离子之间无电荷转移, 不产生作用。这表明在含多种金属离子的复合氧化物载体上, 被负载的金属氧化物可优先与载体中的一种金属离子产生相互作用。Raman、原位DRIFTS和XPS结果表明, 在界面上形成的O₂⁻和O₂²⁻亲电氧离子是CuO/La₂Sn₂O₇催化剂表面的活性中心, 其含量决定了催化剂碳烟颗粒燃烧的活性。在CuO负载量低于单层分散容量时, 这些表面活性亲电氧离子含量随着CuO的负载量升高而增加, 直至单层分散容量时达到最大。在CuO负载量高于单层分散容量时, CuO微晶开始形成, 并对表面活性亲电氧离子的生成产生负面影响。上述结果表明, CuO/La₂Sn₂O₇催化剂用于碳烟颗粒燃烧具有明显的单层分散阈值效应; 并可通过在La₂Sn₂O₇载体表面负载单层分散量的CuO获得活性最佳的催化剂。

关键词: CuO/La₂Sn₂O₇催化剂; 碳烟燃烧; DFT计算; 优先相互作用; 烧绿石载体上的单层分散; O₂⁻和O₂²⁻活性位点

收稿日期: 2020-05-11. 接受日期: 2020-06-20. 出版日期: 2021-03-05.

*通讯联系人. 电话: 15979149877; 电子信箱: xwang23@ncu.edu.cn

基金来源: 国家自然科学基金(21962009, 21567016, 21666020); 国家重点研发计划(2016YFC0209302); 江西省自然科学基金(20181ACB20005, 20171BAB213013, 20181BAB203017); 江西省环境与能源催化重点实验室(20181BCD40004).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).