available at www.sciencedirect.com

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

Article

Three-dimensionally ordered macroporous SnO₂-based solid solution catalysts for effective soot oxidation

Cheng Rao ^{a,†}, Rui Liu ^{a,†}, Xiaohui Feng ^a, Jiating Shen ^a, Honggen Peng ^a, Xianglan Xu ^a,
Xiuzhong Fang ^a, Jianjun Liu ^b, Xiang Wang ^{a,*}

^a Institute of Applied Chemistry, College of Chemistry, Nanchang University, Nanchang 330031, Jiangxi, China

^b Jiangxi Baoan New Material Technology Corporation, Ltd, Pingxiang 337000, Jiangxi, China

ARTICLE INFO

Article history:

Received 28 April 2018

Accepted 28 May 2018

Published 5 October 2018

Keywords:

Three-dimensionally ordered
macroporous catalyst

Soot combustion

SnO₂ solid solution

Lattice doping

Oxygen vacancies

ABSTRACT

A series of three-dimensionally ordered macroporous (3DOM) SnO₂-based catalysts modified by the cations Ce⁴⁺, Mn³⁺, and Cu²⁺ have been prepared by using a colloidal crystal templating method and tested for soot combustion under loose contact condition. XRD and STEM mapping results confirm that all the secondary metal cations have entered the lattice matrix of tetragonal rutile SnO₂ to form non-continuous solid solutions, thus impeding crystallization and improving the surface areas and pore volumes of the modified catalysts. In comparison with regular SnO₂ nanoparticles, the 3DOM SnO₂ displays evidently improved activity, testifying that the formation of the 3DOM structure can anchor the soot particulates in the macro-pores, which ensures that the contact of the soot particles with the active sites on the 3DOM skeleton is more easily formed, thus benefiting the target reaction. With the incorporation of the secondary metal cations, the activity of the catalyst can be further improved due to the formation of more abundant mobile oxygen species. In summary, these effects are believed to be the major factors responsible for the activity of the catalyst.

© 2018, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Soot particulate emitted from diesel engines is one of the most hazardous pollutants that threatens the health of people and harms the environment [1,2]. For the elimination of soot particles, the combination of diesel particulate filter and oxidation catalysts [3,4] is the most efficient after-treatment technique developed to date. An efficient soot combustion catalyst should typically have a certain surface area and porous structure that permits adequate interactions with the soot particu-

lates in the form of a solid-solid-gas reaction. Three-dimensionally ordered macroporous (3DOM) materials [5–8] with big pore sizes (>50 nm) permit solid reactants to enter the pores and develop sufficient contact with the active sites. Recently, it was reported that 3DOM materials such as Co₃O₄ [9], Ce-Zr-O_x [10], LaFeO₃ [11], and LaMnO₃ [12] showed good catalytic activity for several heterogeneous catalytic reactions, including soot combustion [13–16]. Zhao et al. [11] reported that 3DOM Au/LaFeO₃ catalysts prepared with three-dimensional structural supports and containing nano-

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

[†] These authors contributed equally.

This work was supported by the Natural Science Foundation of China (21567016, 21503106), the Natural Science Foundation of Jiangxi Province (20171BAB213013), the Education Department Foundation of Jiangxi Province (KJLD14005), National Key Research and Development Program of China (2016YFC0209302), the Innovation Fund Designated for Graduate Students of Jiangxi Province (YC2015-B017) and the Innovation Fund Designated for Undergraduate Students of China (201701035)

DOI: 10.1016/S1872-2067(18)63123-7 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 10, October 2018

particle active sites might be useful in fundamental research on metal-support synergistic effect, and also has potential for applications in the catalytic oxidation of solid particles. Dai et al. [17] found that three-dimensional macroporous perovskites exhibited excellent catalytic activity for methane combustion, because the unique nanovoid 3D structure of the catalysts can provide larger surface areas and pore volumes, uniform pore sizes, higher accessible surface oxygen concentrations, and better low-temperature reducibility in comparison to regular samples.

SnO_2 is an n-type semiconductor metal oxide having both reactive surface-deficient oxygen and lattice oxygen. Furthermore, its melting point is as high as 1630 °C, proving it has good chemical and thermal stability. All these factors indicate that it is a promising and potential catalytic material [18]. Therefore, over the past five years, our group has systematically investigated the catalytic chemistry of SnO_2 for various reactions [19–21]. It was found that SnO_2 with a rod shape showed the reaction behavior of supported precious metals because of preferentially exposed (110) facets [19]. Moreover, doping the lattice of SnO_2 nano-rods with a small amount of In, Cr, and Al cations can further enhance its activity, as evaluated for the complete oxidation of toluene. An Al-doped $\text{Sn}_{99}\text{Al}_1$ rod shows the highest activity among all the catalysts owing to its optimized surface-active oxygen species and acidic sites [20]. If the crystal matrix of SnO_2 is modified by suitable amounts of Nb and Mn cations to form pure rutile tetragonal structured solid solutions, the best activity can be generally obtained for CO and CH_4 oxidation [22]. Based on our work, we have developed an easy and reliable X-ray diffraction (XRD) extrapolation method for the first time to evaluate the lattice capacity of a solute cation in a solvent metal oxide lattice [23].

Some other researchers have used SnO_2 -based materials for different catalytic reactions. Li et al. [24] reported that a Ce-Sn binary oxide catalyst revealed promising activity for the selective reduction of NO by NH_3 . The major reason for this is the synergistic effect between the Ce and Sn oxides, which not only enhances the redox property of the catalyst but also increases its Lewis acidity, thus promoting the adsorption and activation of the NH_3 reactant. In addition, it was revealed by another group that Ce-doped SnO_2 catalysts were also active for methane combustion. The surface Sn^{4+} cations are found to be the active sites, and the surface lattice oxygen species plays an important role in determining the activity [25]. Our studies also testified that the catalytic performance of SnO_2 could be enhanced by substituting a fraction of the Sn^{4+} ions in the crystal lattice with other cations such as Ce^{4+} [26], Mn^{3+} [22], and Cu^{2+} [27] to form solid solutions having the tetragonal rutile structure, which improves oxygen mobility, thermal stability, and eventually, the activity for CO and CH_4 oxidation.

In recent years, 3DOM SnO_2 materials have been used for gas sensing [28–31], anodes for Li-ion batteries [32], photoanodes for dye-sensitized solar cells [33], electrodes for degrading benzoic acid [34] and as catalysts for Suzuki cross coupling reactions [35]. For instance, O'Dwyer et al. [35] reported that Pd nanoparticles highly dispersed on ordered SnO_2 IO supports showed superior catalytic performance for liq-

uid-phase Suzuki coupling reactions and allow the easy removal of the catalyst substrate after the reaction. Compared to the commercialized Pd/C catalysts, a higher mass electrocatalytic activity is also demonstrated over SnO_2 -Pd IOs for formic acid oxidation, which is due to better access of the reactants to the active sites. However, the study on using 3DOM- SnO_2 -based materials for soot combustion has not been reported yet. It is reasonably presumed that doping the lattice matrix of SnO_2 with other transition metals such as Cu^{2+} , Mn^{3+} , or Ce^{4+} to form a solid solution and then developing them into a 3DOM structure could enhance the activity of the resulting catalysts for soot combustion. Therefore, in this study, a series of Cu-, Mn-, or Ce-doped SnO_2 solid solution catalysts with 3DOM structures have been prepared and used for soot particulate combustion. Indeed, it has been revealed that with the modification of the SnO_2 matrix by Ce^{4+} , Mn^{3+} , or Cu^{2+} and the formation of the 3DOM structure, the soot combustion activity of the prepared catalysts evidently improved; among these, the Cu-modified catalyst exhibits the best promotional effect. Using different characterization techniques, the influence of the 3DOM solid solution structure on the properties of SnO_2 catalysts has been analyzed and elucidated, and correlated with their soot combustion activities.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of PMMA colloidal crystal templates

Volumes of 115 mL of PMMA (Guoyao, CP) monomer and 1300 mL of distilled deionized (DDI) water were added to a 3000 mL three-necked round-bottomed flask. A N_2 flow rate of 100 mL min^{-1} through the flask was used to remove the air inside it, and the mixture was constantly stirred magnetically. The temperature of the reaction system was controlled at 70 °C; 50 mL of a potassium persulfate solution (0.03 mol L^{-1}) was added to the mixture to initiate the polymerization reaction, and held at this temperature for 60 min. Afterwards, it was cooled to room temperature. The solution mixture containing

Fig. 1. SEM images of the PMMA template (A) and 3DOM- SnO_2 (B). TEM images of 3DOM- SnO_2 (C), 3DOM- Ce_1Sn_9 (D), 3DOM- Mn_1Sn_9 (E), and 3DOM- Cu_1Sn_9 (F).

monodispersed PMMA microspheres was then centrifuged at the rate of 4500 r min⁻¹ for 50 min to obtain the PMMA precipitate, which was then dispersed in DDI water and dried using an 80 °C water bath to obtain the final highly ordered PMMA colloidal crystal templates (Fig. 1(A)).

2.1.2. Synthesis of 3DOM-SnO₂

The unmodified 3DOM-SnO₂ sample was prepared via the thermal decomposition of the Sn precursor and the PMMA template mixture. In detail, SnCl₄·5H₂O (Guoyao, AR) was dissolved in a certain amount of DDI water to form a stable solution (0.1 mol L⁻¹). Then, 5 g PMMA templates were permeated into 5 mL of this Sn precursor solution for 2 h, and the solution was filtered and dried at room temperature. Subsequently, the dried PMMA colloidal crystal templates containing the Sn precursor were calcined, with the temperature increasing linearly at 1 °C min⁻¹ to 300 °C and kept for 2 h in N₂ flow, before cooling to room temperature. After this, the sample was calcined again by increasing the temperature at the rate of 1 °C min⁻¹ to 700 °C and maintaining it for 4 h in air flow.

2.1.3. Synthesis of 3DOM-M₁Sn₉

Ce⁴⁺, Mn³⁺, and Cu²⁺-doped 3DOM-SnO₂ were synthesized by similar processes, except that the SnCl₄·5H₂O precursor was dissolved with a certain amount of Ce (NO₃)₃·6H₂O (Aladdin, AR), Mn (NO₃)₂ (Guoyao, 50 wt%), or Cu (NO₃)₂·3H₂O (Guoyao, AR) in DDI water. The Ce/Sn, Mn/Sn, or Cu/Sn molar ratio for the different catalysts was always controlled at 1/9. The final catalysts were named 3DOM-Ce₁Sn₉, 3DOM-Mn₁Sn₉, and 3DOM-Cu₁Sn₉, respectively, according to the chemical compositions.

2.2. Catalyst characterization

Scanning electron microscopy (SEM) images were recorded on a Hitachi S-4800 field emission scanning electron microscope. Similarly, transmission electron microscopy (TEM) images were taken using a TecnaiTM F30 transmission electron microscope. Elemental phase mapping and surface scans were also obtained by energy-dispersive spectroscopy (EDX) using the TecnaiTM F30 microscope equipped with an Oxford EDX detector operated at 300 keV.

Nitrogen adsorption-desorption experiments of the samples were performed at -196 °C on an ASAP2020 instrument. The specific surface areas of the catalysts were calculated using the Brunauer-Emmett-Teller method in the relative pressure (p/p_0) range 0.05–0.25. The pore size distributions of the samples were calculated using the Barrett-Joyner-Halenda method, and the pore sizes were obtained from the peak positions of the distribution curves. The total pore volume was accumulated at $p/p_0 = 0.99$.

Powder XRD patterns were obtained using a Bruker AXS D8Focus diffractometer operating at 40 kV and 30 mA with Cu K α irradiation ($\lambda = 1.5405$ Å). The scans were performed in the 2θ range 10° to 90° using a step size of 2° min⁻¹. To keep the data comparable, all the samples were tested continuously.

Raman spectra of the catalysts were recorded on a Ren-

ishaw inVia Raman spectrometer equipped with an argon laser excitation source operating at 532 nm and a Renishaw RenCam CCD detector. The scanned Raman shift range was from 200 to 800 cm⁻¹.

Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out on a FINESORB 3010C instrument. Generally, 0.01 g of the catalyst was used for the tests. Before the experiments, the catalysts were recalcined in high-purity air flow at 120 °C for 30 min to remove any possible surface impurities. After purging with ultrahigh purity Ar flow at room temperature for 30 min, the temperature was then increased from room temperature to 800 °C at the rate of 10 °C min⁻¹ with 10% H₂/Ar gas mixture flow (30 mL min⁻¹). 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 desorption (O₂-TPD) measurements were carried out on a Huasi DAS-7000 adsorption instrument equipped with a TCD detector. Typically, 0.05 g of the sample was placed in a quartz reactor pretreated in 30 mL min⁻¹ ultrahigh purity Ar flow at 300 °C for 60 min. Afterwards, the sample was cooled to 50 °C and saturated in 10% O₂ + Ar flow (30 mL min⁻¹), which was followed by purging with ultrahigh purity Ar flow (30 mL min⁻¹) for 60 min to remove any physically adsorbed O₂. The TPD experiments were then carried out from 50 to 800 °C at the heating rate of 10 °C min⁻¹ in ultrahigh purity Ar flow (30 mL min⁻¹).

X-ray photoelectron spectroscopy (XPS) tests were performed on a PerkinElmer PHI1600 system using a single Mg K α X-ray source operating at 300 W and 15 kV. The spectra were obtained at ambient temperature using ultrahigh vacuum. The binding energies were calibrated using the C 1s peak of graphite at 284.6 eV as the standard.

2.3. Activity evaluation

Temperature-programmed oxidation technique (TPO) was used to evaluate the activity of the prepared catalysts for soot combustion. The tests were carried out in a fixed-bed quartz tube microreactor with an inner diameter of 6 mm. To evaluate the activity of the catalyst under loose contact condition, typically 5 mg of soot (Printex-U, diameter of 25 nm, purchased from Degussa) were mixed with 50 mg of the catalyst powder and stirred for 2 min to obtain a loose contact mixture. Before loading onto the reactor, the prepared mixture was diluted with 100 mg of inert silica containing a soot/catalyst/silica weight ratio of 1/10/20 to avoid the formation of hotspots during the activity test. A K-type thermocouple was used to monitor the temperature of the catalyst bed accurately, with the thermocouple head point touching the bed. To measure the reaction behaviors of the catalysts, all the data were collected by increasing the temperature to 800 °C at the rate of 10 °C min⁻¹. The volume composition of the feed gas was 10% O₂ balanced by high-purity Ar, with the flow rate (30 mL min⁻¹). To accurately quantify the amount of O₂ consumed, prior to entering the TCD, the formed CO₂ was removed thoroughly using soda lime trap. The catalytic activity was evaluated based

on the ignition temperature (T_i) and the highest combustion temperature (T_p) reflected in the TPO profiles. In order to obtain the selectivity of the products on the samples, soot combustion on the catalysts was performed again without the soda lime trap, and the products were monitored through online SHP8400PMS mass spectrometry. The $m/z = 44$ signal corresponds to CO_2 ; and the $m/z = 28$ signal obtained by subtracting the fragment from CO_2 is of CO. The selectivity towards CO_2 production ($S(\text{CO}_2)$) is obtained according to the equation $S(\text{CO}_2) = C(\text{CO}_2)/(C(\text{CO}) + C(\text{CO}_2))$. Here, $C(\text{CO}_2)$ and $C(\text{CO})$ are the outlet concentrations of CO_2 and CO, respectively.

3. Results and discussion

Fig. 2. HRTEM images and SnO_2 size distributions of SnO_2 -based catalysts with 3DOM structures. (A, B) 3DOM- SnO_2 ; (C, D) 3DOM- Ce_1Sn_9 ; (E, F) 3DOM- Mn_1Sn_9 ; (G, H) 3DOM- Cu_1Sn_9 .

3.1. SEM, TEM, and HRTEM results

The morphologies and macroporous structures of all the samples have been investigated by using SEM and TEM. Fig. 1(A) shows that the obtained PMMA template consists of highly uniform colloidal microspheres with narrow size distributions that are closely packed in a well-organized 3D arrangement, with the average size being around 350 nm. Fig. 1(B) (SEM) and Fig. 1(C) (TEM) of the 3DOM- SnO_2 sample show that it has a well-defined 3DOM structure, and visible SnO_2 nanoparticles are present on the skeleton of the framework. With the addition of Ce^{4+} , Mn^{3+} , and Cu^{2+} cations, all the samples still have a well-defined 3DOM structure, as shown in Fig. 1(D)–(F) in sequence. The average pore size of the 3DOM- SnO_2 -based samples is about 300 nm, and the voids interconnected through the open windows are around 95 nm in diameter. Apparently, both modified and unmodified SnO_2 samples with well-defined 3DOM structures have been successfully synthesized. This structure could be favorable for mass transfer and the contact of the soot particles with active sites and oxygen because of the presence of abundant macropores and continuous pore connectivity [36].

The nanoparticles visible on the skeleton of the 3DOM samples were further studied by HRTEM, with the corresponding images shown in Fig. 2. Irregular microspheres are observed for all the samples, both modified and unmodified. In addition, both the exposed (110) and (101) facets are observed in all the samples, indicating that the addition of secondary Ce^{4+} , Mn^{3+} , and Cu^{2+} ions with a M/Sn molar ratio of 1/9 did not evidently influence the crystallization process or the growth direction of SnO_2 . As listed in Table 1, all the samples have an average particle size of around 6.0 nm. With the addition of the secondary metal cations, the average particle size only slight decreases, which might imply that Ce^{4+} , Mn^{3+} , and Cu^{2+} could have been incorporated into the SnO_2 lattice to form a solid solution structure [22,26,37] that impedes the aggregation of the SnO_2 crystallites.

3.2. N_2 adsorption-desorption studies

The N_2 adsorption-desorption technique was used to discern the textural properties of the catalysts, with the isotherms and pore diameter distribution profiles displayed in Fig. 3 and the quantification results in Table 1. All the catalysts exhibit the typical type II isotherm, and the hysteresis loop in the relative pressure (p/p_0) range 0.7–1.0 belongs to H3-type, which is typ-

Table 1

Physicochemical properties measured by N_2 adsorption-desorption, XRD, and HRTEM for SnO_2 -based catalysts with a 3DOM structure.

Sample	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Mean pore diameter (nm)	Mean particle size ^a (nm)
3DOM- SnO_2	52	0.28	17.97	6.6
3DOM- Ce_1Sn_9	64	0.37	16.41	5.8
3DOM- Mn_1Sn_9	56	0.33	10.67	5.6
3DOM- Cu_1Sn_9	57	0.32	15.56	5.5

^a Determined from TEM images.

Fig. 3. N_2 adsorption-desorption profiles of SnO_2 -based catalysts with 3DOM structures. (A) Isotherms; (B) Pore size distribution profiles.

ical of the interstice mesoporous structure formed by the nanoparticle assembly. As listed in Table 1, after calcination at 700 °C, the 3DOM- SnO_2 catalyst has a surface area of 52 $m^2 g^{-1}$, an average pore volume of 0.28 $cm^3 g^{-1}$, and an average pore size of 17.97 nm, which are much higher than those of the regular SnO_2 nanoparticles prepared by traditional methods [21]. In comparison, the addition of the secondary metal ions increases the surface areas and average pore volumes apparently, but decreases the average pore sizes, testifying that the modified catalysts have a larger amount of smaller pores in the structure, which could be favorable for the diffusion of reactants and products. In summary, the addition of the secondary metal cations can evidently alter the texture properties of 3DOM- SnO_2 , which might produce a porous structure that benefits the soot combustion activity.

3.3. Activity evaluation

The soot combustion activity over the prepared catalysts has been tested in the loose contact condition to simulate the real application process, and the TPO profiles are shown in Fig. 4. For better clarity, the combustion of pure soot and over regular SnO_2 nanoparticles (NP- SnO_2) are also evaluated under the same conditions, and the results are presented in Fig. 4(A) and Table 2.

Without any catalyst, the combustion of pure soot starts at 530 °C (T_i) and the highest rate is obtained at 630 °C (T_p). In addition, the selectivity towards CO_2 is only 68%, indicating that the oxidation of the soot is incomplete. On NP- SnO_2 , the corresponding T_i and T_p values drop, and the CO_2 selectivity improves to 86%. On the 3DOM- SnO_2 catalyst, T_i and T_p further

Fig. 4. Soot combustion activity of SnO_2 -based catalysts with 3DOM structures under loose contact condition. (A) TPO profiles of different catalysts; (B) Stability test of 3DOM- Cu_1Sn_9 for four continuous TPO experiments.

Table 2

Soot combustion activity of SnO₂-based catalysts with 3DOM structures under loose contact condition.

Sample	<i>T</i> _i (°C)	<i>T</i> _p (°C)	<i>S</i> (CO ₂) (%)
Soot	530	630	68
NP-SnO ₂	470	620	86
3DOM-SnO ₂	390	580	89
3DOM-Ce ₁ Sn ₉	380	575	76
3DOM-Mn ₁ Sn ₉	370	560	81
3DOM-Cu ₁ Sn ₉	370	545	95

decrease by 80 and 40 °C, respectively, though the CO₂ selectivity has only slightly increased, suggesting that the formation of the 3DOM structure is favorable for the soot combustion activity. The incorporation of the secondary cations more or less improves the soot combustion activity of the catalysts. It is observed that Cu²⁺ addition results in much better promotional effects for the activity and CO₂ selectivity compared to the other two dopants. Over 3DOM-Cu₁Sn₉, with the combustion starting at 370 °C (*T*_i) and the highest rate being obtained at 545 °C (*T*_p), the CO₂ selectivity reaches 95% even under the loose contact condition. In summary, the soot combustion activities of all the catalysts follow the sequence 3DOM-Cu₁Sn₉ > 3DOM-Mn₁Sn₉ > 3DOM-Ce₁Sn₉ > 3DOM-SnO₂ > NP-SnO₂. It is apparent that both the formation of the 3DOM structure and the incorporation of the secondary metal cations can benefit the soot oxidation activities of the catalysts.

The stability of 3DOM-Cu₁Sn₉, the best catalyst observed in this study, has been tested to evaluate its application potential by performing four continuous TPO experiments, and the results are shown in Fig. 4(B). It is observed that from the first to the last test, *T*_p increases from 545 to 570 °C, indicating that the catalyst has experienced some deactivation.

3.4. XRD and STEM mapping analysis

The phase compositions and crystalline structures of all the samples have been analyzed by XRD, with the patterns shown in Fig. 5. For unmodified 3DOM-SnO₂, tetragonal rutile SnO₂ is the only crystalline phase detected, as evidenced by the typical diffraction peaks at (110) = 26.659°, (101) = 33.979°, and (211) = 52.177° (JCPDS no. 41–1445). As listed in Table 3, for the unit cell of 3DOM-SnO₂, the lattice parameters are *a* = *b* = 4.7106 Å, *c* = 3.1810 Å, and all the intersection angles are 90°, which is typical for a cell with tetragonal structure.

Interestingly, with the incorporation of the secondary Ce⁴⁺, Mn³⁺, and Cu²⁺ into SnO₂, all the samples still display the typical

Fig. 5. XRD patterns of SnO₂-based catalysts with 3DOM structures.

diffraction characteristics of the tetragonal rutile SnO₂ phase, without the detection of any diffraction peaks related to the corresponding secondary oxides; however, the diffraction peaks of the SnO₂ phase become less intense. Compared with the unmodified 3DOM-SnO₂ sample, the lattice parameters of the 3DOM-Ce₁Sn₉, 3DOM-Mn₁Sn₉, and 3DOM-Cu₁Sn₉ samples distinctly change (Table 3), which proves that the secondary cations entered the lattice matrix of SnO₂ to form a solid solution structure with lattice distortion and structural defects [23,38,39]. As reported, the radii of Ce⁴⁺, Mn³⁺, and Cu²⁺ with a coordination number of 6 are 0.87, 0.65, and 0.73 Å in that order, which are close to that of the Sn⁴⁺ ion (0.69 Å) with the same coordination number. Theoretically, Ce⁴⁺, Mn³⁺, and Cu²⁺ can enter the matrix of the SnO₂ lattice to form stable non-continuous solid solutions with certain lattice capacities [22,23,40]. It has previously been found that lattice distortion and charge imbalance could arise with the formation of a non-continuous solid solution structure, thus generating more mobile oxygen species. Furthermore, the formation of the solid solution structure can also inhibit the crystallization process, thus stabilizing the surface areas of the catalysts [22,23]. The smaller crystallite sizes listed in Table 3 and the higher surface areas observed in Table 1 for the modified 3DOM-SnO₂ catalysts prove this hypothesis. In summary, the XRD results are in good agreement with the N₂ adsorption-desorption results, indicating that both the presence of the 3DOM structure and the doping of the secondary metal cations into the SnO₂ lattice are effective ways to enhance the soot combustion activities of the catalysts.

To further confirm that the doped cations have been effectively incorporated into the lattice matrix of the tetragonal ru-

Table 3

XRD results of SnO₂-based catalysts with 3DOM structures.

Sample	Mean crystallite size ^a (nm)	SnO ₂ (101)		SnO ₂ (211)		Lattice parameters		
		2θ (°)	<i>d</i> (Å)	2θ (°)	<i>d</i> (Å)	<i>a</i> (Å)	<i>c</i> (Å)	<i>a</i> / <i>b</i> / <i>γ</i> (°)
3DOM-SnO ₂	5.7	33.979	2.6362	52.023	1.7564	4.7106	3.1810	90
3DOM-Ce ₁ Sn ₉	4.3	33.899	2.6422	51.941	1.7590	4.7146	3.1903	90
3DOM-Mn ₁ Sn ₉	4.8	33.979	2.6362	52.016	1.7566	4.7116	3.1807	90
3DOM-Cu ₁ Sn ₉	5.4	34.042	2.6314	51.897	1.7604	4.7369	3.1646	90

^a Calculated by Scherrer's equation for the (110) reflection of SnO₂.

Fig. 6. STEM mapping images of 3DOM-Cu₁Sn₉ catalyst.

tile SnO₂ for the three-dimensionally ordered samples to form solid solution structures, 3DOM-Cu₁Sn₉, the most active catalyst obtained in this study, has been subjected to a STEM mapping study. As shown in Fig. 6, in the mapped zone, elemental Cu and Sn are distributed uniformly along with O, which provides further proof of the XRD results and demonstrates that the Cu²⁺ cations replace a fraction of the lattice Sn⁴⁺ to form a homogeneous solid solution structure.

3.5. Raman characterization of the catalysts

Raman technique has been used to study the structures of the catalysts, and the spectra are shown in Fig. 7. For purposes of comparison, the spectrum of regular NP-SnO₂, without the 3DOM structure, which was calcined at 700 °C for 4 h, has also been collected and included. Fig. 7 shows three Raman bands at about 773, 633, and 476 cm⁻¹, which can be assigned to the B_{2g}, A_{1g}, and E_g vibration modes of tetragonal rutile SnO₂ of D_{4h}¹⁴ group, based on group theory [41]. Interestingly, 3DOM-SnO₂, a

Fig. 7. Raman spectra of SnO₂-based catalysts with 3DOM structures.

pure SnO₂ sample having a 3DOM structure, did not reveal any Raman peak that could be detected. The 3DOM structure is believed to be responsible for the disappearance of the peaks, since the abundant surface macropores can scatter and weaken the Raman signals. Therefore, for 3DOM-Ce₁Sn₉, a strong peak assigned to the F_{2g} vibration mode of CeO₂ is observed at 449 cm⁻¹, and another peak observed at 617 cm⁻¹ can be attributed to ceria surface oxygen vacancies [42,43]. For 3DOM-Mn₁Sn₉, an intense peak at 627 cm⁻¹ is observed, which is assigned to the out-of-plane bending mode of Mn₂O₃ [44]. For 3DOM-Cu₁Sn₉, a peak centered at 609 cm⁻¹ is observed, corresponding to the B_g vibration mode of CuO [45]. In addition, for 3DOM-Mn₁Sn₉ and 3DOM-Cu₁Sn₉, a peak at 495 cm⁻¹ is observed, which is assigned to the A_{2u}TO mode due to surface defects such as oxygen vacancies (O_{vs}) and lattice disorder [46].

In summary, it is apparent that the addition of the secondary metal cations into the lattice matrix of tetragonal rutile SnO₂ to form solid solutions can improve the lattice disorder and create more surface oxygen vacancies, thus altering the surface properties of the prepared catalysts.

3.6. H₂-TPR studies

The H₂-TPR technique was used to investigate the redox properties of the catalysts, and the profiles are shown in Fig. 8. Pure 3DOM-SnO₂ shows a major reduction peak at 626 °C, which can be assigned to the reduction of SnO₂ to metallic Sn [23]. With the addition of Ce⁴⁺, Mn³⁺, or Cu²⁺, the temperature corresponding to the major reduction peak shifts to a lower value. This indicates the alteration of the chemical environment of Sn⁴⁺ in different samples that accompanies the formation of the more reducible lattice oxygen species, which is generally beneficial for soot oxidation activity. The 3DOM-Cu₁Sn₉ sample reveals the lowest temperature for SnO₂ reduction, which may be one of the reasons for its highest catalytic activity for soot combustion. It must be mentioned that the quantified O/Sn atomic ratios of all the samples are around 2.0/1, indicating that the Sn species has fully oxidized to Sn⁴⁺, in agreement with the XRD and XPS results.

More interestingly, for all the catalysts, a reduction peak below 450 °C is observed, as indicated by the enlarged profiles in Fig. 8(B). It has been reported that the surface of SnO₂ con-

Fig. 8. H₂-TPR profiles of SnO₂-based catalysts with 3DOM structures. (A) complete profiles, (B) Enlarged profiles (between 100 and 450 °C).

Table 4Quantified H₂-TPR results of SnO₂-based catalysts with 3DOM structures.

Sample	H ₂ consumption (< 450 °C) (mmol g _{cat} ⁻¹)	H ₂ consumption (> 450 °C) (mmol g _{cat} ⁻¹)	H ₂ consumption (> 450 °C) (mmol g _{SnO2} ⁻¹)	O/Sn atomic ratio
3DOM-SnO ₂	0.23	13.35	13.35	2.01
3DOM-Ce ₁ Sn ₉	0.18	11.92	13.43	2.02
3DOM-Mn ₁ Sn ₉	0.44	11.81	13.18	1.99
3DOM-Cu ₁ Sn ₉	1.71	12.54	13.28	2.00

tains a lot of oxygen vacancies, which results in a certain amount of active deficient oxygen species [23]. With the addition of Ce⁴⁺, Mn³⁺, or Cu²⁺, a larger amount of this type of oxygen species is formed in all the samples, except for the case of 3DOM-Ce₁Sn₉, as listed in Table 4 for the amounts of H₂ consumed for the peak below 450 °C.

It is noted here that owing to the reduction of CuO_x to metallic Cu in the 3DOM-Cu₁Sn₉ sample, as evidenced by the intense peak at 198 °C, an extremely high H₂ consumption amount below 450 °C is observed [37]. The quantified results indicate that the Cu⁺/Cu²⁺ atom ratio is 0.19, proving that the Cu²⁺ cations predominantly exist in the bulk of 3DOM-Cu₁Sn₉. The result also confirms that the Cu²⁺ cations substitute a fraction of the Sn⁴⁺ cations in the SnO₂ crystalline lattice, which is consistent

with the theoretical analysis discussed above that suggested that some Sn⁴⁺ cations can be replaced by Cu²⁺ in the SnO₂ lattice to form a solid solution structure.

3.7. XPS studies

The surface compositions and in particular the surface oxygen properties of the catalysts have been analyzed by XPS, and the corresponding spectra are shown in Figs. 9 and 10 and the quantified results listed in Table 5. The spectrum of 3DOM-SnO₂ (Fig. 9(A)) displays two Sn 3d peaks at 486.4 and 494.9 eV, which are assigned to Sn 3d_{5/2} and 3d_{3/2}, respectively, and attributed to Sn⁴⁺ [21], indicating that Sn is fully oxidized in all the samples. As listed in Table 5, with the addition of the

Fig. 9. XPS patterns of SnO₂-based catalysts with 3DOM structures. (A) Sn 3d for all the catalysts; (B) Ce 3d for 3DOM-Ce₁Sn₉; (C) Mn 2p for 3DOM-Mn₁Sn₉; (D) Cu 2p for 3DOM-Cu₁Sn₉.

Fig. 10. XPS patterns of SnO₂-based catalysts with 3DOM structures. (A) O 1s spectra; (B) T_p versus O_{ads}/O_{latt} molar ratio.

Table 5

Calculated XPS and ICP results of SnO₂-based catalysts with 3DOM structures.

Sample	Sn 3d binding energy (eV)			Surface compositions of the catalysts measured by XPS (molar ratio)		Bulk compositions of the catalysts measured by ICP (molar ratio)
	3d _{3/2}	3d _{5/2}	ΔE			
3DOM-SnO ₂	494.9	486.4	8.5	—	—	—
3DOM-Ce ₁ Sn ₉	494.9	486.5	8.6	Sn:Ce = 7.4:1.0	Ce ³⁺ :Ce ⁴⁺ = 0.1:1.0	Sn:Ce = 9.1:1.0
3DOM-Mn ₁ Sn ₉	495.2	486.6	8.6	Sn:Mn = 7.1:1.0	Mn ³⁺ :Mn ⁴⁺ = 1.9:1.0	Sn:Mn = 9.0:1.0
3DOM-Cu ₁ Sn ₉	495.2	486.7	8.5	Sn:Cu = 7.4:1.0	Cu ⁺ :Cu ²⁺ = 3.7:1.0	Sn:Cu = 9.0:1.0

secondary metal ions (Ce⁴⁺, Mn³⁺, Cu²⁺), the Sn 3d peaks shift and the ΔE between the two peaks experiences only a slight change, revealing the change in the chemical environment of the Sn cations.

For 3DOM-Ce₁Sn₉, two sets of peaks corresponding to Ce 3d_{3/2} and Ce 3d_{5/2} of the Ce cation with different valence states are observed (Fig. 9(B)). The peaks at 907.9 and 883.7 eV are assigned to the surface Ce³⁺ species [47], while all the other peaks are ascribed to the surface Ce⁴⁺ species [24]. The quantified Ce³⁺/Ce⁴⁺ molar ratio is 0.06, suggesting that the surface of 3DOM-Ce₁Sn₉ is enriched by the Ce⁴⁺ cations. It has been reported that surface Ce³⁺ can induce the formation of oxygen vacancies and unsaturated chemical bonds, which is in line with the Raman results of 3DOM-Ce₁Sn₉, and improve the activity of the catalyst for soot combustion [38,48].

For 3DOM-Mn₁Sn₉, two XPS Mn 3p_{3/2} peaks at 641.6 and 645.4 eV are observed (Fig. 9(C)), which are assigned to Mn³⁺ and Mn⁴⁺ [49,50], respectively. The Mn 3p_{1/2} peak at 653.7 eV is also characteristic of Mn³⁺. The calculated Mn³⁺/Mn⁴⁺ molar ratio is 1.86, proving the surface of 3DOM-Mn₁Sn₉ is enriched by the Mn³⁺ cations, which is in accordance with the fact that Mn₂O₃ is the stable manganese oxide under normal conditions and that the Mn³⁺ cations enter the SnO₂ lattice matrix to form a solid solution structure [21]. It has been reported that the presence of the Mn⁴⁺ species is beneficial for the activity towards soot combustion [51].

For the 3DOM-Cu₁Sn₉ sample, the clear split in the Cu 2p spectrum (Fig. 9(D)) indicates the mixed oxidation state of Cu. The two peaks at 954.5 eV for Cu 2p_{1/2} and 934.5 eV for Cu 2p_{3/2} are attributed to the Cu²⁺ species; and the two peaks at 952.6 eV for Cu 2p_{1/2} and 932.8 eV for Cu 2p_{3/2} are attributed to

the Cu⁺ species [38,52,53]. Interestingly, the calculated surface Cu⁺/Cu²⁺ molar ratio is 3.70, suggesting Cu⁺ enrichment on the surface of the 3DOM-Cu₁Sn₉ sample, where the concentration is different from the bulk compositions identified by H₂-TPR. This testifies that the formation of the 3DOM solid solution structure favors the formation of surface Cu⁺. According to previous studies on SiO₂(CuO_xSnO_y) and Cu_{4-x}Mo₃O₁₂ catalysts [53,54], Cu⁺ is the most active species capable of initiating soot combustion [54]. Therefore, the presence of abundant surface Cu⁺ species could be an important reason for the highest soot combustion activity of the 3DOM-Cu₁Sn₉ catalyst.

The oxygen species on the surface of the catalysts are particularly investigated, with the results displayed in Fig. 10 and Table 6. Two peaks at about 530.0 and 532.0 eV are observed for all the samples, which are assigned to the surface lattice oxygen (O_{latt}) and loosely adsorbed surface oxygen (O_{ads}), respectively [21]. Interestingly, the incorporation of different doping cations not only shifts the binding energies but also alters the O_{ads}/O_{latt} molar ratios of the catalysts (Table 6). Furthermore, the O_{ads}/O_{latt} ratios increase in the order 3DOM-SnO₂

Table 6

Calculated XPS O 1s signals for SnO₂-based catalysts with 3DOM structures.

Sample	O _{ads}		O _{latt}		O _{ads} /O _{latt} (a.u.)
	B.E. (eV)	Amount (a.u.)	B.E. (eV)	Amount (a.u.)	
3DOM-SnO ₂	531.9	22	530.4	69	0.32
3DOM-Ce ₁ Sn ₉	531.8	22	530.2	47	0.47
3DOM-Mn ₁ Sn ₉	531.9	23	530.3	45	0.51
3DOM-Cu ₁ Sn ₉	531.7	36	530.3	64	0.56

< 3DOM-Ce₁Sn₉ < 3DOM-Mn₁Sn₉ < 3DOM-Cu₁Sn₉, indicating increasing abundance of mobile surface oxygen species in that sequence. According to the literature [21], the loosely bonded surface oxygen species could play a vital role in redox reactions such as soot combustion. To depict this clearly, the T_p on the catalysts has been plotted against the O_{ads}/O_{latt} molar ratio in Fig. 10(B). It is evident that the T_p decreases with increasing O_{ads}/O_{latt} molar ratio, testifying the formation of more abundant mobile oxygen species, which is another important reason for the high soot oxidation activity.

3.8. O₂-TPD analysis

O₂-TPD experiments have been performed to further study the oxygen properties of the SnO₂ samples, and the results are shown in Fig. 11 and Table 7. For all the samples, three oxygen desorption peaks are observed below and above 200 °C. For the convenience of discussion, the peaks are divided into two groups: the low-temperature peak at around 100 °C is named the α peak, and the two overlapping high-temperature peaks above 200 °C are named the β peak. The α peak is assigned to the desorption of loosely bonded surface oxygen, and the β peak to the desorption of mobile surface lattice oxygen [20,21]. For better clarity, the two groups of peaks for each sample have been integrated and normalized to the sample amount, and the results are listed in Table 7. While the amounts of loosely bonded surface oxygen follow the order 3DOM-Ce₁Sn₉ $\approx$ 3DOM-Cu₁Sn₉ > 3DOM-Mn₁Sn₉ $\approx$ 3DOM-SnO₂ and the amounts of surface lattice oxygen follow 3DOM-Cu₁Sn₉ > 3DOM-Mn₁Sn₉ > 3DOM-SnO₂ > 3DOM-Ce₁Sn₉, the total amounts of oxygen desorbed follow the order 3DOM-Cu₁Sn₉ > 3DOM-Mn₁Sn₉ > 3DOM-Ce₁Sn₉ $\approx$ 3DOM-SnO₂. Compared with the activity results, it is apparent that if a catalyst is more active, it contains a larger amount of total desorbed oxygen species. In brief, if the H₂-TPR results demonstrate that more reducible oxygen species has been formed in a more active catalyst, the O₂-TPD results prove directly that it contains a higher amount of active surface oxygen species, which is in agreement with the Raman and XPS results.

Indeed, the formation of the more facile oxygen species

Fig. 11. O₂-TPD profiles of SnO₂-based catalysts with 3DOM structures.

Table 7

Calculated O₂-TPD results of SnO₂-based catalysts with 3DOM structures.

Sample	α peak		β peak		Total amount (a.u.)
	T (°C)	Amount (a.u.)	T (°C)	Amount (a.u.)	
3DOM-SnO ₂	100	5.0	360/500	72.0	77.0
3DOM-Ce ₁ Sn ₉	90	9.5	450/580	67.3	76.8
3DOM-Mn ₁ Sn ₉	100	4.9	455/570	81.1	86.0
3DOM-Cu ₁ Sn ₉	100	9.3	340/475	90.7	100.0

through the formation of 3DOM solid solution structures with secondary cations is believed to be favorable in enhancing the soot combustion activities of the prepared catalysts. In addition, the anchoring of the soot particulates in the macropores of the 3DOM catalysts, which ensures that the contact of the soot particles with the active sites on the 3DOM skeleton is achieved more easily, is another major reason for the enhancement in the activity of the catalysts.

4. Conclusions

To improve the reaction performance of SnO₂-based catalysts for soot combustion, a colloidal crystal templating method has been adopted to prepare a series of 3DOM catalysts. SEM, TEM, and HRTEM results have revealed that interconnected networks of the 3DOM structure can be successfully achieved using all the catalysts. The formation of the 3DOM structure can anchor the soot particulates in the macropores, which ensures that the contact of the soot particles with the active sites on the 3DOM skeleton is established more easily, thus benefiting the target reaction. XRD and STEM mapping results have confirmed that all the doped cations are incorporated into the crystal lattice of SnO₂ to form a non-continuous solid solution structure that impedes the crystallization process and improves the surface areas and pore volumes of the catalysts. Raman, H₂-TPR, XPS, and O₂-TPD results testify that a more abundant mobile oxygen species has also been formed, which is important for the soot combustion activity. The formation of the 3DOM solid solution structure and the more abundant mobile oxygen species are the critical reasons for the activities observed of the catalysts. 3DOM-Cu₁Sn₉ contains the largest amount of mobile oxygen species, thus revealing the highest activity among all the catalysts.

References

- [1] R. A. Kerr, *Science*, **2013**, 339, 382.
- [2] Q. Li, Y. Xin, Z. Zhang, X. Cao, *Chem. Eng. J.*, **2018**, 337, 654–660.
- [3] T. V. Johnson, *Int. J. Engine Res.*, **2009**, 10, 275–285.
- [4] D. Fino, S. Bensaid, M. Piumetti, N. Russo, *Appl. Catal. A*, **2016**, 509, 75–96.
- [5] A. Stein, B. E. Wilson, S. G. Rudisill, *Chem. Soc. Rev.*, **2013**, 42, 2763–2803.
- [6] P. D. Yang, T. Deng, D. Y. Zhao, P. Y. Feng, D. Pine, B. F. Chmelka, G. M. Whitesides, G. D. Stucky, *Science*, **1998**, 282, 2244–2246.
- [7] K. Sasahara, T. Hyodo, Y. Shimizu, M. Egashira, *J. Eur. Ceram. Soc.*,

Graphical Abstract

Chin. J. Catal., 2018, 39: 1683–1694 doi: 10.1016/S1872-2067(18)63123-7

Three-dimensionally ordered macroporous SnO₂-based solid solution catalysts for effective soot oxidation

Cheng Rao, Rui Liu, Xiaohui Feng, Jiating Shen, Honggen Peng, Xianglan Xu, Xiuzhong Fang, Jianjun Liu, Xiang Wang*
Nanchang University;
Jiangxi Baoan New Material Technology Corporation

3DOM SnO₂-based solid solution catalysts modified by Ce⁴⁺, Mn³⁺, or Cu²⁺ cations have been prepared using a colloidal crystal templating method. 3DOM-Cu₁Sn₉ shows the best soot combustion activity among all the studied catalysts.

2004, 24, 1961–1967.

- [8] T. Sun, N. Shan, L. Xu, J. Wang, J. Chen, A. A. Zakhidov, R. H. Baughman, *Chem. Mater.*, **2018**, 30, 1617–1624.
- [9] Z. Wu, J. Deng, Y. Liu, S. Xie, Y. Jiang, X. Zhao, J. Yang, H. Arandian, G. Guo, H. Dai, *J. Catal.*, **2015**, 332, 13–24.
- [10] Y. Cheng, J. Liu, Z. Zhao, W. Song, Y. Wei, *Chem. Eng. Sci.*, **2017**, 167, 219–228.
- [11] Y. Wei, J. Liu, Z. Zhao, Y. Chen, C. Xu, A. Duan, G. Jiang, H. He, *Angew. Chem. Int. Ed.*, **2011**, 50, 2326–2329.
- [12] Y. Wang, H. Arandian, H. A. Tahini, J. Scott, X. Tan, H. Dai, J. D. Gale, A. L. Rohl, S. C. Smith, R. Amal, *Nat. Commun.*, **2017**, 8, 15553.
- [13] Y. Wei, J. Jiao, Z. Zhao, W. Zhong, J. Li, J. Liu, G. Jiang, A. Duan, *J. Mater. Chem. A*, **2015**, 3, 11074–11085.
- [14] Y. Wei, J. Jiao, X. Zhang, B. Jin, Z. Zhao, J. Xiong, Y. Li, J. Liu, J. Li, *Nanoscale*, **2017**, 9, 4558–4571.
- [15] Y. Wei, Q. Wu, J. Xiong, J. Liu, Z. Zhao, *Chin. J. Catal.*, **2018**, 39, 606–612.
- [16] V. Alcalde-Santiago, A. Davó-Quinónero, D. Lozano-Castelló, A. Bueno-López, *Appl. Catal. B*, **2018**, 234, 187–197.
- [17] H. Arandian, J. Scott, Y. Wang, H. Dai, H. Sun, R. Amal, *ACS Appl. Mater. Interfaces*, **2016**, 8, 2457–2463.
- [18] Y. Inomata, K. Albrecht, K. Yamamoto, *ACS Catal.*, **2017**, 8, 451–456.
- [19] X. Wang, L. Xiao, H. Peng, W. Liu, X. Xu, *J. Mater. Chem. A*, **2014**, 2, 5616.
- [20] Y. Liu, Y. Guo, Y. Liu, X. Xu, H. Peng, X. Fang, X. Wang, *Appl. Surf. Sci.*, **2017**, 420, 186–195.
- [21] C. Rao, J. Shen, F. Wang, H. Peng, X. Xu, H. Zhan, X. Fang, J. Liu, W. Liu, X. Wang, *Appl. Surf. Sci.*, **2018**, 435, 406–414.
- [22] Q. Sun, X. L. Xu, H. G. Peng, X. Z. Fang, W. M. Liu, J. W. Ying, F. Yu, X. Wang, *Chin. J. Catal.*, **2016**, 37, 1293–1302.
- [23] X. Xu, F. Liu, X. Han, Y. Wu, W. Liu, R. Zhang, N. Zhang, X. Wang, *Catal. Sci. Technol.*, **2016**, 6, 5280–5291.
- [24] Z. Liu, X. Feng, Z. Zhou, Y. Feng, J. Li, *Appl. Surf. Sci.*, **2018**, 428, 526–533.
- [25] C. Liu, H. Xian, Z. Jiang, L. Wang, J. Zhang, L. Zheng, Y. Tan, X. Li, *Appl. Catal. B*, **2015**, 176–177, 542–552.
- [26] X. Xu, R. Zhang, X. Zeng, X. Han, Y. Li, Y. Liu, X. Wang, *ChemCatChem*, **2013**, 5, 2025–2036.
- [27] H. G. Peng, Y. Liu, Y. R. Li, X. H. Zhang, X. Tang, X. L. Xu, X. Z. Fang, W. M. Liu, N. Zhang, X. Wang, *ChemCatChem*, **2016**, 8, 2329–2334.
- [28] T. Hyodo, K. Sasahara, Y. Shimizu, M. Egashira, *Sens. Actuatur. B*, **2005**, 106, 580–590.
- [29] L. Yuan, T. Hyodo, Y. Shimizu, M. Egashira, *Sens. Mater.*, **2009**, 21, 241–250.
- [30] M. D'Arienzo, L. Armelao, A. Cacciamani, C. M. Mari, S. Polizzi, R. Ruffo, R. Scotti, A. Testino, L. Wahba, F. Morazzoni, *Chem. Mater.*, **2010**, 22, 4083–4089.
- [31] F. Gu, H. Wang, D. Han, Z. Wang, *Sens. Actuatur. B*, **2017**, 245, 1023–1031.
- [32] C. H. Yim, E. A. Baranova, F. M. Courtel, Y. Abu-Lebdeh, I. J. Davidson, *J. Power Sources*, **2011**, 196, 9731–9736.
- [33] K. N. Li, Y. F. Wang, Y. F. Xu, H. Y. Chen, C. Y. Su, D. B. Kuang, *ACS Appl. Mater. Interfaces*, **2013**, 5, 5105–5111.
- [34] Y. Chen, Y. Tu, Y. Zhang, J. Lu, B. Fang, *Chem. Eng. J.*, **2017**, 311, 100–110.
- [35] G. Collins, M. Bloemker, M. Osiak, J. D. Holmes, M. Bredol, C. O'Dwyer, *Chem. Mater.*, **2013**, 25, 4312–4320.
- [36] B. F. Jin, Y. C. Wei, Z. Zhao, J. Liu, G. Y. Jiang, A. J. Duan, *Chin. J. Catal.*, **2016**, 27, 923–933.
- [37] X. Bai, S. Chai, C. Liu, K. Ma, Q. Cheng, Y. Tian, T. Ding, Z. Jiang, J. Zhang, L. Zheng, X. Li, *ChemCatChem*, **2017**, 9, 3226–3235.
- [38] P. Sudarsanam, B. Hillary, B. Mallesham, B. G. Rao, M. H. Amin, A. Nafady, A. M. Alsalmeh, B. M. Reddy, S. K. Bhargava, *Langmuir*, **2016**, 32, 2208–2215.
- [39] X. Wang, Y. C. Xie, *Appl. Catal. B*, **2001**, 35, 85–94.
- [40] A. R. Denton, N.W. Ashcroft, *Phys. Rev. A*, **1991**, 43, 3161–3164.
- [41] K. N. Yu, Y. H. Xiong, Y. L. Liu, C. Xiong, *Phys. Rev. B*, **1997**, 55, 2666–2671.
- [42] I. d. C. Silva, F. A. Sigoli, I. O. Mazali, *J. Phys. Chem. C*, **2017**, 121, 12928–12935.
- [43] G. Gao, J. W. Shi, C. Liu, C. Gao, Z. Fan, C. Niu, *Appl. Surf. Sci.*, **2017**, 411, 338–346.
- [44] B. L. Vijayan, S. G. Krishnan, N. K. M. Zain, M. Harilal, A. Yar, I. I. Misnon, J. O. Dennis, M. M. Yusoff, R. Jose, *Chem. Eng. J.*, **2017**, 327, 962–972.

- [45] D. Q. Gao, G. J. Yang, J. Y. Li, J. Zhang, J. L. Zhang, D. S. Xue, *J. Phys. Chem. C*, **2010**, 114, 18347–18351.
- [46] V. Bonu, A. Das, A. K. Sivasadan, A. K. Tyagi, S. Dhara, *J. Raman. Spectrosc.*, **2015**, 46, 1037–1040.
- [47] C. W. Yang, X. J. Yu, S. Heissler, A. Nefedov, S. Colussi, J. Llorca, A. Trovarelli, Y. M. Wang, C. Wöll, *Angew. Chem. Int. Ed.*, **2017**, 56, 375–379.
- [48] H. He, X. Lin, S. Li, Z. Wu, J. Gao, J. Wu, W. Wen, D. Ye, M. Fu, *Appl. Catal. B*, **2018**, 223, 134–142.
- [49] Z. Feng, Q. Liu, Y. Chen, P. Zhao, Q. Peng, K. Cao, R. Chen, M. Shen, B. Shan, *Catal. Sci. Technol.*, **2017**, 7, 838–847.
- [50] L. J. France, Q. Yang, W. Li, Z. Chen, J. Guang, D. Guo, L. Wang, X. Li, *Appl. Catal. B*, **2017**, 206, 203–215.
- [51] Q. Tang, J. Du, B. Xie, Y. Yang, W. Yu, C. Tao, *J. Rare Earths.*, **2018**, 36, 64–71.
- [52] J. Choi, H. Oh, S. W. Han, S. Ahn, J. Noh, J. B. Park, *Curr. Appl. Phys.*, **2017**, 17, 137–145.
- [53] G. E. Yalovega, T. N. Myasoedova, V. A. Shmatko, M. M. Brzhezinskaya, Y. V. Popov, *Appl. Surf. Sci.*, **2016**, 372, 93–99.
- [54] P. G. Chigrin, N. V. Lebukhova, A. Y. Ustinov, *Kinet. Catal.*, **2013**, 54, 76–80.

三维有序大孔 SnO_2 基固溶体用于有效燃烧碳烟颗粒

饶 成^{a,†}, 刘 瑞^{a,†}, 冯小辉^a, 沈家庭^a, 彭洪根^a, 徐香兰^a, 方修忠^a, 刘建军^b, 王 翔^{a,*}

^a南昌大学化学学院, 江西南昌330031

^b江西宝安新材料科技有限公司, 江西萍乡337000

摘要: 柴油车尾气排放的碳烟颗粒对人类的生存环境和身体健康带来了严重危害。催化燃烧是消除碳烟颗粒污染的有效途径。碳烟颗粒催化燃烧是固-固-气相反应, 因此催化剂本身具有活泼的氧中心且其能与碳烟颗粒有效接触是提高反应效率的关键因素。为改善碳烟颗粒与催化剂的接触, 设计制备三维有序大孔(3DOM)催化剂, 使碳烟颗粒可以进入催化剂孔道内部, 增加其与催化剂的有效接触, 是提高反应活性的有效途径。此外, 在催化剂晶格中掺杂其它金属离子形成固溶体结构, 可提高其氧化还原性能, 也可有效提高其碳烟燃烧活性。

SnO_2 富含活泼的表面缺位氧和可还原的晶格氧, 且其熔点高达1630 °C, 具有良好的热稳定性, 被广泛用于制备气体传感、电化学和催化等材料。在过去的6年中, 本课题组在 SnO_2 催化化学领域做了大量系统的工作, 将 SnO_2 基催化材料用于多种环保和能源反应。发现通过其它阳离子 Fe^{3+} , Cr^{3+} , Ta^{5+} , Ce^{4+} 和 Nb^{5+} 等的掺杂, 替换晶格中部分 Sn^{4+} 形成金红石型 SnO_2 固溶体结构, 可显著提高催化剂氧物种的流动性、活性和本身的热稳定性。

本文采用胶体晶体模板法制备出了 Ce^{4+} , Mn^{3+} 和 Cu^{2+} 离子掺杂的 SnO_2 三维有序大孔固溶体催化剂用于松散接触条件下的碳烟催化燃烧。采用SEM, TEM, XRD, STEM-mapping, O_2 -TPD和XPS等手段对催化剂进行表征, 研究其碳烟催化燃烧性能。SEM和TEM结果表明已成功合成三维有序大孔结构样品。XRD, Raman和STEM-mapping结果表明, Ce^{4+} , Mn^{3+} 和 Cu^{2+} 离子均进入四方金红石型 SnO_2 晶格形成固溶体结构。另外, Raman, H_2 -TPR, XPS和 O_2 -TPD等结果发现上述离子掺杂三维大孔 SnO_2 后, 催化剂表面形成了更活泼、丰富的氧物种, 有利于碳烟颗粒燃烧。其中3DOM- Cu_1Sn_9 催化剂具有最丰富的活泼氧中心, 因此表现出最高的活性。

关键词: 三维有序大孔催化剂; 碳烟燃烧; SnO_2 基固溶体; 晶格掺杂; 氧空位

收稿日期: 2018-04-28. 接受日期: 2018-05-28. 出版日期: 2018-10-05.

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

[†]共同第一作者.

基金来源: 国家自然科学基金(21567016, 25103106); 江西省自然科学基金(20171BAB213013); 江西省教育厅基金(KJLD14005); 国家重点研发项目(2016YFC0209302); 江西省研究生创新创业训练基金(YC2015B017); 中国大学生创新创业训练基金(201701035).

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>).