RSC Advances



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

RSC Advances

An international journal to further the chemical sciences



RSC Advances is an international, peer-reviewed, online journal covering all of the chemical sciences, including interdisciplinary fields

The criteria for publication are that the experimental and/or theoretical work must be high quality, well conducted and demonstrate an advance by adding to the development of the field

RSC Advances 2013 Impact Factor* = 3.7

Thank you for your assistance in evaluating this manuscript.

Guidelines to the referees

 Guidelines to the referees

 Referees have the responsibility to treat the manuscript as confidential. Please be aware of our Ethic.

 Guidelines, which contain full information on the responsibilities of referees and authors, and our Refereeing Procedure and Policy.

 It is essential that all research work reported in RSC Advances is well-carried out and well-characterised. There should be enough supporting evidence for the claims made in the manuscript.

When preparing your report, please:

- comment on the originality and scientific reliability of the work;
- comment on the characterisation of the compounds/materials reported has this been accurately interpreted and does it support the conclusions of the work;
- state clearly whether you would like to see the article accepted or rejected and give detailed commented (with references, as appropriate) that will both help the Editor to make a decision on the article and the authors to improve it.

Please inform the Editor if:

- there is a conflict of interest
- there is a significant part of the work which you are not able to referee with confidence
- the work, or a significant part of the work, has previously been published
- you believe the work, or a significant part of the work, is currently submitted elsewhere
- the work represents part of an unduly fragmented investigation.

For further information about RSC Advances, please visit: www.rsc.org/advances or contact by email: advances@rsc.org.

*Data based on 2013 Journal Citation Reports®, (Thomson Reuters, 2014).

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Three dimensionally ordered macroporous (3DOM) SiOC on cordierite monolith inner wall and its properties for soot combustion

Jia Ma,^a Yunlong Ning,^a Cairong Gong,^a⁺ Gang Xue^b and Guoliang Fan^b

Three dimensionally ordered macroporous (3DOM) SiOC was successfully fabricated on the cordierite monolith inner wall of a polystyrene spheres (PS) template through a colloidal crystal templating (CCT) method (named as 3DOM SiOC/cordierite). And perovskite-type LaCoO₃ (LCO) mixed metal oxides, prepared by a facile sol-gel process, were coated onto the wall of 3DOM SiOC/cordierite by a simple impregnation-sintering approach (named as LCO/3DOM SiOC/cordierite). The morphological and physicochemical properties studies indicate that 3DOM structure has excellent connectivity, large specific surface area, and applicable pore size. And 3DOM structure plays an important role in preventing aggregation of the targeted catalyst particles, improving the contact condition between catalysts and soot as well as enhancing the reducibility of the LCO. The subsequent investigation on the catalytic performance of the 3DOM samples for diesel soot combustion shows that the 3DOM texture offers the catalyst with lower soot combustion temperature than conventional catalyst, and the LCO/3DOM SiOC/cordierite reduces the combustion temperature even further while avoid the rise of back-pressure effectively as well.

1. Introduction

Diesel engines have **dominated** heavy-duty trucks and off-road vehicles all over the world due to their great advantages overtaking other type **engines**, **including longer** durability, lower costs, and higher efficiency. Diesel particulate matter (PM, mainly containing soot) and nitrogen oxides (NO_x), undesired by-products of diesel engines in combustion process, **have been recognized among the top threads** to environment and human health **which has driven research focusing on solutions.**^{1,2}

Diesel particulate filter (DPF) is an effective technology in engine development to reduce diesel soot onsite efficiently. As a physical entrapment, the onsite capture of soot in DPF requires a desired durability or continuous regeneration, as the increase of backpressure from a blocking trap will damage the engine.³ However, passive regeneration generally started at the temperature above 550°C which is much higher than the exhaust-gas temperature (200-400°C)

† Footnotes relating to the title and/or authors should appear here. Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

This journal is © The Royal Society of Chemistry 20xx

under normal working condition of the engine. Catalyst coatings were commonly used to lower the regeneration temperature, which will enable continuous regeneration under normal working condition.4-7 Some catalysts exhibited excellent performance in simultaneous removal of soot and NOx.⁸⁻¹⁰ Several factors of catalysts preliminarily govern the catalytic activity: chemical composition, specific surface area,¹¹ grain size,¹² surface contact condition with soot,^{13,14} as well as porosity and pore structure.¹⁵ Additionally, being a sootcatalysts-gas three-phase reaction, the fluidity and permeability of gas are also important factors in the soot combustion process. Over decades of fundamental study and practical application demonstrate that catalytic coatings over DPFs are efficient after-treatment technique. Unfortunately, normal coating techniques often provide the catalyst coating with small specific surface area, small pore size and unsatisfying contact condition with soot and thus limit their catalytic activity. Furthermore, catalyst particles agglomerate easily and block the DPF wall channels, resulting in the deterioration of fluidity of gas and the increase of backpressure which eventually overheat the engine.

Three dimensionally-ordered macroporous (3DOM) materials **demonstrated** excellent properties, such as an open connected macropore structure and nanosized wall components,¹⁶ and numerous successful applications benefited from these properties. As for the features of 3DOM materials, 3DOM catalysts showed better properties than **conventional**



^a School of Material Science and Engineering, Tianjin University, Tianjin 300072, P. R. China

^{b.} Institute of Power Source & Ecomaterials Science, Hebei University of Technology, Tianjin 300130, P. R. China

ARTICLE

catalysts, as a result of higher specific area, better surface contact condition with soot, excellent connectivity and pores structure.17-21 It offers an efficient way to improve the properties of the catalysts. To date, various kinds of 3DOM catalysts have been successfully fabricated by different methods. M. Sadakane et al.¹⁹ prepared 3DOM perovskite-type La_{1-x}Sr_xFeO₃ (x=0-0.4) mixed metal oxides by using a new facile colloidal crystal templating method, compared with nonporous catalysts, the T_{50} (a temperature where half of carbon were burned) of the catalyst was reduced by 16°C and the specific surface area increased by 30m²/g, demonstrating that the 3DOM perovskite-type materials have superior catalytic activity for combustion of nanosized carbon. Y. Wei et al.²⁰ successfully fabricated a series of catalysts of 3DOM Ce_{0.8}Zr_{0.2}O₂-supported gold nanoparticles with controllable sizes by a gas bubbling-assisted membrane reduction (GBMR), as reported, 3DOM Au_{0.04}/Ce_{0.8}Zr_{0.2}O₂ may achieve the lowest T_{10} (a temperature where 10% of carbon were burned) temperature (218°C) for soot oxidation under the loose contact condition.

Motivated by the analysis **mentioned** above, in this study, the 3DOM structure was applied in catalyst coatings process for the real-life DPF device. 3DOM SiOC structure **was firstly fabricated** on the inner wall of the cordierite monolith through a colloidal crystal templating method, **following another coating of the LCO to reduce** the combustion temperature of soot. 3DOM structure showed excellent connectivity, large specific surface area, and applicable pore size. The 3DOM structure also effectively restrained the aggregation of the catalyst particles, **leading to the improved surface** contact condition between catalysts and soot **as well as the reducibility of LCO**. Moreover, as the 3DOM structure formed on the cordierite walls, LCO/3DOM SiOC/cordierite **effectively prohibits** the **chance for** backpressure increase and further enhances the catalytic activity.

2. Experimental section

2.1. Synthesis of 3DOM SiOC cordierite

The general scheme of a synthesis of 3DOM SiOC/cordierite is relatively straightforward: dip-coating SiOC thin film onto the cordierite monolith inner wall, depositing closed-packed polystyrene (PS) spheres template on the SiOC coating, filling the empty volume between PS spheres with SiOC solution and then removing the PS spheres. All **reagents** used below are of analytic grade.

For preparation of the PS spheres, Tetrabutyl titanate was added into water/ethanol (10:3 in volume) solution, whose pH was adjusted to 9 with NaOH solution (1mol/L), then it was stirred at 40°C for 40min. After that, styrene (purified by vacuum distillation), sodium dodecyl sulfate and ammonium persulfate (provided by Tianjin Guangfu Fin Chemicals Research Institute) were added, followed by stirring at 80°C for 8h in nitrogen atmosphere.

The second step was to coat SiOC on the cordierite monoliths. The SiOC precursor solution was prepared by

Journal Name

simply mixing of Polymethylhydrosiloxane (PMHS), 1,3,5,7-Tetravinyl-1,3,5,7-tetramethylcyclotetrasiloxane (D₄Vi) and Karstedt catalyst solution (provided by Aladdin), which were then ultrasonically dispersed. The cordierite monoliths (provided by Yixing Jintai Refractory Material Co., Ltd), having 64 cells per square centimeter, were cut into pieces of 10mm×10mm in section and 15mm long. The pieces were first washed in acetone/ethanol (3:1 in volume) solution for 3h and then in nitric acid for another 3h. Finally, after being washed with deionized water, the cordierite monoliths pieces were dried at 60°C for 4h. Then the pretreated monoliths were immersed into the prepared SiOC precursor solution for 30min to coat SiOC thin film, followed by blown to remove the excess of slurry. After that, the monoliths were dried at 60°C for 4h. The cycle of immersion-blowing-drying was repeated for three times. We named them as SiOC/cordierite monoliths.

The prepared SiOC/cordierite monoliths were immersed into 100ml PS precursor solution (35wt%) in the centrifugation tubes, followed by centrifuging at 4000r/min for 24h to coat a thin film of PS spheres. After centrifugation, the monoliths were blown at 60°C for 72h to remove the excess of slurry. Then, the coated monoliths were soaked in the SiOC precursor solution for 5d. **After blowing away excessive solution**, the obtained samples were incubated at 50°C for 4h. The product was crosslink of SiOC/cordierite monoliths and PS spheres.

To obtain 3DOM **SiOC/cordierite monolith**, the crosslinked monoliths were heat-treated at 800°C for 1h in nitrogen atmosphere and then calcined at 800°C for 2h in air.

2.2. Synthesis of the perovskite-type LaCoO₃ (LCO) mixed metal oxides supported on 3DOM SiOC/cordierite

The perovskite-type oxides of $LaCoO_3$ (LCO) were prepared by sol-gel method.²² The 3DOM SiOC/cordierite monoliths **were immersed** into the catalyst precursor solution prepared previously for 30min, and then **was preheated** at 100°C for 1h, after preheating, the samples were sintered at 450°C for 1h. The immersion-preheating-sintering-cooling cycle was repeated for several times to obtain a maximum upload. After uploading, the samples were calcined at 800°C for 2h. The products were named as LCO/3DOM SiOC/cordierite.

2.3. Structure Characterization

The microstructures of the catalysts and 3DOM samples were observed by scanning electron microscope (SEM. HitachiS4800, HITACHI, Japan) using accelerating voltages of 0.5-30kV, and 0.1kV per step, samples (grinded into powder) were glued to the sample holder by conducting resin and then coated with a gold layer to improve the images obtained. The elemental chemical analysis was performed using the energydispersive X-ray analysis (EDX, Genesis XM2, EDAX, USA) system, which was equipped to the SEM instrument. The porosity, pore volume and BET were measured by N2 adsorption at -196°C using NOVA 2000 gas sorption analyzer, and the pore-size distribution (PSD) of samples were calculated using the Barrett-Joyner-Halenda (BJH) algorithm. Specific surface areas were calculated by Brunaure-Emmert-Teller (BET) method. The crystal phases of the prepared catalysts

Journal Name

were identified on X-ray diffractometer (XRD D/MAX-2500, Rigaku, Tokyo, Japan) using Cu- $K\alpha$ radiation. The XRD patterns were recorded for 2 θ angles between 10° and 90° with increments of 0.02° and counting time of 0.5s⁻¹ per step. The structures of the prepared catalysts were analyzed by Fourier transform infrared spectrometry (FTIR, Nicolet 6700, USA) with 2cm⁻¹ resolution. The IR wafers were prepared by mixing KBr powder with LCO (*ca.* 1% sample in KBr).

Hydrogen temperature-programmed reduction (H₂-TPR) experiments were carried out on a ChemBET Pulsar TPD/TPR analyzer (Quantachrome). 20mg of LCO or 200mg of LCO/3DOM SiOC (40-60mesh) was loaded to a fixed-bed-U-shaped quartz microreactor. The sample was pretreated in a helium flow of 30 mL/min at 500°C for 30min and cooled at the same atmosphere to room temperature. The pretreated sample was exposed to a flow (50mL/min) of 5% H₂ balanced Ar and heated from 50°C to 750°C at a rate of 10°C/min. The variation in H₂ concentration of the effluent was monitored on-line by the chemical adsorption analyzer.

2.4. The catalytic activity test

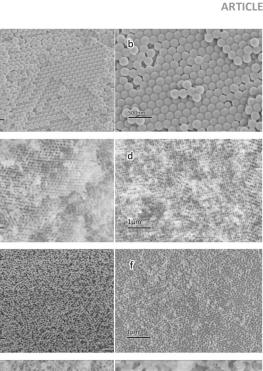
The activity of 3DOM samples and catalysts for carbon particle combustion were tested using the TG-DSC (Mettler Toledo, USA). 20 mg of the prepared samples were placed in a alumina crucible, then is heated under a gas flow (100ml/min) containing 10% O2 and 500ppm NO balanced N2 at a rate of 10°C/min in a temperature range of 50°C to 800°C. The performance of the samples were evaluated by the values of $T_{\rm m}, T_{10}, T_{50}$, and $T_{90}, T_{\rm m}$ was defined as the temperature at which the conversion rate of carbon black is the most rapid, and T_{10} , T_{50} , T_{90} were defined as the temperatures at which 10%, 50%, 90% of carbon black were oxidized, respectively. Carbon black, purchased from Evonik Degussa, was used in the test as a replacement of diesel soot due to its similar chemical components and specific surface area. Before being used, carbon black was pretreated at 100°C for 3h. To imitate the real situation, carbon black was dispersed into anhydrous ethanol, and 3DOM contact was obtained by immersing the 3DOM samples into the suspension solution, and did ultrasonic dispersion for 30min to make the carbon black disperse onto the inner walls of 3DOM samples. As a comparison, the catalytic activity of catalyst powders (catalyst to carbon black. 9:1, mass ratio, loose contact) was also studied.

3. Results and discussion

3.1. The microstructure of 3DOM samples

The morphology and pore structure of PS microspheres and 3DOM samples (3DOM SiOC, 3DOM SiOC/cordierite and LCO/3DOM SiOC/cordierite) were investigated by SEM.

Fig. 1a and Fig. 1b show the SEM images of PS **microspheres**, they depict that a dispersion of monodisperse PS **microspheres** are assembled into close-packed arrays. It shows a face-centered cubic (fcc) structure.²³ The diameter of the PS spheres measured from the SEM images is at a range of 120 to 150nm.



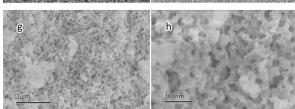


Fig. 1 SEM images of PS spheres and 3DOM samples: (a) the flatsurface of PS spheres template, (b) the section of PS spheres template, (c) 3DOM SiOC sintered at 800°C in Ar atmosphere, (d) 3DOM SiOC annealing treatment at 800°C in air, (e) the corner of 3DOM SiOC/cordierite wall, (f) the center of 3DOM SiOC/cordierite wall, (g) LCO/3DOM SiOC/cordierite, (h) the enlarged image of LCO/3DOM SiOC/cordierite.

Fig. 1c-f all demonstrate that the samples obtained by CCT method have the 3DOM structure. Concretely, Fig. 1c gives the SEM images of 3DOM SiOC sintered at 800°C in Ar atmosphere. It can be seen that the 3DOM SiOC exactly copies the fcc structure of PS template. As to the ideal model of fcc structure, this structure highly improves the specific surface area and negotiability of gas flow.

It can also be found that the pore size, wall thickness and morphology varied **under** different treatment, as listed in Table 1. From Table 1 and Fig. 1c, it can be seen that, the wall thickness ranges from 50 to 100nm, **indicating a** sheet structure. Macropores diameter measured from the SEM images ranges from 100 to 150nm, **which is** narrowed compared with the size of PS microspheres, and the macropores show irregular roundness. It **might caused by melting of PS microspheres during sintered.**²¹

Fig. 1d shows the SEM image of 3DOM SiOC after annealing treatment at 800°C in air. The SEM image of the material shows partial collapse, but the general macropores structure is reserved.

Samples	Spheres (Pores) Size/nm	Wall Thickness/nm
PS microspheres	120-150	
3DOM SiOC (before anneal)	100-150	50-100
3DOM SiOC (after anneal)	100-400	20-100
3DOM SiOC/cordierite	100-120	40-50
LCO/3DOM SiOC/coridirite	200-600	

Table 1 The spheres (pores) size and wall thickness of PS spheres and 3DOM sample

Compared with Fig. 1c, the macropores are more irregular, **ranging from 100 to 400nm**, **of which** several pores combined into larger pores. The possible reason is the oxidation of carbon element during sintering of PS microspheres and SiOC, which **serve as** skeleton of the 3DOM structure. This speculation was further confirmed by the following test of EDX.

Compared with 3DOM SiOC, 3DOM SiOC/cordierite monoliths (Fig. 1e and Fig. 1f) have more integrated structure. It owes to the supporting role of the cordierite to the 3DOM structure, decreasing the degree of collapse. The interaction of the cordierite and 3DOM structure improves the performance of both.

The SEM analysis were performed **on** different regions of 3DOM SiOC/monolith, Fig. 1e and Fig. 1f show the morphology of the corner and the center of the wall, respectively. From the images, we can see that the layer thickness is not homogeneous, being thicker at the corner of the walls, **but** only one layer at the center of the walls. The difference in thickness is caused by the fluid dynamic phenomena during the blowing step of making template on walls and filling process.^{24,25} Generally speaking, the adherence force of the corners is stronger than **that of** the centers, which may be another reason for the different layer thickness.

After several times of immersion-sintering process, LCO supported 3DOM SiOC/cordierite monoliths were investigated by SEM. Fig. 1g and Fig. 1h show that after several times of sintering, 3DOM materials collapsed locally. Macropores combined to form larger pores, whose sizes range from 200 to 600nm, larger than other 3DOM samples, and the shape of the macropores show more irregular roundness. But the materials still present 3DOM structure. The SEM images demonstrate the excellent properties for the catalysts. From the images, we can see that the catalyst particles uniformly distributed on the 3DOM walls, and their sizes range from 30 to 50nm, much smaller than the catalyst particles made under solgel method (the corresponding SEM images were showed in Fig. S1), indicating the 3DOM structure played an important role in restraining the aggregation of catalyst particles, which is good for improving the contact condition between catalysts and soot. In addition, from the image we can see a connectivity structure of 3DOM structure, which is convenient for the gas flow, making it easier for gas diffusion into soot and catalysts.²⁶ The phase structure of the catalysts was also demonstrated by XRD and FTIR, as shown in Fig. S2 and Fig. S3.

The EDX analysis of 3DOM SiOC (Fig. 2) confirmed the reason for the collapse of the 3DOM structure when annealing in air. The EDX analysis shows that the main elements of the

two materials (before and after annealing in air) are still Si, O and C. However, after annealing process, the **content of carbon** element declined obviously. The relative average atomic ratios was Si:32, O:36, C:31 before annealing process (Fig. 2a), and Si:61, O:26, C:12 after annealing process (Fig. 2b). The decline of carbon element led to the change of 3DOM materials' structure. There is still some carbon element after annealing process, which is from the skeleton of SiOC amorphous structure.

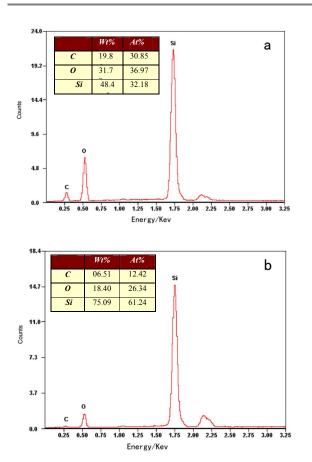


Fig. 2 EDX analysis of 3DOM SiOC: (a) 3DOM SiOC sintered at 800°C in Ar atmosphere, (b) 3DOM SiOC annealing treatment at 800°C in air.

ARTICLE

Table 2 Total pore volume, average pore radius and BET of 3DOM samples

Samples	3DOM SiOC	LCO/3DOM	Cordierite Monolith
Total pore Volume (ml/g)	0.083	0.076	
Average Pore Diameter (nm)	53.98	96.22	
BET (m^2/g)	61.33	33.69	14.44

Fig. 3 shows the EDX analysis of LCO/3DOM SiOC/cordierite. From the EDX we can see that although the main elements are Si, O and C, there are still La and Co elements remaining in the corresponding position. It precisely demonstrate that the catalysts had **been** immersed into the interior of the macroporous structure after several times **of** immersion-sintering process. The active element kept the approximate stoichiometric radio. It demonstrated that LCO were successfully coated onto 3DOM SiOC/cordierite.

In order to **further exact** the morphology and the properties of the pores (**Fig. S4 and Fig. S5**) of the 3DOM structure, pores volume, pores size and BET of the samples were measured.

The results are summarized in Table 2. The results of **the pore-size** distribution **are** precisely the same as the results of the SEM. This kind of pore sizes is suitable for soot and catalysts **to pass**, and catalysts to load. And the BET results clearly demonstrate that the 3DOM structure enlarged the specific surface area significantly, which has an important effect on the contact condition with soot and diffusion of gas and thus improving the catalysts activity.

3.2. The reducibility of LCO

H₂-TPR experiments were conducted to investigate the reducibility of the samples, and their profiles are illustrated in Fig. 4. For the two samples, there are two reduction peaks: the first reduction peak was due to the reduction of surface Co^{3+} to Co^{2+} and the adsorbed oxygen species, the

second reduction peak was due to the reduction of Co^{2+} to Co^{0} . ^{27,28} The two reduction peaks of LCO/3DOM SiOC (435°C and 595°C) were much lower than those (468°C and 633°C) of LCO, indicating the reduction of LCO/3DOM SiOC exhibited better reducibility than LCO due to the 3DOM structure. And the reduction peaks of LCO/3DOM SiOC/cordierite are similar to those of 3DOM LCO. ²⁹

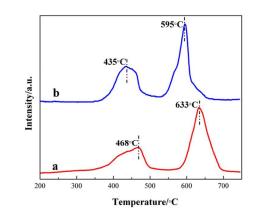


Fig. 4 H₂-TPR profiles: (a) LCO, (b) LCO/3DOM SiOC.

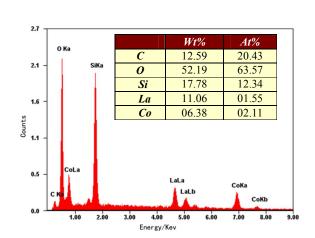


Fig. 3 EDX analysis of LCO/3DOM SiOC/cordierite.

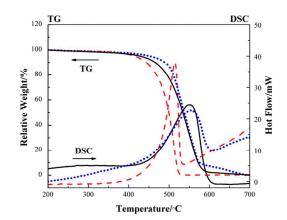


Fig. 5 TG-DSC curves of (a) solid curves: the soot and SiO_2 mixture, (b) short dot: the soot and SiOC mixture, (c) dash curves: soot supported on 3DOM SiOC.

	$T_{10}/^{\circ}\mathrm{C}$	<i>T</i> ₅₀ /°C	$T_{\rm m}^{\ a}/{\rm ^oC}$	<i>T</i> ₉₀ /°C
Sample A	470	535	551	570
Sample B	490	538	555	575
Sample C	443	499	514	518

^a temperatures at which the soot conversion rate is the most rapid, showed in Fig. S6.

3.3. The 3DOM structure for the soot combustion

In order to assess the activity of 3DOM structure for the soot combustion, the soot and SiO₂ mixture (SiO₂ to soot, 9:1, mass ratio, tight contact, Sample A), the soot and SiOC mixture (SiOC to soot, 9:1, mass radio, tight contact, Sample B), and soot supported on 3DOM SiOC (Sample C) were tested by TG-DSC. The combustion curves are showed in Fig. 5 and the corresponding temperatures are listed in Table 3. Sample A and Sample B have similar characteristic temperatures, which clearly demonstrates that the carbon element remained in SiOC has no obvious effects on combustion temperature of soot. Compared with Sample A, T_{10} , T_{50} , T_m , T_{90} of Sample C are decreased by 27°C, 36°C, 37°C, 52°C, respectively. In conclusion, the 3DOM structure has excellent quality for soot combustion, listed as follows: First, 3DOM structure has fine connectivity which is convenient for gas flow. Secondly, 3DOM structure enlarges the specific surface area efficiently. The two features above contribute to diffusion of gas into the soot.²⁶ Thirdly, 3DOM structure has uniform pore size which assists soot to spread. All these excellent properties of 3DOM structure add to the unique performance in lowering of the combustion temperature.

3.4. LCO supported on 3DOM structure for the soot combustion

At present, we further studied the feature of LCO/3DOM SiOC/cordierite for soot combustion. As Fig. 6, Fig. S6 and Table 4 showed, compared with soot over 3DOM SiOC/cordierite and SiO2, T10 of soot over LCO/3DOM SiOC/cordierite are decreased by 50°C and 77°C, respectively, T_{50} are decreased by 21°C and 57°C, $T_{\rm m}$ are decreased by 10°C and 47°C, and T₉₀ are decreased by 0°C and 52°C. They all showed obvious advantage of 3DOM SiOC/cordierite over SiO₂ especially in the middle and later stages of soot combustion. The explanation for this phenomenon is that in the process of non-catalytic combustion, the initiatory combustion of soot begins in a partial area, and then gradually diffuses to the whole area with the heat temperature rising. Once the soot combustion began, huge energy was released and transferred, which could partly fulfill the activation energy for soot combustion. At this stage, the diffusion of gas to the soot surface is another important factor influencing the sootcatalysts-gas three phases reaction. 3DOM structure has larger specific surface area and better connectivity, so gas could more easily diffused to the surface of soot for soot combustion, therefore, as Fig. 6 depicts, in the early stage, the combustion temperature of a and b are similar, in the middle and later stage, 3DOM structure could reduce the temperature of soot combustion efficiently, and this phenomenon obviously coincided with the rising of the temperature. As for catalytic combustion, there are three kinds of active oxygen species on the surface of LCO,³⁰ LCO/3DOM SiOC/cordierite could

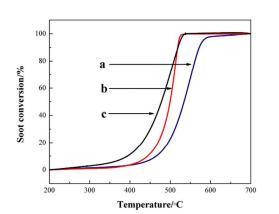
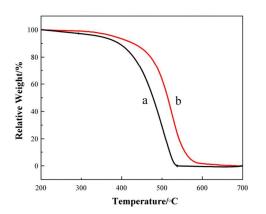


Fig. 6 Soot conversion curves over different supports: (a) SiO₂, Fig. 7 TG curves: (a) 3DOM contact, (b) loose contact. (b) 3DOM SiOC/cordierite, (c) LCO/3DOM SiOC/cordierite.



Supproting samples	$T_{10}/^{\circ}\mathrm{C}$	<i>T</i> ₅₀ /°C	$T_{\rm m}/^{\circ}{\rm C}$	T ₉₀ /°C
SiO ₂	470	535	551	570
3DOM SiOC/cordierite	443	499	514	518
LCO/3DOM SiOC/cordierite	393	478	504	518

reduce the combustion temperature greatly. As a result, the combustion of soot was dominated by both the 3DOM structure and catalysts in the early and middle stages, and dominated by the 3DOM structure in the later stage.

3.5. Contact condition between LCO and soot on the 3DOM structure

The catalysts supported on 3DOM SiOC/cordierite had showed excellent property for soot combustion. LCO catalysts particles for soot combustion (loose contact) were carried out to further prove the advantage of 3DOM structure has on the contact condition between catalysts and soot. LCO/3DOM SiOC/cordierite was immersed into the carbon black-ethanol solution to simulate the practical situation (3DOM contact). From the Fig. 7, compared with loose contact, T_{10} , T_{50} , T_{90} of 3DOM contact decrease by 36°C, 37°C, 37°C respectively. As J. Xu et al. 29 reported, compared with nanoparticles LCO, the T_{50} of 3DOM LCO is lower by 15°C, in this study, the T_{50} of LCO/3DOM SiOC/cordierite is lower by 37°C, indicating better properties for soot combustion. We can draw the conclusion that 3DOM structure improved the contact condition between soot and catalysts for the excellent structure properties of 3DOM structure, and thus the soot combustion temperature is further reduced.

Conclusion

Three dimensionally ordered macroporous (3DOM) SiOC/cordierite has been successfully fabricated. 3DOM SiOC/cordierite has excellent connectivity (convenient for gas flow and diffusion onto solid surface), large specific surface area (much larger than cordierite monolith), and applicable pore size (100 to 400nm), 3DOM SiOC/cordierite can significantly reduce the soot combustion temperature for these excellent properties of 3DOM structure, T_{10} , T_{50} , $T_{\rm m}$, T_{90} of soot over 3DOM SiOC/cordierite decrease by 27°C, 36°C, 37°C, 52°C, respectively.

Perovkite-type LaCoO₃ (LCO) mixed metal oxides prepared by sol-gel method are loaded onto 3DOM SiOC/cordierite, LCO/3DOM SiOC/cordierite could further reduce the combustion temperature of soot, avoiding the back-pressure rising effectively. Compared with 3DOM SiOC/cordierite and bare soot, T_{10} of soot over catalysts supported on 3DOM SiOC/cordierite decreased by 50°C and 77°C, respectively, T_{50} decreased by 21°C and 57°C, $T_{\rm m}$ decreased by 10°C and 47°C, and T_{90} decreased by 0°C and 52°C. And the contact condition between soot and LCO/3DOM SiOC/cordierite is better than loose contact of soot and catalysts.

Acknowledgement

This study was supported by the Natural Science Foundation of Tianjin (12JCQNJC05700) and the Natural Science Foundation of Hebei Province of China (E2014202194).

References

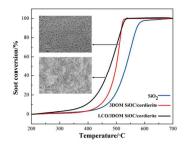
- J. Neeft, M. Makkee and J. A. Mouliin. Fuel Process. 1 Technol., 1996, 47, 1-69.
- 2 B. Giechaskiel, B. Alföldy and Y. Drossinos, J. Aerosol Sci., 2009, 40, 639-651.
- 3 J. Adler, Int. J. App. Ceram. Tec., 2005, 2, 429-439.
- 4 J. Yang, M. Stewart, G. Maupin, D. Herling and A. Zelenyuk, Chem. Eng. Sci., 2009, 64, 1625-1634.
- 5 M. Dhakad, T. Mitshuhashi, S. Rayalu, P. Doggali, S. Bakardjiva, J. Subrt, D. Fino, H. Haneda and N. Labhsetwar, Catal. Today, 2008, 132, 188-193.
- A. Mishra and R. Prasad, Int. J. Appl. Eng. Res., 2014, 9, 9-16. 6
- S. Fang, L. Wang, Z. Sun, N. Feng, C. Shen, P. Lin, H. Wan 7 and G. Guan, Catal. Commun., 2014, 49, 15-19.
- 8 N. Nejar, J. M. Garcia-Cortes, C. Salinas-Martínez de Lecea and M. J. Illán-Gómez, Catal. Commun., 2005, 6, 263-267.
- 9 W. F. Shanggua, Y. Teraoka and S. Kagawa, Appl. Catal., B, 1998, 16, 149-154.
- 10 I. S. Pieta, M. García-Diéguez, C. Herrera, M. A. Larrubia and L. J. Alemany, J. Catal., 2010, 270, 256-267.
- H. Shimokawa, H. Kusaba, H. Einaga and Y. Teraoka, Catal. 11 Today, 2008, 139, 8-14.
- D. D. Javaseelan, W. E. Lee, D. Amutharani, S. zhang, K. 12 Yoshida and H. Kita, J. Am. Ceram. Soc., 2007, 90, 1603-1606
- 13 J. Neeft, M. Makkee and J. A. Moulijn, Appl. Catal., B, 1996, 8, 57-78.
- 14 J. Neeft, O. P. van Pruissen, M. Makkee and J. A. Moulijn, Appl. Catal., B, 1997, 12, 21-31.
- 15 L. Li, X. Shen, P. Wang, X. Meng and F. Song, Appl. Surf. Sci., 2011, 257, 9519-9524.
- A. Stein, B. E. Wilson and S. G. Rudisill, Chem. Soc. Rev., 16 2013, 42, 2763-2803.
- G. Zhang, Z. Zhao, J. Xu, J. Zheng, J. Liu, G. Jiang, A. Duan 17 and H. He, Appl. Catal., B, 2011, 107, 302-315.
- J. Zheng, J. Liu, Z. Zhao, J. Xu, A. Duan and G. Jiang, Catal. 18 Today, 2012, 191, 146-153.
- 19 M. Sadakane, T. Asanuma, J. Kubo and W. Ueda, Chem.

ARTICLE

Mater., 2005, 17, 3546-3551.

- 20 Y. Wei, J. Liu, Z. Zhao, A. Duan, G. Jiang, C. Xu, J. Gao, H. He and X. Wang, *Energ. Environ. Sci.*, 2011, **4**, 2959-2970.
- 21 J. Xu, J. Liu, Z. Zhao, J. Zheng, G. Zhang, A. Duan and G. Jiang, *Catal. Today*, 2010, **153**, 136-142.
- 22 C. Gong, C. Song, Y. Pei, G. Lv and G. Fan, *Ind. Eng. Chem. Res.*, 2008, 47, 4374–4378.
- 23 B. T. Holland, C. F. Blanford, T. Do and A. Stein, *Chem. Mater.*, 1999, 11, 795-805.
- 24 J. M. Zamaro, M. A. Ulla and E. E. Miró, *Chem. Eng. J.*, 2005, 106, 25-33.
- 25 E. D. Banús, V. G. Milt, E. E. Miró and M. A. Ulla, *Appl. Catal.*, *B*, 2013, **132**, 479-486.
- 26 B. R. Stanmore, J. F. Brilhac and P. Gilot, *Carbon*, 2001, **39**, 2247-2268.
- 27 T. Nakamura, G. Petzow and L. J. Gauckler, *Mater. Res. Bull.*, 1979, 14, 649-659.
- 28 B. Sextori, A. Hughes and T. Turney, *J. Catal.*, 1986, 97, 390–406.
- 29 J. Xu, J. Liu, Z. Zhao, C. Xu, J. Zheng, A. Duan and G. Jiang, J. Catal., 2011, 282, 1-12.
- 30 H. Liang, Y. Hong, C. Zhu, S. Li, Y. Chen, Z. Liu and D. Ye, *Catal. Today*, 2013, 201, 98-102.





Three-dimensionally ordered macroporous (3DOM) SiOC were successfully fabricated on the cordierite monolith, and $LaCoO_3$ was coated onto 3DOM SiOC/cordierite. The 3DOM structure produced a positive effect on soot combustion.