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Chapter

Reducing Green House Effect Caused by Soot via Oxidation Using Modified $LaFe_{1-x}Cu_xO_3$ Catalysts

Paritosh C. Kulkarni

Abstract

Soot has been the cause of global warming since the dawn of diesel engines. Soot oxidation in the diesel particulate filters fixated at the exhaust of the engine has been a boon to reduce the particulate matter from entering the atmosphere. Here we have attempted to synthesize the smooth powder of supported and macro-porous perovskite $LaFeO_3$ and its doped variant with 5, 10, 20, and 30% copper on B site. Subsequent catalysts, termed as LFO and LFCO- (5, 10, 20, 30) with formula $LaFe_{1-x}Cu_xO_3$, were investigated as catalysts for soot oxidation reaction. The structural and physical and chemical attributes of $LaFe_{1-x}Cu_xO_3$ and $LaFeO_3$ are characterized by XRD patterns, FESEM, BET, particle size analysis measurements. Undoped $LaFeO_3$ with desired textural structures were successfully prepared, employing the citric-acid auto combustion method, and the porous sample exhibits the best activity towards redox reactions, pointing out the enriched activity at redox sites of fabrication of porous perovskite for the responses. By correlating with the catalytic activities and the physical and chemical properties, of both doped and undoped samples, it is inferred that the best activity obtained from the porous $LaFe_{0.9}Cu_{0.10}O_3$ is attributed to its extensive surface area corresponding to least particle size, precious active lattice oxygen, high oxygen storage capacity and vigorous surface activity.

Keywords: heterogeneous catalysis, green chemistry, perovskite-type oxides, soot oxidation, sustainability, green and clean synthesis, global warming, greenhouse effect

Highlights

- Copper-doped LFO and pure LFO were analyzed as catalysts for soot oxidation.
- It is useful in oxidizing carbon particulate in comparison with pure $LaFeO_3$.
- We have correlated mechanism of soot oxidation with the function of LFO and LFCuO.
- We have proposed the optimized route to install the catalysts using the TGA chart of conversion of soot, T_{50} temperature, and catalytic performance.
- The enhanced stability and reusability indicated its potential for practical use.

1. Introduction

The literature [1] indicates a strong relationship between the rising of soot concentration in the environment and the increasing intensity of global warming over the past 20 years. Greenhouse effect and global warming are the most pressing issues the world is facing in 2019. The noticeable problem is the are average 0.17°C per year global warming since pre-industrial levels (1970–2019), also the 0.09°C warming and increasing pH of oceans 1950s, 3.2 cm sea-levels growth per decade, a large number of extreme heatwaves in last decade [2, 3]. Unless the in 2019 we act to reduce the causes of global warming, we unite and commit, and pledge that the changes to mitigate global warming are fully implemented, the adverse effects of climate change will go on.

The natural phenomenon of the greenhouse effect plays a vital role in climate change for decades. The burning of fossil fuels has contributed intensely to the natural greenhouse effect. This aggregated greenhouse effect stems from a rise in the atmospheric concentrations termed greenhouse gases. Greenhouse gases in the atmosphere lead to climate change. Soot, along with NO_x, CO, and CO_2 are considered significant greenhouse gases and pollutants.

In recent years after the industrial revolution, diesel engines are used extensively in multiple areas for their fewer CO_2 emissions, better fuel efficiency, and improved economy [4]. Soot or unburnt hydrocarbons (UHC) present in the exhaust of internal combustion diesel engines. To be in accord with the intense emission levels imposed by the law, destruction of above mentioned delirious compounds is the necessity of the era. Their conversion into a nonparticulate form before these toxic substances released into the surrounding environment is also another alternative. Soot has been counted in the chief scale of severity among such classification. For this purpose, it is proposed, the of a mixture of catalytically active components coated with perovskites will cause the parallel conversion of UHC into subsequent oxides while could be absorbed in the exhaust filters and by the environment.

While soot continues to harm human race in metropolitan cities its effect is unseen to healthy eyes, when carbon black enters your bloodstream, it can cause a wide array of severe health issues, including respiratory problems, infections, shortness of breath, bronchitis, asthma, stroke, heart attack, cancer, and premature death. Soot not only causes smog that decreases visual clarity but stays in the atmosphere longer than carbon dioxide. Carbon dioxide can be absorbed by trees, but soot cannot be 'fixed' by natural means. Soot causes global warming by absorbing sunlight and directly heat the surrounding air. **Figure 1** clearly

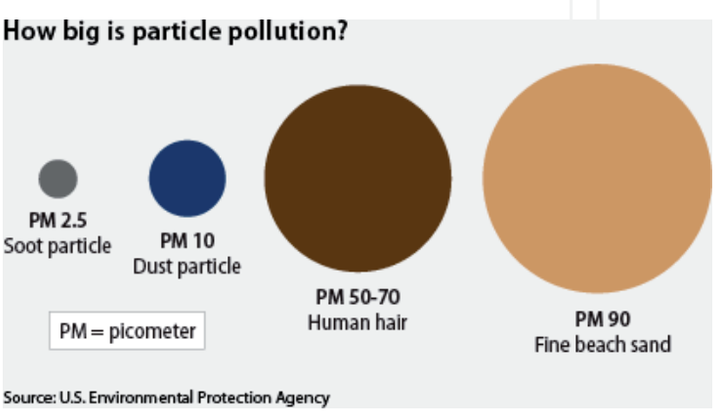


Figure 1.
Pollution caused by particulate matter.

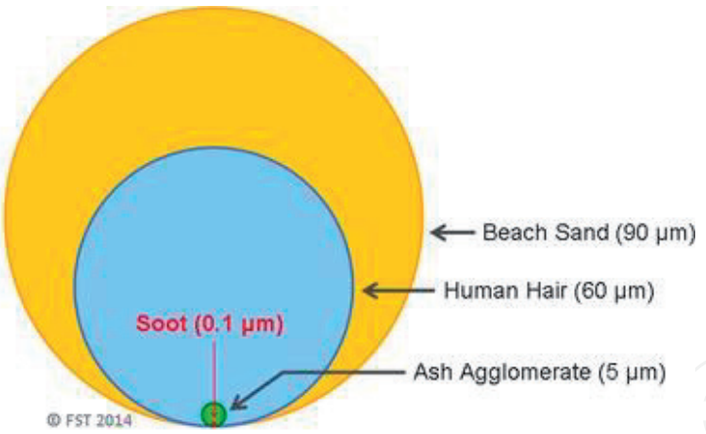


Figure 2.
Size of soot as the comparison with other particulate matter.

demonstrates how particulate matter is contributing to global warming as a significant global pollutant. **Figure 2** zones in the culmination of sizes of PM towards soot indicating inversely proportional relationship between the size of PM and its banality [5, 6].

This particulate matter (pm) in the form of soot released from the diesel combustion process has grasped plenty of attention. The reason for that is it can give rise to serious environmental and health problems [7–9]. Particulate matter is filtered with diesel particulate filters (DPF) in the current scenario [10] which captures soot and requires regeneration to maintain performance. To tackle this issue, researchers have conducted some works about regeneration, but none led to satisfaction. Methods involving in oxidation of particulate matter directly are researched upon. But they all need a high temperature above 600°C which might destroy DPF [11].

Therefore oxidation of soot is important to resolve environmental issues in many parts of the world. However, soot oxidation is not a process that can occur under natural conditions, and so further analysis is needed.

Following reactions take place for soot oxidation:

$$C_{soot} + O_2 \rightarrow CO_2 + H_2O$$

$$2CO + O_2 \rightarrow 2CO_2$$

$$C_{soot} + NO \rightarrow \tfrac{1}{2}N_2 + CO_2 + H_2O$$

As seen soot oxidation mainly involves the reaction of formation of CO_2, so does the enthalpy of reaction is enthalpy of formation. Enthalpy at 298.15 K for carbon dioxide formation is 393.5 kJ/mol and the formation of carbon monoxide is 110.53 kJ/mol. Soot oxidation is a slow process at high temperatures with relatively high activation energy.

Activation energy of above reaction at various temperature is found as follows:

770–1250 K:143.5 kJ/mol

800–1000 K:161.2 kJ/mol—Accurate and depends on the partial pressure of O_2 (root pO_2)—(7)

1100–1400 K:164 kJ/mol

Thus, the catalyst is required to increase the rate and decrease the time of the process. Various catalysts are proposed, and perovskites are discussed in detail. Because oxidation and reduction reactions must co-occur, perovskites are efficient owing to their high redox properties and high oxygen storage capacity (OSC) in some perovskites. In this work, we prepared a series of $LaFe_{1-x}Cu_xO_3$ perovskite-type nanopowder by sol–gel auto-combustion technique following calcination under the same experimental conditions. The metal nitrates and EDTA along with citric acid were dissolved in water, the homogeneous mixtures then added with ammonia to balance pH and kept to form a gel, and later combusted and calcined in the air at last. The as-prepared samples were characterized by XRD, FE-SEM, BET, particle size, TGA/DTA, and carbon dioxide analysis techniques to investigate the effect of the introduction amount of Cu^{2+} on the morphology, structure and redox abilities of the catalysts [12].

2. Methodology

2.1 Materials

Lanthanum nitrate hexa-hydrate ($La(NO_3)_3{\cdot}6H_2O$, ≥99.9% purity), copper nitrate ($Cu(No_3)_2$, ≥99.9% purity), and iron nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, ≥99.9% purity) were obtained from Alfa Aesar.

2.2 Catalyst preparation

All catalyst powders were prepared using the EDTA-citrate auto combustion method [5]. Metal nitrates were employed as desired metal pre-cursors for support. A 2 g-scale preparation for $LaFe_{1-x}Cu_xO_{3-\Delta}$ is described below as an example. Lanthanum nitrate ($La(NO_3)_3{\cdot}6H_2O$) was dissolved in deionized water (100 mL), followed by mixing into an aqueous solution of copper and iron nitrates in stoichiometric ratios at room temperature. EDTA (3.8 g) dissolved in an aqueous NH_3 solution was then dropped into the mixed solution, followed by the addition of solid citric acid (3.7 g) upon stirring. Molar ratio of total metal ions (La + Fe-Cu), EDTA, and citrate is 1.0:1.0:1.5, respectively. NH_4OH was used to adjust the pH of the solution to the desired value of 11 [12–14]. The solution was then heated above 80°C slowly and became dark brown after being brown-orange at the beginning.

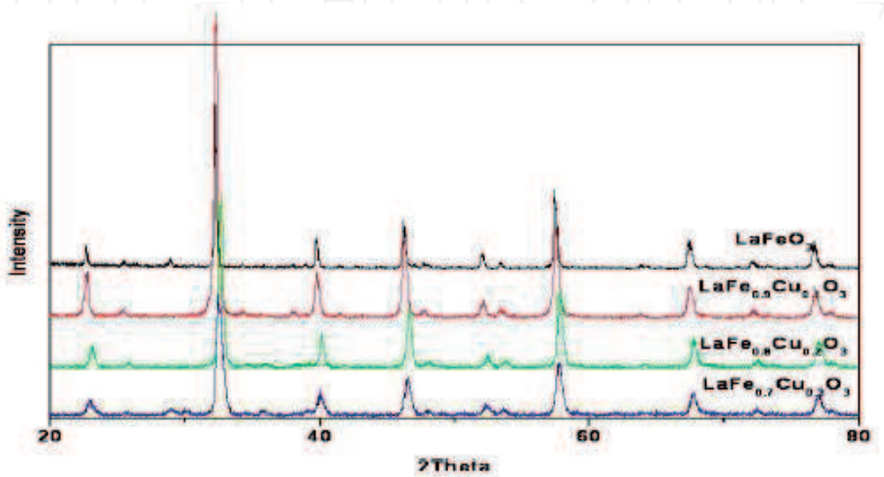


Figure 3.
XRD plot of $LaFeO_3$ doped with copper on B site.

The gel was placed in a hot air oven at 200°C for 12 h to combust and convert into flaking solid powders. Next, the powders were crushed and calcined at 800°C for 6 h in air to yield $LaFe_{1-x}Cu_xO_{3-\Delta}$ which was ground and solid power was obtained. The preparation method for undoped LFO samples is the same as above (**Figure 3**) [13].

3. Results

As shown in **Figure 4**, doping of copper of the perovskite did not affect the crystal structures of $LaFe_{1-x}Cu_xO_3$ samples (LFCO-10–LFCO-20). The peaks were in negligible deviation to the peaks of LFO. The characteristic diffraction peaks were at 22.6°, 32.2°, 38.0°, 39.6°, 46.3°, 53.3°, 57.4°, 67.4°, and 76.7° in the diffraction data of all samples can be correlated to the indices of the crystal planes of (101), (121), (112), (220), (141), (311), (240), (242), and (204), signifying that the fabricated samples were finely crystallized with three-dimensional orthorhombic structure (JCPDS No. 37-1493) [15, 16]. **Figure 4** zooms in the XRD graph of LFCO-10 and contrasts it with the pure LFO synthesized in-situ and in agreement with the JCPDS data.

Table 1 shown below depicts the a, b, c values for lattice constants of the perovskite $LaFeO_3$ and [17] $LaFe_{1-x}Cu_xO_3$. The introduction of Cu(II) with a larger ionic radius (0.730 Å) to replace Fe(III) with smaller ionic radius (0.645 Å) did not result in the expansion of LFO unit-cell [18, 19]. The smaller cell volume of $LaFe_{1-x}Cu_xO_3$ might be caused by the defects in the form of anionic vacancies, which maintained the electroneutrality in $LaFe_{1-x}Cu_xO_3$ [17, 20–26]. In **Table 1**, the crystallite sizes of Cu-doped LFO samples were smaller than that of undoped sample and decreased with increasing amount of Cu dopant.

This concurs with the literature, it shows that increasing Cu doping could cause lattice distortion and hinders the growth of large crystallites in the samples. The large degree of crystallinity with minute defects fosters the reduction in the recombination of electron–hole pairs, leading to enhanced efficiency of the soot oxidation reaction [15].

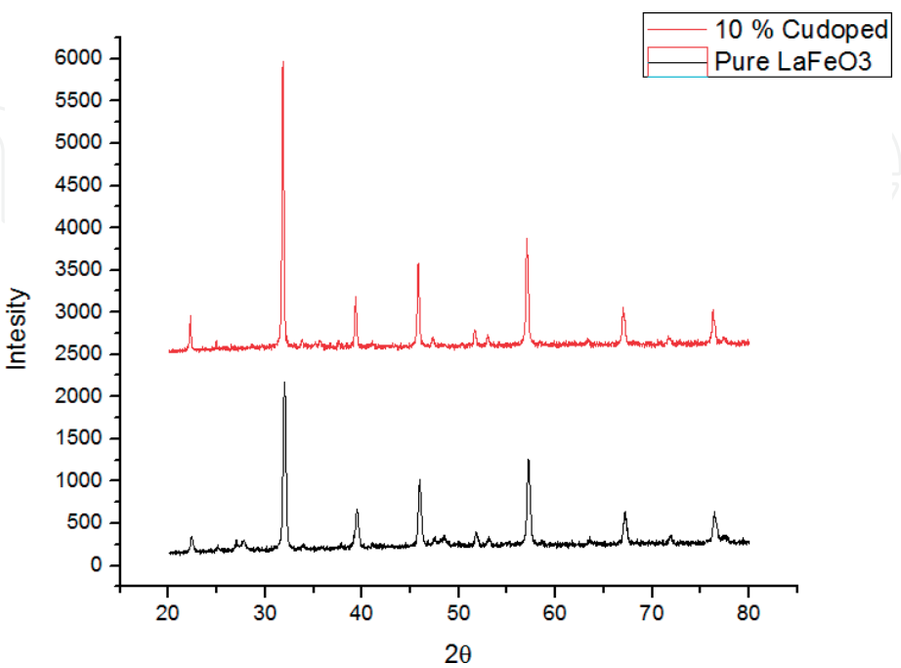


Figure 4.
Zoomed in image of XRD LFCO-10.

	a (A^0)	b (A^0)	c (A^0)	Cell volume ($Å^3$)
$LaFeO_3$	5.576(3)	7.857(3)	5.550(2)	242.160
$LaFe_{0.9}Cu_{0.1}O_3$	5.554(4)	7.854(4)	5.554(2)	241.580
$LaFe_{0.8}Cu_{0.2}O_3$	5.567(3)	7.869(3)	5.563(2)	241.074
$LaFe_{0.7}Cu_{0.3}O_3$	5.571(4)	7.862(4)	5.560(2)	240.499 238.101

Table 1.
Lattice parameter and cell volume calculations inferred from XRD analysis.

Sample	Structural property		
	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
LFO-0Cu	17.63	0.099	45.66
LFO-5Cu	19.01	0.068	32.90
LFO-10Cu	21.37	0.11	35.52
LFO-15Cu	25.33	0.12	39.29
LFO-20Cu	24.57	0.14	37.95

Table 2.
Calculations obtained from BET analysis about structural properties.

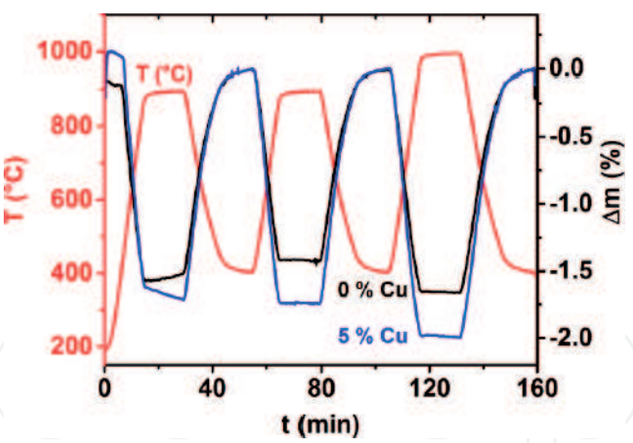


Figure 5.
TGA analysis of LFCO-5.

The information can be observed from **Table 2**, the prepared samples exhibited similar morphology, relating to the pore size consisting of nano and spherical particles. That the Cu-doping did not significantly affect the morphology and particle size of sample. The decrease in the pore size signifies that the Cu ions have been inserted into the lattice. On the other hand the XRD shoes no distortion into the lattice, which in turn explains the possible structural acceptance capability of the LFO towards favorable Cu doping.

TGA analysis results shown below proves that the catalyst is acting on the soot to reduce the carbon black particles in the controlled environment (here fixed air velocity was used) (**Figure 5**).

4. Discussion

The focus of the research is to dissect the problem of global warming by understanding scope doping of copper on the LFO structure, then to analyze the effect on the properties of the LFO and correlate them with the performance characteristics of the catalyst with the reaction of soot oxidation. Following the results, we are attempting to circumnavigate the altered properties of LFCO to the catalytical performance.

Firstly, no crystalline Cu peaks were observed and the congruent, perovskite phase formed in all cases (LFO-10Cu–LFO-30Cu). However, the amount of Cu doping in the inverse proportion with the intensity of diffraction peaks because it was broadening them.

Cell volume can be calculated for orthorhombic structure as V = abc.
For the LFCO-10-
*(since a = c), V = (5.554^2)*7.845 A°m^3 = 242.16 A°m^3 and so on*
Which gives the below inverse relation

The cell volume of $LaFe_{1-x}Cu_xO_3$ is marginally smaller than that of LFO; this value decreased with increasing Cu doping.

We can observe the trend in the BET analysis when synthesized at maximum Cu doping concentration; the particles may have fused to form large convolutions, This may also explain the more significant pore volumes and sizes for the samples of LFO-10Cu and LFO-20Cu when compared with others [8]. Increasing pore volume is the indication of more room for oxygen ions to combine with carbon, following reaction will spread light on the intricacies of the steps involved. Now as we see in the culmination of discussion, we are relating how the catalyst could have acted on the UHC (soot) and where rate-limiting step where the most unstable species carbon trioxide is formed and exactly in that step the LFO-Cu will facilitate the conversion in the diesel particulate filter (DPF) It will lower the temperature required for reaction to attain 50% conversion. From the TGA, we could infer the temperature to be around 350°C which is significantly lower than 600°C observed in reality and 500°C observed in the 0.

The controlled environment of the TGA equipment.

The chemical aspects of soot oxidation as discussed earlier indicated a need for catalyst. Here we can infer from TGA data that indeed the 50% conversion temperature of the catalyzed reaction is near to the exhaust temperature of the diesel engine, which in turn follows the possibility of soot oxidation reaction in the DPFs. Once installed the catalyst will reduce the amount of soot exiting the exhaust. The decrease in soot

$$O_{2(g)} \rightarrow O_{2(ads)} \rightarrow 2O_{(ads)}$$

$$CO_{(g)} \rightarrow CO_{(ads)}$$

$$CO_{(ads)} + 2O_{(ads)} \rightarrow CO_{3(ads)} \text{ (rate limiting step)}$$

$$CO_{3(ads)} \rightarrow CO_{2(ads)} + O_{(ads)}$$

$$CO_{2(ads)} \rightarrow CO_{2(g)}$$

Figure 6.
Possible reaction mechanism and role of catalyst—soot oxidation.

emissions from diesel engines will reduce the amount of carbon in the atmosphere, quantification of which can be extrapolated as 6 g hold per liter of diesel burnt.

As stated earlier, the formation of reactive carbon and oxidation of that species the basis of soot oxidation first order recombination reaction takes place,

$$H* + OH* + C_{(free)} - H_2O + C_{(reactive)}$$

And concerning **Figure 6**, soot oxidation mainly involves the reaction of formation of CO_2; soot oxidation is a slow process at high temperatures with relatively high activation energy (143 kJ/mol at average of 600°C) However due to increased surface activity of LFCO-20% it would be effective at the exhaust temperature itself (350°C). This would mean the catalyst is effective in converting soot to its subsequent oxides.

5. Conclusions

An attempt was made to understand the issue of global warming from all aspects, it was then established that the emission of soot contributes to global warming [1]. Soot does cause a greenhouse effect and reducing the concentration of unburnt hydrocarbons is a possible solution to combat global warming.

Soot is harmful to humans and pollutes the atmosphere, thus, soot oxidation is a necessity in today's environmental conditions, as proved soot oxidation does not take place at standard temperature and pressure and requires high temperature and stoichiometric conditions also it is slow process. Therefore, a catalyst is needed to make it feasible. To mitigate the issue of soot we undertook this research to semantically and objectively evaluate the scope doping of copper on the LFO structure, then to analyze the effect on the properties of the LFO and correlate them with the performance of the catalyst with soot oxidation.

Perovskite-type oxides were reviewed in relation to their application in soot oxidation. The main advantage of these materials is their robust crystal structure that can be used to catalyze redox reactions due to their flexible oxygen content. The possibility to accommodate simultaneously different metal cations at A- and B-sites allows tuning the catalytic properties for a specific application such as soot oxidation, which requires redox properties with high thermal stability. As such, perovskite-type oxides exhibit good oxidation activity. Cu-doped $LaFeO_3$ ($LaFe_{1-x}Cu_xO_3$) samples were prepared by a citric-acid auto combustion method and used as heterogeneous catalysts for the process of soot oxidation. The results showed that LFO-10Cu with a theoretical 10 mol% Cu doping was more effective and stable than the sample of $LaFeO_3$ (LFO) in terms of cell size and pore volumes and active surface area. The partial substitution of Cu into LFO improved oxidation rate by approximately 60%; which could be ascribed to the formation of more free oxygen during the adsorption of carbon particulates over the perovskite. The encouraging data also indicated the high stability and reusability of LFO-10Cu; therefore, it shows possible potential as a promising catalyst for soot pollutant removal in the field of diesel particulate filters [27–29]. As DPFs are optimized soot will be reduced and so global warming [1].

As of scope for further research the prepared catalyst can be manufactured at a scaled-up laboratory such facility in an industry or in the research laboratory of Pollution Control Board, Govt of India and is proposed to be implemented in public transport and custom DPFs for trials as the cost of manufacturing has to be calibrated over the years.

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Author details

Paritosh C. Kulkarni
Department of Chemical Engineering, Manipal Institute of Technology, MAHE, Manipal, India

*Address all correspondence to: paritosh.chandrashekhar@learner.manipal.edu

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References

[1] Quaas J. Global warming: The soot factor. Nature. 2011;**471**:456-457. DOI: 10.1038/471456a

[2] Levitus S et al. World ocean heat content and thermosteric sea level change (0-2000 m), 1955-2010. Geophysical Research Letters. 2012;**39**:L10603. DOI: 10.1029/2012GL051106

[3] Climate change increases the likelihood of catastrophic avian mortality events during extreme heat waves. DOI: 10.1098/rsbl.2009.0702. Published: 30 September 2009

[4] Keav S, Matam SK, Ferri D, Weidenkaff A. Structured perovskite-based catalysts and their application as three-way catalytic converters—A review

[5] Harshini D, Lee DH, Jeonga J, et al. Applied Catalysis B: Environmental. 2014;**148-149**:415-423

[6] Simonsen SB, Dahl S, Johnson E, Helveg S. Catalytic soot oxidation studied by environmental transmission electron microscopy. In: Richter S, Schwedt A, editors. 14th European Microscopy Congress (EMC 2008); 1-5 September 2008; Aachen, Germany. Berlin, Heidelberg: Springer; 2008

[7] Labhasetwar N et al. Perovskite-type catalytic materials for environmental applications. Science and Technology of Advanced Materials. 2015;**16**:036002

[8] Fino D, Bensaid S, Piumetti M, Russo N. A review on the catalytic combustion of soot in diesel particulate filters for automotive applications: From powder catalysts to structured reactors. Applied Catalysis A: General. 2016;**509**:75-96. DOI: 10.1016/j.apcata.2015.10.016. ISSN: 0926-860X

[9] Guo H, Anderson P, Sunderland P. Optimized rate expressions for soot oxidation by OH and O_2. Fuel. 2016;**172**. DOI: 10.1016/j.fuel.2016.01.030

[10] Singh M, Gaddam CK, Wal RLV, Xu C, Yezerets A, Kamasamudram K. Reconciliation of Carbon Oxidation Rates and Activation Energies Based on Changing Nanostructure. John and Willie Leone/Department of Energy & Mineral Engineering (EME)/Institutes of Energy and the Environment (IEE)/ Materials Research Institute (MRI)

[11] Jung H, Kittelson D, Zachariah M. Kinetics and visualization of soot oxidation using transmission electron microscopy. Combustion and Flame. 2004;**136**:445-456. DOI: 10.1016/j.combustflame.2003.10.013

[12] Ovejero G, Sotelo JL, Romero MD, Rodríguez A, Ocaña MA, Rodríguez G, et al. Multiwalled carbon nanotubes for liquid-phase oxidation. Functionalization, characterization, and catalytic activity. Industrial & Engineering Chemistry Research. 2006;**45**(7):2206-2212. DOI: 10.1021/ie051079p

[13] Thirumalairajan S, Girija K, Hebalkar NY, Mangalaraj D, Viswanathan C, Ponpandian N. Shape evolution of perovskite $LaFeO_3$ nanostructures: A systematic investigation of growth mechanism, properties and morphology dependent photocatalytic activities

[14] Industrial & Engineering Chemistry Research. 2014;**53**(24):10090-10096. DOI: 10.1021/ie501277x. Publication Date: May 23, 2014

[15] Dacquin JP, Lancelot C, Dujardin C, Cordier-Robert C, Granger P. Support-induced effects of $LaFeO_3$ perovskite on the catalytic performances of supported

Pt catalysts in DeNOx applications. Journal of Physical Chemistry C. 2011;**115**(5):1911-1921. DOI: 10.1021/jp1069779. Publication Date: 06 January 2011

[16] Di Sarli V, Landi G, Lisi L, Saliva A, Di Benedetto A. Catalytic diesel particulate filters with highly dispersed ceria: Effect of the soot-catalyst contact on the regeneration performance. Applied Catalysis B: Environmental. 2016;**197**:116-124. DOI: 10.1016/j.apcatb.2016.01.073. ISSN: 0926-3373

[17] Kulkarni PC, Neelapala SD, Uppara HP, Dasari H, Van Esch N. $SmFe_{1-y}Co_yO_3$ perovskite-type oxides for soot oxidation. International Journal of Recent Technology and Engineering (IJRTE). 2019;**8**(1S4). ISSN: 2277-3878

[18] Trovarelli A, Hutchings GJ, editors. Catalysis by Ceria and Related Materials (Università di Udine, Italy). Catalytic Science Series. Vol. 2. London: Imperial College Press; 2002. vviii + 508p. ISBN: 1-86094-299-7

[19] Swartz SL. Journal of the American Chemical Society. 2002;**124**(43):12923-12924. DOI: 10.1021/ja025256e. Publication Date: September 24, 2002

[20] Xiao P, Zhong L, Zhu J, Hong J, Li J, Li H, et al. CO and soot oxidation over macroporous perovskite $LaFeO_3$. Catalysis Today. 2015;**258**(Part 2):660-667. DOI: 10.1016/j.cattod.2015.01.007. ISSN: 0920-5861

[21] Yaghi OM, O'Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J. Reticular synthesis and the design of new materials. Nature. 2003;**423**:705-714

[22] Wei Y, Liu J, Zhao Z, Chen Y, Xu C, Duan A, et al. Highly active catalysts of gold nanoparticles supported on three-dimensionally ordered macroporous $LaFeO_3$ for soot oxidation. Angewandte Chemie, International Edition. 2011;**50**:2326-2329. DOI: 10.1002/anie.201006014

[23] Lukashuk L, Yigit N, Li H, Bernardi J, Föttinger K, Rupprechter G. Operando XAS and NAP-XPS investigation of CO oxidation on meso- and nanoscale CoO catalysts. Catalysis Today. 2019;**336**:139-147. DOI: 10.1016/j.cattod.2018.12.052. ISSN: 0920-5861

[24] Ma BQ, Sun HL, Gao S. The design and synthesis of a non-centric diamond-like network based NH_4^+ ion. Chemical Communications. 2003:2164-2165

[25] Mangal S et al. Materials Today: Proceedings. 2018;**5**:16378-16389

[26] Ramirez JH, Maldonado-Hódar FJ, Pérez-Cadenas AF, Moreno-Castilla C, Costa CA, Madeira LM. Azo-dye orange II degradation by heterogeneous Fenton-like reaction using carbon-Fe catalysts. Applied Catalysis B: Environmental. 2007;**75**(3-4):312-323. DOI: 10.1016/j.apcatb.2007.05.003. ISSN: 0926-3373

[27] Mishra A, Prasad R. Preparation and application of perovskite catalysts for diesel soot emissions control: An overview. Catalysis Reviews. 2014;**56**(1):57-81. DOI: 10.1080/01614940.2014.866438

[28] Li L, Wang X, Zhang Y. Materials Research Bulletin. 2014;**50**:18-22

[29] Sannino D, Vaiano V, Ciambelli P, Isupova LA. Catalysis Today. 2011;**161**:255-259