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ORIGINAL RESEARCH ARTICLE



Synthesis, characterization and catalytic activity of partially substituted $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ ($x \geq 0.1 \leq 0.4$) nano catalysts for potential soot oxidation in diesel particulate filters in diesel engines

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ABSTRACT

The sol gel method was used in preparing a series of A site partially substituted $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ ($x \geq 0.1 \leq 0.4$) perovskite catalysts coded LBC1, 2, 3, and 4 and their potential as catalysts for soot oxidation were evaluated. The Brunauer–Emmett–Teller (BET), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES), Thermogravimetric/Differential Thermal Analysis (TGA/DTG), X-ray analysis (XRD) were used in characterizing the prepared perovskite catalyst. The result shows that at ($x \geq 0.2 \leq 0.4$), there was an increase in surface area when we compare it with that of $x = 0$. The increase in surface area helps in increasing the catalytic performance of the catalyst. Also, when evaluating the catalytic performance of the synthesized catalysts, it was observed that doping the perovskite catalysts helped in the general improvement of the catalytic performance for soot oxidation. The best performance in this research study with a T_{50} of 484 °C was observed at $x = 0.2$ catalyst (LBC2). This shows that the non-noble perovskite catalysts prepared in this research study has the potential to replace the noble metal based catalysts used presently in the diesel automotive industry.

KEYWORDS

soot oxidation, perovskites, catalysts, sol gel, barium

1. INTRODUCTION

Diesel engines in recent times have been widely used as a means of transportation. However, these automotive systems suffer from a high level of discharges which are most times soot [1–3]. In the advent of this, reducing diesel exhaust to permitted environmental levels is of utmost importance and cannot be achieved by engine modifications alone, but by also considering the catalytic after treatment process [4]. Literature review reveals that one of the most widely used techniques for soot reduction in diesel engines is the wall-flow filter, which involves the entrapment of the soot, after which the deposited soot is burned off as a result of the catalyst placed on the filter [5, 6]. This technology has proven to be successful worldwide. Several reports have argued that the perovskite metal oxide has the ability to promote the conversion of soot into CO_2 in catalytic traps. The perovskite metal oxide is a general formula ABO_3 , in which the A site is generally occupied by the lanthanide and actinides groups, while the B site is generally occupied by the transition metal groups coordinated to oxygen atom. The metal on the A site usually gives stability to the perovskite structure, while the metals on the B sites are the ones responsible for the catalytic activity of the perovskite metal oxide. The partial substitution of the A or/and B site can give structural modifications which can result

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into crystal lattice distortion as well as oxygen vacancies generation, hence the thermal stability and catalytic activities can be tailored. Some of the factors affecting the catalytic activity for soot oxidation (surface area of catalyst, the redox properties of catalyst, the position at which the substitution of the catalyst is taking place) have been given a consequential attention in recent times. Several reports have shown that perovskite catalyst can be an effective catalyst for soot oxidation in diesel engines. However, out of all the researched catalyst, LaCoO_3 has been found to be the most responsive to soot oxidation due to the fact that it possesses high catalytic capability and can form well-structured perovskite crystallite at highly substituted conditions. However, the effect of dopant on the catalytic activity of soot in DPFs has been properly dealt with in literature.

Therefore, in this research study, the A site component of LaCoO_3 was partially substituted with Ba in the range of 0–0.4. The prepared catalyst was characterized using the various characterization techniques such as the X-ray analysis (XRD), ICP-AES, EDAX, Brunauer–Emmett–Teller (BET), Thermogravimetric/Differential Thermal Analysis (TGA/DTA), while catalytic evaluation for soot oxidation was performed using the TGA method. The results obtained tend to help in the formulation of a viable commercially available perovskite catalyst for diesel exhaust purification.

2. MATERIALS AND METHODS

2.1. Synthesis of $\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ perovskite catalyst

All the chemicals used for this experiment were purchased from Sigma Aldrich Ltd, and were used as purchased without further purification. The method used for the preparation of the above mentioned perovskite catalyst was the citrate EDTA sol gel synthesis method. According to this method, the appropriate metal nitrate solutions were mixed with EDTA and Citric Acid, which acts as chelating agents. The mixture was stirred at 90 °C for 4 h on a hot plate. The gel like material obtained after a temperature raised to 100 °C was calcined at 750 °C for 5 h to obtain the final perovskite structure. Several catalysts were prepared by varying the ratio of barium used ($x = 0, 0.1, 0.2, 0.3, 0.4$ coded LBC 0, 1, 2, 3, 4, respectively).

3. RESULTS AND DISCUSSION

The TGA/DTA analysis of the prepared perovskite catalyst is shown in Fig. 1 below. A representative catalyst LBC2 dried at 200 °C for 5 h was used for the thermal behaviour investigation of the prepared catalyst.

The phase changes mechanism of the prepared catalysts was monitored by the percentage weight loss in relation to the temperature from the range of 0–1,000 °C. The weight losses that were observed at temperatures below 600 °C can be attributed to the thermal decomposition of water, citrate

precursor, and carbon monoxide [5, 7, 8]. At temperature higher than 600 °C, no change in weight was observed. From the TGA/DTA profiles, about three major weight loss stages were observed. The first endothermic weight loss (A_1) was observed around 0–150 °C, which could be credited to the loss of surface water molecules [1, 9, 10]. The second weight loss (A_2) was observed around 150–260 °C, which is attributed to the loss of crystalline water. The major decomposition stage (A_3) was observed at the temperature between 250 and 400 °C and can be credited to the decomposition of the citrate, EDTA and organic precursors. The minor weight losses that were observed above 400 °C are ascribed to the decomposition of the organic materials under the O_2 condition resulted in the large DTA peak [13–15]. The stages of the weight loss observed from the TGA along with the chemical processes that was observed in the DTA suggests that the stepwise thermal decomposition of the prepared perovskite catalysts came to an end at about 600 °C.

The Xrd diffraction pattern of the prepared catalyst is as shown in Fig. 2. Figure 2 shows the evolution of the crystalline phases of the precursor (LBC0) dried at 200 °C and the doped catalysts (LBC1-4), calcined at 750 °C. It was observed that the XRD diffractogram of the precursor appears to be completely amorphous. This suggests that at a temperature of 200 °C, the formation of the perovskite phase has not been achieved, which could be a result of impurities contained in the precursor which has not been completely burnt off. However, there was clear and distinct peak when the catalysts were calcined at 750 °C. Also, the peaks corresponding to LaCoO_3 perovskite phase (JCPDS-ICCD 48-0123) were observed and indexed using the QualX software.

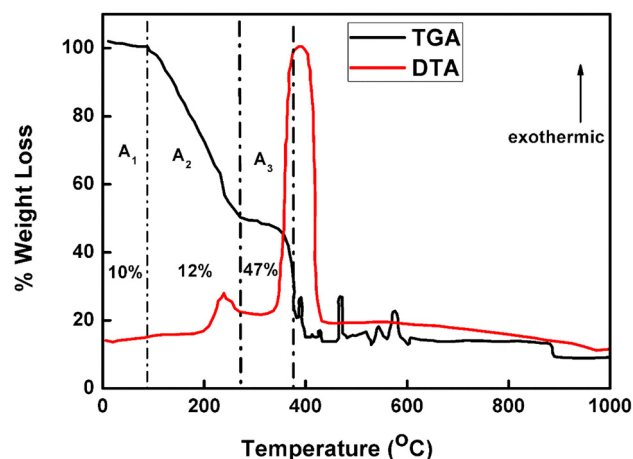


Figure 1. TGA/DTA of LBC2 dried at 200 °C



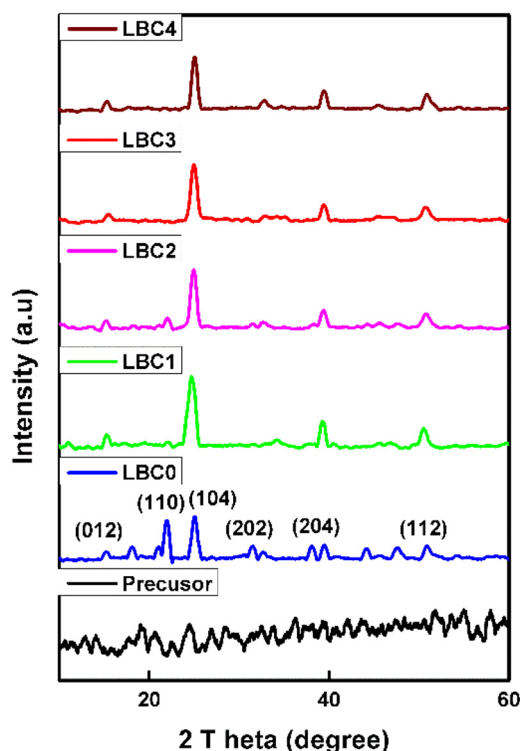


Figure 2. XRD diffractograms of all the prepared catalysts

Isolated phase or impurity such as $\text{La}_2\text{Ba}_2\text{O}_5$, BaLaCoO_4 , metal-EDTA, metal nitrate, metal citrate was noticed in the Xrd diffractogram [16, 17]. This indicates that the preparation technique used and the calcination temperature was effective in the attainment of the single phase perovskite structure.

Also, upon the introduction of Ba into the perovskite structure, there was a shift at the angle ($2\theta = 32-33$, as shown in Fig. 3) towards the lower angle 2θ . This shift can be said to be a result of the structural and stoichiometry changes occurring due to the charge difference created between the exchanged lanthanum cation (+3) and the barium cation (+2).

Similarly, the unit parameters of the prepared catalysts were carried out using the software QualX and the results are recorded in Table 1. The results obtained from both the doped and undoped catalysts are well in agreement with previous reports in literature [13]. It was observed that the partial substitution of the La^{3+} by the Ba^{2+} cations resulted into the increase of the cell volume and c (\AA) parameter. Also, the average crystallite size was calculated using the QualX software and also validated by the Scherrer equation using the (104) peak. The result obtained is recorded in Table 1. It was noticed that upon the doping of the perovskite catalysts, there was a significant drop in the crystallite sizes of the catalysts. The crystallite sizes range between 25 nm and 32 nm. This is similar to what has been previously reported in literature [18]

The elemental composition of all the prepared perovskite catalysts was done using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES) and the result is as

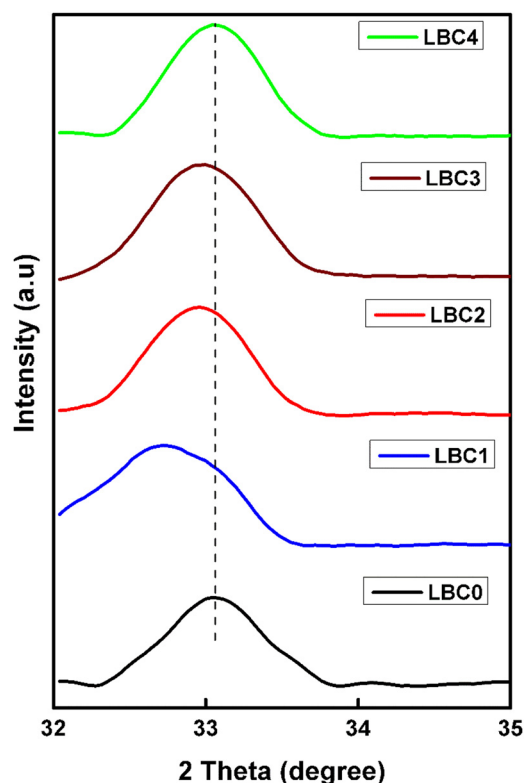


Figure 3. Extended XRD plots of the prepared catalysts

shown in Table 2. The results validate the percentage composition of all the elements present in the perovskite catalyst. The percentage composition of La, Ba, Co obtained from the ICPAES was observed to be close to that obtained from the theoretical values (in parenthesis). This indicates that the metals were well mixed during the preparation stage and that the method used is efficient for the intended perovskite catalyst design.

Also, the SEM-EDAX of the prepared catalysts is as shown in Fig. 4. The SEM-EDAX of the catalysts confirms the presence of La, Ba, Co and O, hence suggesting that the designed perovskite catalyst have been formed. The bar chart presented in Fig. 4 compares the differences between the theoretical values and the experimental values which show that they are close, hence validating the earlier results from the ICPAES.

The specific surface area analysis of the prepared catalysts was done using the BET method and the result

Table 1. Physio chemical properties of the prepared catalysts

Catalysts	a (\AA)	c (\AA)	Unit cell volume (nm^3)	Crystallite size (nm)
LBC0	5.4403	13.112	0.3361	32.5
LBC1	5.4516	13.147	0.3385	30.3
LBC2	5.4357	13.184	0.3394	29.6
LBC3	5.4471	13.200	0.3401	27.5
LBC4	5.4406	13.218	0.3408	25.2

Table 2. Elemental analysis of the prepared perovskite catalyst

Catalyst	Surface Area (m ² /g)	% La	% Ba	% Co	% O
LBC0	18.80	66.34 (63.45)	0.00 (0.00)	11.34 (10.98)	22.32 (25.57)
LBC1	23.78	54.67 (55.6)	3.20 (3.50)	21.2 (22.2)	23.61 (17.7)
LBC2	24.66	52.78 (53.7)	4.60 (4.20)	21.30 (22.50)	21.32 (19.60)
LBC3	25.75	50.35 (51.0)	5.79 (5.90)	21.4 (22.30)	22.46 (20.80)
LBC4	26.37	48.30 (47.30)	6.89 (6.30)	21.62 (22.40)	23.19 (24.00)

obtained is as recorded in Table 2. The surface area obtained in this research appears to be low, which could be a result of the calcination temperature used, although various materials scientists have reported that calcination temperature generally lowers the surface area of perovskites [19–21]. In this research study, the surface area ranges from 18.80 to 26.37 m²/g. It was observed that the surface area of the catalysts increases upon doping with barium suggesting that doping the catalysts has the ability to improve the surface area. There was no specific trend in the increase of the surface area upon doping and this might be a result of a randomly dispersed carbonate of barium (formed from the combustion of EDTA and Citric acid), which may have blocked the pores of the perovskite catalysts, thereby suppressing the surface area [22–24]. The surface area obtained in this study was observed to be

greater than the ones earlier reported in literature (1–11 m²/g) [4, 25, 26].

The plots of the data obtained from the TGA oxidation of the soot is as presented in Fig. 5. The plots were standardized by removing the weight loss, which occurred below 300 °C. This is because several reports have suggested that at 0–300 °C, only weight loss associated with surface water, desorption of adsorbed water and decomposable oxygen complexes on soot happens [27]. The standardized oxidation plots of the soot over the prepared catalysts LBC1, LBC2, LBC3 and LBC4 are shown in Fig. 5. In order to appropriately evaluate the catalytic performance of the soot, a blank soot was run without the catalyst mixed with it. The catalytic performance of the soot was studied by evaluating the T₅₀ of the catalysts. (This is considered as the soot ignition temperature of the

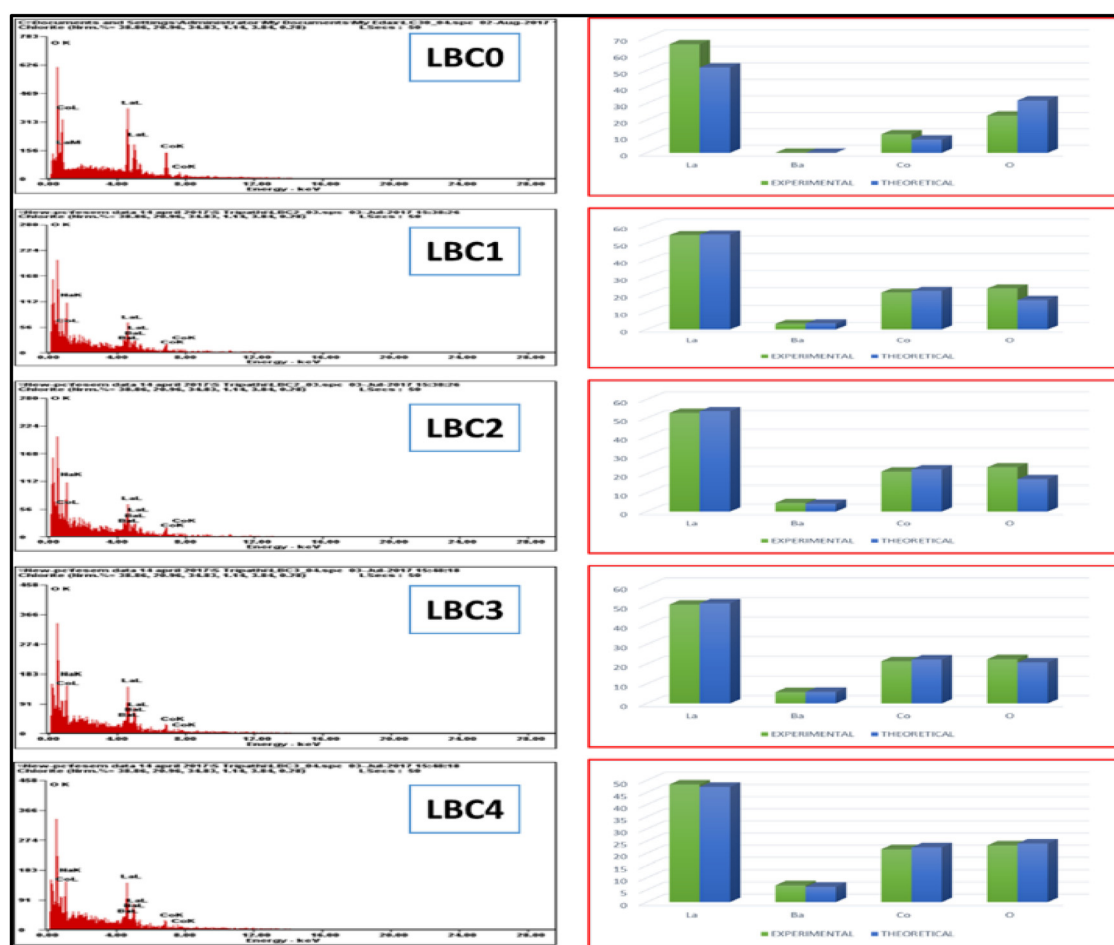


Figure 4. SEM-EDAX of prepared perovskite catalysts

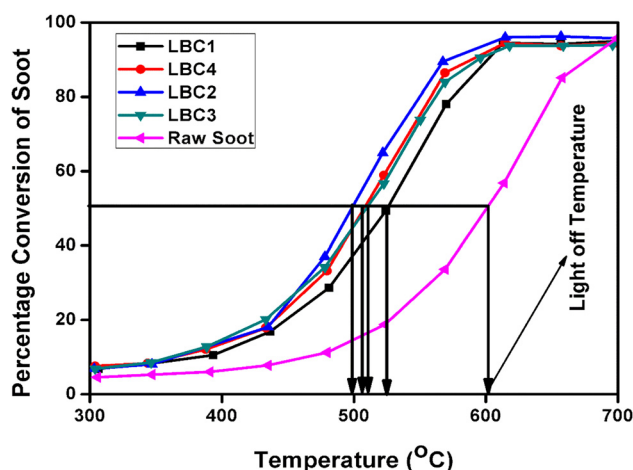


Figure 5. Catalytic activity graph of the prepared catalysts

soot i.e., the temperature at which 50% of the soot is oxidized or converted.) It was observed that the T_{50} of the raw soot was about 610 °C. However, upon the introduction of doped catalysts into the soot, the T_{50} reduces to 550, 530, 520 and 490 °C for LBC1, LBC3, LBC4 and LBC2, respectively. Furthermore, out of all the catalysts prepared, LBC2 gave the best catalytic performance with a T_{50} of 490 °C indicating that the reactivity of the surface oxygen was higher in the LBC2 catalyst than in the other prepared catalysts. Several literature reviews have reported that the high catalytic activity of perovskite and ceria based catalysts are as a result of the presence of oxygen species and not because of the various reactants such as soot, carbon monoxide, propane or methane [21, 28, 29]. Therefore with all the above explanations, we can argue that in this study, the oxygen species in the catalyst is what is responsible for the catalytic activities of the catalyst. One other factor that could be responsible for LBC2 having been the best catalysts might be a result of Ba enriched surface and larger amount of mobile surface bound oxygen species [30].

4. CONCLUSION

$\text{La}_{1-x}\text{Ba}_x\text{CoO}_3$ ($x \geq 0.1 \leq 0.4$) nano perovskite catalysts have been successfully prepared using the sol gel method. The prepared nano perovskite catalysts were also characterized using the various characterization techniques. The results obtained from the TGA/DTG analysis confirmed that the metal complexes pyrolysis occurred at temperature range 0–350 °C and that the perovskite phase was obtained at temperature around 750 °C. No isolated phase was observed from the XRD analysis confirming the formation of pure perovskite nano catalysts. The phase confirmation was further proven using the QualX software. The partial substitution of the A-site parent perovskite catalysts by barium help in improving the catalytic activity of the catalysts when compared with the one without barium. The LBC2 was observed to give better catalytic activity than other prepared

catalysts. In conclusion, the perovskite prepared in this research study have proven to be a potential alternative to the noble metal catalysts presently used in the DPF in diesel engines.

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REFERENCES

- [1] A. Jiamprasertboon, Y. Okamoto, Z. Hiroi, and T. Siritanon, "Thermoelectric properties of Sr and Mg double-substituted LaCoO_3 at room temperature," *Ceramics Int.*, vol. 40, no 8, pp. 12729–12735, 2014.
- [2] M. S. Kamal, S. A. Razzak, and M. M. Hossain, "Catalytic oxidation of volatile organic compounds (VOCs) – A review," *Atmos. Environ.*, vol. 140, pp. 117–134, 2016.
- [3] E. V. Kondratenko, M. Schlüter, M. Baerns, D. Linke, and M. Holena, "Developing catalytic materials for the oxidative coupling of methane through statistical analysis of literature data," *Catal. Sci. Technol.*, vol. 5, no. 3, pp. 1668–1677, 2015.
- [4] C. Lee, J. I. Park, Y. G. Shul, H. Einaga, and Y. Teraoka, "Ag supported on electrospun macro-structure CeO_2 fibrous mats for diesel soot oxidation," *Appl. Catal. B: Environ.*, vol. 174–175, pp. 185–192, 2015.
- [5] K. Krishna, A. Bueno-López, M. Makkee, and J. A. Moulijn, "Potential rare earth modified CeO_2 catalysts for soot oxidation," *Appl. Catal. B: Environ.*, vol. 75, no. 3–4, pp. 189–200, 2007.
- [6] C. Lee, Y.-G. Shul, and H. Einaga, "Silver and manganese oxide catalysts supported on mesoporous ZrO_2 nanofiber mats for catalytic removal of benzene and diesel soot," *Catal. Today*, vol. 281, pp. 460–466, 2017.
- [7] Z. Z. Jian Liu, C. Xu, A. Duan, and G. Jiang, "Simultaneous removal of soot and NO_x over the $(\text{La}_{1.7}\text{Rb}_{0.3}\text{CuO}_4)_x/\text{nmCeO}_2$ nanocomposite catalysts," *Ind. Eng. Chem. Res.*, vol. 49, pp. 3112–3119, 2010.
- [8] S. Kumar Megarajan, S. Rayalu, Y. Teraoka, and N. Labhsetwar, "High NO oxidation catalytic activity on non-noble metal based cobalt-ceria catalyst for diesel soot oxidation," *J. Mol. Catal. A: Chem.*, vol. 385, pp. 112–118, 2014.
- [9] C. Lee, Y. Jeon, S. Hata, J.-I. Park, R. Akiyoshi, and H. Saito, "Three-dimensional arrangements of perovskite-type oxide nanofiber webs for effective soot oxidation," *Appl. Catal. B: Environ.*, vol. 191, pp. 157–164, 2016.
- [10] A. P. Kumar, B. P. Kumar, A. B. V. K. Kumar, B. T. Huy, and Y.-I. Lee, "Preparation of palladium nanoparticles on alumina surface by chemical co-precipitation method and catalytic applications," *Appl. Surf. Sci.*, vol. 265, pp. 500–509, 2013.



- [11] N. Jiang, J. Hu, J. Li, K. Shang, N. Lu, and Y. Wu, "Plasma-catalytic degradation of benzene over Ag-Ce bimetallic oxide catalysts using hybrid surface/packed-bed discharge plasmas." *Appl. Catal. B: Environ.*, vol. 184, pp. 355–363, 2016.
- [12] E. Aneggi, N. J. Divins, C. de Leitenburg, J. Llorca, and A. Trovarelli, "The formation of nanodomains of Ce₆O₁₁ in ceria catalyzed soot combustion," *J. Catal.*, vol. 312, pp. 191–194, 2014.
- [13] S. Rousseau, S. Lorient, P. Delichere, A. Boreave, J. P. Deloume, and P. Vernoux, "La(1-x)Sr_xCo_{1-y}FeyO₃ perovskites prepared by sol-gel method: Characterization and relationships with catalytic properties for total oxidation of toluene." *Appl. Catal. B: Environ.*, vol. 88, no. 3–4, 438–447, 2009.
- [14] M. Piumetti, S. Bensaid, T. Andana, N. Russo, R. Pirone, and D. Fino, "Cerium-copper oxides prepared by solution combustion synthesis for total oxidation reactions: From powder catalysts to structured reactors," *Appl. Catal. B: Environ.*, vol. 205, pp. 455–468, 2017.
- [15] O. U. Osazuwa, H. D. Setiabudi, S. Abdullah, and C. K. Cheng, "Syngas production from methane dry reforming over SmCoO₃ perovskite catalyst: Kinetics and mechanistic studies," *Int. J. Hydrogen Energy*, vol. 42, no. 15, pp. 9707–9721, 2017.
- [16] H. Ranji-Burachaloo, S. Masoomi-Godardi, A. A. Khodadadi, and Y. Mortazavi, "Synergetic effects of plasma and metal oxide catalysts on diesel soot oxidation," *Appl. Catal. B: Environ.*, vol. 182, pp. 74–84, 2016.
- [17] M. Popa and J. M. Calderon-Moreno, "Lanthanum cobaltite nanoparticles using the polymeric precursor method," *J. the Eur. Ceram. Soc.*, vol. 29, no. 11, pp. 2281–2287, 2009.
- [18] D. H. Prasad, S. Y. Park, E. -O. Oh, H. Ji, H. -R. Kim, and K. -J. Yoon, "Synthesis of nano-crystalline La_{1-x}Sr_xCoO_{3-δ} perovskite oxides by EDTA-citrate complexing process and its catalytic activity for soot oxidation," *Appl. Catal. A: Gen.*, vol. 447–448, pp. 100–106, 2012.
- [19] M. Assadi, B. Kalaji, S. Saidur, H. Hanaei. "Recent progress in perovskite solar cells," *Renew. Sustain. Energy Rev.*, vol. 81, no. 45, 2017.
- [20] F. Bin, C. Song, G. Lv, J. Song, C. Gong, and Q. Huang, "La_{1-x}K_xCoO₃ and LaCo_{1-y}FeyO₃ Perovskite oxides: Preparation, characterization, and catalytic performance in the simultaneous removal of NO_x and diesel soot." *Ind. Eng. Chem. Res.*, vol. 50, no. 11, pp. 6660–6667, 2011.
- [21] W. Y. Hernández, M. N. Tsampas, C. Zhao, A. Boreave, F. Bosselet, and P. Vernoux, "La/Sr-based perovskites as soot oxidation catalysts for gasoline particulate filters," *Catal. Today*, vol. 258, pp. 525–534, 2015.
- [22] A. Hernández-Giménez, D. Castelló, and D. Bueno-López, "Diesel soot combustion catalysts: Review of active phases," *Chem. Pap.*, vol. 68, no. 9, 2014.
- [23] M. Jabłońska and R. Palkovits, "Nitrogen oxide removal over hydrotalcite-derived mixed metal oxides," *Catal. Sci. Technol.*, vol. 6, no. 1, pp. 49–72, 2016.
- [24] J.-H. Choy, J. Yukwon, D.-H. Park, J.-I. Park, S.-H. Yoon, M. Isao, et al., "Hollow fibers networked with perovskite nanoparticles for H₂ production from heavy oil," *Sci. Rep.*, vol. 3, pp. 2902, 2013.
- [25] Z. Li, M. Meng, Y. Zha, F. Dai, T. Hu, and Y. Xie, "Highly efficient multifunctional dually-substituted perovskite catalysts La_{1-x}K_xCo_{1-y}Cu_yO_{3-δ} used for soot combustion, NO_x storage and simultaneous NO_x-soot removal." *Appl. Catal. B: Environ.*, vol. 121–122, pp. 65–74, 2012.
- [26] H. Liu, X. Dai, K. Wang, Z. Yan, and L. Qian, "Highly efficient catalysts of Mn_{1-x}Ag_xCo₂O₄ spinel oxide for soot combustion," *Catal. Commun.*, vol. 101, pp. 134–137, 2017.
- [27] C. Cao, L. Xing, Y. Yang, Y. Tian, T. Ding, and J. Zhang, "The monolithic transition metal oxide crossed nanosheets used for diesel soot combustion under gravitational contact mode." *Appl. Surf. Sci.*, vol. 406, pp. 245–253, 2017.
- [28] M. Benjaram, P. L. Reddy, P. Bharali, et al., "Influence of Alumina, Silica, and Titania supports on the structure and CO oxidation activity of Ce_xZr_{1-x}O₂ nanocomposite oxides," *J. Phys. Chem. C*, vol. 111, pp. 10474–10483, 2007.
- [29] X. Han, Y. Wang, H. Hao, R. Guo, Y. Hu, and W. Jiang, "Ce_{1-x}La_xO_y solid solution prepared from mixed rare earth chloride for soot oxidation," *J. Rare Earths*, vol. 34, no. 6, pp. 590–596, 2016.
- [30] H. Nasiri, J. V. Khaki, M. H. Sabzevar, "Fast prepared Ni-Al₂O₃ nanocomposite through solution combustion synthesis," *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.*, vol. 45, no. 8, pp. 1241–1244, 2015.