

Preface

Diesel engines have been widely employed in heavy and light duty vehicles, locomotive, ships, etc. because of their high fuel efficiency, low cost, durability and reliability but the major drawback associated with them is emission of significant amount of particulate matter (PM/soot) along with other pollutants. Apart from health problems, PM also causes pollution of air, water and soil, soiling of buildings, reductions in visibility impact agriculture productivity, global warming and climate change, etc. As the regulations on diesel engine emissions are becoming more stringent, engine modification and exhaust treatment are needed for improved emission control systems for PM. However, diesel soot elimination is known to be a hard task, since this material burns above 600°C in air, while the temperature of diesel exhaust generally lies between 150-450°C. Therefore, in order to lower the required combustion temperature of soot, oxidation catalyst coated diesel particulate filter (DPF) is suggested. The DPF are becoming widespread as an effective measure to reduce soot emissions from diesel vehicles as they have filtration efficiencies of > 98%. As the filters accumulate PM, it builds-up backpressure that has many negative effects such as decreased fuel economy and possible engine and/or filter failure. To prevent these negative effects, the DPF have to be regenerated by oxidizing (i.e. burning) trapped PM. An attractive option to remove PM is passive regeneration of PDF. The passive regeneration involves the catalytic combustion of the trapped PM during the normal operation of the engine. The soot is burned out by the oxidation catalysts deposited onto the filter. The key challenge is to find a catalyst that is active within the window of the exhaust temperature.

Perovskite oxides with general formula ABO_3 have been tried as catalysts for a variety of reactions, due to double research attractions of tailoring flexibility and thermal stability at high temperature. Such catalysts also have been extensively investigated as

potential substitutes for costly PGM-based catalysts in automotive emission control. Thus, the objective of the present work is to develop an efficient perovskite catalyst for diesel soot combustion active within the temperature range of diesel exhaust. To design and develop PGM-free improved perovskite catalysts, reactive grinding technique followed by a novel route of reactive calcination of catalyst precursors were used, based on rational correlations of various physico-chemical parameters to achieve the eventual goal of ultra-low emission norms.

The thesis entitled “**Studies on Catalytic Oxidation of Diesel Soot over Perovskite Oxides**” comprises of ten chapters together with a bibliography.

Chapter 1 is introductory in nature which contains a brief account of diesel soot, its structure, classification and Mechanism of Soot Formation in Diesel Engines. It also includes the impacts of particulate matter on human health, environment, legislations on the diesel soot emissions and soot abatement technologies. Further, the objectives of the work is defined in this chapter.

Chapter 2 describes a brief prologue of various conventional catalysts and their alternative for diesel soot oxidation with a relevant literature survey. The major content of this chapter is published in *Catalysis Reviews: Science and Engineering*, 56:1, 57-81, Taylor & Francis.

Chapter 3 presents materials and methods used to prepare and characterise the catalyst samples and diesel soot. The details of experimental setup for activity evaluation and for kinetics study of the diesel soot oxidation are also integrated in this chapter.

Chapter 4 consists of preparation of real soot and its characterisation by different techniques i.e. proximate analysis, particle size analysis, calorific value calculation and XRD analysis.

Chapter 5 describes the effect of preparation methods (co-precipitation, sol-gel and solution combustion synthesis) and calcination temperature (600-800°C) on the efficiency of LaCoO₃ catalysts for soot oxidation. The catalyst prepared by co-ppt method show highest surface

area and lowest crystallite size than the catalysts obtained by other two methods. The co-ppt method results the best catalyst calcined at 750°C exhibiting total soot oxidation at 370°C within the temperature window of diesel exhaust (150-450°C). The content of this chapter is published in Canadian Chemical Transactions 3(1) (2015) 82-95.

Chapter 6 is divided into two sections. Section one deals with the effect of the intrinsic factors including the structure, nature of B-site ions in the perovskite-type oxide (ABO_3) catalysts $LaCoO_3$, $LaNiO_3$, $LaFeO_3$ and $LaZnO_y$. The external factors of catalyst-soot contacting model and the operating parameters such as air flow rate and temperature on the catalytic performances for the combustion of diesel soot are also reported. Activity of the catalyst for soot oxidation was evaluated on the basis of light off temperature characteristics T_i , T_{50} and T_{100} . $LaCoO_3$, $LaFeO_3$ and $LaNiO_3$ samples possessed the perovskite structure, and gave high activities for the total oxidation of soot below 445°C. Whereas, $LaZnO_y$ catalyst was not showing the ABO_3 perovskite structure by XRD analysis and existed as a mixture of metal oxides. Second section consists of effect of substitution in perovskite catalyst. In this study we substituted La by Sr/K and Co by Fe/Cu/Ni in pure $LaCoO_3$ perovskite. In first step by single substitution of La by Sr/K we optimize the composition of single substituted catalyst shows the best activity for soot oxidation. In next step substitution of the Co by Fe/Cu/Ni in optimized single substituted $La_{0.9}Sr_{0.1}CoO_3$ was done and screening of the best perovskite catalyst for diesel soot oxidation was determined. The content of this chapter is published in (i) International Journal of Applied Engineering Research, 9 (1) (2014) 9-16; (ii) International Journal of advances in Science and Technology, Science publication and communicated to (ii) Iranian Journal of Chemistry and Chemical Engineering.

Chapter 7 deals with a novel route of reactive calcination (RC) of the perovskite catalyst precursors, for the preparation of highly active catalysts for oxidation reactions.

Thus, in the present chapter, double-substituted perovskite, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{1-x}\text{Fe}_x\text{O}_3$, were prepared, calcined conventionally in stagnant air as well as by RC, characterized by various techniques and examined for catalytic performance of the diesel soot combustion. The catalyst reactively calcined (RC) in CO-air mixture which reveals the lowest temperature ($T_f = 325^\circ\text{C}$) for total soot oxidation amongst all the catalysts. The content of this chapter is published in (i) Clean Technology and Environmental Policy 17 (2015) 2337-2347, Springer and communicated for publication in (ii) special issue of Catalysis Today, Elsevier.

Chapter 8 reports a total environmental friendly approach for synthesis of nano-size green perovskite catalysts, using oxide powders of various components, by reactive grinding (RG) in a planetary ball mill. The catalysts synthesised by RG possess higher surface area and smaller crystallites than one prepared by sol-gel (SG) method. The perovskite $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3$ prepared by RG with ZnO additive exhibits the highest surface area, smallest crystallites and the best activity for diesel soot oxidation thus, shows potential as an effective catalyst for use in the passive regenerative catalytic diesel particulate filter (DPF) for a secure sustainable environment. The content of this chapter is communicated to (i) RSC advances for publication.

Chapter 9 describes the kinetics of diesel soot oxidation over $\text{La}_{0.9}\text{Sr}_{0.1}\text{Co}_{0.5}\text{Fe}_{0.5}\text{O}_3$ catalyst with air under isothermal conditions. A kinetic model of pseudo-first order reaction for the soot oxidation with high air flow rate in the temperature range $325\text{-}355^\circ\text{C}$ can be represented by the following rate expression:

$$\text{Rate (r)} = 6.46 * 10^{10} \exp(-101.08 \text{ kJ/RT}) \text{ (m) g/g cat-s}$$

The value of activation energy was found to be 101.08 kJ/mol which was lesser compared to the reported activation energy for different PGM-free catalysts in the literature.

Chapter 10 contains the summary of the present work and scope for future work in this area. The list of references and the appendices are appended at the end of the thesis.

Seven papers from the work have already been published in the referred journals and seven have been presented in the international conferences. Further, three papers have been communicated for the publication.