Chapter 1

Introduction

1.1 Background of the work

Human activities generate three broad sources of air pollution: stationary, mobile (outdoor) and indoor (Rao and Rao, 2007; Bera and Hegde, 2010). Air pollution generated from mobile sources such as automobiles has been a burning issue and contributes major air quality problems in urban and industrialized areas (Wei, 1975; Neeft et al., 1996; Fino et al., 2003c; Kaspar et al., 2003; Labhsetwar et al., 2006; Bera and Hegde, 2010). Automobile market has been increased exponentially day to day (Labhsetwar et al., 2006; Bera and Hegde, 2010; Prasad and Singh, 2012). About 50 million cars are produced every year and over 700 million cars are used worldwide (Kaspar et al., 2003; Shinjoh, 2006; Prasad and Singh, 2012). Vehicle population is going to increase 1300 million by the year 2030 (Pundir, 2007).

Automotive vehicles are one of the main sources for carbon monoxide (CO), unburned hydrocarbons (HC), nitrogen oxides (NO_x) and particulate matter (PM) emissions in the atmosphere (Furfori et al., 2009, 2010; Prasad and Singh, 2012). The unburned hydrocarbons are also called volatile organic compounds (VOCs) which are composed of large variety of hydrocarbons out of which mainly present HC in automobiles are methane (CH_4), ethylene
(C₂H₄), acetylene (C₂H₂), propane (C₃H₈) and propene (C₃H₆) (Pundir, 2007). Due to incomplete combustion in the engine, there are number of incomplete combustion products emitted. CO and HC form because the combustion efficiency is less than 100% due to incomplete mixing of the gases and the wall quenching effects of the cold cylinder walls. The temperature of combustion chamber reaches to around 1500 °C during oxidizing conditions which forms NOx by combining nitrogen (N₂) in air with oxygen (O₂) (Wei, 1975; Acres, 1996; Fritz and Pitchon, 1997; Heck and Farrauto, 2001; Srinivasan, 2001; Pundir, 2007).

There are three types of emissions observed from automobiles (a) Exhaust emissions – The tail pipe releases exhaust gases along with pollutants (CO, HC, NOx and PM) to the atmosphere (b) Crank case emissions – It emits blow by gases and fuel vapors (HC) into the atmosphere and (3) Evaporative emissions – The fuel tank and fuel lines emit fuel vapors (HC) into the atmosphere (Acres, 1996; De Nevers, 2000; Srinivasan, 2001; Bartholomew and Farrauto, 2006; Rao and Rao, 2007). Typical exhaust gas composition for petrol driven vehicles at the normal engine operating conditions is: CO (0.5 vol.%), HC (350 vppm), NOx (900 vppm), H₂ (0.17 vol.%), H₂O (10 vol.%), CO₂ (10 vol.%) and O₂ (0.5 vol.%) (Heck and Farrauto, 2001; Kaspar et al., 2003).

Carbon monoxide is a poisonous gas which reduces the capacity of blood to transfer oxygen to the various parts of the body and most dangerous to the persons having heart problems (Wei, 1975; Heck and Farrauto, 2001; Pundir, 2007; Bera and Hegde, 2010). The formation of secondary pollutants such as ozone (O₃), nitrogen dioxide (NO₂), peroxyacetyl nitrate (PAN) and photochemical oxidants occur as a result of photochemical reactions between HC and NOx. These oxidants can cause eye irritation, retard the functioning of lung and also cause damage to the vegetation and rubber tires (Wei, 1975; Neeft et al., 1996; Fritz and Pitchon, 1997; Heck and Farrauto, 2001; Zhang et al., 2008b; Bera and Hegde, 2010). Particulates matter irritates the eyes and nose, can penetrate the cell membranes, enter the blood and even reach to the brain, create respiratory problems, cause diseases like asthma, bronchitis, cancer and in long term damage the lung (Neeft et al., 1996; Fino et al., 2003c, 2004, 2006a; Cauda et al., 2007). Emissions from automobiles contribute a major role to create the global environmental problems such as acid rain, the green house gas effect and depletion of the ozone layer in addition to the photochemical smog. The auto exhaust also affects the cultural heritage, historical places, monuments and architecture etc. (Neeft et al.,
These pollutants have negative impact on human health, air quality and the environment which introduce stringent regulations regarding automotive exhaust gas emissions in the form of emissions norms. These regulations are now being adopted and tightened all over the world (Neeft et al., 1996; Teraoka and Kagawa, 1998; Belton and Taylor, 1999; Srinivasan, 2001; Fino et al., 2003c, 2006a; Labhsetwar et al., 2006; Bera and Hegde, 2010). Because of such regulations, it is necessary to develop more active and durable emission control system. A number of alternative technologies such as improvement in engine design, fuel pretreatment, use of alternative fuels, fuel additives, exhaust treatment and better tuning of the combustion process etc. are being used to satisfy the regulations regarding automotive exhaust gas emissions (Fino et al., 2003c, 2006a; Mescia et al., 2008; Bera and Hegde, 2010; Prasad and Singh, 2012). Among available technologies, one of the best ways of controlling exhaust emissions is three way catalytic converter that simultaneously promote the removal of CO, HC and NOx from petrol driven vehicles (Fritz and Pitchon, 1997; Belton and Taylor, 1999; Heck and Farrauto, 2001; Srinivasan, 2001; Uenishi et al., 2005b; Shinjoh, 2006; Sartipi et al., 2008; Khanfekr et al., 2009; Bera and Hegde, 2010). Diesel particulates filter (DPF) and oxidation catalytic converter also known as diesel oxidation converter (DOC) is used to control emissions from diesel driven vehicles (Neeft et al., 1996; Heck and Farrauto, 2001; Labhsetwar et al., 2006; Fino, 2007). The catalysts are the heart of catalytic converter and responsible for treating poisonous gases release from the tail pipe of the vehicles (Ferri and Forni, 1998; Labhsetwar et al., 2006; Tian et al., 2009; Bera and Hegde, 2010). The conversion of these poisonous gases such as CO, HC and NOx to CO2, H2O, N2 and O2 using catalysts is a challenging task. Therefore, environmental catalysis or exhaust catalysis has been growing as a new and broad area of research in heterogeneous catalysis as well as in autocatalysis (Zhang et al., 2006d; Bera and Hegde, 2010). There are various catalysts composition including base metals, oxides of base metals, mixture of oxides, noble metals, supported noble metals, spinel structure materials, perovskite structures (mixed oxides), alloys etc. used in catalytic converters (Wei, 1975; Bartholomew and Farrauto, 2006; Zhang et al., 2006a; Cheng et al., 2007; Pundir, 2007; Zhang et al., 2008a; Bera and Hegde, 2010; Royer and Duprez, 2011; Biabani-Ravandia and Rezaei, 2012; Prasad and Singh, 2012) The most effective catalysts used today in commercial catalytic converters are platinum group
metals (PGM) (also known as precious metals or noble metals) platinum (Pt), palladium (Pd) and rhodium (Rh) because of their higher catalytic activity for treatment of pollutants such as CO, HC and NOx and thermal stability over other catalysts (Belton and Taylor, 1999; Farraruto and Heck, 1999; Heck and Farraruto, 2001; Kaspar et al., 2003; Tanaka et al., 2006; Bera and Hegde, 2010).

Economical reasons as well as limited resources of platinum group metals motivated the researchers to develop alternative catalytic materials or reduce the amount of platinum group metals used for catalytic removal of pollutants from automobiles (Liu et al., 2002; Labhsetwar et al., 2006; Vaz and Salker, 2007; Sartipi et al., 2008).

1.2 Scope of the work

Automotive emissions regulations related to low emission vehicle (LEV), ultra-low emission vehicle (ULEV), super ultra low emission vehicle (SULEV) and partial zero emission vehicle (PZEV) are getting stringent all over the world to protect the environment (Heck and Farraruto, 2001; Kaspar et al., 2003; Twing, 2003). These stringent regulations require new or further improvement in exhaust emission control technology based on the catalytic converter (Farraruto and Heck, 1999). The Pt-Pd-Rh/CeO₂-ZrO₂-γ-Al₂O₃ is widely used as three-way catalysts (TWCs) in catalytic converter for the abatement of automotive exhaust gas emissions (Kaspar et al., 2003; Zhang et al., 2007). Due to the position of catalytic converter close to the engine, sometimes during high speed cruising condition, platinum group metal catalysts experience high temperature (T > 600 °C) redox fluctuations of the exhaust which transforms γ-Al₂O₃ (used as a catalyst support) into less active phase α-Al₂O₃ which decreases its specific surface area significantly. These lead to the sintering of platinum particles and forms agglomeration of platinum particles on the catalyst support which can be further accelerated by steam present in the exhaust while rhodium metal is to be oxidized to Rh³⁺ cation and diffuse into alumina. These issues result in a loss of active surface area of precious metals and lower down the catalytic activity (Kaspar et al., 2003; Nishita et al., 2005; Uenishi et al., 2005b; Tanaka et al., 2006; Shinjoh, 2006; Screen, 2007; Zhang et al., 2007; Sartipi et al., 2008; Khanfekr et al., 2009). Poisoning due to the presence of phosphorus, zinc and calcium which are present as a wear inhibiting agents in the engine oil and sulfur which is present in the fuel deactivate the platinum group metal catalysts mainly by blocking the pores or even by direct blockage of the active sites which causes loss of catalytic activity (Shelef et al., 1979; Beck et al., 1997; Kaspar et al., 2003; Layla et al., 2008). In order
to compensate this deterioration and also to satisfy new emissions norms, conventional catalytic converter is loaded with excess amount of precious metals which increase the large demand of the platinum group metals as auto exhaust catalysts (Uenishi et al., 2005b; Screen, 2007; Sartipi et al., 2008; Khanfekr et al., 2009). The increasing prices of platinum group metals motivate the researchers to search for alternatives catalytic materials or reduce the amount of platinum group metals (Uenishi et al., 2005b; Zhang et al., 2007; Seyfi et al., 2009).

The requirements of future emission standards (LEV, ULEV and SULEV vehicles) cannot be met by conventional three way catalytic converter which comprises of noble metals as they cannot be effectively remove CO and HC from the outlet of the engine in the cold-start phase (Heck and Farrauto, 2001). About 60-80% of the pollutants release to the atmosphere for the first 60-90 s of vehicle starting (cold start phase) which is due to catalysts in catalytic converter are not reaching to the light-off temperature (T_{50}-the temperature corresponding to 50% conversion) during this period to initiate the reactions. To meet the stringent emission standards for cold start, catalysts have to achieve the light-off (operating) temperature very fast (Heck and Farrauto, 2001; Layla et al., 2008). In order to achieve light-off temperature immediately, various ways are implemented such as close-coupled catalysts (CCC), electrically-heated catalysts (EHC) and HC trap which improve the cold-start behavior of catalytic converters around the world (Zhenming et al., 2001). Heating the catalytic converters create difficulties with respect to cost, complexity and durability of catalytic converters (Layla et al., 2008). In order to reduce the cold start emission, Pd-based close couple catalyst is used which exhibits good low temperature catalytic activity. Looking to the usage of Pd as close-coupled catalyst which increases the demand for Pd as automotive catalyst from 15 to over 150 t per year. A new automotive catalyst technology is required that reduces precious metals consumption especially Pd (Heck and Farrauto, 2001; Uenishi et al., 2005b; Tanaka et al., 2006; Khanfekr et al., 2009).

Currently used three-way catalysts are exposed to high operating temperature due to the use of closed-coupled catalysts near the engine. Three way catalysts should have life-time of at least 80,000 to 100,000 km or five years. The new emission limits as per EURO V and US TIER II norms which extent the durability of catalyst to 160,000 km and new restrictions are set for the new materials used in three way catalytic converter applications have to be
thermally stable under the redox fluctuation of exhaust gas conditions (Farrauto and Heck, 1999; Nishihata, 2002; Nishihata, et al., 2003; Uenishi et al., 2005b; Screen, 2007).

The number of limitations posed by noble metals which include high cost, volatilization, poisoning and sintering at high temperature that lead the researchers (Koltsakis et al., 1997; Forni and Rossetti, 2002; Qis et al., 2005; Labhsetwar et al., 2006; Sartipi et al., 2008; Russo et al., 2009a; Seyfi et al., 2009) to develop new catalytic materials for automotive exhaust emission control which exhibit the following criteria

- High activity and selectivity (conversion > 98%) which increase up to 99% to satisfy SULEV standards
- Attain very fast light-off temperature within less than 10-20 s means could attain high activity at low temperature
- High thermal stability
- High oxygen storage capacity (OSC) (Kaspar et al., 2003)

Perovskite type oxides of general formula ABO$_3$ (where A and B are rare earth, alkaline earth, alkali metal and transition metal cations respectively) are being developed as an alternative catalytic material for automotive exhaust emissions control because of their low cost, thermal stability at high temperature, high mechanical stability and excellent redox properties (Ciambelli et al., 2001a, 2001b, 2002; Szabo et al., 2003a; Sartipi et al., 2008; Doggali et al., 2010).

As reported in the literature, perovskites are mainly prepared by ceramic and wet chemical methods. One major problem of perovskites prepared by ceramic method is that it involves high calcination temperature at least 800 °C which results in low specific surface area (SSA) and limits its commercial application (Shu and Kaliaguine, 1998; Porta et al., 1999; Xiulan and Yuan, 2000; Kalinguine and Neste, 2000; Kalinguine et al., 2001; Zhang et al., 2002; Royer et al., 2004; Zhang et al., 2006a, 2006b, 2006c, 2006d; Niu et al., 2007; Zhang et al., 2007, 2008b; Abdolrahman et al., 2010; Ghasdi et al., 2010, 2011; Sui et al., 2011). Wet chemical methods such as sol-gel, co-precipitation, citrate complexation etc. provide the improved specific surface area compared to ceramic method. These methods are complicated, the reagents used are normally expensive and the use of large amount of water as well as formation of large amounts of gaseous or liquid wastes which create additional environmental problems (Shu and Kaliaguine, 1998; Zhang and Saito, 2000a; Kalinguine and
Neste, 2004; Sompech et al., 2012). However, the drawbacks with all of these methods are that either low specific surface area due to high calcination temperature or they are complicated and expensive to put into practice. Therefore limited applications of them are found in place of noble metal based catalysts used in catalytic converter for abating automotive exhaust gas emissions (Kalinguine and Neste, 2004). There is a scope for the development of another synthesis method for preparing perovskites which can overcome the limitations of conventional methods used. The novel synthesis method called reactive grinding also known as mechanochemical synthesis using high energy ball mill is developed which is simple, low in production cost, eliminating heating step to synthesize crystalline perovskites and also overcome the limitations of conventional methods used for preparing perovskites (Zhang and Saito; 2000a; Nguyen et al., 2002; Ito et al., 2004; Merino et al., 2006; Zhang et al., 2006a, 2006d, 2006e; Pourghahramani et al., 2008; Zhang et al., 2008b; Sompech et al., 2012).

The process of reactive grinding starts with mixing of the starting materials (mainly oxides) as per stoichiometric proportion and loading the powders mixture along with the grinding medium (generally steel balls) in high energy ball mills e.g. planetary ball mills, SPEX shaker mills, vibratory mills and attritors etc. and high energy induced due to intense milling which cause the chemical reaction between oxide powders and thereby synthesize the crystalline perovskite catalysts. During milling, there are three processes occur such as cold welding, plastics deformation and further fragmentation of the particles. In order to prevent or minimize excessive cold welding of powder particles among themselves sometimes a process control agent (PCA) is added. This mixture (with or without the PCA) is then milled for the require length of time until a steady state is reached between cold welding and fracturing and finally perovskites form with improved specific surface area (Kalinguine and Neste, 2004; Suryanarayana, 2004; Chicinas, 2006).

Volin and Tuxedo (1979) (U.S. Pat. No. 4,134,852 ) disclosed synthesis of perovskite crystal structure by subjecting a mixture of powders to dry high energy impact milling (SPEX mill and attritors) to form mechanically alloyed product and subsequently it was heated in oxidizing atmosphere at high temperature between 900 and 1200 °C to obtain single phase perovskite. Kalinguine and Neste (2000) disclosed about process called mechanical alloying or mechanochemical for synthesized metal oxides having a perovskite or perovskite like crystal structure using high energy ball mill (SPEX shaker mill) in U.S. Pat. No. 6,017,504.
The perovskites prepared by this method exhibit high density of lattice defects which is responsible for higher catalytic activity even though the proposed method used heating step and also mill operated at high rpm to synthesize perovskites. Ito et al. (2004) synthesized LaCoO$_3$ perovskite using planetary ball mill (Fritsch Pulverisette-7) in which starting oxides mixture were milled at approximately 700 rpm under atmospheric condition. They used zirconia pot and zirconia balls as grinding medium and milled for different period of time. According to their result, pure crystalline LaCoO$_3$ was formed after 3 h of grinding but the specific surface area was observed only of 3 m$^2$/g. The perovskites synthesized by reactive grinding method reported by Volin and Tuxedo (1979), Kalinguine and Neste (2000), Royer et al. (2004, 2005b), and Bolarin et al. (2007) require high energy ball mills mainly SPEX shaker mills, longer milling time and a heating step to synthesize crystalline pure perovskites structure. Zhang and Saito (2000a, 2001), Zhang et al. (2002), Ito et al. (2004), Sompech et al. (2012) prepared perovskites using planetary ball mills for that they mentioned that high speed (rpm) and heat treatment is required to synthesize pure crystalline perovskites.

There is a scope to design indigenous planetary ball mill that simultaneously grind the oxide powders and cause the chemical reaction among oxide powders and thereby synthesizes the crystalline perovskite catalysts without heat treatment. There is a scope to optimize various operating conditions for reactive grinding method using planetary ball mill such as basic disc (sun wheel) direction and revolution speed, grinding jar direction and rotation speed, ball to powder weight ratio, milling time, extent of jar filling and heat treatment to form pure crystalline perovskites.

It is reported in the literature that cobalt, manganese and iron based perovskites are most suitable catalysts for automotive CO and CH$_4$ oxidation (Song et al., 1999; Ciambelli et al., 2001b, 2002; Zhang-Steenwinkel et al., 2002; Cimino et al., 2003; Royer et al., 2005a; Labhsetwar et al., 2006; Royer et al., 2006; Zhang et al., 2006c; Levasseur and Kaliaguine, 2008; Bera and Hegde, 2010). The oxidation activity of perovskite depends on reducibility of transition metal, anion vacancies and higher oxygen mobility (Forni and Rossetti, 2002; Royer et al., 2005b; Deng et al., 2008; Russo et al., 2009a). Zhang et al. (2006e) and Royer et al. (2005b) pointed out that the physicochemical properties of perovskites can be modified by partial substitution in A and/or B-sites with metals of different oxidation states which plays an important role in various redox reactions.
It is reported in the literature that partial substitution in the A-site by Sr or Ce enhances the catalytic activity of the catalysts (Zhong et al., 1997; Ciambelli et al., 2001a; Ran et al., 2005; Niu et al., 2007). Ran et al. (2005) studied the effect of Ce and Sr in PrMnO$_3$ as a three way catalysts (CO, HC oxidation and NO reduction). They observed that Pr$_{0.6}$Sr$_{0.4}$MnO$_3$ and Pr$_{0.8}$Ce$_{0.2}$MnO$_3$ can exhibit higher catalytic activity as a three way catalysts and larger specific surface area than PrMnO$_3$. The Ce-doped catalysts exhibit better catalytic activity than the Sr-doped due to presence of CeO$_2$ phase which enhances the redox properties of Ce-doped PrMnO$_3$.

According to several studies, partial substitution of 10% of La by Ce in cobalt or manganese-based perovskites leads to an increase in catalytic oxidation activity for propane (Rida et al., 2008), CO (Zhang-Steenwinkel et al., 2002), CH$_4$ (Ferri and Forni, 1998; Forni and Rossetti, 2002; Fabbrini et al., 2003; Royer et al., 2005c) and NO (Wen et al., 2007). Song et al. (2006) reported that the partial substitution of La$^{3+}$ by Sr$^{2+}$ in LaFeO$_3$ significantly enhances the reducibility of the catalysts. The incorporation of Pd at B-site of most reducible catalyst La$_{0.6}$Sr$_{0.4}$FeO$_{3.5}$ among the La$_{1-x}$Sr$_x$FeO$_{3+δ}$ perovskites i.e. La$_{0.6}$Sr$_{0.4}$Fe$_{0.95}$Pd$_{0.05}$O$_{3+δ}$ enhances both low-temperature oxygen mobility and catalytic activity by decreasing the reduction temperature of the perovskite and also improves the thermal stability. Russo et al. (2009a) reported that catalytic activity for CH$_4$ combustion is improved by partial substitution with 10% of Pd at the B-site of LaBO$_3$ (where B = Cr, Mn, Fe) perovskites over LaBO$_3$ perovskite because substituted perovskites enhance the capability of delivering higher amount of intrafaicial oxygen responsible for combustion of CH$_4$. Large numbers of oxygen (anion) vacancies are generated after substitution of Co$^{3+}$ by Cu$^{2+}$ due to a positive charge deficiency which significantly enhances the amount of a-O$_2$ desorption (Porta et al., 1999; Zhang et al., 2006a, 2006b, 2006c, 2006d, 2007, 2008b). Zhang et al. (2006a) pointed out that these anion vacancies plays an important role in catalytic reduction of NO by CO by providing the adsorption sites for NO and CO as well as promoting the dissociation of adsorbed NO species. Partial substitution of Cu can also enhance not only anion vacancies but also increases the mobility of lattice oxygen which promotes the CO oxidation and also regenerates the anion vacancies. According to their studies (Zhang et al., 2006a, 2006b, 2006c, 2008b), catalytic performance of NO reduction using C$_3$H$_6$ or CO is significantly improved by introduction of Cu ions into the B-sites of LaBO$_3$ (B = Co, Mn, Fe) perovskites. They also pointed out that
(Zhang et al., 2006b, 2007) the incorporation of Pd at B-site of LaFeO$_3$ perovskite significantly improves the reduction of NO by C$_3$H$_6$.

Limited work has been carried out for the development of suitable perovskites by reactive grinding method using high energy ball mills mainly planetary ball mills for automotive CO oxidation and also the various compositions are not developed in order to reduce the light-off and 100% CO conversion temperature. In the present study, emphasis has been given to develop cobalt, manganese and iron based perovskite catalysts for automotive CO oxidation by citrate complexation, co-precipitation and reactive grinding methods. The various operating conditions are optimized for reactive grinding method to synthesize pure crystalline perovskites using planetary ball mill which include milling time, size and number of balls, extent of jar filling, ball to powder weight ratio, direction of basic disc (sun wheel) and jar, basic disc (sun wheel) revolution speed, grinding jar rotation speed and atmosphere for milling etc. In order to improve the catalytic activity for CO oxidation, the partial substitution of Sr or Ce at A-site and Cu at B-site was given in the present study. The incorporation of small amount of Pd at B-site of ABO$_3$ perovskite has also been given in order to improve further catalytic activity for CO oxidation as well as the stability of the catalyst.

1.3 Objectives

The main objective of proposed research work is to develop perovskite (non-noble metal) based catalysts which possess exhaust catalytic combustion properties. This characteristic of perovskite is to be used for developing automotive exhaust catalyst for CO oxidation.

The specific objectives are as follows:

- Preparation of perovskite based catalysts by citrate complexation, co-precipitation and reactive grinding methods.
- Investigation of suitability of these catalysts for minimization of automotive CO oxidation.
- Enhancement of activity of selected catalysts.
- Detailed characterization of catalysts and to understand the relation between catalytic properties and catalytic activity.
Development of most appropriate perovskite catalyst in terms of catalytic activity for automotive CO oxidation.

Optimization of operating conditions for reactive grinding method to synthesize crystalline perovskites using planetary ball mill such as milling time, size and number of balls, extent of jar filling, ball to powder weight ratio, direction of basic disc (sun wheel) and jar, basic disc (sun wheel) revolution speed, grinding jar rotation speed and atmosphere for milling etc.

Time-on-stream activity study.

Study of effect of operating parameters such as contact-time and reaction temperature on automotive CO oxidation using selected catalyst.

Kinetic study.

### 1.4 Organization of thesis

This thesis is composed of the following sections: Introduction, a review of the relevant literature, a description of the materials and experimental methods used and the sections of results and discussion and finally summary and conclusions with recommendations for future research work.

In Chapter 1, the background and scope of the research work are explained. Based on the scope of the work, the specific objectives of the research work are also incorporated.

In the literature review of this thesis, a general perspective of the theory behind automotive emissions, formation of CO and their adverse effects, automotive CO emission control technology, limitations of platinum group metal catalysts for automotive CO emissions control along with its alternative are discussed in Chapter 2. Introduction about perovskites, its preparation methods with limitations of conventional methods are also discussed. The theory behind reactive grinding, equipment used for reactive grinding along with process variables in milling are discussed in detail. The preparation of perovskites by reactive grinding method is also discussed. The important topics on catalytic activity for CO oxidation over perovskites prepared by various methods, kinetic studies, reaction mechanisms and deactivation studies over perovskites for automotive CO oxidation are also discussed. Finally, conclusions are made from the literature reviews which are used to plan for experimental works.
The experimental part of this research is discussed in Chapter 3. The experimental part is organized as follows: catalysts preparation procedures to prepare perovskite catalysts by citrate complexation, co-precipitation and reactive grinding methods, characterization techniques, catalytic activity tests for CO oxidation, kinetic studies and time-on-stream activity for CO oxidation. The various operating conditions optimized for reactive grinding method to synthesize crystalline perovskites using planetary ball mill are also discussed.

Chapter 4 presents the results of automotive CO oxidation over various catalysts compositions prepared by citrate complexation, co-precipitation and reactive grinding methods. In this chapter, the integration of results with physicochemical properties of the catalysts is carried out. Key literature in the respective fields is also discussed in this chapter to support the experimental results.

Finally, in the last chapter i.e. Chapter 5, the summary and conclusions based on the results of earlier chapters are drawn and recommendations for future work are given.