IdeaLab Project ID- 14-10-CH-09
Design and Fabrication of Pd substituted perovskite based catalytic converter for CO emission control

Submitted By

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IdeaLabProject ID-31-07-CH-08
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Under the mentorship of

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Declaration

We do hereby declare that the technical project report submitted is original, and is the outcome of the independent investigations/research carried out by us and contains no plagiarism. The research is leading to the discovery of new facts/techniques/correlation of scientific facts already known. This work has not been submitted to or supported by any other University or funding agency.

We do hereby further declare that the text, diagrams or anyother material taken from other sources(including but not limited to books, journals and web) have been acknowledged, referred and cited to the best of our knowledge and understanding.

Date: 30/4/2016
Place: AHEMEDABAD

Signature of Student1	Signature of Student2	Signature of Student 3	Signature of Mentor
13BCH154	12BCH007	12BCH010	Dr. Femina Patel

NIRMAUNIVERSITY
INSTITUTEOF TECHNOLOGY
IDEALAB
Chemical Engineering Department

Annual /final report of the work done on the idea lab project

1. Idea Lab Project ID: 14-10-CH-09

2. Project Title: Design and Fabrication of Pd substituted perovskite based catalytic converter for CO emission control

3. Period of Project: 25/08/2014 to 31/03/2016

4. (a) Name of Student (RollNo.): Dhruvin Patel (13BCH154)

Department: Chemical Engineering

(b) Name of Student (RollNo.): Chandni Dholakia (12BCH007)

Department: Chemical Engineering

(c) Name of Student (RollNo.): Brinda Gangdev (12BCH010)

Department: Chemical Engineering

(d) Name of Mentor: Dr. Femina Patel

5. Project Start Date: 15/09/2015

6. (a) Total Amount Approved: Rs. 30, 000/-

(b) Total Expenditure: Rs. 26, 810/-

(c) Report of the work done:

i. Brief objective of the project: As per Sr. No. 1.4

ii. Work done: Pls refer Annexure - I

iii. Results achieved from the work : Participated in SAE BAJA competition

iv. Results achieved : Yes

v. Please indicate the technical difficulties, if any, experienced in implementing the project: N.A.

vi. If the project has been completed, please enclose a summary of the findings o the study: Attached

Signature of Student	Signature of Student	Signature of Student
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Signature of Mentor
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Signature of Idea Lab Co-ordinator	Signature of Section Head
Idea Lab Co-ordinator Name	Respective Section Head Name
Idea Lab Co-ordinator:	Section Head:
Department Name:	Department Name:
Institute of Technology,	Institute of Technology,
Nirma University, Ahmedabad.	Nirma University, Ahmedabad.

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Contents

Abstract

One of the main sources of air pollution in large cities is automotive exhaust gas emissions which contain pollutants like CO, HC, NO_x and particulate matter. These pollutants have negative impact on air quality, environment and human health that leads in stringent norms of pollutant emission. These regulations require the need for more active and durable emission control system. Highly efficient durable emission control system is Three Way Catalytic Converter (TWC_s) with noble (Platinum Group – Pt, Pd and Rh) metals for treatment of pollutants such as CO, HC and NO_x. Noble metals pose problems due to limited resources, expensive as it is noble metals, it vaporize and metal lost at high operating temperature of exhaust, so it is necessary for a researcher to search for new catalytic material that reduce or replace the noble metals for auto exhaust applications.

Perovskite oxides of general formula ABO_3 (where A and B are usually rare earth and transition metal cations respectively) is promising alternatives to supported noble metals for treatment of pollutants such as CO, HC and NO_x from auto exhaust because of their low cost, good thermal and mechanical stability at high temperatures and excellent redox properties. During synthesis of perovskite, high calcinations temperature (around 800 ^{0}C) is require to form crystalline phase which sintered the perovskite catalyst and limits their practical application due to low specific surface area. To overcome the limitation of low specific surface area, perovskite phase synthesized on alumina or other support reported by many researchers. Large particle size due to sintering react with alumina support at high temperature and form undesirable phases like mulite and metal aluminates which also limits their application. To overcome above limitations, small amount of noble metals substitute into perovskite structure which can prevent their sintering, reduce losses due to volatilization at high operating temperatures and avoid reactions with the support that lead to catalyst deactivation and remarkably enhances the catalytic activity.

Pd substituted perovskite catalyst wash coated using dip coating method on ceramic monolith for fabrication of catalytic converter. For wash coating of Pd substituted perovskite based catalyst on the ceramic monolith structure in which aluminium oxide used as a binder and nitric acid as a pH regulator. The wash coated ceramic monolith structure is fitted into the actual catalytic converter. The converter has mainly three sections. (1) Divergent cone (2) Throat section (3) Convergent cone. Such design creates anti-venturi effect in the converter so that the pressure will increase and velocity will decrease at the throat section and maximum residence time is given to the exhaust gases. Such design may exhibit higher CO/HC conversion. This design gives almost negligible amount of pressure drop. The Catalytic converter based on Pd substituted perovskite catalyst is also tested on engine for automotive emission control.

1. Introduction

Today, with increasing industrialisation and rising traffic, the air pollution is creating an adverse effect on health of all living organisms and environment. Automotive exhaust emissions are considered to be the main culprit behind the increasing levels of air pollution. Automobiles are the main source of transportation and the number of vehicles manufactured yearly is increasing exponentially. The commonly used fuels are crude oil derivatives like gasoline, petrol, diesel, kerosene etc. Other fuels that are used are LPG (Liquefied Petroleum Gas), CNG (Compressed Natural gas), hydrogen, biodiesel and others. Ideally, a combustion engine operates at the stochiometric ratio of air to fuel of 14.7 on weight basis for gasoline based fuel engines expecting a complete combustion with carbon dioxide, water vapour and nitrogen as the products. But the combustion is incomplete yielding poisonous gases like CO, HC, and NOx which are released into the atmosphere causing air pollution.

2. Limitations of platinum group (noble) metal catalysts:

Apart from technology developments in platinum group metal catalyst for engine exhaust emission control has limitations that motivated the investigation of alternative catalyst materials for catalytic combustion.

The stringent emissions standards today require high catalyst efficiency quickly after vehicle start up. In order to achieve high efficiency quickly after vehicle start, the catalyst are moved close to the engine and Pd based catalyst are widely used [8]. Because it is close to the engine, sometimes in the harsh conditions experienced in the exhaust stream with temperatures up to 1000ºC, the metal in the catalyst is prone to deactivation by sintering, leading to a reduction in surface area of precious metals caused by grain growth in high-temperature redox (reduction–oxidation) fluctuations of the exhaust gas and hence catalytic activity. To meet tightening legislative emissions control targets, conventional catalysts are loaded with excess amounts of precious metals. Also need to guarantee catalyst performance over the typical vehicle lifetime of 80,000 km also means that excess metal must be added, since the performance of the catalyst drops off over time.

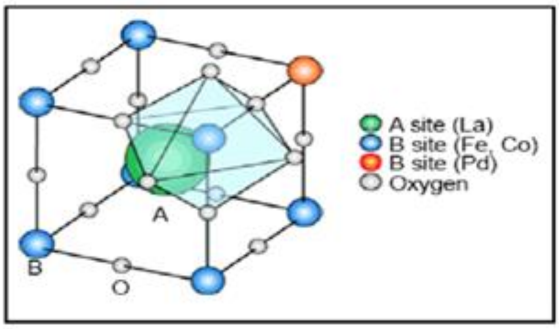
About 50 % of Pt and Pd and about 90 % of Rh are consumed as the active components of automobile catalysts. It should also be noted that consumption of platinum group metals (PGM) for automobile catalysts has significantly increased in the last few years (approx. two fold for Pt and four fold for Pd). The demand for palladium use in automotive catalyst has increased from 15 to over 150 ton per year become even more important as the Euro 5 requirements also include an extension of catalyst lifetime to 160,000 km. Due to the high cost of the PGM used in three way catalysts, reduction is required in amounts or replacement of TWCs in automotive exhaust catalytic converters would be highly desirable. In addition, rising PGM demand and costs are incentives towards achieving lower metal loadings and higher activity.

The compounds of the PGM are generally considered highly toxic while the Pd and Rh are carcinogenic in nature. Due to the fact that the PGM are produced due to the abrasion of automotive catalyst washcoat. That is why the road traffic is responsible for metallic and organic pollutant – emissions which contaminate the environment.

The catalytic converters in the exhaust system become deteriorated by several mechanisms e.g. thermal deterioration and poisoning. Thermal deterioration occurs as a result of exposure of the catalyst to high temperature conditions. This cause sintering of the PGM, loss of support surface area and phase transformation. Poison also cause loss of activity mainly by blocking the pores leading to active sites or even by direct blockage of the active sites themselves.

3. Perovskite:

Perovskite is a metal oxide having a well defined structure similar to $CaTiO_3$ (Calcium Titanate). The general formula is $AB0_3$. Here, A is the larger cation and B is the smaller one and O is the anion bonded to both the cations. The larger cation A which is surrounded to twelve oxygen in a dodecahedral structure can be rare earth, alkali or alkaline metals like Pb^{+2}, Bi^{+3} while cation B is usually 3d,4d or 5d transition metal and is surrounded by six oxygen atoms forming an octahedral structure. In a unit cell of a pervoskite, if B occupies the body centre then oxygen ion occupies the face centre and A occupies the corners of the unit cell. While if cation A is at the body centre, oxygen ion are at the middle of the edge and B in the corner of the unit cell.



Multi component Perovskite synthesized by partial substitution of the cation A and B which exhibit notable catalytic characteristics. It enhances the activity of oxidation of CO, combustion of CH_4 and conversion of NO to less harmful gases. The partial substitution of cation A and B by other metal of lower or higher oxidation state enhances the catalytic activity.

Due to wide range of properties and compositions, perovskite has found an area of application in many important fields like solid state chemistry, separation membranes, fuel cells, chemical sensors etc.

1.3 Major Objectives Proposed

- Preparation of Pd substituted pervoskite based catalysts by co-precipitation and reactive grinding using planetary ball mill.
- Investigation of suitability of these catalysts for minimization of automotive CO emission.
- Detailed characterisation of pervoskite based catalysts and to understand the relation between catalytic properties.

- Design and fabrication of a catalytic convertor based on Pd substituted perovskite catalyst.
- Testing of Pd substituted perovskite based catalyst on real engine.

1.4 Objectives Achieved

- Prepared Pd substituted perovskite catalyst by co-precipitation and and reactive grinding using planetary ball mill.
- Developed Pd substituted perovskite based catalytic converter for automotive emission control

1.5 Objectives Not Achieved: N.A.

1.6 Technical Difficulties Faced: N.A.

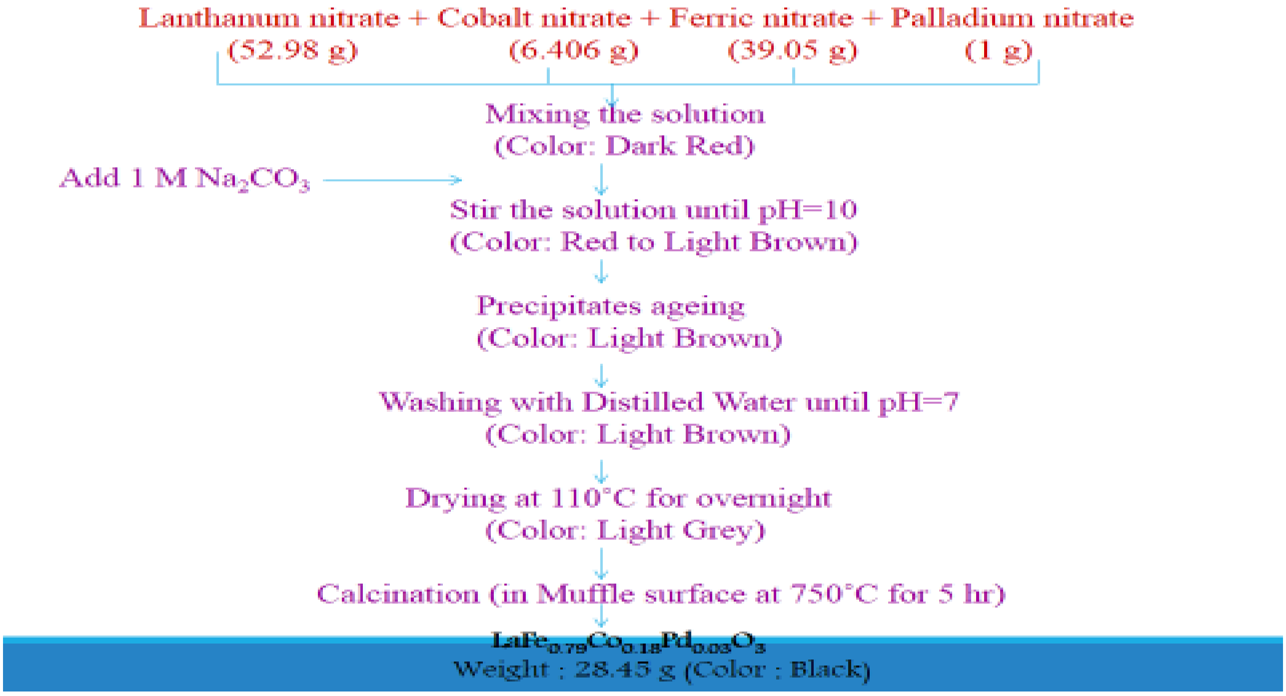
1.7 Experimental Setup and Results

Synthesis of Perovskite

Synthesis by Co-Precipitation Method:

A typical preparation method for the synthesis of perovskite catalyst is as follows:

Calculations were done and specific amount of salt precursors were taken and dissolved in 25ml of distilled water and mixed. 1M Na_2CO_3 solution was quickly added drop wise to the precursor solution under vigorous stirring until the pH reaches 10. The precipitates were allowed to age at room temperature for 30mins. The obtained precipitate was filtered and washed with distilled water several times until a pH of 7 was reached in order to remove sodium salts. The precipitates was then dried at 110ºC overnight in hot air oven and crushed to a fine powder. It was further calcined in a muffle furnace at 750ºC (ramp = 10ºC/min) under atmospheric conditions for 5hrs.



Limitations of Co-precipitation method:

This process requires high calcination temperature for formation of crystalline phase and to remove organic precursors. Also higher temperature leads to reduction in surface area hence decreasing the catalytic activity. To improve the surface area, lower calcination temperature is required which does not ensure proper crystalline phase formation. Moreover it requires reagents which are expensive and also use a large amount of water well as formation of large amount of gaseous and liquid wastes which add to environmental pollution. It also requires complex equipment due to their method of producing the perovskite. To improve the surface area, the perovskite are wash coated on alumina. But several perovskite compositions and their precursors are reactive to alumina and hence cannot be used in all the cases.

Synthesis by Reactive Grinding Method

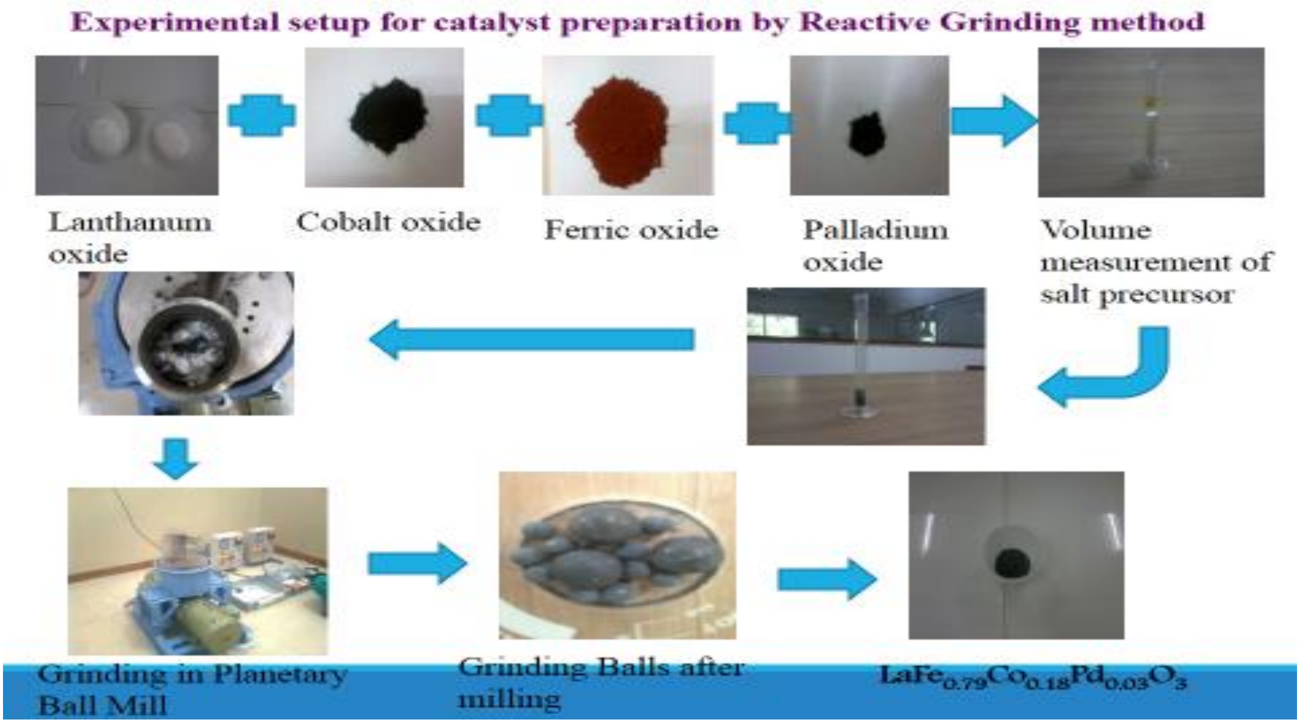
Reactive Grinding is a powder processing technique. Here, chemical reaction and phase transformation take place due to high intensity milling due to application of mechanical energy. Due to severe mechanical action on the solid surface, chemical and mechanical changes take place. The mechanical energy is converted to chemical energy which causes the reaction which commonly occurs at higher temperatures. This method is used to synthesis metal oxides, carbides, nitrides and nanosized particles. The materials prepared by this method are used in electrochemistry, catalysis, absorbers etc.

Reactive grinding involves synthesis of material by high energy ball mills e.g. Planetary ball mill, SPEX shaker mills, attritor mills in which salt precursors are milled and high energy is induced due to intense milling causing chemical reaction to occur. The powder particles undergo cold welding, fracturing and rewelding. Process control agents (PCA) can be added to minimize cold fracturing of powder particle among them. The powder particle is milled for a specific duration until a steady state is reached. Metal powder material are milled using a liquid medium, it is called wet grinding. Here, the liquid only facilitates milling but does not take part alloying to the powder. If no liquid is involved, it is called dry grinding.

The perovskite-type catalyst was prepared, by reactive grinding ($LaFe_{0.79}Co_{0.18}Pd_{0.03}0_3$). The compositions were synthesized by grinding the single oxides of La_2O_3 (CDH, 99.99%), Co_3O_4 (CDH), Fe_2O_3 (CDH), MnO (CDH), PdO (Otto, 85%). The La_2O_3 powder was calcined at 600 ^{0}C for

24 h to transform any $La(OH)_3$ to La_2O_3 before grinding. The mixed powder was then loaded into stainless steel jar (250 cm^3) with stainless steel balls under air atmosphere. The ball to powder weight ratio was 15:1. The jar was closed with a thick cover and sealed with O-ring.

The grinding jar temperature increased slightly above room temperature due to the collisions and friction among balls during the milling process. Therefore, the grinding jar wall temperature was fan cooled and kept below 40 ^{0}C.The milling atmosphere in the grinding jar was controlled by using a filter paper ring in order to continuously seep some air into the grinding jar. Finally the perovskite was calcined under air 600 ^{0}C for 5 h in muffle furnace.



Operating conditions	
Material of grinding jar and grinding balls	Stainless steel
Milling atmosphere	Air

Jar speed (rpm)	350 (Clock wise)
Sun wheel speed (rpm)	200 (Anti clock wise)
Speed ratio (Sun wheel and jar speed ratio)	1 : - 1.75
Ball to powder weight ratio	15:1
Ball number and diameter[a] (mm)	04 (19), 07 (14), 07 (10)
Mass of powder in jar (g)	15
Grinding jar dimension (mm)	Jar inside diameter (d_i) = 67.5, Jar outside diameter (d_o) = 78, Jar height (h) = 71.5
Grinding jar volume (cm^3)	250

Coating on Ceramic Monolith

Ceramic Monolith used in this study is composed of $2MgO.2Al_2O_3.5SiO_2$. The monolith is a honeycomb structure called cordierite which has low thermal expansion, is less expensive and light in weight. The cell size varies from 400 cpsi(cells per square inch) to 1200 cpsi. The cell with a size of 1200 cpsi is considered best but is used rarely due to high cost. The cell can be of various shapes- triangular, square, hexagonal etc. Hexagonal shape provides 10-12 % lower pressure drop whereas triangular shape provides up to 30 % higher pressure drop than square shaped cell. The cell used in this study is square shaped as it is easy to manufacture and also catalyst becomes operational at low temperature. Cordierite honeycomb monolith of square channels (Dia. = 97 mm, L= 44.5 mm, volume = 328 cc). Other characteristics of ceramic supports are mentioned in the table below:

Alumina slurry was prepared under the acidic condition, and with continuous stirring for 2- 4 hr. Dilute nitric acid was used t adjust the initial pH of slurry at around 3.5 to 4. Alumina undergoes peptization and also some amount of aluminium nitrate may be formed in the process, which imparts the thyrotrophic rheology to alumina slurry. Then 22 g of $LaFe_{0.79}Co_{0.18}Pd_{0.03}0_3$ perovskite catalyst was added to the slurry and the pH was again maintained to 3.5 to 4 by adding HNO_3. Wash coating of ceramic substrate was carried out following the dip coating technique. The ceramic substrate was dipped into slurry and the excess slurry was removed from channels by using blower. The outer faces of substrate were covered so that the depositions were performed only inside the channels. Substrate was initially dried by applying the hot air through a blower or alternatively by keeping the substrate in hot air oven at 200 ^{0}C for 30 minutes, followed by calcination at 700 ^{0}C for 5 h for anchoring of particles on ceramic substrate and consolidation of wash coat layer. This entire procedure was repeated to achieve the desired level of catalyst incorporation. Dimensions of catalytic converter such as length and diameter, pressure drop across the catalytic converter were calculated theoretically and based on that LaCo$_{0.95}$Pd$_{0.05}$O$_3$ perovskite based catalytic converter fabricated. The LaCo$_{0.95}$Pd$_{0.05}$O$_3$ perovskite based catalytic converter was applied on 300 CC petrol engine and the amount of emission was monitored with Five Gas Analyzer.

Result of emission test on catalytic convertor

The perovskite catalyst LaFe$_{0.79}$Co$_{0.18}$Pd$_{0.03}$0$_3$ is wash coated on a ceramic monolith and Catalytic Convertor is fabricated. When tested in the exhaust of an engine using a Five Gas Analyser, the results obtained were as follows.

Catalyst LaFe$_{0.79}$Co$_{0.18}$Pd$_{0.03}$0$_3$	CO (ppn)		% CO conversion	HC (ppm)		% HC conversion	NOx (ppm)		%NO conversion
Based on	Before CC	After CC		Before CC	After CC		Before CC	After CC	
Reactive Grinding	2.419	1.98	18	906	95	89	1061	213	81
Co-Precipitation	2.419	0.919	62	906	281	69	1061	350	67

1.8 Budget Analysis

1. Budget Sanctioned: Rs. 30, 000/-

2. Budget Utilized: Rs. 26, 810/-

Sr. No.	Name of Product	Amount	Bill No.	Date	Consumables/Non-Consumable	Dead Stock Number (if any)
1	Chemicals				Consumables	
2	Chemicals				Consumables	
3	Chemicals				Consumables	

3. Budget Unutilized: Rs. 3190/-