CHAPTER 4

Synthesis and Characterization of a PalladiumLoaded Perovskite MCM-41 material and its Application as anAutomotive Catalyst
4.1 INTRODUCTION:

Automotive catalysts designed to detoxify the exhaust were implemented in production in US on vehicles of the model year 1975 and, as we are reaching a full quarter century of their use, there is ample information available to allow us to declare that these devices, which are the principal emission control tools, have proved to be an unqualified success. Following the positive experience in US, in short order Japan and thereafter Europe, in 1986, adopted the use of automotive catalysts. Less affluent developing societies have come to the realization that emission control in heavily populated areas is not a costly frill but a tangible benefit for the quality of life and the use of automotive catalysts is rapidly spreading around the globe. Even a subjective, casual visitor to urban centers where these devices have not yet been widely implemented will quickly notice the difference in air quality. The ubiquity of automobiles, and by extension of catalysts, has made catalysts and their function much more familiar to the population at large.[1]

The significant environmental implications of vehicles cannot be denied. The need to reduce vehicular pollution has led to emission control through regulations in conjunction with increasingly environment-friendly technologies. In India, it was only in 1991 that the first stage emission norms came into force for petrol vehicles and in 1992 for diesel vehicles. The following chart indicates, step wise enforcement of norms for emission of pollutants from two wheelers.

![Fig. 4.1 Progressive Reduction of Indian Emission Norms 2 Wheelers (Both 2 and 4 stroke):](image)
### Table 4.1 Stepwise enforcement of norms for emission of pollutants from two wheelers

<table>
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<tbody>
<tr>
<td>CO g/km</td>
<td>12</td>
<td>4.5</td>
<td>2.0</td>
<td>1.5</td>
</tr>
<tr>
<td>HC+NOx g/km</td>
<td>8</td>
<td>3.6</td>
<td>2.0</td>
<td>1.5</td>
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</tbody>
</table>

From April 1995 mandatory fitment of catalytic converters in new petrol passenger cars sold in the four metros of Delhi, Calcutta, Mumbai and Chennai along with supply of Unleaded Petrol (ULP) was effected. Availability of ULP was further extended to 42 major cities and now it is available throughout the country. The emission reduction achieved from pre-89 levels is over 85% for petrol driven and 61% for diesel vehicles to 1991 levels. Since the year 2000, passenger cars and commercial vehicles have been meeting Euro I equivalent India 2000 norms, while two wheelers have been meeting one of the tightest emission norms in the world. Euro II equivalent Bharat Stage II norms are in force from 2001 in 4 metros of Delhi, Mumbai, Chennai and Kolkata. Since India embarked on a formal emission control regime only in 1991, there is a gap in comparison with technologies available in the USA or Europe. Currently, we are behind Euro norms by few years, however, a beginning has been made, and emission norms are being alligned with Euro standards and vehicular technology is being accordingly upgraded. Vehicle manufactures are also working towards bridging the gap between Euro standards and Indian emission norms.

### 4.2. AUTOMOTIVE EXHAUST PURIFICATION CATALYSIS- TERMS AND CONCEPTS:

**Catalytic converter** is an exhaust emission control device which converts toxic chemicals in the exhaust of an internal combustion engine into less toxic substances. Inside a catalytic converter, a catalyst stimulates a chemical reaction in which toxic byproducts of combustion are converted to less toxic substances by way of catalysed chemical reactions. The specific reactions vary with the type of catalyst installed. Most present-day vehicles that run on gasoline are fitted with a "three way" converter, so named because it converts the three main pollutants in automobile exhaust: an oxidizing reaction converts carbon monoxide (CO) and unburnt hydrocarbons (HC), and
a reduction reaction converts oxides of nitrogen (NO\textsubscript{x}) to produce carbon dioxide (CO\textsubscript{2}), nitrogen (N\textsubscript{2}), and water (H\textsubscript{2}O).

The catalytic converter consists of several components:

**The catalyst core.** For automotive catalytic converters, the core is usually a ceramic monolith with a honeycomb structure. Metallic foil monoliths made of FeCrAl are used in some applications. This is partially a cost issue. Ceramic cores are inexpensive when manufactured in large quantities. Metallic cores are less expensive to build in small production runs. Either material is designed to provide a high surface area to support the catalyst washcoat, and therefore is often called a "catalyst support". The cordierite ceramic substrate used in most catalytic converters was invented by Rodney Bagley, Irwin Lachman and Ronald Lewis at Corning Glass, for which they were inducted into the National Inventors Hall of Fame in 2002.

**Monolith**

The combined requirements of compactness, high volumetric flow rates and low back pressure led to the adoption of a monolithic embodiment for automotive catalysts, quite different from the packed-bed forms that prevailed in almost all industrial and petroleum catalysis. The monoliths were multi-channeled ceramic catalyst bodies (square, triangular or honeycomb channel configurations), with the exhaust gas flowing through the channels on whose walls there is a coated high surface area porous layer with finely dispersed noble metal catalytic particles. (At the dawn of the implementation period, some manufacturers stuck to the more familiar granular catalysts. In use, these catalyst granules or beads suffered from attrition and ultimately were abandoned in favour of the monoliths and also due to poorer warm-up characteristics.) Presently, monolithic catalysts (mostly ceramic but also metallic in some special instances) are universally used in automotive catalysis. Moreover, the “monolith” catalytic technology is migrating into the realm of industrial catalysis, most often in processes for treatment of industrial effluents.

**The washcoat.** A washcoat is a carrier for the catalytic materials and is used to disperse the materials over a high surface area. Aluminum oxide, Titanium dioxide, Silicon dioxide, or a mixture of silica and alumina can be used. The catalytic materials are suspended in the washcoat prior to applying to the
core. Washcoat materials are selected to form a rough, irregular surface, which greatly increases the surface area compared to the smooth surface of the bare substrate. This in turn maximizes the catalytically active surface available to react with the engine exhaust.

Precious metal. The catalyst itself is most often a precious metal. Platinum is the most active catalyst and is widely used, but is not suitable for all applications because of unwanted additional reactions and high cost. Palladium and rhodium are two other precious metals used. Rhodium is used as a reduction catalyst, palladium is used as an oxidation catalyst, and platinum is used both for reduction and oxidation. Cerium, iron, manganese and nickel are also used, although each has its own limitations.

Types of catalytic converters:

Two-way
A two-way (or "oxidation") catalytic converter has two simultaneous tasks:
1. Oxidation of carbon monoxide to carbon dioxide:
   \[2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2\] (4.1)
2. Oxidation of hydrocarbons (unburnt and partially burnt fuel) to carbon dioxide and water:
   \[\text{C}_x\text{H}_{2x+2} + [(3x+1)/2] \text{O}_2 \rightarrow x\text{CO}_2 + (x+1) \text{H}_2\text{O} \text{ (a combustion reaction)}\] (4.2)

This type of catalytic converter is widely used on diesel engines to reduce hydrocarbon and carbon monoxide emissions. They were also used on gasoline engines in American- and Canadian-market automobiles until 1981. Because of their inability to control oxides of nitrogen, they were superseded by three-way converters.

Three-way
Since 1981, "three-way" (oxidation-reduction) catalytic converters have been used in vehicle emission control systems in the United States and Canada; many other countries have also adopted stringent vehicle emission regulations that in effect require three-way converters on gasoline-powered vehicles. The reduction and oxidation catalysts are typically contained in a common housing, however in some instances they may be housed separately. A three-way catalytic converter has three simultaneous tasks:
I. Reduction of nitrogen oxides to nitrogen and oxygen:

\[ 2\text{NO}_x \rightarrow x\text{O}_2 + \text{N}_2 \]  \hspace{1cm} (4.3)

II. Oxidation of carbon monoxide to carbon dioxide:

\[ 2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2 \]  \hspace{1cm} (4.4)

III. Oxidation of unburnt hydrocarbons (HC) to carbon dioxide and water:

\[ \text{C}_x\text{H}_{2x+2} + [(3x+1)/2]\text{O}_2 \rightarrow x\text{CO}_2 + (x+1)\text{H}_2\text{O} \]  \hspace{1cm} (4.5)

These three reactions occur most efficiently when the catalytic converter receives exhaust from an engine running slightly above the stoichiometric point. This point is between 14.6 and 14.8 parts air to 1 part fuel, by weight, for gasoline. The ratio for Autogas (or liquefied petroleum gas (LPG)), natural gas and ethanol fuels is each slightly different, requiring modified fuel system settings when using those fuels. In general, engines fitted with 3-way catalytic converters are equipped with a computerized closed-loop feedback fuel injection system using one or more oxygen sensors, though early in the deployment of three-way converters, carburetors equipped for feedback mixture control were used.

Three-way catalysts are effective when the engine is operated within a narrow band of air-fuel ratios near stoichiometry, such that the exhaust gas oscillates between rich (excess fuel) and lean (excess oxygen) conditions. However, conversion efficiency falls very rapidly when the engine is operated outside of that band of air-fuel ratios. Under lean engine operation, there is excess oxygen and the reduction of NO\(_x\) is not favored. Under rich conditions, the excess fuel consumes all of the available oxygen prior to the catalyst, thus only stored oxygen is available for the oxidation function. Closed-loop control systems are necessary because of the conflicting requirements for effective NO\(_x\) reduction and HC oxidation. The control system must prevent the NO\(_x\) reduction catalyst from becoming fully oxidized, yet replenish the oxygen storage material to maintain its function as an oxidation catalyst.

**Light off Temperature:** Car catalyst do not work at low temperature due to kinetic considerations and if the temperature of the catalyst is increased, increase in conversion from zero to high levels occurs over a short temperature range, the inflexion point of this curve is often called the light off temperature. It is important that this temperature is as low as possible for
efficient conversion quickly after the cold start of the engine. This is especially so since the testing cycle require the catalyst to achieve total averaged conversion from a cold start and include cycles of low temperature operation. Precious metals are highly active materials which encourage low temperature light-off, but below this temperature the metals tend to be covered by carbon monoxide and light off only occurs when this begins to desorb from the surface and liberate surface sites for reaction. Of late, the light off temperature has gained significance in defining the efficiency of automotive catalysts, and the definition has been conveniently labeled for individual pollutants (CO, Hydrocarbon and NOx) as the temperature at which 50% conversion is achieved for the respective pollutant gas.

**Air fuel ratio (Lambda, $\lambda$):**

Air–fuel ratio (AFR) is the mass ratio of air to fuel present in an internal combustion engine. If exactly enough air is provided to completely burn all of the fuel, the ratio is known as the stoichiometric mixture. AFR is an important measure for anti-pollution and performance-tuning reasons. For gasoline fuel, the stoichiometric air–fuel mixture is approximately 14.7; i.e. for every one molecule of fuel, 14.7 molecules of $O_2$ are required (the fuel oxidation reaction is: $25/2 \text{O}_2 + \text{C}_8\text{H}_{18} \rightarrow 8 \text{CO}_2 + 9 \text{H}_2\text{O}$). Any mixture less than 14.7 to 1 is considered to be a rich mixture; any more than 14.7 to 1 is a lean mixture – given perfect (ideal) "test" fuel.

Lambda ($\lambda$) is the ratio of actual AFR to stoichiometry for a given mixture. Lambda is 1.0 at stoichiometry, less than 1.0 for rich mixtures, and greater than 1.0 for lean mixtures. There is a direct relationship between lambda and AFR. To calculate AFR from a given lambda, multiply the measured lambda by the stoichiometric AFR for that fuel. Alternatively, to recover lambda from an AFR, divide AFR by the stoichiometric AFR for that fuel. This last equation is often used as the definition of lambda.

$$\lambda = \frac{\text{AFR}}{\text{AFR}_{\text{Stoichiometric}}} \quad (4.6)$$

Because the composition of common fuels varies seasonally, and because many modern vehicles can handle different fuels, when tuning, it makes more sense to talk about lambda values rather than AFR.
Oxygen storage

Three-way catalytic converters can store oxygen from the exhaust gas stream, usually when the air-fuel ratio goes lean. When insufficient oxygen is available from the exhaust stream, the stored oxygen is released and consumed. A lack of sufficient oxygen occurs either when oxygen derived from NO\textsubscript{x} reduction is unavailable or when certain maneuvers such as hard acceleration enrich the mixture beyond the ability of the converter to supply oxygen.

Thermal stability

The catalyst can cycle from cold start to temperatures as high as 900°C, and this is a very demanding situation not usually experienced by catalysts in chemical processing. Thus both mechanical and chemical stability are required. Mechanical support and thermal shock resistance are provided by monolith support, as stated earlier. Clearly, the chemically active components of the catalyst must also be thermally stable and this eliminates many possible elemental compositions, including low melting metals and oxides which may be reducible to more volatile species during the engine cycle. Platinum group metals (Pt, Pd and Rh) are relatively high melting point metals, compared to other base metals like Cu and Ag.

Lifetime

The catalyst must have considerable longevity and maintain high conversion over at least 50000 miles operation in Europe or 100000 miles in the USA. Thus all the materials used are also designed for great time stability and many of the features described above would aid in catalyst engineering.

Catalyst Architecture

The automotive catalyst assembly is required to operate with very high efficiency at high gas flows. As a result much care must be taken in design and construction of the catalyst to ensure that these requirements are met. Of particular interest are the pore size distribution in the catalyst, the metal particle size and the distribution of active metal within the pores. Two main factors influence the design: the requirement for effective mass transport so that reactant gases can reach the catalyst and product can be efficiently removed, and chemical considerations to ensure that catalysis is effectively
carried out with minimum need for expensive resources, particularly precious metals. The mass transport usually needs a network of both macropores \((d>500 \text{ Å})\) which carry most of the gas load, and meso pores \((20 \text{ Å}<d<500 \text{ Å})\) where most of the precious metal component is located and catalysis occurs.

### 4.3 MATERIALS USED AS AUTOMOTIVE EXHAUST PURIFICATION CATALYSTS:

Gasoline-powered passenger cars, which comprise a large majority of the US market, emit CO, unburnt HC and oxides of nitrogen (NOx). Starting in 1981, the automobile industry was mandated to sharply reduce the emissions of all three (previously only CO and HC had to be removed). This required "three-way-conversion" (TWC): the simultaneous oxidation of CO/HCs and reduction of NOx, a feat without precedent in the chemical industry. It can only be accomplished by keeping the exhaust gas composition extremely close to the stoichiometric point. Cerium oxide was soon recognized as indispensable to the success of the TWC catalyst, due to its ability to rapidly change oxidation states at the surface. This enables it to "store" and "release" oxygen in response to changes in the gas phase composition. The use of ceria was greatly expanded by the addition of zirconia; the ceria-zirconia was far more thermally stable than ceria itself and allowed the TWC catalyst to survive much higher temperatures.

Diesel exhaust differs from gasoline exhaust in important respects. It is always "lean" (i.e., net oxidizing) and three-way conversion is thus ruled out. The chief concern is particulate matter, which includes dry soot and a "soluble organic fraction" (SOF), comprised of mainly \(C_{20}-C_{28}\). Prior to 2000, attention was mainly focused on SOF conversion, as dry soot emissions could be controlled within the standards by optimizing fuel delivery, air intake systems, and the combustion process. To meet the new emission standards proposed for 2007-2009 in the U.S, Europe and Japan, the diesel particulate filter (DPF) was created, in which the channel wall filters out the soot particles. The latter are burned off, at suitable intervals, by raising the temperature. DPFs were originally limited to trucks and buses, but their proven effectiveness has led to their planned use on passenger cars as well.
A final topic in diesel after treatment is NOx removal. A successful approach, already in place in Europe, is the use of urea, carried on-board as an aqueous solution. Urea hydrolyzes to release NH₃, which is a highly effective agent for converting NOx to N₂.

**Zeolites:**

With the continued improvements in three-way catalyst (TWC) technology, most of the hydrocarbon (HC) emissions from gasoline engines occur during engine cold start before the TWC would reach its effective operating temperature. Since the TWC is deemed to be at or near its lowest feasible light-off temperature, alternate approaches to achieve the reduction are necessary. One approach is to use a zeolite to adsorb HC at low temperatures followed by desorption at temperatures where the TWC is active. Several Japanese car manufacturers have reported the use of zeolites as HC traps for gasoline powered passenger cars to meet these stringent emission standards [2, 3]. The concept of using zeolites as hydrocarbon traps can be traced back to the early 1970s [4,5], and various zeolites have since been considered as adsorbents for trapping exhaust HCs [6–15]. For example, silicalite (MFI) was studied because of its hydrophobic properties that lead to the ability to preferentially adsorb HCs over water present in the exhaust [7]. Other zeolites such as H-ZSM-5 [7, 12], Ag-ZSM-5 [8], Beta zeolite [9, 12], mordenite [10], EUO [10], SSZ-33 [11] and USY [12] have also been investigated as HC trapping materials.

In diesel automotive emission control systems, zeolites have been incorporated into the diesel oxidation catalysts (DOC) to help reduce HC emissions [13]. Zeolites Beta and ZSM-5 have been considered to be effective for DOC [14, 15].

**Perovskites:**

Perovskite-type oxides have general formula as ABO₃. Fig. 4.2 shows structure of perovskite where red spheres are oxygen atoms, the blue spheres are B atoms (a smaller metal cation, such as Ti⁴⁺), and Green spheres are the A-atoms (a larger metal cation, Ca²⁺). When A is rare earth or alkaline earth metal and B is transition metal, the perovskite are typically P-type semiconductors.
Pictured is the undistorted cubic structure, however the symmetry is lowered to orthorhombic, tetragonal or trigonal in many perovskites. Their composition can be varied in a wide range by partial substitution of lower valent cation in A or B site yielding additional mobile anion vacancies. Their mixed conductivity by both ion and electron migration and their high nonstoichiometric composition have resulted in the applications of this group of materials in the areas such as electrochemistry, catalysis, solid oxide fuel cells, oxygen separation membranes, chemical sensors for the detection of humidity, alcohol and gases such as oxygen, hydrocarbon and nitric oxide [16]. Earlier studies reported on perovskite oxide LaCo$_x$Fe$_{1-x}$O$_3$ mainly involved methane oxidation catalysis.

Recently, noble metals combined with perovskites have developed into an emerging field. Addition of small amounts of noble metals to perovskites could improve their catalytic activity. Incorporation of small amounts of precious metals into a perovskite structure can prevent their sintering, reduce losses due to volatalization at high operating temperatures and avoid reactions with the support that slow down the catalyst. Further, attention has been concentrated on the use of palladium based catalyst for TWC (three way catalyst) formulation. Pd is well known to have a good resistance to thermal sintering, is much cheaper than Pt and Rh and also has a good activity for oxidation of CO and hydrocarbons [16].
Oxygen Storage and release in Perovskites:

Y. Zhang-Steenwinkel et al [17] have studied the oxygen storage/releasing property by reduction of La$_{0.8}$Ce$_{0.2}$MnO$_3$ type Perovskite, using labeled 1 vol.% C$^{18}$O and balance He(99%), as reducing gas mixture over the catalyst and monitoring the production of C$^{16}$O, C$^{18}$O, C$^{18}$O$^{16}$O and C$^{16}$O$^{18}$O, and have provided following reaction mechanism of CO oxidation on Perovskite surface.

**Fig.4.3** The reaction mechanism of the reduction of La$_{1-x}$Ce$_x$MnO$_3$ by C$^{18}$O at 473 K [17].

### 4.4 SYNTHESIS STRATEGIES FOR AUTOMOTIVE CATALYSTS-A LITERATURE SURVEY

LaMnO$_3$ perovskites supported noble metal (Pt, Pd, Rh) catalysts prepared by the citrate method are used for the total oxidation of methane and it is observed that the oxidation activity is enhanced [18]. Tanaka [19] prepared LaFe$_{0.95}$Pd$_{0.05}$O$_3$ perovskite catalyst by the alkoxide method. “The intelligent catalyst” has a self-regenerative function. Pd in this catalyst moves back and forth between the B-site in the perovskite structure and the metal lattice.

Furthermore, La(Fe, Co)PdO$_3$ [20,21] (La$_{0.6}$Sr$_{0.4}$)(Co$_{0.94}$Pt$_{0.03}$Ru$_{0.03}$)O$_3$ [22,23] and LaMn$_{0.976}$Rh$_{0.224}$O$_{3.15}$ [22,24] perovskite composition were explored for TWC catalysis for exhaust treatment from single cylinder engine and compared with synthetic CO + NO + C$_3$H$_6$ mixture.

Co-precipitation [25], sol-gel methods [26, 27] and combustion methods [28, 29, 30–33] are common synthetic approaches for synthesis of
perovskites. Amongst these synthetic methods, the solution combustion is an attractive route. It is very facile and energy efficient. It can produce high purity, homogeneous crystalline product with high specific surface area [28, 29,30–33]. However, not much attention has been focussed towards the preparation of perovskite catalysts incorporating noble metal, using a solution combustion method. There is very limited information available on developing new active catalysts, especially the perovskite oxides substituted by Pd via solution combustion method. Perovskite-type oxides have been used for simultaneous catalytic removal of NOx and diesel soot [34]. LaCoO3 has excellent catalytic activity for oxidation. Pd could modify its structure and the physical properties and increase its catalytic activity [22].

4.5 AIM AND SCOPE OF THE PRESENT WORK

Although perovskite materials have not yet found application as commercial catalysts, their importance in efforts to correlate solid-state chemistry with catalytic properties, dependence of their properties on the preparation methods, and the fact that they can be tailored for specific catalytic needs make these oxides, prototype models for heterogeneous catalysts.

Perovskite produced via conventional synthesis methods are found to exhibit relatively low specific surface areas and low catalytic activity in the reactions, thus its commercial applications are limited. Siliceous MCM-41 a material with a neutral framework exhibits negligible catalytic activity. However, one can encash its advantageous properties such as high surface area, chemical inertness, high thermal and chemical stability. Thus, one of the approaches for overcoming the limitations of Perovskites is to support them on to materials with high surface area inert materials like MCM 41. Supporting Perovskites on a high surface area inert material can ensure uniform and high dispersion throughout the surface of carrier along with thermal stability of resultant material and hence durability of the catalyst and generating structural defects due to interaction with support and thereby improvement of redox functionality.

In the present endeavor LaCoO3 Perovskites(LC) have been synthesized on the surface of siliceous MCM 41 materials by citric acid
solution combustion method abbreviated as LCM. Different wt.% Pd was loaded by equilibrium adsorption using excess solution of palladium nitrate. The materials have been characterized for XRD, BET surface area and temperature programmed reduction (TPR). Catalytic activity of these materials have been evaluated in a down flow tubular micro reactor using a simulated exhaust gas mixture, where in concentration of CO, HC and NOX in the gas mixture passing through the catalyst bed has been monitored as a function of catalyst bed temperature.

4.6 EXPERIMENTAL

Materials:
Lanthanum nitrate, Cobaltous nitrate, Palladium nitrate and citric acid were procured from Merck India Ltd. as AR grade reagents.

Synthesis of Perovskite based automotive catalysts
The synthesis consists of three parts.

(i) Synthesis of MCM 41
The synthesis has been performed as described in Chapter 2 section 2.10.

(ii) Synthesis of LC onto siliceous MCM 41-(LCM)
In a typical set up for preparation of LCM, lanthanum nitrate and cobaltous nitrate were dissolved in water in a 1:1 mole ratio. To this solution was added an aqueous solution of 20% citric acid. (Amount of Citric acid solution was taken such that weight of citric acid was equivalent to oxide weight of resultant LaCoO₃). To this resultant solution, MCM 41 powder was added and kept under agitation for 0.5 h. The slurry was transferred to a ceramic crucible, dried at 120°C for 6 h and then calcined at 550 °C for 3 hrs at the rate of 2 °C/min. This sample was designated as LCM. For comparison, LaCoO₃ was prepared following the same procedure as described above except that MCM 41 was not added. This sample was designated as LC.

(iii) Incorporation of precious metal (Pd) onto LCM to give Pd-LCM:
Palladium impregnation on LCM sample was carried out using equilibrium adsorption using excess solution of Pd(NO₃)₂. In a typical set up, 1 g LCM powder was kept with 1 % solution of palladium nitrate for 12 hours. After 12 hours, powder was separated by filtration, dried at 120°C, followed by
calcination at 550°C for 3 hrs at a heating rate of 2°C/min. This sample was designated as Pd-LCM.

In the present study following materials were prepared LC, LCM-15 wt.%-LC loading, LCM-40wt%-LC loading, 0.2wt%Pd-LCM-15wt%-LC loading, 0.2 wt%Pd-LCM 40 wt%-LC loading, 1wt%Pd-LCM and 1wt%-Pd-MCM-41.

**Instrumental methods of characterization**

X-ray diffractograms ($2\theta$=5-90°) were obtained on X-ray diffractometer (Bruker D8) with Cu-Kα radiation and Nickel filter. Surface area measurement (BET method) was carried out on Micromeritics Gemini 2120 at -196°C using nitrogen adsorption isotherms. TPR was carried out on Micromeritics 2720, using 10 % H₂+N₂ gas up to 800°C at a heating rate of 10°C/min.

**Evaluation of Catalytic Activity**

Catalytic activity of the above synthesized materials was evaluated using a simulated exhaust gas mixture in a down flow tubular micro reactor, fitted with a programmable furnace and data recording device which logs the data of gas concentration and temperature at every 10 seconds to the computer attached. Catalyst pellets were placed in the middle of the reactor tube on a sintered disc and a thermocouple placed near the catalyst bed detects the temperature and sends temperature signals to computer every 10 seconds. In a typical test set up, 1 g of material was pelletized using a hydraulic die press and placed inside the reactor on the disc. Gas mixture containing 0.4 % CO, 0.13 % H₂, 0.04 % Propylene, 12.5 % CO₂, 0.06 % NOx, 0.4 % O₂ and balance N₂ was passed through the reactor at the rate of 125 L/h to give gas hourly space velocity of 125 KL/h. Temperature ramp up was given at the rate of 10°C/min. from room temperature to 450°C and temperature and composition of gases flowing through the reactor were recorded using a Horiba gas analyzer. Air to fuel ratio ($\lambda$) of the exhaust gas composition was calculated as,

$$\lambda = \frac{2 \times O_2 \text{ Volume } \% + NO \text{ Volume } \%}{CO \text{ Volume } \% + 10 \times \text{propylene volume } \%}$$ (4.7)

Catalytic activity of the materials tested has been reported as (i) Light off temperature for CO, HC and NOx and (ii) conversion of CO, HC and NOx at 400 °C, the temperature at which activation energy is enough for conversion
to take place on the active sites, and there are no thermodynamic limitations for CO and HC conversion.

4.7 RESULTS AND DISCUSSION

XRD of LC is presented in Fig. 4.4 and matches with LaCoO$_3$ structure with cubic morphology (JCPDS card no.-075-0279). XRD of LCM-40 wt% LC loading is presented in Fig. 4.5 and matches with LaCoO$_3$ structure with cubic morphology (JCPDS card no.-075-0279). The intensity of peaks is very less for 40 wt% LCM sample compared to 100 % LC sample, indicating that LaCoO$_3$ is well dispersed on the surface of MCM-41.

![Fig.4.4 XRD of LC](image)

![Fig.4.5 XRD of 40wt% LCM](image)

![Fig.4.6 TPR patterns of LCM and Pd LCM](image)

![Fig.4.7 Conversion curves for 1 % Pd LCM](image)
Since the materials are proposed to be used as automotive exhaust catalysts, thermal stability is an important aspect of the same, as stated earlier in the introduction part. In order to check the thermal stability, the materials were subjected to calcination at 1000 °C in a muffle furnace for 3 h. and checked for BET surface area. BET surface area of MCM-41, MCM-41(LCM) fresh and aged samples are presented in (Table-4.2). BET surface area of MCM-41 decreases after impregnation with perovskite. This may be attributed to pore blockage by loading of perovskite on MCM-41. Further drop in surface area is observed after thermal ageing at 1000 °C. This may be attributed to sintering of perovskite structure as well as collapse of MCM-41 pores after severe thermal treatment.

**Table 4.2:** BET surface area of fresh and thermally aged samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m²/g)</th>
<th>Fresh</th>
<th>Aged</th>
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<tbody>
<tr>
<td>MCM-41</td>
<td>1126</td>
<td></td>
<td>700</td>
</tr>
<tr>
<td>LC</td>
<td>16</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>LCM-15 wt.%-LC loading</td>
<td>535</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>LCM-40 wt.%-LC loading</td>
<td>158</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>0.2 wt%Pd-LCM-15 wt% - LC loading</td>
<td>487</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>0.2 wt% Pd-LCM 40 wt% - LC loading</td>
<td>119</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>1% Pd-LCM</td>
<td>89</td>
<td>2</td>
<td></td>
</tr>
</tbody>
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TPR patterns of LCM and Pd LCM (Fig. 4.6) shows peaks due to hydrogen consumption for reduction of perovskite materials. As observed,
reduction temperature of perovskite decreases post impregnation with Pd which may be attributed to Pd catalyzing reduction of perovskite resulting in a lower reduction temperature. Area under the curve in TPR pattern indicates amount of metal being reduced. It is observed that area of TPR curve increases after Pd metal loading and as a function of amount of Pd metal loading. The decrease in reduction temperatures can be explained by the activated hydrogen atoms on the Pd particles [35]. These H atoms could reduce the Co\textsuperscript{n+} species at lower temperature [18]. Similar results have been reported for Pd doped LaFeCoO\textsubscript{3} catalysts [36] and LaMnPdO\textsubscript{3} catalysts [18].

Lowering in the reduction temperature may be attributed to Pd catalyzing complete reduction of perovskite material. Reduction temperature in TPR pattern can be correlated with flexibility of oxygen uptake and release (redox functionality) under transient conditions (rich and lean) in automotive exhaust. Lower the reduction temperature, lower the temperature of oxygen release in rich condition in exhaust. Hence, from the TPR pattern it can be concluded that LCM indicates potential as oxygen storage material for automotive exhaust catalyst. Pd impregnation of LCM enhances reducibility of perovskite and oxygen storage capacity of the material.

To check the activity of Perovskite for conversion of CO and HC, 15 % LCM without Pd was evaluated first. As seen from (Table 4.3) entry no 2, no light off for either CO or HC was observed for this sample and conversion of CO was 8% at 400 °C, while no HC conversion was observed. Thus 40 wt% LCM entry no 3 was subjected to light off with no response to CO and HC though active sites were increased, however conversion of CO and HC at 400 °C improved marginally (Table-4.4) entry no 3.

Further it is observed that when Pd is introduced in samples to provide active sites for CO and HC conversion (Table-4.3 entry no 4 & 5) while light off was not observed, for 15 % LCM, CO and HC conversion were dramatically improved and for 40 % LCM, CO and HC light off were observed at ~ 400 °C. These observations indicate that, CO and HC conversion occur on Pd metal surface, and Pd is the active site for CO and HC conversion. ~ 10 % conversion of CO and HC for samples without Pd may be attributed on account of free radical oxygen being released from Perovskite and reacting with CO and HC.
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Pd concentration was further increased to 1 wt. % on 40 % LCM sample and as seen from table 4.3 (entry no 6), CO and HC light off were significantly improved to 220 °C. There was no unreacted CO and HC at 400 °C for 1 % Pd on 40 % LCM sample (table 4.4 entry no 6).

For all the samples tested, NOx light off is not observed, which is expected since there is no Rhodium present, which is necessary for NOx reduction to occur.

For comparison purpose a catalyst with 1 % Pd on MCM 41 (Table-4.3 entry no 7) was evaluated for catalytic activity for which no light off for CO and HC was observed upto 400 °C. This indicates that, CO and HC are oxidized only when Pd is present as an active site on catalyst. Since Perovskites reduce the activation energy of oxidation of CO and HC, it may even help to reduce precious metal content in commercial catalysts.

Table 4.3: Light off temperatures for synthesized catalysts

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>CO Light off T, °C</th>
<th>HC light off T, °C</th>
<th>NOX Light off T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LC</td>
<td>No light off</td>
<td>No light off</td>
<td>No light off</td>
</tr>
<tr>
<td>2</td>
<td>LCM-15 wt%-LC loading</td>
<td>No light off</td>
<td>No light off</td>
<td>No light off</td>
</tr>
<tr>
<td>3</td>
<td>LCM – 40 wt% -LC loading</td>
<td>No light off</td>
<td>No light off</td>
<td>No light off</td>
</tr>
<tr>
<td>4</td>
<td>0.2wt% Pd-LCM-15 Wt% LC Loading</td>
<td>No light off</td>
<td>No light off</td>
<td>No light off</td>
</tr>
<tr>
<td>5</td>
<td>0.2wt% Pd-LCM -40 Wt% LC Loading</td>
<td>410</td>
<td>394.5</td>
<td>No light off</td>
</tr>
<tr>
<td>6</td>
<td>1% Pd-LCM</td>
<td>220</td>
<td>223.5</td>
<td>No light off</td>
</tr>
<tr>
<td>7</td>
<td>1% Pd-MCM41</td>
<td>No light off</td>
<td>No light off</td>
<td>No light off</td>
</tr>
</tbody>
</table>

Table 4.4: Conversion of CO, HC and NOx at 400 °C

<table>
<thead>
<tr>
<th>No</th>
<th>Sample</th>
<th>CO Conversion, %</th>
<th>HC Conversion, %</th>
<th>NOX Conversion, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LC</td>
<td>15.5</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>LCM-15 wt%-LC loading</td>
<td>8</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>LCM – 40 wt%-LC loading</td>
<td>10</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>0.2wt% Pd-LCM-15 Wt% LC Loading</td>
<td>25</td>
<td>20</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>0.2wt% Pd-LCM -40 Wt% LC Loading</td>
<td>37.5</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>1% Pd-LCM</td>
<td>100</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>7</td>
<td>1% Pd-MCM41</td>
<td>10</td>
<td>25</td>
<td>3</td>
</tr>
</tbody>
</table>
4.8 CONCLUSIONS

In the present endeavour a humble attempt has been made towards synthesis of materials that could be probably used for automotive catalysts. Since it is evident that storage oxygen is used for oxidation, a material that can store oxygen is highly essential for automotive catalyst, which is met with by use of perovskite (LC) in the present study.

Oxidation of CO and HC by free radical oxygen, released from surface of Perovskite(LCM) has been demonstrated. The conventional precious metal used is Pt. Using Pd makes the catalyst cost effective. In view of the relatively larger drop of surface area of the samples post thermal ageing, and due to low conversion for NOx, in the synthesized materials, it could be useful for diesel oxidation catalyst, wherein exhaust temperatures are low, and only oxidation function of the catalyst is required, since NOx reduction is treated separately in diesel exhaust treatment system. It is also proposed that further work on LCM system with incorporation of Rh can be studied, for three way catalysis wherein NOX reduction will also occur on the same catalyst.
REFERENCES