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Application of supported perovskite-type catalysts for vehicular emission control

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Catalytic control of auto-exhaust emissions is one of the most successful applications of heterogeneous catalysis, both in commercial and environmental point of views. Although noble metal-based catalysts have dominated this area, efforts were always put in towards development of low cost non-noble metal-based catalysts. With the recent need of closed-coupled catalytic converter, thermal stability requirements have also become more severe, leading to the search for stable catalytic materials. Mixed oxides, including those perovskite type compounds with ABO_3 structure have been extensively studied, mainly for their catalytic and electrical properties. Low surface area of these catalysts has so far been the most important limitation for their catalytic applications involving high space velocities, e.g. auto-exhaust catalysis. Various synthesis routes have been earlier attempted to improve their surface area, yet this was much inferior than the noble metal catalysts, dispersed on high surface area alumina. The *in situ* synthesis of these oxides on alumina is often associated with the formation of undesired phases, due to the reactive nature of perovskite precursors. However, alumina washcoat, commonly used for improving the surface area of ceramic and metallic catalyst supports, can be modified for perovskite applications. *In situ* synthesis of stabilized perovskites on modified alumina-washcoated supports offer high surface area and excellent catalyst adhesion. Although, it is difficult to ascertain the presence of pure perovskite type materials on support, such improved synthesis has resulted in remarkable improvement in their catalytic activity for their applications in auto-exhaust catalytic converters. This review presents our work on synthesis of various improved perovskite-type mixed oxides supported on modified alumina-washcoated cordierite honeycomb, their characterization, and detailed catalytic evaluations for possible application in automobile pollution control.

KEY WORDS: Perovskite; catalytic converter; alumina washcoat.

1. Introduction

1.1. Auto-exhaust emission control

Automobile exhaust pollution contributes significantly to the air pollution. With fast increasing vehicle population even in developing countries, enormous amount of obnoxious emissions like CO, HC, NO*x* and particulate matter are being emitted. These pollutants have hazardous effects on environment and human health. Looking towards the exponential growth of vehicular population, control strategies for auto-exhaust pollution are essential. Out of various technologies available for automobile exhaust emission control, a catalytic converter is found to be the best option to control the CO, HC, and NO*x* emissions from petrol driven vehicles, while diesel particulate filter and oxidation catalytic converter or diesel oxidation catalyst have so far been the most potential options to control particulate emissions from diesel driven vehicles [1].

The basic function of the catalyst in a catalytic converter is to perform the following reactions in the automobile exhaust [1]:

Oxidation of CO and HC to CO_2 and H_2O

$$C_yH_n + (y + n/4)O_2 \rightarrow yCO_2 + (n/2)H_2O$$
$$CO + 1/2O_2 \rightarrow CO_2$$
$$CO + H_2O \rightarrow CO_2 + H_2$$

Reduction of NO/NO_2 to N_2

$$NO\,(\text{or}\,NO_2) + CO \rightarrow 1/2N_2 + CO_2$$
$$NO\,(\text{or}\,NO_2) + H_2 \rightarrow 1/2N_2 + H_2O$$
$$(y+n/2)\,NO\,(\text{or}\,NO_2) + C_yH_n \rightarrow (y+n/4)\,N_2 + yCO_2 + (n/2)\,H_2O$$

1.2. Catalytic converter

A catalytic converter consists of following main parts and each part is important for its specific function:

- Substrate (catalyst support)
- Alumina washcoat
- Catalyst
- Canning.

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Cordierite honeycomb monolith and corrugated metallic types of catalyst substrates are most commonly used for auto-exhaust catalytic converter. The cordierite substrate has several advantages e.g.:

- Thermal shock fracture resistance through an inherently low thermal expansion coefficient and high thermal stability
- Suitable porosity and pore size distribution for washcoat application
- Sufficient mechanical strength for their use in automotive catalytic converter
- Lighter weight and high geometric surface area
- Low back pressure
- Low cost.

While the metallic substrates are being used because of certain specific advantages such as

- Low pressure drop due to thinner cell wall
- Better thermal conductivity and
- Better mechanical strength [1,2].

The choice of the support is generally based on the application. Although, ceramic supports are most commonly used but metallic substrates are popular for two wheeler applications, mainly due to the pressure drop advantages. The ceramic substrates having channel density of 400 cpsi with wall thickness of approx. 0.15 mm was mainly used in the present study. The contribution of substrate porosity towards the overall specific surface area is not significant, while the major contribution comes from the alumina washcoat. The substrate porosity, however, is important for applying alumina washcoat as well as its adhesion. The standard method of Brunauer, Emmett and Teller (BET) has been used for measuring specific surface area. The sample of ceramic substrate was degassed at temperature of 300 °C for about 1 h to remove the adsorbed gases. The BET surface area of ceramic substrate was observed in the range of 0.6–1.0 m^2/g. As there is no porosity in case of metallic substrate, specific surface area determination is not carried out. Porosity of ceramic substrate walls helps adherence of alumina washcoat layer, therefore, optimum porosity of support is vital for washcoat and catalyst application. Porosity of the ceramic substrate was determined using mercury porosity meter. The porosity was observed in the range of 30–42%. The difference in bulk density and actual density determines the porosity. The particle size of alumina and pore diameters of the substrates have to be in appropriate proportion for the effective intrusion of alumina slurry into the pores of ceramic substrate walls.

Bulk properties of ceramic substrates, viz. thermal expansion coefficient, heat capacity, thermal conductivity, melting point, bulk density etc are important for auto-exhaust application, however, these are already optimized by the substrate manufacturers. Table 1 depicts the various physical properties of ceramic substrates (some of the data are provided by the substrate manufacturers).

Table 1
Physical properties (approximate values) of ceramic substrate

1.	Substrate material	Cordierite
2.	Channel density	400 cpsi
3.	Wall thickness	0.15 mm
4.	Geometric surface area	3.7 m^2/L
5.	Porosity	39%
6.	Bulk density	1.480 g/mL
7.	Coefficient of thermal expansion	$8–12 \times 10^{-7}/°C$
8.	Pore size	4–15 microns
9.	Open frontal area	76%
10.	Thermal conductivity	0.1–0.8 W/m K
11.	Heat capacity	1.05 kJ/g K

2. Alumina washcoat

This is one of the important components of a catalytic converter and is responsible for achieving high specific surface area, which is the critical requirement for auto-exhaust catalysis, considering the very high space velocity encountered. Though ceramic substrate provides good geometrical surface area, its specific surface area is very low and is insufficient for auto-exhaust catalysis. A layer of high surface-area oxide is generally applied over the ceramic substrate to increase their specific surface area. Alumina, silica, zirconia are some of the oxides used for this purpose, most suitable and commonly used material being high specific surface area γ-alumina. In the present work, a process for alumina washcoating on ceramic substrate has been developed [3–5]. The first step in this process is preparation of alumina slurry with desired properties. This was achieved by systematic optimization of parameters for the preparation of alumina slurry. The further details of preparation and optimization of alumina slurry are given here.

2.1. Optimization of alumina slurry

Commercially available aluminas (Versal 900 and Versal-GH from La-Roche, USA) were used for washcoating. Alumina slurry was prepared by hydrothermal treatment at 60–110 °C using autogenous pressure, under the acidic condition, and with continuous stirring for 2–4 h. Dilute nitric acid was used to adjust the initial pH of slurry at around 5. Alumina undergoes peptization and also some amount of aluminium nitrate may be formed in the process, which imparts the thixotropic rheology to alumina slurry. The viscosity of alumina slurry is controlled by varying the % solids, particle size, acid content and reaction time. The most typical slurry prepared is having 15% solid content, initial pH of 5 and process time of 3 h at 90 °C. Alternatively, the alumina slurry was also prepared by treating the acidified alumina suspension in a high speed blender/attriter. Alumina slurry is required to be characterized for its % solids, density, viscosity with respect to time, particle size analysis and proximate analysis for alumina, residual acid and other properties [5].

Particle size analysis carried out using laser particle size analyzer-Fritsch Analysett 22, reveals that the mean particle size i.e. value of d_{50} is about 6 μm and d_{10} is about 2 μm. This particle size distribution is not very appropriate for intrusion of alumina slurry into the micropores of ceramic substrate walls. A mechanical grinding treatment was given to alumina slurry in a high-speed blender for particle size reduction [3]. Different methods have been employed for alumina slurry preparation such as variation in dispersibility of alumina and extent of mechanical treatment. Alumina slurry resulted from each method has been characterized for physicochemical analysis. Alumina slurry exhibited thixotropic behavior, while viscosity was observed to be changed with time and shear applied. This behaviour is believed to be depending on the % solids, residual acid content, aluminium nitrate content and extent of thermo-mechanical treatment. Viscosity of different time intervals was observed for different alumina slurries prepared under the different conditions.

2.2. *Alumina washcoating of substrate*

Alumina washcoating of ceramic substrate was carried out following the dip coating technique. The ceramic substrate was dipped into alumina slurry and the excess alumina slurry was removed from channels by applying compressed air. Substrate was initially dried by applying the hot air thorough a blower or alternatively by keeping the substrate in oven at 105 °C, followed by heating at 500 °C for anchoring of alumina particles on ceramic substrate and consolidation of alumina washcoat layer. This cycle was repeated to achieve the desired level of alumina incorporation [5]. Alumina-washcoated substrate was then characterized for the BET surface area. Different samples were prepared with various weight percent loading of the substrate weight. The substrate samples were of same size and were cut from the same monolith substrate. Figure 1 shows the behavior of BET surface area with respect to % alumina loading. The alumina loading is maintained at 15–25 wt.% of the support weight and the BET-SA observed for washcoated ceramic support was in the range 25–35 m^2/g.

2.3. *Thermal stability of alumina washcoat*

Alumina washcoat needs to be characterized for its thermal stability as it is subjected to severe environment of automobile exhaust. Various oxide materials have been reported to improve the thermal stability of alumina washcoat. Such washcoat offers a better anchoring for the catalytic material and also possess high surface area. The thermal stability after the catalyst coating also needs to be evaluated. Various oxides such as La_2O_3, Ce_2O_3, BaO and ZrO_2 have been studied as stabilizers, mainly to improve its thermal stability and also to improve its oxygen storage capacity (in case of Ce_2O_3). The percentage of this stabilizer was varied as 5, 10 and 15% of the weight of alumina. Addition of lanthanum oxide and barium oxide has shown considerable improvement in thermal stability of alumina washcoat.

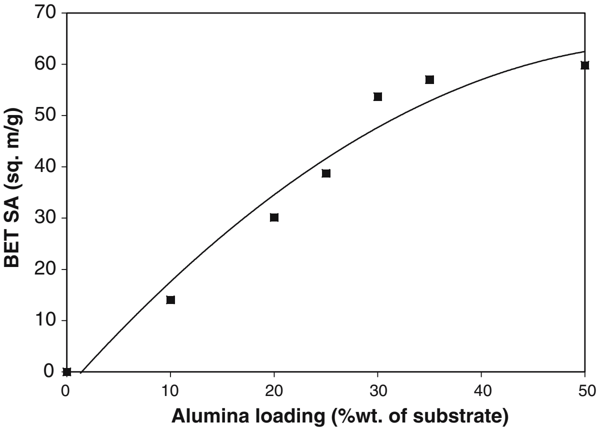

Figure 1. Effect of alumina loading on BET SA [5].

Inner thermal cycling (ITC) tests have been carried out on small, cylindrical, alumina-washcoated cordierite supports to evaluate their thermal stability and adhesion. A laboratory test assembly was used to generate alternating flow of hot air of 850 and 600 °C at every 1-min interval. The test sample was subjected for 400 such cycles and then characterized for the washcoat loss and BET- surface area. No significant loss of alumina was observed after the test, while the BET-surface area was found to be reduced by up to maximum of 15% in some of the experiments. This sample was also investigated under the electron microscope and shows slight deterioration of alumina layer near the support inlet but this effect was found to be confined in a very small inlet zone only. After initial loss of surface area, the washcoated supports were found to be stable under the prolonged exposure to high temperature.

2.4. *Surface morphology*

The topography of the surface of ceramic substrate without and with alumina washcoating was observed by scanning electron microscope – model JEOL-840A. The washcoated supports have been investigated for their micro-structural analysis using scanning electron microscopy. Formation of a thin uniform layer of alumina firmly adhering to the wall of ceramic substrate was confirmed by SEM investigations. Finally, a layer containing suitable oxides, mainly lanthanum oxide was developed *in situ* by soaking precursor solution on alumina-washcoated supports, and subsequent heating under the controlled atmosphere, following a predetermined heating cycle. This precoated alumina was used for the synthesis of supported perovskite catalysts as the normal alumina washcoat is found to be quite reactive towards perovskite precursors leading to the formation of undesired phases.

3. Catalyst

The catalyst is sometimes referred as the heart of catalytic converter, as it is actually responsible for treating the obnoxious gases. Although noble metal-based catalysts have clearly dominated the area of auto-exhaust catalysis, mainly because of their high activity and thermal stability, their limited availability and high cost has always been a reason for the search of alternative catalysts. Their limited tailoring capability is also one aspect, which prompted for more investigations on mixed oxides, zeolites and perovskite-based catalysts. In the present work, various perovskite-type catalysts have been developed both in un-supported and supported forms and evaluated for their catalytic activity towards auto-exhaust emission control.

3.1. Perovskites

Perovskites are mainly attractive due to their lower cost for commercial reasons, but more importantly because of their thermal stability as well as great flexibility in their composition and structure, offering tremendous tailoring capability for the development of future auto-exhaust catalysts for lean burn and selective de-NOx applications. These catalysts also show potential for the direct decomposition of nitrogen oxides, a very important reaction of immense practical importance for the catalytic control of emissions from both mobile and stationary sources. Perovskite-type materials have been specially investigated in details for their possible applications in heterogeneous catalysis [6–10]. These are one of the most fascinating groups of catalytic materials having densely packed cubic lattice of the formula ABO_3. ‘A’ ion can be rare earth, alkaline earth, alkali and other large ions such as Pb^{2+}, Bi^{3+} that fits in to the dodecahedral site of the framework. The ‘B’ ion can be 3d, 4d and 5d transition metal ions, which occupy the octahedral sites. They crystallize in the ABO_3 form only when specific conditions of physico-chemical and crystallographic parameters of the A and B metal ions are fulfilled. Large classes of perovskite-like materials are comprised of layers such as alkaline earth oxides. Perovskite compounds can also tolerate significant partial substitution and non-stoichiometry, while still maintaining the perovskite structure. Metal ions having different valence can replace both A and B ions. This may generate a non-integral number of oxygen atoms. Because of their varied structure and composition, perovskites have been considered as prototype material for fundamental areas of solid-state chemistry, physics and catalysis. Due to their diverse applications, the optimum preparation of these materials has proved challenging, requiring many synthetic approaches, determined by the ultimate end use [10]. Although, perovskites have been frequently reported for studies of their catalytic properties, these materials could not find significant practical applications in environmental catalysis including auto-exhaust emission control. In seventies, cobaltate and manganate type of perovskites were reported as potential substitutes for noble metal based auto-exhaust catalysts. However, their low surface area, comparatively low catalytic activity and sulfur poisoning later dampened the initial enthusiasm for their applications in automotive exhaust catalysis [11]. Some sulfur-tolerant perovskite compositions have also been later reported. However, their surface area and inferior catalytic properties remain major limitations for their practical feasibility, particularly in automotive exhaust catalysis. These catalysts are also not suitable for their dispersion on alumina washcoat, applied for the surface area enhancement of commonly used ceramic and metallic catalyst supports. Larger particle size of perovskites and their reactivity with alumina are the major limitations in this regard.

Recent studies on perovskites confirm the renewed interest in these versatile materials [12–16]. Nishihata *et al.* have demonstrated excellent dispersion of noble metal in perovskites and their practical applications in auto-exhaust emission control. Efforts have also been made to improve the surface area of perovskites, particularly by exploiting suitable preparative techniques, and also by using suitable anions in perovskite precursors [17–19]. Although this specialized synthesis often leads to several fold increase in the surface area of perovskites, this is certainly not sufficient to meet the requirements of auto-exhaust catalysis. This has prompted for efforts towards using alumina washcoat as a surface area enhancement tool even for perovskites. However, large particle size of perovskite was often found unsuitable to get the surface area advantages from commonly used alumina, which is more suitable for dispersion of atomic size moieties. Several perovskite compositions and their precursors (in case of *in situ* synthesis) are found to be reactive toward alumina at higher temperature, leading to the formation of undesired phases like mulite and metal aluminates. Some of the reported works, however, mention about the synthesis of perovskites on alumina and other supports. But, it was almost always found difficult to properly characterize the presence and location of perovskite compounds on various supports [20–23]. In this way, the renewed interest in these non-conventional catalytic materials can be justified due to following reasons:

- Good flexibility in their chemical compositions with still the freedom to influence the properties of active 'B' ion
- High thermal stability which makes them suitable even for closed-couple applications
- Great degree of possible tailoring in their physical and chemical properties for future requirements e.g. lean-burn catalyst
- Poison resistant nature.

In the present work, attempts have been made to design suitable perovskite compositions for their improved catalytic properties and to synthesize them in the supported form to improve their surface area and make them suitable for auto-exhaust applications.

3.2. Synthesis of supported perovskites

A range of perovskite-type catalytic materials with different compositions have been synthesized. The following optimized composition: $La_{(1-x)}Sr_{(x)}Mn_{(1-y)}Pt_{(y)}O_3$ has also been synthesized in both un-supported and supported forms following the three different methods:

- Co-precipitation
- *In situ* synthesis on alumina, pre-coated with lanthanum oxide and
- Synthesis on lanthana pre-coated alumina using "deposition-precipitation" technique [24].

In co-precipitation method, mixed metal hydroxides were co-precipitated using aqueous ammonia. The precipitate was washed, oven-dried and platinum was then added in the co-precipitated mass. The dried precipitate was subsequently heated at about 850 °C to obtain the perovskite phase, following the reported procedures [3,17]. This sample is designated as LMO–Coppt. Another sample was prepared *in situ* on alumina pre-coated with lanthana. About 15–20wt% lanthana was incorporated on commercial γ-?alumina (La-Roche, USA), using wet impregnation technique. Alumina powder was suspended in an aqueous solution of lanthanum acetate, filtered, oven-dried and heated in air at 600 °Cfor 4 h. This cycle was repeated to achieve the desired loading. Finally the material was heated in air at 900 °C for 12 h. This sample is designated as "La-alumina". An *in situ* sample of alumina supported $La_{(1-x)}Sr_{(x)}Mn_{(1-y)}Pt_{(y)}O_3$ was prepared by wet impregnation of La-alumina with precursor mixed metal ion solution, and subsequent heating at 900 °C for 10 h. The procedure was repeated to obtain 10 wt.% catalyst loading. This sample was designated as "LMO-*in situ*". The third sample was prepared following the deposition–precipitation method (precipitation from homogeneous solution) as described by Cimino *et al*. [14]. The sample was designated as LMO–DP. These later two samples are supported perovskites, while first sample (co-precipitated) is used mainly for comparison [24]. The *in situ* synthesis of the catalyst provides best dispersion on alumina washcoat. The only problem in this method is that the perovskite precursors react with alumina to form undesired phases. However, deposition-precipitation method offers high dispersion with better purity of perovskite material on substrate.

3.3. Characterization of catalysts

The catalysts have been characterized by X-ray powder diffraction analysis for perovskite phase formation as well as to study the formation of other phases especially in case of supported perovskites. Specific surface area was measured following the standard BET N-adsorption method, using BELSORB-ASAP-200 instrument.

We have observed that alumina pre-calcined at higher temperature (about 900 °C) is relatively better for perovskite applications, with respect to its suppressed reactivity and pore characteristics [3]. As evident from many previous attempts and also considering its obvious reactivity, the preparation of perovskites directly on alumina has almost always lead to the formation of many undesired phases, making it difficult to get the targeted perovskite phase. A pre-coat of suitable material is therefore, almost essential for preparing the perovskite directly on alumina. Pre-coat material, pre-coat loading and pre-coating technique can be regarded as the most important parameters in this regard. Although pre-coat material should be selected

Table 2
X-ray diffraction analysis results [24]

Sr. No.	Sample	$La_2 O_3$	$LaAlO_3$	$LaMnO_3$	MnO_2	Other Phases
1.	γ-Alumina	NO	NO	NO	NO	YES
2.	La-Alumina	YES	YES	NO	NO	YES
3.	LMO Co-ppt	NO	NO	YES	NO	NO
4.	LMO-*in situ*	NO	YES	YES*	NO	YES
5.	LMO–DP	YES	YES	YES	NO	YES

*Relatively lower intensity peaks.

Table 3
BET surface area results [24]

Sr. No.	Sample	BET surface area (m^2/g)
1.	γ-Alumina	273
2.	Post-heated Alumina	62
3.	La-Alumina	97
4.	LMO–Coppt	3.7
5.	LMO-*in situ*	61
6.	LMO–DP	54

considering the composition of perovskite to be supported, lanthanum and cerium oxides were found suitable for many of our previous preparations. The lanthana-based pre-coat of the present study has been found the most adequate to synthesize lanthanum manganate and similar perovskites.

The BET-SA results (table 3) show decrease in the surface area of alumina after the pre-coat, however, this is still higher than the bare alumina heated at the same temperature. The process of pre-coating also plays important role, and we observed that repeated cycles of pre-coating is always better than pre-coating of the targeted amount at once. This might also help achieving a relatively complete coat on alumina particles. Although, a reasonably small amount of pre-coating materials should be theoretically sufficient to form single coat on alumina particles, however, it is better to incorporate a much larger amount of pre-coat to ensure a better coating on alumina particles, even with some tradeoff in surface area. Lombardo *et al.* have explained this by considering a reaction at preferential sites on the so-called potential nucleation centres [25]. The pre-coating does not have any adverse impact on washcoat adhesion as observed by washcoat adhesion tests, in our previous studies [3,14].

Although supporting pre-synthesized perovskites on cordierite or alumina support ensures presence of properly characterized catalyst phase, large sintered particles of perovskites almost always result in loss of surface area, achieved through high surface area materials like γ-alumina. Their adhesion on cordierite honeycombs were also often found inadequate for the severe conditions encountered in auto-exhaust catalysis. XRD analysis of co-precipitated $LaMnO_3$ (LMO–Coppt) confirms synthesis of highly crystalline, single-phase perovskite, with a low surface area value of 3.7 m^2/g (table 3). Further improvements in the surface area can be achieved using the various reported methods of perovskite synthesis, however, most of these methods either do not result in the desired improvement in the surface area or suffer practical feasibility, with regard to the synthesis conditions or reactants. We have been using the *in situ* route for perovskite synthesis on pre-coated aluminas. The method has been successfully used to prepare full-scale prototypes of catalytic converters, while the same method is also convenient for large scale production. The XRD analysis (table 2) of LMO-*in situ* sample shows presence of targeted $LaMnO_3$ perovskite as the main phase, but a small amount of other phases were also present. This could be due to the reactions of perovskite precursors with any un-coated or improperly coated alumina particles. Lower synthesis temperature was found to minimize the formation of such phases. Temperature beyond 1000 °C is seldom encountered in auto-exhaust catalytic converters, and the perovskite reactivity with pre-coated alumina is unlikely to pose problem under this temperature. However, formation of other phases and thermal deterioration of perovskites cannot be ruled out for high temperature applications like combustion reactions. The BET-surface area of this material (61 m^2/g) is much higher than unsupported perovskites prepared by any of the synthesis methods or pre-synthesized perovskites supported on high surface area supports [3,24].

The preparation of perovskite catalysts using this method is found to be dependent on several factors. Precursor metals, suitable salts of precursors, and synthesis temperature are some of the most important factors. Reactivity of alumina and even pre-coated alumina also depends on the precursor metal ion. Cobalt ions are reported to penetrate alumina at relatively lower temperature due to its larger concentration driving force [5] Formation of manganate type perovskites is therefore, associated with relatively less amount of undesired phases. Although difficult to characterize, such supported perovskites have been found to show excellent catalytic performance with the required adhesion on cordierite honeycombs [3,26].

The third supported catalyst sample prepared by "DP" method (sample LMO–DP) shows XRD pattern containing perovskite peaks with better intensity than the *in situ* sample. XRD peaks corresponding to other compounds, including La_2O_3 and $LaAlO_3$, were also present, though their intensity was relatively much lower. This indicates that the DP method presents rather better conditions for perovskite formation. Precursor metals in hydroxide form may be less reactive towards alumina, thereby minimizing the formation of alumina based other phases. The BET-surface area (table 3) shows a value of 54 m^2/g, which is slightly lower than the LMO *in situ* sample. However, once again, this value is several folds higher than the un-supported perovskites [3,24,27].

3.4. Laboratory evaluation of the catalytic activity

The catalytic evaluations of three different samples of $LaMnO_3$ perovskites have been investigated for their catalytic activity towards CO and HC oxidation and NO reduction under the stoichiometric conditions, considering their potential applications in conventional 3-way catalytic converters. These laboratory evaluation data are presented in figures 2–4. There is a marked

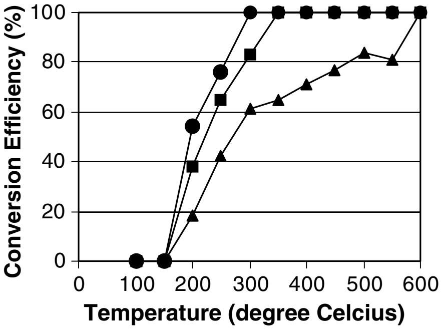

Figure 2. Laboratory evaluation results for CO oxidation. ▲ Catalyst LMO–Coppt, ● Catalyst LMO-*in situ*, ■ Catalyst LMO–DP.

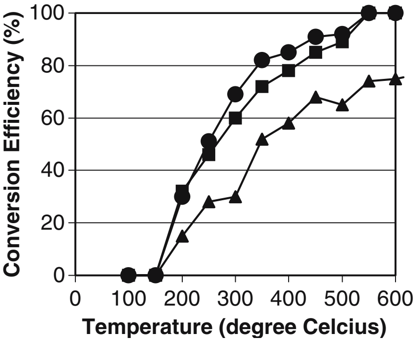

Figure 4. Laboratory evaluation results for NO reduction. ▲ Catalyst LMO–Coppt, ● Catalyst LMO-*in situ*, ■ Catalyst LMO–DP.

improvement in the CO oxidation activity of both *in situ* and DP samples as compared to the co-ppt. sample. As the later catalyst shows presence of rather well crystalline perovskite phase, the improved catalytic activity can be attributed to the improved surface area of the other two supported catalysts. A similar trend has been observed for NO reduction activity, where co-ppt. catalyst could not achieve100% conversion even at higher temperature. The activity of the *in situ* catalyst was slightly better than DP catalyst in both these cases, though the difference is not very significant to be interpreted for. All the three catalysts show relatively inferior catalytic activity for HC oxidation as compared to the CO oxidation. About 100% conversion was observed only beyond 400 °C for both DP and *in situ* catalysts. This is considerably inferior to the noble metal catalysts. However, our studies on Sr substituted and Pt promoted lanthanum–manganate-type perovskites show higher activity for both CO and HC oxidation and 100% conversion was observed around 320 °C. The HC oxidation activity of DP catalyst is slightly better than the *in situ* catalyst. The almost similar trends observed for the catalytic activity of these three catalysts also support the fact that the catalytic material of all the samples is same and the difference in activities should be due to the difference in the surface area. These results infer that the catalytic performance of perovskite type materials can be remarkably improved by supporting them on suitable high surface area supports.

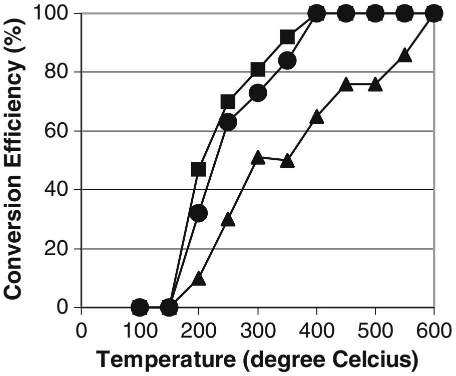

Figure 3. Laboratory evaluation results for HC oxidation. ▲ Catalyst LMO–Coppt, ● Catalyst LMO-*in situ*, ■ Catalyst LMO–DP.

3.5. *Mass emission tests*

Most of the earlier experiments carried out on perovskite type catalysts, report laboratory evaluations using pure gases. These catalysts were often found unsuitable for the engine and chassis dynamometer tests on actual converter prototypes. Obviously, their applications in actual vehicles were seldom attempted, where high space velocity and extremely good catalyst adhesion are important requirements. However, application of such catalysts on modified alumina-washcoated catalyst supports can rejuvenate the possibility of their applications in automobile pollution control. Auto-exhaust control devices need to be tested for their mass emission conversion efficiencies on chassis dynamometer following the standard test procedure. A test lasting a total of 648 seconds and comprising six Indian driving cycles (IDC) was used. The mass emissions of CO, HC, NO*x* and CO_2 were measured with and without the catalytic converter fitted on the vehicle. Such mass emission tests are representative of performance of vehicle and control system in actual road conditions. The instrumentation for Chassis Dynamometer testing consists of motor exhaust gas analyzer of Horiba make Mexa 9200D, constant volume sampler (CVS) 9100 system, 20'' roller test bed of Zollner, Germany, and drives aid portable analyzer of Horiba CRDS-2000 [3].

A number of mass emission tests have been conducted on various vehicles using full scale prototypes. The test results for a three-way catalytic converter prototype for passenger car is shown in table 4. These mass emission results confirm the high efficiency of converter for all the three pollutants CO, HC and NO*x*. The activity of the converter for NO*x* reduction is especially appreciable and, suggests its potential for practical application in three way catalytic converter.

Table 4
Mass emission test results [3]

Converter details	Substrate volume		1.2L
	Channel density		400 cpsi
	Washcoat		Alumina washcoat with protective overcoat
	Catalyst		$La_{(1-x)}Sr_{(x)}Mn_{(1-y)}Pt_{(y)}O_3$ (promoted by noble metal)
Vehicle	Maruti Gypsy with 1.0 L (approx.) engine swept volume		
Test Procedure	Indian Driving Cycle with standard "Cold-start" test procedure		
Pollutant Component	Emissions in grams per kilometer		Conversion efficiency (%)
	Without converter	With converter	
CO	11.84	2.12	82.09
HC	2.24	0.28	85.96
NO_x	1.26	0.37	70.63
CO_2	169.94	192.76	–

3.6. Durability tests

Two types of converter durability tests have been carried out on different test prototypes of catalytic converters.

Engine dynamometer ageing test
Catalytic converter was also tested on engine dynamometer for its durability and poison resistance. The engine dynamometer was run at different rpm and load for about 50 h. The test run was not continuous due to the technical limitations of dynamometer, however, severe conditions were created on dynamometer to test the durability of converter. Subsequently converter was tested for its conversion efficiencies. Less than 10% deterioration was observed when these data are compared with the engine dynamometer data of fresh catalyst. The converter was also subjected to the so-called post-martem analysis after the ageing test [28, 29].

Field trials
The converter was subjected to the actual field trial to test its performance, mechanical durability, thermal durability and lead tolerance. Actual field trial although costly, time consuming and cumbersome, but is the most reliable durability test particularly for several less developed countries where fuel quality, road quality and vehicle maintenance are not of the desired standards. Vehicle specific converter prototype was fitted on a test vehicle and was run for more than 28,000 kms under the control and supervision, following the normal vehicle use and maintenance practices.

The vehicle was regularly monitored for its idling emissions and physical condition of converter during the field trial. Mass emission tests were carried out after 12,000 and 28,000 kms of field run. These durability test results confirm the high conversion efficiencies of the converter even after using it for such a long duration on a vehicle running on commercial grade petrol. The successful field trial also confirm about the excellent mechanical durability, thermal durability and prolonged performance of the converter under the normal maintenance of vehicles.

4. Conclusion

A comprehensive approach can be adopted to overcome the perovskite's limitations related to their

- Surface area
- Reactivity of precursors with alumina and other support materials, and
- Low temperature catalytic activity.

Our detailed investigations on supported perovskites have validated that the following approach can substantially improve the performance of perovskite based catalytic converters:

- Use of modified alumina with suitable precoat to make it inert towards perovskite precursors
- Synthesis of perovskites directly on alumina-washcoated support using modified alumina
- Use of metallic supports to improve their light-off characteristics
- Use of substituted perovskite compositions, specially promoted by a small amount of noble metals.

This study was aimed to investigate the effect of various methods for supporting perovskites on commonly used γ-alumina. However, further detailed investigations are warranted to properly characterize the presence of perovskite phase on alumina and to understand the support-precoat-catalyst interactions. The supported perovskites can be prepared directly on a high surface area alumina support. However, it is necessary to apply a suitable precoat on alumina prior to perovskite synthesis. The properties of precoat largely depend on the precoat material, amount of precoat loading and precoating technique. Perovskite type catalytic materials can be directly prepared on such precoated alumina supports, using either *in situ* or "deposition-precipitation" techniques. A small amount of phases other than the desired perovskite may also be formed. The main factors effecting the formation of supported perovskites with minimum secondary phases are:

- Nature of precursor metal ions and their salts (for *in situ* method)
- Synthesis temperature and atmosphere
- Repeated deposition of perovskite material on support
- Synthesis technique.

The supported perovskites show remarkably improved catalytic activity and adhesion on alumina-washcoated cordierite supports. Their thermal stability should also not be a matter of concern for auto-exhaust applications. These supported perovskites can rejuvenate the possibility of their practical applications as low-cost conventional 3-way catalytic converters, and oxidative type catalytic converters for two-stroke vehicles. Their high thermal stability could be especially useful for closed coupled applications, and a more judicious use of noble metals can be practiced in view of their limited abundance. These techniques to prepare supported perovskites can be easily extended for the preparation of other perovskite phases to improve their surface area and catalytic activity.

5. Future perspectives

The development of perovskites with new compositions and their synthesis in the supported forms has resulted in their improved catalytic properties. These perovskites are being further investigated for their possible applications as soot oxidation catalysts for regeneration of diesel particulate filter to control the diesel exhaust emissions. “A” site substituted perovskites with desorption of α-oxygen at lower temperature also appears to show potential catalytic properties for soot oxidation reaction. It is interesting to mention here that substituted perovskites are also being recognized as potential catalysts for selective catalytic reduction (SCR) of NOx and active research is underway at NEERI to develop the perovskite based SCR and NO/N_2O decomposition catalysts, under the CSIR network project. A few thermally stable perovskites have also been successfully developed including those ruthenium-based perovskites. These catalytic materials are being investigated for their activity towards methane combustion for cleaner energy production.

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