Application of catalytic materials for diesel exhaust emission control

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Perovskite type non-noble metal-based catalytic materials have been developed for their possible applications in diesel exhaust emission control. These materials have been evaluated for their applications in regeneration of diesel particulate filter (DPF) and also as diesel catalytic converter (DCC). Both the applications require low temperature oxidation catalysis properties. Temperature-programmed desorption studies revealed the low-temperature oxygen desorption of perovskite catalyst, which may be useful for the oxidation of carbon/soot at lower temperature. Laboratory evaluation results on activated carbon show the carbon oxidation activity of the catalyst in a temperature range of 300–450°C. However, this was achieved under the tight contact of carbon and catalyst. Catalyst coated-ceramic foams have been used to fabricate laboratory prototype of regenerative type DPF. Although its evaluation on a vehicle shows significant reduction in smoke density, however, the regeneration temperature was still higher than desired. The DCC shows 10–25% reduction in smoke density depending on engine conditions. The perovskite-type catalyst appears to follow a redox mechanism for soot oxidation through oxygen removal and replenishment, while hydrocarbons adsorbed on soot particles may also help in oxidation of the carbonaceous part.

Diesel exhaust emissions have been increasing alarmingly specially in urban settlements. The most potential after-exhaust treatment options so far to control diesel exhaust emissions are diesel particulate filter (DPF) and diesel catalytic converter (DCC). Catalytic materials have two important roles to play in diesel exhaust emission control. The first is related to the catalytic regeneration of particulate laden DPF at a lower temperature and possibly at the exhaust temperature, to make it ‘continuously regenerative type’ DPF. Efficient regeneration of DPF is probably the only important limitation of this otherwise effective particulate control option. Development and detailed investigations on a large number of catalytic materials for DPF regeneration have been well documented during the last decade⁹. Progress has been substantial to achieve lower soot oxidation temperature; however, most of the results are reported under laboratory conditions, often using tight soot-catalyst contact.

Another important application of catalytic materials is directly oxidizing the soluble organic fraction (SOF) of the diesel exhaust emissions. In-cylinder diesel particulate matter (PM) control has greatly reduced the PM emission levels in modern engines. Progress has been especially effective in reducing the soot portion of PM emissions, so the SOF of particulate matter now accounts for a much larger share. Oxidation catalysts of a diesel catalytic converter can oxidize a large portion of the hydrocarbons present in the soluble organic fraction of PM emissions, as well as gaseous hydrocarbons, carbon monoxide and odour. Unlike a catalytic trap, the oxidizing catalytic converter does not collect solid particulate matter, which passes through the exhaust. This eliminates the need for a regeneration system. These catalysts obviously have a negligible effect on fuel consumption due to low back pressure of the device¹¹. Chemical stability of catalysts could be a challenging task, especially in view of higher sulphur content of diesel¹²–¹⁴. However, it is likely to be acceptable, especially with the continuous reduction of diesel sulphur content.

As explained, catalysts can be used either as soot oxidation catalysts for regeneration of DPF or directly as oxidation catalysts to mainly control the SOF portion of diesel emissions. Perovskite-type oxides are good oxidation catalysts and show potential as effective soot oxidation catalysts for DPF regeneration as well as for the oxidation of SOF. Perovskites are binary oxides with general formula ABO₃. Availability of a large number of cations, which can fit at both A and B positions, offer the perovskite structure a versatile flexibility in its chemical composition. Their structure and properties can also be modified due to the great extent of substitution possible at both A and B sites. The oxygen absorption and desorption properties of perovskites can play a crucial role for the low-temperature oxidation of soot/particulate. A number of perovskite type and other mixed oxide-based catalytic materials have been reported for their activity towards diesel soot emission control¹⁵–⁰. Development of perovskite-type catalytic materials with low-temperature oxidation properties and their laboratory evaluations in powder form as well as evaluation of DPF and DCC prototypes for soot and SOF oxidation, have been attempted in the present study, in view of the possible applications in diesel exhaust emission control.

A few catalyst compositions have been designed and characterized. These catalysts were first evaluated in the laboratory for their oxidation properties and also for carbon oxidation activity. The following basic perovskite composition has been used for the present studies:

Lₐ(A₁₋ₐ)₂₋ₓMnO₃,

where cation A represents lower valence substitution at the ‘A’ site of perovskite structure. The catalyst was prepared following co-precipitation and impregnation methods with
a heat treatment in oxidative atmosphere at 800°C for 8 h to get a crystalline perovskite phase (patent filed). Catalyst-coated honeycomb and ceramic foams were prepared following the in situ method described elsewhere. Synthetic catalyst sample was characterized by X-ray diffraction for perovskite phase, and BET surface area, following the standard N-adsorption method using Micromeritics ASAP-2000 instrument. Temperature Programmed Desorption (TPD) of oxygen was investigated using BEL–TPD instrument, equipped with both Thermal Conductivity Detector (TCD) and Quadruple Mass Spectrometer (Q-Mass). The sample was pre-treated by heating at 800°C in helium flow, followed by evacuation and oxygen exposure with decreasing temperature. Desorption was carried out by controlled heating with estimation of oxygen release up to 900°C. The soot oxidation activity was evaluated following a temperature-programmed reaction procedure. Activated carbon was used as a substitute for soot. The catalyst powder and activated carbon (ca. 5 wt%) were well mixed by grinding for 10 min in an agate mortar. Although this mixing procedure gives tight contact conditions, better reproducibility can be achieved for catalyst screening. The carbon–catalyst mixture was palletized, crushed and sieved to 20–100 mesh. The mixture was packed in a fixed-bed flow reactor with a programmable heater controller. A gas mixture containing 15% oxygen was flown with the increasing temperature. The outlet gas was analysed for CO₂ and CO by a TCD-based gas chromatograph.

The DPF and DCC prototypes were also prepared. The DCC was prepared using 200 cpsi cordierite honeycomb support. The catalyst was applied using two different methods. The pre-synthesized catalyst was powdered using a planetary ball mill, and catalyst slurry was prepared by optimizing the solid content. Alternatively, catalyst was also prepared using in situ technique directly on alumina wash-coated and lanthana pre-coated honeycomb ceramic support. Details of the methods are described elsewhere. The DPF prototypes were prepared using the ceramic foams and an aggregation chamber. DPF and DCC prototypes were evaluated on commercial diesel vehicles using both free-acceleration test and also on engine dynamometer at various rpm–load conditions. In free-acceleration test, the acceleration pedal at idle condition is pushed rapidly and completely for full throttle condition. The engine is kept at high idle for about 1 s before releasing the acceleration pedal. Due to the moment of inertia of rotating masses of the engine and coupled drive line, a smoke burst at maximum injected fuel is produced. The instantaneous values of opacity are measured and peak opacity is recorded. Engine dynamometer set-up is a unit used for performance evaluation of auto-exhaust emission control device as well as various engine-related performances. It is used to generate different speed–torque engine operating conditions for performance evaluation. The dynamometer unit comprises an eddy current dynamometer and a flexible mounting bed for the engine. An Ambassador-make diesel-driven engine of 1500 cc capacity was used for evaluation of DPF and DCC. Various rpm–load conditions were generated using a computerized dynamometer control system and smoke density measurements were done using a Hartridge MK-III smokemeter.

The TPD analysis of catalyst (Figure 1) infers significant desorption of oxygen between 220 and 400°C. Another small desorption peak was observed at temperature above 800°C. The low-temperature desorption is generally related to surface-adsorbed oxygen and also from oxygen vacancies of perovskites, created by cation substitution. This low-temperature oxygen desorption indicates the large redox capacity of the catalyst, while confirming the easy availability of oxygen at lower temperature. This could be useful for the oxidation of particulate as well as SOF under the low temperature of diesel exhaust. Another oxygen desorption at higher temperature is due to the reduction of B-site cation, and this kind of beta-oxygen desorption is quite typical for perovskite-type materials.

The laboratory results on carbon oxidation activity of perovskite-type catalyst are presented in Figure 2. The catalyst appears to get activated immediately after 200°C.
However, significant oxidation of the carbon material is observed beyond 300°C. The peak oxidation temperature corresponding to maximum activity is around 425°C. The exothermic carbon oxidation reaction is expected to propagate the reaction rate after it achieves significant activity. This activity could be considered as reasonably good, in view of the very low surface area of the catalyst used. There was practically no CO generation, which is sometimes present as a product of incomplete combustion. The sudden drop in CO₂ generation is because of the consumption of carbon material in the reaction mixture. Therefore, this does not indicate the lowering of activity and rather confirms the complete oxidation of carbon. The catalyst shows unaffected structure up to about 1000°C even after prolonged exposure. Such a thermal stability is certainly sufficient, even considering the failure-mode scenarios like soot oxidation after excessive accumulation, generation of high localized temperature due to delayed soot oxidation, etc.

The DCC prototypes were tested on a mini truck following both free acceleration and full-load tests on an engine dynamometer test rig. The DCC did not show significant smoke reduction activity under the free acceleration tests, probably due to relatively lower exhaust temperature during these test procedures. Diesel engines are inherently cleaner than petrol engines and the exhaust temperature is relatively much lower, which is generally not sufficient for the catalyst to become active. The full-load trials on the engine dynamometer however, show the effectiveness of the catalyst. The results are presented in Table 1. The maximum smoke reduction achieved was about 25% at relatively lower rpm conditions. The smoke reduction efficacy of DCC depends on several factors including SOF content of diesel emissions. In this way, DCC shows only a moderate activity towards smoke emission reduction.

The catalyst-incorporated DPF was also evaluated following both free acceleration and full-load test procedures. Soot particles get deposited on the ceramic foam both on the surface and inner voids. Although the void structure of the ceramic foam requires a long time to get clogged compared to ceramic honeycomb, it still requires regeneration. Two different methods have been followed for regeneration of DPF, viz. heating at high temperature and catalyst-assisted oxidation of soot. In case of thermal regeneration, the ceramic foam was withdrawn from the DPF and heated at 650°C for 1 h. This results in the cleaning of the ceramic foam, which is again installed in the DPF. Catalyst-assisted regeneration was achieved by heating the DPF to the light-off temperature either by exhaust gas or external heating, while perovskite-type catalyst was used for catalytic combustion of soot. These regeneration processes required simple heating of the device externally at around 400–500°C. This low heating temperature helps in combustion of the soot with the help of an oxidation catalyst coated on the filter material. However, this regeneration temperature is not low enough for auto-regeneration of DPF at the vehicle exhaust temperature. Efforts are underway to further lower the regeneration temperature of catalyst-incorporated DPF to avoid energy-intensive external heating.

A number of catalytic materials have been reported for soot oxidation as well as soot–NOₓ reactions. These can be categorized into noble metals, oxides, and mixed oxides including those of perovskite type. Accordingly, a number of mechanisms have also been proposed for these environmentally important reactions. According to Shangguan et al.¹⁵,¹⁶–¹⁷, gasous oxygen is adsorbed dissociatively on the catalyst surface and the resulting atomic O ads species then attack the reactive free carbon site to give an intermediate like C*=[O]. The reaction between this intermediate and gaseous O₂ results in the formation of CO₂. It is also reported that some of the oxides can oxidize carbon even in the absence of any gaseous oxidizing agent. Thus we can infer about oxygen donor mechanism rather than an electronic mechanism. It was pointed out that carbon adsorbs metal-bound oxygen atoms faster than molecular-bound oxygen.²⁰ Neri et al.²⁰ described the oxygen spillover effect from the noble metal promoter, and requires good contact between the carbon and the catalyst. This effect was also found in many other reported studies²⁵.

Perovskite-type catalytic materials are frequently reported for soot–NOₓ as well as soot–NOₓ–oxygen reactions. It is understood that oxygen ions move through the lattice vacancy in the perovskite-type oxides. Teraoka et al.¹²–¹⁵ reported extensive results on perovskite-type catalytic materials for soot–NOₓ reactions. Hong et al.¹³ confirmed that the oxygen ion conductivity of perovskite structure can play an important role in carbon or soot oxidation. As it is well established that oxygen ions can move through the lattice vacancy in perovskite-type oxides, they can be removed by oxidation of reducing molecules on the surface. This results in increased vacancies of oxygen and consequently absorp-

### Table 1. Test results for full load test of diesel catalytic converter on mini-truck engine

<table>
<thead>
<tr>
<th>RPM</th>
<th>Torque (Nm)</th>
<th>Smoke density (HSU)</th>
<th>Reduction in smoke density with device (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A2000</td>
<td>153.2</td>
<td>44.0</td>
<td>25.0</td>
</tr>
<tr>
<td>B2000</td>
<td>145.0</td>
<td>33.0</td>
<td></td>
</tr>
<tr>
<td>A2200</td>
<td>149.0</td>
<td>24.0</td>
<td>24.0</td>
</tr>
<tr>
<td>B2200</td>
<td>141.0</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>A2400</td>
<td>142.9</td>
<td>16.0</td>
<td>15.6</td>
</tr>
<tr>
<td>B2400</td>
<td>134.0</td>
<td>13.5</td>
<td></td>
</tr>
<tr>
<td>A2800</td>
<td>137.0</td>
<td>12.0</td>
<td>16.7</td>
</tr>
<tr>
<td>B2800</td>
<td>125.0</td>
<td>10.0</td>
<td></td>
</tr>
<tr>
<td>A3200</td>
<td>130.9</td>
<td>19.0</td>
<td>10.5</td>
</tr>
<tr>
<td>B3200</td>
<td>118.2</td>
<td>17.0</td>
<td></td>
</tr>
</tbody>
</table>

A. Without DCC; B. With DCC.
tion of NO on oxygen vacancy sites, where it can react with carbon to form CO$_2$ and N$_2$. This mechanism$^{17,35}$ explains carbon or soot oxidation with NO$_x$.

As the present catalytic material shows activity in the presence of both oxygen and NO$_x$, we assume that the following reported mechanisms can explain soot oxidation:

The ‘A’ site substitution by a lower valence cation in perovskite adds to its redox capacity due to its increased α-oxygen content. This loosely bound oxygen may help oxidizing the carbon/soot particles, although catalyst-carbon contact should play an important role in catalytic activity. The increased oxygen vacancy is also likely to increase the oxygen ion conductivity of perovskite structure, which can have favourable impact on its oxidative catalytic activity$^{32}$. Another possibility for carbon oxidation by oxygen could be dissociative adsorption of oxygen on perovskite surface and its reaction with carbon, as explained by Shangguan$^{31}$ and Hong et al.$^{17,35}$ respectively. Hong et al.$^{17,35}$ have given details of this mechanism in which the dissociatively adsorbed O$_{ad}$ species attack the reactive free carbon to give an oxygen-containing active intermediate, which finally produces CO$_2$. These mechanisms are depicted in Figure 3 a and b.

In the case of soot/carbon oxidation by NO, there could be two reaction mechanisms in the presence and absence of oxygen, as explained by Hong et al. The following mechanism will be more suitable in the presence of oxygen, which is normally the case for diesel vehicle exhaust. According to this reported mechanism, NO gets oxidized to NO$_2$. The resulting NO$_2$ is dissociatively adsorbed on the catalyst surface to form O$_{ad}$ and NO$_{ad}$ species. The carbon particulate is said to be directly oxidized by O$_{ad}$ to give CO$_2$ and also accelerates the reduction of NO to give a reactive carbon–NO complex by reacting with adsorbed NO on catalyst surface$^{17,35}$, which results in the formation of N$_2$ as depicted in Figure 3 c.

Perovskite-type lanthanum manganate-based catalytic materials have been synthesized and studied for their catalytic activity towards diesel exhaust soot oxidation for catalytic DPF regeneration and also for SOF oxidation in DCC. The catalyst shows low-temperature oxidation activity, which may be correlated with its low-temperature oxygen desorption properties. The TPD studies support this explanation of low-temperature catalytic activity. These catalytic materials have been incorporated to ceramic foam-based DPF and honeycomb-based DCC developed in-house. The prototypes of DPF and DCC were evaluated for their efficacy of soot reduction using different test protocols. The catalyst-incorporated DPF shows relatively better lowering of regeneration temperature; however this is still not enough to regenerate the DPF at vehicle exhaust temperature. Substitution by a lower valence cation at the ‘A’ site of the perovskite structure appears to improve its oxidative properties, while the catalytically active ‘B’ site cation also plays an important role in soot oxidation reaction. Although efforts should be continued for improved design of perovskite with better oxidation properties, it may also be useful to increase the temperature at DPF by means of its optimum location and prevention of heat losses through the exhaust system. The long-term durability of catalytic materials also needs to be thoroughly investigated, especially in view of the prevailing high sulphur content of diesel in several countries. Nevertheless, perovskite-type catalytic materials appear to be potential for further investigations in this field.


Figure 3. Schematic representation of carbon/soot oxidation mechanism. a, Carbon/soot oxidation through release of oxygen from catalyst. b, Carbon/soot oxidation through dissociative adsorption of oxygen on catalyst. c, Carbon/soot oxidation through NO$_2$ formed on catalyst surface through NO oxidation (from Fino$^3$).
RESEARCH COMMUNICATIONS


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Prospects for nitrogen incorporation into humic acid as evidenced by alkaline extraction method

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Nitrogen-fixation is an important process in nature, transforming atmospheric N2 into biological forms either via enzymatic pathways by nitrogen fixing microorganisms7 or by chemical methods using the Haber–Bosch process in industry14. However, other pathways contributing to the global nitrogen cycle may exist. We made an attempt to show that the nitrogen content in humic acid extracted under air and pure N2 gas increased compared with extraction under argon gas. 15N abundance in humic acid was increased to 1.7% by 15N gas tracer measurement. Further evidence for the actual bond formation between nitrogen and humic acid was determined by FTIR spectroscopy. In addition, structural analyses using 13C nuclear magnetic resonance with cross polarization, magic angle spinning (CPMAS 13C NMR) and UV absorbance revealed structural changes in aromatic and aliphatic properties of the humic acid structure. Hence we envisage that alkaline humic acid might be undergoing a novel non-enzymatic N2-fixation when extracted with air and N2 through an unknown mechanism that consumes free radicals in the humic acid structure.

HUMIC substances are complex polymers originated from chemical and biological degradation of plant, animal residues and microorganisms and may contain 2–6% of elemental nitrogen6. Humic acid is considered as a high quality growth substance for agricultural purposes7. Approaches towards characterizing N-content in humic substances utilize acid/base hydrolysis to separate nitrogen into acid insoluble-N, NH4-N, amino acid-N, amino sugar-N, and hydrolysable

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