Low Cost Catalysts for Regeneration of Diesel Particulate Filters

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ABSTRACT

A range of perovskites including the substituted and promoted perovskite type catalytic materials have been designed and synthesized using various techniques. In this work we have studied the catalytic activities of a praseodymium substituted La₈₀Pr₂₀MnO₃ and La₉₀K₀₁Pr₀₂MnO₃ based perovskites synthesized by coprecipitation, which is further improved by incorporation of alkali metals like potassium (K). Potassium substituted La₉₀K₀₁Pr₀₂MnO₃ perovskite shows good catalytic activity for soot/carbon oxidation probably promotional effect of potassium. The La₉₀K₀₁Pr₀₂MnO₃ showing T_{initial} at 300°C and T_{final} at 510°C, which is almost 110°C lower than the non-catalyzed reaction. The synergetic effects of Pr incorporation in perovskite and presence of a small amount of potassium appears to be responsible for the high soot oxidation activity of these perovskite type materials. The La₉₀K₀₁Pr₀₂MnO₃ type catalyst can also be synthesized directly on commercially available diesel particulate filters (DPF). Suitability of perovskite type catalysts for flow-through type DPF and their improved stability with low sulfur diesel add to their potential for their application in regeneration of DPF. These studies should actually pave the way towards practical application of this class of catalysts in the field of diesel exhaust emission control.

Key words: Catalytic regeneration of DPF; perovskite; praseodymium substituted lanthanum-magnates perovskite

INTRODUCTION

The particulate matter (PM) emissions from diesel engines cause serious environmental and health related problems. The most promising approach to reduce the PM emissions appears to be use of Diesel Particulate Filter (DPF), however, its effective regeneration is a challenge for its practical feasibility. Catalytic regeneration has already been proposed as the best approach, and intensive efforts are being made to develop suitable catalysts. The use of catalysts in soot removal from particulate traps is a logical choice. Catalysts for the oxidation of carbonaceous materials, e.g. graphite, activated carbon, and coal, have been studied for a long time. Catalytic oxidation of soot is in many ways analogous to these oxidation reactions, in which many catalysts have appeared to be active. Perovskite type catalytic materials are quite potential for diesel exhaust emission control. Perovskites are binary oxides with a general formula ABO₃. Availability of a large number of cations, which can fit at both A and B positions, offer perovskite structure a versatile flexibility in their chemical composition. Their structure and properties can also be modified due to the great extent of substitution possible at both A and B sites. Positive holes and oxygen vacancies can be easily created at perovskite matrix and this adds to the excellent tailoring capabilities of perovskite structure. The oxygen absorption and desorption properties of perovskites can play a crucial role for the low temperature oxidation of soot/particulate. The low temperature release of Ω-oxygen may be especially important, incorporation of a small amount of alkali metals improved their catalytic activity [ref].

We have already reported the development of supported perovskites and their applications on both two- and four wheelers catalytic converters [1-3]. Some perovskite type materials have also been reported to show good catalytic activity towards the reactions involving soot and soot NOx reactions [4-12].

In this study we have synthesized La₉₀Pr₂₀MnO₃ and La₉₀K₀₁Pr₀₂MnO₃ perovskite type catalytic materials, which is further improved by incorporation of potassium inside the structure. Performance of these improved catalysts is compared with that of LaMnO₃ type catalysts with basic perovskite structure. Their catalytic activity for carbon/soot oxidation has been studied for their possible application in DPF regeneration.

EXPERIMENTAL

Co-precipitation method was used to synthesize La₉₀Pr₂₀MnO₃ and La₉₀K₀₁Pr₀₂MnO₃ type perovskite materials. Acetate salts of lanthanum, Praseodymium, potassium and manganese (E-Merck) were mixed together and stirred for 15 minute with heating. 300 ml of 2 N NH₄OH solution was then slowly added to the above metal solutions at a rate of 100 ml / min with a stirring of 100 rpm .The precipitate thus obtained was allowed to settle overnight followed by filtration with thorough washings with de-ionized water. The precipitate cake was then dried at 80°C and the resultant mass was then calcined at 450°C for 5 hrs followed by grinding and further calcination at 900°C for 8 hrs.
Characterization

XRD patterns were recorded on a Rigaku Rint-220HF diffractometer, operated at 40 kV and 50 mA with a monochromator and using Cu-Kα radiation (λ = 0.15418 nm). Indexing of XRD peaks was done, by using the JCPDS cards for the respective phases. Surface area was measured by nitrogen adsorption using the automatic gas adsorption apparatus BELSORP 28SA (produced by Nippon Bell Co.) and evaluated by BET method. The samples were pretreated at 300°C before the nitrogen adsorption experiments.

The catalytic evaluations for the oxidation of carbon black have been studied by thermogravimetric analysis (TG), with a Rigaku-TAS-200 apparatus. Commercially available carbon black was used as model soot (Degussa S.A, Printex-U). For oxidizing carbon black, a mixture of carbon black and catalyst (in a catalyst: carbon ratio of 95:05) was heated at 5°C/min rate from 50-800°C in an atmospheric air atmosphere. The catalyst: carbon black weight ratio used was 95:5.

Experiments have been performed in loose contact conditions, i.e., by physically mixing catalyst and carbon black and subsequent homogenization using a spatula. This sample preparation represents more realistic conditions, as the catalyst-carbon contact is relatively poor. The carbon blank experiments were also performed with only catalyst samples to account for any weight loss, due to moister desorption. Some of the experiments were also performed using steady state laboratory gas evaluation assembly, which show quite similar results. The catalytic materials were examined for any effect on their structure after using for the catalytic reactions for 24 hours continuously. This was done through X-ray diffraction and BET surface area measurements on used catalyst samples.

RESULTS AND DISCUSSION

LaMnO₃ and La₀.8Pr₀.2MnO₃ perovskite sample were found to be well crystallized by XRD analysis, which is shown in fig1, 2. No prominent peaks of La₂O₃ and Mn₂O₃ are observed in the diffraction pattern of the perovskite synthesized at 950°C without Pr incorporation conforms a pure LaMnO₃ phase formation. Pr incorporation (0.1-0.3) in perovskite lattice has been attempted. The XRD patterns of all these synthesized materials show a prominent peak of Pr₂O₃, whose intensity increases with increasing Pr content. From the elemental analysis conducted for evaluating the content of Lanthanum, praseodymium, manganese and potassium into the perovskite lattice, the experimental values closely agree with the theoretically calculated values.

The BET surface area of these materials is shown in table.1, which is expected range considering the higher synthesis temperature.

These catalytic samples were also studied for its thermal stability experiment. The TG isothermal studies confirm practically no loss of material, while isothermal heating in steady state catalyst evaluation assembly also shows similar results. High thermal stability requirement for soot oxidation application.

Catalytic activity

Diesel particulate (soot) is normally composed of carbon core associated with hydrocarbons (SOF, which includes polyaromatic hydrocarbons (PAH (polyaromatic hydrocarbon) and nitro-PAH), sulphates, water, trace amounts of zinc, phosphorus, calcium, iron, silicon, and chromium [21]. The non-catalytic combustion temperature of soot depends on the contents of adsorbed hydrocarbons, and experimental conditions, but generally exceeds 550°C. Moreover, the composition of diesel particulate is affected by several engine operation parameters. Thus, it is difficult to collect batches of soot with constant properties and therefore, the model soot is often used. The model soot used in this study is a carbon black from Degussa S.A. (Printex-U) with following physicochemical properties: fraction of adsorbed hydrocarbons (5.2%), ash (<0.1%), C (92.2%), H (0.6%), N (0.2%) and S (0.4%).

Fig-1 shows the soot/carbon oxidation evaluation (TG) results. This figure gives temperature values T₀ (start of the carbon combustion) and Tₚ (complete combustion of carbon). The value ∆T = T₀ - Tₚ determines the reaction velocity. Catalytic activity of various catalysts was evaluated by comparing these values with and without catalysts under the same experimental conditions. As mentioned before, the experiments were performed under loose contact conditions as described by van Setten et al. [22]. Loose contact offers more realistic conditions as compared to that of tight contact and therefore has been used in the present study. There is considerable difference observed between non-catalyzed reaction of carbon and oxygen as compared to the catalyzed reaction. The non-catalyzed carbon oxidation starts above 400°C, and maximum activity was observed at about 560°C with a sharp weight loss due to carbon oxidation in CO₂.

The carbon oxidation activity results for LaMnO₃, La₀.8Pr₀.2MnO₃ and La₀.8K₀.2Pr₀.2MnO₃ are presented in Fig. 2. The La₀.8Pr₀.2MnO₃ catalyst appears to get activated after 250°C, however, significant oxidation of the carbon material is observed beyond 300°C only. The peak oxidation temperature corresponding to maximum activity is around 480°C. The exothermic carbon oxidation reaction is expected to propagate the reaction rate after it achieves significant activity. The introduction of Pr in the perovskite lattice seems to modify significantly the catalytic activity of this perovskite series. This activity could be considered as a good catalytic activity, in view of the very low surface area of the catalyst used. A slight improvement was observed in the carbon oxidation activity of K incorporated La₀.8Pr₀.2MnO₃ which indicates its promoting effect.

The catalyst containing potassium La₀.8K₀.2Pr₀.2MnO₃ shows the excellent activity and the potassium present in the lattice plays a synergistic role in enhancing both the activity and selectivity. Therefore La₀.8K₀.2Pr₀.2MnO₃ is the most active catalyst for carbon/soot oxidation reaction. The La₀.8K₀.2Pr₀.2MnO₃ shows Ti at 300°C and Tf at 510°C, which is almost 110°C lower than the non-catalyzed reaction.

The catalytic properties of La₀.8Pr₀.2MnO₃ are different from the physical mixture of LaMnO₃ and Pr₂O₃. Mechanism: It is well known that when a perovskite is heated at high temperature, oxygen vacancies can be formed (23-27). Two types of chemisorbed oxygen species are desorbs from perovskite lattice; at lower temperature about 300º-600ºC, alpha species is desorbs and at about 600º-900ºC beta species is desorbs. The alpha oxygen species is not always observable because it strongly depends on the concentration of surface oxygen vacancies. Oxygen vacancies formed by partial substitution of A-site cations by lower valence ions or even by...
vacancies of B-site cations (28). The beta oxygen species is strictly depends on the nature of the B cation. The oxidation mechanism of alpha species is generally referred as “superafacial” because it is connected with the presence of anionic vacancies on the perovskite surface and the mechanism of beta species is referred as “intrafacial” because connected to the presence of lattice species in layers near to surface.

LaMnO$_3$ perovskite can easily accept structural under-occupation on the A as well as on the B-site up to a certain amount. (29).

On the other hand, it must be stressed here that introducing La$^{3+}$ vacancies, which alter also the electronic configuration of the BO6 octahedra by lowering the binding energy of oxygen, may activate surface oxygen (alpha oxygen), which is responsible for soot/carbon oxidation. It is possible that this alpha oxygen could undergo spillover on the carbon agglomerates in touch with the catalyst (30). This would result in an increase of the number of sites in which the carbon particles are simultaneously attack by the oxygen to the benefit of reaction kinetics. It has been reported in the literature the non-stoichiometric materials can easily release oxygen and become more active than the stoichiometric. It has been shown that the non-stoichiometry can increase the catalytic activity in the carbon/soot oxidation but only in structure where Mn is defective. In such case the types of vacancies introduced should be responsible for alpha oxygen desorption. (31).

Various mechanisms have been proposed for the catalytic soot oxidation by molecular oxygen. It is difficult to consider the good catalyst-soot interaction under the loose contact conditions, and also due to the fact that both soot and catalysts are in solid phase. We therefore, presume that dissociative adsorption of molecular oxygen on catalyst surface followed by its reaction with the solid soot/carbon can be more acceptable under the practical conditions. Further, the soot oxidation should involve intermediates and their decomposition can be the rate-determining step. These carbon intermediates are known as surface oxygen complexes (SOC’s) [32]. Hong et al. proposed a mechanism based on dissociative adsorption of oxygen for soot-oxygen reaction from their kinetic analysis of the reaction [33].

As per this mechanism by Hong et al., gaseous oxygen is dissociatively adsorbed on the surface of perovskite catalysts, and the resulting atomic O$_{\text{ad}}$ species then attack the reactive free carbon site, C$_f$ to give an oxygen-containing active intermediate, C$_f$ $^*$ [O]. The reaction between C$_f$ $^*$ [O] intermediate and either O$_{\text{ad}}$ or gaseous O$_2$ produces CO$_2$ through reaction or, reproducing the reaction C$_f$ sites on the soot surface. It is natural that the removal of one carbon atom from the soot surface leaves more, probably two or three reactive surface carbon sites as described under this mechanism.

The oxidation of carbon/soot was studied over a series of La$_{0.7}$Pr$_{0.3}$MnO$_3$ perovskites calcined at 900°C for 8 h. It has been observed that, without catalyst, carbon/soot oxidation take place for temperatures at about 560°C.

**CONCLUSION**

The present study has showed the appearance of the synergistic effect of Pr, and K in the La$_{0.7}$K$_{0.1}$Pr$_{0.2}$MnO$_3$ catalyst for soot/carbon oxidation reaction and the most active catalyst is La$_{0.7}$K$_{0.1}$Pr$_{0.2}$MnO$_3$. Small substitution of lanthanum by Pr, creating a defective perovskite, results in a highly active oxidation catalyst having good thermal stability. The higher activity of the defective perovskite is related to the increased oxygen mobility. Incorporation of alkali metal into the perovskite lattice, result in the increasing activity and selectivity. The stability of the perovskites was tested by repeating the carbon/soot oxidation experiments for each perovskite twice or thrice, for the temperature ranging from 200-600°C. A similar activity was observed suggesting that the perovskite are stable under these conditions.

**Table: 1.BET surface area for lanthanum manganate based catalysts**

<table>
<thead>
<tr>
<th>S.N o.</th>
<th>Catalysts</th>
<th>Co-precipitation Surface Area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>LaMnO$_3$</td>
<td>3.09</td>
</tr>
<tr>
<td>2</td>
<td>La$<em>{0.7}$Pr$</em>{0.2}$MnO$_3$</td>
<td>2.719</td>
</tr>
<tr>
<td>3</td>
<td>La$<em>{0.7}$K$</em>{0.1}$Pr$_{0.2}$MnO$_3$</td>
<td>2.52</td>
</tr>
</tbody>
</table>

**Table: 2. Activated Carbon oxidation results of lanthanum manganate**

<table>
<thead>
<tr>
<th>S. N o.</th>
<th>Samples</th>
<th>$T_i$ (°C)</th>
<th>$T_{20%}$ (°C)</th>
<th>$T_f$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bare carbon</td>
<td>380</td>
<td>530</td>
<td>620</td>
</tr>
<tr>
<td>2</td>
<td>LaMnO$_3$</td>
<td>350</td>
<td>500</td>
<td>580</td>
</tr>
<tr>
<td>3</td>
<td>La$<em>{0.7}$Pr$</em>{0.2}$MnO$_3$</td>
<td>282</td>
<td>450</td>
<td>510</td>
</tr>
<tr>
<td>4</td>
<td>La$<em>{0.7}$K$</em>{0.1}$Pr$_{0.2}$MnO$_3$</td>
<td>235</td>
<td>445</td>
<td>487</td>
</tr>
</tbody>
</table>
Fig. 1. XRD Pattern for LM-1(LaMnO$_3$) Sample

Fig. 1: XRD Pattern for LCM-1 (La$_{0.8}$Pr$_{0.2}$MnO$_3$) Sample
References: