RECENT TRENDS IN CATALYST DEVELOPMENT FOR DIESEL ENGINE EXHAUST EMISSION CONTROL

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ABSTRACT

The increased industrialization and particularly increased traffic in developing countries has been accompanied by a negative impact on air quality, the environment and human health. Diesel engines have both carbon monoxide and unburned hydrocarbon outlet concentrations much lower than those produced by spark-ignition engines (gasoline engines). But diesel engines emit large quantities of particulate matter (called PM) and nitrogen oxides (NOx), both precursors of photochemical smog. Growing alarms on health effect and pressure to fulfill the governmental directives for the reduction of pollutants emissions from diesel engines are paving the way for the development of tailored treatment systems. These cannot be accomplished by engine modifications, fuel pretreatments or simply better tuning of the combustion process; thus a convenient way of treating diesel off-gases is needed.

Perovskite type oxides of general formula ABO_3 where A and B are usually rare earth, alkali earth, alkali or other large ions and transition metal cation respectively are less expensive, thermally more stable, diverse physicochemical properties, increase thermal stability of the support, store and release oxygen under conditions fluctuating between oxidizing and reducing than noble metal used in catalytic converter to reduce emission from diesel engines.

This paper discusses use and potential of perovskites based catalysts for simultaneous removal of soot and nitrogen oxides in a single, suitably catalyzed trap from diesel engine. The various synthesis methods like citric acid, co-precipitation, sol–gel, freeze drying, combustion synthesis, reactive grinding of catalysts are incorporated. Perovskite compounds can also tolerate significant partial substitution and non-stoichiometric while still maintaining the perovskites structure. Metal ions having different valence can replace both A and B ions. This may generate a non-integral number of oxygen atoms. It is explained the mechanism of generation of a non-integral number of oxygen atoms and doping of PGM in perovskites which work as highly active and clean catalyst and can also reduced 70 – 90 % amount of precious metals needed to meet new emission vehicle standards.

Keywords: Catalytic converter; Perovskite; Automotive emission; Catalyst; Diesel soot combustion; Nitrogen oxide reduction

INTRODUCTION :

The increased industrialization and particularly increased traffic in developing nations have been accompanied by a negative impact on air quality, the environment and human health[1-6]. Automobile market has been increased expotentially day to day[5]. About 50 million cars are produced every year and over 700 million cars are used worldwide[6].

Due to shortage of petroleum resources, lean burn engines (diesel engines) have become the main option for the vehicles[7]. Diesel engines have higher thermal efficiency (higher fuel efficiency resulting from higher compression ratios) than gasoline engines so they can reduce the use of the limited amount of fossil fuel in the future as well as reduce the global warming, longevity, less heavily taxed than gasoline (in Europe)[7-9]. Diesel fuel is injected into a highly compressed charge of air where the temperature is sufficiently high that combustion occurs. Thus, unlike the spark-ignited engine, the diesel is a compression-ignited process. The liberal design of the combustion process result in larger quantities of unburned fuel, lubricating oil emissions and dry soot. Diesel emissions represent all three phases of matter: (1) Solid: Particulate matter (is the matter consists of carbon particles as well as engine oils, debris, soot and ash particulates. The diesel particulate matter is the visible cloud of black smoke on start up and can be categorized into two groups: PM_{10} which are particles of 2.5 micons to 10 microns and $PM_{2.5}$ are particles of less than 2.5 microns in size) (2) Liquid: unburned fuel, lubricating oil (collectively soluble organic fraction - SOF) and liquid sulfates primarily, sulfuric acid (H_2O associated with the SO_3 is included as a component of the liquid particulate) (3) Gas: carbon monoxide (CO), hydrocarbons (HC), NO_x and sulfur[2,3,6,8,10-16].

Carbon monoxide is a noted poison which has an affinity for hemoglobin in the blood 210 times greater than the oxygen affinity prolonged exposure to levels above 9 ppm can lead to reduce mental acuity for some individuals[6]. HC and NO_x lead to photochemical smog in sunlight giving rise to the photochemical oxidant, ozone, nitrogen dioxide and peroxyacetyl nitrate. Exposure to these oxidants above 0.08 ppm can cause eye irritation and impairment of lung function in person with chronic pulmonary disease. The oxidants also cause damage to vegetation and rubber tires[5,6,12,16-21]. PM irritates the eyes and nose thereby entailing respiratory problems, can penetrate the cell membranes, enter the blood and even reach the brain, can also induce inheritable mutations[2,3,12,17,22-25]. In addition to photochemical smog, global environmental issues such as acid rain, the green house gas effect and

depletion of the ozone layer are also attributable in part to emissions from motor vehicle[4,5,26-28]. The automotive industry is currently facing challenges to reduce the emissions from vehicles. As per Euro IV norms introduced in January 2005 (by European legislation), diesel cars have emit the NO_x upto 0.25 g km^{-1} and particulate matter upto 0.025 g km^{-1} (0.005 g km^{-1} as per EURO V). Due to adverse effect on health and pressure to fulfill the governmental directives for the reduction of pollutants emissions from diesel engines are paving the way for the development of tailored treatment systems. These cannot be accomplished by engine modifications, fuel pretreatments or simply better tuning of the combustion process; thus a convenient way of treating diesel off-gases is needed[2].

RECENT DEVELOPMENTS IN DIESEL ENGINE EXHAUST EMISSION CONTROL :

Diesel engines emit HC and NO_x at ppm levels (300–800 ppm) and large amounts of O_2 (5–15%), water and CO_2 (each 10–12%)[29]. A number of other alternative technologies like improvement in engine design (as high pressure fuel injection, small injection nozzle hole area, high swirl ratio, large volume ratio of the piston cavity, improvement of combustion chamber shape and high response turbo charge), fuel pretreatments or more simply by a better tuning of combustion process or modification of fuel formulation or use of alternative non fossil fuels such as natural gas, alcohols or esters, fuel additives, exhaust gas recirculation (EGR), exhaust treatment and finally the use of filtering or non filtering after treatment devices, NO_x storage and reduction (NSR) etc. are being considered to reduce the emission levels of the diesel engine[6,30].

Diesel engines are most fuel efficient compared to gasoline based vehicle but diesel engine face two problem of NO_x reduction under lean conditions (a large excess of oxygen) and control of soot particles. Under lean conditions, the conventional three way catalytic converters (TWCs) based on noble metals are completely ineffective for NO_x reduction. Therefore, diesel engines are equipped with oxidation converters (DOC) for the abatement of HC and CO emissions and diesel particulate filters (DPF) to trap soot particles[1,4,6,11,15,31-35]. To reduce the PM emissions of vehicles is to retrofit them with a particulate filter. Several diesel particulate filter systems are currently on the market. Wall-flow monoliths are the most common type. Adjacent channels in the wall-flow filters are alternatively plugged at each end thus forcing the gas to flow through the porous wall which acts as a filter medium. The only problem with diesel particulate traps with regeneration of diesel traps. Various strategies for regeneration of diesel traps have been considered including catalyzed filter substrates, fuel-borne catalysts, continuous regenerating traps, electric heaters, fuel burners, microwaves[2,4,5,11,36]. The research

carried out worldwide in this field is aimed mainly at two different solutions: (1) Filtration of particulate in a first catalytic converter in which the soot is trapped and burned out due to the presence of a catalyst thoroughly deposited onto the filter with NO_x eliminated in a second catalytic converter either by reaction with suitable reducing agents (e.g., light hydrocarbons, fuel, ammonia) or by direct decomposition (2) Simultaneous removal of soot and nitrogen oxides in a single, suitably catalyzed trap[2-4,10,11]. The second approach has advantages over first because it may offer reduction in both investment cost and pressure drop. It is well known that 10–15% of NO_x is generally reduced during regeneration of soot-laden traps. This reduction mostly involves NO_2 molecules by direct reaction with soot to form NO and to a much lesser extent, N_2 and N_2O[2,3].

Martyn V Twigg and other researcher have pointed out the exhaust gas recirculation (EGR) with continuous regenerating trap (CRT) system is as efficient as for HC, CO and PM reduction and additionally lowers NO_x by 45-58%[36,37]. R Heck et al. pointed out that cerium metallo organic fuel bound additive coupled with exhaust gas recirculation claims to simultaneously decrease PM and NO_x in diesel engine[6].

Johnson Matthey developed the continuous regenerating trap (CRT). In this approach an oxidation catalyst turns NO into NO_2 upstream from the DPF. The DPF collects the PM and NO_2 generated over the catalyst combusts this PM at temperatures much lower than is the case for combustion with oxygen (250 ^{0}C instead of 550 ^{0}C)[2,31,38]. Selective catalytic reduction of NO_x with hydrocarbons or NH_3 in form of urea as reducing agent in presence of oxygen has been pointed out by J Kaspar et al. and many other researchers[1,5,31,33,37-39].

C. Millet et al. has introduced the concept of 4-way catalytic converter that simultaneously convert CO, HC, NO_x and PM on a single support. As CO and HC catalytic oxidation functions are also present on the deNO$_x$ system, the catalyst can be named a '4 way catalytic converter' (4WCC). Its main advantage is that it decreases the space needed along the exhaust line for the set of catalysts. It allows diesel vehicle to obey to increasing stringent emission regulations while at the same time decreasing the space needed by the exhaust after treatment system[31].

Despite the fact that several technical problems remain to be solved (e.g., determining the best catalyst deposition route on the trap and the best trap design so as to allow intimate contact between the reactants and the catalyst itself), it is deemed necessary to develop suitable catalyst which is capable of promoting both soot oxidation and NO_x reduction at comparatively low temperatures (possibly within

the range typical of diesel exhaust, 150–380 ^{0}C)[10]. A literature shows that perovskite based catalysts are the most promising catalysts for this purpose because perovskites are less expensive, thermally more stable, diverse physicochemical properties, increase thermal stability of the support, store and release oxygen under conditions fluctuating between oxidizing and reducing than noble metals used in catalytic converter to reduce emission from diesel engines.

DIESEL EXHAUST EMISSIONS CONTROL BY PEROVSKITES :

Introduction about perovskites

Perovskites (any material with the same type of crystal structure as $CaTiO_3$) take their name from this compound which was first discovered in the Ural Mountains of Russia by Gustav Rose in 1839 and is named after Russian mineralogist, Count Lev Aleksevich Von Perovski who discovered the naturally occurring mineral calcium titanate ($CaTiO_3$) (1792-1856)[40]. The general chemical formula for perovskite compounds (is ABO_3)[26,29,38,40-48], where 'A' and 'B' are two cations of very different sizes and O is an anion that bonds to both. The 'A' atoms are larger than the 'B' atoms[22,26,40,41,49]. A ion (A coordinated by 12 oxygen) 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 (B surrounded by six oxygen in octahedral coordination) can be 3d, 4d and 5d transition metal ions[26,29,41,43,44,46,48-50].
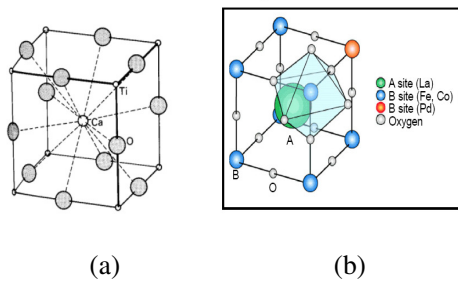

(a)   (b)

Fig. 1: (a) Perovskite structure ($CaTiO_3$) (b) Structure of Perovskite (ABO_3)

Pure perovskite crystals are formed when their tolerance factor $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$ defined by Goldschmidt was around 0.8–1.0, where r_A, r_B and r_O are ionic radii of A, B and O respectively[40,41,51,52]. Due to this tolerance factor, wide variety of elements can be combined without change in the original structure.

Perovskite compounds can also tolerate significant partial substitution (A and/or B with metals A', B' correspondingly of different oxidation states i.e. AA'BO$_3$, ABB'O$_3$ etc. or $A_{1-x}A'_xB_{1-y}B'_yO_{3\pm\delta}$) and oxygen non-stoichiometry (oxygen excess as well as deficiency) indicated by the δ subscript in the formula while still maintaining the perovskite structure. A large number of metal ions having different

valence can replace both A and B ions. By appropriate formulation many desirable properties can be tailored[29,38,40,41,43-45,48,50,53].

The catalytic properties of perovskite-type oxides basically depend on the nature of A and B ions and on their valence state. The A site ions are catalytically inactive. The nature of these ions also influences the stability of the perovskite phase. Catalytic activity is generally determined by the B cation. The substitution at A site with ions having lower valence can allow the formation of structural defects such as anionic or cationic vacancies and/or a change in the oxidation state of the transition metal cation to maintain the electro neutrality of the compound. When the oxidation state of B cation increases, the relative ease of the redox process generates larger quantities of available oxygen at low temperature and the overall oxidation activity enhances. Moreover, the oxygen vacancies favour the catalytic activity in oxidation reaction because they increase the lattice oxygen mobility[40,44,45,47,54,55]. When a perovskite is heated at high temperature, oxygen vacancies can be formed. The oxidation activity of perovskites has been ascribed to their ionic conductivity, to oxygen mobility within their lattice, to their reducibility and to their oxygen sorption properties[48]. Indeed, two possible mechanisms, a suprafacial and an intrafacial one are proposed for oxidation reduction over these catalysts. The former mechanism rises from the interaction of surface oxygen with reactants and it is operative at low temperature ($< 400\ ^0$C). The latter is effective at higher temperature ($> 400\ ^0$C) and involves a Mars Van Krevelen redox cycle. In it, bulk oxygen migrates towards the surface becoming available for the oxidation of the adsorbed substrate and it is quickly replaced by oxygen coming from the gaseous phase. The mobility of O^{-2} ions within the crystalline framework determines the mechanism of the catalytic reaction[12,47,48]. The released oxygen species can be divided into two categories depending on temperature (1) α oxygen: low-temperature suprafacial species, weakly chemisorbed on the surface of the perovskite, desorbed in the 300–600 ^{0}C range and related to surface oxygen vacancies (2) β oxygen: high-temperature intrafacial one, less easy to desorb and therefore more bound to the perovskite structure, desorbed above 600 ^{0}C and related to the bulk nature of the catalyst.

Generally speaking, A-site replacement mainly affects the amount of sorbed oxygen whereas B-site replacement influences the nature of sorbed oxygen. Therefore, such isostructural substitution would produce modifications of the perovskites catalytic behavior[29].

Synthesis of Perovskites

Synthetic perovskites may be prepared by a range of methods.

(1) Solution combustion synthesis (SCS): To produce any metal oxide by combustion synthesis, an aqueous solution of metal nitrates (oxidisers) and the appropriate amount of urea (fuel) is brought to the boil; shortly thereafter the mixture ignites and the fast self-sustaining redox reaction takes off which generates a large amount of gaseous products in a very short period of time which leads to a spongy catalyst morphology and also form rough interfaces for the catalyst powder agglomerates which helps in maximizing the number of contact points between catalyst and carbon (soot) and promoting carbon combustion and consequently, NO reduction[2,12,36].

In recent years, this technique has been used to produce homogeneous, very fine, crystalline powders without the intermediate decomposition and/or calcining steps which other conventional synthesis routes would require. Powders prepared via SCS generally have higher specific surface areas as well as pure phases and the desired chemical compositions[12,42,48]. However, the main drawback of this method is that hazardous or polluting compounds are emitted during the synthesis (mainly NH_3 or NO_x)[42,45]. (2) Citrate complexation: Nitrates of constituent metals of the required perovskite were dissolved in water and mixed with an aqueous solution of citric acid (molar ratio of citric acid to total metals 1:l). Water was evaporated from the mixed solution using a rotary evaporator at 330-340 K until a sol was obtained. The sol was further dehydrated at the same temperature under vacuum for 5 h[3,22,26,42,44]. Citrate method normally produces solids with a higher degree of crystallinity[22]. Citrate method is most effective route to create higher surface areas[56].

(3) Sol gel methods: The precursor in a sol-gel preparation can either be a metal salt/alkoxide dissolved in an appropriate solvent (organic solvent) or a stable colloidal suspension of preformed sols. Commonly, gels are obtained by a hydrolysis step followed by a condensation reaction. The destabilization of a sol into a gel which mainly occurs by modifying the pH of the dispersion can also be performed[22,26,40,42]. Sol gel technique is one of the most efficient methods since it permits a better control of stoichiometry, high reactivity, controlled dimensions and nanoparticles[15,22].

(4) Co-precipitation: Synthesis of perovskites is by co precipitation from soluble precursors of the constituent metals in suitable solvent and then coprecipitated as a gel by adding an acid/base or another reagent to cause the precipitation. These can be readily converted to oxides by heating. Precipitation has three stages: supersaturation, nucleation and growth. An amorphous or crystalline precipitate or a

gel is obtained which is aged, filtered, washed thoroughly until salt free. This is then followed by further steps: drying, shaping, calcination and activation. Various characterization techniques confirmed that the co-precipitation method produces lower crystallinity and higher surface area than the citrate method[22,26,43]. In addition, the final material obtained from the alkali coprecipitation route suffers from the contamination of alkaline metals as well as the formation of large amount of environmental wastes (e.g., salts from hydrolysis and washwater)[57].

(5) Reactive grinding: A reactive grinding (high-energy mechanical synthesis) allowing to attain a pure perosvkites phase at room temperature without the thermal treatment[18,26,41,42,51,53]. Mechanical impact during the process reduces the precursors crystallite size to nano scale provides a homogeneous mixture and enhances the solid state diffusion. The synthesis is performed in a closed environment without generating any waste[58].

Application of perovskites in diesel engines exhaust emission control

Catalytic materials have two important roles to play in diesel exhaust emission control. 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. Lots of development and detailed investigations took place on a large number of catalytic materials for DPF regeneration. However, most of the results are reported under laboratory conditions often using tight soot–catalyst contact. 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.

The oxygen adsorption and desorption properties of perovskites can play a crucial role for the low-temperature oxidation of soot/particulate matter. A number of perovskite based catalytic materials have been reported for their activity towards diesel soot emission control. Teraoka *et al*. reported extensive results on perovskite-type catalytic materials for soot–NO_x reactions. 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 that can have favorable impact on its oxidative catalytic activity. 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 and Hong *et al*. respectively. According Hong *et al,* 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 which results in the formation of N_2[2,3,10,13,20,23,24,49]. The perovskites catalyst favors the reaction between the nitrate species and the soot particulates which makes this system promising for the simultaneous abatement of both contaminants. The soot combustion peak appears at lower temperatures for nitrated catalysts suggesting that the reaction C(soot) + nitrate species occurs in addition to the combustion with gaseous oxygen[10]. Rundo Zhanga et al. and other researches was proposed a mechanism for NO reduction by propene in which organo nitrogen compounds generated from the interaction between nitrate species and adsorbed C_3H_6. Subsequently, an isocyanate intermediate formed from organo nitrogen intermediates can react with NO and/or O_2 to get the desired products[25].

A special self-regeneration character on Pd-containing perovskite was described by Nishihata et al. who showed that Pd can move back and forth between the B-site in the perovskite and the metal oxide when exposed to fluctuations in the redox characteristics of the emission exhaust. Incorporation of small amount of precious metals into a perovskite structure can prevent their sintering, reduce losses due to volatilization at high operating temperatures and avoid reactions with the support that lead to catalyst deactivation. Some of these perovskites materials are now in commercial use resulting in a 70% decrease in precious metal usage compared with conventional automotive catalysts[49].

CONCLUSION :

Diesel emissions from mobile sources have raised health and welfare concerns but a number of technologies exist that can greatly reduce emissions from diesel-powered vehicles. New emission standards have created the need for even better catalyst for NO_x and PM control in engines along with CO and HC. Perovskites based catalyst can simultaneously reduced CO, HC, NO_x (in lean conditions) and PM due to their high activity, versatile and stable structure and low PGM content. Our further efforts will be aimed at fully exploiting the potential of perovskite (non noble metals) in the automotive catalyst so that we can approach the eventual goal of zero emission and cost minimization.

Table 2 : The applications of perovskites based catalyst in diesel exhaust emission control.

Catalyst	Pollutants	Result
$LaFeO_3$ $LaFe_{0.8}Cu_{0.2}O_3$ $LaFe_{0.97}Pd_{0.03}O_3$	NO by propane	$LaFe_{0.97}Pd_{0.03}O_3$ with a N_2 yield of 67 % and C_3H_6 conversion of 68 % at 623 K (350 ^{0}C). The catalytic performance over $LaFeO_3$ is poor but can be improved significantly by incorporating Cu into its lattice resulting in N_2 yields over $LaFe_{0.8}Cu_{0.2}O_3$ of 81% at 723 K (450 ^{0}C) and 97% at 973 K (700 ^{0}C).
$BaCoO_{3-y}$ $BaCoO_{2.74}$	NO_x, and diesel soot	$BaCoO_{3-y}$ is an active phase for both NO_x trapping and soot combustion in diesel exhausts.
$LaCoO_3$ $LaCo_{1-x}Cu_xO_3$ $LaCo_{0.8}Cu_{0.2}O_3$	NO (SCR of NO by C_3H_6)	Blank test run in empty reactor up to T = 1073 K (800 ^{0}C) : No NO conversion to N_2, No C_3H_6 conversion observed below 773 K (500 ^{0}C). Yield of N_2 of 19% (unsubstituted) at 773 K (500°C) at a space velocity 55,000h^{-1} (3000 ppm NO, 3000 ppm C_3H_6, 1% O_2 in helium).Yield of N_2 of 46 % by Cu substitution at 773 K (500 ^{0}C).Yield of N_2 = 73% (in absence of oxygen, the reduction of NO by C_3H_6).

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