CHAPTER 2

LITERATURE REVIEW

Several types of catalysts have been investigated for the soot combustion i.e. platinum group metals (PGM), rare earth metal oxides, mixed transient metal oxides, spinel-type oxides, hydrotalcite and perovskite-type oxides, etc.

2.1 Platinum Group Metal Catalysts for Diesel Soot Oxidation

Regeneration of catalytic diesel particulate filter (DPF) requires active, selective and stable catalyst. The most conventional catalysts used for soot oxidation are noble metal based (Pt, Pd). Ample of work have been done and reviewed on the platinum group metal (PGM) catalysts. Recently, Prasad and Bella [2010] reviewed the catalytic control of diesel soot emission and reported that PGM catalysts are most active for the soot oxidation. Pt supported on γ-Al_2O_3 shows high activity even at low loadings is explained by the spillover effect [Neri et al. 1997]. Pt also shows high selectivity for CO_2 however the addition of Pd to Pt significantly reduces the selectivity [Cooper and Thoss 1989]. It has been discussed that the use of Pt is significantly important when the fuel contains low Sulphur, while NO oxidation should be maximized. Other possible solution to regenerate the filter in the sulphur dioxide atmosphere is the use of Pt along with the Vanadium.

Huang et al. [2004] applied a Pt/Mg/V catalyst coated onto a tungsten doped TiO_2 washcoat. The Pt/V catalyst may reduce sulphate, due to the effect of V as a sulphate suppressant. Regeneration of the soot loaded filter took place at a temperature of 350 °C. The TiO_2 washcoat was favored over Al_2O_3 to avoid interaction between Mg and Al_2O_3, resulting in a loss of surface area and catalyst deactivation. Matarrese et al. [2008] replace Pt by K/Ba and prepared K/Ba/Al_2O_3, catalyst. They found that the K/Al_2O_3 is very active for the oxidation of soot even better than Pt/Al_2O_3. Also, a synergistic effect is observed for the case of the K and Pt containing (i.e. Pt-K/Al_2O_3) catalyst.

2.2 Alternative to PGM Catalysts

PGM catalysts are highly active but unfortunately they are expensive and due to low abundance vulnerable to further price increases upon increasing demand. Therefore, the search for catalysts free of or low in noble metals is of global importance. Recently, a considerable amount of research has been carried out to develop cheaper and efficient PGM free catalysts for diesel soot removal. PGM free catalysts for soot oxidation are discussed under the following categories:

i) Metal oxides [Li et al. 2005, hu et al. 2005, Tikhomirov et al. 2006],

ii) Spinel catalysts [Shangguan et al. 1998, Fino et al. 2008, Zawadzki et al. 2011],

iii) Hydrotalcite catalysts [Wang et al. 2006, Zhang et al. 2007],

iv) Perovskite catalysts [Teraoka et al. 2001, Peng et al. 2007].

2.2.1 Metal Oxides for Soot Oxidation

Transition metal oxide, Lanthanide group oxides and alkaline earth metal oxide are widely used for soot oxidation. In a rigorous study performed by Neeft [Neeft et al. 1996] Single-component metal oxides are arranged for the relative activities in the oxidation of carbonaceous material in following order Pb > Co > V > Mo > Fe > La > Mn > Sb > Bi > Ca > Cu > Ag > Ni > Cr > Zr > Ba > Zn > Ce > Mg > Nb > W > Sn > Ge. Neeft et al. [1996] in his work discussed that CaO form $CaCO_3$ during soot oxidation. Further, they suggested the need of calcination at 727°C so that La_2O_3 containing $La(OH)_{3-2x}(CO_3)_x$ with x=0.1 must be calcined to break all the carbonate and -OH linkage into oxide form. CrO_3 is much more active than Cr_2O_3 [Neeft et al. 1994a, Neeft et al. 1994b] for soot oxidation. For copper, a higher combustion temperature is required for cuprous oxide ($T_{comb.}Cu_2O$ = 524°C) than for cupric oxide ($T_{comb.}CuO$ = 490°C). Neeft et al. [1996] also concluded that the activity in loose contact is always lower (resulting in higher combustion temperatures) than the activity in tight contact however, few oxides are almost as active as in tight contact mode (i.e. Sb_2O_5, MoO_3).

CeO_2 has the property to store NOx at low temperature (200°C) which can be decomposed at high temperature [Li et al. 2004, Setiabudi et al. 2004]. This is one of the reasons to show high activity of CeO_2 for soot oxidation in NOx/O_2. Atribak et al. [2007] did comparative study of the catalytic activity of TiO_2, ZrO_2 and CeO_2 for soot oxidation under NO*x*/O_2, and found that CeO_2 is more active than TiO_2 and ZrO_2, because TiO_2 and ZrO_2 do not catalyse conversion of NO to NO_2. He also concluded that the catalytic activity of all the three oxides decreases when calcined at higher temperature (600 to 800°C).

Abdullah et al. [2008] performed experiments on zeolite supported oxides (i.e. on 15% (w/w) V_2O_5/CuO/Fe_2O_3/ZSM-5) and found that V_2O_5/ZSM-5 showed best activity with the peak activity occurred at 450°C. Incorporation of K_2O to V_2O_5/ZSM-5 below 4.5wt% of K_2O shows promotional effect. This promotional effect is attributed to the mobility of V_2O_5 due to the melting of K_2O above 350°C. Castoldi et al. [2009] studied the intrinsic reactivity of alkaline (Na, K, Cs) and alkaline-earth (Ca, Ba, Mg) oxide catalysts in the oxidation of model soot sample (Printex U). With the aim of obtaining information about the intrinsic reactivity of catalytic elements, catalyzed soot samples have been prepared in which the active species have been directly deposited on the soot. It has been found that the combustion of soot is greatly enhanced by the presence of either alkaline or alkaline-earth oxides, with Cs and Mg exhibiting the highest and the lowest activity, respectively. The reactivity in the soot combustion of the selected elements well correlates with the electro-positivity of the investigated metal ions, in line with literature mechanistic proposals for the soot oxidation pointing out the relevance of the electron-donor characteristics of the active elements. The correlation between electro-positivity and activity in the soot combustion is however not apparent when a ‘‘full contact’’ is not guaranteed between the catalytic elements and the soot, e.g. under loose contact conditions.

Under loose contact conditions there activity of alkaline compounds is still remarkable, whereas that of the alkaline-earth compounds is very poor. It has been suggested that under these conditions the catalytic activity is governed by other factors, and particularly by the mobility of the surface species which favors the soot–catalyst contact and hence the reactivity. The poor performances observed in the case of the alkaline-earth metal oxides may suggest for these elements a poor mobility of the active surface species, as opposite to alkaline oxide based catalysts which show a high reactivity even under loose contact conditions.

Several studies have been conducted on ceria containing catalyst due to its oxygen storage capacity in vehicular pollution control. Shan et al. [2010] studied soot oxidation by ceria lattice incorporated by Mn ions. The features and catalytic behaviors of MnOx-CeO_2 catalyst strongly depended on their preparation conditions. MnOx-CeO_2 catalyst prepared in mild acid condition exhibited much higher catalytic activity with a decrease of about 150^oC in the temperature values at the exothermic peak for soot oxidation compared with that of un-catalytic soot. Jian et al. [2010] studied soot oxidation on CeO_2-supported vanadium oxide catalysts. Vanadium shows an optimum loading for soot oxidation and reason for this is explained by the different structure of Vanadium depending on loading. At low V loading isolated mono-vanadate species were present on the surface, and VOx existed predominantly as poly-vanadate at medium V loading, and further increase in V loading resulted in the formation of $CeVO_4$ crystallites after full coverage of the surface. The poly-vanadate species were more active than mono-vanadate species and $CeVO_4$ for soot oxidation. Shimizu et al. [2010] also worked on CeO_2 loaded silver metal nanoparticles. It is concluded that reducibility of the lattice oxygen of CeO_2 is enhanced by an adjacent silver nanoparticle, which results in the enhanced catalytic activity for soot oxidation.

Shimizu et al. [2011] concluded that among various metals (Ag, Cu, Pd, Pt, Rh, and Ru) supported on SnO_2, Ag/SnO_2 showed highest soot oxidation activity. They also concluded an interesting fact about Ag-O-Sn bond stabilization at cluster-support interface which was preserved after the treatment under oxidizing condition at 800^oC. The effect of high-temperature (800^oC) redox-cycle on the soot oxidation activity showed that the large Ag_3Sn particles once formed during reductive condition were re-dispersed to Ag metal nanoparticles under oxidizing conditions owing to self-regeneration.

Wu et al. [2011] studied MnOx-CeO_2 mixed oxide and found that Al_2O_3-modified (ie. MnOx-CeO_2-Al_2O_3) mixed oxides catalyst exhibits the superior thermal stability mainly ascribed to retarding the sintering of MnOx and CeO_2 crystallites as well as preventing the phase separation of MnOx-CeO_2 solid solutions to some extent. Lin et al. [2013] also prepared MnOx-CeO_2-Al_2O_3 by three different methods and found MnOx-CeO_2 deposition on Al_2O_3 powders as appropriate modification method that preserves the synergetic Mn-Ce effect than the other two methods (Al^{3+} doping at the precursor stage, mechanically mixture of the oxide powders).

Yeqin et al. [2013] also worked on the incorporation of transition metals (Cr, Mn, Fe, Co, Ni, and Cu) into CeO_2 can greatly enhance its low-temperature redox properties, resulting in high catalytic activity for soot oxidation. In particular, the amount of active oxygen released at 200-400^oC plays an important role in improving combustion performance. Doping CeO_2 with structure promoter metals will mainly improve its moderate-temperature redox properties, which leads to a higher combustion rate without affecting soot ignition temperature. Modification of CeO_2 with alkali and alkaline earth metals can improve its ability to catalyze soot oxidation because the low melting points of the resulting materials improve the contact between soot and catalyst, rather than by changing the redox properties of CeO_2.

2.2.2 Spinel Catalysts for Soot Oxidation

The spinel oxide structure of chemical formula, AB_2O_4 always formed by a nearly close packed face centered cubic array of oxygen ions with tetrahedral A and octahedral B sites partly occupied by cations A and B [Hamedoun et al. 1986]. However, these materials may change their crystal structure for an inverse spinel or mixed spinel structure, a process that depends on the particle size. Shangguan et al. [1996] prepared Spinel-type catalysts, characterized and tested for potential applications in the treatment of diesel exhaust emissions. In the experiments carried out by on spinel catalyst, ACr_2O_4 (A=Cu, Mg, Co, Mn), $CoMn_2O_4$, AFe_2O_4 (A=Cu, Co, Ni) in NO/O_2 atmosphere under tight contact shows catalytic performance of the spinels depended significantly on the constituent metal cations and $CuFe_2O_4$ was the most excellent catalyst with the intermediate ignition temperature of soot (295^{o}C).

Fino et al. [2006] tested $CoCr_2O_4$ catalyst for the simultaneous NO and soot abatements. The authors found that the prepared catalyst shows activity better than the perovskite catalyst ($LaCrO_3$) and this success is related in part to the particular synthesis method adopted-solution combustion synthesis, which enables the formation of fine catalyst crystals (< 20 nm) and a very foamy structure of their agglomerates maximizing the number of contact points between catalyst and soot. Lin et al. [2009] performed redox reaction between soot and NO*x* under lean-burn condition by $BaAl_2O_4$ and found it an effective catalyst. The reaction processes were investigated and discussed in detail. The interaction of nitrate with oxygenated intermediates C(O) on soot surfaces was found to be the key step of soot oxidation by NO*x* over $BaAl_2O_4$. The C(O) intermediates are produced from the direct oxidation of soot by NO*x* and O_2. On the other hand, the nitrates can come from NO_2 adsorption or from oxidation of nitrites by oxygen. Hence, the presence of O_2 promotes nitrates formation, and thus soot oxidation and NO*x* reduction.

Zawadzki et al. [2009] performed experiments on the Cu containing $ZnAl_2O_4$ spinel and suggests that impregnated catalyst, 5%Cu/$ZnAl_2O_4$ is more active than the bare support ($ZnAl_2O_4$) and substituted catalyst ($Zn_{0.95}Cu_{0.05}Al_2O_4$) which is attributed to increase in reducibility of copper. Zawadzki et al. [2011] showed $CoAl_2O_4$ spinel catalyst has activity for soot combustion similar to that of the Pt/Al_2O_3 reference catalyst. This soot combustion activity of $CoAl_2O_4$ is attributed to its high NO*x* chemisorption capacity, which allows fast NO oxidation to NO_2.

2.2.3 Hydrotalcite Catalysts for Soot Oxidation

Hydrotalcite (HT) and Hydrotalcite-like compounds (HTlcs), also called layered double hydroxides (LDH), are widely applied in catalysis and adsorption. These materials can be chemically expressed by the formula $[M(\text{П})_{1-x}\ M(\text{Ш})_x(OH)_2]^{x+}[(A^{n-})_{x/n}.mH_2O]^{x-}$ where M(П) represents any divalent metal cation, M(Ш) any trivalent metal cation, and A^{n-} an anion; the value of x is equal to the molar ratio of M(П)/(M(П)+M(Ш)) and generally ranges between 0.2 and 0.4 [Vaccari 1998].

Zhang et al. [2007] tested soot oxidation on MgAlO and potassium promoted MgAlO hydrotalcite and found marked decreases in all characteristic temperatures. He also studied catalyst stability for soot oxidation over used KNO_3/K_2CO_3/MgAlO and found retained activity with slight enhancement in characteristics temperature. In TGA experiment for soot oxidation in absence of air, no exothermic peak was observed for MgAlO, while the potassium promoted samples gave an exothermic peak indicating unambiguously bulk O_2 is incorporated in soot combustion in potassium promoted samples. MgAlO did not show any catalytic activity in the absence of gaseous oxygen, while in the presence of air it decreased soot combustion temperature slightly. This suggests that, in the presence of MgAlO, the reaction occurs through the adsorption of gaseous O_2 on the catalyst surface, generating an active species that is capable of oxidizing soot. Li et al. [2009] also examined for the promotional effect of K on CoMgAlO hydrotalcite and found that the addition of K increases the amount of active Co sites as well as the mobility of bulk lattice oxygen species due to the low melting point of K-containing compounds, the low valence of K^+ and the strong interaction between K and Mg(Al). The K-promoted catalysts decrease the activation energy of soot combustion from 207 to 160 kJ/mol.

Recently, Wang et al. [2012] prepared a series of CuMgAl hydrotalcites derived oxides by co-precipitation and calcination methods and tested for the simultaneous catalytic removal of NO_x and soot. The Cu incorporation into hydrotalcites strongly influenced the crystal phases, porous structures and redox properties of the catalysts. The enhancement of redox properties after Cu incorporation and/or the promotion effects of NO_x species result in the high activity and selectivity for soot oxidation. Among the catalysts studied, CuAlHT calcined at 800°C sample shows the best activity with T_i = 260°C.

2.2.4 Perovskite Catalysts for Soot Oxidation

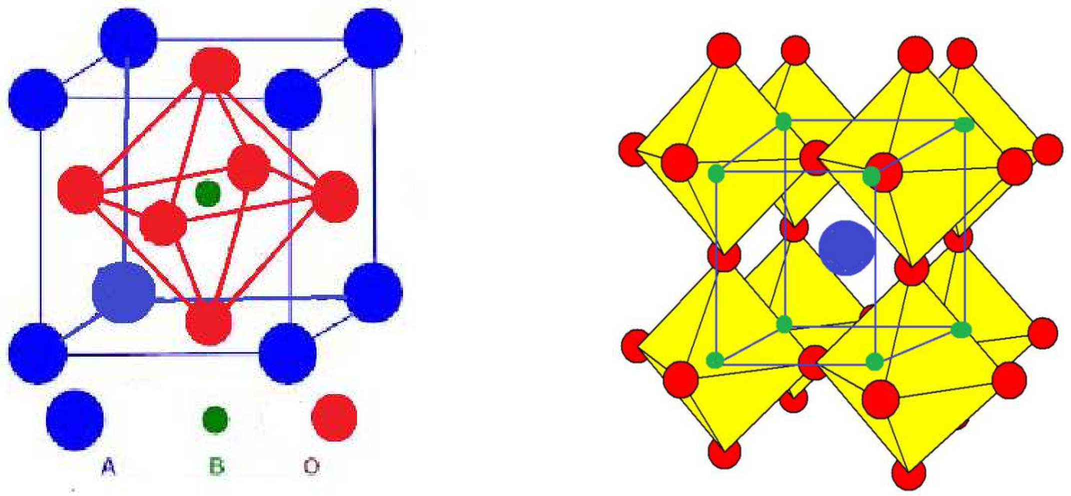
Perovskite oxides appear as an important family of catalysts and show potential as effective soot oxidation catalyst for the diesel particulate filter (DPF) because of their low cost, high thermal stability, and tailoring flexibility [Labhsetwar et al. 2007, Xiaoying 2012, Bin 2010, Li 2013].

2.2.4.1 Perovskite Catalysts Structure and Properties

The mineral perovskite ($CaTiO_3$) was first discovered by Gustav Rose in 1839 and is named after the Russian mineralogist, Count Lev Aleksevich Von Perovski [Screen 2007]. The general chemical formula for perovskite compounds is ABO_3 [Kaliaguine 2006, Zhang et al. 2007], where “A” and “B” are two cations of very different sizes, and O is the anion that bonds to both, as shown in Figure 2.1a [Ciambelli et al. 2007, Zhang et al. 2006]. “A” is rare earths (La, Ce, Pr) alkali and alkaline earths (Cs, Sr, Ba, Ca) larger (radius of A ~ 0.90 Å,) than "B" transition metals (Co, Fe, Cu, Ni, Mn, Cr, Al) (radius of B ~ 0.51 Å). In the idealized cubic unit cell of such a compound, type "A" atom sits at cube corner positions (0, 0, 0), type "B" atom sits in body centre position (1⁄2, 1⁄2, 1⁄2) and oxygen atoms sit at face centered positions (1⁄2, 1⁄2, 0). "A" ion (co-ordinated by 12 oxygen) fits into the dodecahedral site of the framework (Figure 2.1b). The "B" ion (surrounded by six oxygen in octahedral coordination) can be 3d, 4d, and 5d transition metal ions [Civera et al. 2007, Zhong et al. 1997]. A large number of metal ions having a different valence can replace both A and B ions. By appropriate formulation many desirable properties can be tailored [Russo et al. 2009, Zhang et al. 2006]. 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 a 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 favor the catalytic activity in oxidation reaction because they increase the lattice oxygen mobility [Zhong et al. 1997]. When a perovskite is heated at high temperature, oxygen vacancies can be formed. The oxidation activity of perovskite has been ascribed to their ionic conductivity, to oxygen mobility within their lattice, their reducibility, and their oxygen sorption properties [Russo et al.

2009]. The released oxygen species can be divided into two categories depending on temperature (i) oxygen: low temperature superficial species, weakly chemisorbed on the surface of the perovskite, desorbed in the 300-600^{o}C range and related to surface oxygen vacancies; (ii) oxygen: high temperature interfacial one, less easy to desorb and therefore more bound to the perovskite structure, desorbed above 600^{o}C and is related to the bulk nature of the catalyst [Patel & patel 2012].



(a) (b)

Figure 2.1 (a) ABO_3 ideal cubic perovskite structure **(b)** Perovskite framework

Perovskite can be classified as pure perovskite like ABO_3, single substituted perovskite similar to $A_{1-x}A'_xBO_3$ or $AB_{1-x}B'_xO_3$ and double substituted perovskite such as $A_{1-x}A'_xB_{1-y}B'_yO_3$. The application of different types of perovskite catalysts for diesel soot oxidation is described below:

2.2.4.2 Pure Perovskite Catalysts

Such as $LaCoO_3$ [Tanaka et al. 2003, Yang et al. 1998, Russo et al. 2008, Li et al. 2010, Li et al. 2012a, Li et al. 2012b, Jiménez et al. 2010, Pecchi et al. 2013], $LaFeO_3$ [Pena et al. 2001], $LaCrO_3$ [Ifrah et al. 2007], $SrCoO_3$ [Dhakad et al. 2008], etc., provide excellent catalytic activity for soot oxidation. Dhakad et al. [2008] reported the exceptional thermal stability and stable activity under repeated cycles of $SrCoO_3$ catalyst. Pecchi et al. [2013] synthesized the solids $MNbO_3$ (M = Li, Na, K, Rb) by a citrate method, calcined at 450-750°C, and characterized by various techniques. It was observed that catalytic activity depends mainly on the nature of the alkaline metal and the calcination temperature. At the calcination temperature of 650 °C the catalytic activity follows an atomic number dependent order, namely: $KNbO_3 > NaNbO_3 > LiNbO_3$. As described by Pena et al. [2001] around 90% of the metallic elements of the periodic table are stable in a perovskite structure. This gives the possibility of synthesizing multi-component perovskites by the partial substitution of cations in positions A and B giving compounds with the formula $A_{1-x}A'_xB_{1-x}B'_xO_3$.

2.2.4.3 Single-substituted Perovskite

Catalysts with general formula $A_{1-x}A'_xBO_3$ or $AB_{1-x}B'_xO_3$, where A' and B' may be alkali or alkaline earth or noble metals fall under single-substituted perovskite. Fino et al. [2003] prepared layered-type La-K-Cu-V perovskite catalysts, by the citrates method and characterized by BET, XRD, and reported that it is an effective catalyst in the simultaneous removal of soot and nitrogen oxides. Jiménez et al. [2010] studied the effect of Ca substitution in $La_{1-x}Ca_xFeO_3$ perovskites on the catalytic activity for soot combustion and found a significant enhancement of the catalytic activity by increasing the degree of La^{3+} substitution by Ca^{2+} with an optimum value of (x = 0.4) in the perovskites.

Zhao et al. [2009] prepared a series of the $La_{1-x}Ce_xNiO_3$ perovskite catalysts for simultaneous removal of nitrogen oxides and diesel soot by the citric acid complexation method. The partial substitution of Ce for La increases the concentration of Ni^{2+}, enhancing the catalytic activities. The $La_{0.97}Ce_{0.03}NiO_3$ catalyst shows the highest activity. The capacity to store and release oxygen is one of the particular properties of ceria that makes this material exceptionally effective in several catalytic applications [Trovarelli et al. 1999]. The redox properties of the $Ce^{3+/4+}$ couple and the capacity of cerium oxide to exchange oxygen with the gas phase are also behind the good catalytic performance of ceria-based materials as soot combustion catalysts [Bueno-López 2013]. Perovskite-type catalysts with $SrCoO_3$ and $Sr_{0.8}Ce_{0.2}CoO_3$ compositions prepared by co-precipitation and other methods Dhakad et al. [2008] show excellent thermal stability and catalytic activity for soot oxidation, despite their low surface area and under the loose contact condition. Strontium titanates partially substituted with potassium ($Sr_{1-x}K_xTiO_3$, x = 0.1-0.5) prepared by the sol-gel citric acid method [Ura et al. 2011a] show that substitution of strontium by potassium lowers the temperature of soot ignition by 270^oC. The positive effect of potassium addition on the catalytic activity of strontium titanate in soot oxidation can be interpreted in terms of two mechanisms of potassium action: enhancement of oxygen surface mobility and oxygen vacancies formation in the oxygen sub lattice of perovskite structure depending on the potassium localization [Ura et al. 2011b]. The $La_{3.5}Ru_{4.0}O_{13}$ can be synthesized easily using the various synthesis methods and shows good catalytic activity for carbon oxidation, which is important for auto-exhaust applications related to regeneration of the DPF. The material possesses excellent thermal stability, which could be due to the presence of ruthenium in the more stable Ru^{4+} oxidation state in the perovskite structure [Labhsetwar et al. 2007]. Recently, Doggali et al. [2013] synthesized $Pr_{0.7}Sr_{0.2}K_{0.1}MnO_3$, Sr and K substituted praseodymium manganite-type perovskite for catalytic oxidation of diesel soot. The catalytic materials show good thermal stability, while their cost would also add to their potential for practical applications.

Nano-sized perovskite $La_{0.8}K_{0.2}MnO_3$ (LKMO) catalyst is prepared by citric acid complexation method [Wang et al. 2006]. The LKMO catalyst has a porous structure and shows a capture effect of soot and a catalytic activity for soot combustion. Nano-structured bulk Li-substituted La-Cr perovskites ($La_{0.8}Cr_{0.9}Li_{0.1}O_3$, $La_{0.8}Cr_{0.8}Li_{0.2}O_3$, and $La_{0.8}Cr_{0.7}Li_{0.3}O_3$) are prepared by the combustion synthesis method, in comparison with the reference $LaCrO_3$. The progressive increase in the Li content of the catalysts induces an increase in the catalytic activity for the diesel soot oxidation [Fino et al. 2006, Fino et al. 2003].

2.2.4.4 Double Substituted Perovskite

Catalysts with general formula, $A_{1-x}M_xB_{1-y}N_yO_3$ where M and N are alkali or alkaline earth or noble metals form double substituted perovskite. Li et al. (2010) prepared a series of nano-metric Fe-substituted $La_{0.9}K_{0.1}Co_{1-x}Fe_xO_{3-\delta}$ (x = 0, 0.05, 0.1, 0.2, 0.3) perovskite catalysts by citric acid complexation method for soot combustion. They reported that the partial substitution of Co^{3+} by Fe^{3+} in $La_{0.9}K_{0.1}Co_{1-x}Fe_xO_{3-\delta}$ (x = 0-0.3) perovskite catalysts largely improved the catalytic activity of the catalyst $La_{0.9}K_{0.1}CoO_{3-\delta}$ for soot combustion, NO_x storage, and simultaneous soot-NO_x removal. Among all the prepared catalysts the $La_{0.9}K_{0.1}Co_{0.9}Fe_{0.1}O_{3-\delta}$ perovskite was the most active one Li et al. [2010]. The K/Cu simultaneously substituted perovskite catalysts $La_{1-x}K_xCo_{1-y}Cu_yO_{3-\delta}$ possess much higher catalytic performance towards simultaneous No*x*-soot removal as compared with un-substituted $LaCoO_3$ and K or Cu single substituted perovskite catalysts [Li et al. 2012]. Li et al. [2012] proposed that there are mainly four reaction pathways: (i) soot oxidation on the solid–solid interface of the catalyst and soot by the active O^{2-} and O^{-} species which can be continuously supplemented by gaseous O_2 through the oxygen vacancies; (ii) NO oxidation to NO_2 on catalyst surface forming surface adsorbed species, which migrate to solid-solid boundary and oxidize the soot; (iii) adsorption and oxidation of gaseous NO to nitrite and/or nitrate species, which can oxidize the soot and give out the products CO_2 and N_2; and (iv) adsorption and oxidation of gaseous NO_2 to nitrate species, which can directly react with soot or decompose into NO*x* species during heating to take part in soot oxidation.

A series of dually substituted perovskite catalysts $La_{1-x}K_xCo_{1-y}Pd_yO_{3-\delta}$ (x = 0, 0.1; y = 0, 0.05) were synthesized by Guo et al. (2013) through sol-gel process, and employed for soot combustion in the presence of nitrogen oxides. The catalysts were characterized by N_2-sorption, XRD, XPS, SEM, HRTEM, XANES, EXAFS, H_2-TPR, soot-TPR, FTIR, and TG/DTA. The activity evaluation results show that among all catalysts $La_{0.9}K_{0.1}Co_{0.95}Pd_{0.05}O_{3-\delta}$ possesses the highest performance, exhibiting the lowest Ti and Tm (219^{o}C and 360^{o}C), the narrowest temperature range (Tm-Ti= 162^{o}C) and the lowest activation energy (93.6 kJ/mol) for soot combustion. The catalyst $La_{0.9}K_{0.1}Co_{0.95}Pd_{0.05}O_{3-\delta}$ shows relatively larger BET surface area, smaller crystallite size and higher dispersion of Pd.

2.2.4.5 Precious Metal Supported on Perovskite

Four $LaBO_3$ perovskite catalysts (B = Cr, Mn, Fe and Ni), supporting 2% by weight of gold, were prepared via the so-called Solution Combustion Synthesis (SCS) method. The performance of these catalysts, in powder form, was evaluated towards the simultaneous oxidation of soot and CO [Hong et al. 2008]. The 2 wt% Au-$LaNiO_3$ showed the best performance with a peak carbon combustion temperature of 431^{o}C and a half CO conversion of 156^{o}C. A series of perovskite type oxide catalysts ($La_{0.6}Ce_{0.4}CoO_3$) derived with Ag were prepared [Russo et al. 2008]. The influences of pre-treatment and Ag loading on catalytic activity for diesel soot oxidation were studied. An increase in activity with Ag addition was observed, especially with more than 5% Ag loading. It is claimed that this catalyst could be a promising candidate for the catalytic elimination of diesel soot. Substituted lanthanum magnate-type perovskites were synthesized following co-precipitation and a modified *in situ* method. These perovskites were supported on cordierite honeycomb with and without alumina washcoat. Alumina washcoated supports with lanthana pre-coat, were found suitable for the *in situ* synthesis of perovskites. This modified synthesis resulted in remarkable improvement in surface area while excellent catalyst adhesion was also observed. The catalyst composition was also promoted by a small amount of platinum, which resulted in improved catalytic activity [Labhsetwar et al. 2001].

2.2.4.6 Macroporous perovskite catalysts

It was found that the macro-porous catalysts showed higher catalytic activities for soot combustion than that of the corresponding nanometric sample. The macro-porous catalyst $La_{0.9}K_{0.1}CoO_3$ was the best candidate catalyst for soot combustion, the activity of which was as good as supported Pt catalysts [Zhang et al. 2009]. Three dimensionally ordered macro-porous (3DOM) $LaMn_{1-x}Fe_xO_3$ catalysts had good catalytic performances for diesel soot combustion and the main product of soot combustion was CO_2 whose selectivity values were almost above 97% for the 3DOM catalysts tested [Zheng et al. 2012]. Xu et al. concluded that 3DOM $LaCo_xFe_{1-x}O_3$ catalysts had improved catalytic performances for diesel soot combustion when compared with the particle perovskite-type catalysts. Among the studied samples, the 3DOM $LaCo_{0.5}Fe_{0.5}O_3$ catalyst had the highest catalytic activity for soot combustion [Xu et al. 2010]. Table 2.1 shows the literature at a glance for various perovskite catalysts preparation methods, experimental conditions for soot oxidation and important findings.

Table 2.1: The applications of perovskites catalysts in diesel soot emission control

Ref.	**Catalyst**	**Preparation method**	**Experimental Conditions**	**Remarks**
Dhakad et al. 2008	$SrCoO_3$ & $Sr_{0.8}Ce_{0.2}CoO_3$	Co-ppt	Catalyst/soot 95:5 & 66:33 Loose contact	$SrCoO_3$ has (T_i, T_{50} & T_f) at 300, 460 & 520^{o}C and $Sr_{0.8}Ce_{0.2}CoO_3$ has 241, 420 and 500^{o}C at 95:5 wt ratio
Russo et al. 2005	a)$LaCrO_3$, b)$La_{0.9}CrO_3$, c)$La_{0.8}CrO_3$, d)$La_{0.9}Rb_{0.1}CrO_3$ e)$La_{0.9}Na_{0.1}CrO_3$ f)$La_{0.9}K_{0.1}CrO_3$, g)$La_{0.8}Cr_{0.9}Li_{0.1}O_3$	SCS	Tight contact Carbon/Catal = 1/9 & silica pellet 150 mg Air flow rate 100NmL/min	$La_{0.8}CrO_3$ showed the best activity with T_{50}=441^{o}C, Larger Na, K, Rb make them host at A site while Li at B.
Ifrah et al. 2007	La-Cr-O perovskite	Co-ppt	5% of O_2 in He, flow rate of 6 L/hr	activity order; $LaCrO_3$ (470^{o}C) > 94%$LaCrO_3$-6%La_2O_3 (475^{o}C) > La_2CrO_6 (481^{o}C) > 86%$LaCrO_3$ 14%La_2CrO_6 (497^{o}C) > La_2O_3 (477^{o}C).
Labhsetwar et al. 2001	$La_{0.6}Ce_{0.4}Co_{1-x}M_xO_3$ M= Fe, Ni, Cu.	Co-ppt	Loose contact Catal/soot = 10/1, 10%O_2 in N_2, flow rate 100cm^3/ min	5%Ag/$La_{0.6}Ce_{0.4}CoO_3$ showed the best activity with T_{50}=400^{o}C
Wu et al. 2009	$LaMn_{0.7}Ni_{0.3}O_{3+\lambda}$ (LMN_3)	Citric acid sol-gel	Loose contact 10%O_2 in N_2, 1,000 ppm NO	Reduction peak, 370^{o}C for $LaMnO_3$ (LMNO)(Mn^{4+}-Mn^{3+}) decreases with Ni doping, it shifts to higher temp after ageing due to particle growth.
Li et al. 2010	$La_{0.9}K_{0.1}Co_{1-x}Fe_xO_{3-\delta}$ LKCFy where y is wt % of Fe present	Citric acid sol-gel	Tight contact, Soot/catal = 1/20, 600ppm NO, 10%O_2 in N_2, flow rate= 100ml/ min^{-1}.	$La_{0.9}K_{0.1}Co_{0.9}Fe_{0.1}O_3$ showed the best activity with T_{50} =395^{o}C
Li et al. 2012a	$La_{1-X}K_XCo_{1-Y}Cu_YO_{3-\delta}$	Citric acid sol-gel	Tight contact, Soot/ catal= 1/20, 500 ppm NO, 10%O_2 in N_2 flow rate = 100ml/ min^{-1}	$La_{0.9}K_{0.1}Co_{0.9}Cu_{0.1}O_3$ showed the best activity with T_{50} = 360 ^{o}C
Li et al. 2012b	$La_{1-X}K_XCo_{1-Y}Ni_YO_{3-\delta}$	Citric acid sol-gel	Tight contact, Soot/ catal = 1/20, 500ppm NO, 10%O_2 in N_2, flowrate=100mlmin^{-1}	$La_{0.9}K_{0.1}Co_{0.9}Ni_{0.1}O_3$ showed the best activity with T_{50} = 370 ^{o}C
Pena & Fierro 2001	$KNbO_3$, $NaNbO_3$ $LiNbO_3$.	Citric acid sol-gel	Tight contact Soot/catal = 1/4,12% O_2 in He , Flow rate =180 mL/min	Catalytic activity order: $KNbO_3$ > $NaNbO_3$ > $LiNbO_3$.
Hong et al. 2008	$La_{1-x}K_xCo_{1-y}Pd_yO_{3-\delta}$ (x=0, 0.1; y = 0,0.05) & Pd/Al_2O_3	Citric acid sol-gel	Tight contact Soot/catal = 1/15 10%O_2 in N_2 flow rate = 100 mL/min	Activity order: $La_{0.9}K_{0.1}Co_{0.95}Pd_{0.05}O_{3-\delta}$ > $LaCo_{0.95}Pd_{0.05}O_{3-\delta}$ > Pd/$La_{0.9}K_{0.1}CoO_{3-\delta}$ > Pd/$LaCoO_3$>$La_{0.9}K_{0.1}CoO_{3-\delta}$ > $LaCoO_3$ > Pd/Al_2O_3
Mishra & Prasad 2015	$LaCoO_3$ $La_{0.9}Sr_{0.1}CoO_3$ $La_{0.9}Sr_{0.1}Co_{0.5}Ni_{0.5}O_3$ $La_{0.9}Sr_{0.1}Co_{0.5}Cu_{0.5}O_3$ $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_3$	Citric acid sol-gel	Tight contact Soot/catal = 1/10 flow rate = 150 mL/min	Activity order: $La_{0.9}Sr_{0.1}Co_{0.5}Fe_{0.5}O_3$ > $La_{0.9}Sr_{0.1}Co_{0.5}Cu_{0.5}O_3$ > $La_{0.9}Sr_{0.1}Co_{0.5}Ni_{0.5}O_3$ > $La_{0.9}Sr_{0.1}CoO_3$ > $LaCoO_3$

2.3 Mechanism for Catalytic Oxidation of Soot

There are two explanations given for catalytic combustion of soot particle. First one, less accepted, is electron transfer mechanism, suggests a redistribution of the pi electrons in the carbon matrix. Second one, which is widely accepted, is oxygen transfer mechanism where the catalyst is considered as a renewable activated oxygen donor. Catalysts are capable of delivering active oxygen species to the reacting carbon particulate which help in lowering activation energy for soot oxidation. Oxygen chemisorbed on the catalyst surface is the active oxygen center for soot oxidation. Higher the capacity of catalyst to deliver active oxygen species the superior is the activity of catalyst toward carbon oxidation.

Transient thermal analysis studies (oxygen TPD plots) were quite helpful in understanding the behavior of the catalysts toward soot oxidation. Lower the temperature at which oxygen species are desorbed the higher the soot combustion activity. From this standpoint, Fino et al. [2006] compare the activity order of spinel catalysts toward soot combustion as $CoCr_2O_4$> $MnCr_2O_4$> $CoFe_2O_4$. Comparing the TPD plots of the $CoCr_2O_4$ and $MnCr_2O_4$ catalysts, Fino et al. [2006] suggested that the temperature at which the oxygen species can be released is even more important than the amount of such oxygen species.

Physical contact between soot and catalyst is also an important parameter for soot oxidation. Without physical contact the catalyst could still act as a renewable activated oxygen donor. But activated oxygen radicals recombine themselves too rapidly in the gas phase before reaching carbon. For supported catalysts it was proposed that activated oxygen could migrate on the support to the carbon. This is called the spillover effect theory [Neri et al. 1997]. Otherwise the catalyst could also catalyze other oxidation reaction of the gas phase. It could accelerate the transformation of NO to NO_2, which can oxidize the carbon. Or it can oxidize the CO from the thermal carbon oxidation to CO_2, releasing some heat that can accelerate the carbon combustion. In affirmation with this fact Fino et al. [2006] comparing the results of the runs performed under loose or tight contact conditions and found that there are 60 to 80°C temperature difference for soot combustion, higher value for loose contact.

2.3.1 Soot-Catalyst Contacts

Catalyst-soot contact is a key element for the performance of soot oxidation [Van Setten et al. 2000]. Some catalytic elements are mobile enough under reaction condition to ‘wet’ the soot surface and effectively disperse their activity and move to non-reacted soot. Other catalysts remain as discrete particles but are mobile enough to maintain contact with the soot. More static catalytic elements require the soot to contact them. Van Setten et al. has described two modes of soot catalyst contact, loose and tight [Van Setten et al. 2000]. For experimental studies the soot-catalyst mixture, in an appropriate ratio, are milled in an agate mortar for ‘‘tight contact’’ or mixed carefully with a spatula for ‘‘loose contact’’. Loose contact mode is found to best simulate contact of soot and catalyst in a DPF environment. Tight contact provides higher reaction rates and may correspond closer to certain types of soot oxidation catalyst, such as fuel borne catalysts [Van Setten et al. 2000].

In order to find out the difference between the loose contact and tight contact, these mixtures were examined by SEM, as shown in Figure 2.2. For tight contact, almost all the catalyst surface was covered by finely dispersed soot particles. However, for loose contact, only a small portion of the soot was attached to the catalyst. In other words, most of the soot particles were separated from the catalyst. This might be the reason why the starting temperatures of soot oxidation for both loose and tight contacts were the same but the peak temperatures were quite different.

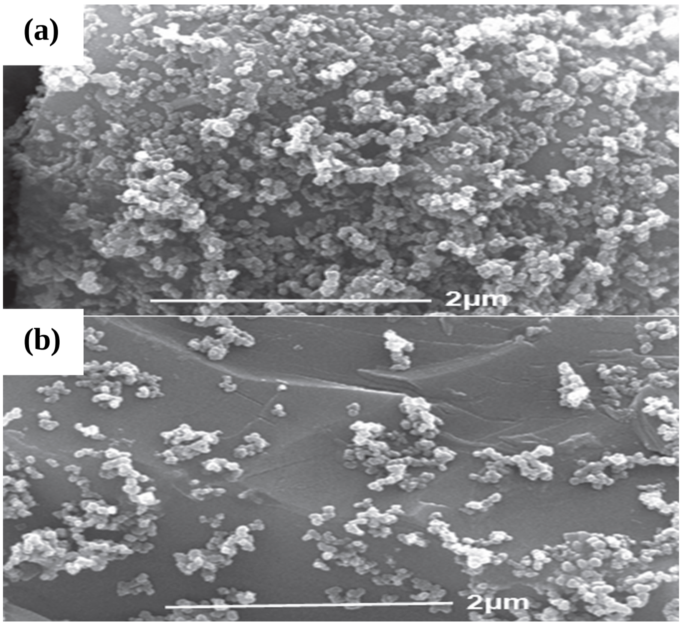


Figure 2.2 SEM images of catalyst-soot mixture with (a) tight contact and (b) loose contact

To see the effect of catalyst-soot contact Wang, et al. [2011] prepared three types of contact: "tight contact" by a mortar and pestle; "wet loose contact" by dropping a ethanol slurry solution of soot to catalyst powder followed by drying at 90 ^oC; "dry loose contact" by shaking the reactor tube for 20 seconds. The result of different $K_2Ti_2O_5$ catalyst-soot contacts by temperature programmed oxidation (TPO) test is shown in Figure 2.3.

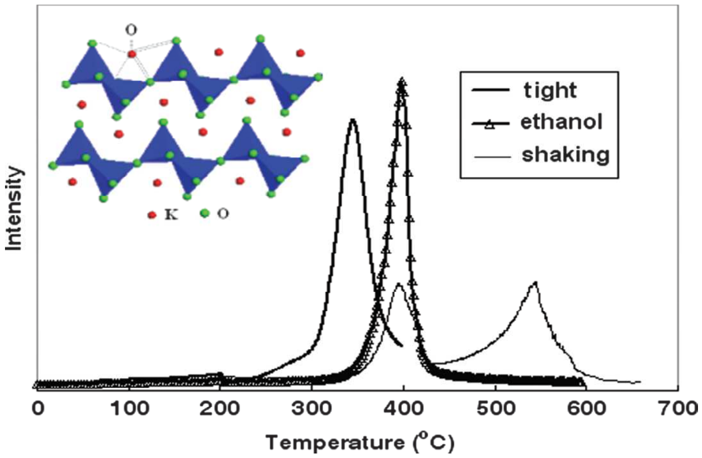


Figure 2.3 Temperature programmed oxidations of soot over $K_2Ti_2O_5$ with different types of contact. The inset shows the atomic structure of $K_2Ti_2O_5$.

Tight contact exhibited the lowest peak temperature, *Tp* at 340 °C. The other two types of loose contact showed the same *Tp* at 390 °C, except that the *in-situ* shaked showed an additional peak with *Tp* at 540 °C. The same patterns of two peaks with higher *Tp* located at 550-570 °C were also observed when catalyst-soot was mixed with spatula [Tikhomirov et al. 2006]. The higher *Tp* was caused by insufficient contact between the catalyst and soot.