

CHAPTER - 3

LITERATURE REVIEW & OBJECTIVES

3.1 Literature Review

The different types of catalysts have been used for simultaneous control of diesel soot and NO_x. PGM catalysts are highly active but unfortunately they are expensive and due to low abundance are 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 research has been carried out to develop cheaper and efficient PGM free catalysts for simultaneously diesel soot and NO_x removal. PGM free catalysts reviewed in this treatise for soot oxidation and NO_x reduction are discussed under the following categories.

- i) Perovskite catalyst
- ii) Noble metals catalyst
- iii) Spinel catalyst
- iv) Hydrotalcite catalyst
- v) Mixed metal oxides catalyst

A wide variety of catalysts like noble metals, spinel structured, hydrotalcite, mixed metal oxides, perovskite structured catalysts have shown activity for the simultaneous control of diesel soot and NO_x. In the subsequent sections work done by various researchers has been summarized.

3.1.1 Perovskite Catalyst

Perovskites are mixed-metal oxides that are attracting much scientific and application interest owing to their low price, adaptability, and thermal stability, which often depend on bulk and surface characteristics. The perovskites have been explored

for a variety of environment-related and energy-related applications, including automobile exhaust purification, fuel cells, N₂O decomposition. These materials have been extensively explored for their catalytic, electrical, magnetic, and optical properties. They are promising candidates for the photocatalytic splitting of water and have also been extensively studied for environmental catalysis applications. Oxygen and cation non-stoichiometry can be tailored in a large number of perovskite compositions to achieve the desired catalytic activity, including multifunctional catalytic properties. Despite the extensive uses, the commercial success for this class of perovskite-based catalytic materials has not been achieved for vehicle exhaust emission control or for many other environmental applications. With recent advances in synthesis techniques, including the preparation of supported perovskites, and increasing understanding of promoted substitute perovskite-type materials, there is a growing interest in applied studies of perovskite-type catalytic materials. The various perovskite catalysts were studied based on Co, Mn, Na, and Fe and their substituted compositions for their catalytic activity in terms of simultaneous reduction of diesel soot-NO_x. The enhanced catalytic activity of these materials is attributed mainly to their altered redox properties, the promotional effect of co-ions, and the increased exposure of catalytically active transition metals in certain preparations [Teraoka *et al.*, 2000, Wei *et al.*, 2006, Liu *et al.*, 2010, and Wang *et al.*, 2010].

3.1.1.1 Perovskite-Type Catalyst Structure

The general chemical formula for perovskite compounds are ABO₃ and A₂BO₄. These are a very important class of functional materials that exhibit a range of stoichiometries and crystal structures. Where “A” and “B” are two cations of very different sizes, and O is the anion that bonds to both, as shown in Figure 3.1a. “A” is rare earths (La, Ce, Pr) alkali and alkaline earths (Cs, Sr, Ba, Ca) larger ($r_A \sim 0.90 \text{ \AA}$),

than “B” transition metals (Co, Fe, Cu, Ni, Mn, Cr, Al) ($r_B \sim 0.51 \text{ \AA}$). 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). “An” ion (co-ordinated by 12 oxygens) fits into the dodecahedral site of the framework (Figure 3.1b). The “B” ion (surrounded by six oxygen’s in octahedral coordinations) can be 3d, 4d, and 5d transition metal ions (35, 36). 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.

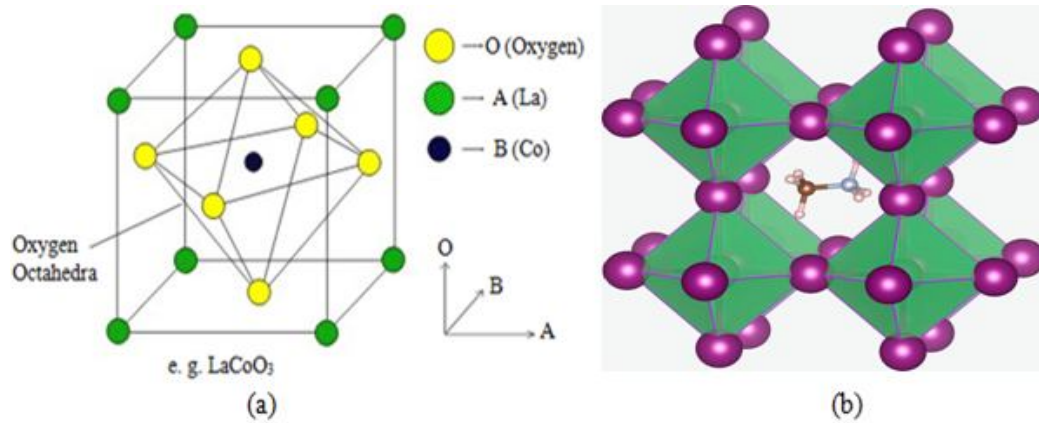


Figure 3.1 (a) ABO_3 ideal cubic perovskite structure and (b) the perovskite framework

The stability of the perovskite phases is largely governed by geometric considerations that are best summarized by the Goldschmidt tolerance factor (t), which is used to define the range of the ionic radii of A and B defined by Equation 3.1, which is applicable at room temperature.

$$t = \frac{(r_A + r_O)}{\sqrt{2} (r_B + r_O)} \quad (3.1)$$

Equation 3.2 is for an ideal perovskite, where t is unity

$$(r_A + r_O) = \sqrt{2} (r_B + r_O) \quad (3.2)$$

Where r_A , r_B , and r_O are the respective radii of A, B, and oxygen ions. The value of the Goldschmidt tolerance factor must be in the range from 0.8 to 1.00 nm in order to obtain the perovskite structure [Li *et al.*, 2016].

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.

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, their reducibility, and their oxygen sorption properties. 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°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°C and is related to the bulk nature of the catalyst.

The application of the various type of perovskite substituted catalyst is used for simultaneous control NO_x and soot i.e.

- i. Pure perovskite ABO₃
- ii. single substituted perovskite catalyst (A_{1-x}M_xBO₃ or AB_{1-x}M_xO₃)
- iii. double substituted perovskite catalyst (A_{1-x}M_xB_{1-x}N_xO₃)
- iv. Double Perovskite (A₂BO₆)
- v. Precious metal supported perovskite catalyst
- vi. Macro-porous perovskite catalyst

In general, the A-site is usually occupied by a lanthanide ion, usually La, and the B-site is occupied by a transition metal ion. For an un-substituted perovskite, the catalytic activity is predominantly attributable to the metal ion at the B site. The A site metal has a strong effect on stability and provides the possibility to improve catalyst performance through synergistic interactions with metals at the B site [Navarro *et al.*, 2007]. Partial substitution at the A and/or B site with alternative A' and B' metal ions results in the composition A_{1-x}A'_xB_{1-y}B'_yO₃ of the dually substituted perovskite structure. This substitution induces structural modifications related to the generation of crystal lattice defects and oxygen vacancies, thus allowing the improvement in thermal stability and catalytic performance.

Perovskite-type catalysts have drawn the great attention of the researchers, due to their higher chemical, thermal and structural stability than the single oxides, lower cost and higher thermal stability than precious metals, and diverse catalytic performance. The partial replacement of the A-site ions by alkali metal and rare-earth metal in perovskite-structure enhances the activity and selectivity for simultaneous removal of NO_x and soot [Teraoka *et al.*, 2001].

Hong *et al.*, 2000 reported enhancement in the catalytic activity of LaCoO_3 catalyst for carbon particulate oxidation and NO conversion due to partial substitution of A-site with Cs. A slight decrease in the soot ignition temperature was observed for the Cs – substituted catalyst in B- site in the order $\text{Co} > \text{Mn} > \text{Fe}$ with almost same NO conversion. However, NO conversion decreased by increasing the NO concentration and decrease in soot ignition temperature was observed for NO concentration more than 1000ppm. The authors have reported $\text{La}_{0.75}\text{K}_{0.25}\text{MnO}_3$ oxides catalyst obtained by the citric acid-ligated method is good candidate catalysts for the soot particle removal reaction, and the combustion temperatures of soot particle are between 285°C and 430°C when the contact between catalysts and soot is loose, and their catalytic activities for the combustion of soot particle are as good as supported Pt catalysts

Wang *et al.*, 2008 studied the activity of alkali- substituted nanometric $\text{La}_{1-x}\text{K}_x\text{CoO}_3$ perovskite-type oxides, prepared by citric acid complexation method under “loose” contact condition. The high activity of the catalyst was proposed to be attributed to the formation of high valance ion (Co^{4+}) at B-sites, the formation of oxygen vacancy, and formation of oxide catalysts with nano-metric size. The role of particle size in the catalytic performance of catalyst was also examined. Catalyst with the particle size in nano-metric range was much more active than the ones with the particle size in the range of micrometers. Best activity was shown by $\text{La}_{0.7}\text{K}_{0.3}\text{CoO}_3$ catalyst with the oxidation temperature for soot particle over the catalyst between 289 and 461°C , and the NO_x to N_2 conversion 34.6% under loose contact conditions.

Wang *et al.*, 2010 studied the influence of partial replacement of La^{3+} ions of LaMnO_3 perovskite oxide by Ag^+ ions and reported that $\text{La}_{0.7}\text{Ag}_{0.3}\text{MnO}_3$ catalyst produced the good catalytic performance for simultaneous removal of NO_x and diesel

soot particulates under loose contact conditions with a maximum NO_x conversion of 72%. The authors concluded that the partial substitution of Ag⁺ for La³⁺ at A- site ions enhanced the catalytic activity due to the increase of oxygen vacancy concentration and the over-stoichiometric oxygen content. The oxygen vacancy enhanced the adsorption and activation of NO or molecular oxygen, while over-stoichiometry oxygen accelerated the mobility of oxygen in the catalyst. Thus, Ag substitution not only accelerated the combustion rate of soot particulates but also promotes the reduction rate of NO.

Bin *et al.*, 2011 synthesized a series of La_{1-x}K_xCoO₃ catalysts and reported performance of La_{0.6}K_{0.4}CoO₃ as the best with 41% NO conversion and lowest T_{ig} of 283°C soot conversion. A Co₃O₄ phase was reported to be produced by the excess K ions adhering to the perovskite crystals. The effect of potash (K) doping in perovskite catalysts on the activity and selectivity for simultaneous reduction of NO_x-soot is studied by several researchers (Fino *et al.*, 2006). A peculiar effect of potassium at optimum doping levels was observed in promoting the activity and the NO_x reduction selectivity for perovskite type of catalyst. The effect of K content was investigated in detail on perovskite-related La_{1-x}K_xCoO₃ and La_{2-x}K_xCu_{0.95}V_{0.05}O₄ and it was found that the catalytic property of catalyst became highest at an optimum composition.

Li *et al.*, 2010 prepared a series of La_{0.9}K_{0.1}Co_{1-x}Fe_xO_{3-δ} and the best results were found for x= 0.1 with T_{ig} of 251°C and X_{NO}= 12.5%. The Fe-substitution enhanced the mobility of surface lattice oxygen improving their catalytic activity for soot combustion and the formation of high valence ion (Fe⁴⁺) at B-site increased the oxidation of NO to NO₂ facilitating the simultaneous soot-NO_x reaction. The K/Cu simultaneously substituted perovskite catalysts La_{1-x}K_xCo_{1-y}Cu_yO_{3-δ} possess much higher catalytic performance towards simultaneous NO_x-soot removal as compared with un-substituted LaCoO₃ and K or Cu single substituted perovskite catalysts 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 [Arens *et al.*, 2001].

Li *et al.*, 2012 reported that the K/Cu simultaneously substituted perovskite catalysts $La_{1-x}K_xCo_{1-y}Cu_yO_{3-\delta}$ possessed much higher catalytic performance towards soot combustion, NO_x storage and simultaneous NO_x -soot removal than the unsubstituted $LaCoO_3$ and K or Cu single substituted perovskite catalysts. Among all the catalysts, the nanometric $La_{0.9}K_{0.1}Co_{0.9}Cu_{0.1}O_{3-\delta}$ exhibited the highest catalytic activity, showing the lowest soot combustion characteristic temperature (T_m) of $360^\circ C$, the highest NO_x storage capacity (NSC) of $284 \mu mol.g^{-1}$ and the highest NO_x reduction of 32%. Better redox properties of the dually substituted perovskite were found to be attributed to enhanced oxygen vacancies, the larger amount of surface adsorbed oxygen species and more Co^{4+} ions, due to the K/Cu simultaneous substitution.

Li *et al.*, 2012 reported that the nanometric substituted perovskite catalysts $La_{1-x}K_xCo_{1-y}Ni_yO_{3-\delta}$ ($x = 0, 0.1$; $y = 0, 0.05, 0.1$) synthesized by citric acid complexation method was showing higher performance for soot combustion, NO_x storage and simultaneous NO_x -soot removal has been achieved by the simultaneous substitution of La^{3+} and Co^{3+} by K^+ and Ni^{3+} in $LaCoO_3$ perovskite. Among all the catalysts, the

$\text{La}_{0.9}\text{K}_{0.1}\text{Co}_{0.95}\text{Ni}_{0.05}\text{O}_{3-\delta}$ with a size of ~ 80 nm, exhibits the highest performance, showing a T_m of 367°C , a NSC of $269 \mu\text{mol g}^{-1}$ and a NO_x reduction percentage of 21%.

Teraoka *et al.*, 1996 revealed that perovskite-type and Cu-based K_2NiF_4 -type oxides catalyze the simultaneous removal of NO_x and diesel soot particulate and that these perovskite related oxides are superior to transition metal simple oxides and $\text{Pt}/\text{Al}_2\text{O}_3$ with respect to the selectivity to NO_x reduction. The catalytic activity evaluated from the ignition temperature of the soot and the selectivity to NO_x reduction changed significantly by the sort and composition of A- and B-site cations.

Teraoka *et al.*, 2001 reported that mixed metal oxides (e.g., La–K–Mn–O system) demonstrate activity toward the simultaneous removal of NO_x and soot. Activity toward soot oxidation and NO_x -reduction selectivity was strongly dependent on potassium content. Fino and Specchia [2003] have prepared nano-structured PrCrO_3 on CeO_2 through combustion synthesis, which showed even better catalytic activity than $\text{Pt}/\text{Al}_2\text{O}_3$ when the catalyst was coated onto a monolith.

Teraoka *et al.*, 2001 showed that for the $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ series, the activity and N_2 selectivity of the catalysts are dependent significantly on K content and that the oxides with K contents varying in the range of 0.2-0.25 exhibited the highest activity and selectivity. Wang *et al.*, 2008 also studied nano-sized perovskite-type $\text{La}_{1-x}\text{K}_x\text{MnO}_3$ (LKMO) catalyst. Soot is significantly reduced after the LKMO catalyst treatment. $\text{La}_{0.8}\text{K}_{0.2}\text{MnO}_3$ showed best comprehensive catalytic performance. Peng *et al.*, 2006 further substituted a portion of Mn with Cu and evaluated the porous $\text{La}_{1-x}\text{K}_x\text{Mn}_{1-y}\text{Cu}_y\text{O}_3$ oxides with highest NO conversion efficiency to N_2 of 54% and T_{ig} (soot ignition temperature) of 260°C for $\text{La}_{0.8}\text{K}_{0.2}\text{Mn}_{0.95}\text{Cu}_{0.05}\text{O}_3$.

Peng *et al.*, 2007 reported a highly efficient catalyst ($\text{La}_{0.8}\text{K}_{0.2}\text{Cu}_{0.05}\text{Mn}_{0.95}\text{O}_3$) for simultaneous removal of NO_x and diesel soot. The catalytic properties of this catalyst were tested under simulated diesel engine exhaust using temperature programmed reduction (TPR) and it was found that this catalyst showed promise for the simultaneous removal of NO_x and diesel soot 54.8%.

Mescia *et al.*, 2008 synthesized nano-structured perovskite-type lanthanum ferrites $\text{La}_{1-x}\text{A}_x\text{Fe}_{1-y}\text{B}_y\text{O}_3$ ($\text{A} = \text{Na}, \text{K}, \text{Rb}, \text{B} = \text{Cu}$). The best compromise between soot and NO_x abatement was shown by the La-K-Cu-FeO_3 catalyst which exhibits the highest catalytic activity towards complete combustion of black carbon and the highest NO conversion activity of 79% at 384°C (Figure 3.2). In succession, Lie *et al.*, 2013 reported that the nanocrystalline $\text{La}_{0.8}\text{K}_{0.2}\text{Fe}_{0.5}\text{Mn}_{0.45}\text{Co}_{0.05}\text{O}_3$ (LKFMCO) catalyst exhibits a high soot conversion catalytic activity.

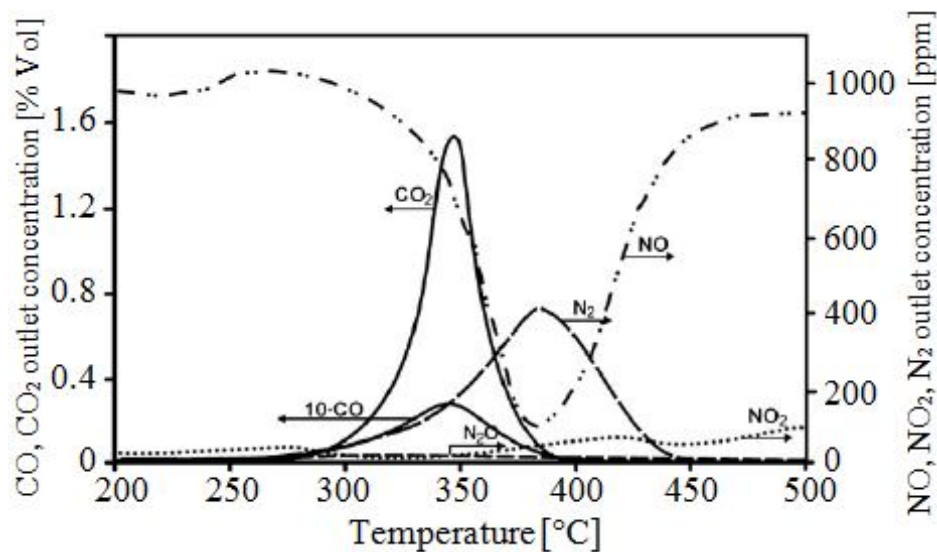


Figure 3.2 Outlet gaseous species concentration in a TPSR run performed with La-K-Cu-FeO_3 catalyst

Teraoka *et al.*, 2001 also reported that Co, Mn, and Fe perovskite-type and Cu-based K_2NiF_4 -type oxides (all with La^{3+} partial substituted by alkaline metal or alkaline

earth metal cations) catalyze the simultaneous removal of NO_x and diesel soot particulates and that these perovskite-related oxides are superior to transition metal simple oxides and Pt/Al₂O₃ with regards to their selectivity towards NO_x reduction. Fe-based perovskites have also displayed good activity for soot combustion and NO_x reduction. The coordination radius of iron ion is larger than that for cobalt ion, so the substitution of Co by Fe can promote the release of active oxygen in the reaction.

Teraoka *et al.*, 1995 reported that the result of the temperature-programmed reaction (TPR) over La_{0.9}K_{0.1}Cu_{0.7}V_{0.3}O₃. The formation of carbon dioxide due to the oxidation of the soot and the reduction of NO, to nitrogen took place at the same temperature range, evidencing the occurrence of the simultaneous removal of NO, and soot. The sudden drop of carbon dioxide and nitrogen formation at higher temperatures is of course due to the exhaustion of the charged soot.

Liu *et al.*, 2002, 2007, 2010, and 2011 studied thoroughly simultaneous reduction of soot-NO_x over perovskite catalysts and published a series of papers. In 2002, the authors reported improved activity with silver loading on La_{0.6}Ce_{0.4}Co_{1-x}M_xO₃ (M=Fe, Ni, Cu) catalyst with an optimal loading of 5%. They found that highly dispersed Ag⁺ not only favors absorption- activation of NO on the catalyst but also introduces in the form of anionic vacancies favoring absorption-activation of oxygen on the catalyst and transport of lattice and surface-oxygen species. Further in 2007, they prepared La_{2-x}K_xCuO₄ catalysts by auto-combustion method using citric acid as a ligand, the partial substitution of K for La at A-site leads to the increase of the concentrations of Cu³⁺ and oxygen vacancy. The best formulations of the catalyst is La_{1.5}K_{0.5}CuO₄, which shows T₁₀, T₅₀, T₉₀ as 376, 438, 487°C and S_{N2} is 22%, respectively, for simultaneous removal of NO_x and soot under loose contact conditions.

Next in 2008, the authors synthesized nanometric La-Na-Cu-O perovskite-like complex oxide catalysts by sol-gel auto-combustion method and reported that the catalysts have good catalytic activities for the simultaneous removal of diesel soot and NO_x under loose contact conditions. Additionally in 2010, the authors have prepared two double layers catalysts La_{0.6}K_{0.4}CoO₃/Al₂O₃ + W/HZSM-5 and La_{0.5}K_{0.5}MnO₃/Al₂O₃ + W/HZSM-5, where the alumina supported perovskites prepared by impregnation method, show the peak temperature of soot combustion as 421 and 448°C, respectively. It was decreased by more than 200°C compared with the peak temperature of the bare soot combustion (without catalyst). The conversion of NO to N₂ was above 70%; the temperature of the HC total combustion was below 364°C, and the maximum selectivity of CO₂ production was above 97%.

Jiménez *et al.*, 2010 reported that the effect of Ca substitution in La_{1-x}Ca_xFeO₃ perovskites on the catalytic activity for soot combustion and found a significant enhancement of the catalytic activity by increasing the degree of La³⁺ substitution by Ca²⁺ with an optimum value of (x = 0.4) in the perovskites.

Guo *et al.*, 2013 doped a small amount of Pd into LaCoO₃ perovskite to partially substituting the Co ions and the La ions at A-sites were also partially substituted by K to obtain a series of Pd-containing dually substituted perovskite catalysts (La_{1-x}K_xCo_{0.95}Pd_{0.05}O_{3-δ}) and compared the activity with a series of supported catalysts Pd/La_{1-x}K_xCoO_{3-δ}. Formulation, La_{0.9}K_{0.1}Co_{0.95}Pd_{0.05}O_{3-δ} give the best result for NO reduction 26.7% at 360°C. The dually substituted sample was reported to possess the large specific surface area, good reducibility, and the high NO oxidation. The Pd ions with high valence (Pd³⁺, Pd⁴⁺) in distorted octahedral coordination environment (in dually substituted system) were found to be more active for NO oxidation and soot combustion than the Pd²⁺ ions with square-planar coordination symmetry (in supported

catalyst) as they greatly increased the concentration of reactive NO₂ species during the reaction, enhancing soot combustion.

Ma *et al.*, 2011 prepared a series of La_{2-x}A_xB_xNi_{1-x}O₃ with the simultaneous substitution of both the sites A and B sites of the catalyst. The La_{1.8}Sr_{0.2}NiO₃ catalyst showed the best activity with a maximum yield of N₂ up to 71% just at 300°C with lowest ignition temperature of 160°C.

Zhao *et al.*, 2009 studied a series of catalyst La_{1-x}Ce_xNiO₃ (0 ≤ x ≤ 0.05) and the results indicated that Ni²⁺ were the active centers. The partial substitution of Ce for La was found to be responsible for increasing the concentration of Ni²⁺, enhancing the catalytic activities. Among all, La_{0.97}Ce_{0.03}NiO₃ catalyst showed the highest activity. The maximum productivity of N₂ and the ignition temperature were 11.8% and 300°C, respectively. He also reported that only less than 5% La can be substituted by Ce in the LaNiO₃ catalyst due to the instability of LaNiO₃ for higher substitution. The instability was confirmed by the presence of crystalline CeO₂ and NiO phases besides the perovskite phase.

Zhao *et al.*, 2009 prepared a series of La₂Ni_{1-x}Cu_xO₃ (0 ≤ x ≤ 1.0) catalysts displaying the single orthorhombic K₂NiF₄-like phases and reported that Cu-doping increased the orthorhombic distortion and decreased the capability of the catalyst to accommodate non-stoichiometric oxygen. The B-site nickel ions were found to be varying in oxidation state gradually from Ni²⁺ to Ni³⁺ with increasing Cu content. Cu²⁺ substitutes for B-site Ni²⁺ leads to an increase of the reducibility of lattice oxygen, improving catalytic activities. The La₂Ni_{0.4}Cu_{0.6}O₃ catalyst with proper ratio of Ni³⁺ and Ni²⁺ (0.63) showed the highest activity. The maximum conversion of nitrogen oxide to molecular nitrogen achieved was 15.6% and the ignition temperature decreased from

440 to 246°C, as compared with the non-catalyzed soot combustion reaction. The application, results, preparation method and literature review of perovskite-type catalysts for simultaneous control of soot and NO_x from diesel exhaust emissions described in Table 3.1.

Table 3.1 The application of perovskite-type catalysts used for simultaneous catalytic reduction of soot and NO_x emissions from diesel engine exhaust

Catalyst and Preparation method	Experimental Parameter	Remarks	Reference
La _{1-x} K _x Co _{1-y} Pd _y O _{3-δ} (x=0,0.1; y=0,0.05), Nitrate, Sol-gel	Soot/Cat mixture = 1/15, Flow 100 cc/min, 400ppm NO _x + 10% O ₂ , Tight contact, Heating - 5°C/min, Temp.- 25-600°C	La _{0.9} K _{0.1} Co _{0.95} Pd _{0.05} O _{3-δ} the best cat, T _i , T ₅₀ , T _f = 219, 331, 387°C; X _{NO} = 26.7%, x _{soot} = 100%	Guo <i>et al.</i> , 2013
La _{1-x} K _x Co _{1-y} Cu _y O _{3-δ} (x=0,0.1; y=0,0.03), Nitrate, Sol-gel	Soot/Cat = 1/20, Tight contact, total flow 100 cc/min, 600ppm NO _x + 10% O ₂ , Heating - 10°C/min , Temp.-100-700°C	La _{0.9} K _{0.1} Co _{0.9} Cu _{0.01} O _{3-δ} best cat, T _i , T _{m-NO} = 300, 360°C; X _{NO} =32%	Li <i>et al.</i> , 2012
La _{1-x} K _x Co _{1-y} Ni _y O _{3-δ} (x=0,0.1; y=0,0.05), Nitrate, Sol-gel	Soot/Cat = 1/20, Tight contact, Flow 100 cc/min, 500ppm NO _x + 10% O ₂ , Heating - 10°C/min, Temp.- 100 - 700°C	La _{0.9} K _{0.3} Co _{0.95} Ni _{0.05} O _{3-δ} the best cata, T _i , T _{m-NO} = 345, 367°C; X _{NO} = 21%	Li <i>et al.</i> , 2012
La _{2-x} A _x B _x Ni _{1-x} O ₄ (A=Sr, Ba; B=Mn, Fe), Nitrate, Sol-gel	Soot/Cat = 1/10, Tight contact, Flow 50 cc/min, 1.0 vol. % NO + 5 vol. % O ₂ , Heating - 5°C/min, Temp. 200 - 800°C	La _{1.8} Sr _{0.2} NiO ₄ best cata., T _i , T _{m-NO} , T _P = 160, 300, 400°C; X _{NO} = 72%	Ma <i>et al.</i> , 2011
La _{1-x} K _x CoO ₃ , LaCo _{1-y} Fe _y O ₃ Nitrate, Sol-gel	Soot/Cat = 1/10, loose contact, Flow 200 cc/min, 800ppm NO + 10% O ₂ , Heating - 2°C/min, Temp. - 100-800°C	La _{0.6} K _{0.4} CoO ₃ the best cata., T _i , T _{m-NO} =283, 382°C; X _{NO} = 41% ; S _{CO2} = 96.2%	Bin <i>et al.</i> , 2011

La _{0.9} K _{0.1} Co _{1-x} Fe _x O _{3-δ} Nitrate, Sol-gel	Soot/Cat = 1/20, Tight contact; Flow 100 cc/min, 600ppm NO _x + 10% O ₂ , Heating - 10°C/min, Temp. - 100-700°C	La _{0.9} K _{0.1} Co _{0.9} Fe _{0.1} O _{3-δ} the best cat, T _i , T _{m-NO} , T _f = 251, 362, 429°C, X _{NO} =12.5%	Li <i>et al.</i> , 2010
La _{1-x} A _x Fe _{1-y} B _y O ₃ (A=Na,K, Rb) and B=Cu), nitrate, SCS method	Soot/Cat = 1/9, Tight contact; Flow 100 cc/min, 1000ppm NO + 10% O ₂ , Heating - 5°C/min, Temp. - 200-700°C	La-K-Cu-FeO ₃ the best Cat T _p =359°C; T _{m-NO} = 384°C X _{NO} =79%	Mescia <i>et al.</i> , 2008
La _{1-x} K _x Co _{1-y} Pd _y O _{3-δ} (x=0,0.1; y=0,0.05), Nitrate, Sol-gel	Soot/Cat = 1/15, tight contact, Flow 100 cc/min, 400ppm NO _x + 10% O ₂ , Heating - 5°C/min, Temp. - 25-600°C	La _{0.9} K _{0.1} Co _{0.95} Pd _{0.05} O _{3-δ} the best cat, T _i , T ₅₀ , T _f =219, 331, 387°C; T _{m-NO} = 371°C, X _{NO} = 26.7%.	Guo <i>et al.</i> , 2013
La _{1-x} K _x Co _{1-y} Cu _y O _{3-δ} (x=0,0.1; y=0,0.03), Nitrate, Sol-gel	Soot/Cat = 1/20, Tight contact; Flow 100 cc/min, 600ppm NO _x + 10% O ₂ , Heating - 10°C/min, Temp. - 100-700°C	La _{0.9} K _{0.1} Co _{0.9} Cu _{0.01} O _{3-δ} the best cat, T _i , T _{m-NO} = 300,360°C; X _{NO} = 32%	Li <i>et al.</i> , 2012

The highest conversion NO_x and temperature reported by various workers are: Wang *et al.*, 2012, 78.2% at 685°C. which is beyond the diesel exhaust temperature. Zhaoqiang Li *et al.*, 2012, 32% at 360°C which is comparatively less. Xiaosheng *et al.*, 2006 yield of NO to N₂ 54.8% also used extra reductant 5% H₂. Ma *et al.*, 2011, the yield of N₂ is up to 72% just at 300°C but they used 10% hydrogen as a reductant and Ni (precious metal) in at B position of spinel catalyst. Bin *et al.*, 2011, 41% at 382°C which is relatively less.

4.1.2 Noble Metal Catalysts

Noble metal catalysts have been widely used in many applications because of their high activity and selectivity. Palladium-based, platinum-based, Iridium Based, Gold-

based, and ruthenium-based bi-noble metal catalysts have activities for simultaneously removing soot and NO_x and their activities are greatly affected by combinations of novel metals. Ohtsuka *et al.*, 2001 reported that the bicomponent noble metal catalysts Rh-Pt and Pd-Pt were more active than the corresponding single noble metals. However, a controllable preparation of noble metal catalysts still remains as a significant challenge and the noble metals tend to be valuable [Piumetti *et al.*, 2015, Cheng *et al.*, 2017].

Setiabudi *et al.*, 2007 investigated two standard soot catalytic filter configurations and a so-called TU Deift (TUD) catalytic filter in laboratory equipment and evaluated it as a promising system for potential application for the simultaneous soot- NO_x removal. The first configuration, where Pt/SiC foam catalyst was placed upstream of soot loaded on SiC foam, showed the lowest NO₂-slip and the lowest soot oxidation rate. In the second configuration, soot was loaded on Pt/SiC foam, which gives rise to higher soot oxidation rate at the expense of a higher NO₂-slip. An improvement on the utilization of NO₂ with lower NO₂-slip was observed in the TUD catalytic filter in addition with the highest soot oxidation rate. As with all diesel particulates filter TUD catalytic filter up to 10% CO (around 50 ppm) is formed as soot combustion product, whereas for the miniaturization of the commercially available continuously regeneration trap (CRT) system at the same diesel soot oxidation rate 120-140 ppm CO is observed.

Castoldi *et al.*, 2006 investigated the potentiality of a typical Pt-Ba /Al₂O₃ NSR catalyst in the simultaneous removal of particulate matter (soot) and NO_x, and compared with that of a Pt/Al₂O₃ sample. The results showed that in presence of only oxygen, soot oxidation occurs slowly even .at a temperature as high as 400 °C. On the other hand, the presence of NO greatly increased the rate of soot conversion, which

became significant at 350°C. The capability of the Pt-Ba/Al₂O₃ and Pt/Al₂O₃ catalysts to accomplish the removal of NO_x in the absence and in the presence of soot was investigated under cycling conditions, i.e. alternating lean-rich phases according to the typical NSR strategy. It was found that the Pt-Ba/Al₂O₃ sample is able to simultaneously remove both soot and NO_x, as opposite to the Pt/Al₂O₃ catalyst which effectively performs the soot oxidation but is not able to remove gas phase NO_x to a significant extent. The presence of soot does not significantly affect the activity in the NO_x reduction of the PtBa/Al₂O₃ catalyst. The comparable level of activity in the soot combustion which was observed between the Pt/Al₂O₃ and the Pt-Ba/Al₂O₃ sample in spite of the fact that the ternary sample accomplishes the removal of NO_x in the gas phase was tentatively ascribed to specific oxidizing properties of the stored nitrate species.

Shuang *et al.*, 2012 reported that Pt-Mg/ Al₂O₃ catalyst derived from magnesium acetate exhibited a higher soot oxidation activity than that prepared with magnesium nitrate due to the larger Pt particle size on the catalyst. The large particle size of Pt improved the NO oxidation leading to the NO₂ formation which ultimately promoted the catalytic oxidation of soot. Also, Pt-Mg/ Al₂O₃ produced more amount of NO₂ in the temperature range of soot oxidation than Pt/Al₂O₃ catalyst with a similar Pt particle size, promoting the ignition of soot and thus confirming synergistic action of Pt and Mg for the NO oxidation activity and NO_x storage capacity of catalyst.

Miyoshi *et al.*, 1995 studied Pt-Ba-Al₂O₃.catalyst, and found that NO after being oxidized with oxygen reacts with Ba (storage component) to form a nitrate. The amount of NO storage capacity in such catalysts was reported to be strongly affected by the basicity resulting in more stable nitrates. NO_x absorbers reduced NO_x by more than 90%, however they were very sensitive to sulphur poisoning. This technology is still

under development. Specifically, SO₂ derived from the sulfur in the fuel can catalytically react with oxygen and then with the NO_x storage components, such as BaCO₃, forming stable sulphates (BaSO₄) and rendering the NO_x adsorbing capabilities of the system ineffective.

Lately, a three-dimensionally ordered macroporous (3DOM) Ce_{0.8}Zr_{0.2}O₂-supported platinum catalyst has also been synthesized [Wei *et al.*, 2012]. The 3DOM structure is presumed to improve the contact efficiency between catalyst and soot, and the synergistic effect between the metal and the support (Ce) increases the amount of active oxygen species delivered to the Soot. The 3DOM Pt/Ce_{0.8}Zr_{0.2}O₂ catalysts thus exhibited a high catalytic activity and thermal stability for soot combustion.

Zhu *et al.*, 2008 investigated the potentiality of Ir/ γ -Al₂O₃ catalyst for the simultaneous removal of soot and NO_x in the presence of O₂. The simultaneous removal paths are that the NO₂ formation, by the Oxidation of NO promotes the soot oxidation and the CO formation by the soot oxidation reduces NO. Furthermore, the adsorbed-dissociation of NO₂ also promotes the NO_x reduction, Ir/ γ -Al₂O₃ proved to be more effective catalyst for the simultaneous removal of soot NO_x than Pt/ γ -Al₂O₃. Support material also has an impact on the catalytic activity of Ir/ γ -Al₂O₃. For soot oxidation the activity order was recorded as Ir/ZSM-5 > Ir/ γ -Al₂O₃ > Ir/SiO₂ and for NO_x reduction the order was Ir/ γ -Al₂O₃ > Ir/ZSM-5 > Ir/SiO₂ [Gu *et al.*, 2012].

Matarrese *et al.*, 2006 studied Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ LNT catalysts for simultaneous removal of soot and NO_x, when operating under cycling conditions, i.e. alternating lean-rich phases according to the typical LNT strategy. The data showed that the storage capacity of the two investigated systems is comparable, but the K-containing sample was far more active in the soot combustion than the Ba-based catalyst. The high

activity of the K-containing catalyst in the soot combustion was proposed to be related to the function of mobile potassium surface compounds which enhance the catalyst-soot contact and improve activity.

Although, noble metal catalysts have been employed in various commercial emission control techniques, emphasis on the development of cheap and efficient noble-metal-free catalysts is being given due to the high cost and their inability to simultaneous removal of soot and NO_x in the presence of SO₂ as discussed above. Though some platinum supported metal oxide were found to be sulphur resistant but the cost problem still survived [Lin *et al.*, 2009]. The application, results, preparation method and literature review of noble metal catalysts for simultaneous control of soot and NO_x from diesel exhaust emissions described in Table 3.2.

Table 3.2 The application of noble metal catalysts used for simultaneous catalytic reduction of soot and NO_x emissions from diesel engine exhaust

Catalysis Preparation Technique	Experimental Parameters	Remarks	Author & Year
Pt-Mg/ Al ₂ O ₃ , wetness, acetate, Impregnation	Soot/Cat =1/10, Loose contact, heating 10°C/min, Flow 500 cc/min, 1000ppm NO + 10% O ₂ , Temp. - 100-500°C	Pt-Mg/ Al ₂ O ₃ prep from Mg-Ac the best, T ₁₀ , T ₅₀ = 330, 432°C, S _{Co} > 98%	Shuang <i>et al.</i> , 2012
Pt/Ir/ γ-Al ₂ O ₃ , wetness Impregnation with H ₂ IrCl ₆ .6H ₂ O	Soot/Cat=1/10, Loose contact, Heating 4°C/min, Flow 100 cc/min, 420ppm NO + 4.4% O ₂ , Temp. - 100-750°C	1% Ir/ γ-Al ₂ O ₃ , best cat T ₁₀ , T ₅₀ , T ₉₀ = 442, 452, 625°C, S _{Co} =6%	Gu <i>et al.</i> , 2010
Pt-Ba/ Al ₂ O ₃ , acetate, wet Impregnation method	Soot/Cat=1/9, Loose contact, Heating 15°C/min, Flow 100 cc/min, 1000 ppm, NO + 3% O ₂ , Temp. - 100 -800°C	Barium improves soot combustion, X _{Soot} =55% (350°C), 100% (400°C)	Matarrese <i>et al.</i> , 2006

3.1.3 Spinel Catalysts

Spinel generally refers to the metal oxides having general formula $A_xB_{3-x}O_4$ (where A = a divalent cation like Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd; B= a trivalent cation like Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Ni etc.) with stoichiometric or even non-stoichiometric compositions, have recently attracted great interest in electrochemical energy storage systems (ESSs). The spinel-type transition metal oxides exhibit outstanding electrochemical activity and stability, and thus, they can play a key role in realizing cost-effective and environmentally friendly ESSs [Liu *et al.*, 2003]. The normal structures are cubic closed packed oxides with one octahedral and two tetrahedral site per formula unit. B^{3+} ions occupy half the octahedral holes, while A^{2+} ions occupy one-eighth of the tetrahedral holes. The spinel that is most popularly known is $MgAl_2O_4$ as shown in Figure 3.3.

Teraoka *et al.*, 1996 studied simultaneous removal of NO_x and diesel soot particulate in the presence of excess oxygen with ternary AB_2O_4 . The catalyst studied were ACr_2O_4 (A = Cu, Co, Mn), $CoMn_2O_4$ and AFe_2O_4 (A = Cu, Co, Ni) and it was found that the catalytic performance was considerably dependent on the metal cations used. The performance of $CuFe_2O_4$ spinel catalyst was reported better than that of simple metal oxides and their mixtures with high selectivity for N_2 formation and low ignition temperature ($\sim 285^\circ C$). Higher selectivity for N_2 of $CuFe_2O_4$ than $CuO-Fe_2O_3$ mixture was ascribed to -Cu-O-Fe- structure which promotes N_2 formation.

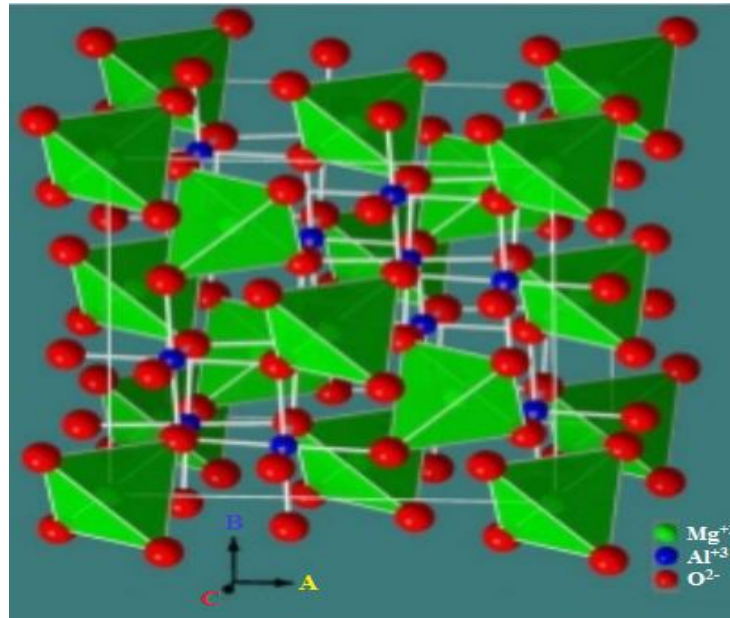


Figure 3.3 Crystal Structure of Spinels

Shangguan *et al.*, 1996 investigated ternary AB_2O_4 spinel oxides for simultaneous removal of NO_x and diesel soot particulate in the presence of excess oxygen. The catalytic performance of the spinels depended significantly on the constituent metal cations and $CuFe_2O_4$ was the most excellent with the highest selectivity to nitrogen formation, lowest selectivity to nitrous oxide and the intermediate ignition temperature of soot. They suggested that the coordination state of metal cations was of less importance and that the catalytic performance was almost exclusively determined by constituent metal cations.

In succession, Shangguan *et al.*, 1998 prepared a series of $Cu_{1-x}A_xFe_2O_4$ ($A = Li, Na, K, Cs, V, Pt$) catalysts and investigated the effect of doping. Comparison with the unsubstituted $CuFe_2O_4$ revealed that Cs substitution enhanced the activity for soot combustion without altering selectivity to N_2 formation, K promoted both the activity and selectivity, Na increased the activity but decreased the selectivity, whereas, Li substitution resulted in the deterioration of both the activity and selectivity. Thus, it was concluded that K substituted catalyst promoted the catalytic activity for soot- NO_x

reaction the most. The amount of dopant also played important role in effecting the catalyst performance. Highest activity for soot combustion and selectivity for N₂ formation was obtained for x=0.05.

Liu *et al.*, 2003 confirmed the activity of Cu_{0.95}K_{0.05}Fe₂O₄ by loading it on DPF (diesel particulate filter). The formation of CO₂ and the reduction of NO_x were observed in the temperature range of 150-600°C with T_{ig} =380°C and 15% NO_x reduction. The ignition and exhaustion temperatures of PM was found to be decreased as the order NO >O₂ >NO+O₂.

Fino *et al.*, 2003 reported that layered-type perovskite catalysts (A_{2-x}A'_xB_{1-y}B'_yO_{4±δ}, where A, A' = La, K and B, B' = Cu, V), prepared by the citrates method, the La_{1.8}K_{0.2}Cu_{0.9}V_{0.1}O₄ catalyst was giving outstanding NO abatement efficiencies and low soot oxidation.

Fino *et al.*, 2006 prepared nanostructure spinel-type oxides catalysts AB₂O₄ (where A = Co and Mn, and B = Cr and Fe) which proved to be effective in the simultaneous removal of soot and NO_x in the temperature range of 350-450°C. The activity order for soot combustion was found to be CoCr₂O₄>MnCr₂O₄>CoFe₂O₄, while that for NO_x reduction was CoFe₂O₄>CoCr₂O₄>MnCr₂O₄. The best compromise between soot combustion and NO_x reduction was reported by CoCr₂O₄ catalyst with 36% conversion of NO_x into N₂. The predominant catalytic combustion activity of the chromate catalysts was proposed to be attributed to the higher concentration of superficial, weakly chemisorbed oxygen, which contributes actively to soot combustion.

Szailer *et al.*, 2006 found that BaAl₂O₄ has high NO_x storage ability because of the strong Ba-Al bond. Later, Lin *et al.*, 2009 confirmed that BaAl₂O₄ catalyze the reaction between soot and NO_x under lean-bum conditions, promoting simultaneous

NO_x reduction to N₂ and soot oxidation to CO₂. In the presence of O₂, the catalyst promoted NO adsorption to form nitrites and nitrates. The interaction of nitrate with oxygenated intermediates C (O) which are produced from the direct oxidation of soot by NO_x and O₂ was found to be the key step of soot oxidation by NO_x over BaAl₂O₄. CoAl₂O₄ spinel catalyst also exhibited an activity for soot combustion reaction similar to that of Pt /Al₂O₃ reference catalyst [Zawadzki *et al.*, 2011]. The catalyst also displayed high NO_x chemisorptions capacity leading to rapid NO oxidation to NO₂. The application, results, preparation method and literature review of spinel type catalysts for simultaneous control of soot and NO_x from diesel exhaust emissions described in Table 3.3.

Table 3.3 The application of spinel type catalysts used for simultaneous catalytic reduction of soot and NO_x emissions from diesel engine exhaust

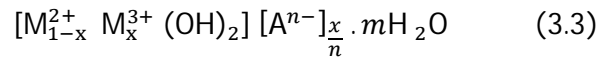
Catalysis Preparation Technique	Experimental Parameters	Remarks	Author & Year
BaAl ₂ O ₄ , nitrates, calcined at 873°C	Soot/Cat= 1/15, Tight contact; heating - 5°C/min, Flow 100 cc/min, 5000 ppm, NO + 10% O ₂ , Temp: 200-800°C	T _i =510°C, S _{N2} (max)=62%	Lin <i>et al.</i> , 2009
Nanostructured spinel-type oxide catalysts AB ₂ O ₄ (where A = Co and Mn, and B = Cr and Fe), prepared by the SCS method	Soot/Cat = 1/9, Tight contact; Heating - 5°C/min, 1000 ppmv NO, 10 vol% O ₂ , He = balance, Temp: 100-750°C	The activity order for soot combustion was found to be CoCr ₂ O ₄ > MnCr ₂ O ₄ > CoFe ₂ O ₄ , whereas the activity order for NO _x reduction was CoFe ₂ O ₄ > CoCr ₂ O ₄ > MnCr ₂ O ₄ . Best activity below 400°C	Fino <i>et al.</i> , 2006
CoCr ₂ O ₄ , MnCr ₂ O ₄ , CoFe ₂ O ₄ , nitrate, combustion synthesis	Soot/Cat = 1/9, Tight contact; Heating 5°C/min, Flow 100 cc/min, 1000 ppm, NO + 10% O ₂ , Temp: 200-700°C	CoCr ₂ O ₄ best cat, T _m = 396°C, X _{No} = 36%	Fino <i>et al.</i> , 2008
CuFe ₂ O ₄ , acetates sol-gel	Soot/Cat = 1/19, Tight contact; Heating 10°C/min, Flow 20 cc/min, 0.5 NO+5% O ₂ , Temp: 100 - 700°C	T _i , T _{m-NO} = 285,410°C, X _{No} =35%	Shangguan <i>et al.</i> , 1996

3.1.4 Hydrotalcite Catalyst

Hydrotalcite is a naturally occurring layered mineral, discovered in Sweden in 1842, of chemical formula: $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ [Cavani *et al.*, 1991]. The name hydrotalcite comes from its resemblance with talc ($Mg_3Si_4O_{10}(OH)_2$), and from its high water content. Similar to talc, the hydrotalcite mineral can be easily crushed into a white powder. Hydrotalcite occurs in nature in foliated and contorted plates and/or fibrous masses [Cavani *et al.*, 1991]. From a crystallographic point of view, this mixed magnesium and aluminium hydroxycarbonate possesses the trigonal structure of brucite, i.e., magnesium hydroxide $Mg(OH)_2$. Hydrotalcite layers are built of octahedral units in which a divalent or trivalent cation is placed in the center of an octahedron and six OH^- groups are placed in the corners of the octahedron (Figure 3.4 a). As with brucite, octahedral units are linked by edges, forming parallel layers. Depending on the arrangement of the layers, the hydrotalcite structure may have rhombohedral or hexagonal symmetry, in which the unit cell is built up from three and two hydrotalcite layers, respectively. For both naturally occurring and synthetic hydrotalcites, the rhombohedral symmetry is generally more common.

In the hydrotalcite brucite-like layers, a part of the divalent magnesium cations has been isomorphously replaced by trivalent aluminium cations. Such substitution is possibly due to the similar ionic radii of Mg^{2+} and Al^{3+} . Thanks to this substitution, the brucite-like layers of hydrotalcite are positively charged. This charge is compensated by carbonate anions present in the interlayer spaces. Water molecules complete the voids in the spaces between the hydrotalcite layers [Evans *et al.*, 2006; Rives *et al.*, 2010 and Forano *et al.*, 2013]. A schematic representation of hydrotalcite structure is presented in Figure 3.4 (b).

Shortly after the discovery of hydrotalcites, a large number of minerals with different compositions but the same hydrotalcite-like structures were developed. Currently, the name hydrotalcite (hydrotalcite-like compounds–HTs, layered double hydroxides–LDHs) is used to describe a large group of naturally occurring minerals and synthetic materials that possess the typical layered structure of hydrotalcite. The general formula of such compounds can be represented as [Forano *et al.*, 2013]:



where M^{2+} , M^{3+} are di- and tri-valent cations; A-interlayer anions; and x -mole fraction of trivalent cations. The part $[M_{1-x}^{2+} M_x^{3+} (OH)_2]$ describes the composition of brucite-like layers and $[(A^{n-})_x \cdot mH_2O]$ describes composition of interlayer spaces.

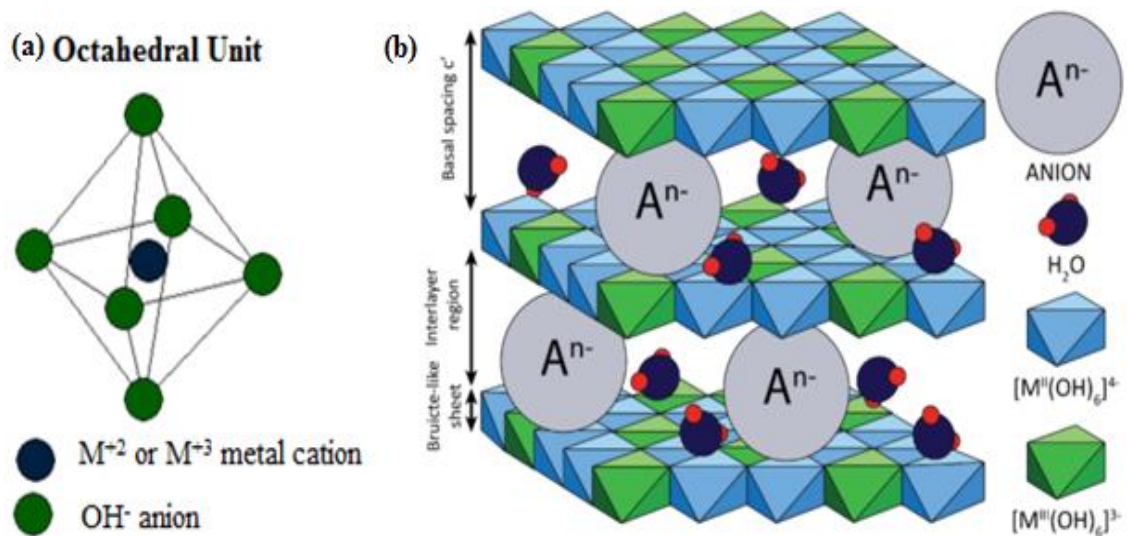


Figure 3.4 (a) The octahedral unit of brucite-like layers in an hydrotalcite structure and (b) Schematic representation of the hydrotalcite structure

Hydrotalcite-derived compounds (HTlcs) modified by transition metal ions have exhibited excellent redox properties owing to their large surface areas, basic properties, high metal dispersions and high thermal stability [Li *et. al.*, 2009, Meng *et. al.*, 2009]. The constituting metal species, amount of constituent species and calcinations

temperature of the catalysts have phenomenal effect on their redox performances. At higher temperatures hydrotalcites can be transformed into mixed metal oxides or spinels, which are excellent catalysts or catalyst support.

Wang *et al.*, 2007 reported that calcinations of Co-Al mixed oxides (CAO) prepared from hydrotalcites (HT) at 500°C and 800°C, results into a non-stoichiometric spinel phase. The properties were found to be affected by the Co content and calcinations temperature. Among all catalyst with the Co/Al ratio of 4 and calcinations temperature of 800°C showed a medium activity ($T_i = 290^\circ\text{C}$) and high selectivity to N_2 formation ($S [\text{N}_2] = 3.5\%$).

It is well known that the catalysts doped with alkali metals, such as potassium, are much more active for the catalytic combustion of soot than the undoped ones [Milt *et al.*, 2009, Ura *et al.* 2011; Li *et al.*, 2009]. The presence of K increases the mobility of surface oxygen species on the catalysts [Xu *et al.*, 2011], and enhances the activity. Co-based perovskite, mixed oxides and hydrotalcite-derived oxide catalysts have displayed excellent catalytic oxidation ability [Dai *et al.*, 2012].

Li *et al.*, 2009 evaluated a series of K-promoted hydrotalcite-derived CoMgAlO catalysts for soot combustion, NO_x storage and simultaneous soot- NO_x removal. Addition of potassium to the CoMgAlO catalyst accelerated soot combustion such that the temperature (T_m) for maximum soot conversion lowered by at least 50°C. Moreover, soot facilitated the NO_x reduction over the catalysts calcined at 500-700°C. The K-containing catalyst calcined at 600°C not only showed the highest soot combustion rate, but also the maximum NO_x reduction percentage of 32% which was thought to be ascribed to the high surface K/Co atomic ratio and the strong interaction between K and Co. In situ DRIFTS revealed that NO is readily oxidized to NO₂ and stored as nitrates

over K-promoted catalysts, which are reduced by soot efficiently, [Shangguan *et al.*, 1997].

Dai *et al.*, 2012, doped CoMgAlO catalyst with oxygen storage and activation materials like cerium oxide. It was reported that $\text{Co}_{2.5}\text{Mg}_{0.5}\text{Al}_{1-x}\text{Ce}_x\text{O}$ hydrotalcite-derived catalysts (CMACex) with different Ce/Al atomic ratios exhibited better activity than the unsubstituted-CoMgAlO catalyst. Ce-substitution was found to increase the specific surface area, the redox properties and the amount of surface lattice oxygen species of the catalyst. Also, it was found that NO is readily oxidized to NO_2 and stored as nitrates over Ce-substituted catalysts, which very reactive intermediates for simultaneous NO_x -soot removal. Among the catalysts, CoMgAlCeO had the lowest maximal soot oxidation rate temperature ($T_{\text{max-soot}}$) of 384°C for the, largest NO_x storage capacity ($336 \mu\text{mol g}^{-1}$), and the largest NO_x reduction percentage of 15.4%.

Mn-based oxides possess novel catalytic activity, thus extensively investigated by many researchers [Tikhomirov *et al.*, 2006, Saab *et al.*, 2007, Escribano *et al.*, 2008, Li *et al.*, 2009, Qi *et al.*, 2003]. As a combination, Li *et al.*, 2010 prepared a series of hydrotalcite-derived Mn-containing catalysts, namely $\text{Mn}_x\text{Mg}_{3-x}\text{AlO}$ ($x=0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0$) for the simultaneous soot- NO_x elimination. $\text{Mn}_{1.0}\text{Mg}_{2.0}\text{AlO}$ proved to be most proficient in promoting simultaneous soot- NO_x reduction. It was found that Mg_2MnO_4 and MnAl_2O_4 phases co-existed for $x \leq 5$. The existence of Mn^{4+} in Mg_2MnO_4 , was proposed to contribute the formation of ionic nitrate, meanwhile, the Mn^{2+} in MnAl_2O_4 is proposed as the active site for the reduction of NO_x by soot. Both of the features promoted the NO_x removal process.

Meanwhile, Zhang *et al.*, 2007 found that KNO_3 or K_2CO_3 can increase the catalytic activity of Mg-Al hydrotalcite-derived mixed oxides for soot combustion.

Takahashi *et al.*, 2007 also reported that the NO_x storage performance of the potassium-based NO_x storage material could be improved at high temperature by using hydrotalcite-derived MgAl₂O₄ spinel as support. Thus, a series of hydrotalcite-derived K/MnMgAlO catalysts were synthesized and the effect of K- loading on simultaneous soot-NO_x removal was examined [Li *et al.*, 2012]. In situ DRIFTS results indicated that optimal amount of K can facilitate the formation of mono-dentate nitrate, which shows higher reactivity with soot than nitrite, chelating bi-dentate nitrate and ionic nitrate species, Also, a new phase K₂Mn₄O₈ formation was discovered, which was found to be highly active for NO_x reduction by soot. The phase possessed more active surface lattice oxygen species, which could easily oxidize NO to NO₂, making the NO_x be stored as nitrates on K species, and subsequently reduced by soot.

Hydrotalcites derived mixed oxides CuAlO were found to show good activity for simultaneous catalytic control of soot and NO_x due to the higher redox performance [Kannan *et al.*, 2006]. Consecutively, a series of Cu_xMg_{3-x}Al HT derived oxides [xCu-Y HT] with different Cu-contents and different calcinations temperatures(Y) were prepared for the simultaneous NO_x soot removal by Zhang *et al.*, 2007. The crystal phases, porous structures and redox properties of catalysts were found to be strongly influenced by Cu substitution contents and calcinations temperatures. Among all the catalysts, 3.0 Cu-800 sample shows the best activity with Ti =260 °C and VN₂=6.0 x 10⁵ mol [Marquez *et al.*, 2001].

Recently, a series of Co-Mn-Al nonstoichiometric spinel-type oxides were synthesized from hydrotalcites precursors prepared through co-precipitation method, and their catalytic activities for the simultaneous removal of soot and NO_x were investigated by Wang *et al.*, 2013. Nonstoichiometric spinel-type oxides were obtained on thermal decomposition at 800°C. Authors concluded that Co-Mn-Al ternary oxides

exhibited much higher NO_x storage capacities than Co-Al and Mn-Al binary oxides and that soot oxidation activity gets significantly increased in the presence of NO [Wang *et al.*, 2013]. It was proposed that in O₂/NO atmosphere, NO was easily oxidized to NO₂ over the mixed oxides. NO₂, being more powerful oxidant, acted as an intermediate which oxidized soot to CO₂ at a lower temperature with itself being reduced to NO N₂, resulting in the high catalytic performances in simultaneous soot-NO_x removal. The application, results, preparation method and literature review of hydrotalcite type catalyst for simultaneous control of soot and NO_x from diesel exhaust emissions described in Table 3.4.

Table 3.4 The application of hydrotalcite type catalyst used for simultaneous catalytic reduction of soot and NO_x emissions from diesel engine exhaust

Catalysis Preparation Technique	Experimental Parameters	Remarks	Author & Year
Co _{2.5} Mg _{0.5} Al _{1-x} Ce _x O nitrate, co-precipitation	Soot/Cat = 1/20, Tight contact, Heating 10°C/min, Flow 150 cc/min, 600 ppm, NO + 10% O ₂ , Temp: 100-700°C.	Co _{2.5} Mg _{0.5} Al _{0.92} Ce _{0.08} O the best cat, T _{m-NO} = 449°C, X _{NO} = 15.4%	Dai <i>et al.</i> , 2012
Mn _x Mg _{3-x} AlO acetate, nitrate co-precipitation	Soot/Cat = 1/20, Tight contact, Heating - 10°C/min, Flow 240 cc/min, 750 ppm, NO + 10% O ₂ , Temp: 100-700°C	Mn _{1.0} Mg _{2.0} AlO the best cat, T _i , T _{m-NO} = 320, 380°C, X _{NO} = 24%	Li <i>et al.</i> , 2010
Co-Al HT mixed oxide, nitrates, co-precipitation	Soot/Cat = 1/20, Tight contact, Heating - 10°C/min, Flow 80 cc/min, 1000 ppm, 0.25% NO + 5 vol% O ₂ , Temp: 250-350°C	4Co-Al HT the best cat, T _i = 290°C, S _{N₂/C} = 3.5%	Wang <i>et al.</i> , 2007

4.1.5 Mixed Metal Oxides Catalyst

Noble metals catalysts are highly active for complete oxidation of pollutants; however their high cost, limited availability and sensitivity to deactivate have motivated the research for their substitute. Metal oxides are attractive substitute for noble metals as total oxidation catalysts. The single metal oxide catalysts for total oxidation of variety

of compounds are oxides of Cu, Ag, Fe, Cr, Co, V, and Ni Cu [McCarty *et al.*, 1997; Tahir & Koh, 1997]. The single metal oxides are less active to noble metals, but some combinations of oxides have high catalytic activity and stability as compared noble metal catalysts [Wang *et al.*, 1999; Prasad & Singh, 2012]. Such as spinel AB_2O_4 ($CuCr_2O_4$, $NiCo_2O_4$, $CuFe_2O_4$, $CuCo_2O_4$ etc.), perovskite ABO_3 ($LaFeO_3$, $LaKO_3$, $LaMnO_3$ etc), hydrotalcite ($CoMgAlO$, $CuMgAlO$, $MnMgAlO$ etc.). Figure 3.5 depicts importance applications of mixed metal oxides catalyst in various fields including environmental pollution control.

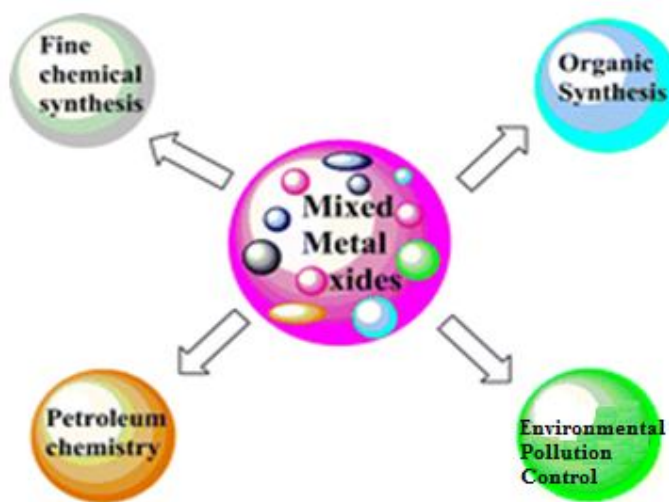


Figure 3.5 Application of mixed metal catalyst oxides

Pisarello *et al.*, 2002 conducted a study of the effect of the supports (MgO , La_2O_3 and CeO_2) on the activity of catalysts containing Co, K and/or Ba. Among the catalysts, Co K/ La_2O_3 and Co K/ CeO_2 displayed activity for the simultaneous removal of soot and nitric oxide whereas Ba / CeO_2 and Ba K/ CeO_2 were found to be effective in NO_x absorption in the form of nitrates. These nitrates are stable up to $490^\circ C$. The addition of Co to .Ba, K/ CeO_2 system lowered this temperature to $370^\circ C$ [Milt *et al.*, 2003]. A $BaCo_{0.93}$ perovskite phase was detected, which was absent in the Co, Ba/ CeO_2 system. The perovskite was proposed to be responsible for the instability of

nitrate species, due to the formation of surface N-bound nitrate species (O-Ba- NO₂) which readily gets decomposed in reducing environment. Soot particles were also oxidized by surface nitrate species trapped in the catalyst.

Ciambelli *et al.*, 2000 investigated the effect of NO on the activity of a Cu/V/K/Cl based catalytic filter in the combustion of soot and found that activity was significantly enhanced in the presence of NO in the gas phase. NO oxidizes to NO₂ and the oxidation of carbon by NO₂ occurs which in turn reduces to NO. Later, the activity of two bimetallic catalysts (K-Cu and K-Co) ,which were directly incorporated into soot was studied for the simultaneous removal of NO_x and soot. K-Co catalyst was found to be more active, achieving total NO_x reduction to N₂, at 350°C with the high soot consumption rate [Nejar *et al.*, 2005. Posterior to it, performance of K-Cu and K-Co supported on alumina was evaluated for varying ratios of K/Cu or Co. Copper-based catalyst K-Cu/Al₂O₃ (with K/Cu=5/5) displayed the highest activity for NO_x/soot removal at 450°C [Nejar *et al.*, 2007].

Ceria based oxide are known for oxygen storage capacity and hence in accelerating the soot combustion [Reddy *et al.*, 2007, Setiabudi *et al.*, 2004]. Cerium has the ability to switch between the Ce⁴⁺ and Ce³⁺ oxidation states and to incorporate more or less oxygen into their crystal structure depending on various parameters, such as the gaseous atmosphere in contact, temperature, and pressure [Trovarelli, 2002]. It was proposed that the formation of active oxygen was initiated by NO₂ in the gas phase. A synergetic effect was observed as a result of the surface nitrate decomposition, which resulted in the gas phase NO₂ and desorption of active oxygen [Tikhomirov *et al.*, 2006].

Reddy *et al.*, 2007 evaluated the activity of Cu-containing ceria/ceria-zirconia catalysts for NO_x-assisted soot oxidation reaction. Aged at 800°C in flow air, the CuO-CeO₂ catalyst showed the maximum oxidation rate at 321°C and nearly 100% selectivity to CO₂ production [Wu *et al.*, 2007]. The behavior was suggested to be related with the morphology of CuO with insertion into the ceria lattice, and the fine dispersion of Cu on ceria which brings a strong synergistic effect between Cu and Ce species ameliorating the oxygen activation and NO adsorption on the catalyst. Further, addition of Al₂O₃ to the CuO-CeO₂ was done by Wu *et al.*, 2008, producing Cu-Ce-Al mixed oxides catalyst. Al₂O₃ not only increased the textural stability of the catalyst but also improved the dispersion of CuO and CeO₂, resulting into lowering of soot oxidation temperature and a higher simultaneous NO reduction. After ageing of the catalyst at 800°C in air, high soot oxidation rate and a 34% NO reduction at 455°C is achieved.

Atribak *et al.*, 2008 studied CeO₂ and Ce-Zr mixed oxides with varying Ce/Zr ratios. Among the different mixed oxides prepared, Ce_{0.76}Zr_{0.24}O₂ gave the best results. The catalyst was found to be more active than pure CeO₂ for soot oxidation by NO_x/O₂ with a high soot oxidation rate of 14.9 µg soot/s. Although the catalytic activity of both the catalyst decayed significantly as calcinations temperature changed from 500 to 1000°C, Ce_{0.76}Zr_{0.24}O₂ presented enhanced thermal stability at temperatures as high as 1000°C. Also, Ce_{0.76}Zr_{0.24}O₂ catalyzed the reduction of NO_x increases in presence of soot at nearly 500°C more efficiently than CeO₂, thereby contributing to the decreased NO_x emission levels.

Neeft *et al.*, 2007 studied soot oxidation over CoO and NiO in tight contact mode and observed moderate activity. Later, Rao *et al.*, 2009 evaluated the activity of CuO-CoO/Ce-Zr and CuO-NiO/Ce-Zr combination catalysts towards oxidation of diesel

soot particulates. The bimetallic CuO-CoO/Ce-Zr combination catalyst exhibited high activity ($T_{50} = 636\text{K}$) and selectivity for $\text{CO}_2 \sim 99\%$. The high activity and stability of the catalyst was suggested to be attributed to $\text{Ce}_{0.76}\text{Cu}_{2.24}\text{O}_2$ solid solution formation similar to that of Co_3O_4 , facile reduction and oxygen vacancies as well as the size of the metal particles and their specific surface area.

Iron containing oxides have also been proven to be effective catalysts for the direct NO_x /soot conversion [Wu *et al.*, 2007]. Zhang *et al.*, 2010 accounted for the activity of Fe-doped ceria with Fe-O-Ce species as the active sites for soot combustion in the O_2 gas.

Shen *et al.*, 2012 prepared and evaluated Fe-Ce mixed oxide with varying proportions of Fe/Ce. They proposed that Fe increased the oxygen vacancy concentration and decreased the crystallite sizes of the catalyst. Among all the catalysts prepared, the one with Fe/Ce ratio of 1/9 exhibited best activity for the soot combustion, and more than 10% NO_x conversion at 410°C under tight contact condition. The catalyst calcined at 600°C possessed highest oxygen vacancy concentration on its surface and maximal storage ability for nitrite/nitrate species on its surface which played key role in influencing the catalytic soot combustion and the NO_2 -assisted soot combustion.

Several transition metal oxides, viz. Co_3O_4 , V_2O_5 , CuO , Fe_2O_3 , have been studied alone and in combination with alkali compounds, such as K, which act as promoters, favouring soot-catalyst contact [Gálvez *et al.*, 2012] and formation of active oxygen species. Gálvez *et al.*, 2011 synthesized alumina-supported K-Me (Me = Cu, Co, V) catalysts and tested for soot oxidation and the simultaneous removal of soot and NO . K-Cu / Al_2O_3 (with K/Me=10/5) showed best result with 100% NO reduction at

475°C and almost full soot conversion, Soot oxidation activity was highest for Cu-containing catalysts, followed by Co and V. On increasing the K content in the catalysts composition higher soot oxidation rates were achieved, Increase in metal content, however, resulted in higher set off temperatures for NO reduction.

Recently, Ascaso *et al.*, 2013 studied the influence of the alkali-earth promoters such as K and Ba on Cu, Co, Fe based catalyst for simultaneous control of soot and NO_x. K and Ba enhanced both NO_x adsorption and contact between soot and catalyst. K showed higher mobility than Ba whereas Ba contributed to a greater extent to the adsorption of N-species and higher thermal stability than on K-catalysts. Thus, K-catalysts were more active towards soot oxidation than Ba-catalyst. Ba-containing catalysts showed increased activity towards NO_x reduction but at temperatures higher than K-catalysts. Fe-based catalyst was found to be less active both in soot oxidation and NO_x reduction than Co and Cu-based ones.

Further, the effect of Cs as promoter on the catalytic performance of Me (Me= Cu, Co, Fe)/ Al₂O₃ was also assessed by Ascaso *et al.*, 2013. The use of Cs as alkali promoter resulted in lower soot oxidation activity as compared to K-containing catalyst. However, considerable deNO_x activity was exhibited, reaching 55% conversion for Fe-Cs catalyst followed by 42% and 32% for Co-Cs and Cu-Cs systems respectively. The application, results, preparation method and literature review of mixed metal oxides type catalysts for simultaneous control of soot and NO_x from diesel exhaust emissions described in Table 3.5.

Table 3.5 The application of mixed metal oxides type catalyst used for simultaneous catalytic reduction of soot and NOx emissions from diesel engine exhaust

Catalyst and Preparation method	Experimental parameter	Remarks	Reference
Ce/Zr based catalysts, K/Me-doped (Me= Fe, Pt, Au, Ru) Ce/Zr mixed oxides with a Ce/Zr molar ratio 3/1, modified citrate method	Comparison with model Pt-K/Al ₂ O ₃ LNT catalyst. Soot/Cat = 1/9, Loose contact. Flow =100 cm ³ /min, O ₂ (3%) in He or O ₂ (3%) + NO 1000 ppm, + H ₂ O (1%), heating 10°C/min	Pt-K/Al ₂ O ₃ -CZKRu catalytic systems ensures high catalytic performances in both the deSoot and deNOx activity. T _i =150°C, T _{NOx-storage} =350°C, T _{m-NO} = 391°C, S _{N₂} (max) = 86%	Matarres <i>et al.</i> , 2017
5% Cu catalysts with Ce _{0.8} M _{0.2} O supports (M = Zr, La, Ce, Pr Nd); NSR method	Soot/Cat = 1/20, Loose contact. Flow (50 ml/min; 850 ppm NOx + 5% O ₂ + N ₂)	Simultaneously reduction of NOx to N ₂ and combustion of soot carried out NSR conditions at 400°C; NSR process improves the catalytic combustion of soot. Best cat 5%Cu/Ce _{0.8} Pr _{0.2} O and with H ₂ micropulses, X _{soot} = 100% at 240°C	Lopez <i>et al.</i> , 2016
Ag-based catalysts, Ag (5%) – Ba(10%) /MO / Sr(10%)/CeO ₂ catalysts, incipient wetness impregnation method	Soot/Cat = 1/20, Loose contact; NO/O ₂ gas flow (10% O ₂ + 500 ppm NO, balance N ₂ ; flow 0.5 l/min), heating 10°C/min, Catalyst Bed temp 100-800°C,	Ag(5%)–Ba(10%)/ Al ₂ O ₃ best catalyst, SA-144 (m ² /g), T _i =250°C, T _{m-NO} =350°C, S _{N₂} (max)= 80%, X _{soot} conversion=85%	Castoldi <i>et al.</i> , 2015
Combination of LNT cat and DPF, 2Pt20Ba/ Al ₂ O ₃ , Impregnation	Temp.: 200-600°C, Flow 100 cc/min, heating 4°C/min, NO 500 ppm +10% O ₂	Simultaneous reduction Over LNT/2Pt20Ba/ Al ₂ O ₃ , X _{NO} =65%, T _{m-NO} = 350°C, Channel flow condition, X _{soot} = 100% at 700°C	Choi <i>et al.</i> , 2014
K-Cu-Co-V/Al ₂ O ₃ ,nitrate, boehmite, sol-gel	Soot/Cat =1/4 , loose contact, Flow 50 cc/min, 500 ppm NO+ 5 % O ₂ , heating 5°C /min, Temp:250-650°C	Co-K/Al ₂ O ₃ best cat. X _{NO} = 53% , X _{soot} ~100% at 545°C	Gálvez <i>et al.</i> , 2013
K/Ba-Cu/Co/Fe-Al ₂ O ₃ , nitrates, oxalates, boehmite, sol- gel	Soot/Cat = 1/5, Tight contact, total flow 50cc/min, 500 ppm NOx + 5% O ₂ , heating 5°C/min, Temp : 250-650°C	Cu-Ba catalyst, T _i , T _{m-NO} , T ₅₀ = 425,650,600°C, X _{NO} , X _{soot} = 100%	Gálvez <i>et al.</i> , 2013
Iron-ceria mixed oxide	Soot/Cat = 1/9, tight contact; Flow 200 cc/min, NO + 5% O ₂ , Heating 10°C/min, Temp: 200-800°C	T _i =410°C,S _{N₂} (max)=10% soot combustion, X _{soot} =100%	Shen <i>et al.</i> , 2013

Cu/MgAl ₂ O ₃ , Cu/SrAl ₂ O ₃ nitrate, wet impregnation	Soot/Cat = 1/4, Loose contact, Flow 500cc/min, 500ppm NO _x + 5% O ₂ , Heating 10°C/min, Temp : 25-800°C	Cu/SrTiO ₃ best cat., T ₅₀ =600°C S _{CO2} = 99 %, T _{m-NO} =425°C, X _{NO} = 20%	López-Suárez <i>et al.</i> , 2012
K-M(M= Cu, Co, V)/Al ₂ O ₃ , nitrates, impregnation	Soot/cata = 1/4, Tight contact, Heating rate 5°C/min, Flow 50 cc/min, 600 ppm NO _x + 5% O ₂ , Temp : 250-650°C	10:5 K-Cu/Al ₂ O ₃ best cat T _i , T _p , T _f =338,417,477°C , X _{NO} =42%, T _{m-NO} = 460	Gálvez <i>et al.</i> , 2011
BaAl ₂ O ₄ , nitrates, calcined at 873°C	Soot/Cat=1/15, Tight contact, Flow 100 cc/min, 5000 ppm, NO+10% O ₂ , Heating 5°C/min, Temp: 200-800°C	T _{ig} =510°C, S _{N2} (max)=62%	Lin <i>et al.</i> , 2009
CoCr ₂ O ₄ , MnCr ₂ O ₄ , CoFe ₂ O ₄ , combustion synthesis	Soot/Cat = 1/9, Tight contact, Flow 100 cc/min, 1000 ppm, NO+10% O ₂ , Heating 5°C/min, Temp: 200-700°C	CoCr ₂ O ₄ the best cat, T _{m-NO} =396°C, X _{No} =36%	Fino <i>et al.</i> , 2008
K-Cu/C, K-Co/C, nitrate, Direct incorporation of metals to soot	Soot/Cat = 1/9, Tight contact, Flow 60 cc/min, 600 ppm NO + 5% O ₂ , Heating 10°C/min, Temp : 200 -500, 350°C	K-Co/C the best cat., complete reduction of NO _x to N ₂ at 350°C , T _{m-NO} = 300°C	Nejar <i>et al.</i> , 2005

Note: T_i = Initial temperature of soot ignition, T_p = Peak temperature, T_f = Total soot oxidation temperature, T₅₀ = Temperature at which 50% soot is converted, X_{soot} = Fractional conversion of soot, T_{m-NO} =Temperature for maximum conversion of NO, X_{NO} = maximum conversion of NO at T_m, S_{N2} =Selectivity to N₂.

3.2 OBJECTIVES

The aim of this work is to illustrate a strategic emission control system for a diesel engine exhaust that can effectively remove NO_x and PM simultaneously. This involves investigating methods of low-temperature diesel exhaust after-treatment technologies used currently and which will be used after modification in the foreseeable future suggested by the present work. This work fills the gap in literature about formulation of an efficient catalyst ($\text{La}_{0.8}\text{K}_{0.2}\text{Fe}_{0.85}\text{Cu}_{0.15}\text{O}_3$) able to oxidize diesel PM as well as reduce NO_x simultaneously within the range of exhaust temperature (150-450°C). The prime objectives of the present studies were as follows:

- To develop the best possible low cost and low temperature efficient catalysts for simultaneous control of diesel soot and NO_x emissions.
- To characterize the catalysts by various techniques such as low temperature N₂ adsorption, XRD, SEM- EDX, and FTIR.
- To screen-out the best catalyst experimentally in the laboratory for simultaneous abatement of diesel soot and NO_x emissions.
- To develop correlations between characteristic and performance of the catalyst in the said reactions.