CHAPTER 2

SIMULTANEOUS CONTROL OF DIESEL SOOT AND NOx

This chapter elaborates the combined control technologies of diesel soot and NOx and discusses the simultaneous catalytic reduction of soot NOx.

2.1 Combined PM and NOx Control Technologies

As the control of PM and NOx both are required simultaneously because of the stricter legislation, several diesel emissions control systems will be combined into a single unit to minimize space requirements, and for, cost and efficiency, considerations [Castoldi *et al.*, 2015, Wang *et al.*, 2012]. The most common configurations are discussed as below.

2.1.1 CRT-SCR System

This system aims at controlling HC, CO, PM and NOx as shown in the Figure 2.1. It consists of oxidation catalyst, filtration and ammonia SCR for NOx control on heavy-duty diesels. The exhaust gas first passes through a platinum oxidation catalyst that oxidises CO and HCs, as well as converting NO to NO that continuously oxidises PM (Soot) in the filter. The exiting NOx is then reduced to N_2 over the SCR catalysts. The ammonia is obtained from the decomposition of urea that is sprayed into the system as an aqueous solution, and any adventitious ammonia is prevented from passing into the environment by a final platinum catalyst that would oxidise it to NO [Faiz *et a1.*, 1996].

Such a system combining a NO_2 based continuously regenerative trap particulate removal techno1ogy with a urea-based Selective Catalytic Reduction (SCR) NOx removal technology leads to simultaneous conversions of 75 to 90% in NOx and PM. The system combines the Johnson Matthey CRT ® filter with a urea SCR system and is known commercially as SCRT® system which is designed to reduce CO, HC and PM by more than 90%. This is followed by a decomposition catalyst to bring the NO_2 down to the levels required as shown in Figure 2.2.

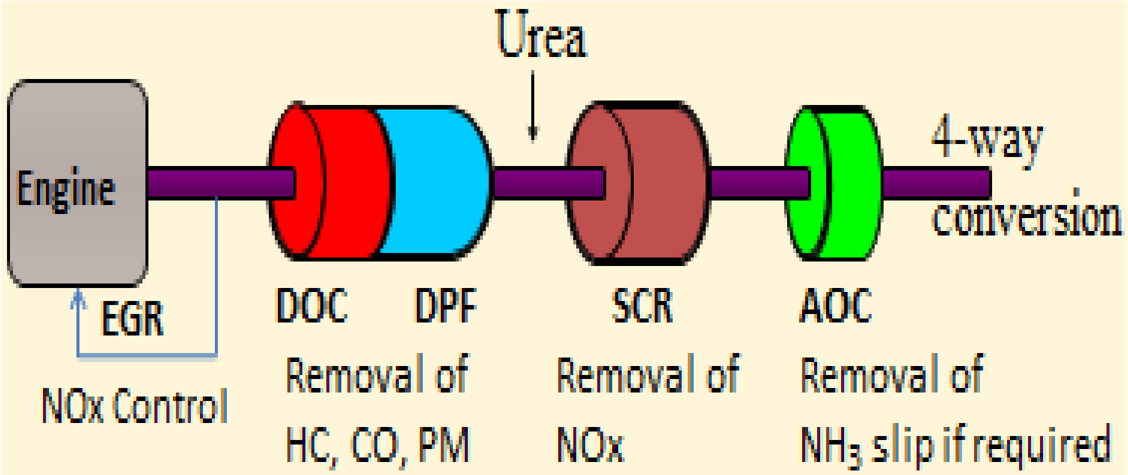


Figure 2.1 4-Way Conversions

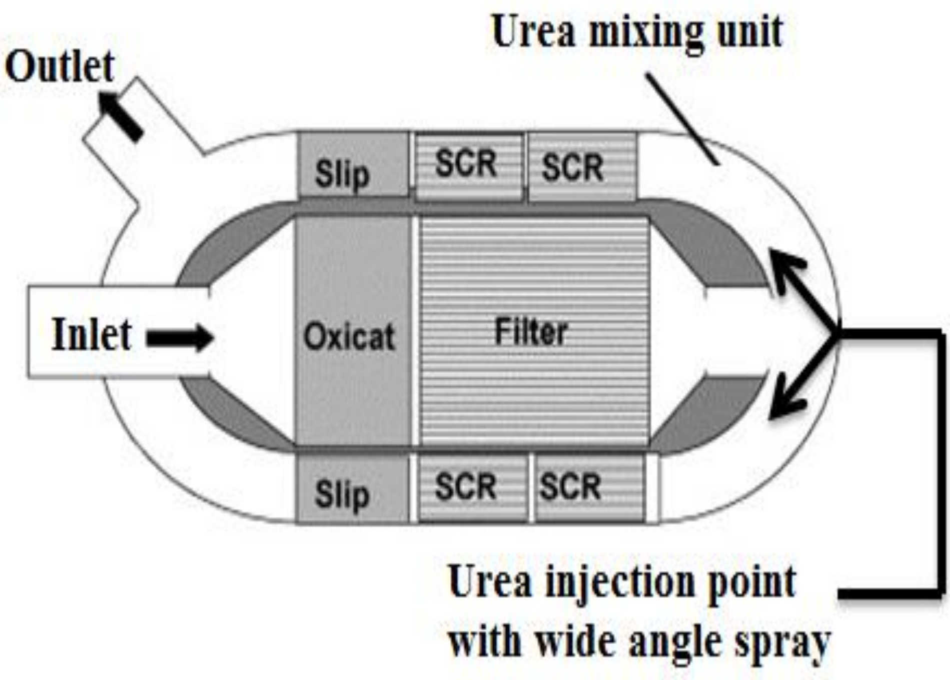


Figure 2.2 Combine CRT-SCR System

2.1.2 Diesel Particulate-NOx Reduction (DPNR)

DPNR (diesel particulate -NOx reduction) system was developed by the Toyota group [Skratakis *et al.,* 2004, Suzuki *et al.,* 2004] and consists of both a catalytic filter and a specific diesel combustion technology, which has the unique capacity to remove simultaneously both soot and NOx. The new catalytic converter for DPNR is a porous ceramic filter coated with a catalytic layer constituted by a high surface area support (e.g. γ -alumina), a noble metal (Pt), and an alkaline or earth-alkaline metal oxide which presents a high NOx-storage capacity as shown in Figure 2.3. These catalytic systems work under cyclic conditions, alternating a lean phase during which the NOx produced by the engine are adsorbed on the alkaline or earth-alkaline metal oxide component (with nitrate species formation), with a short rich phase, during which the stored nitrate species are reduced to nitrogen. The NOx reduction mechanism in the DPNR system correspond to that already proposed by Toyota for lean-burn gasoline engines [Kureti *et al*., 2003], i.e. the so-called NOx storage-reduction (NSR) catalysts. Soot abatement occurs under lean conditions i.e. NOx storage phase and to excess oxygen in the exhaust gas; soot removal is however claimed to occur during rich phase as well which is shown in Figure 2.4 [Liu and Woo, 2006].

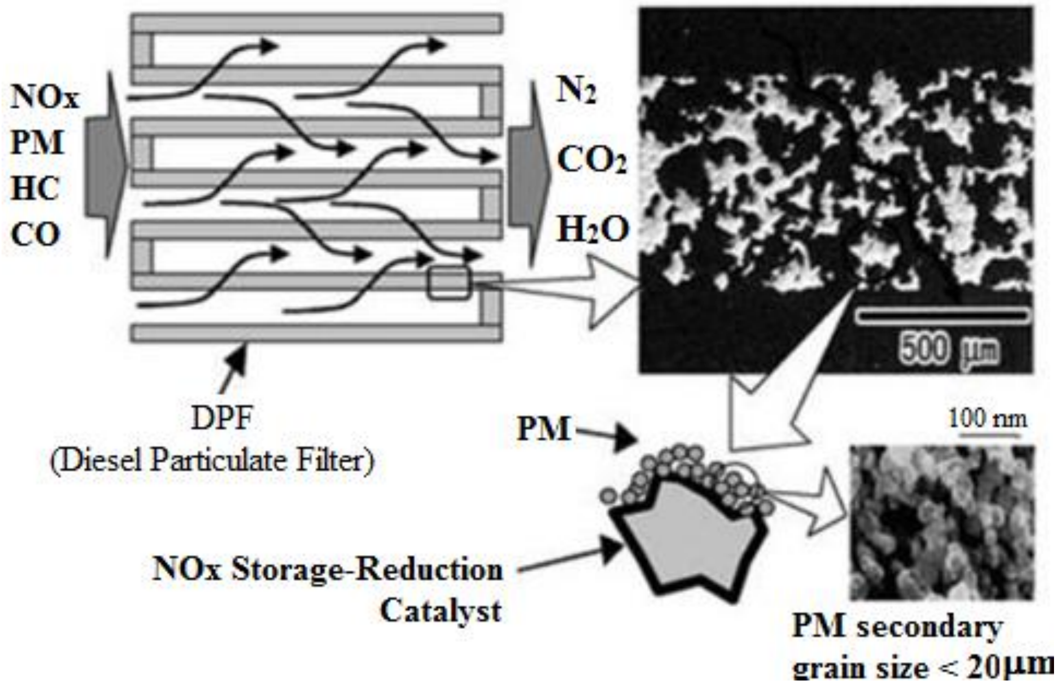


Figure 2.3 Structure of a DPNR catalyst (cross sectional view)

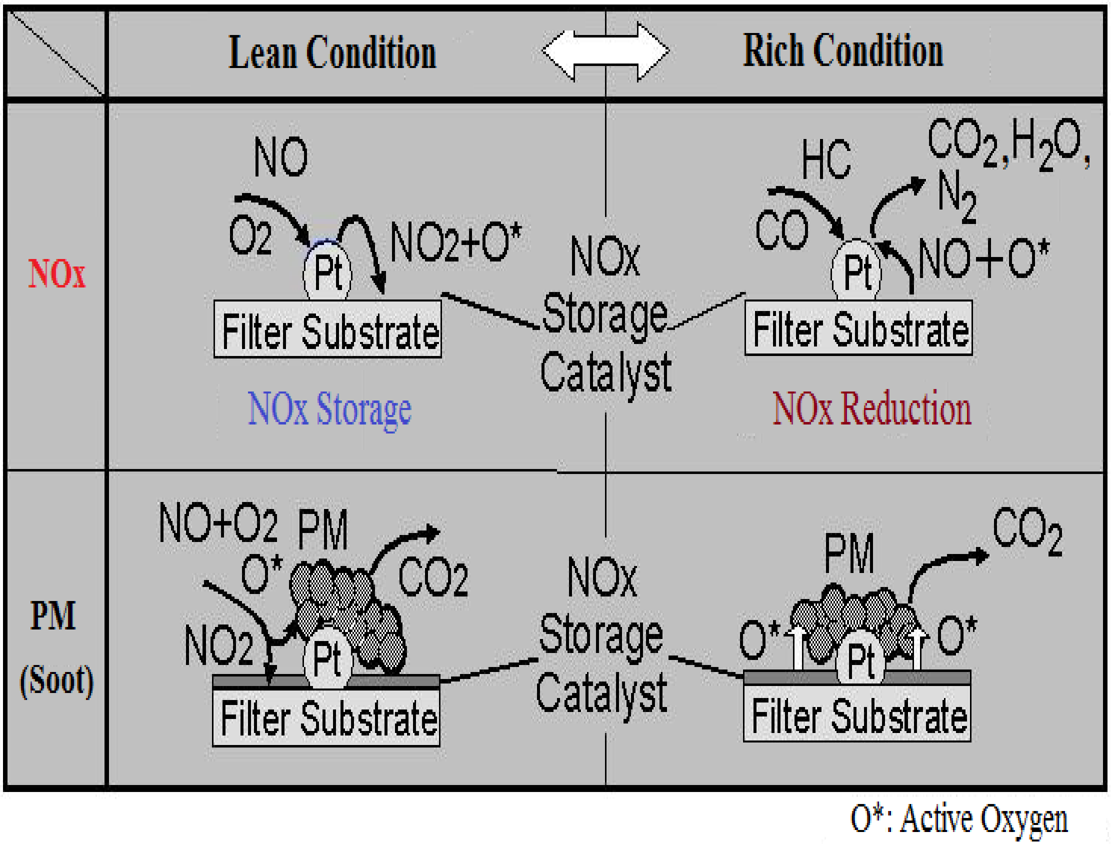


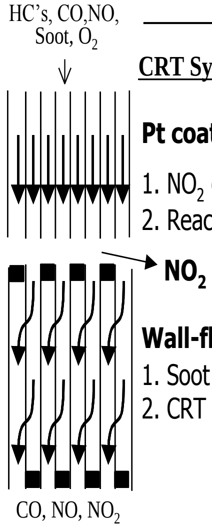
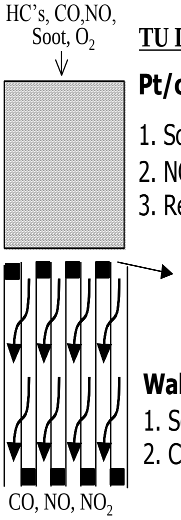
Figure 2.4 NOx and PM (Soot) Reaction Mechanism of DPNR Catalyst

3.1.3 TU Delft Filter

To overcome NO_2 slip, Setiabudi *et al*., 2003 developed the TU Delft catalytic filter, in which Pt/ceramic foam is installed upstream of a wall-flow monolith [Setiabudi *et al.*, 2003]. The filter configuration is capab1e of employing two stages of filtration: deep bed filtration in the foam and surface filtration on the wall-flow monolith. At the same time, two modes of soot oxidation reactions operate. In Pt/ceramic foam the oxidation of NO to NO_2 and multiple NO_2-soot reactions take place, while part of NO will be released as NO_2 slip. The slipped NO_2 subsequently will be used, oxidize the trapped diesel soot particulate on the latter wall flow monolith. This system improves the use of NO_2 and lowers the NO_2 slip. A sufficient amount of NO is required for the formation of NO_2, which then oxidizes soot. Therefore, this technology is more applicable for heavy-duty diesel vehicles despite the fact that the NOx was not actually reduced. The comparison of functions of the components of typical CRT and TU Delft filter system for removal soot and NOx are described in Table 2.1.

CRT and TUD filter systems contain a platinum catalyst upstream of a soot trap. The main differences are discussed. In the CRT system Pt is loaded on a flow-through monolith, while in the TU Delft filter Pt catalyst is loaded on ceramic foam. In the CRT system the Pt coated flow-through monolith functions only as NO_2 generator, no soot trapping or soot oxidation occurs. In the TU Delft filter a Pt/ceramic foam catalyst is designed as a multifunctional reactor that functions not only as NO_2 generator but also as soot filter; a specific advantage is that NO_2 is used catalytically, viz. every NO_2 is used more than once. In both systems NO_2 is generated that passes through the wall-flow monolith where it reacts with the trapped soot.

Table 2.1 Comparisons of functions of the components of typical CRT and TU Delft filter system, [Setiabudi *et al.*, 2003]

	Functions:	**Reactions:**
	**CRT System:** **Pt coated flow-through monolith :** 1. NO_2 generator 2. Reactor for CO and HC oxidation	$NO + \frac{1}{2}O_2 \overset{Pt}{\rightleftarrows} NO_2$ (1) $CO + \frac{1}{2}O_2 \xrightarrow{Pt} CO_2$ (2) $C_xH_y + \frac{1}{2}O_2 \xrightarrow{Pt} CO_2 + H_2O$ (3)
	Wall-flow monolith: 1. Soot filter (total filtration) 2. CRT system utilising NO_2-slip	$NO_2 + C \longrightarrow CO + NO$ (4)
	**TU Delft Filter** **Pt/ceramic foam :** 1. Soot filter (40-70% efficiency) 2. NO_2 generator 3. Reactor for **soot**, CO and HC oxidation	$NO + \frac{1}{2}O_2 \overset{Pt}{\rightleftarrows} NO_2$ $NO_2 + C \longrightarrow CO + NO$ (5) $CO + \frac{1}{2}O_2 \xrightarrow{Pt} CO_2$ (2) $C_xH_y + \frac{1}{2}O_2 \xrightarrow{Pt} CO_2 + H_2O$ (3)
	NO_2-slip: non-reacted NO_2 emitted from Pt/ceramic foam **Wall-flow monolith:** 1. Soot filter (total filtration) 2. CRT system utilising NO_2-slip	$NO_2 + C \longrightarrow CO + NO$ (4)

Therefore, to control NOx with soot simultaneously, the concept of NOx-aided continuously regenerated trap (NOx-aided CRT) was introduced by Cooper and Thoss [Cooper and Thoss, 1989]. It oxidizes all carbon components in diesel exhaust gas, including small particles, and unregulated compounds, and also reduces the NOx concentration by 3-8% [Hawker *et al.*, 1989]. NOx-aided CRT consists of a pre-oxidizer with oxidation catalyst which converts 90% of the CO and hydrocarbons to CO_2 and 20-50% of the NO to NO_2 [Hawker *et al.*, 1989]. Downstream, the particles are trapped on a cordierite wall-flow monolith and subsequently oxidized by the NO_2. Figure 2.5

provides a schematic representation of the system. The CRT system by Johnson Matthey concerning the role NO_2 in diesel particulate combustion consists of a wall-flow trap with an upstream flow-through diesel oxidation catalytic monolith called pre-oxidizer (Figure 2.6).

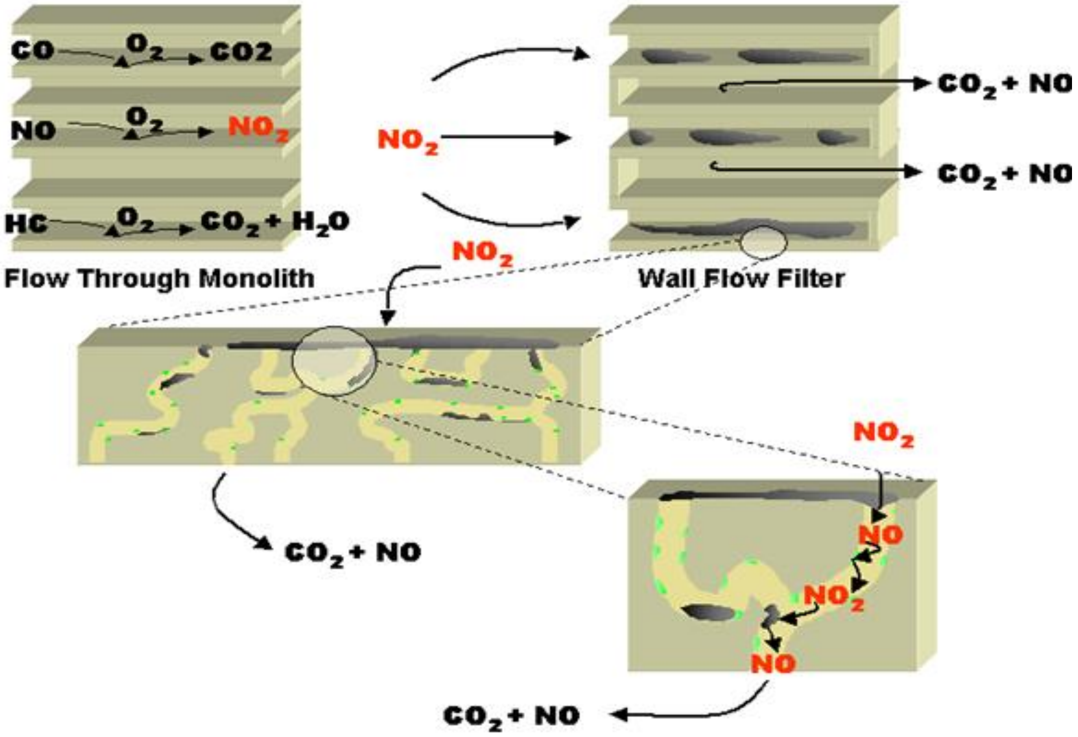


Figure 2.5 NOx- aided continuously regeneration trap

The modular design of the separated and detachable pre-oxidizer and filter facilitates a high flexibility of the system, which is a great advantage for retrofitting of different buses and trucks. In each case, the optimal trap and. pre-oxidizer can be chosen, which can, in many cases, save space, heat loss, backpressure, and system costs. Another advantage of the modular design with clamshells is that the canning can be easily opened in order to remove deposits of inorganic ash.

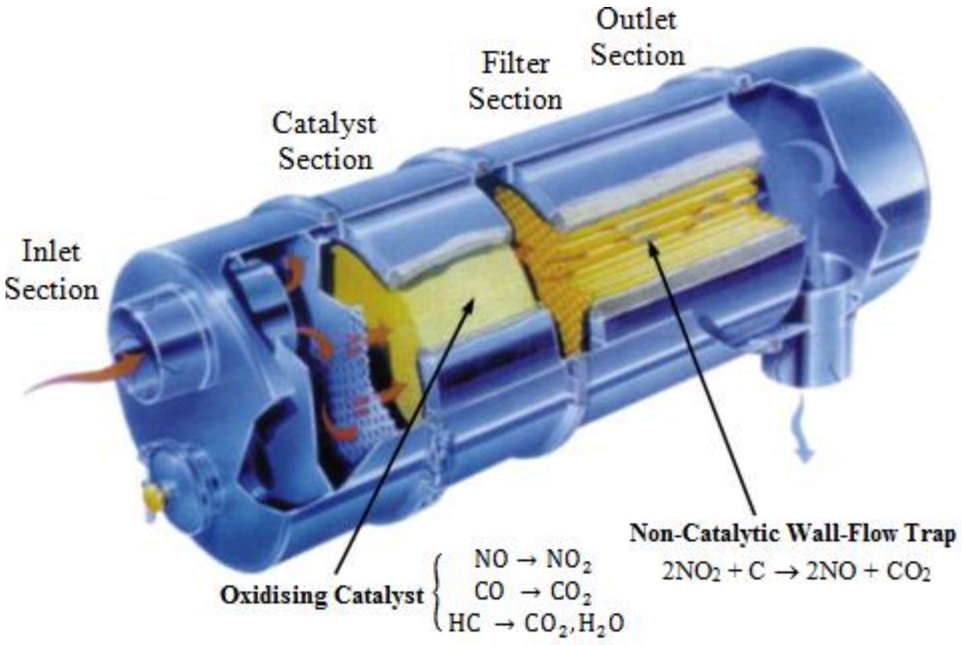


Figure 2.6 The continuously regenerable trap system by Johnson Matthey

The filter should produce a surplus of NO_2 in order to compensate for time periods in which the temperature is too low for regeneration. The surplus NO_2 should not be too high because NO_2 is foul smelling in the vicinity of the vehicle, where it has not yet been diluted sufficiently with ambient air. For the environment, the NO_2 gives no additional problems, because NO is converted to NO_2 anyway in short time scales [Hawker *et al.*, 1989].

The system has not yet been introduced on a wide scale because it requires the use of low-sulfur fuel <50ppm [Allansson *et al.*, 2000], because SO_2 restricts the performance and when oxidized by the platinum catalyst, it adds up significantly to the total particulate mass. Low-sulfur fuel can easily be made available to public transport companies, which often have their own diesel depots, but for many other heavy-duty applications, that is not practical yet. In a few years time, this will, however, change, when low-sulfur fuel becomes widespread in Europe and the United States. Problems may arise for international transport companies that operate in countries that will not introduce low-sulfur fuels on the short term. Another problem of the system is its dependency on NOx, because it is uncertain if the required NOx-to-soot ratio for successful regeneration will be met in future engines.

2.2 Simultaneous Catalytic Control of PM and NOx

The present state of art for controlling soot and NOx are application of separate technology for each. For controlling soot different types of diesel particulate filters (DPFs) are used, such as active DPF, passive DPF and combination of both. In active DPF, the trapped soot is burned occasionally applying flame or electrical heater to regenerate the filter. In passive DPF highly active catalyst is coated over filter to burn the trapped soot to regenerate the filter continuously. To control NOx selective catalytic reduction (SCR) technology is used using ammonia (NH_3) / aqueous solution of urea commercially known as Adblue®. The present separate technologies used to control soot and NOx are cumbersome and tedious [Lietti *et al.,* 2016, Mescia *et al.,* 2008].

Thus, simultaneous catalytic control of soot and NOx is a good alternative compact technology. In this technology, development of a highly active, selective, stable and regenerable catalyst to remove simultaneously soot and NOx is a challenge**.** The reaction between soot and NOx can be represented by Equations 2.1 and 2.2. A potential mechanism scheme for simultaneous soot-NOx removal is proposed by Li *et al.*, 2012 as shown in Figure 2.7.

$$C+2NO \rightarrow CO_2 + N_2 \qquad (2.1)$$

$$C_nH_m(\text{soot}) + \left(2n + \frac{m}{2}\right) NO\ (g) \rightarrow \left(n + \frac{m}{4}\right) N_2(g) + nCO_2(g) + \left(\frac{m}{2}\right) H_2O\ (g) \qquad (2.2)$$

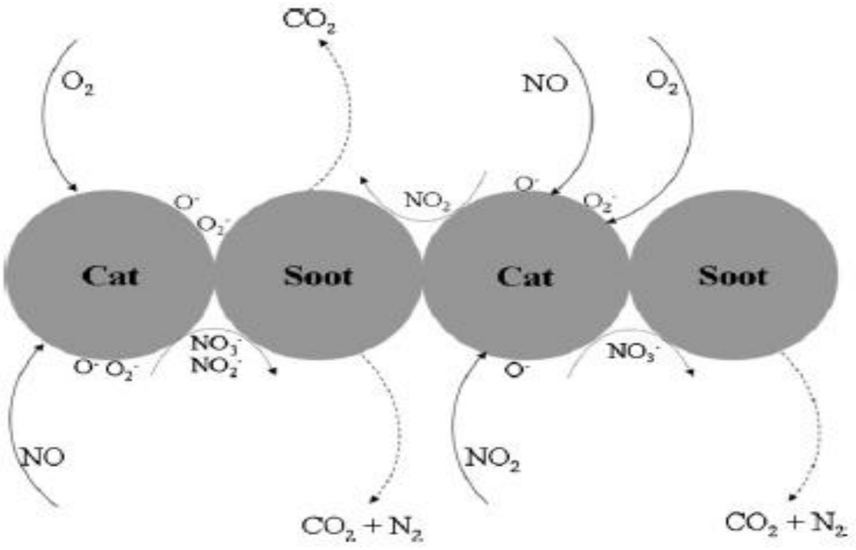


Figure 2.7 Scheme of the reaction mechanisms for the simultaneous NOx-Soot removal (Li *et al.*, 2012)

2.2.1 Reaction mechanism of present work for simultaneous removal of soot and NOx

Reactions of diesel soot and NOx with air were carried out over effective perovskite catalysts. The ignition temperature of soot with the NO+O_2 feed was lower than that in O_2 or NO and the reduction of NOx into N_2 was enhanced by coexisting O_2. Based on these results the possible reaction mechanism of the simultaneous NOx-soot removal with NO+O_2 feed has been proposed according to the following Equations (2.3) - (2.8):

$$O_2 + X \rightleftarrows 2O_{ad} \quad (2.3)$$

$$NO + X \rightarrow NO_{ad} \quad (2.4)$$

$$NO_{ad} + Oad \rightarrow NO_{2ad} \quad (2.5)$$

$$2O_{ad} + C \rightarrow CO_2 \quad (2.6)$$

$$2NO_{ad} + C \rightarrow CO_2 + N_2 \quad (2.7)$$

$$2NO_{2ad} + 2C \rightarrow 2CO_2 + N_2 \quad (2.8)$$

Gaseous oxygen is adsorbed dissociatively on the active site (X) of the catalyst surface (Equation 2.3), and NO is also adsorbed on the active site (X) of the catalyst

(Equation 2.4). The adsorbed species O_{ad} and NO_{ad} react and form NO_{2ad} (Equation 2.5). The adsorbed oxygen (O_{ad}) reacts with adjacent carbon (soot) particles to give CO_2 (Equation 2.6). Further, adsorbed NO_{ad} and NO_{2ad} species react with adjacent carbon (soot) particles to result CO_2 and N_2 (Equationns 2.7, 2.8). Based on the above discussions the proposed mechanism is depicted in Figure 2.8.

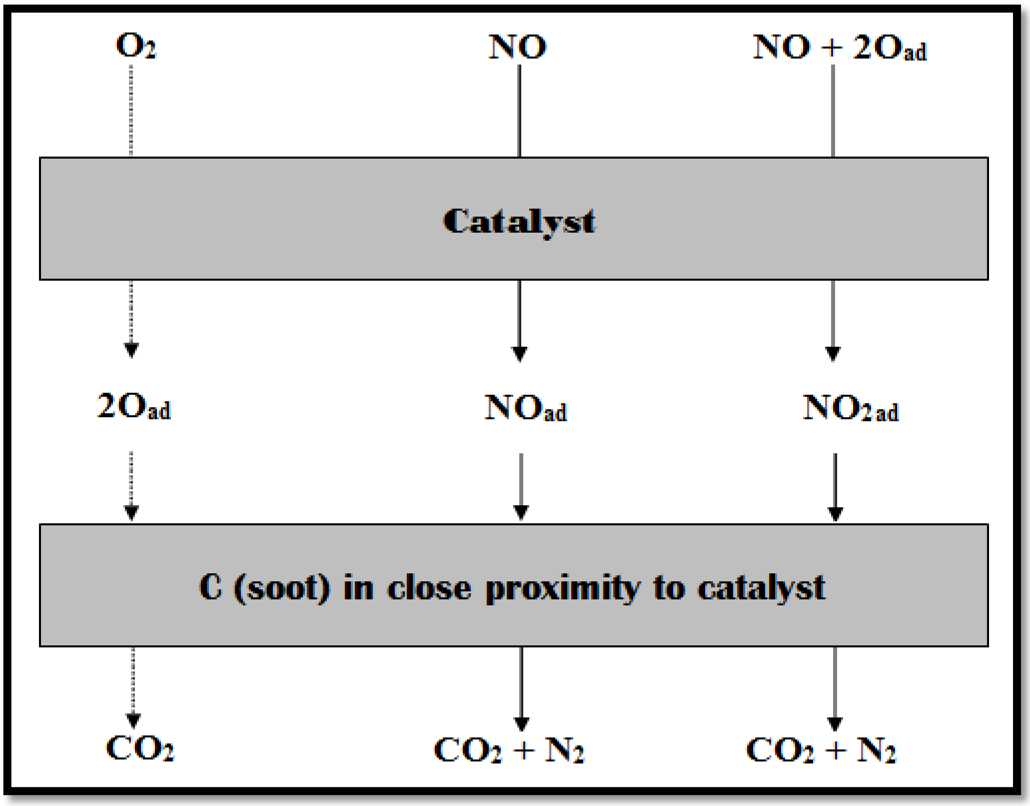


Figure 2.8 Illustrative of the proposed mechanism of the simultaneous NOx-soot removal reaction in NO+O_2 over catalyst

2.2.1 Catalyst Design Parameters

For catalyst design purposes it is first necessary to translate the catalyst performance parameters into a physical picture of catalyst structure. Different performance parameters give rise to different structural features and so a compromise is generally required. For example it is commonly found in industrial applications that initial catalyst activity may be sacrificed in favor of improved catalyst stability, since a lower activity and a prolonged operating catalyst life is in general preferable to a higher initial activity that decays rapidly. Therefore, the relationships between the catalyst performance parameters and physical structure is discussed in order to design suitable catalysts, to decrease the onset temperature for soot combustion and to reduce NOx simultaneously in the presence of O_2 [Cheng *et al*., 2017, Sharma *et al*., 2018].

(i) Activity

In general activity arises from maximizing both the dispersion and availability of the active catalytic material. Ideally, from an activity viewpoint, the catalyst material should be highly dispersed throughout on the external as well as internal pore surfaces of the support. However, there is an inherent conflict as high concentrations of active material become progressively more difficult to disperse [Anderson *et al.*, 1979].

(ii) Stability

By stability it is referred to the loss in activity with time [Kemball and Dowden 1981]. This is due to one or several of four main causes; fouling of the active surface with in-volatile reaction by-products, sintering or crystal growth of the active material, poisoning of the active surface by feed impurities, and blockage of the support pore structure.

(iii) Selectivity

Catalyst selectivity can change due either to physical or chemical reasons. For sequential reactions diffusivity and mass transport through the pore structure can lead to apparent loss in selectivity in the formation of intermediate products. Location of active ingredients and pore-size distributions are therefore again of importance. Variations in selectivity can also arise from changes in intrinsic chemical activity of the active component. Typically this can be affected by use of multi-component catalysts without changing the configuration. A specific example of this type of selectivity arises in the case of multifunctional catalysts in which a hydrogenation function is combined with an acid function. Since the latter is typically provided by the support and the former by the impregnated material, a uniform impregnation is required [Kemball and Dowden 1981].

(iv) Regenerability

Regenerability refers to the reactivation of a catalyst, which typically will involve air combustion of carbonaceous deposits followed in some cases by a re-dispersion of the active components. From the catalyst design viewpoint, this will generally imply enhanced thermal-hydrothermal stability of the support itself, combined with stability of the active components under the high temperature oxidizing environments required for the oxidation of the deactivating carbonaceous deposits. It is now generally recognized that many metals sinter more readily under oxidizing conditions and in extreme cases may even dissolve in the underlying support and become effectively removed from the reaction system. A further complication arises with multi-component catalysts in which the combination ratio is all important, since such combinations frequently are destroyed under oxidizing conditions [Argyle and Bartholomew 2015].

2.2.2 Development of catalysts

In the development of catalyst, the best preparative method is sought and factors considered are bulk and surface chemical composition, microstructure, phase composition thermal and mechanical stability, surface area, porosity, shape, and dimension of the catalyst particle.

The lot of papers has been published for simultaneous catalytic control of NOx and Soot. Based on laboratory studied, many papers are showing highest catalytic activity towards soot combustion as well as the high NOx conversion activity within the exhaust temperature (<500°C) [Mescia *et al.*, 2008]. The various preparation methods have been reported on the priority of the high surface area, selectivity, durability, availability of raw materials, and cost. The sequence of the preparation methods based on the efficiency of the catalyst is incipient Sol-gel > Reactive grinding > solution combustion synthesis (SCS) > Co-precipitation [Fino *et al*., 2003, Mescia *et al.*, 2008, and Castoldi *et al.*, 2015]**.** The soot and catalyst ratio is effective in the range (1/9 to 1/20). Some of the single and double substituted perovskite catalysts are mentioned promising activity toward the simultaneous removal of soot and NOx within the diesel engine exhaust temperature range [Labhasetwar *et al.,* 2015]**.** The lanthanum ferrites catalyst displays the maximum activity for simultaneous Soot-NO conversion, soot is fully oxidized and maximum conversion of NO to N_2 is ~ 84 % below 500°C without adding any extra reductant. Soot catalytically oxidizes itself in presence of NOx at a faster rate than O_2.

The simultaneous NOx–soot removal process is considered to be a promising technique for the after treatment of diesel exhausts [Teraoka *et al*., 1998]. In order to realize the simultaneous NOx–soot removal process, three key technologies should be developed; development of (1) active catalysts, (2) thermally stable and reliable PM (soot) traps and (3) the method of catalyst loading on the trap. PM (soot) traps made of ceramics (wall-flow honeycomb or foam) and metals (foam) have been much developed in these years. As for catalytic materials, [Teraoka *et al.,* 1998; Fino *et al.,* 2003] reported that the mixed metal oxides are superior to simple metal oxides and platinum especially with respect to the NOx reduction into N_2 and that the effect of potassium in promoting both the activity and selectivity is remarkable. Since potassium is volatile, they feel that it should be stabilized in the crystal lattice of mixed metal oxides as in perovskite-related oxides. The potential of Ag-based catalysts considered as a promising alternative to Pt-based catalysts for the simultaneous removal of soot and NOx [Castoldi *et al.*, 2015]. The nanometric perovskite-type oxides, especially the nanometric K-substituted Co-, Mn- and Fe-based catalysts show excellent catalytic performances for the simultaneous elimination of soot particles and NO, and they can greatly lower the combustion temperature of soot particles and enhance the NO conversion [Wang *et al.*, 2012]. Matarrese *et al.*, 2016 reported that Ru-based catalysts show interesting properties for the simultaneous removal of soot and NOx. The performances on NOx adsorption and soot combustion revealed by some catalysts formulations are remarkable, even higher than those of Pt-containing catalysts [Matarrese *et al.*, 2016]. Catalysts derived from LDH precursors have shown great performance on the simultaneous catalytic removal of soot and NOx. Researchers have demonstrated that the LDH derived mixed oxides can not only store NOx but also oxidize soot to CO_2 [Yang *et al.*, 2014].

Till now, there is no patent available for simultaneous catalytic reduction of soot and NOx emissions from diesel engine exhaust. There are very few literature available for simultaneous catalytic reduction for NOx-Soot which is discussed in consecutive chapter.