CHAPTER – 1

INTRODUCTION

1. Introduction

Diesel engines have increased popularity over conventional gasoline engines around the globe, because of their better fuel efficiency, higher durability, superior reliability, lower maintenance cost and lesser CO_2 emissions [1]. Rapidly, they acquired wide applications in various fields such as transportation, agriculture, defence, power generation, mining, construction, etc. (Figure 1). In the current scenario, in spite of vehicles using alternative fuels, diesel vehicles are still holding the main power source behind transport people, goods, and services being employed in autos, cars, buses, trucks, trains, boats and ships. They find wide range of applications in agriculture such as tractors, harvesters, pumping set, etc. In the field of defence they are used in armored fighting vehicles, battle tanks, mechanized mortars, missile carriers, submarines, etc. They play a vital role in power generation and industrial activities. They are also used in construction of buildings, bridges, roads, as well as off-road ships, trains, industrial vehicles such as excavation machineries and mining equipments.

Diesel engines have advantages like:

- Better fuel efficiency, higher durability,
- Better reliability, lower maintenance cost and lesser CO_2 emissions
- Higher compression ratio, higher thermodynamic efficiency,
- No throttle, no knock, no pumping losses,
- Combustion in diesel engine is lean with low heat losses,
- Flexibility about choice of fuel like biodiesel.

Figure. 1. Pictorial view of different diesel engine applications

Air–fuel ratio (A/F) is the weight ratio of air to a fuel used in a combustion process. The lean-burn engines (A/F = 18–21) are more fuel efficient, thus save 30–35% fuel consumption and release less CO_2 [4]. The stoichiometric A/F ratio for diesel is 14.6, but diesel engines always run under lean burn conditions [7].

Apart from the bright side of various applications and advantages of diesel engines, the dark side is emissions of various primary toxic pollutants such as CO, HC, NOx and smoke/particulate matter (PM)/soot. The primary pollutants are hazardous to human health and environment. Further, the primary pollutants react with atmospheric constituents in presence of sun-light and form more toxic secondary pollutants, such as acid rain, ground level ozone, smog, Per Aceto Nitrile (PAN), Per Aceto Hydride(PAH), etc. From the lean burn diesel engines, the concentration of CO and HC is very less almost under the legislation limits in the exhaust. The main concern is emissions of PM and NOx. The PM can be controlled to 99% by the use of diesel particulate filter (DPF). However, control of NOx is not so easy and require special catalytic redox techniques. Therefore, the present work is concerned with the reduction of NOx from diesel exhausts.

1.1. Sources and Effects of NOx

NOx are suspected for a series of adverse impact on human health [8], environment, climate, vegetation, etc. That is why it is being intensely studied by numerous groups from academic as well as industrial research laboratories. The emission of NOx from the exhaust gases of diesel engines is becoming a global–problem of increasing concern. Thus, NOx have been recognized as principal pollutants since the start of industrialization [8]. The interest in the subject is reflected in the number of papers, including a large number of reviews [9-29], a number of Ph. D. degrees [30-38] have been awarded by various universities and numerous patents [39-47] have been sanctioned and many seminars, symposia and workshops organized [48-50] on the topic from 1994-2017. The emission regulations for lean burn engines are becoming stricter because of the need to reduce NOx in the atmosphere. Much research has been done on discovery and improving lean burn catalysts for the control of NOx from automobile exhaust. Emission abatement strategies for lean burn engines are challenging, because of the need to reduce NOx in lean burn exhaust conditions [51]. Several avenues have been pursued to eliminate the harmful NOx from the diesel engine exhaust [52].

1.2. Engine exhaust composition

The exhaust emission contains pollutant in various proportions depending on the type of engine [53]. Inside an engine, the complete combustion of the motor fuels composed exclusively of carbon and hydrogen would only generate CO_2 and H_2O, to the exclusion of any other harmful product. However, the very short time allowed for chemical oxidation processes integration in combustion chambers, the lack of homogeneity in the carbureted mixtures, and the heterogeneity and rapid variations in the temperature do not allow for the state of ideal thermodynamic equilibrium to be reached. Thus, the incomplete combustion of a hydrocarbon results in the formation of a wide range of organic and inorganic compounds distributed among the gaseous, semi-volatile and particulate phases as is given in Table 1.1 [11]. The gaseous phase contains CO, CO_2, NOx, SOx, NH_3, water vapors, volatile organic compounds (VOC), hydrocarbons (HC), polycyclic aromatic hydrocarbon (PAH), organic/inorganic acids, halogenated organic compounds, dioxins, etc.

Table 1.1. Main components and their concentration of various LDV engine exhausts [18]

Exhaust Component	**4-stoke SI engine**	**4-stroke CI engine**	**Diesel engine**
CO_2	10-18%	10-15%	3-13%
CO	0.1-6.0%	0.5-0.9%	150-1200 ppm
HC	0.1-4.0%	0.5-0.7%	50-500 ppm
NOx	100-4000 ppm	800-2300 ppm	200-1000 ppm
SOx	15- 60 ppm	10-50 ppm	10- 100 ppm
PM	Low	Low	50-400 mg m^3

1.2. Nitrogen Oxides (NOx)

Nitrogen is a relatively inert gas that makes up about 80% of the air. Nitrogen can form several different oxides by the combustion of fuels in air. NOx mostly contain nitric oxide (NO) ~95%, nitrogen dioxide (NO_2) about 4.5% and nitrous oxide (N_2O) around 0.5%. NO is a sharp sweet-smelling gas at room temperature, whereas NO_2 has a strong, harsh odour and is a liquid at room temperature [54]. Two of the most toxicologically significant nitrogen oxides are NO and NO_2; both are non-flammable and colourless to brown at room temperature. The family of NOx compounds and their properties [55] are listed in Table 1.2.

Table 1.2. Nitrogen Oxides (NOx)

Formula	Name	Properties
NO	Nitric oxide	colourless gas, slightly water soluble
NO_2	Nitrogen dioxide	red-brown gas, highly water soluble, decomposes in water
N_2O	Nitrous oxide	colourless gas, water soluble

The three typical types of NOx that produced from combustion processes are:

Fuel NOx – It is formed when the nitrogen bound in the fuel is combusted. Obviously, the amount of NO_X formed from this mechanism is a function of the fuel being combusted. Natural gas has no fuel nitrogen, and therefore, no NO_X is formed [56]. Heavy oils tend to have higher nitrogen content than light oils such as residential heating oil. The fuel NO_X reaction mechanism is of most concern when coal is being burned.

Thermal NOx –The most important of these is thermal NO_X formation. In thermal NO_X formation, NO_X is formed by fixation of atmospheric nitrogen, in which the reactions of N_2 from the combustion air with reactants such as O and OH radicals and molecular NO_2 [56].

Thermal NO_X is the primary source of NO from stationary as well as mobile combustion sources.

Prompt NOx – The main feature in the formation of prompt NOx is that the CH radical (methylidyne), which is formed in the early phase at the flame front, reacts with atmospheric N_2 to form HCN (hydrocyanic acid), which reacts further to form NOx [34]. The mechanism of prompt NO_X formation is illustrated in section 1.3.2.

1.3. NOx Formation Mechanism

The formation of NO_2 results only from the subsequent oxidation of NO, so the total NOx (NO + NO_2) is not affected by the amount of NO_2 formed. Therefore, the calculation of NO is sufficient for determining total NOx and the literature review of NOx formation processes focused only on NO formation. There are four well-recognized chemical mechanisms for NOx formation. These include the Zeldovich, prompt, nitrous oxide, and fuel-bound nitrogen mechanism. The following sections provide a description of these four NO-producing chemical pathways.

1.3.1. Zeldovich Mechanism

The Zeldovich Mechanism produces NO by the reaction of atmospheric oxygen and nitrogen at elevated temperatures. The mechanism consists of two chain reactions:

$$O + N_2 \rightleftarrows NO + N \qquad (1)$$

$$N + O_2 \rightleftarrows NO + O \qquad (2)$$

These reactions can be further extended by adding the reaction:

$$N + OH \rightleftarrows NO + H \qquad (3)$$

This three-reaction set is known as the Extended Zeldovich Mechanism [57]. The NO formed through the Zeldovich mechanism is commonly referred to as thermal NO because the formation rates are only significant at high temperatures (~1300°C). This set of reactions is a widely-used and recognized mechanism for NO formation.

1.3.2. Prompt NOx Mechanism

The prompt mechanism was first proposed by Fenimore in 1971 to account for NO formation that occurred very quickly in the primary reaction zone of the combustor [58]. It was later found that the NO is formed from the reaction of hydrocarbon radicals present during the combustion process reacting with atmospheric nitrogen. The primary initiating reaction is:

$$N_2 + HC \rightleftarrows HCN + N \qquad (4)$$

The N atom becomes NO through the last two reactions in the Zeldovich mechanism. The HCN route to NO is complex, but the main path is through NCO, NH, N, and then finally to NO Zeldovich N atom reactions.

1.3.3. Nitrous Oxide Mechanism

The nitrous oxide (N_2O) mechanism was recognized by Malte and Pratt in 1974 [58] as an important NO pathway. It is regarded as being most important in rich-fuel ($\lambda < 0.8$), low-temperature conditions, such as those experienced in lean-premixed combustion. Air–fuel equivalence ratio, λ (lambda), is defined as follows:

$$\lambda = (A/F)_{actual} / (A/F)_{stoichiometric}$$

$\lambda = 1.0$ is at stoichiometry, rich mixtures $\lambda < 1.0$, and lean mixtures $\lambda > 1.0$.

The three main steps in the mechanism of N_2O formation are as follows:

$$O + N_2 \rightleftarrows N_2O \qquad (5)$$
$$H + N_2O \rightleftarrows NO + NH \qquad (6)$$
$$O + N_2O \rightleftarrows NO + NO \qquad (7)$$

1.3.4. Fuel NOx Mechanism

Combustors burning fuel which contains nitrogen show an increase in NO production. This increase in NO results from the conversion of the organically-bound nitrogen in the fuel to NO. The mechanism begins with the pyrolysis of the nitrogen containing fuel to HCN. The HCN then follows the same pathway to NO as the prompt mechanism. Because of this, the fuel and prompt NO are considered linked processes [58]. This mechanism is obviously unimportant in fuels containing no nitrogen, such as natural gas, but contributes significantly when burning nitrogen containing fuels such as coal.

1.4. Other Sources of NOx

Apart from diesel engines which contribute 58% of total NOx emissions, there are several other exhaust emissions come from mobile sources, stationary area sources (oil and gas production and industrial), and stationary point sources including industrial, power plant, and commercial-institutional sources contain large amount of NOx [59]. With the industrial activities and the number of automobiles increasing simultaneously, the NOx emission will significantly increase [60]. NOx are released to the air from the exhaust of motor vehicles, the burning of coal, oil, or natural gas, and during processes such as arc welding, electroplating, engraving, and dynamite blasting. The sum of NOx, HNO_3, PAN and other minor NOx oxidation products is known as the total reactive nitrogen. Pie-chart (Figure 1.2) shows various NOx sources, among all about 58% NOx produced from transportation.

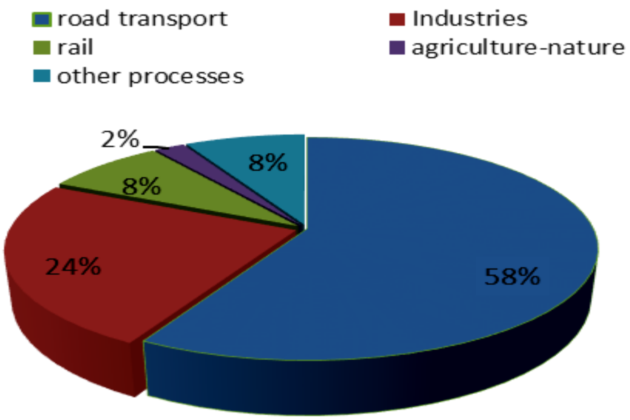

Figure 1.2: Pie-chart for NOx sources

1.4.1. Highway Mobile Sources: Highway vehicles include passenger cars and trucks, diesel vehicles, pickup trucks and vans, multi-trailer trucks, motorcycles, and sport utility vehicles certified for highway use.

1.4.2. Non-Road Mobile Sources: Non-road mobile sources include aircraft, marine vessels, railroads, logging and construction equipment, industrial engines etc.

1.4.3. Natural Sources: Natural sources of NOx compounds may be categorized as biogenic or geogenic sources. Each category is discussed separately in the following sections:

1.4.3.1 Biogenic Sources: biogenic sources are those whose emissions result from natural biological activity (i.e., living organisms). Biogenic NOx emissions can come from soils, forests, volcanoes and croplands. Some of the main factors that influence the quantity of biogenic emissions that are generated include land use and climatology (i.e., temperature).

1.4.3.2 Geogenic Sources: Geogenic sources of NO_x emissions include:

(a) Marine Ecosystems (NO_x, N_2O): NO_x emissions are released from the ocean as a result of the photolysis of nitrates in saltwater at the ocean surface. The contribution of NO_x by marine ecosystems is small and has minimal impact on atmospheric reactions over landmasses.

(b) Lightning (NO_x, N_2O): A natural source of nitrogen oxides occurs from a lightning stroke. The very high temperature in the vicinity of a lightning bolt causes the gases oxygen and nitrogen in the air to react to form nitric oxide.

$$N_2 + O_2 \rightarrow NO \qquad (8)$$

The nitric oxide very quickly reacts with more oxygen to form nitrogen dioxide.

$$NO + O_2 \rightarrow NO_2 \qquad (9)$$

Both of the nitrogen compounds are known collectively as nitrogen oxides or NOx. Nitrogen oxides can also be formed when biomass is burnt and during lightning (Figure 1.3).

Figure 1.3: Lighting as a natural source for NOx

(c) Fires (NOx, NH_3): Burning sources include wildfires, prescribed burning, coal refuse fires, agricultural drums, solid waste burning, and structural fires. Emissions from these sources are highly variable and difficult to quantify.

(d) Stratospheric Intrusion (NOx): Minimal amounts of NOx are formed from stratospheric intrusion. Nitrous oxide in the stratosphere is oxidized and dissociated by solar radiation. The newly formed NOx compounds descend to the troposphere.

(e) Volcanoes and Geysers (NOx, N_2O, NH_3): Only trace amounts of NOx and NO_3 are emitted from geogenic sources. Pollutants of concern for geogenic activity include particulate matter, sulphur dioxide, hydrogen sulphide, and carbon monoxide.

1.5. Adverse effect of nitrogen oxides (NOx)

Atmospheric NOx have been recognized as principal pollutants which adversely affect human health. NOx photo-chemically react with hydrocarbons and other atmospheric constituents to form more toxic secondary pollutants such as ozone, peroxy-acetyl nitrate (PAN), Per Aceto Hydride (PAH), smog, acid rain etc. [61]. The secondary pollutants have more deleterious effect on human health, environment, vegetation and materials as compared to NOx [62]. It acts as indirect greenhouse gases by producing the tropospheric greenhouse gas ozone via photochemical reactions in the atmosphere. It is estimated that (35–38) $\times 10^6$ tonnes of NO are emitted [63] from the exhaust gases of automobiles every year in the world [64].

1.5.1. Effects on health

Current research shows that NO helps to destroy cancerous cells. NO acts as a messenger chemical within the body, assisting the immune system in seeking out and destroying invading bacteria, viruses and parasites [65]. Its presence helps relax blood vessels and improves blood flow, reducing blood pressure. Additionally, nitric oxide helps to obstruct blood clotting within blood vessels, which helps fend off dangerous clots that can cause clogged arteries and lead to heart attack or stroke. But it is more harmful when exposer limit is going to be high, the Occupational Safety and Health Administration (OSHA) has set a limit of 25 ppm of nitric oxide in workplace air during an 8-hour workday, 40-hour work week. Epidemiological studies have revealed that concentrations of NOx having hazardous effects for people in good health are above 0.05 ppm for an exposure of over 24 h [66].

Breathing in small levels of NOx can cause nausea, irritated eyes and/or nose, fluid forming in lungs and shortness of breath [67]. High levels of NOx can lead to burning spasms; swelling of throat; reduced oxygen intake; serious respiratory illness (e.g., asthma, chronic bronchitis). In the presence of air, sunlight and hydrocarbon NO is transformed to NO^* radical. This radical oxide is poisonous for the respiratory and cardiovascular system.

1.5.2. Effects on Materials

Nitrogen dioxide in reaction to textile dyes can cause fading or yellowing of fabrics. Exposure to nitrogen dioxide can also weaken fabrics or reduce their affinity for certain dyes.

1.5.3. Effects on Ecosystems

Ground-level Ozone - It is formed when NOx and volatile organic compounds (VOCs) react in the presence of heat and sunlight [68]. Children, people with lung diseases such as asthma, and people who work or exercise outside, are susceptible to adverse effects such as damage to lung tissue and reduction in lung function [69]. Ozone can be transported by wind currents, and can cause health impacts far from original sources. Other impacts from ozone include damaged vegetation and reduced crop yields [70]. Moreover, tropospheric ozone is the third largest single contributor to positive radiation forcing.

Acid Rain - NO is rapidly oxidized to NO_2 by atmospheric oxidants such as ozone. NO_2 is a precursor of nitric acid that contributes substantially to the so-called acid rain. The acidification is the result of the reaction of NO_2 with water, involving hydroxyl groups (OH-) and gives rise to nitric and nitrous acid. These acids return to earth's surface by dry and wet deposition [69]. Acid rain damages; causes deterioration of cars, buildings and historical monuments; and causes lakes and streams to become acidic and unsuitable for many fish. Acidification of soils causes the loss of essential plant nutrients and increased levels of soluble aluminium that are toxic to plants. Acidification of surface waters creates conditions of low pH and levels of aluminium that are toxic to fish and other aquatic organisms [70]. NOx, which is well known for its role in the formation of ozone, can be oxidized to nitric acid via two important pathways. During the day, NO_2 is oxidized by the hydroxyl radical:

$$NO_2 + OH\cdot \rightarrow HNO_3 \qquad (10)$$

This reaction is responsible for most of the nitric acid formation. A second route takes place mostly at night. First, NO_2 is oxidized by ozone to the nitrate radical, NO_3:

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \qquad (11)$$

$$NO_2 + NO_3 \rightarrow N_2O_5 \qquad (12)$$

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \qquad (13)$$

This reaction is slow in the gas phase, but can occur rapidly on the surface of a particle that contains water. However, the rate of this reaction is very uncertain.

Particles - NOx reacts with ammonia, moisture, and other compounds to form nitric acid and related particles. Human health concerns include effects on breathing and the respiratory system, damage to lung tissue, and premature death. Small particles penetrate deeply into sensitive parts of the lungs and can cause or worsen respiratory disease such as emphysema and bronchitis, and aggravate existing heart disease [70].

Water Quality Deterioration - Increased nitrogen loading in water bodies, particularly coastal estuaries, upsets the chemical balance of nutrients used by aquatic plants and animals. Additional nitrogen accelerates “eutrophication,” which leads to oxygen depletion and reduces fish and shellfish populations in the air are one of the largest sources of nitrogen pollution in the Chesapeake Bay.

Global Warming - One member of the NOx, nitrous oxide, is a greenhouse gas. It accumulates in the atmosphere with other greenhouse gasses causing a gradual rise in the earth's temperature. This will lead to increased risks to human health, a rise in the sea level, and other adverse changes to plant and animal habitat. Global warming is one of the main issues, which refers to an increase in the average temperature of earth. An increase in the mean temperature of the earth’s atmosphere of approximately 0.4-0.8°C has already been measured [71]. Global warming has huge impacts in physical, ecological, social and economic aspects. Rising sea levels, melting glacier and of global warming.

The NOx is the precursor in the atmosphere for the photochemical formation of more toxic secondary pollutants such as PAN, PAH, ground level ozone, smog, etc. N_2O is a greenhouse gas having global warming potential ~310 times than CO_2. Emissions of NOx have negative impact on human health, environment, materials and agriculture. Their effects on human health are respiratory diseases, bronchitis, lung and heart diseases. Effects on environment is more drastic as global warming caused melting of snow caps, increase sea level, natural calamities due to localised cloud burst, draught situations, storms, etc. Acid rain tarnish the beauty of buildings and monuments. Global warming cause heat waves and lead to dehydration and heat stroke cause weather related allergies, respiratory problems and even deaths. These climate change enhances spread of stress diseases through water, food, climate related stress and animals (Figure 1.4).

Figure 1.4: Global warming and its impact

Toxic Chemicals - In the air, NOx reacts readily with common organic chemicals and even ozone, to form a wide variety of toxic products, some of which may cause biological mutations. Examples of these chemicals include the nitrate radical, nitroarenes, and nitrosamines [70].

Visibility Impairment - Nitrate particles and nitrogen dioxide can block the transmission of light, reducing visibility in urban areas and on a regional scale in our national parks.

Smog – When N_2O from automotive exhausts and gaseous HCs from cars and oil refineries, in presence of sunlight, form ozone and photochemical smog.

1.6. Diesel emissions legislation

Due to the adverse impact of diesel emissions, government legislations for permissible exhaust emission limits were first introduced in both Europe and the United States of America in 1982, only for light-duty vehicles and not until 1990 for heavy-duty engines [71, 72, 73]. The first Indian emission regulations for diesel vehicles were introduced in 1992 [74]. Since the year 2000, India started adopting European emission and fuel regulations for four-wheeled light-duty and for heavy-duty vehicles (Table 1.3).

Table 1.3: Emission standards for diesel vehicles [75]

Year	Reference	Light duty diesel (mg/km)		Heavy duty diesel (mg/kWh)	
		NOx	Soot	NOx	Soot
2000	Euro I India 2000	-	140-250	800	360
2005	Euro II Bharat Stage II	-	80-170	700	150
2008	Euro III Bharat Stage III	500-780	50-100	500	100
2010	Euro IV Bharat Stage IV	250-330	25-40	350	20
2011	Euro V	180	5	200	5
2014	Euro VI	80	4.5	40	4.5
2018	Bharat Stage VI	80	4.5	40	4.5

It is quite apparent from Table 1.3 and Figure 1.5 that emission regulations of soot and NOx are becoming more and more stringent, e.g. 5mg km^{-1} for PM and 180 mg km^{-1} for NOx corresponding to 2011 Euro-V regulations will be reduced to 4.5mg km^{-1} for PM and 80mg km^{-1} for NOx by the prescribed pending 2014 Euro-VI regulations, so, it is urgent to control these two kinds of pollutants [75].

From table 1.3 and figure 1.5, it is clear that there are marginal reduction of the PM for both LDV as well as HDV from Euro-5/V to Euro-6/VI i.e. 5 to 4.5 mg/km (LDV) and 5 to 4.5 mg/kWh (HDV) respectively; whereas, reduction of NOx emissions is too much from Euro-5/V to Euro-6/VI i.e. 180 to 80 mg/km (LDV) and 235 to 80 mg/kWh (HDV) respectively [75]. Parallel to Euro norms (Euro1-6/I-VI) Indian standard i.e. Bharat Stage (BS I-IV-VI) has been implemented and recently, from April 2018 Indian Standard jumped from BS IV to BS VI, bypassing BS V [76-77]. Thus, effective emissions control devices need to be developed to enable vehicles to meet the increasingly strict emissions norms for NOx.

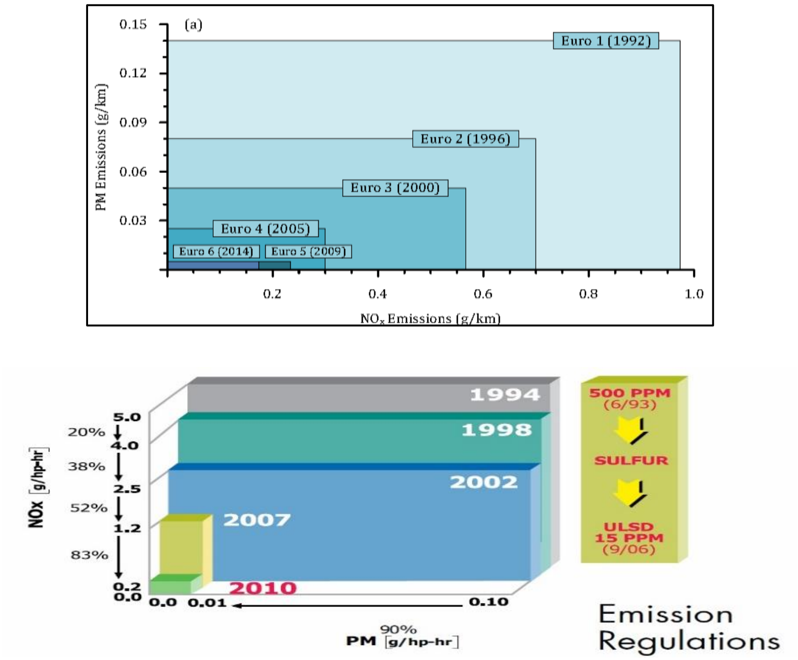

Figure 1.5: European PM and NOx emissions legislation for LDV and HDV diesel vehicles Various technologies have been developed to control the emission of NOx [53].

1.7. NOx emissions control technologies

Abatement of NOx have led to the development of numerous NOx reduction techniques, which can be categorized as pre combustion, fuel modification, engine modifications and post combustion exhaust gas treatment. Pre combustion fuel treatment concerns the reformulation of conventional fuels, treatment of fuels and choice of alternative fuels, which have low NOx emissions. Also the use of fuels with low levels of nitrogen content is an option. Combustion modification is a primary measure intended to minimize NOx formation by designing better burning devices that minimize the oxygen concentration, the flame temperature and the residence time in the combustion zone [78]. Examples of combustion control devices are the low NOx burners, exhaust gas recirculation (EGR), fuel re-burning, staged combustion and water or steam injection. The combustion control technologies are the most cost-effective and energy efficient. On the other hand, post combustion technologies are concerned with the treatment of flue gas before its exhaust out to the atmosphere without changing the combustion parameters.

A drawback of combustion control techniques is sometimes the enhanced N_2O formation [79,80]. The main disadvantage of combustion control methods is the low NOx conversion (<70%) compared to some post-combustion techniques (90- 99%).

Reducing NOx is more complicated than PM from the exhaust of a diesel engine [81, 82]. Thus, it is a significant challenge for the scientific community to improve the efficiency of NOx removal (De-NOx) technologies from diesel engine exhaust. Various technologies developed to control the emission of NOx are as follows:

1.7.1. Exhaust gas recirculation (EGR)
1.7.2. Catalytic decomposition of NOx
1.7.3. Nonselective catalytic reduction (NSCR)
1.7.4. NOx storage and reduction (NSR)
1.7.5. Selective catalytic reduction (SCR)
1.7.6. NOx adsorber catalysts (NAC)
1.7.7. Simultaneous catalytic removal of NOx and PM

1.7.1. Exhaust gas recirculation (EGR)

EGR is effective to reduce NOx because it lowers the flame temperature and the oxygen concentration of the working fluid in the combustion chamber, as the formation of NOx is highly temperature dependent [83]. However, as NOx reduces, PM, CO and unburned hydrocarbons increases, resulting from the lowered oxygen concentration [84]. EGR works by re-circulating 5-10% of the cooled exhaust gases back to the engine air inlet in order to lower the combustion temperature (several hundred degrees), and thus lower NOx emissions (Figure 1.6). Exhaust consists of CO_2, N_2 and water vapours mainly. When a part of this exhaust gas is re-circulated to the cylinder, it acts as diluent to the combusting mixture [85]. This also reduces the O_2 concentration in the combustion chamber. The specific heat of the EGR is much higher than fresh air; hence EGR increases the heat capacity (specific heat) of the intake charge, thus decreasing the temperature rise for the same heat release in the combustion chamber [86].

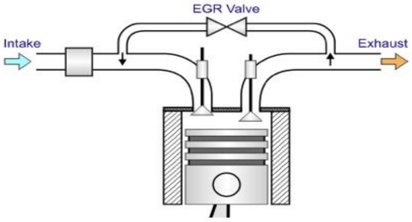

Figure 1.6: Exhaust gas recirculation

Three popular explanations for the effect of EGR on NOx reduction are increased ignition delay, increased heat capacity and dilution of the intake charge with inert gases [87]. The ignition delay hypothesis asserts that because EGR causes an increase in ignition delay, it has the same effect as retarding the injection timing. The heat capacity hypothesis states that the addition of the inert exhaust gas into the intake increases the heat capacity (specific heat) of the non-reacting matter present during the combustion. The increased heat capacity has the effect of lowering the peak combustion temperature. According to the dilution theory, the effect of EGR on NOx is caused by increasing amounts of inert gases in the mixture, which reduces the adiabatic flame temperature [88].

1.7.2. Catalytic Decomposition of NOx

The decomposition of NO represents the most attractive solution in emission control, because the reaction does not require adding any reactant to exhaust gas and could potentially lead to the formation of only N_2 and O_2. Additional reductants such as HC, CO, H_2 or ammonia can lead to the production of secondary pollutants like oxygenated hydrocarbons, CO, N_2O or ammonia or, even, as was often reported in the past, cyanate and isocyanate compounds. This could be completely avoided in this case, except N_2O formation [80]. In the direct NO decomposition reaction, the exhaust containing NO is passed over a catalyst, where the NO bond is split, and N atoms recombine to N_2 while the O atoms recombine to O_2 [81].

$$2\,NO \rightarrow N_2 + O_2 \qquad (14)$$

$$2\,NO \rightarrow N_2O + \tfrac{1}{2}\,O_2\text{`} \qquad (15)$$

The most promising decomposition catalysts are transition metal-exchanged zeolites and perovskites [82]. There are several papers, reviews, patents and Ph.D. thesis on direct decomposition of NOx [83-87]. The direct NO decomposition reaction is thermodynamically favoured at low temperatures below 900^{o}C, but it has proven difficult to find a catalyst that is active, stable and oxidation-resistant.

1.7.3. Nonselective Catalytic Reduction (NSCR)

In non-selective catalytic reduction, CO, NOx and hydrocarbons are converted into CO_2 and N_2 via a catalyst. This technique does not need additional reagents to be injected because the unburned HC and CO are used as reductants. The reactions can be represented by the following equations (16-18):

$$NOx + CO \rightarrow N_2 + CO_2 \qquad (16)$$

$$NOx + HC \rightarrow N_2 + CO_2 + H_2O \qquad (17)$$

$$NOx + H_2 \rightarrow N_2 + H_2O \qquad (18)$$

As may be observed from the reactions above, it requires the presence of the reactants in stoichiometric amounts to remove all of them simultaneously so that none of these compounds remain in flue gas as residuals. But the requirement can be fulfilled by feeding air and the fuel in ratios within a very narrow range, which is maintained by an automatic feedback control loop based upon residual oxygen concentration in the final exhaust. NOx conversion efficiency drops dramatically when the engine is run in the lean regime, while HC and CO conversion efficiency also declines somewhat [82].

The use of NSCR could possibly result in higher CO levels due to the engine's need for a rich mixture, to ensure that CO is available to the catalyst for the removal of NOx. If the CO level is too high after the catalyst, it may be necessary to later employ an oxidation catalyst to oxidize the CO into CO_2 [83]. PGM catalysts are employed as NSCR three way catalysts [84]. This technology controls ~30% of NOx reduction.

1.7.4. NOx storage and reduction (NSR)

NSR/ LNT/ NAC are synonymous technology and is still under development for large-scale applications.

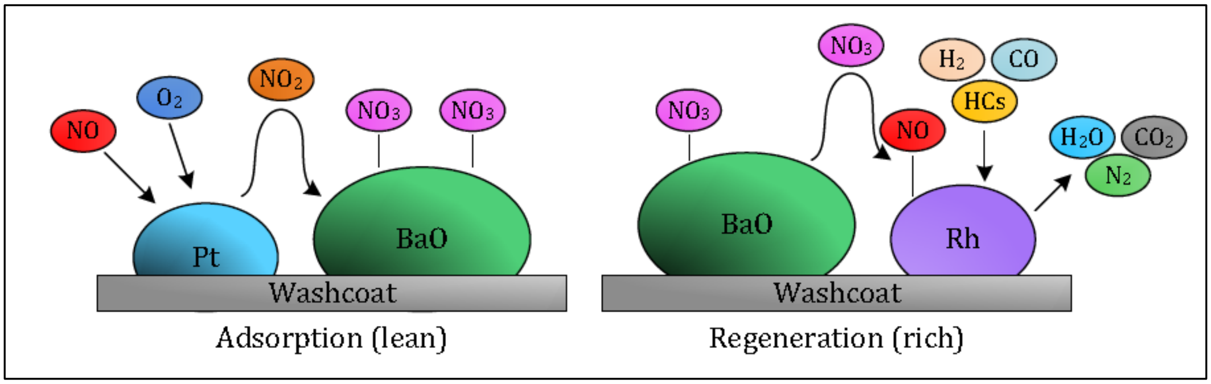

Figure1.7 NOx storage and reduction mechanism [85]

The NSR technology is based upon periodic adsorption and subsequent reduction of NOx. These catalysts contain a precious metal component which promotes the oxidation of NO into NO_2. The resulting NO_2 is then stored by basic adsorbents, e.g. Al_2O_3 and $Ba(OH)_2$. When the storage capacity is reached, rich exhaust conditions are established momentarily by engine management systems. As a result NOx desorbs from the adsorbent and is reduced by H_2, CO and HC present over the precious metal (Figure 1.7). However, a serious constraint of NSC technique is the susceptibility of the basic adsorbents to sulphur poisoning together with the high cost of noble metals [88, 89]. This technology is based on sensing and control devices which make it very complex and costly to use.

1.7.5. Selective catalytic reduction

Selective catalytic reduction (SCR) is a method of controlling NOx emissions from lean-burn diesel engines. Lean-burn engines are characterized by an oxygen-rich exhaust, thereby making the reduction of NOx virtually impossible using SCR catalyst technology [90].

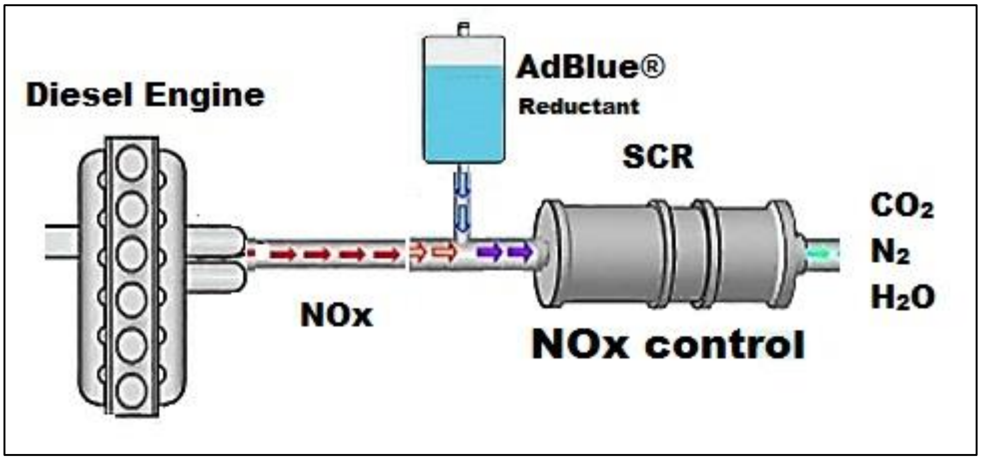

Figure 1.8: A simplified schematic picture of the SCR [89]

However, the reducing agents such as ammonia, urea, hydrocarbon, hydrogen, CO or others are injected upstream of the catalyst bed, which makes the necessary chemical reactions possible for reducing NOx in the presence of a catalyst into N_2 [91]. This approach is called SCR because the catalyst selectively targets NOx reduction instead of oxidation as oxygen is also present in the reactants. The technology was first patented in 1959 in the U.S. Figure 1.8 shows schematic picture of the SCR [92].

Originally, ammonia was used as the reducing agent in these SCR systems. Owning to safety reasons, ammonia has been ruled out and replaced by urea for vehicular NOx control. Other reductants (HC, alcohols, ethanol amine, H_2, etc.) also, have been screened to substitute ammonia [92]. Oxygenated hydrocarbons, later, have been discovered as another potential reductant [93]. The alternative choice, recently, is hydrocarbons which is gaining more attention from researchers [94]. Due to the existence of hydrocarbon in the exhaust gas (passive mode) or in the injected fuel itself (active mode), it is a relatively simple to apply to the passenger vehicles. Now, NOx emissions can be reduced by SCR method, more than 90 percent [42]. The process has been further improved step by step in the recent years. There are dominantly two techniques used; first is ammonia/urea-SCR and the second one is Hydrocarbon-SCR.

1.7.6. Compact SCRT (SCR + CRT)

In future several diesel emissions control systems will be combined into a single unit to minimize space requirements, and for cost and efficiency considerations. Examples of this include the SCRT which refers to the combination of Continuously Regenerating Trap (CRT) with SCR as illustrated schematically in Figure 1.9. Walker, et al. has ingeniously combined oxidation catalyst, DPM filtration and ammonia SCR for NOx control in a single compact container for heavy-duty diesel engines [61].

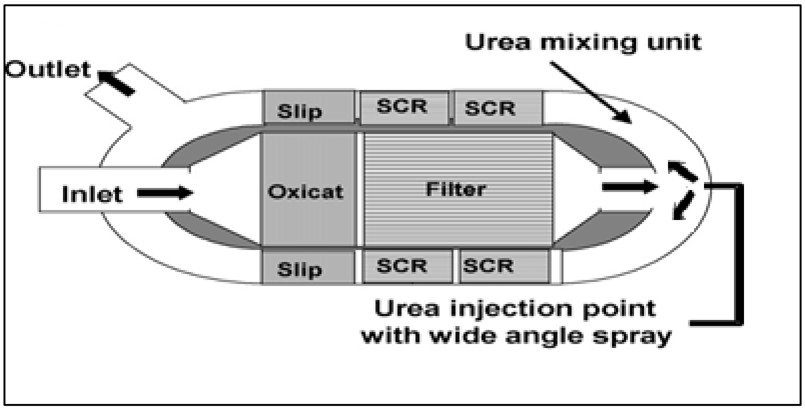

Figure 1.9: A compact emissions control design for heavy-duty diesel vehicles that includes oxidation catalyst, regenerative DPF and urea-SCR [197]

The exhaust gas first passes through a platinum oxidation catalyst that oxidizes CO and HCs, as well as converting NO to NO_2 that continuously oxidizes DPM in the filter. The exiting NOx is then reduced to N_2 over two SCR catalysts. The ammonia here 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 oxidize it to NO. The common problem with all SCR systems is the release of un-reacted ammonia. This is called ammonia slip. Slip can occur when catalyst temperatures are not in the optimal range for the reaction or when too much ammonia is injected into the process. An additional oxidation catalyst called a slip catalyst is typically fitted downstream of an SCR system to reduce such slip.

1.7.7. Simultaneous Soot-NOx removal

Reducing the amounts of PM and NOx from diesel-engine exhaust had become a globally important issue. The soot formula can be approximately given as C_8H [196]. Systems utilizing an oxidizing catalytic converter and a diesel particulate filter (DPF) to reduce PM had been commercialized. However, no system that could reduce PM and NOx at the same time had been commercialized. Therefore, Toyota developed its Diesel Particulate-NOx Reduction System (DPNR), a new purification system that combines the catalytic NOx reduction and oxidation of PM simultaneously [67].

$$C_8H + NO \rightarrow CO_2 + H_2O + N_2 \quad (24)$$

In the DPNR catalytic converter, a NOx adsorption/reduction component is supported on the surface of a porous ceramic wall-flow DPF base material. In order to capture PM with minimal pressure loss, Toyota developed for the DPNR catalytic converter a new cordierite DPF base material having a large number of small, uniformly distributed pores. Figure 1.10 shows mechanism of DPNR. Furthermore, to improve the NOx adsorption/reduction performance, Toyota developed the ideal catalyst for the temperature window of diesel-powered vehicles, as well as a technology that coats the catalyst layer uniformly through slurry atomization, etc. These developments helped realize the DPNR catalytic converter.

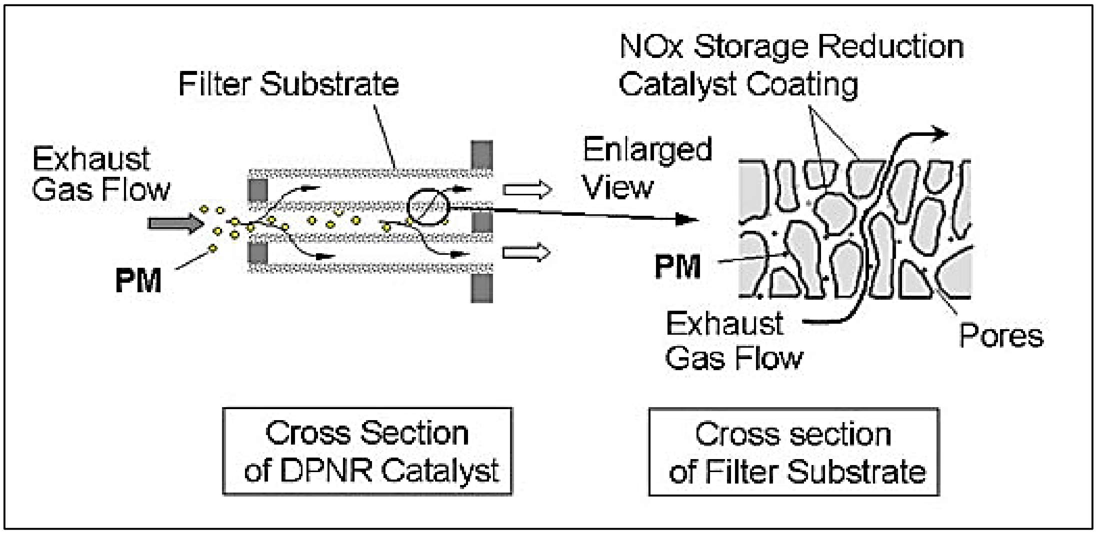

Figure 1.10: Structure of DPNR catalytic system

The DPNR has a high NOx conversion efficiency of ~80% even after 40,000km drive without the desulfurization [68].

1.8.Types of Catalyst used for SCR of NOx

A wide variety of catalysts are known which initiate the reduction of NO such as noble metals, transition metals, spinel structure materials, perovskite structures, hydrotalcite, etc. In the commercial SCR unit for stationary sources, vanadia-based catalysts (V_2O_5/TiO_2 catalyst) mixed with WO_3 and/or MoO_3 as promoters are used as effective catalysts. At present transition metal oxide catalyst V_2O_5/WO_3-TiO_2 are used in stationary sources. But, toxicity due to vanadium content and high selectivity toward toxic N_2O are the disadvantages.

On the other hand noble metal catalysts supported on oxide are widely used in pollution control in mobile sources. Pt, Pd and Rh are important active components in automotive catalysts and considerable number of studies have been performed on PGM supported catalysts to achieve high efficiency and also high durability [73]. However these catalysts have some disadvantages like sensitive to SO_2, high cost and low availability. In order to overcome these disadvantages several catalysts were studied which are described below.

1.8.1. Perovskites

Perovskite-type oxides possessing general formula ABO_3 ($^{XII}A^{2+VI}B^{4+}X^{2-}{}_3$) where 'A' and 'B' are two cations of very different sizes, and X is an anion that bonds to both. A can be rare earths (La, Ce, Pr) alkali and alkaline earths (Cs, Sr, Ba, Ca) while the B sites are usually occupied by transition metals (Co, Fe, Cu, Ni, Mn, Cr). It has generated considerable interest due to their higher chemical, thermal and structural stability than single oxides. As a result, they exhibit good catalytic performance for many reactions. In the idealized cubic unit cell of such a compound (Figure 1.11), type 'A' atom sits at cube corner positions (0, 0, 0), type 'B' atom sits at body centre position (1/2, 1/2, 1/2) and oxygen atoms sit at face centred positions (1/2, 1/2, 0) [99].

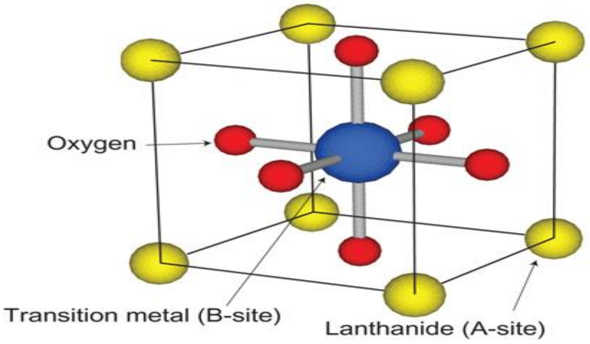

Figure 1.11: ABO_3 ideal perovskite structure

1.8.2. Hydrotalcite

Hydrotalcite is a magnesium aluminium hydroxy carbonate, layered double hydroxide of general formula $Mg_6Al_2(CO_3)(OH)_{16}\cdot 4(H_2O)$ whose name is derived from its resemblance with talc and its high water content (Figure 1.12). It is di-morphous with and often intermixed with manasseite [100].

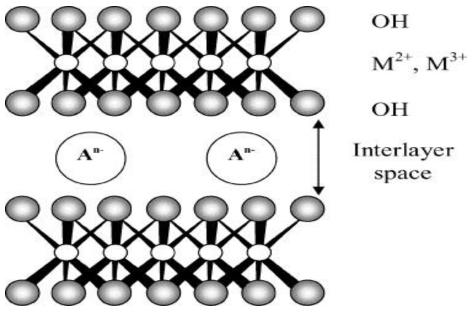

Figure 1.12: Chemical structure of hydrotalcite catalyst

1.8.3. Spinels

Recently, transition-metal oxides with spinel-type AB_2O_4 structure have been extensively employed as catalyst materials in a variety of catalytic reactions mainly owing to their low cost, readily available raw materials, and good redox properties [20−22]. The spinels with the general formulation $A^{2+}B_2^{3+}O_4^{2-}$, where the cations A and B can be divalent, trivalent, or quadrivalent cations, including magnesium, zinc, iron, manganese, aluminium, chromium, titanium, and silicon. The anion is generally oxide. Generally, A in AB_2O_4 occupies the tetrahedral site, while B locates the octahedral site [Figure1.13].

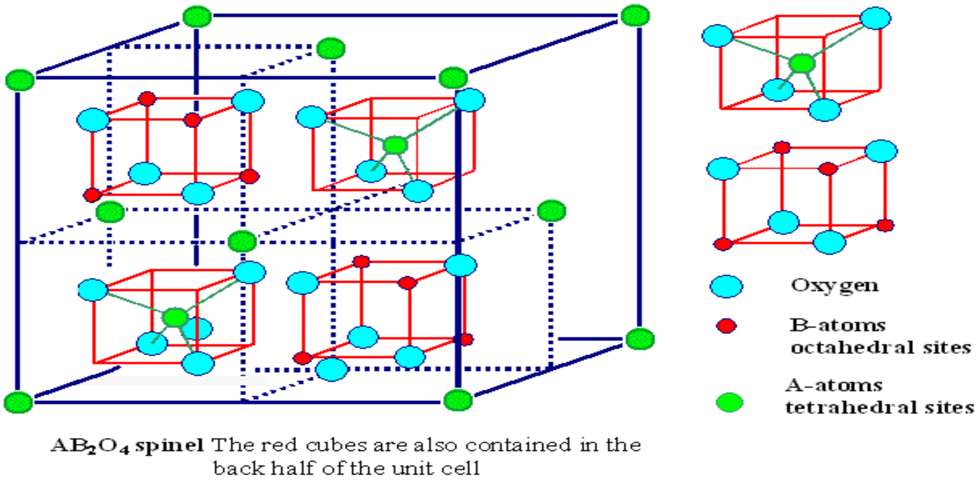

Figure 1.13: Chemical structure of spinel catalyst

The crystal lattice in both tetrahedral and octahedral sites can be substituted by different types of cations. In addition, the cations between A and B sites can mutually transfer, engendering surface-abundant oxygen vacancies [23]. These characteristics are favourable to mediate acid−base sites and redox properties of AB_2O_4, which are able to facilitate catalytic activity in SCR of NOx at low temperature. The synergistic effect of Co and Mn promoted its redox property and surface acidity. In this context, Mn-based spinels possess the advantages of low toxicity and multiple valence states [24], they have been widely studied in other fields than catalysis such as magnetic materials [25] and energy conversion [26]. Few recent studies have been devoted to SCR of NOx using NH_3 reductant [101, 27].

1.8.4. Noble/ Precious metal catalysts

These metals are ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, and gold. They are resistant to corrosion and oxidation in moist air, unlike most base metal catalysts. They tend to be precious, often due to their rarity in the earth's crust. They have role much higher intrinsic activity for the simultaneous conversion of CO, HCs and NOx. Precious metal-based catalysts are also much more resistant to sulphur poisoning at temperatures <750 K [102].

1.8.5. Transition metal Catalysts

Transition metals are the d-block elements of the periodic table like Cu, Ce, Zr, Cr, Co, etc. These are less active catalysts than noble metals but due to high cost and low availability of PGM, there is a constant search for PGM-free catalysts. Some of the transition metal catalysts like $CuCeO_2$, Cu-CeO_2-Zr, Cu-Co, etc. give de-NOx activity comparable to noble metal catalysts [103].

1.9.Reductants used for SCR of NOx

In the SCR process, the reducing agent is competitively consumed by two main pathways, i.e., the selective reduction by NOx and the completed oxidation by oxygen. A lot of investigative research has been devoted to discover the appropriate reductants and catalyst materials for the SCR system [95]. The details of reductants used in SCR of NOx are presented below.

1.9.1 Ammonia and Urea

Ammonia has been used as a reductant for control of NOx in thermal power plants and industrial stationary applications. However, the use of ammonia in automotive vehicles is unsuitable because it is hazardous and toxic. In addition, its high vapour pressure makes it challenging to store and on-board transport safely. To prevent these problems, ammonia is chemically transformed to non-toxic urea. Urea is an organic compound with the chemical formula $(NH_2)_2CO$. It is solid, colourless, odourless and highly soluble in water. The urea-SCR for NOx reduction involves the following steps (Koebel et al., 2000) [96].

$$(NH_2)_2CO\ (l) \rightarrow NH_3 + HNCO \qquad (19)$$

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \qquad (20)$$

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (21)$$

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O \qquad (22)$$

Reaction (19) and (22) are called the standard SCR and fast SCR reactions respectively. Usually, NOx in exhaust from a diesel engine is composed of NO more than 90% [42]; accordingly, the standard SCR is the main reaction for ammonia-SCR. On the other hand, the reaction rate of the fast SCR reaction is much faster than that of the standard SCR reaction [97]. So, to promote the performance of NOx reduction, the fraction of NO_2 in the exhaust is deliberately increased by placing an oxidation catalyst before the SCR catalyst. Nonetheless, the fraction of NO_2 to NO should not exceed 1:1 because the reduction of NO_2 without NO, as shown in Reaction (22), is much slower than Reaction (20) and (21). Although urea SCR is more effective for NOx reduction even though urea is being replaced by other reducing agent due following disadvantages:

(a) ***Emission of iso-cyanic acid*****:** Iso-cyanic acid may be considerable at very low and at very high temperatures (typically up to 50 ppm). The fact that organic isocyanates have become well known for inducing hyper-reactive respiratory diseases in recent years calls for investigation of possible physiological effects of HNCO.

(b) ***The high freezing point of aqueous urea solutions*****:** The proposed eutectic solution has a concentration of 32.5% urea and a freezing point of only -11^oC. This poses technical problems in winter use. It has therefore been suggested to use solid urea. However, the use of solid urea will require a dosing unit for solid urea which is an expensive and critical component. Further, the introduction of solid urea into the exhaust gas stream and the mixing operation are far more difficult to achieve than with urea solution

(c) ***Possible formation of high molecular weight products***: The isocyanic acid formed as an intermediate may react with urea or with itself and lead to higher products like biuret, melamine, cyanuric acid, etc. This problem has been carefully studied earlier due to possible clogging of atomizing nozzles and deposit formation in the flue gas duct. It can be handled technically and the secondary emission of higher products is very small.

An aqueous 32.5% urea solution as reductant, commercially known as AdBlue® is facing challenges like high cost, high operating temperature (>200 ^{0}C) [96]. AdBlue® has several demerits like urea deposits are formed over the catalyst and in the exhaust system during low temperature operation such as cold start or slow urban driving. A minimum exhaust gas temperature >200^{o}C is required to avoid plugging of the spray nozzle and to ensure a complete hydrolysis of urea to ammonia [97]. Therefore, lots of new SCR catalysts utilizing HCs, oxygenated hydrocarbons, H_2 and CO as reductants have been studied [47].

1.9.2. Hydrocarbon-SCR

In the HC-SCR technology, NOx is reduced through catalytic reactions with HCs present in the diesel exhaust under rich condition or injected upstream in case of lean-burn state [48]. The reaction pathways depend on the hydrocarbon used but the following describes the total reaction in the system (Eq. 23):

$$HC + NOx \rightarrow N_2 + CO_2 + H_2O \qquad (23)$$

Additional quantities of hydrocarbons, such as diesel fuel, are often injected upstream of the catalyst to achieve higher NOx reductions. The commercial use of the technology-also known as the “lean NOx catalyst” has been very limited due to low NOx reductions and high fuel economy penalties in systems with HC injection [49]. More active and durable lean NOx catalysts would be necessary for a wider commercial deployment of HC-SCR.

1.9.3. Oxygenated Hydrocarbon

As selective reduction agents, oxygenated hydrocarbons such as ethanol, acetone, and propanol provide high conversions of NOx (above 80%) at 250-400 °C even in the presence of 10% water vapour. After studying various oxygenated hydrocarbons as the reductant for NOx-SCR, He et al. concluded that enolic on Ag/Al_2O_3 catalyst was highly active with NO + O_2, resulting in the formation of isocyanate which was the key intermediate species in the SCR of NOx. They also presented that the conversion of NOx to N_2 by using oxygenated hydrocarbons as the reducing agent was higher than that by using alkanes because surface enolic was formulated only from the partial oxidation of oxygenated hydrocarbons.

1.9.4. Hydrogen-SCR

Hydrogen has been reported to be very active towards catalytic reduction of NO into N_2, and it could potentially be used to reduce NOx emissions (50-54). Hydrogen should act as a promoter for other hydrocarbon reductants as well in similar lean NOx reduction reactions [55]. It has been found that the addition of hydrogen to the up-stream of exhaust in presence of Ag/Al_2O_3 catalyst resulted in a remarkable improvement in the level of NOx reduction [56] in the range of temperature over which NOx could be selectively reduced [57]. Several workers have investigated H_2-SCR using different catalyst like precious metals, base metal oxides, perovskite-related oxides. Savva, and Costa have critically reviewed H_2-SCR over noble metals catalysts up to 2011 [53]. Very recently, Hamada and Haneda have published a review on selective reduction of NO with H_2-SCR over platinum group metal catalysts [54]. H_2-assisted SCR of NOx with ammonia removes only 30% conversion.

1.9.5. Hydrogen assisted hydrocarbon SCR

The discovery of a promoting effect of H_2 on the low-temperature activity of Ag/Al_2O_3 catalysts by Satokawa et al. [11,12] is undoubtedly a major breakthrough for HC-SCR. Since then, many efforts have been devoted to understanding the “H_2 effect” occurring during NOx reduction by lighter hydrocarbons [13–17], higher hydrocarbons [18,19] and alcohols [20] over silver catalysts. At present, the origin of H_2 boosting behaviour on the low-temperature activity of Ag/Al_2O_3 for NOx reduction by hydrocarbons has not been revealed in full detail, while it is clear that the presence of H_2 enhances the transformation of hydrocarbons to partially oxidized species. These oxygenates have been proved to be active intermediates for NOx reduction, leading to an increase in the NOx conversion at low temperatures [15, 21–23]. Ag cluster and Ag metal are reported to be highly active for oxidation of hydrocarbons.

Hydrogen (H_2) as a reductant or promoter have been improved the conversion efficiency especially at low exhaust temperatures. H_2 is a promising and alternative reductant in SCR of NOx and it has been kept as an attracting subject for many researchers. H_2-SCR showed that the addition of hydrogen resulted in conversion of the oxidized nitrogen to N_2 on the catalyst surface. H_2 has an improving effect with HC on SCR activity especially at low temperature. H_2-HC is a promising reductant for SCR applications of NOx without any formation of secondary pollutants and the researches on improving of H_2-HC SCR will continue for a longer time.

1.10. Effect of support

Generally Al_2O_3 is used as support for emission control catalysts as it decreases the cost, provides thermal stability, excellent mechanical property. It possesses large specific surface area and can be easily given to specific shape. These properties of Al_2O_3 make it an excellent support for Mn-based catalysts [69,70]. The high surface area of γ-Al_2O_3 is the key to increase the density of active sites, lowering down catalyst cost and stabilize the catalyst [70].

1.11.Effect of promoters

Rhodium (Rh) catalysts are able to selectively reduce NO in the absence of oxygen in the feed. However, their activity is suppressed with increasing oxygen feed concentration possibly due to the formation of less reactive rhodium oxides [104]. In contrast, oxygen promotes the de-NOx activity of Mn based catalysts but decreases selectivity towards nitrogen [105].

1.12. Improvement in catalytic properties by calcination strategies of precursors

Calcination strategies such as temperature, rate of heating, duration, environment like stagnant air, flowing air and reactive calcination of precursors affect the catalytic properties and morphology [106]. Low calcination temperature may not form the proper structure required for the process [107]. Higher temperature and longer duration may sinter the catalyst and lower the surface area and active sites. Thus, there are optimum temperature, duration, gas atmosphere/ environment for the specific catalyst. The influence of different spinel over the given laboratory conditions was correlated with detailed physico-chemical characterization.

1.13. Literature Review

Literature survey for NOx SCR includes literature classification based on different type of catalysts is given at a glance in Table 1.4

Table 1.4: Recent research in SCR of NO over different catalysts at a glance

Catalyst Preparation method	**Reactant composition, operating parameters**	**Remarks**	**Reference**
Noble/ Precious metals			
Pt-Ti-MCM-41 Ti/Si=0.6, WI	1000 ppm NO, 5000 ppm H_2, 6.7% O_2, GHSV=80,000 h^{-1}	X_{NO} = 89% S_{N2} = 79%, 140°C	118
Ag-Au/Al_2O_3	300ppm NO, 300ppm CO, 300ppmC_3H_6, 2000ppm H_2, 100ppm$C_{10}H_{22}$, 10% CO_2, 10% O_2,5%H_2O in He	X_{NO}=94%, 382ºC	119
3Ag/bauxite, DP	482 ppm NO, 500 ppm NH_3, 0.67% H_2, 3% O_2 in Ar, Total Flow=600mL/min, GHSV=72,000 h^{-1}	X_{NO}>60%, 200°C	120
Ag/MgO-CeO_2-Al_2O_3,WI	500ppm NO, 0.1% C_2H_5OH, 5% O_2, 5% H_2O in He. Total Flow=100 mL/min, GHSV=40,000 h^{-1}.	X_{NO}=60-90%, 400°C, S_{N2}=92-95%	121
Transition metal oxides			
Mn–Ce/TiO, WI	400 ppm NO, 400 ppm NH_3, 2%O_2 in He, Total Flow=150 mL/min.	X_{NO} =93%, 100°C	122
Sn/Cr-MnO, NC	500 ppm NO, 500 ppm NH_3, 3%O_2 in N_2, Total Flow=200mL/min, GHSV=35,000 h^{-1}.	X_{NO}=100%, 150-250°C	123
FeMnTiOx, ICP	500 ppm NO, 500 ppm NH_3, 5% O_2, 100 ppm SO_2 , 3.5% H_2O in N_2, GHSV= 30,000 h^{-1}	X_{NO} =90%, 150–350°C	124
Mn/CeTi WI	500 ppm NO, 500 ppm NH_3, 5% O_2, 100 ppm SO_2 in N_2, GHSV=60,000 h^{-1}.	X_{NO}>90%, 175–300°C	125
$Ce_{0.3}TiF_{1.5}$ CP	0.05% NO, 0.06% NH_3, 5% O_2 in N_2, Total flow 150 mL/min, GHSV=41000 h^{-1}.	X_{NO} =92.19%, 180°C	126
Mn/Ce-ZrO_2 CP	600 ppm NO, 660 ppm NH_3, 6 % O_2, 3 % H_2O, 100 ppm SO_2, in N_2, GHSV 45,000 hr^{-1}, Total Flow = 300 mL/min	X_{NO} =98.6%, 200°C	127
Fe_2O_3, CP	500 ppm NO, 500 ppm NH_3, 3% O_2, 1000 ppm SO_2 in N_2, molar ratio [NH_3]/[NO] = 1	X_{NO} =95%, 180°C	128
MnOx-CeO_2 DP	1000 ppm NO, 1000 ppm NH_3, 3% O_2 in N_2, Total Flow=400 mL/min, GHSV=50,000 h^{-1}	X_{NO}=100%, 80–150°C	129
Mn–CeO_2 SG	[NO] = [NH_3] = 1000 ppm, [O_2] = 2%, GHSV = 42,000 h^{-1}	X_{NO}~100%, 120°C	130
Mn/SSZ-13, CP	600 ppm NO,600 ppm NH_3 ,8% O_2, 5% H_2O Total flow rate 300 ml/m,GHSV 50000 h^{-1}	X_{NO}>90%, 150-450°C	131
V_2O_5/TiO_2, WI	350 ppm NO, 350 ppm NH_3, GHSV 300-1100 h^{-1}	X_{NO}=0.7425, 160°C	132

Cu/zeolite, CP	350 ppm NO, 350 ppm NH_3, 14% O_2, 4.6 % H_2O, 5% CO_2, GHSV 30000 h^{-1}	X_{NO} >90%, 200-300°C	133
VOx/CeO_2, HT	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol %, N2 balance, GHSV = 120,000 $h^{–1}$	X_{NO}=95–100%, 350°C	134
γ-Fe_2O_3, IE	1000 ppm NO, 1000 ppm NH_3, superficial flue gas velocity 0.1 m/s	X_{NO}=90%, 250°C	135
MnO_2/TiO_2,WI	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol %, N_2 balance, GHSV = 24,000 $h^{–1}$	X_{NO}=100% 150–200°C	136
MnOx, CP	[NO] = [NH_3] = 500 ppm, [O_2] = 3 vol %, N_2 balance, GHSV = 47,000 $h^{–1}$	X_{NO} ~100%, 80–150°C	137
V_2O_5/TiO_2, WI	1% V_2O_5/TiO_2 (wt)% ,NO = 500 ppm, NH_3 = 500ppm, O_2 = 50000 ppm	X_{NO}=50%, S_{N2} =93%, 350°C	138
Mixed transition metal Oxides			
Sn/Cr-MnOx, NC	500 ppm NO, 500 ppm NH_3, 35ppm, N_2O 3%, O_2 in Air,200 ppm H_2O,GHSV 35000 h^{-1}	X_{NO} =99%, 200°C	139
Mn-Ce/TIO_2, WI	400 ppm NO, 400 ppm NH_3, 2% O_2 in Fe, Total Flow 150 ml/min	X_{NO}=93%, 100ºC	140
Cu-Ce/ZSM5, IE	[NO] = [NH_3] = 1000 ppm, [O_2] = 10 vol %, He balance, GHSV = 15,000 $h^{–1}$	X_{NO}=90%, 148–427ºC	141
Mn/CeTi, WI	500 ppm NO, 500 ppm NH_3, 5% O_2 in N_2,100 ppm SO_2 in N_2,GHSV 60000 h^1	X_{NO}>90%, 175-300ºC	142
$Ce_{10}Mo_5$/TiO_2, WI	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol %, He balance, GHSV = 128,000 $h^{–1}$	X_{NO} =90%, 275–400ºC	143
Cu-Fe/ZSM5, IE	500 ppm NO, 500 ppm NH_3 10% O_2, 6% H_2O, 1ppm SO_2, flow rate 90cm^3/m, GHSV = 600 h^{-1}	X_{NO}=90%, 450ºC	144
Mn–FeOx, CP	[NO] = [NH_3] = 800 ppm, [O_2] = 5 vol %, N_2 balance, GHSV = 24,000 $h^{–1}$	X_{NO}=100%, 120–300ºC	145
Ce–Sn–Ox, CP	[NO] = [NH_3] = 500 ppm, [O_2] = 5 vol %, N_2 balance, GHSV = 20,000 $h^{–1}$	X_{NO}=90–100%, 200ºC	146
Spinel			
$MnCo_2O_4$, NC	500 ppm NO, 500 ppm NH_3, 5%O_2 in N_2, Total Flow=200mL/min, GHSV 50,000 $h^{–1}$.	X_{NO}=98.5%, 80°C, S_{N2}, T_{50}=60°C.	147

NOx SCR literature survey for different hydrocarbons over various Ag/Al_2O_3 catalysts is given in table 1.5.

Table 1.5. Recent research in NO-SCR over Ag/Al_2O_3 catalysts using different hydrocarbons

Catalyst / Method of preparation	Experimental Conditions	Remarks	Reference
Methane (CH_4)			
$Ag/Al_2O_{3,}$ CG	NO 0.25%, CH_4 2%, 5%O_2, in He, flow rate 100 mL/min.	X_{NO} = 70- 75%, 550°C.	148
Propane (C_3H_8)			
$Ag/Al_2O_{3,}$ WI	NO=1000 ppm, C_3H_8 3000 ppm, 0-10%O_2 with He balance, Flow rate = 20 cc/ min.	X_{NO}= 87%, 200°C-400°C	149
Ag/Al_2O_3, IM, SG	NO 500 ppm, C_3H_8 1500 ppm, O_2 5% in Ar, flow rate 3500 cc/min.	X_{NO}: SG(90%)> IM (78%)	150
Ag/Al_2O_3, SG	NO 500 ppm, 188 C_3H_8, 2% H_2O, 5% O_2 in Ar, $H_2$1000 ppm, flow rate =3500 mL/min.	X_{NO}= 35% at 350°C	151
Ag/Al_2O_3, WI	NO 1000 ppm, C_3H_8 2000 ppm, CO_2 10%, O_2 5%, H_2O 0 or 5%, SO_2 0 or 20 ppm in He, FR 250 mL/min.	X_{NO} = 44%, 623 K	152
Ag/Al_2O_3, WI	0.1% NO, 0.1% C_3H_8, 0.5% H_2, 10% O_2 in He	X_{NO}= 57%, 400°C	153
$Ag/Al_2O_{3,}$ WI	NO 0.1%, C_3H_8 0.1%, O_2 10%, H_2 0.5% with He balanced	X_{NO}= 80%, 450°C	154
Octane (C_8H_{18})			
$Ag/Al_2O_{3,}$WI	NO 720 ppm, O_2 4.3%, C_8H_{18} 4340 ppm (as C1), H_2O 7.2% with He balanced, flow rate 276 cc/min	X_{NO}>95%, 100°C	155
$Ag/Al_2O_{3,}$WI	NO 720 ppm, O_2 4.3%, H_2O 0.53%, CO 7.2%, C_8H_{18} 543 ppm, Catalyst 0.266 g, flow rate 100 cc/min	X_{NO}>60%, 225°C	156
$Ag/Al_2O_{3,}$ BM	NO = 720 ppm, C_8H_{18} 4340 ppm, O_2 4.3%, H_2O 7.2%, 7.2% CO_2 in He, flow rate 100 cc/min	BM (99%, 302°C) > WI (80%, 478°C)	157

Selection of an appropriate reductant for NO reduction at low temperature is very important. The potential use of C_3H_8 as reducing agent is a better alternative to the other reductants as it leads to a strong decrease in the Gibbs free energy values of NO reduction to N_2 than other reductants (Table 1.6) [55]. LPG containing ~72% C_3H_8 is cheap, readily available and is used as a fuel for many utilities and also used in motor vehicles. In addition, LPG offers better system integration that can be installed in the existing emission control set up of vehicles. Therefore, LPG in place of C_3H_8 can be used as reductant for SCR of NOx.

Table 1.6. Gibbs free energy at 227 °C for NO reduction with different reductants

Reductant	H_2	CO	NH_3	CH_4	C_3H_8	C_4H_{10}
$-\Delta G_r$ (kJ/mol)	605.8	646.3	367.5	543.9	603.1	557.7

The PGM catalysts are very costly and scarcely available particularly such catalysts are totally imported in India. Further, literature review shows that the conversion of NOx never achieved 100% over PGM catalysts. On the other hand transition metal oxides specifically, Mn and Co containing catalysts are low cost, abundantly available, highly active and N_2 selective for SCR of NOx at low temperatures. Therefore, the objectives of the present research work are as follows:

1.14. Objective of research work

- To develop a low-cost $MnCo_2O_4$ catalyst for low temperature SCR of NOx.
- To study the effects of promoter Rh doping on the performance of $MnCo_2O_4$ catalysts for SCR of NOx.
- To formulate and characterize the prepared catalysts by various techniques.
- To select one of the best preparation methods of a catalyst for improved NOx reduction.
- To screen out the best catalyst and compare the performance with available commercial catalyst (V-W-Ti) for de-NOx.
- To study the kinetics of SCR of NOx on the best catalyst.