Emission Control in IC Engine - Selective Catalytic Reduction Method

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Abstract - Diesel engines are widely used in many areas like automobiles, locomotive marine engines power generations etc., due to its high power output and thermal efficiency. Even though the diesel engines give more benefits, the human discomforts caused by the pollutant emission of these engines have to be considered. The major pollutant emissions of the diesel engines are particulate matters, smoke and the oxides of nitrogen (NO_x). Out of these pollutant emissions, the oxides of nitrogen are considered as the most harmful pollutants to the human health. Emissions of nitrogen oxides (NO_x) contribute seriously to air pollution, which is a major environmental problem. Emissions of NO_x react with moisture in the air to form nitric acid, contributing to soil and water acidification in sensitive areas. There are many techniques being tried to control NO_x emission from diesel engine. In this paper, the emissions controlled by after treatment of exhaust gases. In the after treatment method, urea solution is sprayed in the exhaust stream which is at a temperature of 300°C to 450°C. At this high temperature of exhaust gas, the urea starts to decompose and form ammonia. The ammonia and zeolite acts as reduction against and converts the oxides of nitrogen (NO and NO₂) into free nitrogen (N₂) and water vapour (H₂O.

Keyword: Emission control, Diesel engine, Urea, Zeolite

1. INTRODUCTION

Internal combustion engines generate undesirable emissions during the combustion process. In this, both SI and CI engines are equally responsible for the same. The emissions exhausted into the surroundings pollute the atmosphere and cause serious problems. The major causes of the emissions are non-stoichiometric combustion, dissociation of nitrogen, and impurities in fuel and air. The emissions of concern are: unburnt hydrocarbons (HC), oxides of nitrogen (NO_x), oxides of carbon (CO_x), oxides of sulphur (SO_x), and solid carbon particulates. It is the dream of the engineers and scientists to develop engines and fuels such that very few quantity of harmful emissions are generated, and these could be let into surroundings without a major impact on the environment.

However, with the present technology this is not possible, and after-treatment of exhaust gases as well as in-cylinder reduction of emissions is very important. In case of aftertreatment it consists of mainly of the use of thermal or catalytic converters and particulate traps. Off late, the economic and industrial growth has caused significant reduction in the quality of ambient air. The main sources of emission from the engine are from the engine exhaust system and other from the crankcase. The former is the main cause of air pollution. The main constituents of the engine exhaust gases are unburnt hydrocarbons, carbon-di-oxide, carbon monoxide, oxides of nitrogen and particulate matter.

Diesel (compression-ignition) engines can be run at higher compression ratios, which result in higher thermal efficiencies compared to gasoline (spark-ignition) engines. As a consequence, Diesel engines can reduce greenhouse gas emissions based on the same mileage driven in comparison to gasoline engines. One challenge for the Diesel engine is the removal of NO_x (nitrogen oxides) from the exhaust, which is a major source of acid rain and chemical smog. It can also cause respiratory problems for people. The selective catalytic reduction (SCR) of NO_x is a promising technology for NO_x reduction. Some of the major catalytic industries are Johnson Mathey India Pvt Ltd, Cats Direct, Emitec Emission Controls Private Limited, Automotiev Merchandising Corporation, Gencat Limited and Cummins India Limited.

1.1 Selective Catalytic Reduction

Selective catalytic reduction systems are the most effective and commonly used post-combustion NO_x reduction processes available. SCR utilize a chemical reaction where vaporized ammonia (NH₃) is injected, via an ammonia injection grid, into the exhaust gas prior to flowing through catalytic modules. The objective is to convert nitrogen oxides (NO_x), to nitrogen and water. The key to optimizing the chemical reaction within the SCR is achieving uniformity of exhaust gas flow rate.

1.2 History And Evolution

Selective catalytic reduction (SCR) of NO_x using ammonia as the reducing agent was patented in the United States by the Englehard Corporation in 1957. Development of SCR technology continued in Japan and the US in the early 1960s with research focusing on less expensive and more durable catalyst agents. The first large scale SCR was installed by the IHI Corporation in 1978. Commercial selective catalytic reduction systems are typically found on large utility boilers, industrial boilers, and municipal solid waste boilers and have been shown to reduce NO_x by 70-95%. More recent applications include Diesel engines, such as those found on large ships, Diesel locomotives, gas turbines, and even automobiles.

Selective Catalytic Reduction (SCR) is a method of converting harmful Diesel oxides of nitrogen (NO_x) emissions, by catalytic reaction, into benign nitrogen gas and water. SCR can deliver near-zero emissions of NO_x , an acid rain and smog-causing pollutant and greenhouse gas, in modern highway clean Diesel engine. This figure illustrates the catalyst geometry designed before, consisted of "pipes" with walls of 5 mm to avoid erosion. Conversion of SO_2 approached 2% for some of these designs, which was not problematic for the early low sulphur content coals.

1.2.1 Oxides Of Nitrogen

Oxides of nitrogen are common atmospheric pollutants arising primarily from high temperature combustion processes. NO_x are formed whenever fuel is burned at high temperatures in air, from nitrogen in the air as well as in the fuel. Apart from automobiles and electric power generation, different chemical plants like urea plants, nitric acid plants, steel mills, gas turbines, fuel fired boilers, cement, steel industries and process heaters are responsible for high emission of NO_x Natural emissions of NO_x arise from bacterial action in the soil. In the atmosphere, nitrogen oxides can contribute to formation of photochemical ozone (smog), can impair visibility, and have health consequences; they are thus considered pollutants.

1.2.2 Formation Of No_x

 NO_x emissions do not form in significant amounts until flame temperatures reach 2800 F. Once that threshold is passed, however, any further rise in temperature causes a rapid increase in the rate of NO_x formation. NO_x production is highest at fuel-to-air combustion ratios of 5–7% O2 (25–45% excess air). Lower excess air levels starve the reaction for oxygen, and higher excess air levels drive down the flame temperature, slowing the rate of reaction.

 NO_x reduction is the area of most concern today. Thermally produced NO_x is the largest contributor to these types of emissions. Thermal NO_x is produced during the combustion process when nitrogen and oxygen are present at elevated temperatures. The two elements combine to form NO or NO_2 . NO_x is generated by many combustion processes other than boiler operation. It combines with other pollutants in the atmosphere and creates O_3 , a substance known as ground level ozone.

 NO_x in boiler burners can be reduced with either precombustion or post-combustion technology. Post-combustion technology allows NO_x to form, then breaks it down in the exhaust gases (a process called catalytic reduction). This method is normally confined to larger, utility-size equipment.

1.2.3 Effect Of No_x

Emission of nitrogen oxides is of a great concern because of their impact on local air pollution as well as on regional environmental risks like acid rain, photochemical smog (ozone) formation. NO_x contribute in the formation of ozone

and acid rain through some complex chemical reactions. Tropospheric ozone is hazardous photochemical air pollutant, which has adverse effect on crops; causes skin diseases, and lead to other environmental trouble that can come up mainly from oxide of nitrogen.

1.2.4 Control Technologies Of Nox

Many methods are available for control of NO_x emissions. They are mainly classified into three categories:

- Control before combustion,
- Control during combustion process

• Control after combustion (post combustion control technique).

Much research has been done to control NO_x emission by combustion modification and post-combustion technologies. Denitrogeneration, which involves the removal of N-content of the fuel before combustion.

The control during combustion reduces the rate of NO_x formation by adding some inert or reduces the combustion temperature by combustion modification, which include low excess air, reduced air preheat temperature, flue gas recirculation, water injection and low- NO_x burner.

In post combustion control technique, NO_x concentration is reduced by reacting NO_x with some specific compound in the presence of catalysts or in the absence of catalyst depending on the type and condition of the reaction process. Postcombustion process of reducing the NO_x emission includes wet methods, as sorption (not commercialized) and a dry method include catalytic reactions like Selective catalytic reduction (SCR) and Selective non-catalytic reduction (SNCR).

Some of control technology for NOx is given below,

- Adblue
- Catalytic Converter
- Exhaust Gas Recirculation
- Lo-Nox Burner
- Selective Non-Catalytic Reduction
- Selective Catalytic Reduction
- Wet Scrubber



Figure 1. Selective Catalytic Reduction

2. LITERATURE REVIEW

• **Zhongbiao Wu et al.** (2006) states experimental study on a low-temperature SCR studied catalyst based on $MnOx/TiO_2$ was prepared by sol-gel method for low-temperature selective catalytic reduction (SCR) of NO with NH₃. Focusing on the effects of the operating parameters, the SCR reaction was investigated at temperatures from 353 to 523K under steady and transient states. Under the optimal conditions, the efficiency of NO removal could exceed 90% at temperature of 423 K.

Within the range investigated, the reaction order of NO, NH_3 , O_2 was determined to be 1, 0, and 0.5, respectively. Apparent activation energy was also calculated to be 38kJ/mol, lower than that for most of the catalysts reported by previous investigations.

• Atsushi Kayo et al. (1983) studied the effect of preparation method on the acidic and catalytic properties of Iron Oxide. The surface and catalytic properties of five kinds of iron oxides prepared from iron alum and iron nitrate by using aqueous ammonia were studied. It was observed that iron oxide prepared from iron alum with urea exhibited pronounced catalytic activities for the ring-opening isomerization of cyclopropane and the dehydration of butanol the activity for the dehydration was about 100-400 times higher than those of the other iron oxides. The preparation from iron alum with urea retained sulfate ion in the resulting oxide, while the other methods gave pure iron oxide. The sulfate ion strongly enhances the acidic properties of the oxide.

• Yong Miao et al. (2009) Study of SCR cold-start by energy method.

Examined the cold-start of a prototype Diesel engine exhaust after treatment system was analyzed using a simplified energy balance to study the impact of system design changes on the performance of the selective catalytic NO_X reduction reactor. The results indicate that without an external energy supply the best way to shorten the selective catalytic reduction (SCR) reactor light-off time is to reduce the system thermal inertia by including an electrical heating applied to the SCR reactors can also reduce the light-off time.

• Tetsuya Nanba et al. (2010) Enhancement of activity of in catalysts for selective catalytic reduction of NO with CO by physical mixing with SiO2 studied that physical mixing of the Ir catalyst with SiO₂, which is inert for CO-SCR, enhanced NOx conversion, and NOx conversion increased with increasing amounts of SiO₂ in the physical mixture. HNCO was formed over the physical mixture at low oxygen concentrations. The dependence of CO-SCR activity on contact time in 0.5% O₂ suggested that HNCO was an intermediate species. In contrast, Ir catalysts that were not mixed with SiO₂ exhibited only trace amounts of HNCO formation, even at low O₂ concentrations. The IR catalyst showed high NH₃ oxidation capacity under NH₃-SCR conditions. The observed enhancement of CO-SCR activity over the mixed IR catalyst was suspected to result from the decrease in the number of NH₃ adsorption sites, which may have caused NH₃ to be oxidized to NO. In this study, he focused on the CO-SCR activity of Ir–Ba/WO₃–SiO₂. To confirm the feasibility of this catalyst under practical conditions, he measured activities under high space velocities. He found that physical mixing of the Ir catalyst withSiO₂, which itself is inert for CO-SCR, improved the CO-SCR activity. He discusses the mechanism of this enhancement effect herein.

• LifengXu et al.(2002) Observed NO_x self-inhibition in selective catalytic reduction with urea (ammonia) over a Cuzeolite catalyst in Diesel exhaust. The effect was strongest at low temperatures (<250°C) and became negligible above 300°C. NO_x self-inhibition effect was observed both for NO and NO/NO₂ mixtures and with both low and high sulfur fuel.The result of the work suggested a dominance of NO_x over NH₃ in competitive adsorption on Cu-zeolite SCR catalyst at low temperatures thus producing low steady-state NO_x reduction efficiency. Cu-zeolite catalyst is superior in effect with large NH₃ adsorption capacity. The observations showed that the zeolite catalyst has strong affinity towards water vapour in the exhaust.

• Min Kang et al. (2007) Investigated manganese oxide catalysts prepared by precipitation method with various precipitants for the low temperature selective catalytic reduction of NO_x with NH_3 in the presence of O_2 . They inferred that the manganese oxide catalysts precipitated with sodium carbonate and calcined with air at moderate temperatures such as 523 K and 623 K, have the high surface area, the abundant Mn_4 species, and the high concentration of surface oxygen on the surface. The carbonate species help to adsorb NH_3 on the catalyst surface, which resulted in high catalytic activity at low temperatures.

• YounghoonYeom et al. (2008) studied that by adding oxygenates over BaNa/Y and Ag/Yzeolites and Ag/g-Al2O3 takes place via complex reaction pathways with a number of common crucial intermediates. Acetate ions are formed by the oxidation of acetaldehyde over these catalysts. These acetate ions react with NO₂ to form nitromethane which decomposes to HNCO via a dinitro-C1 intermediate. HNCO hydrolyzes to form NH₃ which can react with HONO to form ammonium nitrite. This NH₄NO₂ efficiently decomposes to N₂ and H₂O at 100.8^oC, and at even lower temperatures in an acidic environment. The neutral surface species are expected to be in equilibrium with their ions.

The rate-limiting step in these reaction sequences is the reaction of acetate ions to form nitromethane. When nitromethane is directly added to a NOx stream over Ag/Y, 100% conversion of NOx to N2 is achieved at temperatures as low as 140.8° C. In such schemes, NO acts as a reductant of nitrate ions, ammonium nitrate and nitric acid.

J. Muniz et al. (2000). Low temperature selective catalytic reduction of NO over modified activated carbon fibres. In this paper he has investigated Activated carbon fibres (ACFs) have been used for the selective catalytic reduction of NOwith NH3 in the temperature range 100-400C. A model flue gas was used in all experiments. Among all the ACFs studied, polyacrilonitrile (PAN)-based ACFs showed the highest NO reduction activity which is ascribed to the effect of nitrogen functionalities existing on the surface of this material. The curve of NO conversion versus temperature exhibits a minimum in the temperature range 150-200C. The presence of water in the flue gases dramatically diminishes the NO reduction activity at temperatures below 250C. On the other hand, the presence of O2 shows a positive effect on conversion. NO reduction activity of ACFs can be enhanced by means of different pre-treatments which introduce new superficial groups in the fibres.

• Xiang Gao et al. (2010) Studied that Ce-Cu-Ti complex oxide catalyst for the selective catalytic reduction of NO with NH3 was prepared by co-precipitation method. The XRD and H2-TPR reveal that the strong interaction between Ce and Cu results in the production of a new active oxygen species with high reducibility at low temperatures. Compared with Ce-Ti oxide catalyst, the Ce-Cu-Ti oxide catalyst produces better performance at the temperatures lower than 350C and higher SO2-resistent ability. H2O will reduce the SCR activity of Ce-Cu-Ti catalyst at low temperatures while promoting the catalyst performance at the temperatures more than 350C.

AretiKotsifa et al. (2007). Investigated over catalysts supported on six different metal oxide carriers (CeO2, Al2O3, TiO2, YSZ, ZrO2 andW6+-doped TiO2).It has been found that the nature of the dispersed metal affects strongly the lightoff temperature of propylene, the maximum NO conversion to reduction products and the selectivity towards nitrogen. For a given support, Pt catalysts are always more active for both NO reduction and propylene oxidation, but are much less selective towards N2, compared to Rh catalysts. Rhodium catalysts are able to selectively reduce NO even 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. In contrast, oxygen promotes the de-NOx activity of platinum catalysts but decreases selectivity towards nitrogen.

3. OBJECTIVE OF STUDY

Selective Catalytic Reduction (SCR) is a means of converting nitrogen oxides, also referred to as NOx with the aid of a catalyst into diatomic nitrogen, N_2 , and water, H_2O . A gaseous reductant typically anhydrous ammonia, aqueous ammonia or urea, is added to a stream of flue or exhaust gas and is absorbed onto a catalyst. Carbon dioxide, CO₂ is a reaction product when urea is used as the reductant. The SCR system does not alter the design of the modern Common Rail Diesel (CRD) engine therefore it can continue to deliver excellent fuel economy and durability. Rather, SCR provides emissions after-treatment well into the exhaust stack, in a way similar to the soot containment achieved by the Diesel Particulate Filter (DPF). SCR works by injecting Diesel Exhaust Fluid (DEF) such as AdBlue, into the hot exhaust stack. DEF works in conjunction with the hot exhaust gases and catalyst to break NOx into two components of our normal atmosphere water vapour and nitrogen.

The main objective is design the monolithic structure in a manner that it ensures the following,

• The material cost in constructing the monolithic structure should be minimized.

• The structure should not be bulkier, it should be in a manner that it can be easily installed in the exhaust system of an automobile.

• The structure should not add much weight to the vehicle to maintain the fuel efficiency.

• The monolithic structure should not create back pressure and affect the performance of the engine.

The second objective is to select the catalyst that is to be coated on the monolithic structure such that it ensures the following,

• The catalyst used must be cheaper than the conventional catalyst, platinum.

• The catalyst should not be emptied sooner that it requires frequent re-coating.

The catalyst should not change its physical and chemical properties when subjected to high temperatures, i.e., it should withstand high temperatures.

• The catalyst should enable the above mentioned reactions effectively and efficiently.

• The catalyst must not form any new pollutants during the process as

• by products.

Any monolithic structure which satisfies the above requirements could be used and could be coated with a catalyst satisfying the above conditions. The methodology followed in the project work, the approach, the implementation and the validation works are to be done side by side.

- High NOx removal capability >95%
- Large open area & high surface area
- Low SO2 conversion & NH3 slip
- High mechanical & thermal performance
- High poison resistance
- Long catalyst life
- Erosion resistance

4. METHODOLOGY

4.1. Part Description

4.1.1 Engine

The NOx reduction process starts with an efficient CRD engine design that burns clean Ultra Low Sulphur Diesel (ULSD) and produces inherently lower exhaust emissions exhaust that is already much cleaner due to leaner and more complete combustion.

4.1.2 SCR Catalytic Converter

This is where the conversion happens. Exhaust gases and an atomized mist of DEF enter the converter simultaneously. Together with the catalyst inside the converter, the mixture undergoes a chemical reaction that produces nitrogen gas and water vapour.

4.1.3 Control Device

Exhaust gases are monitored via a sensor as they leave the SCR catalyst. Feedback is supplied to the main computer to alter the DEF flow if NOx levels fluctuate beyond acceptable parameters.

4.1.4 Catalysts

SCR catalysts are manufactured from various ceramic materials used as a carrier, such as titanium oxide, and active catalytic components are usually either oxides of base metals (such as vanadium and tungsten), zeolites, and various precious metals. Each catalyst component has advantages and disadvantages. Some of the major catalytic industries are Johnson Mathey India Pvt Ltd, Cats Direct, Emitec Emission Controls Private Limited, Automotiev Merchandising Corporation, Gencat Limited and Cummins India Limited.

4.1.5 Base Metal Catalysts

Such as the vanadium and tungsten, lack high thermal durability, but are less expensive and operate very well at the temperature ranges most commonly seen in industrial and utility boiler applications. Thermal durability is particularly important for automotive SCR applications that incorporate the use of a Diesel particulate filter with forced regeneration. They also have a high catalyzing potential to oxidize SO_2 into SO_3 , which can be extremely damaging due to its acidic properties.

4.1.6 Zeolites Catalysts

It have the potential to operate at substantially higher temperature than base metal catalysts they can withstand prolonged operation at temperatures of 900 K and transient conditions of up to 1120 K. Zeolites also have a lower potential for potentially damaging SO_2 oxidation.

4.1.7 Iron- And Copper-Exchanged Zeolites

Urea SCR has been developed with approximately equal performance to that of vanadium-urea SCR if the fraction of the NO_2 is 20% to 50% of the total NO_x . The two most common designs of SCR catalyst geometry used today are honeycomb and plate. The honeycomb form usually is an extruded ceramic applied homogeneously throughout the ceramic carrier or coated on the substrate.

Like the various types of catalysts, their configuration also has advantages and disadvantages. Plate-type catalysts have lower pressure drops and are less susceptible to plugging and fouling than the honeycomb types, but plate configurations are much larger and more expensive. Honeycomb configurations are smaller than plate types, but have higher pressure drops and plug much more easily.

4.2 Zeolites Introduction

Zeolites are microporous, aluminosilicate minerals commonly used as commercial adsorbents.

The term zeolite was originally coined in 1756 by Swedish mineralogist Axel Fredrik Cronstedt, who observed that upon rapidly heating the material stilbite, it produced large amounts of steam from water that had been adsorbed by the material. Based on this, he called the material *zeolite*, from the Greek $\zeta \dot{\epsilon} \omega$ ($z \dot{\epsilon} \bar{o}$), meaning "to boil" and $\lambda i \theta o \zeta$ (*lithos*), meaning "stone".

As of October 2012, 206 unique zeolite frameworks have been identified, and over 40 naturally occurring zeolite frameworks are known.

Zeolites are widely used in industry for water purification, as catalysts, for the preparation of advanced materials and in nuclear reprocessing. They are used to extract nitrogen from air to increase oxygen content for both industrial and medical purposes. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture.

Zeolites have a porous structure that can accommodate a wide variety of cations, such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral are

analcime, chabazite, clinoptilolite, heulandites, natrolite, phillipsi te, and stilbite. An example mineral formula is: $Na_2Al_2Si_3O_{10} \cdot 2H_2O$, the formula for natrolite.

Natural zeolites form where volcanic rocks and ash layers react with alkaline groundwater. Zeolites also crystallize in post-depositional environments over periods ranging from thousands to millions of years in shallow marine basins. Naturally occurring zeolites are rarely pure and are contaminated to varying degrees by other minerals, metals, quartz, or other zeolites. For this reason, naturally occurring zeolites are excluded from many important commercial applications where uniformity and purity are essential.

Zeolites are the aluminosilicate members of the family of microporous solids known as "molecular sieves." The term molecular sieve refers to a particular property of these materials, i.e., the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. The maximum size of the molecular or ionic species that can enter the pores of a zeolite is controlled by the dimensions of the channels. These are conventionally defined by the ring size of the aperture, where, for example, the term "8-ring" refers to a closed loop that is built from 8 tetrahedrally coordinated silicon (or aluminium) atoms and 8 oxygen atoms. These rings are not always perfectly symmetrical due to a variety of effects, including strain induced by the bonding between units that are needed to produce the overall structure, or coordination of some of the oxygen atoms of the rings to cations within the structure. Therefore, the pores in many zeolites are not cylindrical.

Zeolites transform to other minerals under weathering, hydrothermal alteration or metamorphic conditions. Some examples

• The sequence of silica-rich volcanic rocks commonly progresses from:

Clay \rightarrow quartz \rightarrow mordeniteheulandite \rightarrow epistilbite \rightarrow stilbite \rightarrow thomsonite-mesolitescolecite \rightarrow chabazite \rightarrow calcite.

• The sequence of silica-poor volcanic rocks commonly progresses from:

4.3 Coating Techniques

4.3.1 Vacuum Deposition And Vaporization

In vacuum deposition process, elements, alloys or compounds are vaporized and deposited in a vacuum. The vaporization source is the one that vaporizes materials by thermal processes.

The process is carried out at pressure of less than 0.1 Pa (1 m Torr) and in vacuum levels of 10 to 0.1 MPa. The substrate temperature ranges from ambient to 500°C. The saturation or equilibrium vapour pressure of a material is defined as the vapour pressure of the material in equilibrium with the solid or liquid surface. For vacuum deposition, a reasonable deposition rate can be obtained if the vaporization rate is fairly high. A useful deposition rate is obtained at a vapour pressure of 1.3 Pa (0.01 Torr).

4.3.2 *Physical Vapour Deposition (PVD)*

Physical vapour deposition (PVD) is a variety of vacuum deposition and is a general term used to describe any of a variety of methods to deposit thin films by the condensation of a vaporized form of the material onto various surfaces (e.g., onto semiconductor wafers). The coating method involves purely physical processes such as high temperature vacuum evaporation or plasma sputter bombardment rather than involving a chemical reaction at the surface to be coated as in chemical vapour deposition. The term physical vapour deposition appears

4.3.3 Chemical Vapour Deposition (CVD) And Chemical Vapour Condensation (CVC)

CVD is a well known process in which a solid is deposited on a heated surface via a chemical reaction from the vapour or gas phase. CVC reaction requires activation energy to proceed. This energy can be provided by several methods. In thermal CVD the reaction is activated by a high temperature above 360°C.

A typical apparatus comprises of gas supply system, deposition chamber and an exhaust system. In plasma CVD, the reaction is activated by plasma at temperatures between 300 and 400 $^{\circ}$ C.

In laser CVD, pyrolysis occurs when laser thermal energy heats an absorbing substrate. In photo-laser CVD, the chemical reaction is induced by ultra violet radiation which has sufficient photon energy, to break the chemical bond in the reactant molecules. In this process, the reaction is photon activated and deposition occurs at room temperature.

Nano composite powders have been prepared by CVD. Sic/Si3N composite powder was prepared using SiH4, CH4, WF6 and H2 as a source of gas at 1400°C. Another process called chemical vapour condensation (CVC) was developed in Germany in 1994. It involves pyrolysis of vapours of metal organic precursors in a reduced pressure atmosphere.

4.3.4 D.C Plating

D.C Plating is the process of depositing a coating having a desirable form by means of electrolysis. The main purpose is to alter the characteristics of a surface so as to provide improved appearance, ability to withstand corrosive agents and resistance to abrasion or other desired properties or a combination of them.

After D.C plating, pulse plating emerges as a new technique for deposition of metals and alloys. The main reason for this development is the problem associated with the traditional D.C plating. The continuous current flow through the solution in DC plating leads to rough deposits and sometimes destabilizes the bath producing decomposition products.

The ability to control the distribution of metal over the surface of the cathode is important in successful plating for engineering applications. The main fundamental principle of electroplating depends on the laws of electrolysis formulated by faraday.

It states that the weight deposited on an electrode is proportional to product of current and time where current is the only one variable for a fixed time which flows continuously and fixes the current density of the bath. The current density of the bath cannot be exceeded beyond a limit as it leads to burning appearance. The nucleation process is affected as the DC plating is associated with only one variable- continuous current. This results in non uniform and higher coating thickness. Hence, the raw material consumption is considerably high and the antitarnish property is lowered.

5. EXPERIMENTAL SETUP

The experiment was conducted on a single cylinder, naturally aspirated, water cooled, direct injection diesel engine. The detailed specification of the test engine is given below



Figure 2. Experimental setup with a urea-SCR for NO_x reduction

The Selective catalytic reduction (SCR) is a process in which a reducing agent reacts selectively with NO_x to produce N_2 without consuming excess o_2 . Although a number of reducing agents can be utilized in SCR, ammonia derived from urea is the most effective and widely commercialized, which is called Urea-SCR. The SCR setup includes Urea injection system and SCR catalytic converter. The SCR catalytic converter consists of a catalyst that will enhance the NO_x reduction mechanism. CaO-MnO₂ and CaO-Fe₂O₃ were used as a catalyst. Since combined metal oxide catalysts are difficult to be coated in the substrate, it was decided to use it in the tablet form.

5.1.1 Dosing

Generally applies to feeding chemicals in small quantities into aprocess fluid at intervals to give sufficient time for the chemical to react. Dosing circuit is used to install in setup for the following purpose of spraying the chemicals in intervals.

- 5.1.2 The Injection Nozzles Feature
- 1. Stainless steel construction
- 2. Intelligent atomization principles
- 3. No active cooling needed

This system is classified into two types, they are as below:

5.1.3 Air-Assist Systems

An air-assisted injection system controls the supply of compressed air to the fuel injectors according to the operating status of internal combustion engine.

5.1.4 Airless Systems

An airless injection system controls with the help of singlefluid injection solenoid-actuated injector. Unique return flow design with integral cooling allows airless injection of reagents in challenging high-temperature environments such as exhaust streams. The Compact design with precise.

5.2 Reactor Description

This design is made up of metal cutting method. In this substrate design it consists of eight plates which have 18 large holes and 1 small hole. This 18 large hole is to place two tablets in each of the holes. And the one single will allow a threaded stud pass through it, which is to hold the plates without any disarrangement at the time high pressure. And this reactor designed only to reduce the cost of the SCR setup and to reduce the back pressure created inside the reactor. Because in SCR setup monolithic structure is very costly and it consists of 400squares in 1m.sq so this will create a back pressure inside the reactor. And these plate arrangements have holes in order to hold the tablets. And the plates are covered with wire mesh to eliminate the fall of tablets. And there is about 80mm gap between the two plates which is to divide the reactor into two.

The total length of the reactor is 256mm and the diameter of the plate is 100mm. The hole which is inside the plate is of two diameters the large hole is of 19mm diameter to keep the tablets and the small hole is of 10mm diameter for the stud. And then this reactor is covered with an outer metal covering to eliminate damage of the plates.

5.3 Catalyst Selection

In the past few decades, the backbone of SCR technology is the development of SCR catalysts such as noble metals, zeolites and others. Among them vanadia supported on Titania is known to be the most effective and widely used commercial SCR catalyst due to its high catalytic activity and durability to sulphur compounds. Because this catalyst exhibits high conversions only in the temperature range of 573-673 K. Recently it was found that MnO_x catalysts prepared by a simple precipitation method with sodium carbonate and Ferric oxide prepared with different solutions showed the high catalytic activity for low temperature NH_3 -SCR.

Along with the advances in catalyst technology, the automotive engineers were developing new engine platforms and new sensor and control technology. This has resulted in the full integration of the catalyst into the emission control system. The catalyst has become integral in the design strategy for vehicle operation. During this time period the auto catalyst has progressed through the following development phases. When the automobile first starts, both the engine and catalyst are cold. After start-up, the heat of combustion is transferred from the engine and the exhaust piping begins to heat up. Finally, a temperature is reached within the catalyst that initiates the catalytic reactions. This light off temperature and the concurrent reaction rate are kinetically controlled; i.e. depends on the chemistry of the catalyst since the transport reactions are fast. Typically, the CO reaction begins first followed by the HC and NOx reaction. When all three reactions are occurring, the term three-way catalyst or TWC is used. Upon further heating, the chemical reaction rates become fast and the overall conversions are controlled by pore diffusion.

5.3.1 Catalyst

It is the change in rate of a chemical reaction due to the participation of a substance called a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself. A catalyst may participate in multiple chemical transformations. Catalysts that speed the reaction are called positive catalysts. Catalysts that slow the reaction are called negative catalysts, or inhibitors. Substances that increase the activity of catalysts are called promoters, and substances that deactivate catalysts are called catalytic poisons. Catalytic reactions have a lower rate-limiting free energy of activation than the corresponding un-catalyzed reaction, resulting in higher reaction rate at the same temperature.

However, the mechanistic explanation of catalysis is complex. Catalysts may affect the reaction environment favorably, or bind to the reagents to polarize bonds, e.g. acid catalysts for reactions of carbonyl compounds, or form specific intermediates that are not produced naturally, such as osmate esters in osmium tetroxide-catalyzed di-hydroxylation of alkenes, or cause lysis of reagents to reactive forms, such as atomic hydrogen in catalytic hydrogenation. Kinetically, catalytic reactions are typical chemical reactions, i.e. the reaction rate depends on the frequency of contact of the reactants in the rate-determining step. Usually, the catalyst participates in this slow step, and rates are limited by amount of catalyst and its "activity". In heterogeneous catalysis, the diffusion of reagents to the surface and diffusion of products from the surface can be rate determining. Analogous events associated with substrate binding and product dissociation apply to homogeneous catalysts.

5.3.2 Typical Catalytic Materials

The chemical nature of catalysts is as diverse as catalysis itself, although some generalizations can be made. Proton acids are probably the most widely used catalysts, especially for the many reactions involving water, including hydrolysis and its reverse. Multifunctional solids often are catalytically active, e.g. zeolites, alumina and certain forms of graphitic carbon. Transition metals are often used to catalyse redox reactions (oxidation, hydrogenation). Many catalytic processes, especially those involving hydrogen, require platinum metals.

Some so-called catalysts are really pre-catalysts. Pre-catalysts convert to catalysts in the reaction. For example, Wilkinson's catalyst RhCl $(PPh_3)_3$ loses one triphenylphosphine lig and before entering the true catalytic cycle. Pre-catalysts are easier to store but are easily activated in situ. Because of this pre-activation step, many catalytic reactions involve an induction period. Chemical species that improve catalytic activity are called co-catalysts (co catalysts) or promoters in cooperative catalysis.

Although catalysts are not consumed by the reaction itself, they may be inhibited, deactivated or destroyed by secondary processes. In heterogeneous catalysis, typical secondary processes include coking where the catalyst becomes covered by polymeric side products. Additionally, heterogeneous catalysts can dissolve into the solution in a solid-liquid system or evapourate in a solid-gas system.

5.3.3 Catalyst Shape

5.3.3.1 Extruded Substrate

The process begins by heating the stock material. It is then loaded into the container in the press. A dummy block is placed behind it where the ram then presses on the material to push it out of the die. Afterward the extrusion is stretched in order to straighten it. If better properties are required then it may be heat treated or cold worked. The extrusion ratio is defined as the starting cross-sectional area divided by the cross-sectional area of the final extrusion. One of the main advantages of the extrusion process is that this ratio can be very large while still producing quality parts.

5.3.3.2 Coated Substrate

Coating is a covering that is applied to the surface of an object, usually referred to as the substrate. In many cases coatings are applied to improve surface properties of the substrate, such as appearance, adhesion, wet ability, corrosion resistance, wear resistance, and scratch resistance. In other cases, in particular in printing processes and semiconductor device fabrication (where the substrate is a wafer), the coating forms an essential part of the finished product. Coating and printing processes involve the application of a thin film of functional material to a substrate, such as paper, fabric, film, foil or sheet stock.

6. CONCLUSION

The efficiency of selective catalytic reduction can be expected to increase by combination of both urea and zeolite chemical. By increasing the concentration of urea, NO_x can be reduced. These can be analysing by utilizing the various concentration of urea in selective catalytic reduction technology.

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