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Review Article

A review on Selective Catalytic Reduction technique for diesel engine exhaust after treatment

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Abstract

With globalization and improved economic conditions, there has been a huge increase in the number of vehicles coming out of manufacturing plants. This has led to an exponential increase in the amount of exhaust gases in the environment. The major gases having maximum amount of harmful influence on the environment are unburned hydrocarbons, carbon monoxide, oxides of nitrogen, particulate matter etc. Various technologies have been developed to tackle these gases both in petrol and in diesel engines. Selective Catalytic Reduction is one such advanced emissions control technology used for reduction of NOx emissions in diesel engines. SCR system injects a liquid-reductant agent through a special catalyst into the exhaust stream of a diesel engine thus decomposing NOX into inert nitrogen. This paper reviews the use of various catalysts in SCR technology for reduction of NOx from diesel engine exhaust. The challenge

Keywords: *Selective Catalytic Reduction, NOx emissions, liquid-reductant agent, catalyst*

1. Introduction

In the earlier days of development of automobile, the main issue was to get the car moving in the fastest and safest manner. Increase in number of cars and other vehicles have led to a drastic increase in the amount of exhaust gases releasing in the environment. Strict norms have been set to reduce vehicular emissions and their impact on environment. All vehicles aimed at particular market must satisfy the regional emission norms. Combustion of fuel releases the chemical energy of the fuel in the form of thermal energy. The main components of these exhaust gases are unburned hydrocarbons, carbon monoxide, oxides of nitrogen, particulate matter. There is a need for optimization between particulate emissions and nitrous oxide emissions as an increase in one leads to decrease in other.

Various technologies have been developed in the wake of reducing these emissions. For example, Diesel Oxidation Catalyst is used to minimize the unburned hydrocarbons and carbon monoxide by oxidizing them into H_2O and CO_2. Diesel particulate filter is used to filter out the particulate matter and burn them off before releasing them into atmosphere. Selective Catalytic Reduction has been developed to reduce the oxides of nitrogen (NOx) from the exhaust gases. Selective Catalytic Reduction (SCR) is an advanced active emissions control technology system that injects a liquid-reductant agent through a special catalyst into the exhaust stream of a diesel engine. Automotive grade urea is used as a reducing agent for carrying out the emission reduction reaction. Urea sets off a chemical reaction that converts nitrogen oxides into nitrogen, water and tiny amounts of carbon dioxide (CO_2).SCR technology is designed to permit nitrogen oxide (NOx) reduction reactions to take place in an oxidizing atmosphere. The chemical reaction is known as "reduction" where urea is the reducing agent that reacts with NOx for its reduction. Urea can be rapidly broken down to produce the oxidizing ammonia in the exhaust stream. Reduction in NOx can be as high as 90% using SCR technology.

D. Ravi (2014) carried out the analysis Selective Catalytic Reduction in CI engines. Theaim of this work is to study and optimize NOx reduction in diesel engines using Selective Catalytic Reduction technique. Common catalysts used in SCR system like Cu, Fe, CuFe are studied and the effect of pre-oxidation of the exhaust gases on the rate of reaction at the SCR catalyst has been considered. CuFe SCR catalyst has been found to be the most effective among all due to combined effect of Cu and Fe catalysts.

L.T. Gabrielsson (2004)reviewed urea SCR and its various factors like SCR catalysts, catalytic systems, system performance, choice of reducing agent and durability.

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An experimental study by R. Praveen *et al*. (2014) on SCR on CI engine with diesel-ethanol blend as a fuel determines the maximum reduction varying concentration of aqueous urea solution with reduction catalyst. An aqueous solution of urea was injected in engine exhaust pipe for reduction of NOx emissions in single cylinder light duty stationery DI diesel engine fuelled with diesel and diesel- (10%) ethanol blend. A concentration of urea solution was varied from 30 to 35% by weight with constant flow rates and was tested with fitting Titanium dioxide (TiO_2) coated catalyst.A maximum of 70% of NOx reduction was achieved with diesel-ethanol blend as a fuel and constant flow rate of 0.75 lit/hr. with a urea concentration of 35%.When TiO2 was used as a catalyst, 66% decrement in NOx was observed.

S. Ghosh *et al*. (2013) studied the injection of aqueous solutions of urea and Marine Ferromanganese Nodule as SCR catalyst in the tail pipe of a diesel engine fuelled with Pongamia pinata methyl ester (PPME) for the reduction of oxides of nitrogen (NOx). Injected urea with Marine Ferromanganese Nodule as SCR in the tail pipe yields 64% NOx reduction. The commercial potential of catalyst is also verified in this work.

Optimization of Urea SCR deNOx Systems for HD Diesel Engines was studied by Rinie van Helden *et al*. (2004). Their study gives provides possible SCR system configurations that are required for different stages of future emission legislations. This work showsthe impact of a combination of cold climate and a wintergrade fuel.A comparison with laboratory conditions concludes that engine out NOx can be reduced by upto 30%. Calculations performed show that Euro 4 limits can be met with open loop controlled urea dosage. High speed photography and droplet size measurements can be used for characterizing and modeling aqueous urea spray pattern. The information from these measurements is used as input parameters for simulation tools. Urea mixing analysis in 2D/3D can be done and a 1D SCR system model for development of dosage control and optimization of catalyst dimension can be developed.

Copper ion-exchanged zeolite catalyst in deNOx reaction is reviewed by Hidenori Yahiro *et al*. (2001). Catalytic performance of Cu zeolite for the direct decomposition of NO and the reaction mechanism including the characterization of active sites is studied. The deactivation of the catalyst is described. The adsorption, bonding, and diffusion of NOx in zeolite are also studied. Copper containing zeolites work well in reactions involving nitrogen monoxide, selective catalytic reduction of NO with ammonia, decomposition of N_2O, photocatalytic NO and N_2O reduction as well as the above decomposition and HC-SCR.

2. SCR Process

The catalysts used are non-noble metal catalyst. SCR processes use ammonia as selective reducing agent, the main sub reactions are of nitrogen oxide reactions. Ammonia is added to the exhaust and selectively reduces the NOx rather than being oxidized by excess oxygen in zeolite catalysts, the NOx conversion using NH_3 is independent of the oxygen concentration over a wide range.An SCR system generally has ammonia delivery system and catalyst systemalongwith the sensors, the heated delivery line, dosing module, injector, mixer and control system.

3. SCR Chemistry

The standard SCR follows a 1:1 stoichiometry for ammonia and NO. When equimolar amounts of (50 %) NO and NO_2 are present in the feed, SCR process is accelerated and is termed as "fast SCR" reaction. Fast SCR yields much higher SCR reaction rates than NO or NO2 alone. When pure (100%) NO_2 is present the feed, the reduction process is termed as "NO_2-SCR". Urea is usually atomized as 32.5 % aqueous solution into the hot exhaust gas (250-450°C). Water droplets are evaporated first and then urea is melted. Urea is then thermally decomposed (thermolyzed) into equimolar amounts of ammonia and isocyanic acid.

This easily hydrolyzes according to reaction:

$$4NH_3+4NO+O_2 \rightarrow 4N_2+6H_2O \quad (1)$$
$$4NH_3+2NO+2NO_2 \rightarrow 4N_2+6H_2O \quad (2)$$
$$4NH_3+3NO_2 \rightarrow 3.5N_2+6H_2O \quad (3)$$
$$H_2N\text{-}CO\text{-}NH_2 \rightarrow H_2N\text{-}CO\text{-}NH_2+H_2O(gas) \quad (4)$$
$$HNCO(gas)+H_2O \rightarrow NH_3+CO_2(gas) \quad (5)$$
$$H_2N\text{-}CO\text{-}NH_2 \rightarrow NH_3(gas)+HNCO(gas) \quad (6)$$

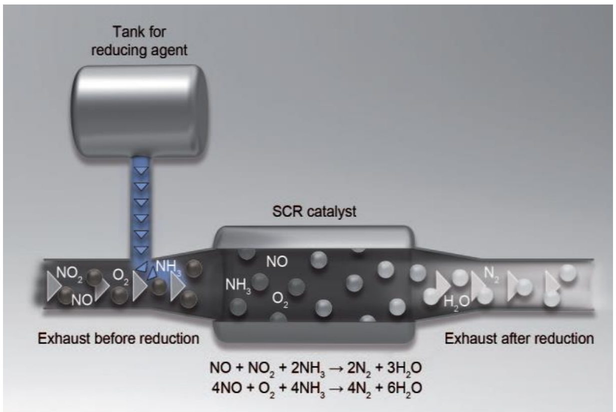

Fig.1 Operating Principle of SCR

4. Catalysts in SCR

There are two different families of SCR monoliths, full or coated. A full catalyst is either an extruded or corrugated structure. The extruded catalyst technologies compete with traditional coated substrates and also with high porosity impregnated substrates.

Zeolites are a well-defined class of naturally occurring crystalline aluminosilicate minerals. They have a three-dimensional structure arising from a framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5+}$coordination polyhedral linked by all their corners. Zeolite based catalysts do not rely on precious metals, have high tolerance to sulfur and have good activity over a wide range of temperature.

The zeolite structure affects a lot of factors including NOx reduction activity, NH3 storage capacity and durability.

4.1 Cu zeolite Catalyst

Cu zeolite provides the best performance at low temperatures. Its sensitivity to NO2 concentration is low from steady state point of view. It is prone to sulfur poisoning. To remove the contamination an occasional high temperature (500°C) cleaning step is required. They are the most preferred catalyst for high performing system.

4.2 Fe zeolite Catalyst

Fe zeolite gives best high temperature performance. NO2 for inlet gases need to be managed for improved low temperature performance. Fe zeolites show no sulfur poisoning but moderate HC poisoning is observed, minimizing the HT cleaning step.

4.3 Vanadium Catalyst

Vanadia is the cheapest of the catalysts, but has poor high temperature durability. It has a tendency to deteriorate at 550-600°C. Its use is not recommended in systems having a DPF that requires active regeneration (T>650°C). Like iron zeolites, the low temperature performance strongly depends on NO2 availability.

SCR catalyst formulations and design are improving both low and high temperature performance through better dispersion of cation in zeolite and with much more durable zeolite structures. Both Cu and Fe zeolites suffer from HC poisoning. Thermal deterioration of catalyst can happen when HCs accumulate at the lower temperatures and then ignite at higher temperatures. Prikhodko *et al*. quantified HC adsorption for Cu and Fe zeolite. They concluded that Fe zeolite adsorbs upwards of 5-10 times more HCs than Cu zeolite, but Cu zeolite oxidizes a higher percentage upon release.

4.4 Cerium Oxide

Cerium Oxide has been used in catalytic converters in automotive applications. Depending on its ambient partial pressure of oxygen, it can give up without decomposing oxygen. It can release or take in oxygen in the exhaust stream. When used in combination with other catalysts, ceria converts CO to CO2.Ceria is comparatively cheaper than platinum for conversion of NOx from diesel engine exhaust emissions.

5. Reducing agent

Different ammonia precursors or reducing agents have been suggested. Liquefied NH_3 has been widely used in larger stationary installations, and has also been suggested for the use on vehicles as described by Funk *et al*. (2011). However, the safety is an issue when such a reducing agent is handled onboard vehicles, and lethal damages cannot be excluded since a rather large amount will need to be transported around to gas stations and also onboard the vehicles, where it is finally used.

Another suggested reducing agent is ammonium carbamate NH_4NH_2COO, which upon heating decomposes into urea $(NH_2)_2CO$ and H_2O. In support of ammonium carbamate is that it is a solid which reduces the volume of the reducing agent which is needed onboard a vehicle compared to urea which is normally dissolved in water to give a 32.5% urea solution. The disadvantage of a solid reducing agent is that the injection system tends to be rather complex.

6. Comparison of performance characteristics

Commercial SCR catalysts in the market are vanadia, copper zeolite, and iron zeolite. The engine used for testing is four stroke single cylinder diesel engine. The above catalysts used in SCR system are studied and also pre-oxidation of the exhaust gases for increasing the rate of reaction at the SCR catalyst is also discussed. On cranking the engine it is allowed to warm up for 15 minutes. The readings on dynamometer scale (load) time are taken for 10cc of fuel consumption. A crypton analyzer is used for emission measurements while smoke measurement is done using smoke meter. The load on the engine is varied from 0 to 20 kg with an interval of 4 kg and the procedure is repeated. The same procedure is followed after fixing the SCR system and the readings are taken for different load conditions (D. Ravi, 2014).

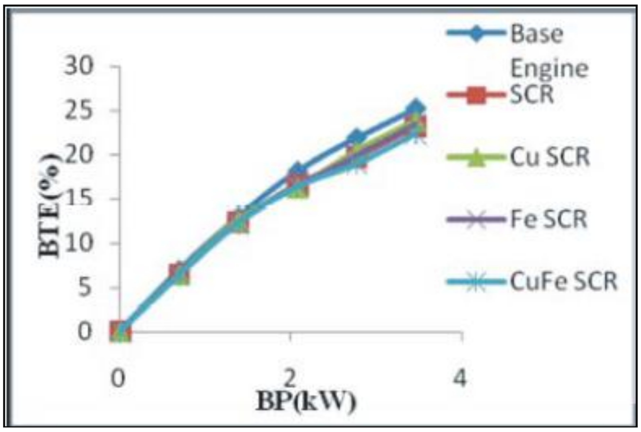

Fig. 2: Engine brake power vs. Brake thermal efficiency

The fig. 2 shows the comparison between the base engine, engine with conventional SCR catalyst, engine with Cu SCR catalyst, with Fe SCR catalyst and with

CuFe SCR catalyst. It can be observed that brake thermal efficiency decreases when SCR is implemented. BTE is found to be maximum for base engine without SCR and decreases with each SCR application. This is due to increased back pressure from alumina ceramic filter affecting combustion efficiency.

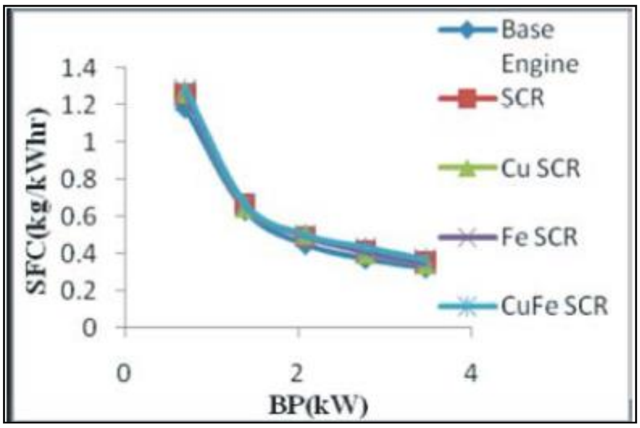

Fig. 3: Engine brake power vs.specific fuel consumption

Fig. 3 shows the engine brake power vs. specific fuel consumption for comparing base engine, conventional SCR catalyst, Cu SCR, Fe SCR, CuFe SCR.The ion exchange process resultschange only in the molecular properties of the zeolites, the physical structure of zeolite and alumina surface remains the same. This can be inferred as back pressure produced is same for conventional SCR, Cu SCR, Fe SCR and CuFe SCR.

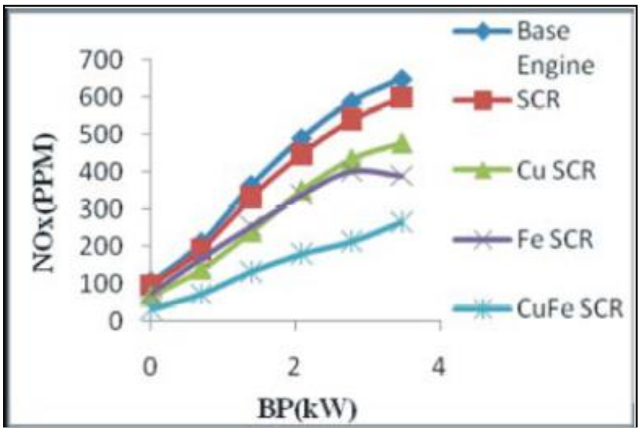

Fig. 4: Engine brake power vs. NOx emissions

Brake power vs. NOx is compared in fig. 4. Base engine without SCR produces maximum NOx. SCR with conventional catalyst reduces NOx production from 650 ppm to 599 ppm at maximum load. Cu SCR catalyst reduces NOx upto476 ppm. Fe SCR reduces NOx by upto 389 ppm. CuFe reduces NOx from 650 ppm to 265 ppm at maximum load compared to base engine without SCR. This is due to the combined effect of copper and iron which increases the conversion efficiency.

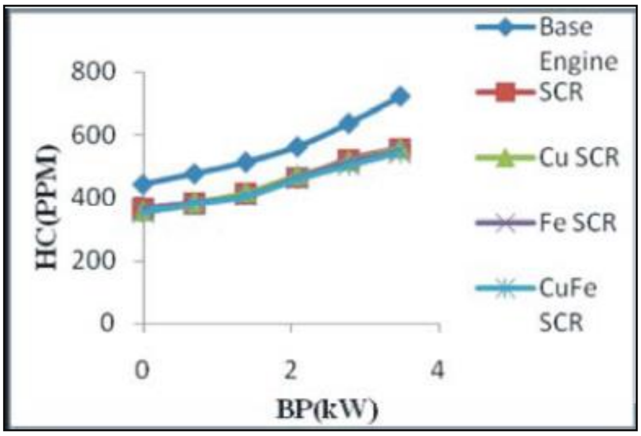

Fig. 5: Engine brake power vs.HC emissions

Comparison of HC emissions is made is fig. 5. Pre-oxidation chamber effectively reduces HC at maximum load. No significant changes in HC reduction is observed for Cu, Fe and CuFe SCR. The ion exchange occurs for the zeolite placed in oxidation without affecting the preoxidation chamber.

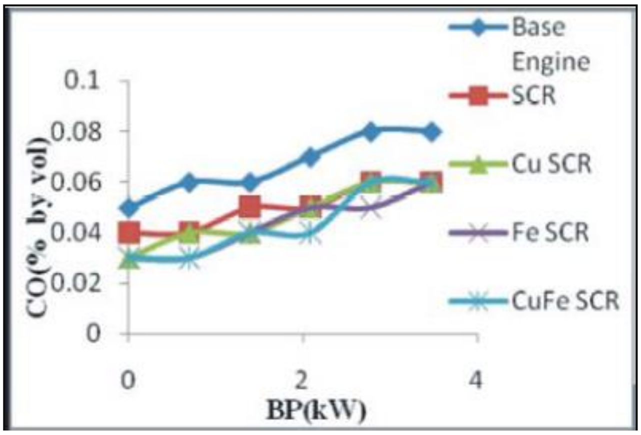

Fig. 6: Engine brake power vs.CO emissions

With increasing brake power, the specific fuel consumption decreases which decreases the CO emissions as indicated in fig. 6. CO reduction is observed in all types of SCR when compared to engine with no SCR due to pre-oxidation chamber.

7. SCR Challenges and Future Prospects

Due to excess amount of ammonia injected for high NOx conversion, some amount of ammonia may go unreacted through the catalyst. To prevent this ammonia slip catalysts may be used but they have a tendency to form N2O.

There is always a demand for new catalysts with enhanced low temperature performance. Low sulfur tolerance of Cu based small pore size zeolite prevents its application in market.

Manganese based mixed oxides are an emerging prospect in SCR technology. Efforts should be made to develop Mn based catalysts which can survive under sulfur containing exhaust gas. Regeneration method can be used to recover the sulfur poisoned Mn based catalysts.

Another alternative for NH3 SCR is H2-SCR. It functions at around 150°C. H2-SCR prevents ammonia slip but excess H2 must be used for high NOx conversion.

Conclusions

Selective Catalytic Reduction technology has been found to be the optimal solution for the increasing NOx emissions issue. With proper use and some modifications it can really help in achieving the emission norms of any particular region.

1) Selective Catalytic Reduction (SCR) technology has great potential to reduce NOx from vehicles with diesel engine. 90% of NOx conversion has been achieved using SCR.
2) Among the commercial catalysts,
3) The optimum concentration of urea should be 32.5% aqueous solution in hot gases for achieving optimum NOx conversion.
4) The NOx conversion efficiency of is maximum among the more commercial catalysts.
5) There is a significant reduction in the HC emissions when the diesel engine is used with Pre-oxidation Urea-CuFe SCR setup.
6) Better SCR mechanism should be followed to reduce the ammonia slip and thus prevent the use of ammonia slip catalysts.
7) Low temperature performance of SCR catalysts should be enhanced for cold start conditions.

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