Reduction of NO_x Emissions in a Diesel Engine Using Selective Catalytic Reduction (SCR)

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ABSTRACT

With CI engines (diesel engines) pollutants such as NO_x along with CO_2 having high global warming potential are emitted in air via engine exhaust. NO_x emissions are responsible for environmental abnormalities like acid rain and ozone layer depletion. These gases are also harmful for direct human contact, as can cause severe respiratory problems and diseases like bronchitis.

Selective Catalytic Reduction (SCR) is a technique used for reducing hazardous nitrogen oxide emissions from diesel engines. Ammonia is a good reducing agent for nitrogen oxide. It reduces nitrogen oxide to non-hazardous emission. But the rate of exhaust from an automobile diesel engine is high. Rate of reduction reaction of ammonia is not enough at these speeds. So, reduction reaction speed is boosted by use of SCR. By implication of this technology, gives satisfactory results considering EURO VI emission norms. The aim is to study various factors affecting NO_x emissions and effect of this technique at different conditions.

Key words: *SCR, EURO VI, Diesel Engines.*

INTRODUCTION

Nitrogen Oxide emissions are generally encountered in diesel engines. If temperature in combustion chamber is low then NO_x formation is negligible, but soot formation is observed to increase due to incomplete combustion of charge (air-fuel mixture). So, to reduce soot formation Diesel Particulate Filter (DPF) is used. Although DPF had limitations, during high soot emission they tend to choke. Replacing DPF is very expensive, difficult and inconvenient. So, temperature in combustion chamber is raised to have complete combustion and cleaner exhaust. Although NO_x (nitrogen oxide) emissions raised due to increase in temperature. Nitrogen in normal conditions is unreactive, but at high temperature and high pressure NO_x is formed. NO_x emissions are seldom observed in spark ignition (SI) engines since, compression ratio of SI engines is less than compression ignition (CI) engines, i.e. lower pressure in SI than CI. NO_x formation is further increased by diesel oxidation catalyst (DOC) used to oxidize soot.

NO_x emissions in diesel engine mainly comprises of nitrogen oxide (NO) and Nitrogen dioxide (NO_2). These gases have high Global Warming Potential. These gases are found in almost same quantity. But during day light NO_2 gets converted into NO, which rise up in atmosphere, react with ozone layer again to form NO_2. Thus depleting ozone layer. It is also responsible for acid rain.

CONSTRUCTION AND WORKING OF SCR

The exhaust form engine is first passed through DOC and DPF. DOC oxidizes the soot particles. DPF filters soot particles which aren't oxidized. Now exhaust consists of NO_x, small traces of SO_x and negligible quantity of soot and carbon monoxide.

After DPF NH_3 is injected in gaseous form. The SCR system can use either aqueous ammonia or anhydrous ammonia for reduction reaction.

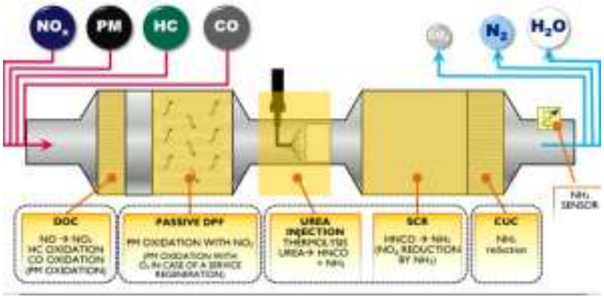

Fig 1: Construction of SCR system with DPF and DOC.

Anhydrous ammonia is 100% ammonia. It is in gaseous form at normal atmospheric temperature and pressure, so it must be transported and stored under controlled high pressure. Anhydrous ammonia is hazardous material and requires special permits and as well as additional equipments for transportation, handling and storage. However, the storage of aqueous ammonia reduces transport and storage problems, since aqueous ammonia is in liquid form at normal pressure and temperature. Aqueous ammonia is concentration of 29.4% ammonia in water, since certain locations won't allow more than 28% lesser percentage of concentration may also be used. But aqueous ammonia requires more storage capacity than anhydrous ammonia.

Since aqueous ammonia offers better security for storage and transportation, with cost of system less than anhydrous ammonia, in automobile aqueous ammonia is used.

The overall reactions of NH_3 with NO_x are as follows:

$4NO + 4NH_3 + O_2 \xrightarrow{\text{catalyst}} 4N_2 + 6H_2O$ [1]

$2NO_2 + 4NH_3 + O_2 \xrightarrow{\text{catalyst}} 3N_2 + 6H_2O$ [1]

The rates of above reactions vary according to the major parameters like catalyst and exhaust temperature. Minor parameters are ability of catalyst to trap ammonia molecules.

At the surface of SCR, surface reaction, it is a bimolecular surface reaction. Mechanism which SCR works is Langmuir-Hinshelwood mechanism adsorption reaction. According to it, two molecules adsorbed on neighboring sites undergo a bimolecular reaction.

Fe-zeolite base SCR

Fe-zeolite SCR leads to faster reduction reaction than vanadium based catalyst. It is able to trap ammonia with much greater efficiency. It has honeycomb monolith structure with catalytically washcoated walls. NO_x and ammonia diffuse from gas stream inside the channel into the pores of the washcoat where ammonia is strongly absorbed on to the catalytic surface. Absorbed ammonia reacts with gas species inside the pores and the products diffuse back through pores and enter into the channel.

There are two types of reactions that happen:

Fast SCR reaction or one with both NO andNO_2 together:

$NO + NO_2 + 2NH_3 \longrightarrow 2N_2 + 3H_2O$ [1]

And standard SCR reaction or one with NO alone:

$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O$ [1]

Since Fe-zeolite base catalyst has better trapping capacity fast SCR reactions occur mostly.

Fe-zeolite base catalyst is observed to have satisfactory conversion of NO and NO_2 within a specific range, also called intermediate temperature. This is the temperature range which mostly occurs when vehicle is running under high load conditions. This range varies from 250 ^{0}C to 400 ^{0}C.

Fe-zeolite base catalyst has better conversion rates for NO_2 than vanadium base catalyst.

NO conversion with Fe-zeolite based SCR:

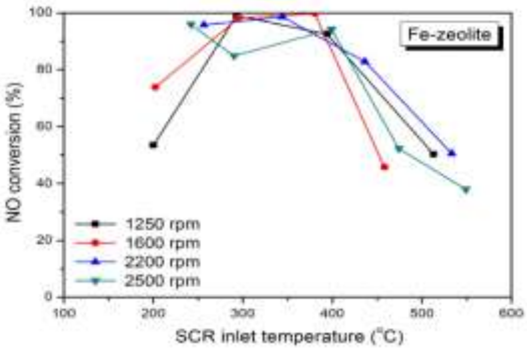

Fig 2: NO Conversion Percentage vs. SCR inlet temperature (^{0}C) for Fe-Zeolite catalyst.[1]

NO_2 conversion with Fe-zeolite base SCR:

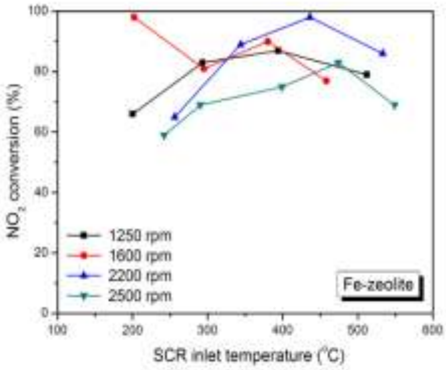

Fig 3: NO_2 Conversion Percentage vs. SCR inlet temperature (^{0}C) for Fe-Zeolite catalyst.[1]

As it can be observed at intermediate temperatures, at different rotational speeds of engines, conversion rate of NO is higher. Similarly for NO_2. But in case of NO; for temperatures higher than intermediate temperature; conversion rates are observed to fall. It is because, as the temperature rises the oxidation efficiency of DOC reduces which results in decrease in NO_2 concentrations. And as learned earlier fast SCR occurs with NO and NO_2 are available in same quantities. Since NO quantity increase due to fall in NO_2, standard SCR reaction occurs. So due to reduced rate of reaction time taken for conversion is more, but the rate of formation of NO is same. Therefore, relatively less NO is converted. On the other hand NO_2 although in less quantity, along with same quantity of NO from its entire quantity goes for fast SCR reaction. So there isn't significant fall in conversion rate of NO_2 by Fe-zeolite based SCR.

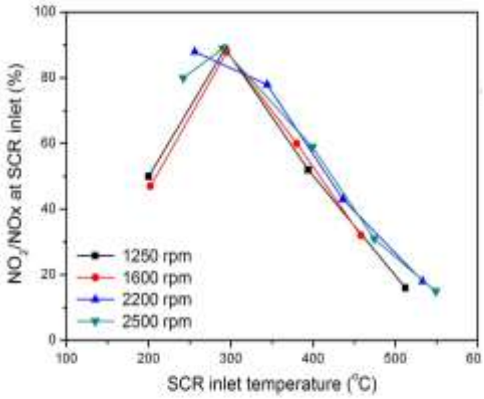

Fig 4: NO_2 Conversion Percentage vs. SCR inlet temperature (^{0}C) for Fe-Zeolite catalyst. [1]

Same thing happens at lower temperatures than intermediate temperatures.
Generally NO_2 always has NO accompanying it, for which conversion reactions were pretty straight forward. But in certain conditions there is no NO. It roughly occurs at 300^{0}C to 320^{0}C when NO_2 quantity is higher than NO. In these conditions an undesirable hazardous by-product is released, N_2O (nitric oxide). It follows the following reactions:

$2NO_2 + 2NH_3 \longrightarrow NH_4NO_3 + N_2 + H_2O$ [1]

Ammonium nitrate (NH_4NO_3) is an intermediate product which further immediately decomposes into nitric oxide

$NH_4NO_3 \longrightarrow N_2O + 2H_2O$ [1]

Since above reactions occurs simultaneously within very less time, combining these reactions give:

$2NO_2 + 2NH_3 \longrightarrow N_2O + 3H_2O + N_2$ [1]

N_2O has global warming potential 298 times CO_2.
Although nitric oxide can also form due to NO and oxidation of ammonia itself:

$4NH_3 + 4NO + 3O_2 \longrightarrow 4N_2O + 6H_2O$ [1][2][3]

$2NH_3 + 2O_2 \longrightarrow N_2O + 3H_2O$ [1][3]

Although,

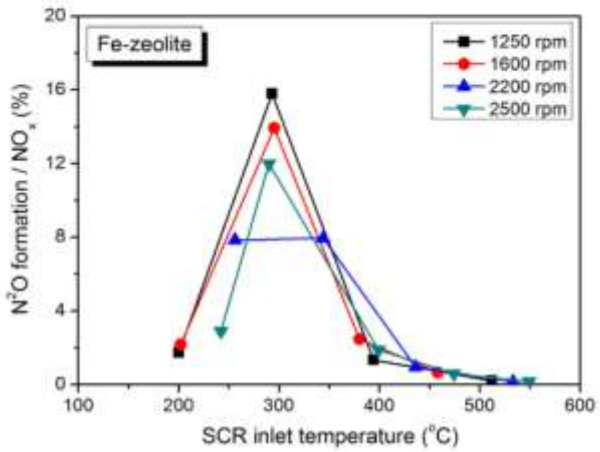

Fig 5: Percent N_2O formation/ NO_x vs. SCR inlet temperature (^{0}C) for Fe-Zeolite catalyst.[1]

This graph of observed nitric oxide clearly draws us to conclusion that it is because of NO_2 reaction alone with ammonia which leads to nitric oxide. Although the amount of nitric oxide is less, it is hazardous.

Except that Fe-zeolite base catalyst leads to formation of nitric oxide, it has shown satisfactory conversion of NO_x.

V_2O_5-WO_3/TiO_2 (vanadium base) SCR: Vanadium base SCR works on similar principle that Fe-zeolite works, with same catalyst structure - honeycomb monolith structure. Although it has different effects on reaction. Titanium di-oxide is not able to trap ammonia alone, so vanadium and tungsten's double bond structure with oxygen helps create larger sites for ammonia adsorption.

Vanadium based catalyst showed better conversion rates for NO at intermediate temperatures.

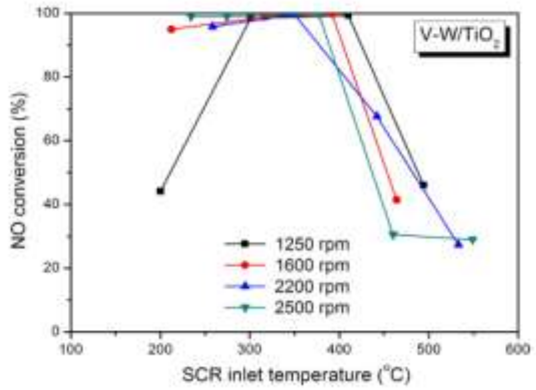

Fig 6: NO Conversion Percentage vs. SCR inlet temperature (^{0}C) for vanadium based catalyst. [1]

Reason for reduced conversion rates after intermediate temperature are same as that for Fe-zeolite SCR. But at temperature range of 250^{0}C to 320^{0}C the NO_2 conversion rate is observed to fall significantly.

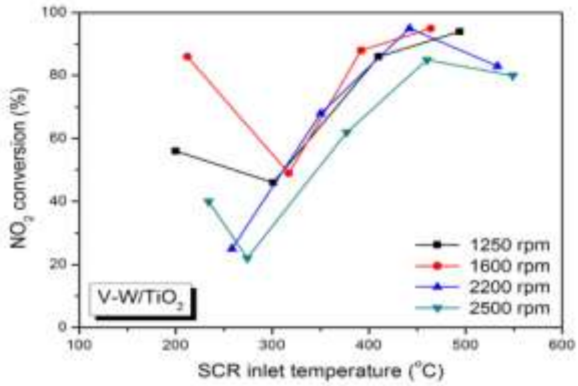

Fig 7: NO_2 Conversion Percentage vs. SCR inlet temperature (^0C) for vanadium based catalyst. [1]

After that range of temperature, rate is noticed to be increased since NO_2 along with NO preforms fast SCR reactions.
In spite of vanadium SCR incapability to convert NO_2 satisfactorily, nitric oxide formation is negligible.

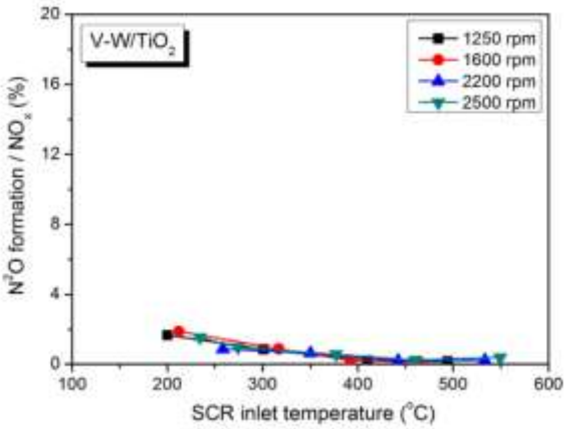

Fig 8: Percent N_2O formation / NO_x vs. SCR inlet temperature (^0C) for vanadium based catalyst.[1]

The intermediate product (as discussed earlier) in formation of nitric oxide, ammonium nitrate (NH_4NO_3) instead of decomposing to form N_2O reacts with NO:

$$2NO + NH_4NO_3 \longrightarrow 3N_2 + 5H_2O$$

So there is almost negligible nitric oxide formation.

COMPARISON OF BOTH CATALYST AND CONCEPT OF HYBYID CATALYST

Advantages of Fe-zeolite base catalyst over vanadium base catalyst

1. Efficiency to trap ammonia is higher. So hardly any ammonia slips as contrast to vanadium base catalyst.
2. NO_2 conversion rates are satisfactory.
3. Since at intermediate temperature range it follows fast SCR reactions, it has faster reaction rates than vanadium SCR.

Advantages of Vanadium base catalyst over Fe-zeolite base catalyst

1) Higher NO conversion rates.
2) Negligible nitric oxide is formed.

Use of hybrid catalyst

Although this concept is under study currently, many experts believe that advantages of both catalyst and out weight disadvantages of each other. Like for instance, the nitric oxide can be avoided by vanadium SCR, on the other hand Fe-zeolite SCR can avoid ammonia slip and give higher NO_2 conversion rates.

CATALYST IN RESEARCH AND EXPERIMENTAL STAGE:

$MnEuO_x$ Catalyst

This catalyst during experiments showed almost constant results of NO_x conversion at intermediate temperature. The conversion rates are satisfactory and due to its consistency in conversion it shows better results than prior catalyst, and most likely to replace them.

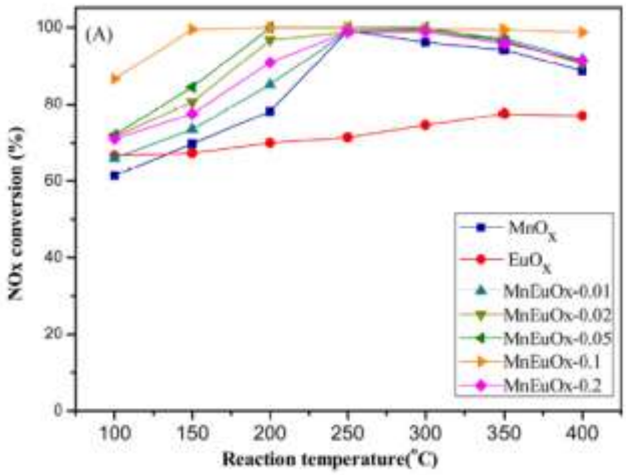

Fig 9. Conversion rates of NO_x for different varients of $MnEuO_x$.[8]

Reaction type it $MnEuO_x$ follows is fast SCR type reaction.

$NO + NO_2 + 2NH_3 \longrightarrow 2N_2 + 3H_2O$[8]

From the experimental graph plotted as shown below $MnEuO_x$-0.1 shows best characteristics than its other variants. This catalyst can avoid NH_3 slip by oxidizing it.

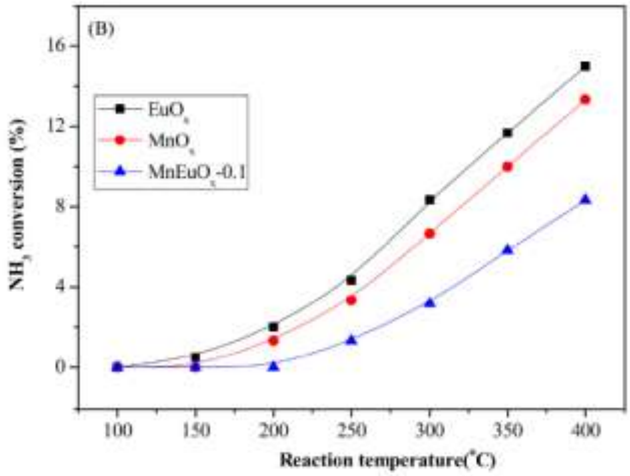

Fig 10. $MnEuO_x$ ammonia oxidation rates w.r.t. temperature.[8]

$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O$[8][9]

Therefore, it can be concluded that it has better conversion rates than Fe-zeolite based catalyst and vanadium based catalyst, also con avoid NH_3 slip. MnO_x alone is not efficient and susceptible to sulphur poisoning due to formation of acidic sulphuric acid. But Europium (Eu), with Eu/Mn molar ratio about 0.1 ($MnEuO_x$-0.1) showed high conversion rates along with resistance to acidic environment.

ADVANTAGES AND LIMITATIONS OF SCR.

Advantages of SCR

1) Conversion of NO_x is greatly accomplished with high reliability under different running and environmental conditions.
2) Use of SCR does not affect in any way to engine running. It is major advantage of SCR over EGR (Exhaust Gas Recirculation) which is also a one of effective techniques to convert NO_x.
3) In EGR exhaust is injected back in combustion chamber. Fine soot particles can go and form sticky sludge layer by mixing with lubricating oil at clearance sites, eventually wearing engine parts much earlier than supposed to be. Where in SCR no such case.

Limitations of SCR

1) Initial investment cost of equipment is high.
2) Susceptible to dusty environments.
3) Have tendency to choke.
4) Does not do well when SO_2 oxidizes (although SO_2 formation is infinitesimally small) to SO_3 which has acidic characteristics damages the catalyst, the catalyst are costly and method to replace them is expensive.
5) It will create inconvenience to vehicle driver to constantly refill ammonia like fuel both economically and physically.
6) SCR includes transportation and storage of hazardous ammonia.

CONCLUSION

1) SCR is capable to provide required reduction of NO_x satisfactorily.
2) At intermediate temperatures both catalyst show important advantages with minor disadvantages.
3) Fe-zeolite base catalyst showed more reliable characteristics than V_2O_5-WO_3/TiO_2 based catalyst. Although Fe-zeolite base catalyst was unable to control N_2O formation.
4) Vanadium base catalyst successfully avoided formation of N_2O, and good NO conversion rate at intermediate temperatures. But, NH_3 slip and inability to satisfactorily convert NO_2 are sever concern for this SCR.
5) Use of Hybrid catalyst enables, reduced N_2O formation by using vanadium base catalyst and avoid NH_3 slips and good NO_2 conversion with Fe-zeolite catalyst.
6) The few of limitations can be avoided by using EGR-SCR hybrid systems.
7) Use of currently under research and experimentation $MnEuO_x$ can replace both Fe-zeolite and vanadium based catalyst, based on characteristics observed and studied so far, unless any other practical setbacks this catalyst has.

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