Emission Reduction in SI Engines by using metal doped Cu- ZSM5 and Ce.Cu- ZSM5 zeolite as Catalysts

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Abstract: ***In recent investigations, it has been found that ZSM5 like catalysts were preferred nor the NOx reduction in the lean burn operating engines. The present experiment is focused on the spark ignition engine emission reduction using metal doped Cu-ZSM5 and Ce.Cu-ZSM zeolite based catalyst. Copper and cerium site was found very much active for the fast reduction of Nitrogen Oxides (NOx), hydrocarbon (HC) and carbon monoxide (CO) emissions. The engine used for the testing is a twin-cylinder petrol fuelled engine coupled with an eddy current dynamometer. The emissions from the engine were measured by AVL DI-gas analyzer. Initially, the emission reading was measured from the commercial catalytic converter that was fitted near to the exhaust and then the emissions were measured from using the Cu-ZSM5 and Ce.Cu-ZSM5 zeolite based catalytic converters. The results indicate that the zeolite based catalysts reduces the exhaust emission more than that of the commercial catalytic convertor.***

Index Terms: SI engine , Emission reduction, Catalysts , Zeolite

I. INTRODUCTION

The Environmental protection Organization of various countries has made strict rules in the field of Automobile to reduce the toxic emissions from the Internal Combustion Engines. Each country having different testing methods for determining the automobile exhaust emission and different emission standards were implemented according to their convenience. The major Spark Ignition(SI) Engine emissions were Hydrocarbons(HC), Carbon Monoxide (CO) and Nitrogen Oxides (NOx) , In Compression Ignition(CI) Engine the emissions were HC, CO, NOx and particulate matter in addition(1). Because the air fuel mixture in CI engine is heterogeneous in nature the atomization of the fuel may not be proper in some conditions which leads to particulate emissions, mostly particulate emissions will be abundant during the starting of the engine & hard acceleration as the engine is operating in rich air fuel mixture in these conditions. There are many technologies that were already in use in the field of emission control, In this paper we have examined one of the post treatment techniques for the reduction of NOx emission in the exhaust pipe. A catalyst is a substance that will enhance the chemical reaction, the existing emission control technologies like three way Catalytic Convertor which is used for controlling Hydrocarbon(HC), Carbon Monoxide (CO), Nitrogen Oxides (NOx) with the help of Platinum, Palladium & Rhodium as a catalyst and Selective Catalytic reduction for the reduction of NOx with a catalyst and ammonia or urea as a reducing agent were used for controlling engine exhaust emissions. In recent development of automobiles, most of the Automobile petrol engine combustion was taking place near to the stoichiometric or lean air fuel mixture ratio commonly known as lean burn engine. But the existing emission control technologies have higher efficiency when the engine is operating at stoichiometric (14.68:1)or rich air-fuel ratio, it shows very less conversion efficiency of toxic exhaust emissions to non-toxic while the engine is working in lean air fuel mixture ratio. If the engine is operating in the lean mixture then the availability of oxygen content in the exhaust is more that tends to support the oxidation process of HC and CO to H20 and CO2 not helping in the reduction process of NOx to nitrogen gas. Here comes the need to develop a catalyst that could able to enhance the reduction process of NOx even the engine is working in a lean air fuel ratio. Zeolites which can be used as a catalyst for the reduction process of NOx, some zeolites may be occurred naturally but they cannot be used as a catalyst as they were mostly unstable, On the other hand the artificially synthesized zeolites place themselves in a special positions in various field as a catalyst as well as a adsorbent of various metals in the micro structure level.BB Ghosh et al, have involved in the testing of a ultra-stable synthetic siliceous crystalline Zeolite ZSM-5 supported by Cu-Pt and Cu-Rh bimetallic catalysts was tested against a lean burn SI engine for its ability to reduce HC, CO &NOx emissions and they have got the better result compared to the conventional three way catalytic convertor(1). BB Ghosh et al, have also involved in the testing of Cu-ZSM5 based catalyst which contains 4% of Cu-4% with ZSM-5 with Copper & Platinum of 4% of Cu-4 & less than 0.1% of Pt as catalyst for the reduction of HC, CO &NOx emission and the results were found to be that the later one was having better efficiency than the previous one(2). J.Ochonska et al, have worked in the area of preparation and coating of Cu exchanged zsm-5 in the monolithic structure for the reduction of NOx they have found that in situ method on non calcined plates have six times more deposition than that of the dip coating method and in situ method on calcined plates have two times more composition than that of the dip coating method (3). SukjinChoung et al, have investigated the NOx emission reduction of emission in a lean burn engine using Pt,Cu and Mg-Cu Ion exchanged zsm-5

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and they have found out that the Mg-Cu-Ion exchanged zsm-5, a bimetallic based zsm-5 shows the maximum efficiency than the other types of zeolites(4). Ismail MohdSaaid et al, have came to a conclusion that the presence of excess amount of oxygen in the exhaust will enhance the NOx reduction using a bimetallic catalyst Pt-Cu-ZSM-5 than in mono metallic catalyst cu-ZSM-5 or Pt-ZSM-5(5). CeO2-Zro2-Al2O3-La2O3 based catalyst was tested against the Natural Gas Operated Vehicle working in a stoichiometric air fuel ratio for the reduction of CH4,NOx and CO and it has been found that the catalyst have high thermal conductivity as well as better reduction of NOx than CH4 and CO(6). It has been found that the 30% ceria content in the catalyst have more efficiency of conversion of HC,CO and NOx, Also ceria content in the catalyst will increase the durability of the catalyst operation(7). The use of Fe-impregnated catalyst in the presence of ammonia shows high catalytic activity compared to other type of catalyst and also it shows higher resistance to Sulpher Dioxide attack in the exhaust gas(8). The 23.6 weight % of Copper-Zinc/ZSM-5 based catalyst that was wash coated in a 400cpsi monolithic for the Selective Catalytic Reduction of Nitrogen oxides emissions in a diesel exhaust shows a high stability and reactivity of the catalyst is a maximum of 88% at 400 deg Celsius temperature(9). Because of the high silica to alumina ratio in the zeolite zsm-5 and with the help of bimetallic catalyst for the NOx reduction in a lean burn engine,we have used this zeolite based ZSM-5 catalyst doped with Cerium-Iron bimetallic catalyst and also with Copper-Iron bimetallic catalyst in addition with the oxidation enhancing catalyst and the results are showing that this type catalytic convertor has the maximum conversion efficiency compared to the existing emission control technologies. The present investigation is focused on SI Engine emissions reduction using Cu-ZSM5 and Ce.Cu-ZSM5 catalysts.

II. METHODS & MATERIALS

2.1 Materials

Commercially used zsm-5 zeolite was purchased from SRL Pvt. Ltd., Mumbai, India. The cordierite monoliths having cell density of 400 CPSI and wall thickness of 0.17 mm with dimensions of 90mm x 90mm diameter and length was purchased from Bocent Advanced Ceramics Co Ltd, China was used to prepare the catalyst.

2.2 Catalyst Preparation method

The ZSM-5 zeolite was impregnated by transition metals like copper and cerium. The weight ratio was 97% zsm zeolite and 1.5% copper and 1.5% cerium. This was made to form a slurry like substance and the same was dried and fired. Thus the hardened surface was formed and this hardened surface was crushed into fine powder and mixed with wet organic and inorganic blends. The resulting paste was washcoated into the honeycomb monoliths.

2.3 Catalyst Characterization

The analysis of XRF, SEM and XRD was carried out on zsm5 zeolite and metal doped zeolites and the results were shown in table 1. From the results it is observed that the weight percentage were decreased in the metal doped zeolite.

Table 1 Chemical composition of zsm5- zeolite and Metal doped zeolites
[Determined by XRF (Mass %)]

Composition	ZSM5	Cu-ZSM5	Ce.Cu-ZSM5
SiO2	88.372	87.012	87.092
Al2O3	3.256	3.091	3.150
Fe2O3	0.114	0.110	5.982
CaO	0.014	0.014	0.011
MgO	1.150	1.050	1.110
SO3	0.134	0.126	0.123
Na2O	7.001	1.515	1.095
K2O	0.00	0.00	0.00
CuO	0.00	5.012	0.00
P2O5	0.00	0.00	0.00
TiO2	0.025	0.22	0.21
BaO	0.00	0.00	0.00
LOi	0.00	0.00	0.00

The SEM analysis (Fig.1&2) shows that the surface of the catalyst microstructure was modified. The particle size of the metal doped catalyst surface was small compared to that of the original one.

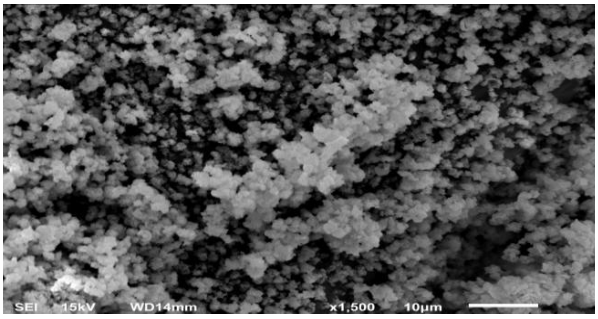
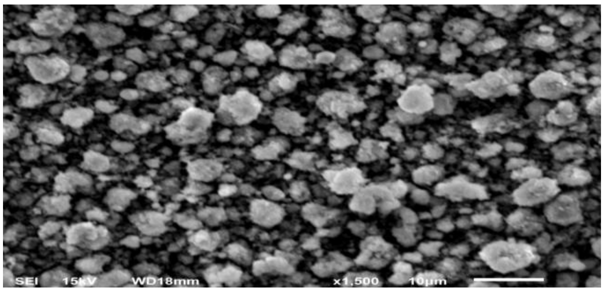
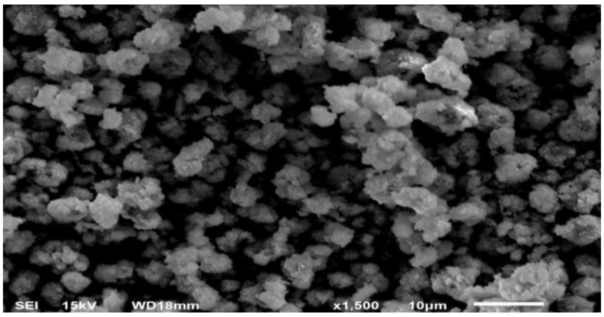


Fig.1 SEM image of zsm5-Zeolite



(a)Cu-ZSM5 zeolite



(b) Ce.Cu-ZSM5 zeolite

Fig.2 SEM image of metal doped Zeolites

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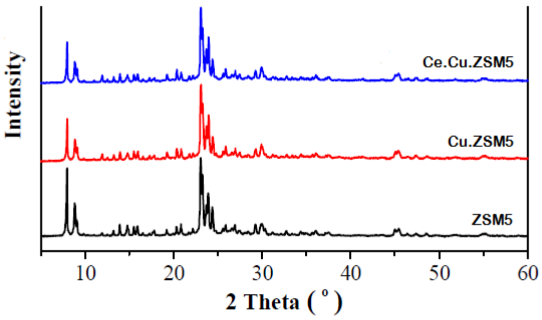

Fig.3 XRD Patterns of ZSM5 zeolites and metal doped Zeolites

2.4 Catalytic Converter

The Cu-ZSM5 and Ce.Cu-ZSM5 zeolite catalysts coated monoliths are housed individually in a steel covering with inlet and outlet cones. The catalytic converters are fabricated as same as commercial catalytic converter. Fig. 4 shows photographic view of all the three catalytic converter.

Fig.4 Photographic view of all the three catalytic converter.

III. EXPERIMENTAL SET-UP

1.Nano Engine 2.Eddy current dynamometer 3.Spark Plug 4.Weighing Balance 5.Fuel tank 6.Fuel pump 7.Air filter 8.AVL Di-gas analyser 9.Pressure transducer 10.Crank angle encoder 11.Charge amplifier 12.Indimeter 13.Monitor 14.Catalytic converter

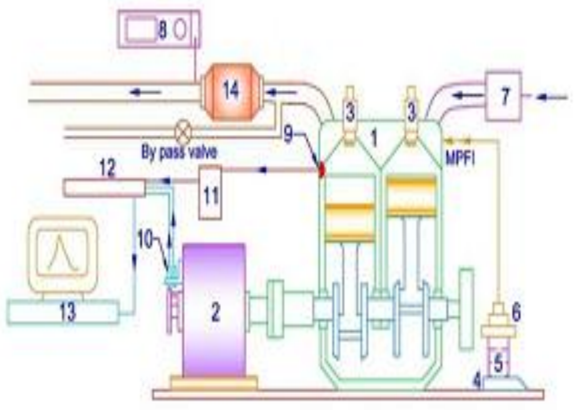

Fig.5 Experimental Block diagram

Table 2 Engine specification

Engine	Nano Engine
Type	Twin Cylinder, 624 cc, MPFI
Bore diameter	73.5 mm
Stroke	73.5 mm
Maximum power	37bhp @5000 rpm
Maximum torque	51 Nm @ 3000 rpm
Dynamometer constant	9549.5
Compression ratio	9.5:1

The experiment were carried out in the SI engine exhaust of a above mentioned specification in table.2 and the block diagram of the experimental setup were shown in the figure.5. The emission from the SI engine were measured using the AVL-Di gas analyzer. The exhaust temperatures as measured by using a Chromel-Alumel thermocouple that was fixed at 3 different places of the catalytic convertor. Engine was allowed to run in different loads (4,7,10,13 and 16kW) without catalytic convertor and the various exhaust emissions were measured. Then the emissions were measured after fixing the commercial catalytic convertor and then the same was replaced by the Cu-zsm5 zeolite and Ce.Cu zsm5 zeolite catalytic convertors and the exhaust emissions were measured.

IV. RESULTS AND DISCUSSIONS

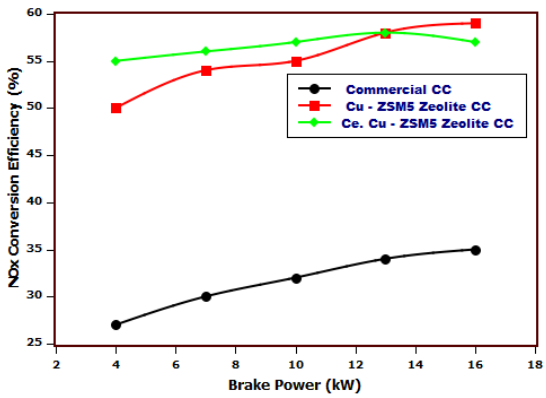

Fig.6 Percentage reduction of NOx Vs load

Figure.6 shows the comparison of Ce.Cu zsm5, Cu, zsm5 and the commercial catalytic convertor on their efficiencies to reduce the nitrogen oxide emissions It is clear from the figure that the Ce.Cu –zsm5 type catalytic convertor shows the maximum reduction of NOx conversion compared to other type of catalytic converter. For 13 kW brake power the efficiency is maximum of about 58%.

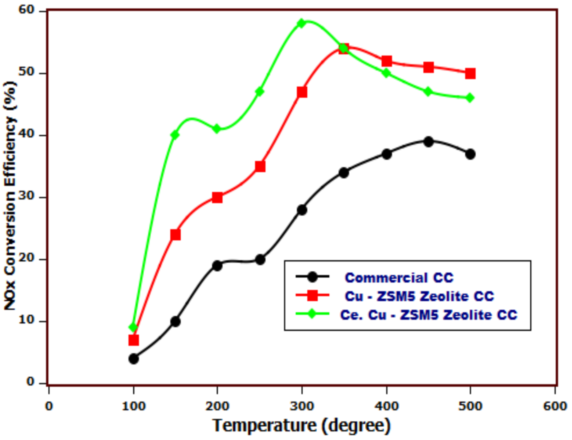

Fig.7 NOx Emission against temperature

Figue 7 shows that the NOx efficiency of the Copper-zsm5 zeolite and the bimetallic catalyst shows the higher conversion efficiency than that of the commercial catalytic convertor. Also the bimetallic catalyst was more effective than the single metal doped zeolite. The conversion efficiency is better even in the lower as well as higher temperatures and the maximum range for the better results were obtained for the exhaust temperatures ranges about 300 to 450 deg celcius.

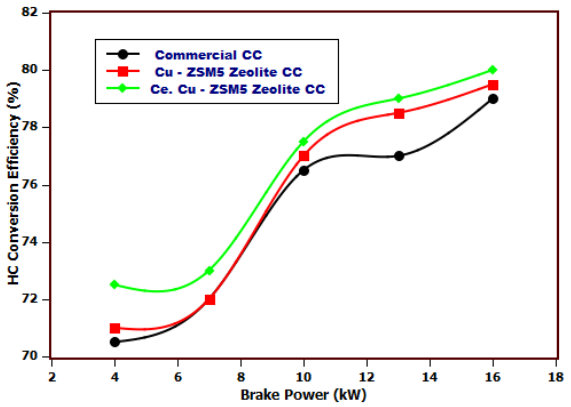

Fig. 8 Hydrocarbon against Brake Power

From the figure 8 it is clear that the HC emission conversion were higher for the bimetallic catalyst and also that the for the increase in the brake power the working of this catalyst is very impressive than the commercial zsm5 catalyst as well as the mono metal doped catalyst.

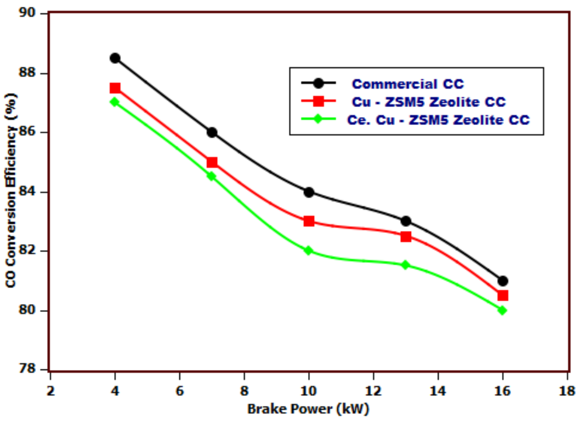

Fig.9 Carbon Monoxide against Brake Power

The CO conversion efficiency against different brake power was shown in the figure 9 and from the graph it is clear that the CO conversion is more in the commercial zsm5 without any metal doped zeolite. The reason is that the oxidation process is required for the CO conversion but the metal doped zeolite will enhance reduction process.

V. CONCLUSION

Thus the zsm5 zeolite was commercially purchased and it was coated in the monolithic structure in two different forms and it was tested to check its emission reducing efficiency. This single and bimetallic catalyst was compared with the commercial catalytic converter. The results shows that the bimetallic Ce.Cu-zsm5 zeolite coated catalytic converter and the mono metal doped Copper-zsm5 coated catalytic convertor shows the maximum conversion efficiency for the reduction process of NOx and HC emission but less for the oxidation of CO emissions.

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