EXPERIMENTAL ANALYSIS OF FLYASH BASED, ION EXCHANGED ZEOLITE AS CATALYST FOR SI ENGINE EXHAUST EMISSION CONTROL

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Abstract

Lean Burn gasoline engines are receiving increasing application because of their potential of improved fuel economy. The conventional three-way converter used in gasoline engines controls effectively the levels of CO and HC, but it displays poor conversion in harmful NOx emission. This study has investigated the use of different materials with metal additives as support for effective NOx control in gasoline engines. In this work, flyash, which is relatively abundant and inexpensive, has been used as a replacement for expensive materials. Development of Catalysts from waste materials is an effective means to enhance the value of the waste. In the present work, X-Zeolite was synthesized from Coal Fly ash. 13-X zeolite was purchased from market. By the process of exchanging Na+ ions present in these zeolites with copper, Silver and Iron metal ions separately, six catalysts were prepared. Investigations were carried out on the 3 cylinder, 4-stroke, water cooled Maruthi Omni Gasoline Engine with a displacement volume of 796 cc and coupled with eddy current dynamometer. The packed catalyst bed was housed in a 100 mm diameter cylindrical pipe and is connected near to the exhaust manifold. AVL Di-gas analyser is used to measure the NOx, CO, HC, CO2, O2 emissions. Experiments were conducted at various loads from no load to maximum load without catalytic converter and then using the Ag-X, Ag-13X, Fe-X, Fe-13X, Ni-X and Ni-13X zeolite catalytic converters. The result reveals that in house made Ag-X, Fe-X and Ni-X Catalysts reduce emission at all levels of load conditions. Ag-X catalyst gives better conversion than Fe-X catalyst and Ni-X catalyst.

Keywords: Synthesis of fly ash, X-Zeolite, Catalytic converter, emission control, 13X Zeolite

1. Introduction

Catalytic Converters have been employed in engine exhaust after treatment systems for more than two decades to reduce pollutant emissions. Since 1990’s Zeolite based catalysts have attracted much attention due to their high activity and relatively wide temperature window. The synthesis of new zeolites and similar shape selective solids and the introduction of catalytic sites into them is one of the most popular areas of research and very recently it finds substantial potentiality in the fabrication of robust catalytic converter for automobiles, exhaust gases which are the major sources of today’s air pollutants. Reduction of SI engine emissions by using X-zeolite based Catalyst was achieved by Bhattacharya and Das [1, 2]. Yuonne Traa et al. [3] reported that many zeolite based materials for the selective catalytic reduction of NOx, with hydrocarbons. Held et al. [4] reported the detailed results of selective NOx reduction over different zeolites in presence of HC, NH3, and urea.

Liu Zhiming et al. [5] reported the activities of various ion-exchanged zeolite-based catalysts (Fe, Mn, Co, Ni, Cu, Ag) under lean-burn engines. Pranit S. Metkar et al. [6] investigated Iron Zeolite Catalysts for selective reduction of NO with NH3. Jan Kaspar et al. [7] reviewed the challenges in the development of new automotive catalysts, which can meet future highly demanding pollution abatement requirements.

Fly ash is mainly composed of some oxides derived from inorganic compounds, which remain after combustion of the coal. The amounts of the main components of ash viz., SiO2 and Al2O3, show few variations with the type of coal. The similar chemical composition of fly ash and some
D. Karthikeyan, C. G. Saravanan

volcanic rocks prompted several research groups to attempt making zeolite from fly ash. In general, zeolite synthesis processes involve the addition of a caustic agent to the fly ash slurry at higher temperatures. Holler and Wirsching [8] first utilized fly ash as the raw material for synthesis of zeolite using hydrothermal method. After that, a number of researchers [9–13] have used this process successfully, varying the hydrothermal temperature within the range of 333–573 K.

Shaobin Wang [14] reported that major components of fly ash are SiO$_2$ and Al$_2$O$_3$. After high temperature combustion, these oxides are formed with high thermal stability, which results in fly ash having good catalyst support. In addition, minor components of other metal oxides such as Fe$_2$O$_3$, TiO$_2$, CaO, MgO could also be used as effective catalyst components. He further stated that Fly ash supported catalysts have shown good catalytic activities for deSO$_x$, deNO$_x$, hydrocarbon oxidation and hydrocracking, which are comparable to commercially used catalysts.

Based on the literature survey, it can be concluded that alkali fusion followed by hydrothermal treatment is the most reliable method of obtaining X-, Y-type zeolites selectively from fly ash of different compositions. It was, therefore, thought desirable to convert fly ashes from some of the Indian thermal power plants to zeolites, which could be used as catalysts for some industrially important reactions, by alkali fusion followed by hydrothermal treatment. Modern commercial three-way catalytic converter is made up of cordierite. Cordierite is the mineral of magnesium, Aluminium, Silicon dioxide (2MgO, 2Al$_2$O$_3$, 5SiO$_2$). All these minerals are naturally found in the fly ash. Hence, Fly ash is chosen as the base material for catalyst preparation.

2. Catalyst preparation

The flyash samples were collected from M/s. Neyveli Lignite Corporation Ltd., Neyveli, Tamilnadu. This fly ash sample was first screened through a sieve of 80 mesh size to eliminate the larger particles. Then the fly ash was treated with Hydrochloric acid to increase the activity in zeolite formation. Then the HCl treated flyash was mixed with NaOH solid powder in a plastic bottle. The weight ratio of fly ash to NaOH powder was 1:1.2. After ball milling, the powders were poured into a stainless steel crucible and heated at 550°C in air for 1 Hr.

The fused flyash powders were ground and poured into a plastic bottle followed by the addition of distilled water. The mixture was aged 1 day with stirring at room temperature and ambient pressure. The mixture was poured into a glass flask with a rubber stopper and cured at 60°C at ambient pressure. All precipitated solids were washed two times with distilled water followed by filtration to remove the residue of sodium hydroxide and soluble impurities. The solid powder was dried at 80°C in air for 12 hours.

The phase of Zeolite was identified by X-ray powder diffraction (XRD). The X-Ray diffraction of 13-X (commercial) zeolite was also obtained and found that both the XRD patterns are exactly matched. Scanning electron microscopy (SEM) studies were conducted both raw flyash and synthesized or treated zeolite. It was found through SEM investigation that the microstructure of catalyst surface was changed. The particle sizes on the treated catalyst surface were smaller than they were for the raw flyash.

The flow diagram of Synthesis Process is shown in Fig. 1.

Then the catalyst was prepared by exchanging the Na$^+$ ion of X-zeolite by Silver, Ferrous and Nickel metal ions. Silver Nitrate (AgNO$_3$), Nickel Chloride (NiCl$_2$.2 H$_2$O) of 20 Wt% of Zeolite was used for preparing Ag-X and Ni-X catalysts. For preparing Fe-X catalyst, 20% unhydrous Ferric Chloride (FeCl$_3$) of zeolite weight was used.

3. Na$^+$ -ion exchange method

X-zeolite was slurried with distilled water. The transition metal salts (Ag, Fe and Ni) were dissolved in distilled water and added to the zeolite slurry and the PH value was maintained at ~6
Experimental Analysis of Flyash Based, Ion Exchanged Zeolite as Catalyst for SI Engine Exhaust Emission Control

Fly ash: NaOH = 1:1.2
Mixing
Heating at 550°C for 1 hour
Grinding
Stirring at Room Temperature
Curing at 60°C
Washing with Distilled Water
Filtration
Drying at 80°C for 12 hours
Zeolite – X

Fig. 1. Synthesis process

by adding HCl. The mixture was continuously stirred at warm temperature and then filtered and washed with distilled water. The resulting slurry was used to make pellets (average diameter of 3.0 mm) and oven dried and then activated by heating at 400°C for 3 hours. By similar method as above, commercial 13-X zeolite pellets were also made.

4. Catalytic converter

The Catalyst Pellets prepared as above are packed and housed in a cylindrical pipe of 100 mm diameter and 100 mm length (with inlet and outlet cones).

5. Experimental study

The experimental study was conducted with exhaust of a stationery, four stroke, three cylinder, water cooled SI engine with a displacement volume of 796 cc. Fig. 2 illustrates the test facility for this study.

Fig. 2. Experimental setup
The Maruthi Omni engine is mounted on the test bed. The engine is directly coupled to an eddy current dynamometer, with suitable switching and control facility for loading the engine. The fuel flow rate was measured on the volumetric basis using a burette and stop watch. The AVL-Di gas analyser was used to measure CO, HC, CO₂, O₂ and NOₓ.

To study the mass flow rate and the effects of space velocity, provision was made for a part of the exhaust gas to by-pass the catalyst bed. Similarly, to study the effects of temperature on Catalyst performance, controlled heating was arranged for the exhaust gas before it enters the Reactor.

Without catalytic converter, the engine was run at different loads from minimum load to maximum load at a rated speed of 2500 rpm. In each case, the concentration of HC, CO, CO₂, O₂ and NOₓ were measured. Then the Ag-X Zeolite Packed Bed Catalytic Convertor was fitted to the Engine exhaust manifold such that the exhaust gas enters the convertor axially. The Convertor bed is insulated with thick layer of asbestos rope to prevent heat loss.

The temperatures of the Exhaust gas was measured by Chromel-Alumel Thermocouple fixed at three different points of the Convertor viz., before the exhaust gas enters the Catalyst bed (T₁), at the centre of the Catalyst bed (which also represents the Catalyst Temperature (T₂), and after the Catalyst bed (T₃) as shown in Fig. 2.

Then the engine was run at the same brake power, as it was when run without catalytic converter, at various load conditions and the concentration of CO, HC, CO₂, O₂ and NOₓ were measured in each case. Then, the process was repeated by replacing Ag-X Zeolite Catalytic Convertor with the other converters viz., Ag-13X, Fe-X, Fe-13X, Ni-X and Ni-13X catalysts. In each case, the converters were screened for a wide range of engine air-fuel ratio, space velocity and the temperature of the exhaust gas.

6. Result and discussion

Figure 3 shows the variation of the NOₓ emission with brake power of the engine. In general, the NOₓ concentration varies linearly with the load of the engine. As the load increases, the overall fuel-air ratio increases resulting in an increase in the average gas temperature in the Combustion chamber and higher NOₓ formation.

![](image)

**Fig. 3. Oxides of nitrogen against brake power**

It is seen from the figure that the in house made metal zeolite catalysts perform marginally best over commercial 13-X zeolite catalysts. Only at lower loads, the 13-X zeolite catalyst performs best. Ni-X catalysts are less active compared to Fe-X and Ag-X catalysts. In agreement with the existing datas, at lower loads, Fe-X catalysts were more active than Fe-X catalysts but at higher loads, Ag-X catalysts reduce NOₓ emission at higher rates.
The reason for this might be that the fly ash after pre-treatment loaded with Silver and Iron gave the highest catalytic activity and NO conversion. When a part of NO molecule contacts the zeolite, the zeolite rips the nitrogen atoms out of the molecule and holds on to it, freeing the oxygen in the form of O\textsubscript{2}. The nitrogen atoms bond with other nitrogen atoms that also stuck to the catalyst forming N\textsubscript{2}. Part of the NO reacts with oxygen to produce some reactive intermediates such as NO\textsubscript{2}, NO\textsubscript{3}. These intermediates react with HC or partially oxidized HC to form N\textsubscript{2}.

Figure 4 shows the comparison of NO\textsubscript{x} conversion efficiencies of six catalysts as a function of temperature. It was seen from the figure that all six catalysts shows significant NO\textsubscript{x} reduction even at temperatures as low as 180°C. The conversion efficiency increases steadily with increase in temperature, attains a peak and then decreases but at a slower rate than the rate of increase. Ag-X catalyst shows peak efficiency within the temperature range of 290 to 350°C. It is seen that the NO\textsubscript{x} conversion efficiency was around 65% at 10.05 kW and 12.56 kW and the temperature recorded in the catalyst bed was 292°C at 10.05 kW and 374°C at 12.56 kW respectively.

Figure 5 shows the percentage CO conversion efficiency with brake power. The result shows that CO emission is reduced considerably while using all the Zeolite based Catalytic Convertors. This is because the catalyst aids the reaction of CO to CO\textsubscript{2} with the oxygen in the exhaust gas. It is evident from the figure that CO reacts preferentially with O\textsubscript{2} at high temperatures and also it is true that oxidation of CO is an advantageous side-effect of reduction of NO\textsubscript{x} over metal-exchanged X-Zeolite Catalysts.

Figure 6 shows the percentage reduction of HC emission with brake power. It was seen that metal-X zeolite catalysts reduces HC emission at all levels of loads. It appears that reduction of the unsaturated HC can be depicted as a NO\textsubscript{x} dissociation reaction occurring the catalyst where the unsaturated HC is responsible for the removal of the adsorbed Oxygen generated by the NO\textsubscript{x} dissociation. Many researchers have said that this is due on one hand to fact that NO\textsubscript{x} always initiates with HC oxidation and on the other hand to the fact that with few exceptions the maximum NO conversion corresponds to maximum HC conversion. It is also observed that the trends for percent reduction in HC and CO are almost similar.

Figure 7 shows the variation of O\textsubscript{2} emission with brake power. It was seen from the figure that the volume of O\textsubscript{2} emission is considerably decreased. It is evident that apart from the oxygen produced from the NO\textsubscript{x} dissociation reaction, the engine-out oxygen is effectively utilized to convert CO to CO\textsubscript{2}. 

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233
Fig. 5 Carbon monoxide against brake power

Fig. 6 Hydrocarbon against brake power

Fig. 7 Oxygen against brake power

Conclusion

– The in-house made metal zeolite catalysts performs better than that of commercial 13-X zeolite catalysts.
– The Ag-Zeolite catalyst showed the best high temperature NOx reduction performance, while
the Fe-zeolite catalyst provided the best low temperature NOx conversion.

- CO and HC emissions were significantly reduced at all levels of load conditions. It is also observed that the trends for percent reduction in HC and CO are almost similar.
- Back pressure developed across the catalyst bed is well within the acceptable limits.
- During 50 hours of experimental evaluation of Catalytic Convertor, no appreciable deactivation of convertor was observed.

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References
