

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

D. Karthikeyan, C. G. Saravanan

Annamalai University
Department of Mechanical Engineering
Annamalainagar, India 608002
e-mail: dkarthi66@yahoo.in

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 NO_x emission. This study has investigated the use of different materials with metal additives as support for effective NO_x 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 NO_x, 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, 13 X 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 NO_x, with hydrocarbons. Held et al. [4] reported the detailed results of selective NO_x 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

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_2O_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_2O_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 , $2\text{Al}_2\text{O}_3$, 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 ($\text{NiCl}_2 \cdot 2 \text{H}_2\text{O}$) 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

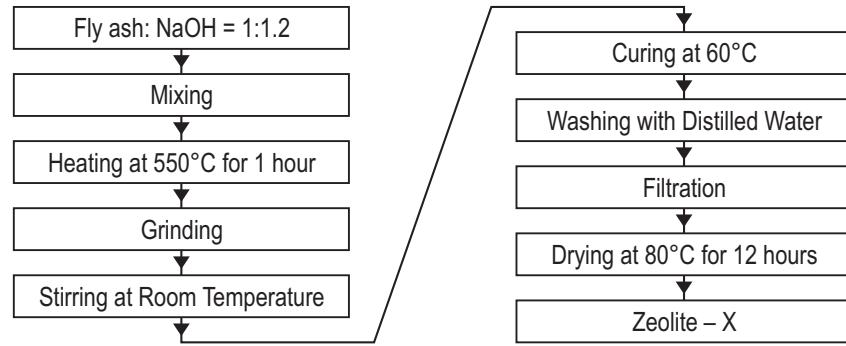


Fig. 1. Synthesis process

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.

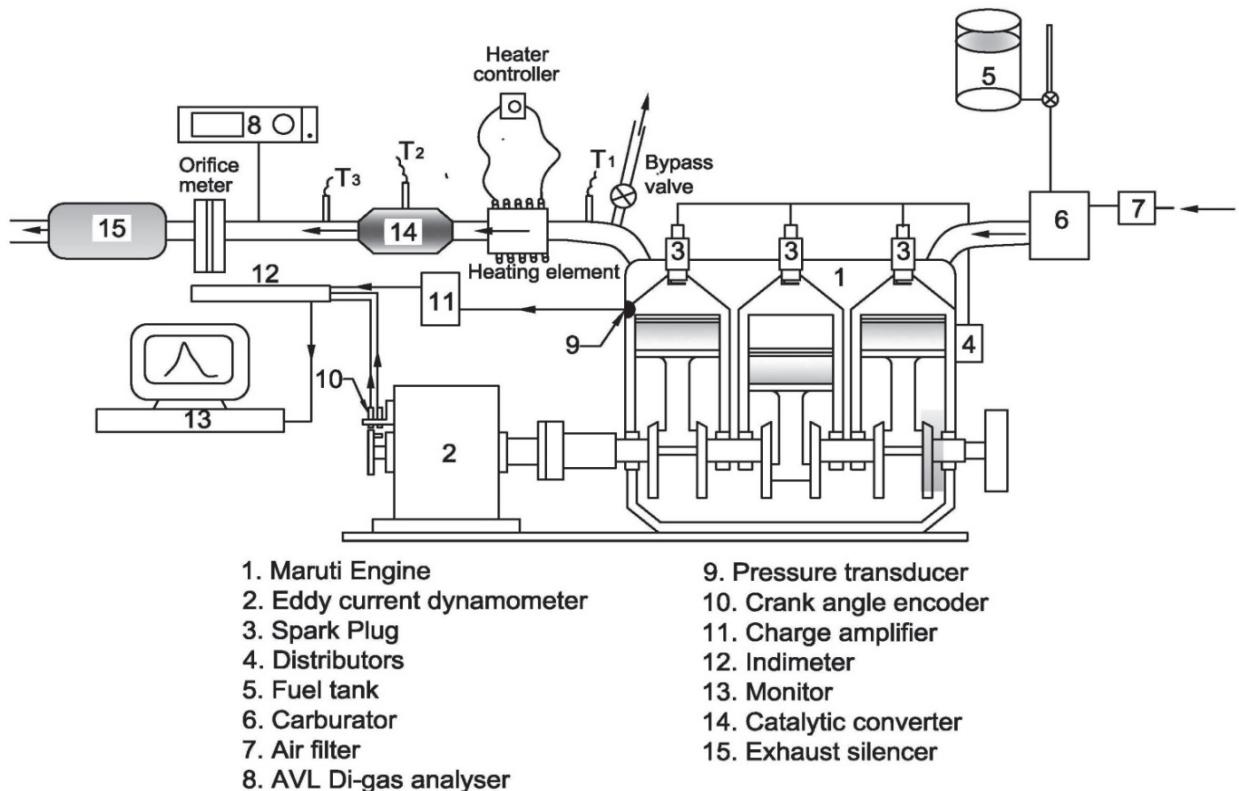


Fig. 2. Experimental setup

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 NO_x.

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 NO_x 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 NO_x 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 NO_x emission with brake power of the engine. In general, the NO_x 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 NO_x formation.

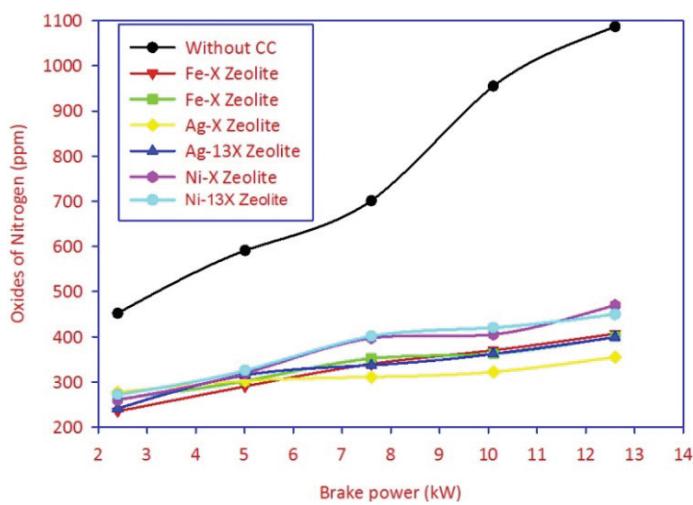


Fig. 3. Oxides of nitrogen against brake power

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 NO_x 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 O₂. The nitrogen atoms bond with other nitrogen atoms that also stuck to the catalyst forming N₂. Part of the NO reacts with oxygen to produce some reactive intermediates such as NO₂, NO₃. These intermediates react with HC or partially oxidized HC to form N₂.

Figure 4 shows the comparison of NO_x conversion efficiencies of six catalysts as a function of temperature. It was seen from the figure that all six catalysts shows significant NO_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_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.

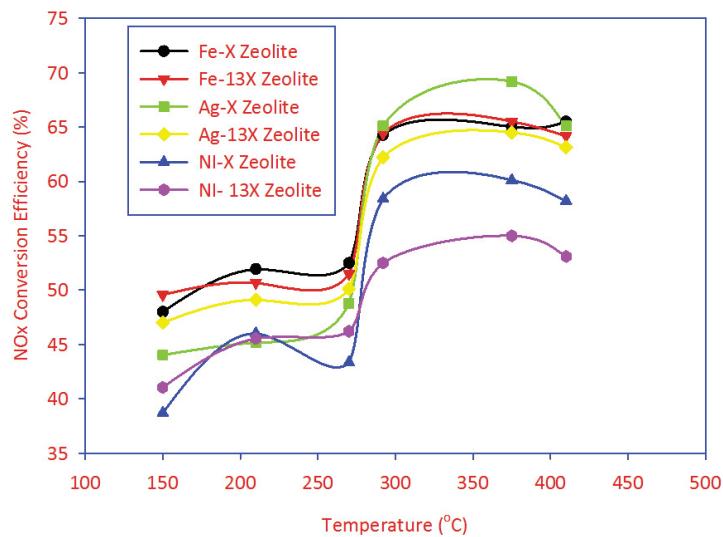


Fig. 4. NO_x Conversion as a function of temperature

CO emission

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 CO₂ with the oxygen in the exhaust gas. It is evident from the figure that CO reacts preferentially with O₂ at high temperatures and also it is true that oxidation of CO is an advantageous side-effect of reduction of NO_x over metal-exchanged X-Zeolite Catalysts.

HC emission

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_x dissociation reaction occurring the catalyst where the unsaturated HC is responsible for the removal of the adsorbed Oxygen generated by the NO_x dissociation. Many researchers have said that this is due on one hand to fact that NO_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.

O₂ emission

Figure 7 shows the variation of O₂ emission with brake power. It was seen from the figure that the volume of O₂ emission is considerably decreased. It is evident that apart from the oxygen produced from the NO_x dissociation reaction, the engine-out oxygen is effectively utilized to convert CO to CO₂.

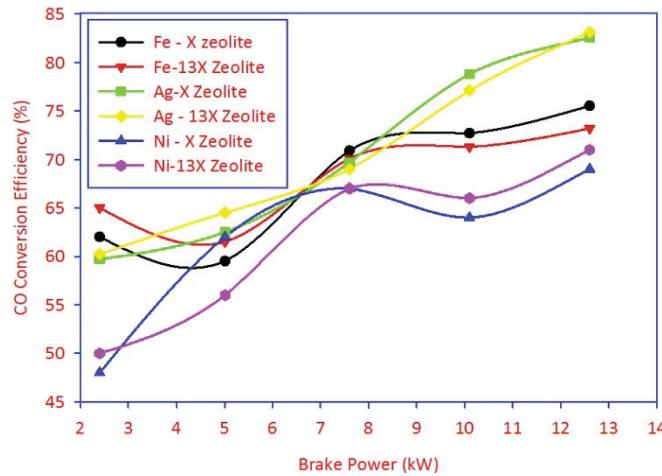


Fig. 5 Carbon monoxide against brake power

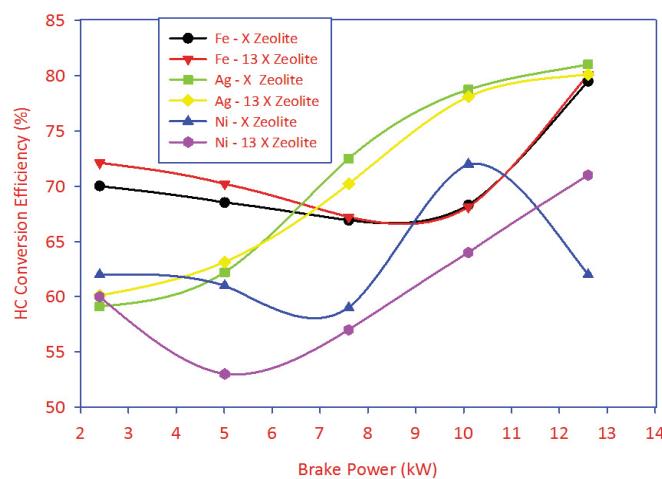


Fig. 6 Hydrocarbon against brake power

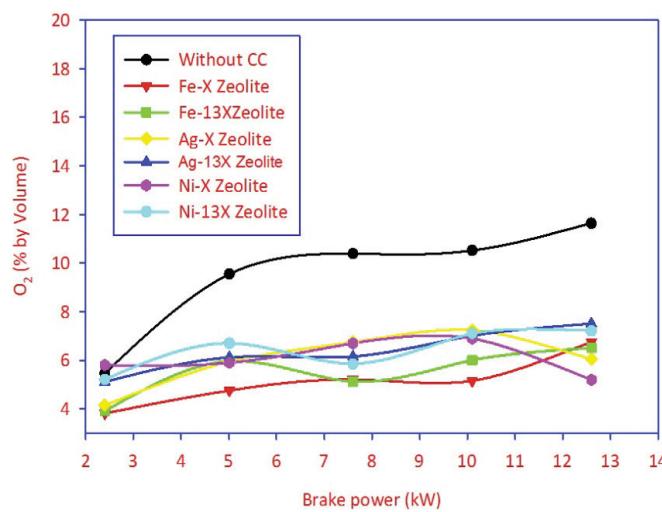


Fig. 7 Oxygen against brake power

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 NO_x 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.

Acknowledgements

The Authors would like to thank M/s. Neyveli Lignite Corporation, Neyveli, Tamilnadu, for providing Fly ash and technical data.

References

- [1] Das, R. K., Bhattacharyya, S., DuttaGupta M., Ghosh, B. B., *Theoretical and Experimental Analysis of Iron-Exchanged X-Zeolite Catalyst for SI Engine Emission Control*, Experimental Thermal and Fluid Science, Vol. 19, pp. 214-222, 1999.
- [2] Bhattacharyya, S., Das, R. K., *Catalytic Reduction of NO_x in Gasoline Engine Exhaust over Copper- and Nickel-Exchanged X-Zeolite Catalysts*, Energy Conversion and Management, Vol. 42, pp. 2019-2027, 2001.
- [3] Traa, Y., Burger, B., Weitkamp, J., *Zeolite-Based Materials for the Selective Catalytic Reduction of NO_x with Hydrocarbons*, Microporous and Mesoporous Materials, Vol. 30, pp. 3-41, 1999.
- [4] Held, W., Konig, A., Richtel, T., Puppe, L., *Catalytic NO_x Reduction in net Oxidizing Exhaust Gas*, SAE Trans., 900496 99 Sec. 4, pp. 209-216, 1990.
- [5] Liu, Z., Hao, J., Fu, L., Li, J., Cui, X., *Advances in Catalytic Removal of NO_x Under Lean-Burn Conditions*, Chinese Science Bulletin, Vol. 49, No. 21, pp. 2231-2241, 2004.
- [6] Metkar, P. S., Salazar, N., Muncrief, R., Balakotaiah, V., Harold, M. P., *Selective Catalytic Reduction of NO with NH₃ on Iron Zeolite Monolithic Catalysts: Steady-State and Transient Kinetics*, Applied Catalysis B, Environmental, doi:10.1016 / j.apcatb. 2011. 02.022, 2010.
- [7] Kaspar, J., Fornasiero, P., Hickey, N., *Automotive Catalytic Convertors; Current status and Some Perspectives*, Catalysis Today, Vol. 77, pp. 419-449, 2003.
- [8] Barth-Wirsching, U., Hoeller, H., *Experimental Studies of Zeolite Formation Conditions*, Eur. J. Mineral., Vol. 1, p. 489, 1989.
- [9] Mondragon, F., Rincon, F., Sierra, L., Escobar, J., Ramirez, J., Fernandez, J., *New Perspectives for Coal Ash Utilization*, Synthesis of Zeolitic Materials. Fuel, Vol. 69, pp. 263-266, 1990.
- [10] Lin, C. F., His, H.-C., *Resource Recovery of Waste Fly Ash synthesis of Zeolite-Like Materials*, Environ. Sci. Technol. Vol. 29, pp. 1109-1117, 1995.
- [11] Querol, X., Moerno, N., Umana, J. C., Alastuery, A., Hernandez, E., Lopez-Solera, A., Plana, F., *Synthesis of zeoliTes from Coal Fly Ash: An Overview*, 1. J. Coal Geol., Vol. 50, p. 413, 2002.
- [12] Shih, W.-H., Chang, H.-L., Shen, Z., *Conversion of Class-F. Fly Ash into Zeolites*. Mater. Res. Soc. Symp. Proc., Vol. 371, pp. 39-44, 1995.
- [13] Ojha, K., Pradhan, N. C., Samanta, A. N., *Zeolite from Fly Ash: Synthesis and Characterization*, Bull. Mater. Sci., Vol. 27, No. 6, pp. 555-564, 2004.
- [14] Wang, S., *Application of Solid Ash Based Catalysts in Heterogeneous Catalysis*, Environ. Sci. Technol., Vol. 42, pp. 7055-7063, 2008.

