

Experimental Investigation on CI Engine Emission Reduction using Metal – Doped ZSM-5 Catalyst Coated Catalytic Converter

Aasthiya bharathinathan¹, karthikeyan. Duraisamy²

¹Research Scholar, ²Associate Professor, Department of Mechanical Engineering, Annamalai University, Chidambaram.

Abstract-- The investigation of ammonia selective catalytic reduction (NH₃- SCR) was done for reduction of NO_x emission by using copper (Cu) & iron (Fe) - Zeolite Socony Mobil-5 (ZSM-5) catalyst. The ZSM-5 zeolite was synthesized from rice husk ash by hydrothermal method. Cu-ZSM-5 & Fe- ZSM- 5 zeolite catalyst were prepared by ion exchange method on to a cordierite honey comb monolith. The honey comb monolith was housed properly. Many catalyst namely Cu-ZSM-5(in house), Fe- ZSM-5(in house), Cu- beta, Fe- beta, Cu- mordenite, Fe-mordenite, Cu- ferrierite & Fe- ferrierite are prepared. All the prepared catalyst are wash coated on monolith and housed separately to form catalytic converters. SCR reduction technique with ammonia as catalyst is used to reduce the NO_x emission. Emission test are conducted in different load condition on twin cylinder Mahindra Maximo engine. All the catalyst coated monolith are tested with the exhaust temperature of 150°C - 600°C. Optimized urea solution was injected on exhausted gas path. The result showed that the NO_x conversion efficiency of ZSM-5 zeolite (in house) is 72% at 225°C and 84% at 375°C. It is noted that the NO_x conversion efficiency is decreased in the order Cu-ZSM-5(in house)> Cu-beta > Cu- mordenite > Cu- ferrierite.

Keywords--NH₃ -SCR; NO_x emission; Cu-ZSM-5 zeolite; Fe-ZSM-5 zeolite; beta zeolite; mordenite zeolite

I. INTRODUCTION

Diesel engines are widely recognized for their high thermal efficiency and lower CO₂ emissions compared to gasoline engines. These attributes make them favorable for energy conservation and reducing greenhouse gas emissions, thus playing a potential role in combating global warming. Despite these benefits, diesel engines emit a range of toxic pollutants that pose significant environmental and health risks. Nitrogen oxides (NO_x), generated through high-temperature combustion, are precursors to ground-level ozone and are linked to respiratory disorders. Carbon monoxide (CO) and unburnt hydrocarbons (UHCs) also contribute to air pollution and ozone formation. Diesel exhaust is a major source of particulate matter (PM), including black carbon, soot, and metallic ash. These ultrafine particles can infiltrate deep into the pulmonary system, leading to cardiovascular, respiratory, and carcinogenic outcomes.

Prolonged exposure to diesel PM is also associated with increased morbidity and mortality. Given the dual challenge of maintaining diesel engine efficiency while reducing harmful emissions, there is a critical need for advanced emission control technologies. Research efforts are increasingly focused on developing sustainable, cost-effective, and high-performance catalysts for NO_x, CO, and PM abatement. Given the dual challenge of sustaining engine efficiency while achieving strict emission targets, there is a critical need for advanced emission control technologies. Strategies such as after-treatment systems, catalytic converters, and selective catalytic reduction (SCR) have shown promise in reducing NO_x, CO, and HC emissions in real-world diesel engine operations. Among available catalyst supports, ZSM-5 zeolite has gained attention due to its high surface area, thermal stability, and tunable acidity. These properties make it effective for the oxidation of CO and UHCs, as well as the reduction of NO_x when combined with transition metals like copper or iron. Agricultural waste management and sustainable resources utilization have become focal points in modern materials science. Among various agricultural byproducts, rice husk (RH) stands out due to its abundance, low cost, and high silica content. Annually, millions of tons of rice husk are generated globally, primarily in rice-producing countries, posing both a waste disposal challenge and a potential raw material opportunity. Rice husk an abundant agricultural by product, contains 70- 90 wt. % silica in its ash form (RHA). Silica derived from RHA is versatile, finding use in ceramics, chromatography column packing adhesives, detergents, semiconductors, pharmaceuticals, and food processing (e.g., as a clarifying agent in vegetable oil refining).the materials wide applicability is attributed to its thermal stability, surface chemistry, and mechanical properties. Extensive literature has established that rice husk ash (RHA) is a reliable and economical source of amorphous silica. Extraction methods such as acid treatment followed by thermal combustion have proven effective in obtaining high – purity silica, which can be used to produce ZSM-5 through hydrothermal and sol-gel methods, promoting waste valorization and green chemistry.

It has been known that SiO_2 in industrial waste RHA can exist in both amorphous and crystalline (mostly cristobalite) forms depending on its heat treatment. More precisely, the operating temperature characteristics of the boiler. The suspension type boilers produce mostly amorphous SiO_2 whilst the Stoker types produce mostly cristobalite. Therefore, industrial waste RHA is a potentially attractive source for the large scale production of ZSM-5 successfully synthesized (W. Panpa et al., 2009). Usually, zeolite ZSM-5 is prepared from alkaline aluminosilicate gel containing an organic nitrogenous compound serving as a structure directing agent (SDA) or templating agent. Aspects related to its synthesis, e.g., effects of precursors, properties, composition and pH of synthesis gel, competitive roles of alkali and other cations, templating agents, sources of required ingredients, etc., have been reported. Crystallization mechanism of ZSM-5 zeolite under various conditions has been discussed in literature. Highly crystalline ZSM-5 can be synthesized from pure chemical commercial starting materials within a period of about 168 h in autoclave at 120–180°C under autogenous pressures (Nilam L. Chauhan., 2012).). The autoclavation time can be reduced to 4–6 h under high pressures and temperatures (about 40–60 atm and 230–250°C). The possibility of synthesizing ZSM-5 from pure chemical commercial starting materials at temperatures between 90 and 100 °C and atmospheric pressure has also been reported (Kordatos et al., 2013). This molecular sieve has an MFI-type structure which promotes the wide use of ZSM-5 zeolite such as for processes involving petrochemicals and fluid catalytic cracking, separation of gases or liquids, synthesis of fine chemicals, in space research, as solid acid catalyst (Zahra Sari et al., 2015). This work introduces a sustainable, cost-effective approach for catalyst synthesis by valorizing rice husk ash—an abundant, underutilized agro-industrial byproduct—as a silicon source for zeolite production. The dual use of Cu and Fe in the zeolite framework, coupled with direct comparison between in-house synthesized and commercial catalysts, provides new insights into material performance. Moreover, the work demonstrates practical implementation by integrating the catalysts into monolithic converters and evaluating them in real engine conditions, bridging the gap between laboratory synthesis and field application. The study confirms that Cu- and Fe-doped ZSM-5 catalysts significantly reduce emissions of NO_x , in CI engine exhaust. Engine tests revealed distinct performance differences between Cu and Fe dopants, highlighting the tunability of emission control based on the choice of metal. Structural analysis verified successful incorporation of metals into the zeolite framework.

The findings suggest that low-cost, RHA-derived ZSM-5 catalysts are a viable alternative to conventional emission control systems, especially in regions with abundant rice production and limited access to advanced exhaust after-treatment technologies.

II. CATALYST PREPARATION

2.1 Rice Husk to ZSM-5 like Material Conversion Process

Raw rice husks (RRH) were sieved to eliminate clay and dust particles. The sieved RRH was then soaked in 10M of concentrated HCl Solution. Subsequently, the mixture underwent washing, filtering, and air-drying, followed by calcination at 850°C for 5 hours. A sample of 50g of acid treated rice husk ash and 30 g of NaOH were dissolved in 500ml of distilled water to obtain solution A. Solution A was stirred continuously for 4 hours at room temperature. In addition, 10g of TPABr and 30g of sodium aluminate (NaAlO_2) was suspended in 500ml of distilled water to obtain solution B. The Solution B was stirred continuously for 4 hours at room temperature. The solution A and B was mixed and stirred continuously for 4 hours at room temperature. The aluminosilicate gel was formed, and the solution was stirred for 24 hours at room temperature to ensure proper dispersion. The above mentioned dispersed solution was transferred into Teflon lined stainless steel autoclave. The autoclave was placed in muffle furnace and heated at 180°C for 24 hours crystallization after this autoclave was cooled and the reaction mixture was filtered, washed several times with copious amount of distilled water until pH had reached 7, dried overnight at 110°C for 12 hours and heated at 550°C for 6 hours in muffle furnace.

2.2 Preparation of Metal Doped Zsm-5

2.2.1 Preparation of Catalyst

ZSM-5 like material is synthesized from rice husk ash is denoted as zsm-5(in house) and commercial Na-form zeolite via, ZSM-5, beta, mordenite and ferrierite are used as base material. Cupric chloride and ferric chloride are used as transition metal.

2.2.2 Na^+ Ion Exchange Method

Metal (Cu, Fe) / zeolite [ZSM-5 (in house), ZSM-5 (commercial), beta, mordenite and ferrierite catalysts are prepared by conventional liquid phase ion exchange method. a sample of 100 gm of zeolite powder is mixed with 1000 ml of 0.5 M metal solution. the mixture is then stirred continuously at room temperature for 24 hours. After ion exchange, the mixture is vacuum filtered and washed with ample amount of de-ionized water until no free ions are present in the mixture.

Then the above sample is dried and calcined in air at 550°C for six hours. The above procedure is followed to prepare ten different catalyst namely, Cu (zsm-5), Fe(zsm-5), Cu-zsm-5|(commercial), Fe-zsm-5(commercial), Cu-

beta, Fe- beta, Cu-Mordenite, Fe- Mordenite, Cu –ferrierite and Fe –ferrierite. The amount of metal (Fe or Cu) content loaded into zeolite is around 12%.

III. CHARACTERIZATION OF RICE HUSK ASH AND ZEOLITES

3.1 X-ray fluorescents (XRF)

Table:1
Chemical Composition Of Rice Husk Ash, Synthesized Zeolites, Commercial Zeolite

COMPOSITION	RHA	ZSM-5 (IN HOUSE)	ZSM-5 (COMMERCIAL)
SiO ₂	78.36	71.91	70.10
Al ₂ O ₃	4.47	6.41	7.20
Fe ₂ O ₃	10.37	0.95	0.00
CaO	3.45	0.90	0.00
MgO	2.47	1.01	0.00
SO ₃	0.45	1.11	0.00
Na ₂ O	0.24	14.2	18.20
K ₂ O	0.10	0.84	0.00
P ₂ O ₅	0.07	1.10	0.00
TiO ₂	0.03	1.31	0.00
BaO	0.00	0.21	0.00
LOI	0.00	-	0.00

Table: 1 shows the chemical composition of rice husk - ash, zsm5 (IH) and zsm5 (commercial). It is noticed from table.1 that there is a marked increase in the percentage of Na₂O in the zeolite material compared to fly-ash.

The weight of Na₂O Is found to increase from 0.24 to 14.2%. This is due to capture of Na⁺ ions needed to neutralize the negative charges on the aluminate in the zeolite during synthesise process.

3.2 Scanning Electron Microscope (SEM)

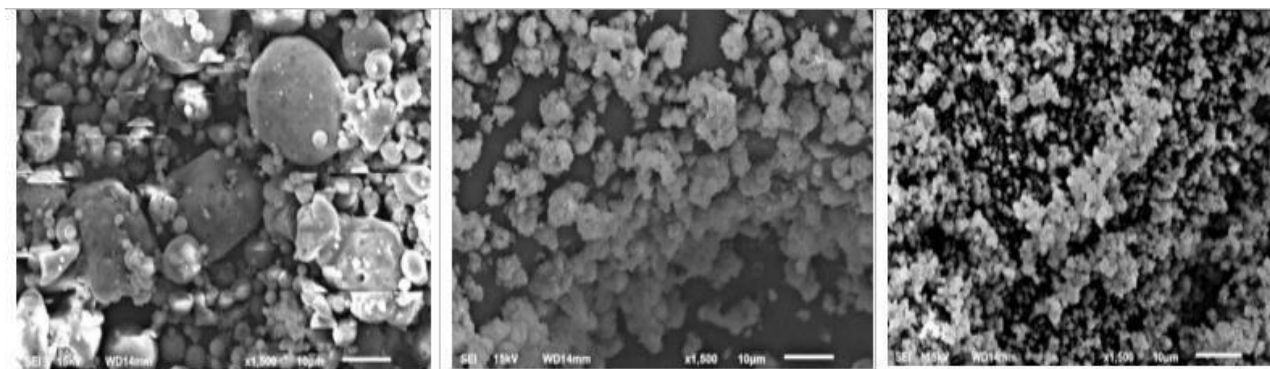
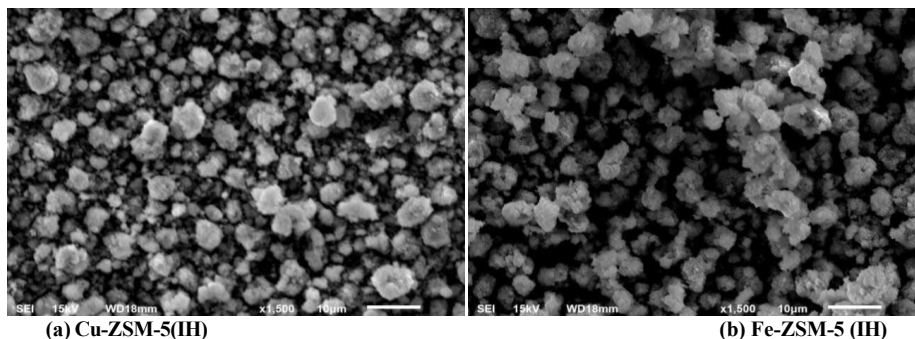


Fig.1 SEM images of raw rice husk ash and ZSM-5 (In House) and (Commercial)

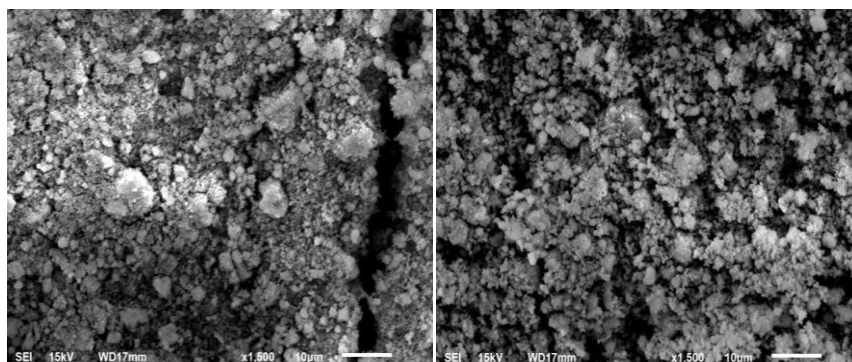
Fig :1 shows the SEM photographs of rice husk ash, ZSM-5 like material (In house) and ZSM- 5 zeolite (commercial) It is observed from the figure that the absence of spherical particles in ZSM-5 like material, indicate high

conversion of rice husk ash into zeolite on hydrothermal treatment. It is also seen that there is no much variation in the crystal structure and similarly, between ZSM-5 (In House) and (Commercial).



(a) Cu-ZSM-5(IH)

(b) Fe-ZSM-5 (IH)



(c) Cu-ZSM-5 (Commercial)

(d) Fe-ZSM-5 (Commercial)

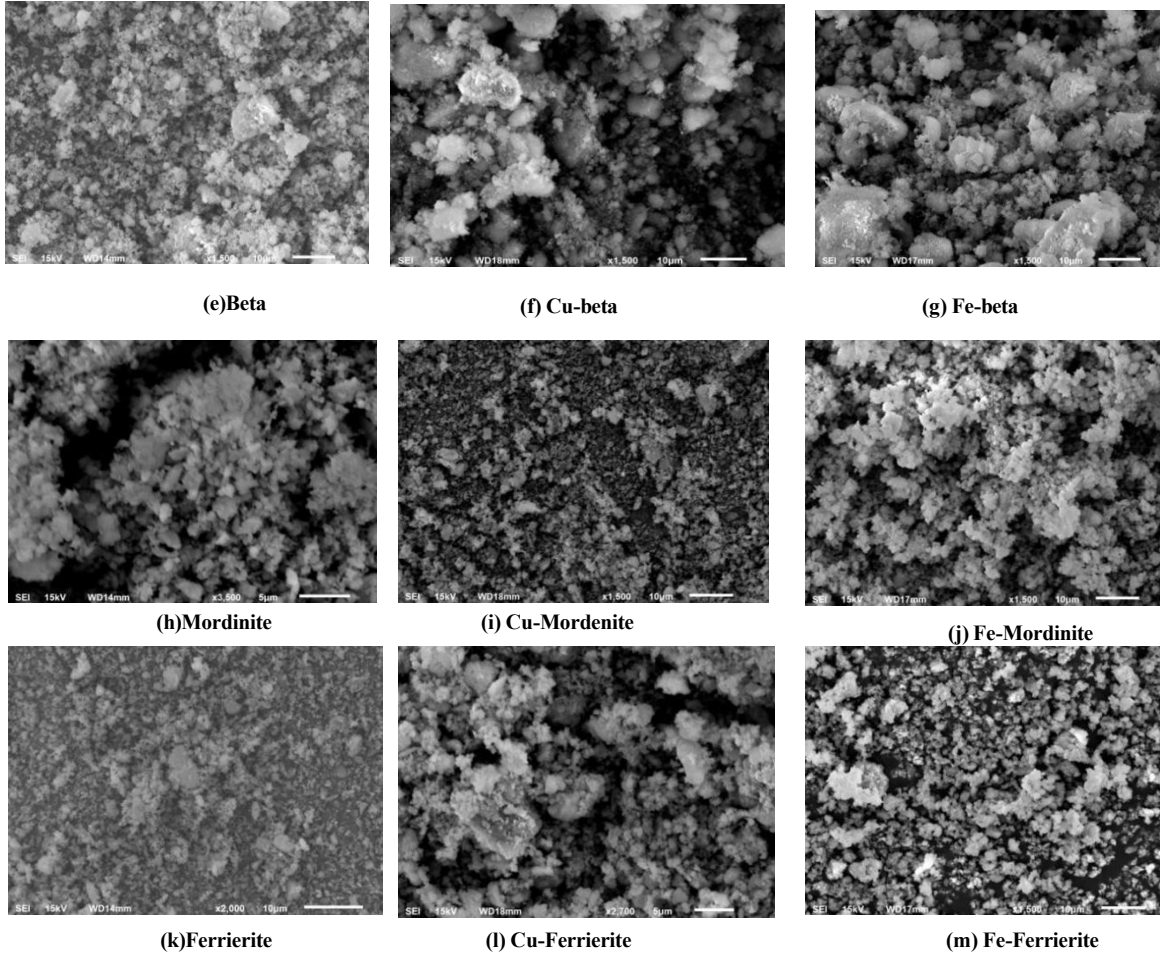


Fig 2. SEM images of metal doped zeolites

Figure: 2 shows the SEM images of various metal doped zeolites and parent zeolites. It is evident from the figure that the microstructure of the metal doped zeolites (Fig. 2 a, b, c, d, e, f, g, h, i, j, k, l and m) are completely changed and the particle size is slightly bigger than that of parent zeolites.

This is because, during ion exchange process, during ion exchange process, the transition metals are distributed or doped on the parent zeolite particles.

3.3 X-Ray Diffraction (XRD)

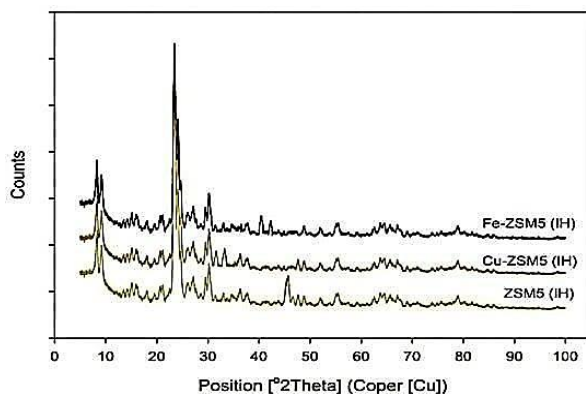
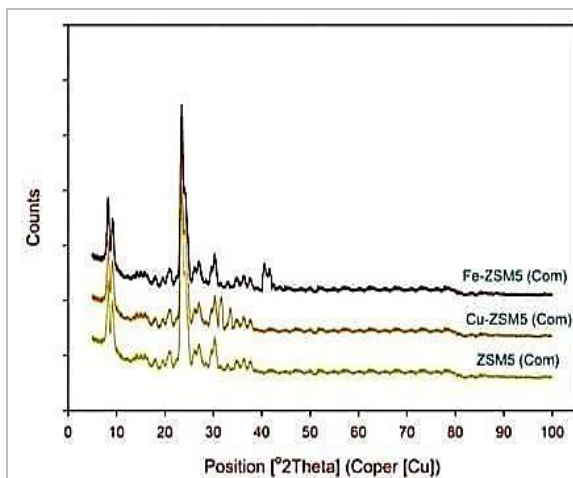
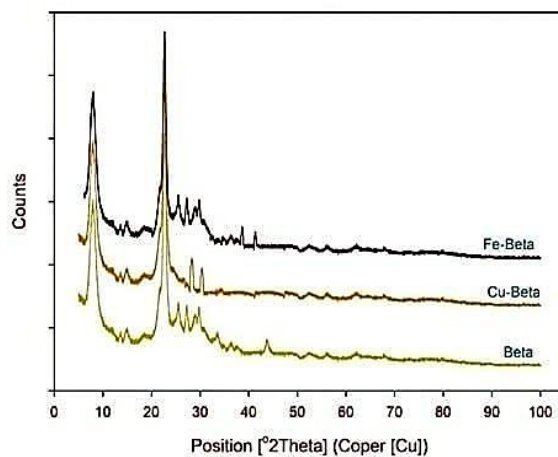


Fig 3a. XRD patterns of ZSM5, Cu-ZSM5, and Fe-ZSM5



(b). XRD patterns of ZSM-5, Cu-ZSM-5 and Fe-ZSM-5 commercial



(c). XRD patterns of beta, Fe-beta and Cu-beta

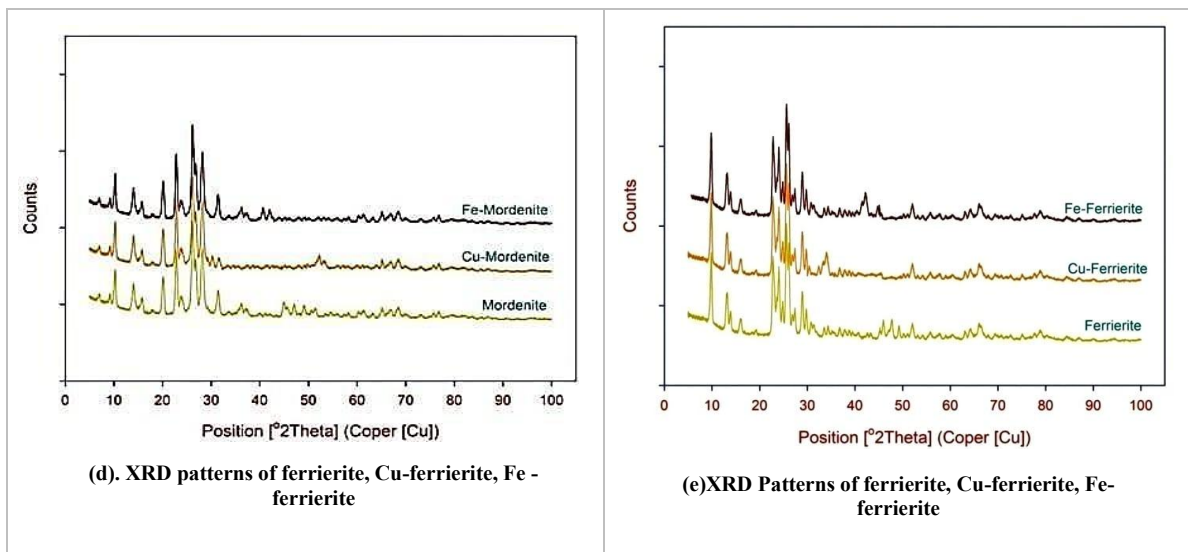


Fig 3b. XRD Patterns of various metal doped zeolites

Fig:3 shows the XRD pattern of various zeolites and metals (Cu, Fe) doped on the zeolites. It is observed from pattern that the major original structure of zeolites (i.e. the major peaks of SiO_2 and Al_2O_3) remains unchanged after the ion exchange process. It is also observed that some low intensity diffraction lines (peaks) disappear and new

diffraction lines are formed, which is identified as metallic (Cu and Fe) species. It is evident from the fig that there is no increase or decrease in the content of the SiO_2 and Al_2O_3 species after the ion exchange process, and only Na^+ ions are replaced by metal ions.

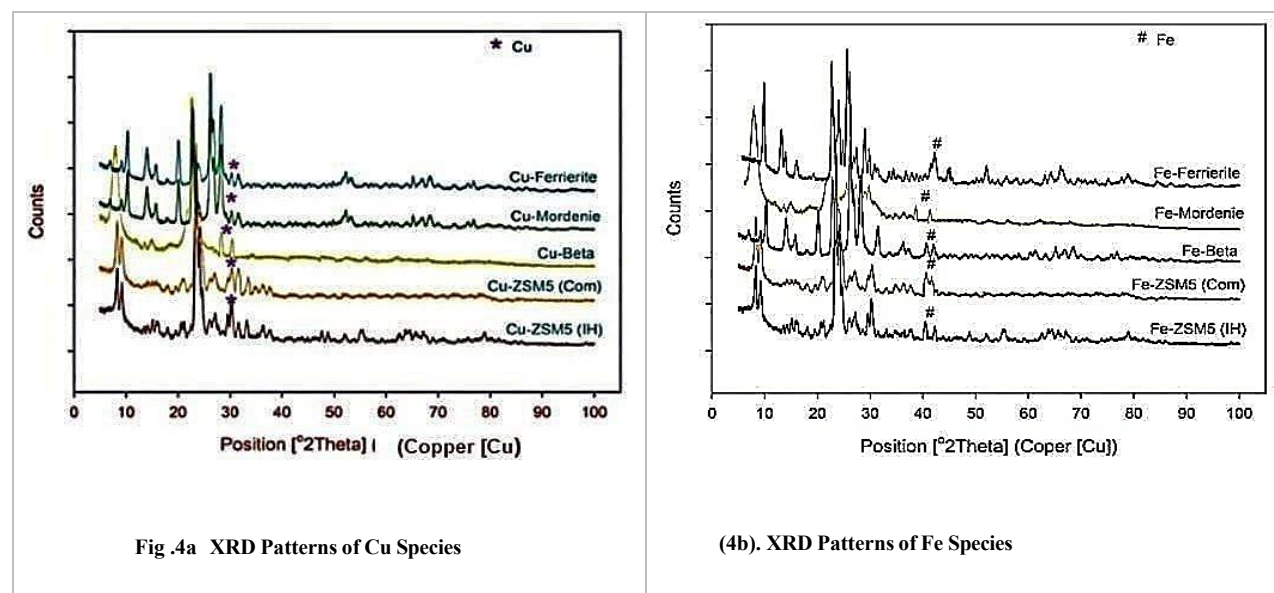


Fig 4. XRD patterns of Cu and Fe species loaded into the various Zeolite structures

Fig: 4 a and b show Cu and Fe species loaded into various zeolites structure after ion exchange process. It the seen from the pattern that low intensity diffraction lines at 37° to 42°

(denoted by# in fig 4b) are attributed to traces of Fe species. Similarly, Cu species are Fe.

3.4 Brunauer-Emmett-Teller's (BET) method and particle size analyzer

Table 2.
Result of average PSA and BET

Sample	Average Particle size Distribution (d.nm)	BET (m ² /g)
Rice husk ash	2519	3.5
ZSM5 (IH)	346.7	405
ZSM5 (Commercial)	315.4	425
Beta	301.3	520
Mordenite	360.2	401
Ferrierite	310.4	448

Table.2 shows the result of average particle size distribution and surface area of raw rice husk ash, ZSM-5 (IH), ZSM-5(commercial), beta, Mordenite and ferrierite.it is observed from the table.2

that the average particle size distribution of raw rice husk - ash is 2519 d.nm, after hydro thermal treatment it is reduced 346.7 d.nm in case of ZSM-5 zeolite. This size reduction indicates the phase of zeolite and it also seen in the result of SEM analysis Figure.1. The surface area of rice husk ash is 3.5 m²/g and it is increased to 332 m²/g and 405 m²/g respectively ZSM-5 (IH).

It is observed that when the particle size is reduced or increased surface area. Higher effective surface area is a favorable advantage for SCR of NO_x emission control.

IV. CORDIERITE MONOLITH

Pt coated monoliths and blank monoliths both with cell density of 400 CPSI, 0.17 mm wall thickness and dimensions of 90 mm diameter and 90 mm length are obtained from Bocent Advanced Ceramics Co Ltd, China Fig. 4 show the photographic view of blank monoliths.



Figure 5. Photographic view of blank monoliths

4.1 Monoliths Washcoating

Among the various methods adopted for deposition of catalyst on the monolith, the conventional dip coating method proves to be effective because of its simplicity and versatility (M.A. Ulla et al., 2003; Valerie Meille, 2006). Slurry is prepared using 50 weight% of Cu-ZSM-5, 4 weight % of silica gel and remaining weight% of water. Two monoliths (Pt-coated and uncoated) are separately immersed into the slurry for 1 minute and excess slurry is removed by passing compressed air through the monolith channel for a fixed time of five seconds from both the ends. Then the monolith is placed in a muffle furnace and dried for two hours at a temperature of 120 °C. The dipping and drying processes are repeated till the desired quantity (i.e. 15% weight of monolith) of wash coat is deposited on the monolith substrate. Finally the substrate is calcined for five hours at 500 °C.

4.2 Fabrication of Catalytic Converter Assembly

In this section, Selective Catalytic Reduction (SCR) of NO_x with NH₃ is adopted for diesel engine to analyse the emission characteristics. The Diesel Oxidation Catalyst (DOC), Diesel Particulate Filter (DPF) and NH₃ reduction monoliths are purchased, the specification of all of which is 90 mm diameter, 90 mm length, wall thickness 0.17 mm and 400 Cells per square inch (CPSI).

The DOC, DPF and NH₃ reduction monoliths are used as such without any modification. The uncoated monoliths are used for washcoating of various metal doped zeolites, the preparation of which have been discussed in the previous chapter. The DOC and DPF monoliths are fabricated as a single unit and SCR and NH₃ reduction monoliths are fabricated as a unit. An expansion box with a heating element is also fabricated separately. DOC and DPF assembly is the first section of the exhaust system followed by the expansion box unit. The SCR and NH₃ reduction assembly is connected downstream of the expansion box. Provision is also made to hold the urea injector on the exhaust pipe line before the expansion box.

4.3 Preparation of Aqueous Urea Solution

In this experiment, the concentration of urea solution is fixed at 32.5% and it may be defined as:

$$\text{Concentration of urea solution (\% by weight)} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100$$

Hence to get 32.5% aqueous urea solution, 325 grams of urea (NH₂ CO NH₂) is dissolved in 675ml of water and kept in a separate tank.

4.4 Urea required for maximum reduction of NO_x

The urea solution is injected into the engine's exhaust path. It gets vaporized and ammonia (NH_3) is produced. Correct quantity of ammonia is to be injected into the engine's exhaust to reduce all the NO_x into N_2 . Hence it is essential to find out the stoichiometric value

Stoichiometric Ratio The stoichiometric ratio " α " represents the ratio between moles of NH_3 added as reducing agent and the moles of NO_x present in the exhaust feed gas.

$$\alpha = \frac{\text{NH}_3 \text{ (in)}}{\text{NO}_x \text{ (in)}}$$

The inlet NO_x is calculated at five different load conditions by diverting the exhaust gas to another path which then reaches the muffler.

5.1 Experimental Setup

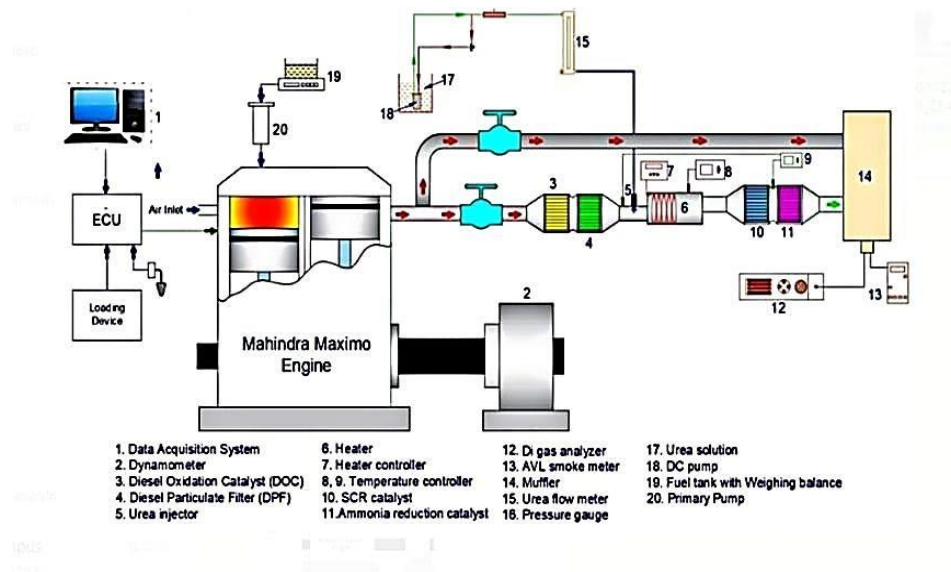


Fig 6. Schematic view of the experimental setup

V. EXPERIMENTAL STUDY

The experimental work was conducted using a Mahindra Maximo, a twin cylinder, four stroke diesel engine equipped with Common Rail Direct Injection (CRDI) and water – cooling, featuring a bore diameter of 83 mm and a stroke length of 84 mm. The engine was coupled with suitable switching and control systems to facilitate load testing. Figure.6 provides a schematic representation of the experimental setup. To achieve a steady-state condition and attain a cooling water temperature of 70°C , the engine was operated for 10 to 15 minutes. Emission measurements, including CO, HC, CO_2 , O_2 , and NO_x , were conducted using the NETEL multi-gas analyzer and smoke was measured by using AVL smoke meter. A Chromel-Aluminum thermocouple was placed at various locations within the converter to monitor exhaust gas temperatures. The test were carried out under varying load and temperature conditions.

VI. RESULT AND DISCUSSION

6.1 Catalytic activity test (SCR)

(a) Low temperature steady state test

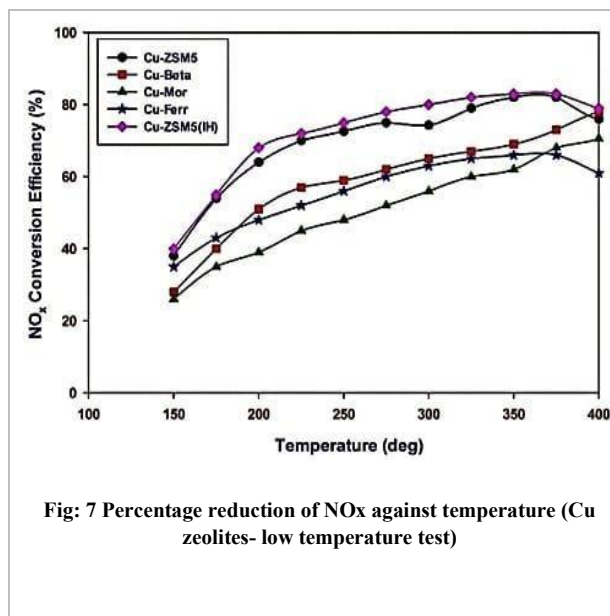


Fig: 7 Percentage reduction of NO_x against temperature (Cu zeolites- low temperature test)

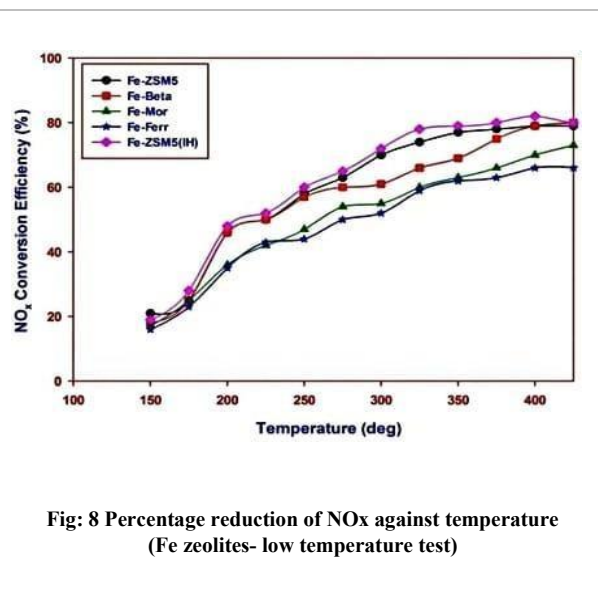


Fig: 8 Percentage reduction of NO_x against temperature (Fe zeolites- low temperature test)

Fig: 8 Shows the percentage reduction of NO_x against temperature of various zeolites. It is observed from the figure that the in-house made Cu-ZSM-5 zeolite and commercial ZSM-5 zeolite shows higher activity throughout the temperature. The NO_x conversion efficiency of Cu-ZSM-5 zeolite (commercial) is around 64% at a temperature of 200 °C and it steadily increases and reaches 82% at 350°C. Whereas, the in-house made Cu-ZSM-5 catalyst shows NO_x conversion efficiency of 65% at 200°C which then steadily increases and reaches 84% at 350°C. Cu-ZSM-5 catalyst exhibits much higher SCR activity at low temperature than other zeolites. The Cu species mainly exists in the form of isolated Cu²⁺ at the exchange sites of ZSM-5 zeolite. Such species are believed to be the active sites for the NH₃-SCR of NO_x. The NH₃ adsorption on lewis and/or bronsted acidic sites is very important for SCR performance. It is spotted that Silica- rich ZSM-5 zeolites possess more ammonia adsorption sites compared to the other zeolites. Therefore, it can be concluded that the abundant isolated Cu-ions acting as lewis acidic site over Cu-ZSM-5 catalysts facilitated the ammonia adsorption, thereby contributing to the enhancement of SCR activity. A maximum of 73% of NO_x conversion efficiency is achieved at 375°C by Cu- beta zeolite.

However the efficiency is marginally low when compared to ZSM-5 zeolite in all the temperature ranges of exhaust gas. Cu-mordenite and Cu-ferrierite exhibit only 60% of NO_x conversion efficiency in the temperature range of 250 to 375°C. It is perceived from the figure that the NO_x conversion efficiency decreases in the Cu-ZSM-5 (in-house) > Cu-ZSM-5 (commercial) > Cu -beta > Cu -ferrierite > Cu -mordenite. Fig 8. Show the NO_x conversion efficiency of Fe-zeolites with exhaust gas temperature. It is noted from the figure that the Fe-ZSM-5 (in-house) zeolites exhibit higher NO_x conversion efficiency when compared to other zeolites. However the conversion efficiency is lower than Cu- ZSM-5 (in-house) zeolites. The conversion efficiency of Fe-ZSM-5 zeolites reaches 60% at 250 °C and then after a steady increase it reaches 80% at 375°C. Fe-beta zeolite performs better than Fe- mordenite and Fe-ferrierite. The order of decrease in efficiency is seen to be Fe-ZSM-5 (inhouse) > Fe-ZSM-5 (commercial) > Fe-beta > Fe-mordenite > Fe- ferrierite. The conversion of Cu- ZSM-5 zeolites perform better than Fe-ZSM-5 zeolite at low temperature range. The reason is that the Cu- species in the ZSM-5 zeolite is more active at low temperature and enhances the oxidation of NO to NO₂ and consequently activities the fast SCR reaction.

b) High temperature steady state test

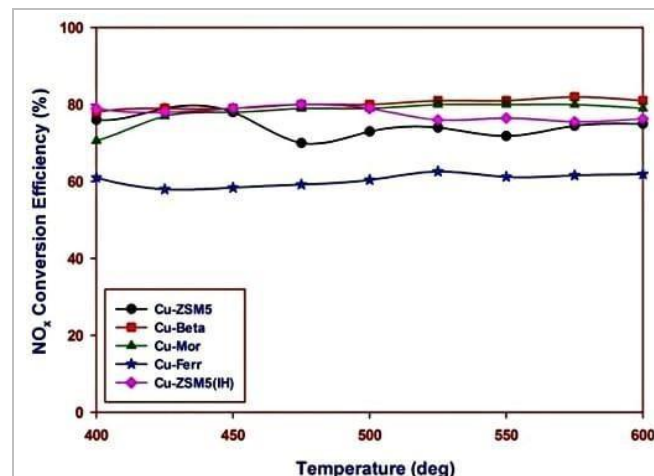


Fig: 9 Percentage Reduction of NO_x against Temperature (Cu Zeolites –High Temperature)

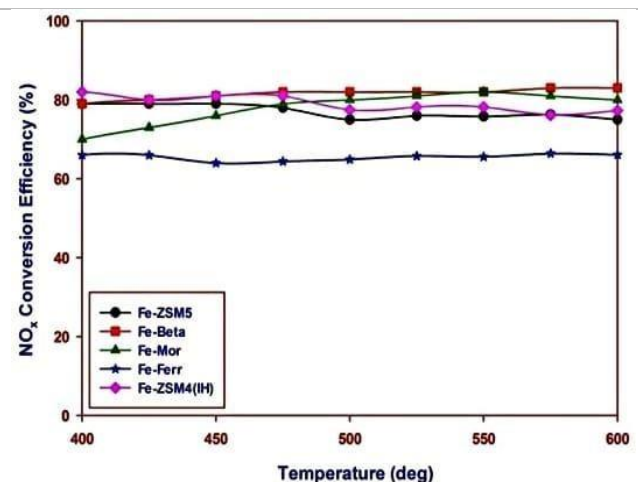


Fig: 10 Percentage Reduction of NO_x against Temperature (Fe Zeolites –High Temperature)

Figure 9. Shows NO_x conversion efficiency against temperature with various zeolites. It is identified from the figure that Cu-beta zeolite shows higher conversion efficiency when compared to other zeolites. The NO_x conversion efficiency of Cu-beta zeolite at 400 °C is around 79% and after steady increase, it reaches 83% at 573°C. Cu-mordenite zeolite also shows higher activity at all levels of temperature of exhaust gas. A maximum of 80% of NO_x conversion is achieved in the temperature range of 525 to 575°C. The in-house made ZSM-5 zeolite exhibit only 75% of NO_x conversion at 550 to 600°C. No remarkable increase of NO_x conversion efficiency is observed throughout the temperature range by the in- house made zeolite. The result of efficiency is decreased in the order being Cu-beta > Cu-mordenite > Cu-ZSM-5 (commercial) > Cu-ferrierite.

Figure10. Shows the NO_x conversion efficiency of various zeolites against temperature. It is seen from the figure that Fe-beta zeolite gives more NO_x conversion efficiency throughout the temperature range of exhaust gas and the conversion efficiency is around 80% at 425°C and it is increased to 83% at 600°C. Fe-mordenite also gives NO_x conversion efficiency of around 80% in the temperature range of 500 to 600 °C. The in- house made Fe-ZSM-5 catalyst shows only 77% NO_x conversion efficiency in the temperature range of 500 to 575°C. The NO_x conversion efficiency is seen to decrease in the order: Fe-beta > Fe-mordenite > Fe-ZSM-5 (in-house) > Fe- ZSM-5 (commercial) > Fe- ferrierite.

In contrast to low temperature results, ZSM-5 zeolites are less active at higher temperature because at higher temperature, the Fe & Cu-ions ions also participate in the oxidation of NH₃, reducing the availability of the reductant and thus decreasing abruptly the NO_x conversion. On the other hand, due to the low oxidation capacity, beta based catalyst does not consume NH₃ and maintains higher NO_x conversion. The NO_x conversion activity of zeolites [ZSM-5 (In House), ZSM-5 (commercial), beta, mordenite and ferrierite] differ each other at various temperatures and load conditions. It is because, even though the preparation root is same for all the zeolites, the physio chemical composition and textural properties are not same for all zeolites. The compositions such as SiO₂ and Al₂O₃, and textural properties such as surface area, micropore volume, mesopores volume, particle size, bulk and absolute density etc. differ from one zeolite to another.

VII. CONCLUSION

This study demonstrated the effectiveness of NH₃-SCR for NO_x reduction using Cu-ZSM-5 and Fe-ZSM-5 catalysts synthesized from rice husk ash, a sustainable silica source. ZSM-5 was synthesized via hydrothermal treatment, and copper and iron were incorporated through ion exchange. The catalysts were wash-coated onto cordierite honeycomb monoliths and tested as catalytic converters.

To evaluate performance, commercial zeolites (ZSM-5, beta, mordenite, ferrierite) were also modified with Cu and Fe, resulting in ten different catalysts. These were tested on a twin- cylinder Mahindra diesel engine under five load conditions, with exhaust gas temperature ranging from 150 °C to 600 °C. Ammonia for all SCR reaction was generated by injecting an optimizing urea solution into exhaust. Among all catalysts, in-house synthesized Cu-ZSM-5 showed the highest NO_x conversion efficiency, achieving 72% at 225 °C and 84% at 375°C. The overall performance order was: Cu-ZSM-5 (In House), Cu -beta > Cu –mordenite > Cu –ferrierite. This confirms that zeolite structure and metal type significantly influence SCR activity, with ZSM-5's MFI framework being particularly effective under high-temperature, lean exhaust conditions. The study highlights the potential of rice husk ash- derived zeolites as eco-friendly, cost- effectively alternatives for diesel engine emission control technologies.

REFERENCES

- [1] Alotibi, M. F., Alshammari, B. A., Alotaibi, M. H., Alotaibi, F. M., Alshihri, S., Navarro, R. M., & Fierro, J.L. G. (2020). ZSM-5 zeolite based additive in FCC process: A review on modifications for improving propylene production. *Catalysis Surveys from Asia*, 24, 1-10.
- [2] Čejka, J., Centi, G., Perez-Pariente, J., & Roth, W. J. (2012). Zeolite-based materials for novel catalytic applications: Opportunities, perspectives and open problems. *Catalysis Today*, 179(1), 2- 15.
- [3] Dhal, G. C., Dey, S., Mohan, D., & Prasad, R. (2018). Simultaneous abatement of diesel soot and NO_x emissions by effective catalysts at low temperature: An overview. *Catalysis Reviews*, 60(3), 437-496.
- [4] Di, Z., Wang, H., Zhang, R., Chen, H., Wei, Y., & Jia, J. (2022). ZSM-5 core-shell structured catalyst for enhancing low-temperature NH₃-SCR efficiency and poisoning resistance. *Applied Catalysis A: General*, 630, 118438.
- [5] Gong, X., Caglayan, M., Ye, Y., Liu, K., Gascon, J., & Dutta Chowdhury, A. (2022). First-generation organic reaction intermediates in zeolite chemistry and catalysis. *Chemical Reviews*, 122(18), 14275-14345.
- [6] Hamoud, H. I., Valtchev, V., & Daturi, M. (2019). Selective catalytic reduction of NO_x over Cu- and Fe- exchanged zeolites and their mechanical mixture. *Applied Catalysis B: Environmental*, 250, 419-428.
- [7] Imoisili, P. E., & Jen, T. C. (2022). Microwave-assisted sol-gel template-free synthesis and characterization of silica nanoparticles obtained from South African coal fly ash. *Nanotechnology Reviews*, 11(1), 3042- 3052.
- [8] Istrate, A., Bică, M., & Simion, M. (2020, December). Compression ignition engine-sources of pollution. In *IOP Conference Series: Materials Science and Engineering* (Vol. 997, No. 1, p. 012148). IOP Publishing.
- [9] Kim, H. S., Kasipandi, S., Kim, J., Kang, S. H., Kim, J. H., Ryu, J. H., & Bae, J. W. (2020). Current catalyst technology of selective catalytic reduction (SCR) for NO_x removal in South Korea. *Catalysts*, 10(1), 52.
- [10] Mohan, S., Dinesha, P., & Kumar, S. (2020). NO_x reduction behaviour in copper zeolite catalysts for ammonia SCR systems: A review. *Chemical Engineering Journal*, 384, 123253.
- [11] Nguyen, D. K., Dinh, V. P., Nguyen, H. Q., & Hung, N. T. (2023). Zeolite ZSM-5 synthesized from natural silica sources and its applications: a critical review. *Journal of Chemical Technology & Biotechnology*, 98(6), 1339-1355.
- [12] Nigam, A. P., & Sinha, S. (2022). Techniques to control IC engine exhaust emissions through modification in fuel and intake air—a review. *International Journal of Ambient Energy*, 43(1), 3418- 3430.
- [13] Reşitoğlu, İ. A., Altinişik, K., & Keskin, A. (2015). The pollutant emissions from diesel-engine vehicles and exhaust aftertreatment systems. *Clean Technologies and Environmental Policy*, 17, 15-27.
- [14] Ruggeri, M. P., Selleri, T., Colombo, M., Nova, I., & Tronconi, E. (2015). Investigation of NO₂ and NO interaction with an Fe-ZSM-5 catalyst by transient response methods and chemical trapping techniques. *Journal of Catalysis*, 328, 258-269.
- [15] Rutkowska, M., Pacia, I., Baśąg, S., Kowalczyk, A., Piwowarska, Z., Duda, M., ... & Chmielarz, L. (2017). Catalytic performance of commercial Cu-ZSM-5 zeolite modified by desilication in NH₃-SCR and NH₃-SCO processes. *Microporous and Mesoporous Materials*, 246, 193-206.
- [16] Schütz, M. B., Xiao, L., Lehnen, T., Fischer, T., & Mathur, S. (2018). Microwave-assisted synthesis of nanocrystalline binary and ternary metal oxides. *International Materials Reviews*, 63(6), 341- 374.
- [17] Treps, L., Gomez, A., de Bruin, T., & Chizallet, C. (2020). Environment, stability and acidity of external surface sites of silicalite-1 and ZSM-5 micro and nano slabs, sheets, and crystals. *ACS Catalysis*, 10(5), 3297-3312.
- [18] Wang, A., Wang, Y., Walter, E. D., Washton, N. M., Guo, Y., Lu, G., ... & Gao, F. (2019). NH₃-SCR on Cu, Fe and Cu+ Fe exchanged beta and SSZ-13 catalysts: Hydrothermal aging and propylene poisoning effects. *Catalysis Today*, 320, 91-99.
- [19] Wang, P., Yu, D., Zhang, L., Ren, Y., Jin, M., & Lei, L. (2020). Evolution mechanism of NO_x in NH₃-SCR reaction over Fe-ZSM-5 catalyst: Species-performance relationships. *Applied Catalysis A: General*, 607, 117806.
- [20] Wang, T., Wan, Z., Yang, X., Zhang, X., Niu, X., & Sun, B. (2018). Promotional effect of iron modification on the catalytic properties of Mn-Fe/ZSM-5 catalysts in the Fast SCR reaction. *Fuel Processing Technology*, 169, 112-121.
- [21] Wardana, M. K. A., & Lim, O. (2022). Review of improving the NO_x conversion efficiency in various diesel engines fitted with SCR system technology. *Catalysts*, 13(1), 67.
- [22] Xue, H., Guo, X., Meng, T., Mao, D., & Ma, Z. (2022). NH₃-SCR of NO over M/ZSM-5 (M= Mn, Co,Cu) catalysts: an in-situ DRIFTS study. *Surfaces and Interfaces*, 29, 101722.
- [23] Yang, J., Li, Z., Yang, C., Ma, Y., Li, Y., Zhang, Q., ... & Cui, J. (2022). Significant promoting effect of La doping on the wide temperature NH₃-SCR performance of Ce and Cu modified ZSM-5 catalysts. *Journal of Solid State Chemistry*, 305, 122700.
- [24] Zhang, C., Li, S., & Bao, S. (2019). Sustainable synthesis of ZSM-5 zeolite from rice husk ash without addition of solvents. *Waste and Biomass Valorization*, 10, 2825-28.
- [25] Proding, S., Derewinski, M. A., Wang, Y., Washton, N. M., Walter, E. D., Szanyi, J., ... & Peden, C. H. (2017). Sub-micron Cu/SSZ-13: Synthesis and application as selective catalytic reduction (SCR) catalysts. *Applied Catalysis B: Environmental*, 201, 461-469.

Corresponding Author, AASTHIYA B Email:
aasthiyabharathi96@gmail.com