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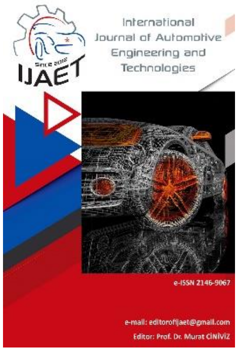

Original Research Article

NO_x emission reduction through selective catalytic reduction using copper-based Y zeolite catalyst: experimental investigation and characterization

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ABSTRACT

Growing concerns surrounding global warming and environmental degradation have prompted the widespread adoption of various emission control methodologies, with a particular emphasis on reducing nitrogen oxide (NO_x) emissions. Selective catalytic reduction (SCR) stands out as a highly effective technique, applicable not only to large-scale industrial machinery but also to smaller vehicles, aimed at converting NO_x emissions into less harmful nitrogen (N_2) using specialized catalysts and reductants. This particular study focuses on synthesizing copper-based Y zeolite and conducting experiments using ethanol as a reductant in the exhaust stream of a two-cylinder diesel engine operating under different loads. Furthermore, the catalyst was subjected to thorough characterization using techniques such as Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), X-ray Diffraction (XRD), and Brunauer-Emmet-Teller (BET) analysis. Results indicate that as temperature and engine load increase, the efficiency of NOx conversion also improves. The highest conversion rate, reaching 94.67%, was achieved at 260°C under a 5 kW load. Additionally, average conversion rates of 90%, 90.70%, and 92.62% were observed for loads of 1 kW, 3 kW, and 5 kW, respectively. These findings not only highlight the effectiveness of SCR technology in reducing NO_x emissions but also underscore the potential of copper-based Y zeolite catalysts in this regard. The comprehensive characterization of the catalyst provides valuable insights into its structural and chemical properties, paving the way for further advancements in emission control strategies.

Keywords: Selective catalytic reduction, NO_x emission, Zeolite, Characterization.

1. Introduction

In the process that has been going on for centuries, human beings have needed energy somehow. While this energy need was provided by using fire at first, with the discovery of external combustion engines, a great innovation has been exhibited especially in transportation and daily life. In the following years, more efficient internal combustion engines (ICEs) have followed.

The advent of commercially viable internal combustion engines (ICE) traces back to Étienne Lenoir's creation around 1860. Subsequently, Nicolaus Otto introduced the modern internal combustion engine, famously known as the Otto engine, in 1876. Rudolf Diesel's significant contribution in 1892 led to the development of the first compression-ignition engine, marking a pivotal milestone in engine technology evolution [1]. With the invention of the diesel engine, heavy-duty work has particularly become even easier. Today, diesel engines find numerous applications, particularly in the fields of transportation and industrial sectors. While their extensive use is often regarded as an advantage, the emissions of diesel engines pose significant health and environmental challenges [2]. Nitrogen oxide (NO_x) emissions are prominent among these pollutants and are recognized as the primary contributor to acid rain formation. In recent years, heightened awareness of global warming and environmental pollution has led to the adoption of various emission control methods, particularly for addressing NO_x emissions. Selective catalytic reduction (SCR) stands out as the most efficient approach for reducing NO_x emissions and can be applied not only to heavy-duty machinery but also to small-scale passenger vehicles [3]. The SCR method is basically a more harmless N_2 conversion of NO_x emissions by using a certain reductant and a specified catalyst [4].

SCR systems are named according to the used reductant. Among the SCR systems, NH_3-SCR is the first and still only commercialized one. The system uses AdBlue for abating the NO_x emissions with a V_2O_5–WO_3/TiO_2 catalyst. NH_3 slip and toxicity and the poor stability of vanadium are the main drawbacks of the NH_3-SCR system [5]. Such disadvantages have pushed research into a broader field. For this reason, different SCR systems were defined by changing the reductants and customized catalysts for these systems were used. Hydrocarbon SCR (HC-SCR), carbon monoxide SCR (CO-SCR), and hydrogen SCR (H_2-SCR) are the other SCR systems that currently exist in the literature [6].

In one of the first studies, Corma and his research group [7] reported that in Cu-beta zeolites, a pronounced enhancement in NO_x conversion is observed upon elevating the reaction temperature from 250 to 350 °C. However, subsequent increments in temperature result in a gradual decline in conversion efficiency. The NO_x reduction experiments were conducted within a fixed-bed quartz tubular reactor. Heimrich and Deviney [8] investigated different zeolites-based catalyst activity for NO_x reduction with copper ion exchange procedure in a real engine exhaust gas stream. They used ethylene as a reductant. Their results reveal that a 95% NO_x reduction can be obtained for a short-term period but 52% percent for long-term usage. Lee and his co-workers [9] studied the impact of varying copper loadings on the catalytic efficacy of different zeolite types for selective catalytic reduction using propene (C_3H_6) under laboratory conditions, maintaining a space velocity (SV) of 12000 h^{-1}. The catalysts were prepared utilizing an impregnation procedure. The incorporation of copper into the zeolite matrices resulted in distinct $DeNO_x$ performances, enhancing NO_x conversion and lowering the required reaction temperatures. Notably, among the synthesized catalysts, 2Cu/ZSM-5 exhibited the most notable NO_x to N_2 conversion, reaching approximately 68%. In the continuation of the previous study, Lee and researchers [10] investigated the effects of both SiO_2/Al_2O_3 ratio and metal additives (Sn, Ce, Mn, and Pt) on 2Cu-ZSM-5 catalyst in detail. The catalysts were synthesized employing the incipient wetness impregnation technique. The $DeNO_x$ performance was particularly affected by the SiO_2/Al_2O_3 ratio. In addition, 1 wt.% metal additives caused a significant increase in catalytic performance. Gao and his team [11] conducted a study about the influence of various copper loadings on catalytic performance and activities on Cu/SAPO-34 in the C_3H_6-SCR system. The various copper-loaded catalysts were synthesized via a pH-controlled ion exchange method. The increase in the pH value caused an increase in the copper loading. The experiments were performed in laboratory conditions at 72000 h^{-1} of SV. It has been observed that copper loading has a significant contribution to $DeNO_x$ performance. Especially, high Cu loadings exhibited more encouraging $DeNO_x$ activity.

When the literature is reviewed, numerous reductants have been tested both in laboratory conditions and under real exhaust gas conditions in conjunction with various zeolite-type catalysts. But these studies are mostly performed in a small-scale reactor and research on real engine exhaust flow is quite limited. In this study, the production of copper-based Y zeolite was conducted, and experiments were carried out using ethanol as a reductant in a two-cylinder diesel engine under different engine loads. Additionally, for catalyst characterization, analyses such as Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS), X-ray Diffraction (XRD), and Brunauer-Emmet-Teller (BET) were performed.

2. Material and Methods

In the study, all preparation and tests were conducted in Laboratories of the Automotive Engineering Department of Çukurova University. However, catalyst characterizations were performed in the center laboratory of Çukurova University.

2.1. $DeNO_x$ performance test system

Performance tests were performed to investigate the NO_x conversion efficiency of the Cu-Y zeolite with ethanol reductant. Commercially available diesel was used as fuel in all tests. The schematic representation of the test system is given in Figure 1, and the technical properties of the test engine are given in Table 1. Experiments were carried out under 3 different engine load conditions (1, 3, and 5 kW) at a temperature ranging from 170 to 260 °C with an SV of 30000 h^{-1}. SV is the ratio of the volumetric flow of exhaust gas to the catalyst volume. For determining the SV, a U manometer was placed with an orifice plate into the exhaust pipe. The engine load was provided with the help of a 10-kW electronic load. To measure the exhaust gas temperature K type thermocouple was placed before the SCR catalyst and the NO_x data were recorded with two Continental $UniNO_x$ sensors. The injection of the reductant is managed by an electric pump and a multipoint electro-hydraulic injector. All obtained data were collected on a laptop with an Arduino-based specified program. The following formula was used to determine the NO_x conversion efficiency of the used catalyst.

$$NO_x \text{ conversion } (\%) = \left(\frac{NO_{x_{in}} - NO_{x_{out}}}{NO_{x_{in}}}\right) x100$$

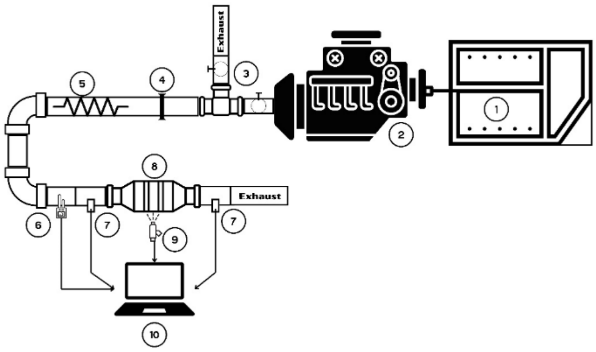


Figure 1. $DeNO_x$ performance test rig schematic (1-Engine load, 2-Engine, 3-SV adjustment valve, 4-Orifice plate, 5-Heater, 6-Temperature sensor, 7-NOx sensor, 8-SCR catalyst, 9-Reductant injector, 10-PC)

Table 1. Technical specifications of the test engine

Type	Diesel
Model	A2CRX08
Cylinder number	2
Cylinder volume	830 cm^3
Compression ratio	23/1
Cooling system	Water-cooled
Engine Speed	3000 rpm

2.2. Catalyst preparation

The SCR catalyst employed in this investigation was synthesized utilizing a commercial Y-zeolite (Alfa-Aesar, SiO_2/Al_2O_3 = 5.1:1) via the conventional liquid-phase ion exchange method, mirroring methodologies outlined in the prior reported study [12]. In the catalyst preparation process, a solution is initially formed by mixing 5 wt. % $CuCl_2$ in 300 mL distilled water, which is heated to 70 °C for 30 min. Subsequently, 50 g of Y-zeolite is introduced, and the pH is carefully adjusted to 8-8.5 using ammonium hydroxide. The system is allowed to undergo an ion exchange process for 24 hours. Afterward, the solution is filtered to separate the solid catalyst, which is then dried at 110 °C for 2 h. The dried catalyst undergoes a first round of calcination at 500 °C for 2 h in a muffle furnace. A solution is prepared by combining 40 g of the powdered catalyst with 0.4 g of colloidal silica. Acidtreated cordierite is immersed in this solution, followed by a drying step at 110 °C for 1 h. The catalyst-coated cordierite then undergoes a second round of calcination at 500 °C for 3 h in a muffle furnace. Finally, copper-based Y-zeolite (Cu-Y zeolite) was ready for performance tests.

2.3. Catalyst characterization

The surface morphology of the catalysts was examined using Scanning Electron Microscopy (SEM) with the FEI Quanta 650 FEG scanning electron microscope. Energy-Dispersive X-ray Spectroscopy (EDS) within the same instrument facilitated the evaluation of catalytic element distribution. Furthermore, the Brunauer-Emmett-Teller (BET) surface area of the catalysts was determined by N_2 gas adsorption measurements using a Sorptometer 1042 device. Crystallographic characteristics were assessed via X-ray diffraction (XRD) analysis conducted with the PANalytical Empyrean diffractometer.

3. Results and Discussions

3.1. DeNO$_x$ performance test of the catalyst

In Figure 2 the NO$_x$ conversion efficiency of the catalyst is illustrated for three different engine loads. With the increase in temperature, it is observed that the conversion efficiencies of NO$_x$ also increase. The increasing NO$_x$ conversion efficiency trend has also been achieved with the rise in engine load. The observed conversion increase, associated with the rise in load, may be attributed to the reducing properties of hydrocarbon emissions, which exhibit higher concentrations in the exhaust gas with the increase in load [13]. The DeNO$_x$ performance results showed that the best NO$_x$ emission conversion rate was obtained at 260 °C for all loads. Also, the highest conversion rate was obtained as 94.67% at 5 kW for the same temperature. Considering the average conversion rates at all temperatures, 90, 90.70, and 92.62% were obtained for 1.3 and 5 kW loads, respectively. In a parallel study conducted by Habib et al. [14], utilizing C_3H_6 as a reductant, a NO$_x$ to N_2 conversion rate of 98% was achieved by employing copper-based Y zeolite.

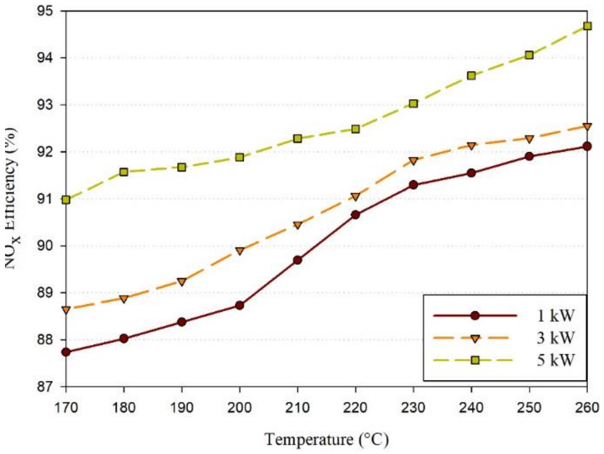


Figure 2. NO$_x$ conversion efficiency at different engine loads

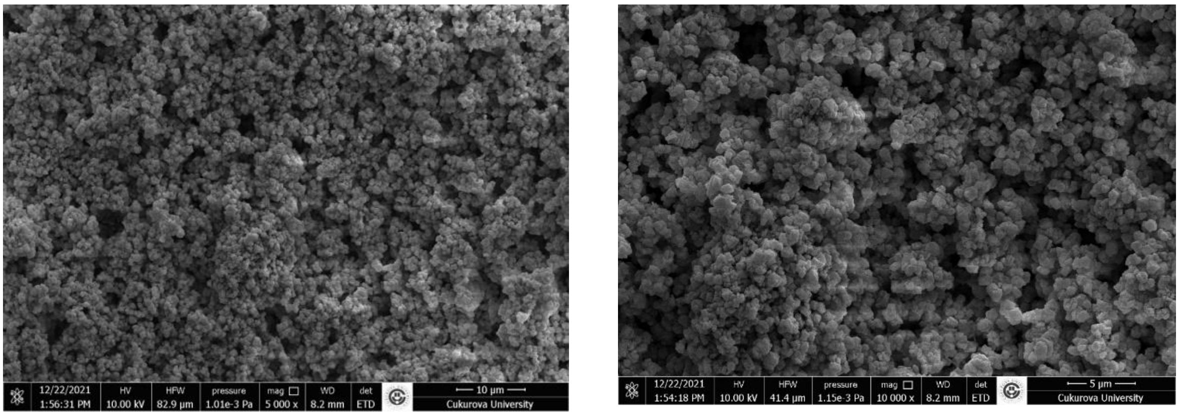
3.2. Catalyst characterization

3.2.1. SEM-EDS analysis

To assess the micromorphology and surface structure of the catalyst analyzed by SEM; a representative micrograph is presented in Figure 3. From a consideration of the SEM images, it has been observed that copper and Y zeolite are uniformly dispersed onto the pores of the cordierite. It has been noted by He et al. [15] that a uniform distribution is achieved in the utilization of zeolites. Furthermore, when compared with the EDS results (Figure 4), this dispersion indicates that the catalyst surfaces were coated with catalytic elements and the catalyst was successfully produced. Upon examining the total EDS images, two predominant colors were identified in the colorization: yellow and green. These colors represent Si and Al elements, respectively. In the element distribution, the proportions of Si, Al, O, Mg, and Cu were determined as 50%, 25%, 20%, 3%, and 3%, respectively. Through XRD analysis, the chemical composition of Y zeolite was investigated, revealing that it primarily consists of Si, Al, and O elements similar to cordierite, except for Mg. It was concluded that the higher proportions of Si, Al, and O are attributed to this composition and are reminiscent of cordierite.

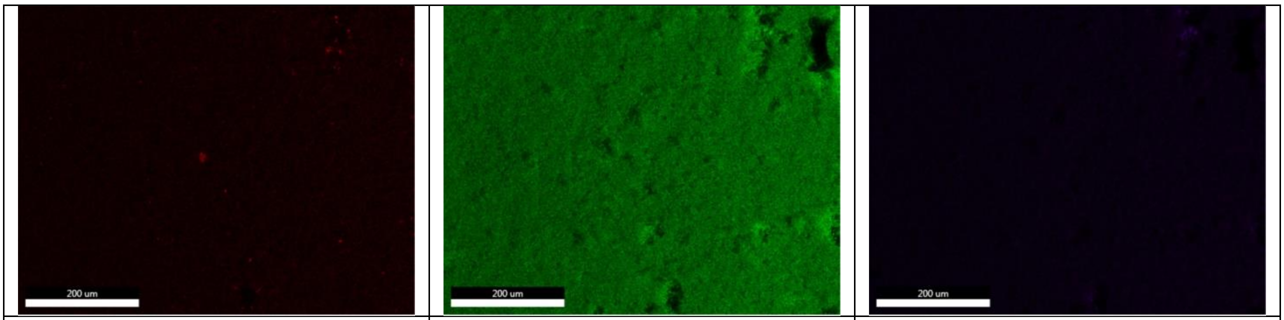
3.2.2. XRD analysis

XRD analysis was employed to characterize the catalysts, providing insights into the crystallization and dispersion of catalytic elements on the surface of cordierite.

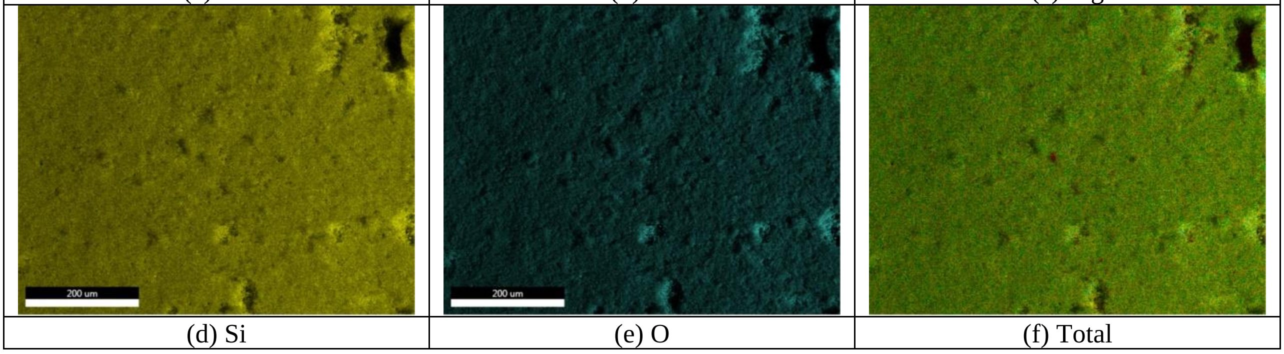


(a) 5000x (b) 10000x

Figure 3. SEM images of Cu-Y zeolite catalyst



(a) Cu (b) Al (c) Mg



(d) Si (e) O (f) Total

Figure 4. EDS mapping of Cu-Y zeolite catalyst

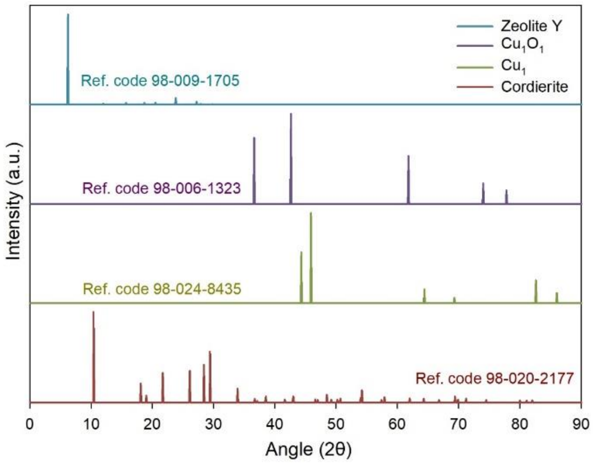


Figure 5. XRD pattern of Cu-Y catalyst

The XRD patterns illustrating the catalysts are depicted in Figure 5. In the pattern, the cordierite peaks are in the hexagonal phase structure. Intensity peaks are determined at 10.42°, 18.10°, 21.70°, 26.35°, 28.40°, 29.43°, 33.89°, and 54.24° [16]. Copper peaks showed different chemical formula Cu and CuO and the peaks are determined at 44.25°, 45.87°, 64.37°, 82.60°, and 86.04° and 36.63°, 42.55°, 61.76°, 74.00°, and 77.89°, respectively. Additionally, it was observed that Cu exhibits a tetragonal crystal structure, while CuO adopts a cubic structure. It can be seen that the characteristic peaks of cubic Y zeolite which located at 6°, 23.75°, and 27.16° over the catalyst [17].

3.2.3. BET analysis

The specific surface area and pore size distribution are important properties that can determine catalyst performance. Typically, a greater specific surface area affords a heightened provision of active sites, thereby enhancing the dispersion of the active component and encouraging the adsorption and activation of reactants. Consequently, this augmentation tends to improve catalytic activity. It is known that the specific surface area of a typical cordierite structure is approximately 0.5 m^2/g. According to the BET analysis, the surface area of the catalyst has been calculated to be 56.0773 m^2/g. Thus, it has been observed that the surface area of the produced catalyst exhibits an increase of more than 100x. This result can be supported by the study of Shigapov and colleagues [18]. This indicates that a greater surface area has been achieved, which is indicative of an increase in active sites. It is attributed that high conversion rates are obtained in conjunction with increasing active sites.

4. Conclusions

The key findings of the current study are summarized as follows:

- Multiple reductants beyond NH_3 can be utilized, offering flexibility in reductant selection.
- Diverse preparation methods for catalysts involving zeolites directly impact NO_x conversion rates.
- Elevated reaction temperatures correspond to increased NO_x conversion rates.
- Copper-supported zeolites demonstrate efficacy in NO_x reduction, particularly in low-temperature scenarios, and emerge as a promising alternative to commercial catalysts.
- SEM analysis reveals a comprehensive coating of catalytic elements on zeolite catalyst surfaces, with EDS mapping confirming homogeneous dispersion within the cordierite substrate.

In further studies, biodiesel and alcohols in different proportions can be mixed with diesel fuel and tested with existing or different catalysts. Also, other types of alcohols rather than ethanol can be used as a reductant for further discussion.

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CRediT authorship contribution statement

Ali Cem YAKARYILMAZ: Investigation, Original drafting, Writing, Editing, Visualization, Graphics, and Methodology. Tayfun OZGÜR: Supervision, Review, and Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

5. References

1. Z. Wang, X. Pan, W. Zhang, Y. Zhao, H. Li, and P. Liu, “The Development Trend of Internal Combustion Engine,” J Phys Conf Ser, vol. 1626, no. 1, p. 012139, Oct. 2020.
doi: 10.1088/1742-6596/1626/1/012139.

2. B. Sajjadi, A. A. A. Raman, and H. Arandiyan, “A comprehensive review on properties of edible and non-edible vegetable oil-based biodiesel: Composition, specifications and prediction models,” Renewable and Sustainable Energy Reviews, vol. 63, pp. 62–92, 84 Sep. 2016.
doi: 10.1016/j.rser.2016.05.035.

3. Arul Gnana Dhas, B. Nagappan, Y. K., A. T., S. Varghese, and C. D., “Effect of nano-86 fluid on reducing the smoke emissions from diesel engine,” Pet Sci Technol, vol. 37, no. 87 22, pp. 2283–2287, Nov. 2019.
doi: 10.1080/10916466.2019.1633349.

4. Ş. U. H. Sümer, S. Keiyinci, A. Keskin, H. Özarslan, and Z. Keskin, “The effect of fusel oil as a reductant over the multi-metallic catalyst for selective catalytic reduction of NO_x in diesel exhaust at low-temperature conditions,” Pet Sci Technol, pp. 1–17, Jul. 2022.
doi: 10.1080/10916466.2022.2097262.

5. M. Zyrkowski, M. Motak, B. Samojeden, and K. Szczepanek, “Deactivation of V2O5−WO3/TiO2 DeNOx Catalyst under Commercial Conditions in Power Production Plant,” Energies 2020, Vol. 13, Page 6200, vol. 13, no. 23, p. 6200, Nov. 2020.
doi: 10.3390/EN13236200.

6. J. Rodríguez-Fernández, A. Tsolakis, R. F. Cracknell, and R. H. Clark, “Combining GTL fuel, reformed EGR and HC-SCR aftertreatment system to reduce diesel NOx emissions. A statistical approach,” Int J

Hydrogen Energy, vol. 34, no. 6, pp. 2789–2799, Mar. 2009.
doi: 10.1016/j.ijhydene.2009.01.026.

7. Corma, V. Fornés, and E. Palomares, “Selective catalytic reduction of NO(x) on Cu-beta zeolites,” Appl Catal B, vol. 11, no. 2, pp. 233–242, Feb. 1997.
doi: 10.1016/S0926-3373(96)00042-2.

8. M. J. Heimrich and M. L. Deviney, “Lean NOx Catalyst Evaluation and Characterization,” SAE Technical Paper, no. x, Mar. 1993.
doi: 10.4271/930736.

9. K. Lee, H. Kosaka, S. Sato, T. Yokoi, B. Choi, and D. Kim, “Effects of Cu loading and zeolite topology on the selective catalytic reduction with C3H6 over Cu/zeolite catalysts,” Journal of Industrial and Engineering Chemistry, vol. 72, pp. 73–86, 2019.
doi: 10.1016/j.jiec.2018.12.005.

10. K. Lee, B. Choi, C. Lee, and K. Oh, “Effects of SiO2/Al2O3 ratio, reaction atmosphere and metal additive on de-NOx performance of HC-SCR over Cu-based ZSM-5,” Journal of Industrial and Engineering Chemistry, vol. 90, pp. 132–144, 2020.
doi: 10.1016/j.jiec.2020.07.005.

11. Z. Gao et al., “Influence of Copper Locations on Catalytic Properties and Activities of Cu/SAPO-34 in C 3 H 6 -SCR,” Ind Eng Chem Res, vol. 60, no. 19, pp. 6940–6949, May 2021.
doi: 10.1021/acs.iecr.0c05809.

12. Y. Zhao, B. Choi, and D. Kim, “Effects of Ce and Nb additives on the de-NOx performance of SCR/CDPF system based on Cu-beta zeolite for diesel vehicles,” Chem Eng Sci, vol. 164, pp. 258–269, 2017.
doi: 10.1016/j.ces.2017.02.009.

13. Z. Keskin, T. Özgür, H. Özarslan, and A. C. Yakaryılmaz, “Effects of hydrogen addition into liquefied petroleum gas reductant on the activity of Ag–Ti–Cu/Cordierite catalyst for selective catalytic reduction system,” Int J Hydrogen Energy, vol. 46, no. 10, pp. 7634–7641, 2021.
doi: 10.1016/j.ijhydene.2020.11.200.

14. H. A. Habib, R. Basner, R. Brandenburg, U. Armbruster, and A. Martin, “Selective catalytic reduction of NOx of ship diesel engine exhaust gas with C3H6 over Cu/Y zeolite,” ACS Catal, vol. 4, no. 8, pp. 2479–2491, Aug. 2014.
doi: 10.1021/cs500348b.

15. H. He, C. Zhang, Y. Wang, L. Zhang, and J. Zeng, “Low-temperature selective catalytic reduction of NO with CO over Nix-MOF-5,” J Mater Sci, vol. 57, no. 4, pp. 2502–2513, Jan. 2022.
doi: 10.1007/s10853-021-06795-0.

16. P. Predecki, J. Haas, J. Faber, and R. L. Hitterman, “Structural Aspects of the Lattice Thermal Expansion of Hexagonal Cordierite,” Journal of the American Ceramic Society, vol. 70, no. 3, pp. 175–182, Mar. 1987.
doi: 10.1111/j.1151-2916.1987.tb04954.x.

17. J. G. Nery, M. V. Giotto, Y. P. Mascarenhas, D. Cardoso, F. M. Z. Zotin, and E. F. Sousa-Aguiar, “Rietveld refinement and solid state NMR study of Nd-, Sm-, Gd-, and Dy- containing Y zeolites,” Microporous and Mesoporous Materials, vol. 41, no. 1–3, pp. 281–293, Dec. 2000.
doi: 10.1016/S1387-1811(00)00304-8.

18. N. Shigapov, G. W. Graham, R. W. McCabe, M. Paputa Peck, and H. Kiel Plummer, “The preparation of high-surface-area cordierite monolith by acid treatment,” Appl Catal A Gen, vol. 182, no. 1, pp. 137–146, Jun. 1999.
doi: 10.1016/S0926-860X(99)00003-4.