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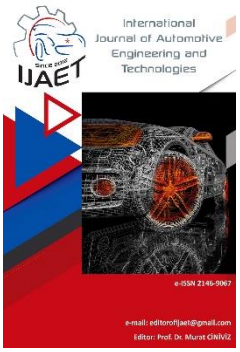

Original Research Article

Production and characterization of AG based catalyst for HC-SCR system

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ABSTRACT

In this study, Ag-Cu-Ce/TiO_2 catalyst was produced by using impregnation method for hydrocarbon-selective catalytic reduction (HC-SCR) system. In this system, as a reducing agent ethyl alcohol and urea solution mixture was used. The NO_X conversion efficiency of the system with using synthesized catalyst was analyzed. Chemical and structural properties of the used catalyst were examined by SEM, BET and XRD analyzes. In the SCR test system, the experiments were conducted in different temperatures ranged from 200 °C to 300 °C in constant gas hourly space velocity (GHSV) (30000 h^{-1}). The tests were carried out by using 2 cylinders, V-type diesel engine with constant speed (3000 rpm) under 3 different loads (1 kW, 3 kW and 5 kW). These tests identified the effects of produced catalyst on NO_x conversion rate of SCR system. In result, NO_x conversion rates were measured between 66 % and 93 %. In 1 kW load, at 300 ° C, SV= 30000 h^{-1}, 100% ethyl alcohol spraying the NO_X conversion rate was reached approximately to 93% which is the highest point.

Keywords: HC-SCR, NO_x, Catalyst, Diesel Engine, Emission

1. Introduction

One of the most important problems of today's world is environmental pollution. Along with the effects of epidemics, wars and natural disasters from the past to the present, environmental pollution has also had a great impact on human life [1, 2]. The impact of environmental pollution on the world has increased with the increase of industrialization and mechanization, especially in the last two centuries [3]. During the industrial revolution, manpower in many areas left its place to internal combustion engines [4]. Although the increase in the number of internal combustion engines provides various advantages, it has also brought significant disadvantages. The most important of these disadvantages are the pollutants released as a result of the operation of internal combustion engines [1, 5–7]. These pollutants cause significant damage to the world [8]. Various problems have arisen as a result of increasing environmental pollution [9, 10]. Global warming and degradation of natural habitats can be given as examples to these problems. Diesel engines are actively used in various areas of the industry and transportation sector [9, 11 , 12]. Therefore, the number of diesel engines in the world is quite high. NO_x and PM (Particulate Matter) emissions that are

emitted from diesel engines have much more negative impact than other emissions emitted from diesel engines [13 – 16]. Due to the negative effectsof diesel emissions scientists have developed various emission reduction technologies [17]. The main ones of these are DPF, DOC, LNT, Catalytic Convertor and EGR [3, 12, 18 – 20]. Like HC, PM and CO emissions emitted from diesel engines have been reduced effectively by the use of these systems. However, NO_X emissions emitted from diesel engines could not be reduced to the desired global levels today with these technologies [20 – 22]. In order to reach the desired current emission levels in diesel engines, scientists have developed the SCR system [5, 10, 15, 23 , 24]. It is seen that SCR systems, in which various catalysts are used with reductants, are quite effective in reducing NO_X emissions from diesel engines [14, 25 – 28]. In this study, a catalyst was produced by the impregnation method in order to be used in the SCR system and the chemical, structural properties of this catalyst were examined. NO_X conversion efficiency was experimentally analyzed by attaching the catalyst to the specially designed exhaust emission test system after the examination of chemical and structural properties of catalyst.

2. Material and Methods

2.1. Material

The cordierite piece used as a carrier material for catalyst production process. Cordierite was prepared for catalyst production by using the facilities of Çukurova University Automotive Engineering Department. Firstly, the cordierite material ($2Al_2O_3 – 5SiO_2 – 2MgO$) to be used during the experiments was prepared to the desired dimensions. The Ag-Cu-Ce/TiO_2 catalyst to be used for HC - SCR system in this study was obtained by using impregnation method. The cordierite material was pretreated with a mixture of 50% by weight of oxalic acid to 50% of distilled water for the purpose of increasing the surface area. This pretreatment was carried out at 90 °C for 3 hours. It was washed with distilled water until its acidity is gone. After that the cordierite was dried in an oven at 110 °C for 1 hour and then calcined at 550 °C for 3 hours. After the pre- treatment process completed, the cordierite material has been ready for coating process. A mixture of catalytic materials was prepared to perform the coating process. For preparing the mixture 5.91 g of silver nitrate ($AgNO_3$), 8.4 g of copper nitrate trihydrate (Cu $(NO_3)_2x3H_2O$) and 17.53 g of oxalic acid ($C_2H_2O_4$) were used. The resulting powder mixture was added to 500 ml of distilled water and stirred with an ultrasonic stirrer for 1 hour. After, 50 g of titanium dioxide (TiO_2) was added to the mixture and continued to stirring. The obtained liquid mixture stirred with an ultrasonic stirrer at a temperature of 90 ^{0}C until the water inside the mixture is evaporated. The mixture was dried in an oven at 110 ^{0}C for 1 hour to completely evaporate the water in the mixture. Then, the mixture was calcined at 550 ^{0}C in oven for 3 hours. After, it grounded into powder. To the 40 g powder mixture containing Ag, Cu and Ti particles, 500 ml of distilled water was added to form a mixture again. 5.55 g of cerium (III) acetate hydrate (Ce $(CH_3CO_2)_3$. xH_2O) was added to the obtained mixture and stirred with an ultrasonic stirrer and the Ag-Cu-Ce/TiO_2 catalyst solution was prepared. In order to start the coating process, firstly the pretreated cordierite material was dipped into the mixture obtained. By use of compressed air gun clogged pores of cordierite piece was opened. At the end, the cordierite material was dried in an oven at 120 ^{0}C for 1 hour and then calcined at 550 ^{0}C for 3 hours. Following these processes, catalyst production was completed.

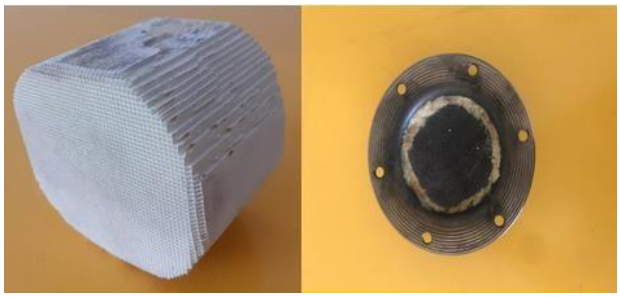

Figure 1. Images of cordierite and produced catalyst

2.2. Method

Surface areas of the cordierite material and produced catalyst were measured by BET analysis.

The analysis was carried out at the Çukurova University Central Research Laboratory using a Costech Sorptometer Kelvin 1042 device.

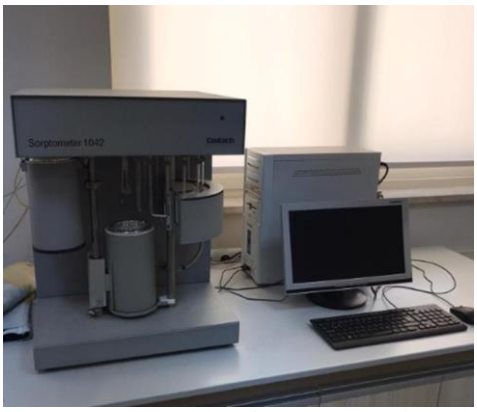

Figure 2. KELVIN Sorptometer 1042

The information about the morphology and size of these materials were determined by SEM analysis using the Quanta FEG 650 branded device at the Çukurova University Central Research Laboratory.

Figure 3. FEI Quanta 650 Field Emission SEM

The structures of the samples were analyzed by XRD analysis using the device branded PANalytical in Çukurova University Central Research Laboratory.

NO_x conversion performance of the produced catalyst was analyzed in a specially designed emission test system in Automotive Engineering Laboratory.

3. Results

3.1. SEM results

SEM analyzes were performed for investigating the surface structure of the cordierite material and Ag-Cu-Ce/TiO_2 catalyst. Images obtained during SEM analysis were taken at 20 kV voltage, x5000 and x10000 magnifications. When SEM analysis images are interpreted, it has shown that cordierite had porous surface structure. According to the information obtained from SEM images, it is seen that the porous structure of the cordierite material was also observed in the Ag-Cu-Ce/TiO_2 catalyst after the coating process. By evaluating the SEM analysis images it can be said that the coating process had occurred correctly. Also, it can be seen from images that there are many pores on catalyst surface for providing NO_x conversion.

Figure 4. PANalytical EMPYREAN XRD

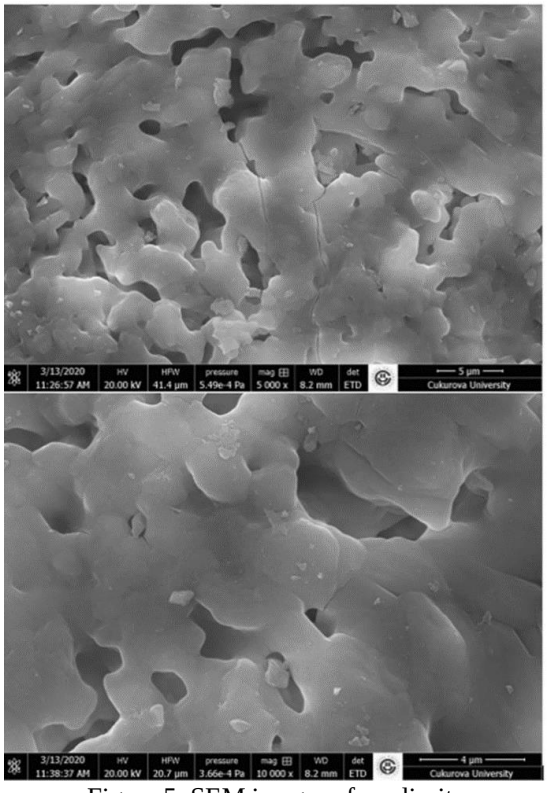

Figure 5. SEM images of cordierite

3.2. BET results

The surface area of the produced catalyst was measured by BET analysis which used nitrogen gas during analysis. While the BET surface area was around 0.5 m^2/g in the cordierite material, it was measured as 34.356 m^2/g in the Ag-Cu-Ce/TiO_2 catalyst produced after acid treatment. Langmuir surface area of the Ag-Cu-Ce/TiO_2 catalyst was measured as 45.061 m^2/g. The obtained values from BET analysis of Ag-Cu-Ce/TiO_2 catalyst gave the micropore volume as 3.279 mm^3/g. Also, the measured micropore area was measured as 9.305 m^2/g.

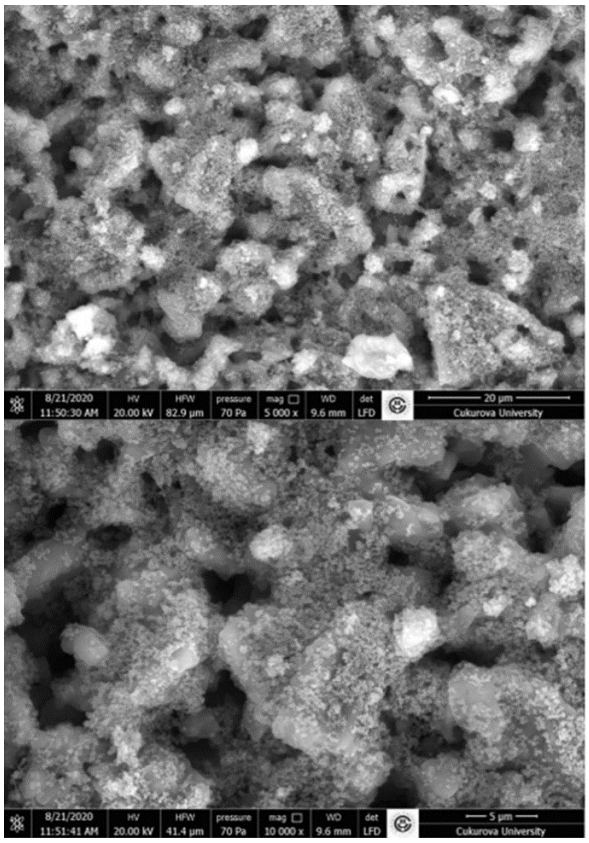

Figure 6. SEM images of catalyst

3.3. XRD Results

Information about crystal structure of materials was obtained from XRD analysis. The XRD analysis results of the cordierite and Ag-Cu-Ce/TiO_2 catalyst are given in the Figure 7 and Figure 8 below. The data obtained after XRD analysis showed that analyzed cordierite sample ($Al_4Mg_2O_{18}Si_5$) has orthorhombic structure. The prominent peaks of the cordierite material were seen during XRD analysis at the points of 2θ = 10.300, 10.420, 22.220, 26.680, 28.810, 29.260, 29.400, 29.630. The compounds have found in synthesized Ag-Cu- Ce/TiO_2 catalyst during XRD analysis were silver oxide (Ag_2O), cuprite (Cu_2O), cordierite ($Al_4Mg_2O_{18}Si_5$) and anatase (TiO_2). Also, cerium (Ce) atoms have found in Ag-Cu-Ce/TiO_2 catalyst during XRD analysis. The silver oxide (Ag_2O) has cubic, cuprite (Cu_2O) has cubic, cordierite ($Al_4Mg_2O_{18}Si_5$) has orthorhombic, anatase (TiO_2) has tetragonal and cerium (Ce) has monoclinic structure. The prominent peaks of the compounds were seen at points 2θ = 32.870, 38.130, 55.030 and 65.600 for silver oxide (Ag_2O), 2θ = 37.230, 43.250, 62.830 and 75.350 for cuprite (Cu_2O), 2θ = 10.360, 10.460, 21.730, 26.330, 28.480 and 29.320 for cordierite ($Al_4Mg_2O_{18}Si_5$), 2θ = 25.330 and 48.080 for anatase (TiO_2) and 2θ = 33.480, 33.950, 34.450, 37.770, 40.220 for cerium (Ce).

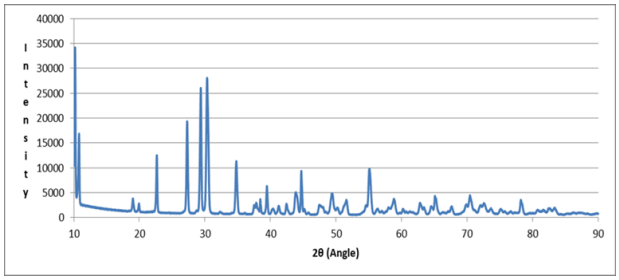

Figure 7. XRD analysis results of cordierite

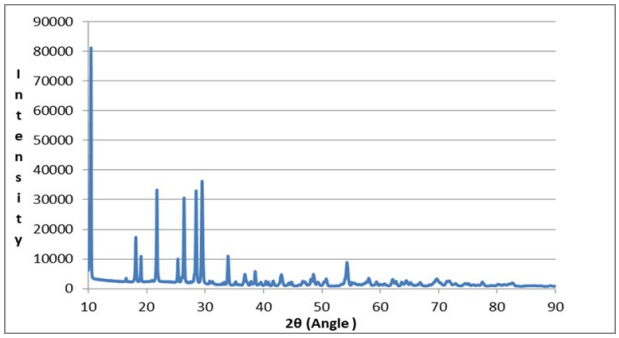

Figure 8. XRD analysis results of Ag-Cu-Ce/TiO_2 catalyst

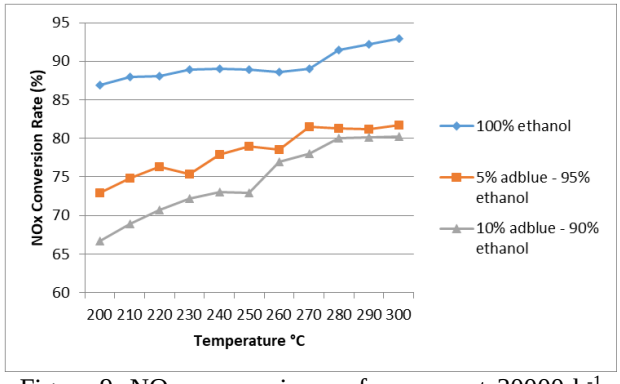

Figure 9. NO_X conversion performance at 30000 h^{-1} and 1 kW with the use of 100% ethanol , 95% ethanol – 5% urea solution and 90% ethanol – 10% urea solution

3.4. NOx Conversion Test Results

NO_x conversion performance of the Ag-Cu-

Ce/TiO_2 catalyst with the use of Ethanol - Urea solution mixtures as reductant analyzed and showed with the variable temperature, engine load and reductant mixture ratios. Emission measurement tests were done between 200 °C and 300 °C, 30000 h-1 space velocity, 1kW - 3kW - 5kW engine loads and 100% ethanol, 95% ethanol- 5% urea solution and 90% ethanol – 10% urea solution conditions.

In the NO_x conversion performance tests, as the temperature decreased from 300 °C to 200 °C, the NO_x conversion performance generally decreased. As it can be seen from the graphs of the NO_x conversion performance test results below, the NO_x conversion efficiency is the highest in the use of 100% ethyl alcohol.

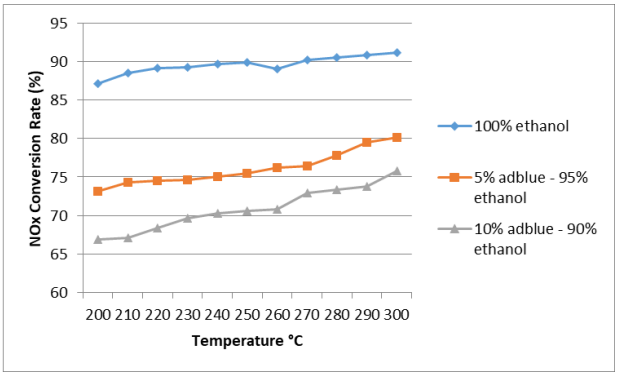

Figure 10. NO_X conversion performance at 30000 h^{-1} and 3kW with the use of 100% ethanol, 95% ethanol – 5% urea solution and 90% ethanol – 10% urea solution

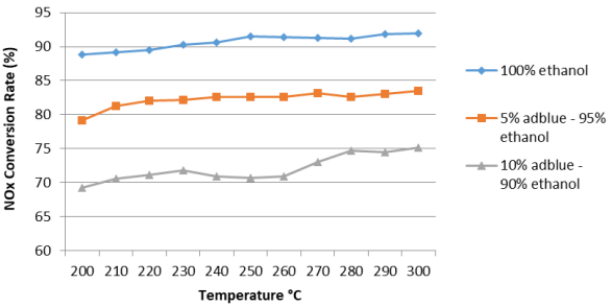

Figure 11. NO_X conversion performance at 30000 h^{-1} and 5kW with the use of 100% ethanol, 95% ethanol – 5% urea solution and 90% ethanol – 10% urea solution

4. Conclusion

Information obtained from SEM analysis showed that the porous structure of cordierite material was preserved after the coating process. By the measurement values obtained from BET analysis it could be seen as the surface area of the catalyst was remarkably increased in comparison to cordierite after the coating process. XRD analysis gives information about elements on the surface of specimen. In this study, by the XRD analysis results it could be said that the coating elements were dispersed effectively to the catalyst surface. At the end by evaluating the exhaust emission test results done by using ethyl alcohol - urea solution mixture as reductant showed that the increase in urea solution content in the mixture effects the NO conversion rate negatively. The maximum NO_x conversion performance during the emission tests was obtained approximately 93 % at SV = 30000 h^{-1}, T= 300 °C, 1 kW engine load and with the use of 100% ethanol as reductant.

Acknowledgement

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Information

This study belongs to master graduation thesis.

Nomenclature

BET : Branauer – Emmet – Teller
CO_2 : Carbon Dioxide
DOC : Diesel Oxidation Catalyst
DPF : Diesel Particulate Filter
EGR : Exhaust Gas Recirculation
GHSV : Gas Hourly Space Velocity
HC : Hydrocarbon
kW : Kilowatt
LNT : Lean NO_X Trap
NO_x : Nitrogen Oxides
PM : Particulate Matter
SCR : Selective Catalytic Reduction
SEM : Scanning Electron Microscopy
XRD : X-Ray Diffraction

5. References

1. I. A. Reşitoğlu, "Dizel motorlarda kirletici emisyonların kontrol edilmesine yönelik Fe_2O_3 esaslı katalizörlerin kullanıldığı DOC ve SCR sistemlerinin geliştirilmesi," Selçuk Üniversitesi, 2016.
2. M. Piumetti, S. Bensaid, D. Fino, and N. Russo, "Catalysis in Diesel engine NO_X aftertreatment: a review," Catal. Struct. React., vol. 1, no. 4, pp. 155–173, 2015.
3. Z. Keskin, "Metal Nano Partiküllerin Kullanımı ile Seçici Katalitik İndirgeme Sistemi

Tasarlanması ve Test Edilmesi Metal Nano Partiküllerin Kullanımı ile Seçici Katalitik İndirgeme Sistemi Tasarlanması ve Test Edilmesi," Tarsus Üniversitesi, 2019.
4. 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.
5. R. Mrad, A. Aissat, R. Cousin, D. Courcot, and S. Siffert, "Catalysts for NO_X selective catalytic reduction by hydrocarbons (HC-SCR)," Appl. Catal. A Gen., vol. 504, no. x, pp. 542–548, 2015.
6. H. T. Xu, Z. Q. Luo, N. Wang, Z. G. Qu, J. Chen, and L. An, "Experimental study of the selective catalytic reduction after-treatment for the exhaust emission of a diesel engine," Appl. Therm. Eng., vol. 147, no. July 2018, pp. 198–204, 2019.
7. Yasar, A. Keskin, Z. Keskin, H. Özarslan, and S. Kaltar, "Low temperature catalytic activity of Ag based SCR catalysts with 2-propanol-Toluene mixture as reductant," Mater. Res. Express, vol. 6, no. 9, 2019.
8. M. Ambast, S. A. Malamis, and M. P. Harold, "Coupled uptake and conversion of $C_{12}H_{26}$ and NO on Pd / SSZ-13 : Experiments and modeling," Chem. Eng. J., vol. 423, no. February, p. 129958, 2021.
9. F. Liu, L. Yang, J. Cheng, X. Wu, W. Quan, and K. Saito, "Low temperature $DeNO_X$ catalytic activity with C_2H_4 as a reductant using mixed metal Fe-Mn oxides supported on activated carbon," Energies, vol. 12, no. 22, 2019.
10. N. Zhang et al., "A MnO_2-based catalyst with H_2O resistance for NH_3-SCR: Study of catalytic activity and reactants-H_2O competitive adsorption," Appl. Catal. B Environ., vol. 270, no. February, p. 118860, 2020.
11. M. Al Cheikh Mohamad Ahmad, A. Keskin, H. Özarslan, and Z. Keskin, "Properties of ethyl alcohol-water mixtures as a reductant in a SCR system at low exhaust gas temperatures," Energy Sources, Part A Recover. Util. Environ. Eff., vol. 00, no. 00, pp. 1–12, 2020.
12. F. Martinovic et al., "Simultaneous improvement of ammonia mediated NO_X SCR and soot oxidation for enhanced SCR-on-Filter application," Appl. Catal. A Gen., vol. 596, no. x, 2020.
13. P. Xu, J. Zheng, F. Jing, and W. Chu, "Influence of support precursor on FeCe-TiO_2 for selective catalytic reduction of NO with ammonia," Mol. Catal., vol. 508, no. February, p. 111586, 2021.
14. T. Qiao, Z. Liu, C. Liu, W. Meng, H. Sun, and Y. Lu, "MnOx location on MnOx-ZSM-5 to influence the catalytic activity for selective catalytic reduction of NOx by NH3," Appl. Catal. A Gen., vol. 617, no. January, p. 118128, 2021.
15. Y. Cao et al., "The effect of Si environments on NH_3 selective catalytic reduction performance and moisture stability of Cu-SAPO-34 catalysts," J. Catal., vol. 391, no. x, pp. 404–413, 2020.
16. I. A. Resitoglu, A. Keskin, H. Özarslan, and H. Bulut, "Selective catalytic reduction of NO_X emissions by hydrocarbons over Ag–Pt/Al_2O_3 catalyst in diesel engine," Int. J. Environ. Sci. Technol., vol. 16, no. 11, pp. 6959–6966, 2019.
17. [17] C. L. Song, F. Bin, Z. M. Tao, F. C. Li, and Q. F. Huang, "Simultaneous removals of NO_X, HC and PM from diesel exhaust emissions by dielectric barrier discharges," J. Hazard. Mater., vol. 166, no. 1, pp. 523–530, 2009.
18. G. Qi and R. T. Yang, "Performance and kinetics study for low-temperature SCR of NO with NH_3 over MnO_X-CeO_2 catalyst," J. Catal., vol. 217, no. 2, pp. 434–441, 2003.
19. A. Åberg, A. Widd, J. Abildskov, and J. K. Huusom, "Parameter estimation and analysis of an automotive heavy-duty SCR catalyst model," Chem. Eng. Sci., vol. 161, pp. 167–177, 2017.
20. L. Valanidou, C. Theologides, A. A. Zorpas, P. G. Savva, and C. N. Costa, "A novel highly selective and stable Ag/MgO-CeO_2-Al_2O_3 catalyst for the low-temperature ethanol-SCR of NO," Appl. Catal. B Environ., vol. 107, no. 1–2, pp. 164–176, 2011.
21. B. Sawatmongkhon, "Modelling of catalytic aftertreatment of NO_X emissions using hydrocarbon as a reductant," no. x, p. 115, 2011.
22. D. Yang et al., "NO selective catalytic reduction with propylene over one-pot synthesized Fe-SAPO-34 catalyst under diesel exhaust conditions," Fuel, no. November, p.

119822, 2020.
23. R. Wu et al., “Enhancement of low-temperature NH_3-SCR catalytic activity and H_2O & SO_2 resistance over commercial V_2O_5-MoO_3/TiO_2 catalyst by high shear-induced doping of expanded graphite,” Catal. Today, no. April, pp. 1–9, 2020.
24. R. Yu, Z. Zhao, S. Huang, and W. Zhang, “Cu-SSZ-13 zeolite–metal oxide hybrid catalysts with enhanced SO_2-tolerance in the NH_3-SCR of NO_X,” Appl. Catal. B Environ., vol. 269, no. February, p. 118825, 2020.
25. Y. Su, N. Wen, J. Cheng, W. Deng, H. Zhou, and B. Zhao, “Experimental study on SCR-C_3H_6 over Cu-Fe/Al-PILC catalysts: Catalytic performance, characterization, and mechanism,” Ind. Eng. Chem. Res., vol. 59, no. 33, pp. 14776–14788, 2020.
26. K. Liu, H. He, and B. Chu, “Microkinetic study of NO oxidation , standard and fast NH_3 -SCR on $CeWO_X$ at low temperatures,” Chem. Eng. J., vol. 423, no. February, p. 130128, 2021.
27. G. Fu et al., “Enhanced hydrothermal stability of Cu/SSZ-39 with increasing Cu contents, and the mechanism of selective catalytic reduction of NO,” Microporous Mesoporous Mater., vol. 320, no. December 2020, p. 111060, 2021.
28. A. Keskin, A. Yaşar, O. C. Candemir, and H. Özarslan, “Influence of transition metal based SCR catalyst on the NO_X emissions of diesel engine at low exhaust gas temperatures,” Fuel, vol. 273, no. x, 2020.