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Preparation and NO_x Reduction Performance of Ag-Ni-TiO_2/Cordierite Catalyst for HC-SCR System

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Abstract

Selective catalytic reduction (SCR) technology in diesel engines is an exhaust after treatment system used for abatement of nitrogen oxide (NO_x) emissions. In order to synthesize Ag-Ni-TiO_2/Cordierite catalyst in the conducted study, a solution including silver nitrate ($AgNO_3$), titanium dioxide (TiO_2), and nickel (II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) were used in the coating of the cordierite ($2Al_2O_3$-$5SiO_2$-2MgO) main carrier structure. The prepared catalyst was characterized for morphological characteristics via scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) analysis. The NO_x reduction measurements as catalytic was carried out at 20 °C intervals in the temperature range from 190 to 270°C at 1 kW and 3 kW motor loads and under 30000 h^{-1} space velocity (SV). Ethanol was used as a reductant during the experiments. As a results of the measurements, it was seen that the Ag-Ni-TiO_2/Cordierite catalyst exhibited a good NO_x conversion efficiency with 93.8 % at 270°C at 3 kW.

Keywords: Selective catalytic Reduction, Catalyst, Cordierite, NO_x emission

HC-SCR Sistemi için Ag-Ni-TiO_2/Kordiyerit Katalizörünün Hazırlanması ve NO_x İndirgeme Performansı

Öz

Dizel motorlardaki seçici katalitik indirgeme (SCR) teknolojisi, nitrojen oksit (NO_x) emisyonlarının azaltılması için kullanılan bir egzoz son arıtma sistemidir. Yapılan çalışmada Ag-Ni-TiO_2/Kordiyerit katalizörünü sentezlemek amacıyla kordiyerit ($2Al_2O_3$-$5SiO_2$-2MgO) ana taşıyıcı yapının kaplanmasında gümüş nitrat ($AgNO_3$), titanyum dioksit (TiO_2) ve nikel (II) nitrat hekzahidrat ($Ni(NO_3)_2 \cdot 6H_2O$) içeren bir çözelti kullanıldı. Hazırlanan katalizör, taramalı elektron mikroskobu (SEM) ve enerji dağılım spektroskopisi (EDS) analizi yoluyla morfolojik özellikler açısından karakterize edildi. Katalitik olarak NO_x azaltım ölçümleri, 190 ila 270 °C sıcaklık aralığında 20°C aralıklarla, 1 kW ve 3 kW motor yüklerinde ve 30000 h^{-1} alan hızında (SV) gerçekleştirildi. Deneyler sırasında indirgeyici olarak etanol kullanıldı. Yapılan ölçümler sonucunda Ag-Ni-TiO_2/Kordiyerit katalizörünün 270°C'de 3 kW'ta %93.8 ile iyi bir NO_x dönüşüm verimi sergilediği görülmüştür.

Anahtar Kelimeler: Seçici katalitik indirgeme, Katalizör, Kordiyerit, NO_x emisyonu

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1. INTRODUCTION

Nitrogen oxide (NO_x) gases are harmful waste gases released into the external environment as a result of the combustion of fuel in diesel engines. It has negative effects on the environment such as acid rain, photochemical smog and ozone depletion [1]. Moreover, it also causes pneumonia, hay fever, bronchitis and cancer [2-3]. To eliminate these drawbacks of diesel engines, many systems are being tried to reduce NO_x. The most efficient and effective among these systems is selective catalytic reduction (SCR) system. In SCR system, ammonia (NH_3) as reductant and V_2O_5-(WO_3 or MoO_3)/TiO_2 catalyst as catalyst are commonly used. However, having a narrow temperature range of 300-400°C and the toxic effects of vanadium species prevent these catalysts from being a satisfactory option [4]. Moreover, in usage of NH_3, there are also negative effects such as ammonia slip and catalyst deterioration [5]. Therefore, recent efforts have been made by researchers to improve the system and overcome these problems. Among these endeavors, various types of reductants and different catalyst structures have been tested in the SCR system. Thirupathi [6] reported that in the NH_3-SCR, the addition of Ni could expand the active temperature range of the Mn/TiO_2 catalyst and improve the NO_x conversion performance. Ning et. al. [7] informed that the addition of Ni on MIL-100 (Fe) catalyst significantly improved the NO_x conversion of C_3H_6-SCR. Ning et. al. [8] reported that the addition of Ni on MIL-100(Fe) catalyst exhibited a 96.6 % NO conversion at 250°C under 2 %O_2 in CO-SCR. Shi et. al. [9] reported that almost 100 % NO conversion performance of $Ni_{0.65}Mn_{0.35}$-MOF-74 catalyst reached at 175 °C in CO-SCR. It also reported that compared with monometallic Ni-MOF-74 or Mn-MOF-74, bimetallic NiMn-MOF-74 catalyst achieved a significant improvement in NO conversion performance. Zhang et. al. [10] reported achieving almost 100% NO conversion in CO-SCR for Ag_1-Ni-MOF-74 catalyst in the temperature range of 200°C to 300°C.

In this study, active nano materials were coated on the cordierite main carrier structure. As a consequence of the coating procedure, Ag-Ni-TiO_2/Cordierite catalyst was prepared. In conducted studies so far in the literature, NO_x abatement studies of nickel with ethanol reductant have been restricted limited. Therefore, the NO_x reduction performances of the cordierite structure-supported catalysts were performed in experiments in the SCR test system with ethanol reductant at low temperatures under real exhaust gas.

2. MATERIAL AND METHODS

2.1. Catalyst Preparation and Characterization

Cordierite material as a main carrier structure is of 400 cells per square inch (cpsi). In this study, 200 cm^3 volume was cut from cordierite and used for catalyst production. First, in the powder catalyst preparation stage, silver nitrate ($AgNO_3$), Nickel (II) Nitrate Hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and titanium dioxide (TiO_2) nanoparticles were added to 200 mL of distilled water at 2.5%, 1% and 96.5% by weight, respectively. The resulting solution was stirred by heating to evaporate the water. The remaining mud-like structure was dried in the oven at 130°C for 3 hours. Then, calcination was carried out in a muffle furnace at 550°C for 3 hours. The completely dried catalyst was ground into powder. The obtained powder catalyst and silicon dioxide (SiO_2), which is 1% of its weight, were added to 500 mL of distilled water and mixed for 1 hour. The cordierite main carrier was immersed in the powder catalyst solution to be completely wetted. Afterwards, drying at 130°C for 3 hours and subsequently calcination at 550°C for 3 hours were carried out. Thus, the catalyst was made ready for experiments in the SCR test system. The main steps of the catalyst preparation process are demonstrated in Figure 1.

Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) method was used to analyze morphologically the surface of the coated cordierite catalyst. In this way, the surface of the catalyst was examined. The produced sample was observed using the FEI Quanta 650 Field Emission model SEM device at 20kV acceleration voltage. The device has the magnification capacity in the range of 6-1.000.000 x times (Figure 2). Before being used in SEM, the non-conductive surface of the catalyst was overlaid with gold material of 2 Å/s by using the Q150R ES spray coating device. The device used for the gold plating process is displayed in the Figure 3.

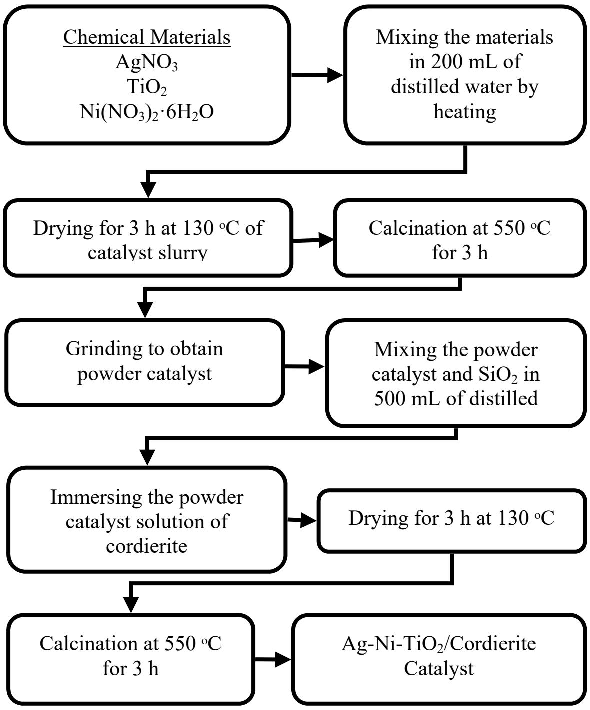


Figure 1. Steps in catalyst preparation

Figure 2. SEM analysis device

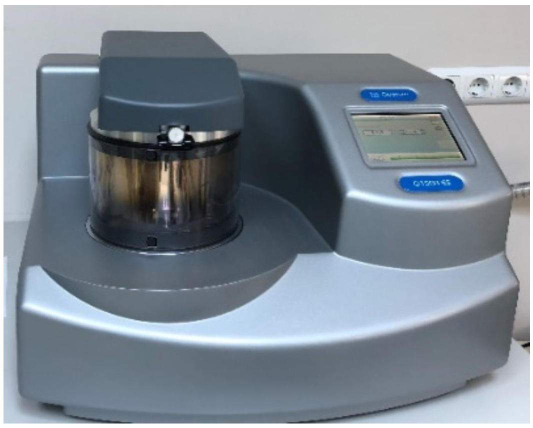


Figure 3. Gold plating process device

2.2. Performance Test of Catalyst

A diesel engine whose technical specifications are given in Table 1 was used in this section. A performance testing system was used to investigate the NO_x conversion rate with the use of ethanol as reductant on Ag-Ni-TiO_2/Cordierite catalyst. The experimental test system is elaborated upon schematically in Figure 4. An orifice plate and manometer in the exhaust system was used in order to evaluate the exhaust gas flow rate within the system. Space velocity (SV) for the gas flow is named as the ratio of the catalyst volume [V_c (m^3)] to the volume flow of the exhaust gas [V_f (m^3/h)] and is expressed as h^{-1}. During the experiment, the desired SV has been adjusted with the help of two valves. An electric loading system of 1 and 3 kW was used to load the engine. The exhaust gas temperatures were adjusted with a heater added to the system. Also, a k-type thermocouple was employed for temperature measurement. Finally, NO_x emission measurements were carried out through a pair of continental model NO_x sensors.

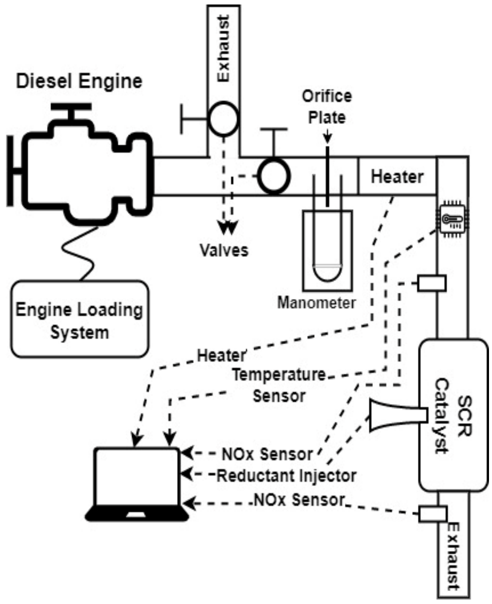


Figure 4. Schematic view of the SCR performance test system

Table 1. Diesel engine technical specifications

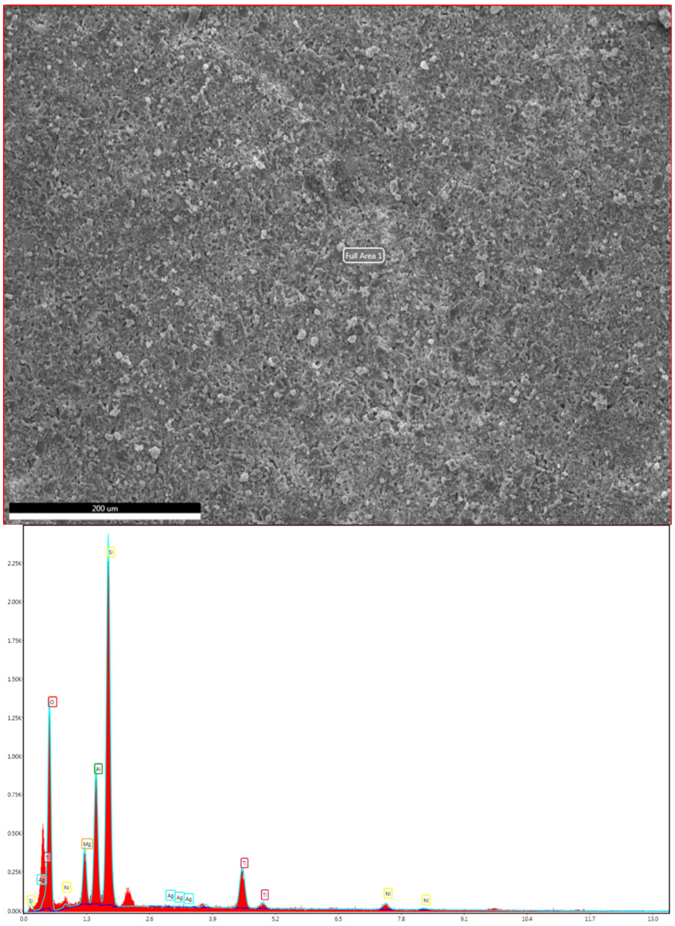
Model	AKSA A2CRX08
Number of cylinders	2
Stroke	79 mm
Bore	80 mm
Cylinder volume	830 cm^3
Compression ratio	23/1
Engine speed	3000 rpm
Cooling system	Water-cooled

The experiments were carried out under the utilization of ethanol reductant and a SV value of 30000 h^{-1}. Moreover, in order to evaluate the efficacy of the catalyst in NO_x reduction, particularly at lower temperatures, measurements of NO_x conversion ratios were conducted at 20°C intervals within the temperature range of 190°C to 270°C.

3. RESULTS AND DISCUSSIONS

3.1. Catalyst Characterization Results

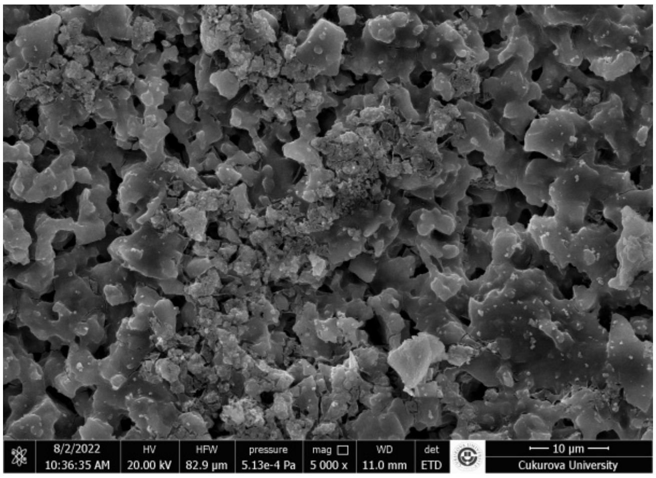
Figure 5 indicates the SEM-EDS image of the catalyst synthesized at 500x magnification. The SEM-EDS results provided information about the change of its surface after coating of the cordierite surface. SEM-EDS analysis was used to scan the entire surface area of catalyst. Peaks of Ag, Ni, and Ti metals on the cordierite structure surface after scanning were observed. Additionally, Mg, Al, and Si elements, which form the main cordierite structure, were also observed. Figure 5 displays the percentages of atomic and weight of the elements in the surface area of the catalyst analyzed. Based on these results of the analysis, it can be concluded that the active components with catalytic effects are distributed on the surface.



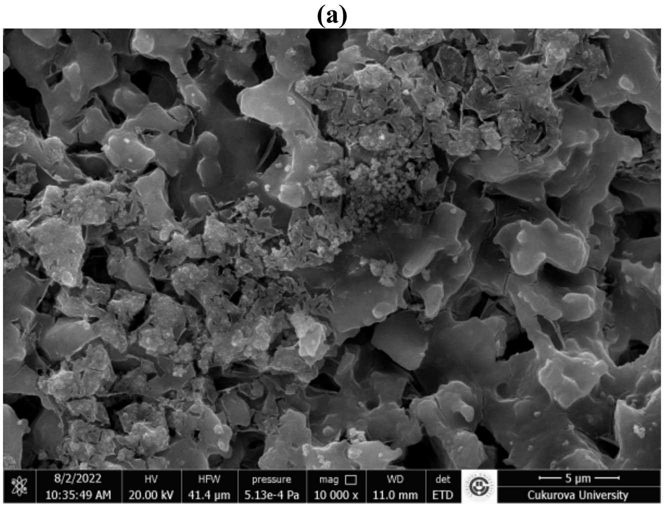
Element	Weight %	Atomic %	Net Int.
O K	45.39	60.87	341.16
Mg K	4.82	4.26	108.08
Al K	10.44	8.3	268.47
Si K	29.19	22.3	759.3
Ag L	0.21	0.04	2.44
Ti K	7.19	3.22	114.21
Ni K	2.76	1.01	20.16

Figure 5. Energy-dispersive X-ray spectroscopy of Ag-Ni-TiO_2/Cordierite catalyst

The SEM images at 5000x, and 10000x magnification in order to determine the morphological properties of the catalyst were illustrated in Figure 6. The images demonstrate that the cordierite has a porous and rough surface. It can be clearly demonstrated at the images of the catalyst that the active coating elements with catalytic effects were irregularly distributed over uneven surface of the cordierite. Besides, the catalytic active elements did not cause clogging of the pores of the cordierite structure, after the coating process. Clustered forms of catalytic active substances were visualized on the surface of the coated cordierite. The images clearly demonstrate the distribution of silver, nickel and titanium nanoparticles on the coated cordierite surface. The catalytic active substances were an irregular structure and different appearance morphologically.



(a)



(b)

Figure 6. SEM image results of Ag-Ni-TiO_2/Cordierite catalyst (a:5000x, b:10000x)

The SEM mapping image of the catalyst sample is displayed at 500x magnification in Figure 7. It has been observed that the coating elements (Ag, Ni, and Ti) that are assumed to show catalytic activity on the surface are distributed equally or homogeneously on the surface. The turquoise spots, the green spots, and the red spots in the mapping image correspond to silver (Ag), nickel (Ni), and titanium (Ti) particles, respectively.

Figure 7. SEM mapping result of Ag-Ni-TiO_2/Cordierite catalyst

3.2. NO_x Conversion Test Results

Figure 8 shows the NO_x conversion rates obtained with ethanol depending on temperature, space velocity, and engine load for the Ag-Ni-TiO_2/Cordierite catalyst. As seen in the figure, the NO_x activity of the catalyst rised with the increment in temperature, and the maximum NO_x conversion ratios were obtained at 270°C. In the experiments, the catalyst activity increased depending on the increment in exhaust gas temperature. It was observed that temperature had a significant effect on catalytic activity in this temperature range. Similar results were available in the literature [11-14]. Additionally, the tests showed that the NO_x conversion rates of the catalyst increased with increment of the engine load. In the experiments, the maximum NO_x conversion rate was obtained under 3 kW engine load. It is thought that this situation occurs because the concentration of O_2 in the exhaust gas decreases due to increased engine loads. Similar results were also found in the literature [15-16].

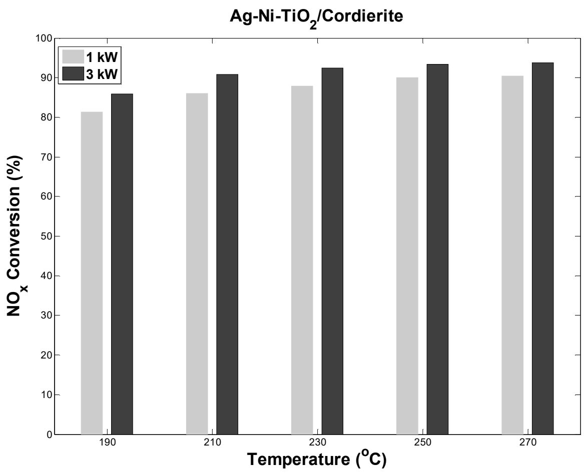


Figure 8. The NO_x conversion results of the catalyst

4. CONCLUSION

The findings obtained in the research are listed as follows.

- SEM images of the catalyst show that the synthesis process was successful.
- Increasing the exhaust gas temperature from 190°C to 270°C enhances the NO_x conversion performance.
- The catalyst has demonstrated promising results. When test results were compared, NO_x conversion efficiencies were achieved as 90.48% at 1 kW and 93.8% at 3 kW for the Ag-Ni-TiO_2/Cordierite catalyst.
- The maximum NO_x conversion rate was obtained at 270°C at 3 kW, reaching 93.8%.

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