

Characterization of SCR Catalyst Based Ag-Nb-Pt

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Abstract

Selective Catalytic Reduction (SCR) is an emission control system used in diesel engines to reduce NO_x emissions. In this study, synthesized of catalyst for SCR system was investigated as experimentally. For this purpose, silver nitrate (AgNO₃), niobium (V) chloride (NbCl₅) and tetra amine platinum (II) nitrate (Pt(NH₃)₄(NO₃)₂) were used to coat the cordierite (2Al₂O₃-5SiO₂-2MgO) structure with impregnation method. X-ray Fluorescence (XRF), Scanning Electron Microscope (SEM) and Brunauer, Emmett, and Teller (BET) analyzes were carried out in order to determine the chemical and physical properties of the catalyst. Results showed that the coating materials penetrate the entire surface of the pores. It was also determined that the BET specific surface areas of the produced catalyst and cordierite are 0.2918 m²/g and 0.4568 m²/g, respectively. The reduction of surface area could be attributed to the increment of crystallization with chemical reactions occurred at the high sintering temperature. Besides, XRF analysis results demonstrated that content of Ag, Pt and Nb in the in the catalyst was found to be 3.67%, 0.19% and 0.12%, respectively, whereas Ag content in cordierite structure was 0.03%.

Keywords: Catalyst, XRF, SEM, BET, SCR, Exhaust emissions

Ag-Nb-Pt Bazlı SCR Katalizör Karakterizasyonu

Öz

Seçici Katalitik İndirgeme (SCR), dizel motorlarda NO_x emisyonlarını azaltmak için kullanılan bir emisyon kontrol sistemidir. Bu çalışmada, SCR sistemi için gümüş esaslı katalizörün sentezlenmesi deneysel olarak incelenmiştir. Bu amaçla, kordiyerit (2Al₂O₃-5SiO₂-2MgO) yapısını daldırma yöntemiyle kaplamak amacıyla gümüş nitrat (AgNO₃), niyobyum (V) klorür (NbCl₅) ve tetra amin platin (II) nitrat (Pt (NH₃)₄ (NO₃)₂) katalizörleri kullanılmıştır. Katalizörün kimyasal ve fiziksel özelliklerini belirlemek için XRF, SEM ve BET analizleri gerçekleştirilmiştir. Sonuçlar, kaplama malzemelerinin gözeneklerin tüm yüzeyine nüfuz ettiğini göstermiştir. Üretilen katalizör ve kordiyeritin BET yüzey alanlarının sırasıyla 0,2918 m²/g ve 0,4568 m²/g olduğu belirlenmiştir. Yüzey alandaki azalmanın, yüksek sinterleme sıcaklığında meydana gelen kimyasal reaksiyonlarla kristalizasyon artışına bağlı olduğu düşünülmektedir. Ayrıca, XRF analizi

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sonuçları, kordierit yapısındaki Ag içeriğinin %0,03 olmasına karşın katalizörde Ag, Pt ve Nb içeriğinin sırasıyla %3,67, %0,19 ve %0,12 oranlarında olduğunu ortaya koymuştur.

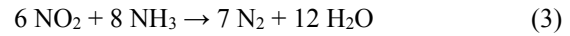
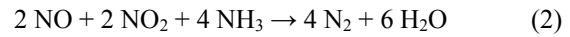
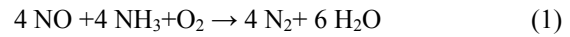
Anahtar Kelimeler: Katalizör, XRF, SEM, BET, SCR, Egzoz emisyonları

1. INTRODUCTION

NO_x emissions deriving from NO and NO₂ forms are a contaminant emission type that can cause negative impacts on the environment and human health worldwide [1]. Acid rains are the most important factor of these negative effects [2].

A significant portion of NO_x emissions comes from the transport sector. Compared to other types of vehicles, diesel-powered vehicles used in the transportation sector have the largest share of NO_x emissions [3]. The high combustion temperature in diesel engines and the high air excess coefficient of diesel engines are the main factors in the formation of these emissions. In the event of a sufficient amount of oxygen in the environment above the 1600 °C temperature, NO_x emissions consist of the result of N₂ and O₂ reactions [1]. Many research activities have been carried out to reduce NO_x emissions from diesel engines. Exhaust Gas Recirculation (EGR) is a system developed for this purpose and widely used in modern vehicles [4]. In this system, a certain amount of exhaust gas is cooled and sent back into the cylinder and thus, the combustion temperature is reduced. Although this situation provides some reduction in NO_x emissions, smoke, CO and HC emissions are adversely affected and an increase in these emissions is observed. Besides, a decrease in combustion efficiency may adversely affect engine performance [5]. Owing to these disadvantages, the interest in the EGR system is gradually decreasing day by day. Apart from the EGR system, the improvement of fuel properties using fuel additives, developing fuel injection systems and controlling engine operating parameters are also effective in reduction of NO_x emissions [6-7]. However, these efforts have not provided a reduction that can meet the NO_x emission values stated in the standards such as EURO, EPA and IPCC. The SCR system was developed as one of an engine emission control systems and has become widespread nowadays. It

provides the desired reductions in NO_x emissions. In this system, NO_x emissions can be reduced by chemical reactions in the presence of a catalyst together with a reductive sprayed into the exhaust gas [8-9]. Ammonia (NH₃) is the most commonly used reductive in SCR systems. Due to the sudden burning of ammonia at high temperatures, the aqueous urea solution called AdBlue have been sprayed on the exhaust gas [10]. NO_x emissions are removed from exhaust gas via the chemical reactions that occur in SCR catalyst. Base reactions for SCR are shown below.



Equation 1 is called as standard SCR reaction where the ratio of NH₃ and NO is 1:1. Equation 2 is referred to as fast SCR reaction due to its 1:1 of NO:NO₂ ratio. Equation 3 is known as slow SCR reaction where pure NO₂ takes place in the reaction. The conventional nanoparticles could gather easily during the catalytic process, leading to catalytic activity reduction. The ordered mesoporous materials having large surface-to-volume ratios and uniform porous structure show many interesting properties in catalysis, energy conversion and storage due to the fact that they have d-shell electrons held to nanosized walls, redox active internal surfaces compared to the nanoparticles, [11,12].

V₂O₅-WO₃/TiO₂ is the most commonly used catalyst species in SCR systems [13]. However, this catalyst does not perform very well at low exhaust gas temperatures, and at the same time it can cause negative effects on the environment and human health due to the toxic effect of vanadium. In previous studies, many different materials (CeO₂-TiO₂, Cu /Al₂O₃, NbCe, Fe-MFI, Fe-ZSM₅, Cu-ZSM₅, Ag/Al₂O₃) have been tested as catalyst

by researchers for SCR systems [14]. Kim et al [15] revealed that Ag based catalyst promoted the oxidation of NH_3 to N_2 , while enhancing the NO_x performance of the conventional HC-SCR, especially at low temperatures. Pang et al [16] examined the NH_3 -SCR activity on $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalysts prepared using the conventional impregnation methods. Kang et al [17] reported that manganese oxides with small amounts of copper oxide having high surface area were the most effective catalyst for low temperature NO reduction with NH_3 in the availability of SO_2 . Wu et al [18] studied Mn/TiO₂ doped with Ce which leads the resistance to SO_2 . It was revealed that Ce addition significantly inhibit the formation of $\text{Ti}(\text{SO}_4)_2$ and $\text{Mn}(\text{SO}_4)_2$. It was also demonstrated that amount of copper species had considerable effect on catalytic performance for Cu-containing SCR catalysts [19].

Many studies were conducted by researchers above mentioned. But there are still gap to understand the nature of Ag based SCR catalyst. Such understanding is especially necessary to establish suitable catalyst production process. The aim of the present study is to investigate the characterization of the Ag based SCR catalyst. In SCR catalyst production process, a lot of chemical matter such as silver nitrate (AgNO_3), niobium (V) chloride (NbCl_5) and tetraamine platinum (II) nitrate ($\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$) were used. These nano particles were utilized in order to coat on the cordierite structure ($2\text{Al}_2\text{O}_3\text{-5SiO}_2\text{-2MgO}$). Furthermore, the characterization of catalyst was determined by XRF, BET and SEM analyzes.

2. MATERYAL VE METHOD

2.1. Catalyst Preparation

The catalyst samples were prepared by an impregnation method. In order to get samples, a solution was prepared composing of 30 g AgNO_3 , 2g NbCl_5 and 1g $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ nano particles. These nano particles were mixed in 500 ml distilled water via ultrasonic mixer for 20 minutes at room temperature. The carrier structure (cordierite) was dried at 110 °C for 2 h. The cordierite was immersed into the formed solution and was dried at 110 °C for 2 h. The same procedure was repeated for coated

cordierite structure. After impregnation process, drying and sintering processes were implemented with 110 °C for 2 h and 550 °C for 5 h, respectively. Finally, the catalyst samples for SEM/EDX, XRF and BET analyzing were prepared in order to determine characterization of the catalyst. Flowchart of catalyst production is given in Figure 1.

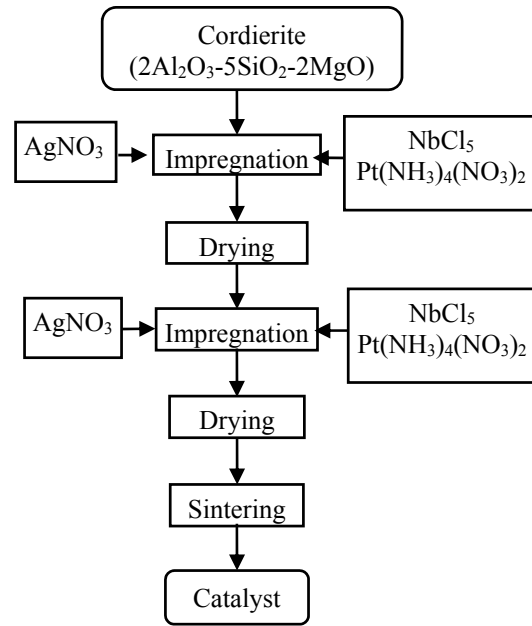


Figure 1. Flow chart of catalyst production

2.2. Catalyst Characterization

SEM analysis of cordierite and synthesized catalyst was performed at Cukurova University Central Research Laboratory (Cumerlab). The device used is Quanta FEG 650 having enlargements of 6-1.000.000x. In order to examine non-conductive samples, the samples was coated with conductive material at a thickness of about 2 Å/sec. Qualitative and quantitative elemental analyzes was performed on the sample using the EDX spectrometer in the instrument. Surface area analysis was conducted using the Micromeritics TriStar II device in Kahramanmaras Sutcu Imam University, USKIM. The surface area was calculated by determining the area covered by a single gas molecule adsorbed to the surface and finding the total number of

molecules adsorbed on the surface. Brunauer-Emmett-Teller method was used in these calculations. Bruker S8 Tiger device located at Kahramanmaraş Sutcu Imam University, USKIM was utilized for XRF analysis which give information on the type of elements contained in the samples and the concentration of these elements.

The catalyst sample was pulverized using a grinder to perform XRF and BET analysis. 10 g of the powder sample was mixed with cellulose of 4 g and the prepared mixture was compressed at 36 MPa pressure and pelletized to use in XRF analysis. BET surface area analysis was performed using nitrogen gas at a temperature of -196 °C.

3. RESULTS AND DISCUSSION

3.1. BET Surface Area Results

The BET data for the cordierite structure and produced catalyst are given in Table 1. The N₂

adsorption-desorption isotherms of Ag-Nb-Pt catalyst and cordierite are shown in Figure 2. The BET specific surface areas of produced catalyst and cordierite are about 0.2918 m²/g and 0.4568 m²/g, respectively. Compared with the cordierite main structure, a reduction of 36.12% in the surface area of the catalyst produced was observed.

Sintering process of the catalyst can be shown as the main reason for the reduction in surface area due to chemical reactions which could increase formation of the metallic particle crystallization. These reactions caused formation of new structures on surface of cordierite. Accordingly, this case caused reduction on surface area of the catalyst. The average pore diameter of the cordierite structure was measured as 21.4072 nm, whereas this value was 54.4758 nm for the produced catalyst. While the cordierite structure was mezopored, it became macro porous after coating since the pore diameter exceeded 50 nm.

Table 1. BET analysis of cordierite and Ag-Nb-Pt catalyst

Summary Report	Cordierite	Ag-Nb-Pt
<i>Surface Area</i>		
BET Surface Area	0.4568 m ² /g	0.2918 m ² /g
Langmuir Surface Area	0.6105 m ² /g	0.3800 m ² /g
BJH adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width	0.183 m ² /g	0.063 m ² /g
BJH desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width	0.1279 m ² /g	0.0647 m ² /g
<i>Pore Volume</i>		
BJH adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width	0.000981 cm ³ /g	0.000856 cm ³ /g
BJH desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width	0.001106 cm ³ /g	0.000857 cm ³ /g
<i>Pore Size</i>		
Adsorption average pore width (4V/A by BET)	83.2510 Å	96.6573 Å
BJH Adsorption average pore width (4V/A)	214.072 Å	544.758 Å
BJH Desorption average pore width (4V/A)	345.889 Å	530.322 Å

Figures 2 and 3 show the variation of relative pressure and absolute pressure with quantity

absorbed, respectively. In isotherm curves shown in Figures 2 and 3, adsorption amount of nitrogen gas

used for determining surface area and pore size distribution takes positive values at low relative pressures. However, as the relative pressure increases, the amount of adsorption decreases to negative values and again positive values at high relative pressure values are obtained. This is believed to be due to the low surface area of the synthesized catalyst. The reduction in surface area is achieved as a result of the reduced NO_x reduction activity of the catalyst.

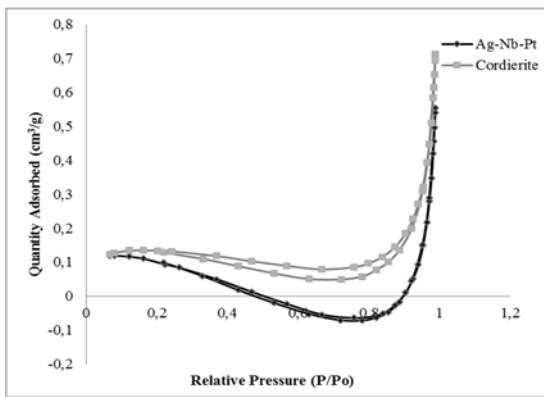


Figure 2. Variaton of relative pressure with quantity absorbed

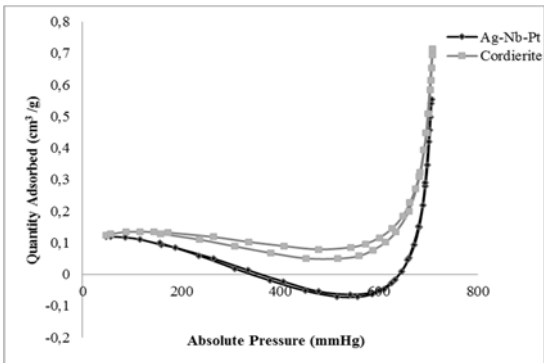


Figure 3. Variaton of absolute pressure with quantity absorbed

Variation of pore width with respect to pore volume is given Figure 4. As shown in Figure 4, pore volume decreases with the increase of pore width. Figure 5 shows the variation of pore width with pore area. As can be seen from Figure 5, when the pore width increases, pore surface area decreases. Eventually, as the pore width increases, the surface

area decreases and surface area increases with the increases of pore volume.

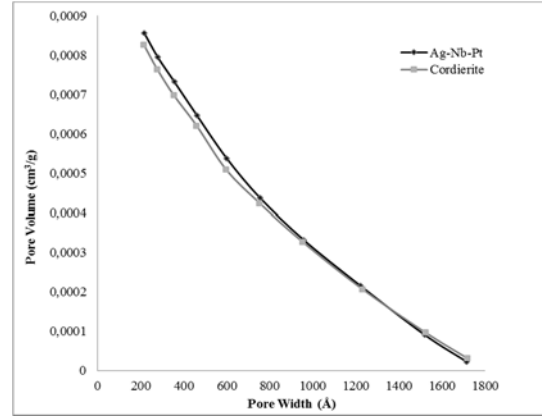


Figure 4. BJH adsorption cumulative pore volume (Larger) Halsey: Faas correction

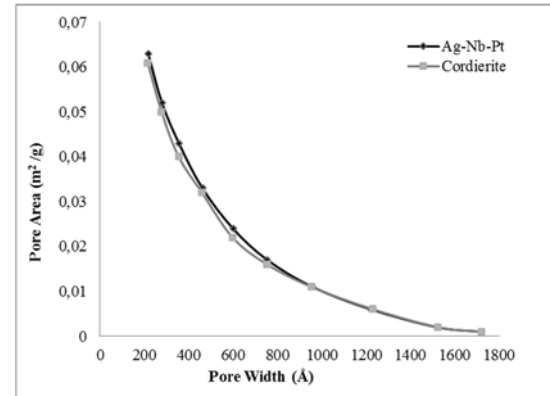


Figure 5. BJH adsorption cumulative pore area (Larger) Halsey: Faas correction

In general, the surface area of the catalysts is the most important factor affecting the catalytic activity. BET graphs were obtained with the determination of the adsorption capacities of cordierite and catalyst. These graphs were attained with the values of the relative equilibrium pressure in the range of 0.05-0.35. When the slope of BET increases, specific surface area decreases. BET surface area is given in Figure 6. As shown in Figure 6, the slope of the catalyst seems to be higher than that of the cordierite. This means that the specific surface area of the catalyst is less than that of the cordierite.

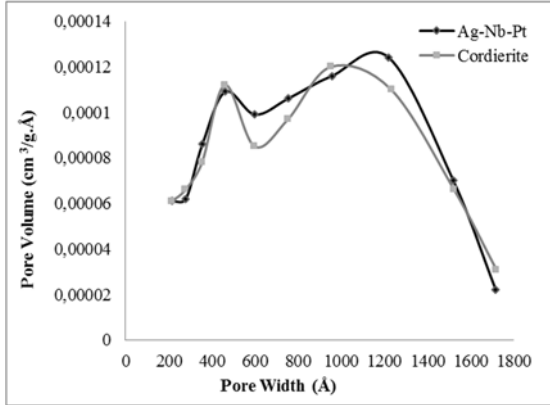


Figure 6. BET surface area plot

Figure 7 displays the variation of pore width with BJH adsorption dV/dw curve which allows the determination of pore volume. In Figure 7, it is seen that pore concentrations increase in pore width values between 10-50 nm for cordierite. This situation is resulted from the presence of mesoporous. In curve belonged to the catalyst, it was determined that pore concentrations decreased with increasing of pore width.

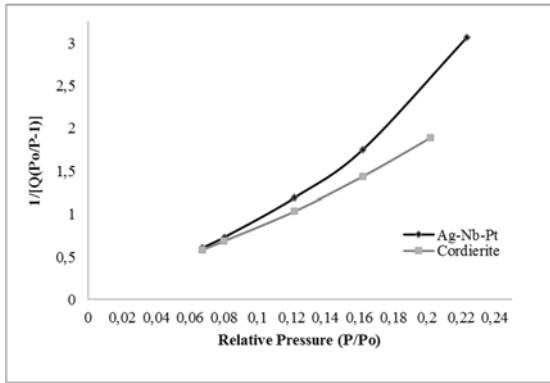


Figure 7. Pore size distribution

3.2. XRF Analysis Results

XRF analysis results of the cordierite structure and produced catalyst with the percentage of the elements and compounds in the sample contents are given in Table 2. According the results, the SiO_2 and Al_2O_3 compounds forming the main structure in the samples were obtained at the highest rate. When Ag content in the cordierite structure was 0.03%,

this ratio was found to be 3.67% in the catalyst. The Pt content in the catalyst is 0.19% and the Nb content is 0.12%.

Table 2. XRF analysis results

Cordierite		Ag-Nb-Pt	
Formula	Concentr.	Formula	Concentr.
SiO_2	34.10%	SiO_2	35.78%
Al_2O_3	24.12%	Al_2O_3	25.96%
MgO	9.85%	MgO	10.63%
Fe_2O_3	0.42%	Ag	3.67%
P_2O_5	0.29%	Fe_2O_3	0.49%
CaO	0.19%	P_2O_5	0.29%
TiO_2	0.15%	CaO	0.21%
K_2O	0.11%	TiO_2	0.16%
PbO	0.06%	Na_2O	0.11%
ZrO_2	0.05%	K_2O	0.10%
Cr_2O_3	0.05%	Pt	0.09%
Ag	0.03%	Nb_2O_5	0.08%
SO_3	0.01%	Cr_2O_3	0.06%
NiO	0.01%	PbO	0.05%
		ZrO_2	0.04%
		SO_3	0.03%
		NiO	0.02%

3.3. SEM/EDX Analysis Results

The structure and morphology of the catalyst are very important parameters as they influence the photocatalytic activity. SEM images of 1000x and 5000x sizes of cordierite and produced catalysts are shown in Figure 8. When the SEM/EDX analysis results are examined, it is determined that the catalysts have a highly porous structure, the coating on the cordierite structure is homogeneous throughout the entire surface, and the coating materials penetrate the entire surface including the pores. In addition, the Ag based catalyst has higher crystallinity.

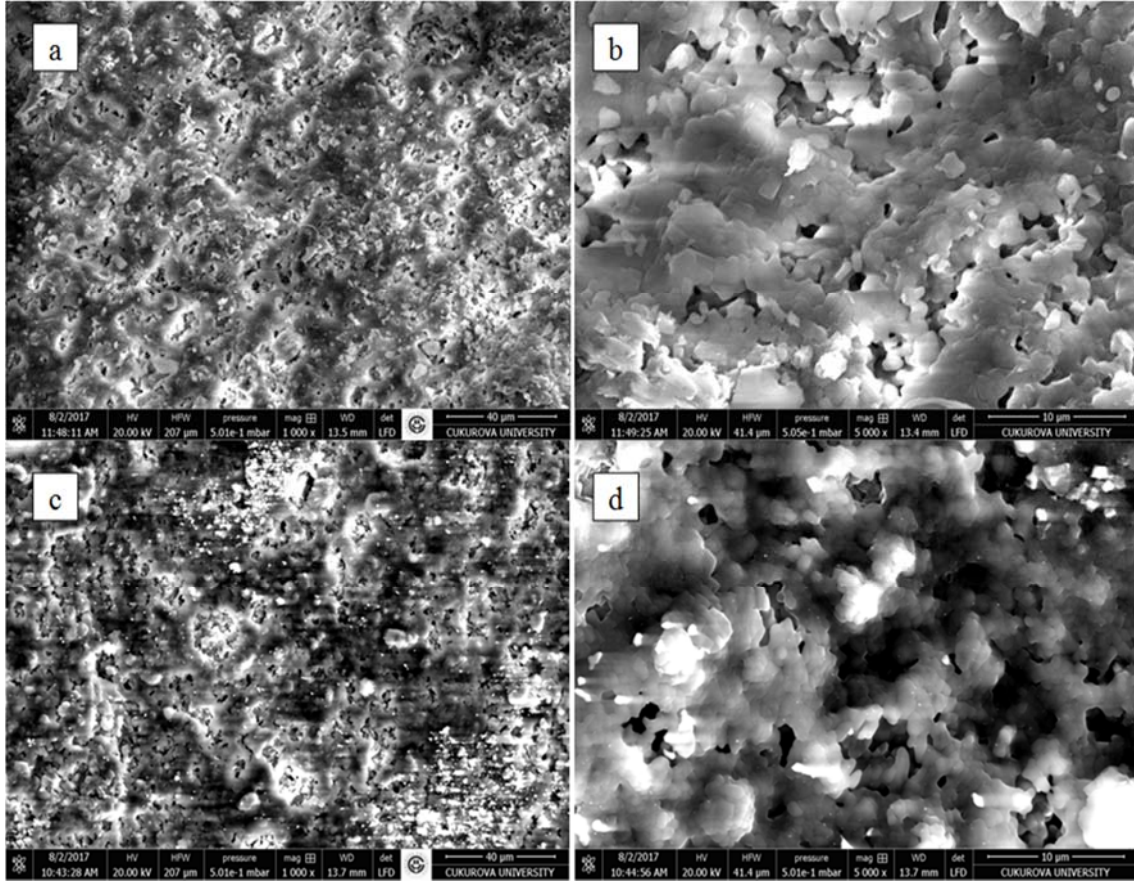


Figure 8. Images of SEM; a) Cordierite 1000x, b) Cordierite 5000x, c) Ag-Nb-Pt 1000x, d) Ag-Nb-Pt 5000x

4. CONCLUSION

In this experimental study, it was aimed to develop and synthesize Ag, Nb and Pt catalysts for use in SCR system. The cordierite structure was immersed in the solution consisting of Ag, Nb and Pt elements and then dried and sintered at high temperature. BET, XRF and SEM/EDX analyzes of the developed catalyst were executed. As a result of the analysis, it was shown that the coating was performed homogeneously. In addition, the Ag, Nb and Pt admixtures penetrate the entire surface and the surface area of the catalyst has decreased due to the high temperature exposure. In further study, it is planned to investigate the effect on the emissions by connecting the produced catalyst to the outlet of an engine.

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