



# The Effect of H<sub>2</sub>O on the Use of Ethanol as Reductant in the SCR System

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## Abstract

In this experimental study, effects of H<sub>2</sub>O on the use of ethanol as reducing agents were investigated on the Ag-Pt-W-Ti/Cordierite catalyst. Ag-Pt-W-Ti/Cordierite catalyst was synthesized using the impregnation method for selective catalytic reduction (SCR) of NO<sub>x</sub>. To investigate the effects of H<sub>2</sub>O addition on the NO<sub>x</sub> conversion ratios, tests were carried out at 200-270 °C under 30000 h<sup>-1</sup> GHSV using three different reductants (ethanol, 5% H<sub>2</sub>O - 95% ethanol, 10% H<sub>2</sub>O - 90% ethanol). The catalytic activity of the catalyst increased with increase in exhaust gas temperature. The highest NO<sub>x</sub> conversion ratio was 89.9% at 270 °C with ethanol. The tests showed that when the H<sub>2</sub>O content of the reductant increased from 5% to 10%, the NO<sub>x</sub> conversion ratios significantly decreased at temperatures below 240 °C. NO<sub>x</sub> conversion ratios enhanced as engine load increased.

**Keywords:** Catalyst, SCR, NO<sub>x</sub>, Diesel engine, Reductant

## 1. INTRODUCTION

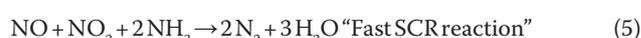
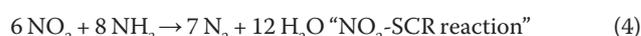
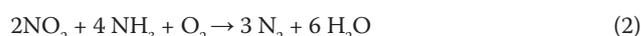
Nitrogen oxides (NO<sub>x</sub>) emitted from vehicles are major air pollutants that require strict environmental regulations because of their toxicity [1,2,3]. Selective catalytic reduction (SCR) of NO<sub>x</sub> using reductant is a one of the most efficient and low cost technology for elimination of NO<sub>x</sub> from engine exhaust gases [4,5,6].

The catalysts are an important factor for SCR technology [7]. A catalyst includes a substrate material, active components such as transition, noble and rare metals and different supported materials such as zeolites, alumina, TiO<sub>2</sub>, active carbon [1,8].

Cordierite (2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>·2MgO) is commonly used as monolith substrate due to strong thermal stability, economic feasibility and low thermal expansion [9,10]. The major disadvantage of cordierite is its low surface area. The surface area of cordierite is about 0.5 m<sup>2</sup>/g. Surface area of cordierite should be increased to provide strong interaction between active components and supports, to obtain high dispersion and highly active catalyst. One way to increase the surface area is coating of supported materials, including alumina, TiO<sub>2</sub>, CeO<sub>2</sub>, active carbon, another way is to pre-treatment of cordierite [11,12]. Surface area of cordierite increases with acid pre-treatment such as nitric acid, hydrochloric acid, sulfuric acid, acetic acid, oxalic acid and EDTA [12,13]. In addition, catalytic activity of catalyst enhances with acid pre-treatment.

Among the supported materials, TiO<sub>2</sub> is predominantly used due to provide large surface area and porosity, which is beneficial for catalytic reaction and catalytic activity [14]. CeO<sub>2</sub> supported materials are used due to their special redox ability and high oxygen storage capacity. However, CeO<sub>2</sub> has small surface area and agglomeration. Therefore, it is not preferred as a support material [15].

The principle of NO<sub>x</sub> conversion reaction is to reduce NO<sub>x</sub> to N<sub>2</sub> by using ammonia (NH<sub>3</sub>), urea, hydrocarbons (HC), and oxygenated hydrocarbons (OHC) and with the help of a catalyst. Ammonia is the commonly used as reductant in the SCR system [3, 14,16]. The main NH<sub>3</sub>-SCR reactions are as follows [14,16]:



In the NH<sub>3</sub>-SCR systems as the source of ammonia are used urea-water solutions. However, urea-SCR systems cause ammonia slip, require heavy urea tank and include complex and costly injection system. These problems can be solved by using HC as reductant in the SCR systems [17,18].

Silver-alumina (Ag/Al<sub>2</sub>O<sub>3</sub>) is extremely effective catalysts for HC-SCR, particularly ethanol [19,20]. Generally, it has

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been reported that the highest catalytic activity is achieved on 2% Ag containing Ag/Al<sub>2</sub>O<sub>3</sub> catalysts [4,18]. However, Ag/Al<sub>2</sub>O<sub>3</sub> catalysts have poor activity at low temperature. The low catalytic activity of these catalysts can be promoted using various catalyst compositions.

Noble metal catalysts such as Pt and Pd are very effective for reducing NO<sub>x</sub> emissions at 200-250 °C [21]. However, noble metals are not suitable catalytic materials due to the high price and limited availability.

Dong et al. investigated Mn-Ce/TiO<sub>2</sub> (M) and Cu-Ce/TiO<sub>2</sub> (C) catalysts for the selective catalytic reduction (SCR) of NO<sub>x</sub> by urea. They found that M phase promotes the low temperature activity and C phase contributes to the high temperature activity [22]. Ma et al. investigated the catalytic activities of tungsten-modified Cu<sub>0.02</sub>Fe<sub>0.2</sub>TiO<sub>x</sub> catalysts (Cu<sub>0.02</sub>Fe<sub>0.2</sub>W<sub>a</sub>TiO<sub>x</sub>; a=0.01, 0.02 and 0.03) with NH<sub>3</sub> in the presence/absence of 5 vol.% H<sub>2</sub>O. They determined that Cu<sub>0.02</sub>Fe<sub>0.2</sub>W<sub>0.02</sub>TiO<sub>x</sub> showed the highest NO conversion, at 235-520°C with >90% NO conversion and high water/sulphur resistance even in the presence of 5 vol.% H<sub>2</sub>O [23].

The aim of this study is investigate the effect of H<sub>2</sub>O on the use of ethanol as reductant in the SCR system. Different catalytic materials was used to improve the SCR activity of Ag based catalyst at low temperature. For this purpose, the Ag-Pt-W-Ti/Cordierite catalyst was produced. The catalytic performance was evaluated using ethanol, 95% ethanol - 5% H<sub>2</sub>O and 90% ethanol - 10% H<sub>2</sub>O, in the temperature range of 200-270 °C, at different engine loads (1 kW, 2 kW, 3kW and 4 kW) and 30000 h<sup>-1</sup> gas hourly space velocity (GHSV).

## 2. MATERIALS AND METHODS

### 2.1. Catalyst synthesis

The low surface area of cordierite was increased for catalyst synthesis. For this purpose, 200 cm<sup>3</sup> a cordierite material was pre-treated with 40 % hot oxalic acid solution for 3 hours. Then, it was washed with distilled water, dried at 110 °C and calcined at 550 °C. Thus it made ready for coating.

The catalyst was synthesized using the impregnation method. For this purpose, 2.5 g AgNO<sub>3</sub> (≥99% Sigma-Aldrich), 2 g (NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (99.9% metal basis Sigma-Aldrich),

2 g Pt (NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> (≥50.0% Pt basis Sigma-Aldrich), 50 g TiO<sub>2</sub> (anatase, ≥99% trace metal basis) and 0.5 g SiO<sub>2</sub> (nano powder, 99.5% trace metals basis) were added into 250 ml distilled water. The mixture was mixed using an ultrasonic stirrer. The pre-treated cordierite was dipped in this mixture and its clogged pores were opened. After the coating, it was dried at 120 °C for 1 hour and calcined at 550 °C for 3 hours. Thus, Ag-Pt-W-Ti/Cordierite catalyst was synthesized. Surface area of the synthesized catalyst was 30.38 m<sup>2</sup>/g. Picture of cordierite used in catalyst production is given in Figure 1. Catalyst preparation flow scheme was given in Figure 2.



Figure 1. Picture of cordierite used in catalyst production

### 2.2. Performance test system

A performance test system was used in the laboratory of the Automotive Department of Çukurova University to investigate the effect of H<sub>2</sub>O on the use of ethanol as a reductant and the NO<sub>x</sub> reduction efficiency of Ag-Pt-W-Ti/Cordierite catalyst. The test system includes a two cylinder V type AKSA diesel engine, an engine loading system and a designed exhaust system. Schematic diagram of the performance test system was given in Figure 3. The technical properties of the test engine were shown in Table 1. The loading unit used consists of 10 resistances, each providing 1 kW loading. The power amount of system pulled from engine has been kept under control using the ammeter and voltmeter on the system. In the test system, an orifice plate was used to determine the exhaust gas flow rate and a heater to adjust the exhaust gas temperatures. Exhaust gas tem-

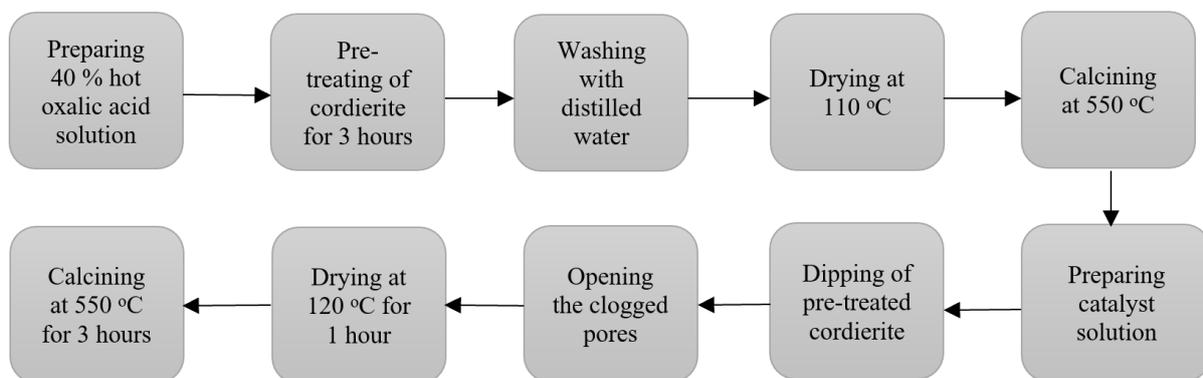
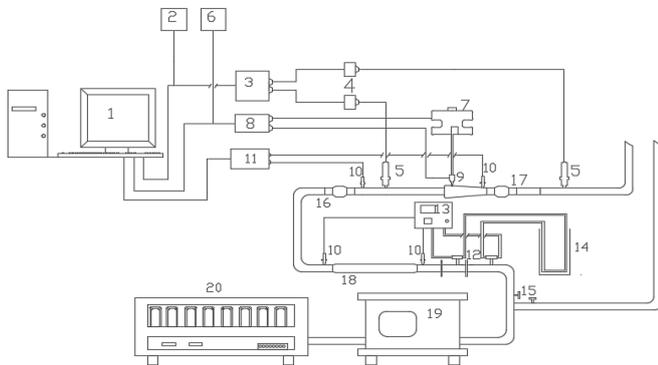


Figure 2. Catalyst synthesis flow scheme

peratures were determined using two K type thermocouple temperature sensors. NO<sub>x</sub> emission reduction ratios were detected using two Continental model NO<sub>x</sub> sensors and the data was monitored by computer. Accuracy values of measuring device are ± 10 ppm for CO, ± 1% for CO<sub>2</sub> and ± 1 ppm for NO<sub>x</sub>.



**Figure 3.** Schematic diagram of performance system (1-Computer, 2- 24V power supply, 3- PEAK CAN, 4- CAN BUS (The Controller Area Network), 5- NO<sub>x</sub> sensor, 6- 12V power supply, 7- Pump and reductant tank, 8- TIVA card, 9- Injector, 10- Thermocouple, 11- Converter, 12- Orifice plate, 13- Digital manometer, 14- U manometer, 15- Valve, 16- DOC (Diesel oxidation catalyst), 17- SCR catalyst, 18- Exhaust gas heater, 19- Diesel engine, 20- Loading system)

**Table 1.** Technical specification of the test engine

Item	Specification
Model	Diesel AKSA A2CRX08
Engine Speed (r/min)	3000
Prime frequency (Hz)	50
Cylinder volume (cm <sup>3</sup> )	794
Stroke (mm)	79
Compression ratio	23/1
Dimensions (mm)	L = 1158 W = 775 H = 1017
Oil capacity (L)	2.3
Water capacity (L)	6.4
Fuel tank capacity (L)	15

### 3. 3. RESULTS AND DISCUSSION

#### 3.1. NO<sub>x</sub> conversion ratios

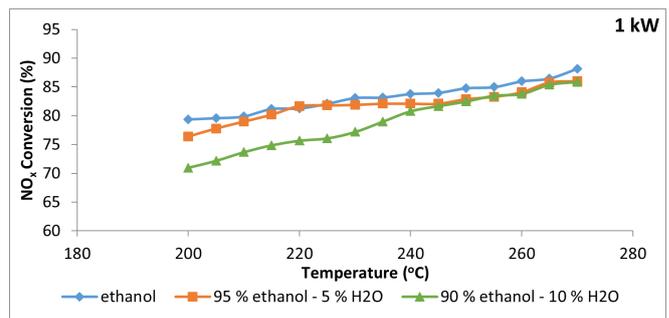
The catalytic performance of the Ag-Pt-W-Ti/Cordierite catalyst was examined under gas hourly space velocity (GHSV) of 30000 h<sup>-1</sup>. The NO<sub>x</sub> conversion ratios of the catalyst were shown in Figure 4-7.

The activity of Ag-Pt-W-Ti/Cordierite is highest for NO<sub>x</sub> reduction using ethanol as reductant. The maximum conversion of NO<sub>x</sub> was 89.9% with ethanol at 270 °C. The catalyst showed different catalytic activity with the addition H<sub>2</sub>O to ethanol. NO<sub>x</sub> conversion ratios with addition 5% H<sub>2</sub>O and 10% H<sub>2</sub>O to ethanol decreased. NO<sub>x</sub> conversion ratios obtained with the addition 5% H<sub>2</sub>O were higher than with the addition 10% H<sub>2</sub>O. Maximum NO<sub>x</sub> conversion ratio with 5% H<sub>2</sub>O-95% ethanol was 89.4% while with 10% H<sub>2</sub>O-90% ethanol was 89.2%. The results with addition 10% H<sub>2</sub>O showed lower NO<sub>x</sub> conversion ratios at temperatures below 240 °C compared to addition 5% H<sub>2</sub>O. The results reveal that H<sub>2</sub>O could inhibit the activation of catalysts.

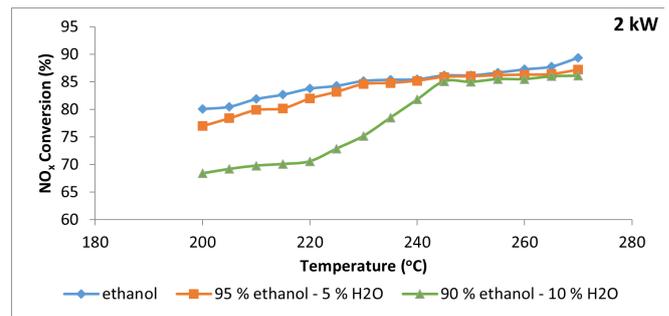
This condition might be due to hydroxyl group formed on catalyst surface in presence of H<sub>2</sub>O. The formed hydroxyl groups prevent NO<sub>x</sub> adsorption on the catalyst surface and reduce the reduction ratio with ethanol and NO<sub>x</sub>. However, above 240 °C, NO<sub>x</sub> conversion ratios increased and similar results were found. Inhibition effect of H<sub>2</sub>O on catalyst activation was proved by Ahmad et al. [24].

In the tests was seen that NO<sub>x</sub> conversion ratios enhanced as engine load increased. Maximum NO<sub>x</sub> conversion ratios were obtained under 4 kW engine load. This situation is thought to be caused by the decrease in O<sub>2</sub> concentration in the exhaust gas due to the increase of engine loads. Similar results were determined by Resitoğlu et al. and Keskin et al. [25, 26].

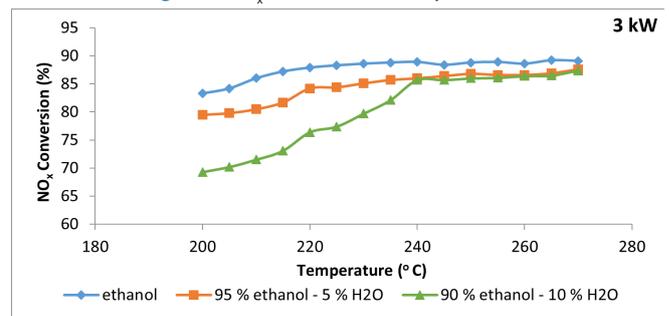
It was seen that temperature had a significant effect on catalytic activity. The catalytic activity of the catalyst increased depending on the increase in exhaust gas temperature. The highest NO<sub>x</sub> conversion ratios were achieved at 270 °C. Similar results were found by Zhao et al. and Du et al. [27,28].



**Figure 4.** NO<sub>x</sub> conversion of catalyst at 1 kW



**Figure 5.** NO<sub>x</sub> conversion of catalyst at 2 kW



**Figure 6.** NO<sub>x</sub> conversion of catalyst at 3 kW

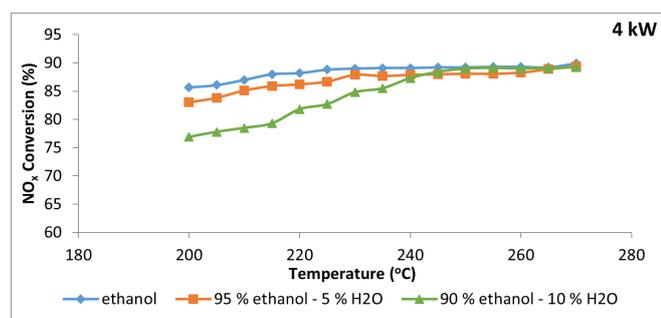


Figure 7. NO<sub>x</sub> conversion of catalyst at 4 kW

#### 4. CONCLUSIONS

NO<sub>x</sub> conversion ratios were compared using ethanol at H<sub>2</sub>O absence/presence in the SCR system. In the tests were determined that NO<sub>x</sub> conversion ratios decreased depending on the H<sub>2</sub>O content. The maximum NO<sub>x</sub> conversion ratio was 89.9 % at 270 °C with ethanol. Addition of H<sub>2</sub>O to the ethanol negatively affected NO<sub>x</sub> conversion ratios. Comparing to 5% H<sub>2</sub>O-95% ethanol, conversion ratios were higher at 10% H<sub>2</sub>O-90% ethanol. NO<sub>x</sub> conversion ratios improved as engine load increased. Highest NO<sub>x</sub> conversion ratios were determined at 4 kW engine load in the all tests. The rise in temperature of exhaust gas significantly enhanced the NO<sub>x</sub> conversion ratios.

#### REFERENCES

- [1] Mousavi, S.M., Panahi, P.N. (2016). Modeling and optimization of NH<sub>3</sub>-SCR performance of MnOx/γ-alumina nanocatalysts by response surface methodology. *Journal Taiwan Institute Chemical Engineers*, 69: 68-77.
- [2] Li, L., Li, P., Tan, W., Ma, K., Zou, W., Tang, C., Dong, L. (2020). Enhanced low-temperature NH<sub>3</sub>-SCR performance of CeTiOx Catalyst via surface Mo modification. *Chinese Journal of Catalysis*, 41: 364-373.
- [3] Zhou, T., Yuan, Q., Pan, X., Bao, X. (2018). Growth of Cu/SSZ-13 on SiC for selective catalytic reduction of NO with NH<sub>3</sub>. *Chinese Journal of Catalysis*, 39: 71-78.
- [4] More, P.M., Nguyen, D.L., Granger, P., Dujardin, C., Dongare, M.K., Umbarkar, S.B. (2015). Activation by pretreatment of Ag-Au/ Al<sub>2</sub>O<sub>3</sub> bimetallic catalyst to improve low temperature HC-SCR of NOx for lean burn engine exhaust. *Applied Catalysis B: Environmental*, 174-175: 145-156.
- [5] Xu, L., Li, X-S., Crocker, M., Zhang, Z-S., Zhu, A-M. (2013). A study of the mechanism of low-temperature SCR of NO with NH<sub>3</sub> on MnOx/CeO<sub>2</sub>. *Journal of Molecular Catalysis A: Chemical*, 378: 82-90.
- [6] Cha, W., Ehrman, S.H., Jurg, J. (2016). CeO<sub>2</sub> added V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst prepared by chemical vapor condensation (CVC) and impregnation method for enhanced NH<sub>3</sub>-SCR of NOx at low temperature. *Journal Environmental Chemical Engineering*, 4: 556-563.
- [7] Wang, J., Peng, Z., Chen, Y., Bao, W., Chang, L., Feng, G. (2015). In-situ hydrothermal synthesis of Cu-SSZ-13/cordierite for the catalytic removal of NOx from diesel vehicles by NH<sub>3</sub>. *Chemical Engineering Journal*, 263: 9-19.
- [8] Rasmussen, S.B., Abrams, B.L. (2017). Fundamental chemistry of V-SCR catalysts at elevated temperatures. *Catalysis Today*, 297: 60-63.
- [9] Fuji, M., Shiroki, Y., Menchavez, R.L., Takegami, H., Takahashi, M., Suzuki, H., Izuhara, S., Yokoyama, T. (2007). Fabrication of cordierite filter by in-situ solidification for high temperature dust collection. *Powder Technology*, 172: 57-62.
- [10] Twigg, M.V. (2007). Progress and future challenges in controlling automotive exhaust gas emissions. *Applied Catalysis B: Environmental*, 70: 2-15.
- [11] Li, F., Shen, B., Tian, L., Li, G., He, C. (2016). Enhancement of SCR activity and mechanical stability on cordierite supported V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst by substrate acid pretreatment and addition of silica. *Powder Technology*, 297: 384-391.
- [12] Shigapov, A.N., Graham, G.W., McCabe, R.W., Peck, M.P., Plummer Jr H.K. (1999). The preparation of high-surface-area cordierite monolith by acid treatment. *Applied Catalysis A: General*, 182: 137-146.
- [13] Liu, Q.Y., Liu, Z.Y., Huang, Z.G., Xie, G.Y. (2004). A honeycomb catalyst for simultaneous NO and SO<sub>2</sub> removal from flue gas: preparation and evaluation. *Catalysis Today*, 93-5: 833-837.
- [14] Chen, C., Cao, Y., Liu, S., Chen, J., Jia, W. (2018) Review on the latest developments in modified vanadium-titanium-based SCR catalysts. *Chinese Journal of Catalysis*, 39: 1347-1365.
- [15] Yang, C., Yang, J., Jiao, Q., Zhao, D., Zhang, Y., Liu, L., Hu, G., Li, J. (2020). Promotion effect and mechanism of MnOx doped CeO<sub>2</sub> nano-catalyst for NH<sub>3</sub>-SCR. *Ceramics International*, 46: 4394-4401.
- [16] Piumetti, M., Bensaid, S., Fino, D., Russo, N. (2015). Catalysis in diesel engine NOx aftertreatment: a review. *Catalysis, Structure & Reactivity*, 1: 155-173.
- [17] Ström, L., Carlsson, P.A., Skoglundh, M., Härelind, H. (2016). Hydrogen-assisted SCR of NOx over alumina-supported silver and indium catalysts using C<sub>2</sub>-hydrocarbons and oxygenates. *Applied Catalysis B: Environmental*, 181: 403-412.
- [18] Gunnarsson, F., Phil, J.A., Toops, T.J., Skoglundh, M., Härelind, H. (2017). Lean NOx reduction over Ag/alumina catalysts via ethanol-SCR using ethanol/gasoline blends. *Applied Catalysis B: Environmental*, 202: 42-50.
- [19] Frobert, A., Raux, S., Rousseau, S., Blanchard, G. (2013). Analysis of the coupling of HC-SCR by ethanol and NH<sub>3</sub>-SCR on real engine emissions. *Topics in Catalysis*, 56: 125-129.
- [20] Deng, H., Yu, Y., He, H. (2015). Discerning the role of Ag-O-Al entities on Ag/γ-Al<sub>2</sub>O<sub>3</sub> surface in NOx selective reduction by ethanol. *The Journal of Physical Chemistry C*, 119: 3132-3142.
- [21] Vliehikki, A., Petalidou, K.C., Kalamaras, C.M., Kolli, T., Huuhtanen, M., Maunula, T., Keiski, R.L., Efstathiou, A.M. (2014). Selective catalytic reduction of NOx by Hydrogen (H<sub>2</sub>-SCR) on WO<sub>x</sub>-promoted Ce<sub>2</sub>Zr<sub>1</sub>-ZrO<sub>2</sub> solids. *Applied Catalysis B: Environmental*, 156-157: 72-83.
- [22] Dong, G-J., Zhao, Y., Zhang, Y-F. (2014). Preparation and performance of V-W/x(Mn-Ce-Ti)/y(Cu-Ce-Ti)/cordierite catalyst by impregnation method in sequence for SCR reaction with urea. *Journal of Fuel Chemistry and Technology*, 42: 1093-1101.
- [23] Ma, S., Zhao, X., Li, Y., Zhang, T., Yuan, F., Niu, X., Zhu, Y. (2019). Effect of W on the acidity and redox performance of the Cu<sub>0.02</sub>Fe<sub>0.2</sub>W<sub>a</sub>-TiO<sub>x</sub> (a=0.01, 0.02, 0.03) catalysts for NH<sub>3</sub>-SCR of NO. *Applied Catalysis B: Environmental*, 248: 226, 238.
- [24] Ahmad, M.A.C.M., Keskin, A., Özarslan, H., Keskin, Z. (2020). Properties of ethyl alcohol-water mixtures as a reductant in a SCR system at low exhaust gas temperatures. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, 1556-7230.
- [25] Resitoglu, I.A., Altinisik K., Keskin A., Ocakoglu K. (2020). The effects of Fe<sub>2</sub>O<sub>3</sub> based DOC and SCR catalyst on the exhaust emissions of

diesel engines. *Fuel*, 262, 116501.

- [26] Keskin A., Yaşar A., Candemir O.C., Özarslan H. (2020). Influence of transition metal based SCR catalyst on the NO<sub>x</sub> emissions of diesel engine at low exhaust gas temperatures. *Fuel*, 273, 117785.
- [27] Zhao B., Ran R., Guo X., Cao L., Xu T., Chen Z., Wu X., Si Z., Weng D. (2017). Nb-modified Mn/Ce/Ti catalyst for the selective catalytic reduction of NO with NH<sub>3</sub> at low temperature. *Applied Catalysis A: General*, 545, 64-71.
- [28] Du X., Gao X., Fu Y., Gao F., Luo Z., Cen K. (2012). The co-effect of Sb and Nb on the SCR performance of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst. *Journal of Colloid and Interface Science*, 368, 406-412.