

# Metal type SCR catalyst with excellent de-NO<sub>x</sub> efficiency at low temperature and sulfur resistance from coal combustion exhaust gas

Woo-Jin Na, Hea-Kyung Park\*

*Research Institute of catalyst Technology, Department of Chemical Engineering,  
Hanseon University, 46 Hanseo 1-ro, Haemi-myun, Seosan, Chungnam 31962, Korea.*

## Abstract

Exhaust gas from power generation facilities using fossil fuels such as coal, oil, natural gas, and byproduct gas contains nitrogen oxides (NO<sub>x</sub>) such as NO and NO<sub>2</sub> which are pollutants causing air pollution and must be removed before being released into the atmosphere.

Especially in case of coal fired power plant, it is necessary to develop a low-temperature de-NO<sub>x</sub> system that should be installed at the rear of FGD unit to solve the breakage and poisoning of catalysts caused by high dust and sulfur-containing fuel due to fuel diversification and deterioration of coal quality.

Therefore, in this study, various attempts have been made to develop an excellent de-NO<sub>x</sub> performance and sulfur resistance catalyst at temperatures below 200 degrees by controlling the amounts of vanadium impregnation, an active component and adding the tungsten, a promoter in the catalyst. De-NO<sub>x</sub> performance and the deactivating effect of SO<sub>2</sub> over the catalyst were evaluated in a laboratory scale atmospheric micro-reactor and the physical and chemical properties of them by analyzers such as BET, SEM-EDX and XRF were also characterized.

As the amount of vanadium impregnation increased, de-NO<sub>x</sub> performance also increased, and the maximum value was recorded at 14% vanadium and decreased afterwards. Durability measurements for sulfur showed that de-NO<sub>x</sub> performance gradually decreased for 180 hours but remained almost unchanged afterwards.

**Keywords:** SCR catalyst, NO<sub>x</sub>, Metal corrugated, Wash coating, Sulfur durability

## I. INTRODUCTION

The NO<sub>x</sub> emission from fossil fuel is considered as a major component to air pollution and contributes health problem to human nature. Therefore, NO<sub>x</sub> emissions have been regulated and controlled worldwide by increasingly stringent regulations [1-4].

And also, most fossil fuels, except LNG, contain sulfur that converts to SO<sub>x</sub> during combustion. Especially coal fired power plant has problems of deactivation and clogging of SCR catalyst by SO<sub>x</sub> and dust in the exhaust gas. In technology for eliminating NO<sub>x</sub> along with SO<sub>x</sub>, SCR(Selective Catalytic Reduction) using NH<sub>3</sub> or urea as reducing agent is well known, proven and efficient technology [5-7].

In case of coal fired power plant, it is necessary to develop a low-temperature de-NO<sub>x</sub> system that should be installed at the rear of FGD (Flue Gas Desulfurization) unit to solve the breakage and poisoning of catalysts caused by high dust and sulfur-containing fuel due to fuel diversification and deterioration of coal quality problems [8-10].

However, the installation of a catalyst at the rear of the FGD unit requires a lot of additional fuel in rising to the active temperature of the existing commercial SCR catalyst due to the low temperature of exhaust gas, making it less economical. Therefore, the development of SCR catalyst with excellent efficiency at low temperature is required. Recently, metal type substrate, which has the advantage of high mechanical strength and superior specific surface area and excellent heat conductivity, is widely used as a catalytic supports [11-16].

In this study, for the purpose of developing a SCR catalyst with excellent de-NO<sub>x</sub> efficiency and sulfur-resistant at low temperature, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was manufactured by changing the amount of vanadium impregnation from 8wt% to 20wt% using metal corrugated support [17-19].

The deNO<sub>x</sub> efficiency of prepared catalyst was measurement out by using laboratory scale atmospheric pressure micro-reactor under condition of temperature 150°C~200°C, space velocity (10,000h<sup>-1</sup>~20,000h<sup>-1</sup>). And the durability measurement of catalyst was conducted over V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst with the additional amount of 10wt% tungsten impregnation in the presence of SO<sub>2</sub> 200ppm. By analyzing the physical properties by analyzers such as BET, SEM(scanning electron microscope), EDX(energy dispersive x-ray spectrometer) and XRF(x-ray fluorescence) were also characterized, the correlation with the de-NO<sub>x</sub> active results was confirmed

## II. EXPERIMENT

### II.1 Catalyst Preparation

The materials of coating slurry were composed of TiO<sub>2</sub> (99%, Cristal Global Co. Ltd., France), V<sub>2</sub>O<sub>5</sub> (99%, Daejung Chemical CO. Ltd., Korea), WO<sub>3</sub>(99 % Sigma-Aldrich Co., Ltd., Germany), Silicasol 30% solution(99%, S-Chemtech. Co., Ltd., Korea) as binder, DispexA 40(83%, BASF CO., Ltd., Germany) as dispersive agent and DI water. The metal corrugated substrate used in this study was cell density of 200cps, 300cps supplied by YIDA Inc., China.

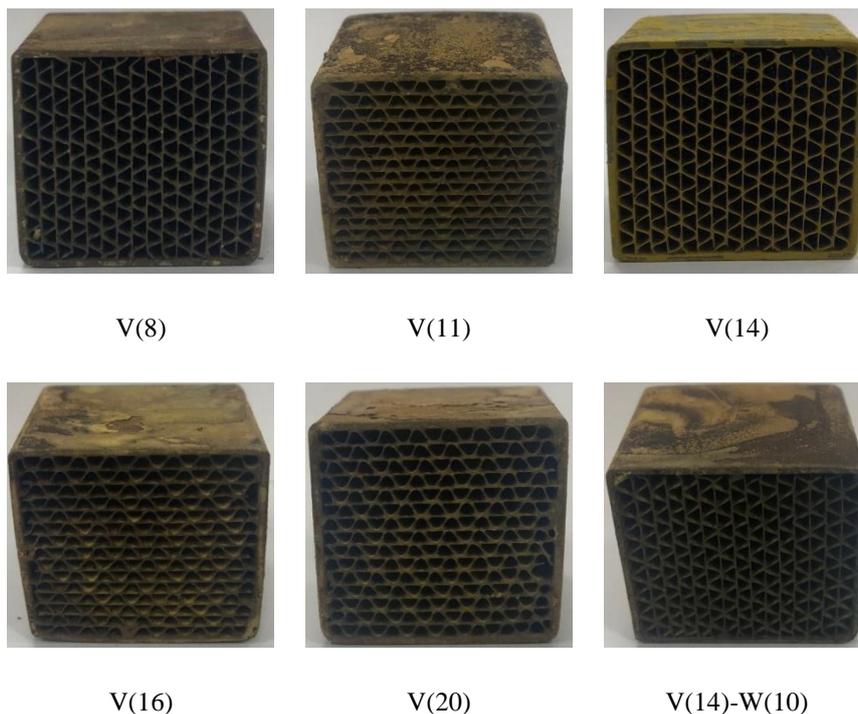
The solution dissolved WO<sub>3</sub> in distilled water and the solution dissolved V<sub>2</sub>O<sub>5</sub> in monoethanolamine (MEA) were mixed and

stirred for 1 h. And then TiO<sub>2</sub> was slowly added to this mixture and stirred for 30 min.

The manufactured slurry was then coated on a 3 cm × 3 cm × 3 cm metal corrugated substrate with a conventional dip-sipping method. The contents of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> were adjusted based on that of TiO<sub>2</sub> and 150 g/L of slurry was controlled to be coated. Finally the coated metal corrugated substrate was dried at 120 °C for 1 h and then calcined at 470 °C for 3 h. The notation and pictures of manufactured catalyst is shown in **Table 1** and **Fig.1**.

**Table 1.** Notation of catalyst

Notation	Catalyst
V(x)	(x) wt% V <sub>2</sub> O <sub>5</sub> / TiO <sub>2</sub>
V(x)-W(y)	(x) wt% V <sub>2</sub> O <sub>5</sub> - (y) wt% WO <sub>3</sub> / TiO <sub>2</sub>



**Fig. 1.** Prepared metal corrugated catalyst.

## II. II Physical characteristics analysis

To analysis of physical characteristics, the slurry used in the catalyst coating was calcined and made into fine powder.

The specific surface area and pore volume was analyzed by BET(TriStar II 3020, Micromeritics Co. Ltd., USA) and the content of metals in the catalyst and surface composition was measured by XRF(X-ray Fluorescence, ZSX Primus, Rigaku Co., Ltd., Japan) and SEM(Scanning Electron Microscope)-EDX(Energy Dispersive X-ray spectrometer, Hitachi SU5000, Hitachi high technology Co., Ltd., Japan) respectively.

## II. III NO<sub>x</sub> removal test condition and apparatus

The schematic diagram of NO<sub>x</sub> removal efficiency test apparatus including continuous atmospheric pressure micro-reactor is shown in **Fig. 2**. The gas flowrate was automatically controlled by MFC (Mass Flow Controller, SM Tech. Co., Ltd.,

Korea). The reaction temperature was controlled by PID controller and test temperature range(150 °C ~ 200 °C) was selected based on the rear condition of FGD (Flue Gas Desulfurizer) unit in coal fired power plant. The composition of simulated gas mixture was adjusted as follows. The 50ppm NO gas(20% in N<sub>2</sub> balance, Sungkang Specialty Gas Co. Ltd., Korea) and NH<sub>3</sub> gas(20% in N<sub>2</sub> balance, Sungkang Specialty Gas Co. Ltd., Korea) were made to flow with the mole ratio of 1:1. The concentration of O<sub>2</sub> gas (99.9%, Sungkang Specialty Gas Co. Ltd., Korea) was maintained at 4% and the total flowrate was balanced with N<sub>2</sub> gas(99.9%, Sungkang specialty gas, Korea). All gases analysis was performed by gas analyzer (MK-II. Seil Co. Ltd., Korea). And the charged catalyst volume was 27cm<sup>3</sup> and the space velocity was set to be at 10,000h<sup>-1</sup>, 15,000h<sup>-1</sup> and 20,000h<sup>-1</sup>. For precise measurement, stabilization was executed for 30min. at each reaction temperature. The catalyst and test condition for NO<sub>x</sub> removal is shown in **Fig. 2** and **Table 2** respectively.

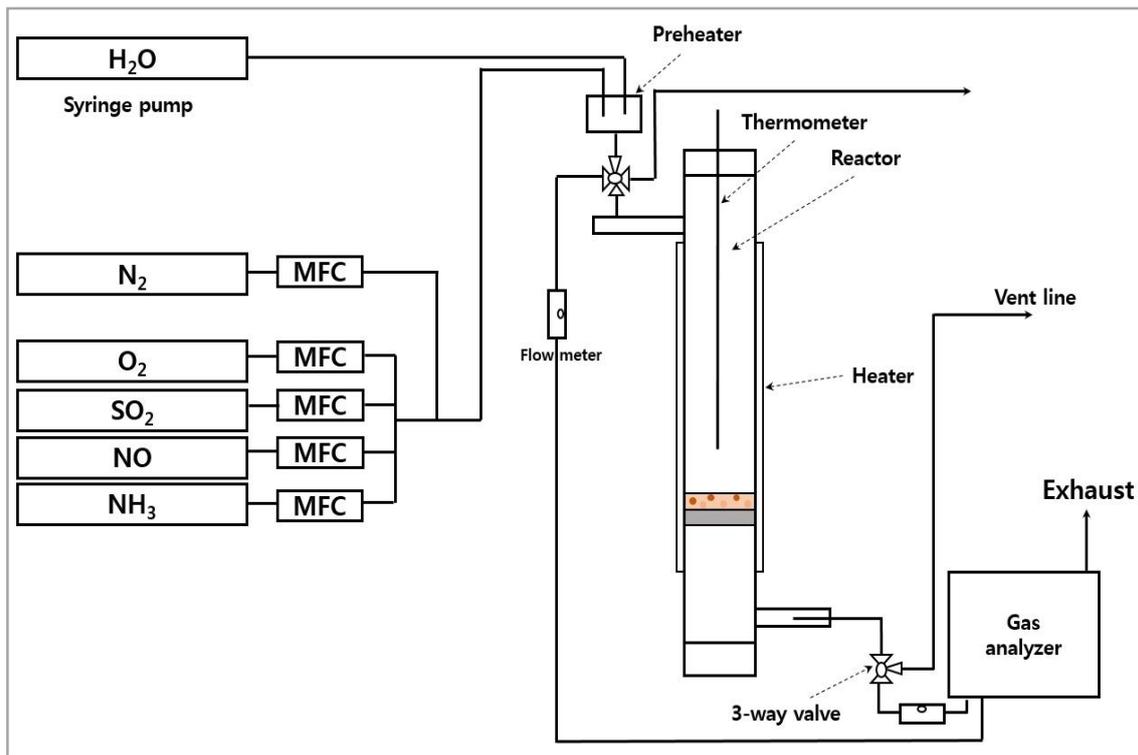


Fig. 2. Schematic diagram of catalyst performance test system

Table 2. NOx removal test condition

Item	Unit	Condition	
S.V	h <sup>-1</sup>	10,000, 15,000, 20,000	
Temperature	°C	150~200	
Simulated gas composition	NO	ppm	50
	SO <sub>2</sub>	ppm	5, 200
	NH <sub>3</sub>	ppm	50
	O <sub>2</sub>	%	4
	N <sub>2</sub>	-	balance

and increased in vanadium content from 8wt% to 14wt% and a decreased in vanadium content from 16wt% to 20wt%. Thus, the maximum value of de-NOx efficiency was at 14wt% vanadium content, 90% at 180 °C and 96% at 200 °C.

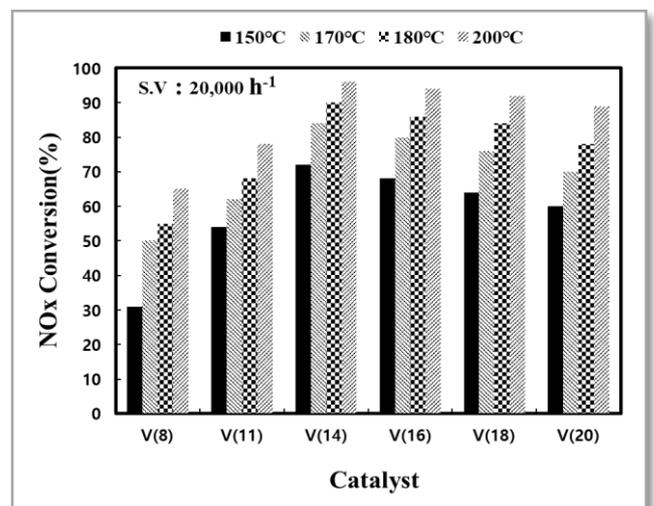


Fig. 3. NOx conversion with the impregnated amount of vanadium changes

### III RESULTS AND DISCUSSION

#### III.1 The evaluation of de-NOx efficiency

The measurement of de-NOx efficiency was carried out over V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst which was manufactured by changing the amount of vanadium impregnation from 8wt% to 20wt% using metal corrugated supports and the result is shown in Fig. 3.

De-NOx efficiency tended to increase with higher temperatures

The de-NOx efficiency was measured with changes in S.V(space velocity) over the V(14) catalyst, which had the highest de-NOx efficiency. As is shown in Fig. 4, the lower S.V, the higher de-NOx efficiency. The de-NOx efficiency was 96%(180 °C) and 98% (200 °C) at S.V 10,000h<sup>-1</sup>. Given that the

current S.V of the SCR system in coal fired power plants is nearly  $5,000\text{h}^{-1}$ , it is thought to be almost completely eliminated.

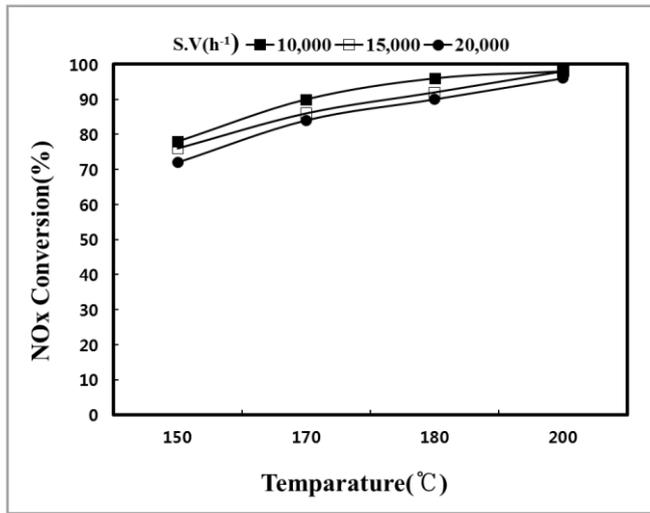


Fig. 4. NOx conversion with the space velocity changes over V(14) catalyst

In Fig. 5, de-NOx efficiency was shown according to cell density(cpsi ; no. cell per square inch)of metal corrugated supports. For 300cpsi metal corrugated catalyst with increased coating surface area due to small cell size, the removal efficiency increased from 98% to 99.4% compared to 200cpsi metal corrugated catalyst at 200°C, 10,000h<sup>-1</sup>.

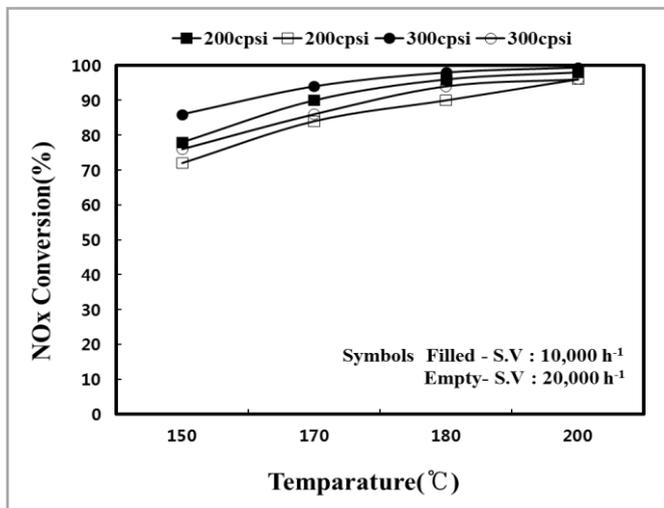


Fig. 5. NOx conversion with metal corrugated (cps) changes over V(14) catalyst

### III.II The evaluation of the effect of sulfur on de-NOx efficiency

To check for sulfur resistance, V(14)-W(10) catalyst was manufactured by adding 10wt% tungsten. Fig. 6 showed the result of de-NOx efficiency over V(14)-W(10) catalyst under

condition of the sulfur dioxide(SO<sub>2</sub>) content increased to 200ppm of simulated gas. It was reduced by about 5% compared to the de-NOx efficiency under condition of 5 ppm SO<sub>2</sub>, but recovered to nearly equivalent levels at high temperatures of 200°C.

Therefore, it was considered possible to maintain sulfur resistance by controlling the amount of tungsten addition and to be very effective attempt.

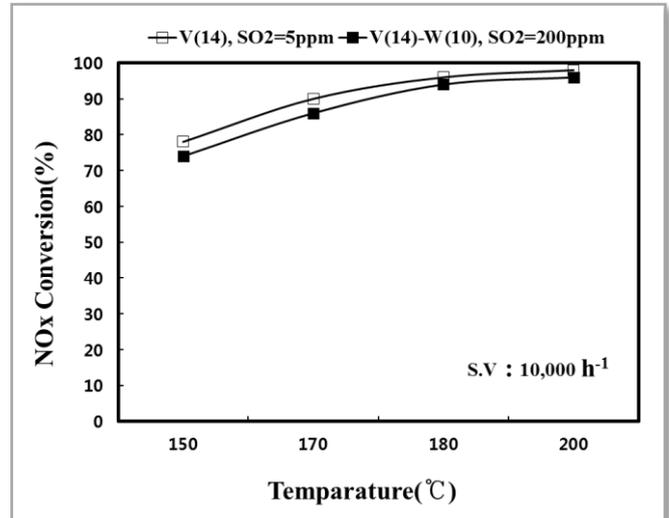


Fig. 6. The effect of sulfur on NOx conversion over V(14) and V(14)-W(10) catalyst

In Fig. 7, for V (10)-W (14) catalyst, the change in de-NOx efficiency over run time was measured for 10 days under conditions of 200 ppm SO<sub>2</sub>. By about a week, de-NOx efficiency had gradually decreased, with a decrease rate of about 10.4% (95.8% → 85.4%), but remained almost unchanged from 7 days until 10 days

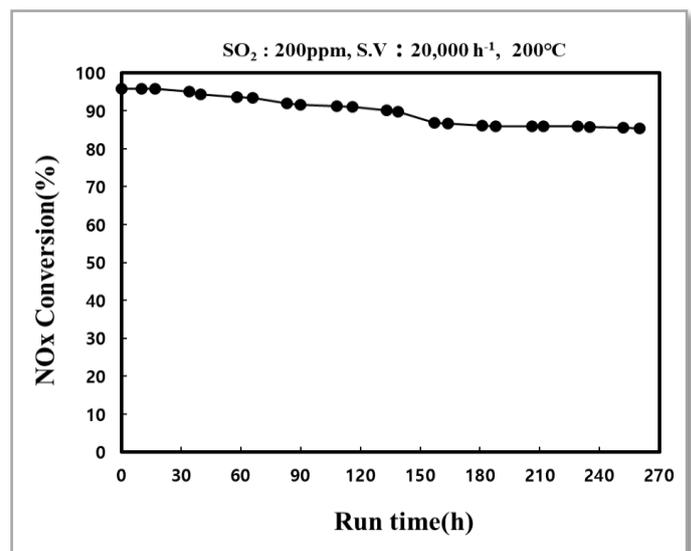


Fig. 7. Durability to sulfur as run time increases over V(14)-W(10) catalyst

### III.III The result of physical characteristics analysis

XRF analysis was conducted to check the difference between the amount of vanadium put into slurry mixing solution and the content of vanadium impregnated in calcined slurry. As shown in **Table 3**, minor differences were identified between each other, confirming that calcined slurry was manufactured to meet the target value of vanadium impregnated content.

**Table 3.** XRF analysis results

	V(8)	V(11)	V(14)	V(16)	V(18)	V(20)	V(14)-W(10)
V <sub>2</sub> O <sub>5</sub> (%)	8.8	12.2	14.5	16.7	18.4	21.1	12.7
TiO <sub>2</sub> (%)	89.3	85.8	83.5	81.8	79.2	76.4	69.8
WO <sub>3</sub> (%)	-	-	-	-	-	-	13.1

EDX analysis was performed to analyze the surface composition of the catalyst manufactured according to vanadium content, and the results are shown in **Table 4**.

Due to little difference from the XRF results, vanadium was thought to be uniformly impregnated inside micro-pores and over the surfaces of the catalyst

**Table 4.** EDX analysis results

	V(8)	V(11)	V(14)	V(16)	V(18)	V(20)	V(14)-W(10)
V (%)	7.64	10.74	12.79	13.76	16.19	18.53	11.13
Ti (%)	92.36	89.26	87.21	86.24	83.81	81.47	74.73
W (%)	-	-	-	-	-	-	14.13

As is shown in **Table 5**, specific-surface area and pore volume tended to decrease as vanadium content increased, and it was considered that the association with de-NO<sub>x</sub> efficiency was not apparent.

**Table 5.** BET analysis results

	V(8)	V(11)	V(14)	V(16)	V(18)	V(20)	V(14)-W(10)
BET surface area (m <sup>2</sup> g <sup>-1</sup> )	34.12	31.17	27.40	23.93	18.23	19.70	19.51
Avg. pore width (nm)	20.75	19.34	18.22	14.00	14.26	14.28	13.73
Pore Volume (cm <sup>3</sup> g <sup>-1</sup> )	0.167	0.151	0.125	0.084	0.065	0.070	0.108

#### IV. CONCLUSION

In this work, the following conclusions were reached by identifying the physical characteristics and de-NO<sub>x</sub> efficiency under condition of temperature and space velocity of exhaust gas in coal-fired power plant for catalysts manufactured by the changes of vanadium content on metal corrugated supports.

1. De-NO<sub>x</sub> efficiency tended to increase with higher temperatures and increased in vanadium content from 8wt% to 14wt% and a decreased in vanadium content from 16wt% to 20wt%. Thus, the maximum value of de-NO<sub>x</sub> efficiency was at 14wt% vanadium content, 90% at 180 °C and 96% at 200 °C
2. It was considered possible to maintain sulfur resistance by controlling the amount of tungsten addition and also to be very effective attempt.
3. As a result of this study, it was fully confirmed its applicability as a low-temperature de-NO<sub>x</sub> catalyst at the rear of the coal-fired power plant by changing the amount of vanadium impregnation

#### ACKNOWLEDGEMENT

This work was supported by Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korean government (MOTIE) (20193410100050, development of new process for low temperature denitrification from coal combustion exhaust gas treatment).

#### REFERENCES

- [1] S. H. Moon, 1999, "A Study on the Catalyst Development for NO<sub>x</sub> Reduction from the Flue Gas of Thermal Power Plant", *J. of KESS*, 21(2), pp 399-408.
- [2] S. M. Palash, M. A. Kalam, H. H. Masjuki, B. M. Masum, I.M. Rizwanul Fattah, and M. Mofijur, 2013, "Impacts of biodiesel combustion on NO<sub>x</sub> emissions and their reduction approaches, *Renewable and Sustainable Energy*", 23, pp 473-490.
- [3] G. J. Song, Y. H. Moon, J. H. Joo, A. Y. Lee, and J. B. Lee, 2018, "SP, PM<sub>10</sub> and PM<sub>2.5</sub> Emission Characteristics in a Coal-fired Power Plant", *JEAHT*, 21(1), pp 52-60.
- [4] M. Gauss, I. S. A. Isaksen, D. S. Lee, and O. A. Søvde, 2006, "Impact of aircraft NO<sub>x</sub> emissions on the atmosphere – tradeoffs to reduce the impact", *Atmos. Chem. Phys.* 6, pp 1529-1548.
- [5] I. Y. Lee, D. W. Kim, J. B. Lee, H. M. Eum and I. S. Nam, 2000, "Long Term Stability of Extruded SCR (Selective Catalytic Reduction) Catalyst for the Reduction of NO<sub>x</sub>", *J. of KESS*, 22(8), pp 1467-1474.
- [6] J.M. Garc'ia-Cortés, J. Pérez-Ram'irez, M. J. Illán-Gómez, F. Kapteijn, J. A. Moulijn, and C. Salinas-Mart'inez de Lecea, 2001, *Appl. Catal. B* 30, pp 399-408.
- [7] S. C. Hong and D. W. Kwon, 2016, "Selective Catalytic Reduction (SCR) Technology Trends for the Nitrogen Oxide Removal of Exhaust Gas, *Prospectives of Industrial Chemistry*", 19(5), pp 12-24.
- [8] K. J. Seong and C. S. Lee, 2017, "Operation and Improvement Cases of FGD Non-leakage Type Gas-Gas Heater (GGH) for Coal Fired Power Plants", *J. Korean Soc. Combust*, 22(4), pp 35-42.
- [9] Zhen Li, Jingkun Jiang, Zizhen Ma, Oscar A. Fajardo, Jianguo Deng, and Lei Duan, 2017, "Influence of flue gas desulfurization (FGD) installations on emission characteristics of PM<sub>2.5</sub> from coal-fired power plants equipped with selective catalytic reduction (SCR), *Environmental Pollution*", 230, pp 655-662
- [10] Isabella, N., Lorenzo, D., Luca, L., Elio, G. and Pio, F., 2001, "Study of thermal deactivation of a de-NO<sub>x</sub> commercial catalyst", *Appl. Catal., B : Environmental*, 35(1), pp 31-42.
- [11] K. H. Park, and W. S. Cha, 2012, "Effect of Vanadium Oxide Loading on SCR Activity and SO<sub>2</sub> Resistance over TiO<sub>2</sub>-Supported V<sub>2</sub>O<sub>5</sub> Commercial De-NO<sub>x</sub> Catalysts", *Appl. Chem. Eng.*, 23(5), pp 485-489.
- [12] Lee, S. J., and Hong, S. C., 2008, "Deactivation and Regeneration of a Used De-NO<sub>x</sub> SCR Catalyst for Wastes Incinerator", *J. Korean Ind. Eng. Chem.*, 19(3), pp 259-263.
- [13] A. Stahl, Zhong Wang, T. Schwämmle, J. Ke, and X. Li, 2019, "Novel Fe-W-Ce Mixed Oxide for the Selective Catalytic Reduction of NO<sub>x</sub> with NH<sub>3</sub> at Low Temperatures", *Catalysts*, 7(2), pp 71.
- [14] J. O. Lee, D. H. Lee, Y. H. Song, D. K. Oh and J. W. Seo, 2013, "Study for SCR Catalyst Reduction in Fast SCR Using Oxidation Catalyst", *Appl. Chem. Eng.*, 24(3), pp 333-336.
- [15] Ha, J. W., and Choi, J. H., 2014, "The Effect of SO<sub>2</sub> and H<sub>2</sub>O on the NO Reduction of V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>/SiC Catalytic Filter", *Korean Chem. Eng. Res.*, 54(5), pp 688-693.
- [16] Ha, H. P., Maddigapu, P. R., Pullur, A. K., Lee, K. J., and Jung, S. H., 2008, "SO<sub>2</sub> resistant antimony promoted V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst for NH<sub>3</sub>-SCR of NO<sub>x</sub> at low temperatures", *Appl. Catal. B*, 78, pp 301-308.
- [17] Shin, B. K., Kim, J. H., Yoon, S. H., Lee, H. S., Shin, D. W., and Min, W. S., 2011, "Preparation and Thermal Degradation Behavior of WO<sub>3</sub>-TiO<sub>2</sub> Catalyst for Selective Catalytic Reduction of NO<sub>x</sub>, *Kor. J. Met. Mater.*, 49(8), pp 596-600.
- [18] Jie Zhang, Xiang cheng Li,\* Pingan Chen, and Boquan Zhu, 2018, "Research Status and Prospect on Vanadium-Based Catalysts for NH<sub>3</sub>-SCR Denitration", *Materials*, 11(9), pp 1632.
- [19] Chuanmin Chen, Yue Cao, Songtao Liu, Jianmeng Chen, and Wenbo Jia, 2018, "Review on the latest developments in modified vanadium-titanium-based SCR catalysts", *Chinese Journal of Catalysis*, 39(8), pp 1347-1365.