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Improvement of sulfur resistance for SCR catalyst at low temperature by HY-Zeolite mixing

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For the purpose of developing an SCR catalyst with excellent sulfur resistance at low temperature, vanadia-tungsta catalyst supported on titania (VWTi) has been prepared and then physically mixed with HY-Zeolite. Before mixing HY-Zeolite, VWTi catalysts are prepared by changing the content of V to 5 wt%, 10 wt%, 14 wt% and 18 wt% with 7.7 wt% of W to identify the optimal NO removal performance. The catalyst with 14 wt% of V(VWC) showed the highest NO removal performance. Therefore, physical mixtures of VWC and HY-Zeolite are prepared by mechanical mixing in a ball mill. The mass ratios of VWC and HY-Zeolite in the mixture are 1:0.5, 1:1 and 1:2. The sulfur resistance experiment over the above catalysts is carried out for10 h under SO_2 exposure and characteristics were also analyzed by BET, XRF, SEM and abrasion resistance is measured using jet erosion tester. It is found that the sulfur resistance increased until the mixing ratio of HY-Zeolite and VWC is equal but decreased slightly when the mixing ratio of HY-zeolite doubled. From these results, it is confirmed that it is necessary to select an appropriate mixing ratio in consideration of the sulfur resistance and material cost.

Keywords: HY-Zeolite, NO removal, SCR Catalyst, Sulfur resistance, Vanadia-tungsta catalyst

Nitrogen oxides (NOx: NO, NO_2, N_2O etc.) are representative air pollutants along with sulfur oxides (SOx), carbon monoxide (CO) and volatile organic compounds (VOC) and are generated from fossil fuels used in stationary sources (power plants, incinerators, industrial boilers etc.) and mobile sources (ships, automobile, motorcycles etc.).

Such NOx can cause acid rain, ozone layer destruction and photochemical smog and not only causes various environmental problems but also has a fatal effect on the human body. Nevertheless, NOx can be efficiently removed from exhaust gases by implementing selective catalytic reduction with NH_3 (NH_3-SCR)[1-3]. Meanwhile, SOx, which is emitted in large quantities during processes such as sintering, coking, and rolling in steel mills, is very harmful to catalyst activity. In particular, sulfur trioxide (SO_3) formed by the oxidation of sulfur dioxide (SO_2) reacts with ammonia (NH_3) at low temperatures below 200°C to produce ammonium bisulfate (ABS). This condensed liquid ABS deposited on the catalyst's surface can physically block the pores in the catalyst, degrading the NO removal performance[4-9].

The V_2O_5-WO_3/TiO_2 catalyst is widely used in NH_3-SCR processes due to its high catalytic efficiency, thermal stability and reasonable resistance to sulfur[10-14]. However, when restarting due to maintenance or defects in stationary source such as power plants, NOx generated in the low temperature range (180°C~250°C) is not removed and is directly emitted into the atmosphere because of the low efficiency of the SCR catalyst[15].

Thus, a reheating system is essential to achieve the optimum catalytic efficiency to meet stringent NOx regulations, but the additional energy input increases operating costs.

In this study, an SCR catalyst with excellent NO removal performance and sulfur resistance was attempted to develop at low temperatures. The V_2O_5-WO_3/TiO_2 catalysts were prepared by changing the content of V to 5 wt%, 10 wt%, 14 wt% and18 wt% and the content of W was kept constant at 7.7 wt%[10,16]. The catalyst (VWC) with V of 14 wt% showed the highest NO removal performance and was mixed with HY-Zeolite by mechanical mixing in a ball mill. The mass ratios of VWC and HY-Zeolite in the mixture were 1:0.5, 1:1, and 1:2.

This physical mixing effect of HY zeolite is found to effectively capture liquid ABS in the micropores of the catalyst and protect most of the V sites from deactivation by ABS, which can be explained by the stable NO removal performance for10hours under

SO_2 exposure at 200°C. It was considered that physical mixing is a cost-effective approach and practical solution that can be easily applied to the industry.

Experimental Section

Preparation of Catalyst and mixing with HY-Zeolite

The substrate used in this experiment is Metal Corrugated Type (200cpsi, YIDA Co., Ltd. In China) and slurry consisted of TiO_2 (99%, Cristal Global Co. Ltd., Saudi Arabia), V_2O_5 precursor (99%, Daejung Chemical Co. Ltd., Korea),WO_3 (99%, Sigma-Aldrich Co. Ltd., Germany), dispersive agent (83%, BASF Co. Ltd., Germany), binder Silica sol 30% solution (99%, S-Chemtech.Co. Ltd., Korea), HY-Zeolite (Zr Catalyst Co., Ltd. China), and distilled water. Vanadium precursor solutions were prepared by adding ammonium metavanadate (99%, Daejung Chemical Co. Ltd., Korea) dissolved in monoethanolamine (99%, Daejung Chemical Co. Ltd., Korea).

The slurry was synthesized by the wet impregnation method. First, WO_3 was dissolved in distilled water, then V_2O_5 precursor was dissolved and stirred for 1 h. TiO_2 was added and stirred for 30 min. The dispersant was then added and stirred for 30 min. The slurry was calcined at 450°C for 4 h. After calcination, the slurry was finely ground and mixed with HY-Zeolite in the ratio of 1:0.5, 1:1, 1:2, and ball milled for 24 h. Binder was added after ball milling to complete the slurry. The slurry was wash-coated on the substrate (Metal Corrugated Type 200 cpsi 3 × 3 × 3 cm) in the conventional manner. The catalysts were calcined at 450°C for 4 h. The notation of the prepared catalysts is shown in Table 1.

Characterization of catalyst

The slurry was calcined into the powder form at the same time as it was coated on the substrate. Specific surface area and pore size distribution were measured by BET (Brunauer Emmett Teller, TriStar II3020, Micromeritics Co., Ltd. In USA).The constituent elements were analyzed by XRF (X-ray Fluorescence, ZSX Primus IV, Rigaku Co. Ltd., Japan). The surface composition was analyzed by SEM (Scanning Electron Microscope, EX-250, Horiba Co., Ltd. In UK). To determine the adhesion of the coated catalytic materials to the metal substrate, the airjeterosiontest of the catalyst was also performed.

Table 1 — Notation of prepared catalysts

Catalyst notation	Conditions
VWA	V_2O_5 5 wt%, WO_3 7.7 wt%
VWB	V_2O_5 10wt%, WO_3 7.7 wt%
VWC	$V_2O_5$14 wt%, WO_3 7.7 wt%
VWD	V_2O_5 18 wt%, WO_3 7.7 wt%
VWCZ-1:0.5	VWC :HY- Zeolite,1:0.5
VWCZ-1:1	VWC :HY-Zeolite,1:1
VWCZ-1:2	VWC :HY-Zeolite,1:2

Experimental conditions of the NO removal performance

The NO removal performance experiment unit is a continuous flow fixed-bed reactor under atmospheric pressure. It is configured as shown in Fig. 1. The flow rate of all gases into the reactor was controlled by MFC (Mass Flow Controller, SMTEK Co. Ltd., Korea). The temperature of the mixing tank and the reactor was controlled at 200℃ using the PID controller. The composition of the gas was measured using a Gas Analyzer (NOVA 9K, MRU Co. Ltd., Germany). Using MFC, NO gas (20%, in N_2 Sung Kang specialty gas, Korea) was introduced into the reactor at 50 ppm (v/v), and NH_3 gas (10%, in N_2 Sung Kang specialty gas, Korea) was introduced at the same concentration as NO. The concentration of SO_2 gas (2%, in N_2 Sung Kang specialty gas, Korea) was at 200 ppm, and that of O_2 gas (99.9%, Sung Kang specialty gas, Korea) was maintained at 4%.N_2 gas (99.9%, Sung Kang specialty gas, Korea) was used to maintain the total flow rate. The space velocity was set to 20,000 hr^{-1} and the temperature was increased at a constant rate. The conditions for measuring NO removal performance are given in the Table 2. The reaction temperature and flow rate were

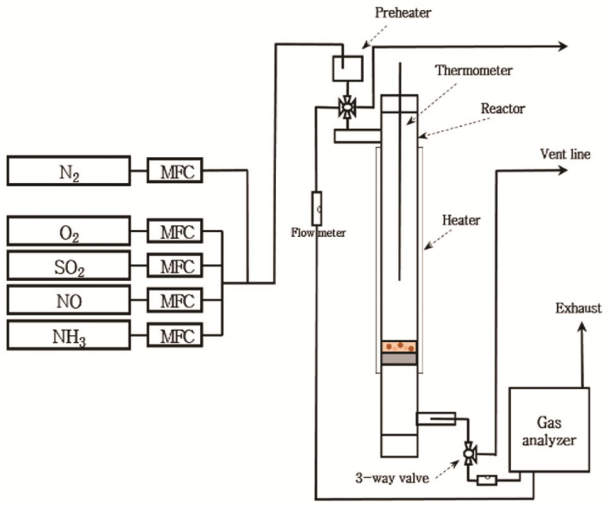

Fig. 1 — Schematic diagram of the NO removal performance experiment unit

stabilized for 30 min before measuring the NO removal performance.

Results and Discussion

NO removal performance

To confirm the NO removal performances, the experiments were conducted at S.V 20,000, 200℃ without the exposure of SO_2.The NO removal performance of the catalysts prepared with various V content is shown in Fig. 2. NO conversion was calculated using the Eq. (1).

$$NO\ conversion(\%) = \left(\frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}}\right) \times 100 \quad \ldots(1)$$

The results for VWA were 93.8%, VWB was 94.6%, VWC was 98.2%, and VWD was 96%, with VWC having the highest NO removal performance. From VWA to VWC, the NO removal performance improved as the V content increased to 14% but that of VWD was worse than VWC.

NO removal performance with the exposure of SO_2

To confirm the effect of SO_2 on the NO removal performance, all prepared catalysts were tested for 10 h of SO_2 200 ppm exposure. The results are shown in Fig. 3.

Table 2 — Experimental conditions

Item	Unit	Condition
S.V	h^{-1}	20,000
Temperature	℃	200
Time	hr	10
NO	ppm	50
O_2	%	4
SO_2	ppm	200
NH_3	ppm	50
N_2	-	Balance

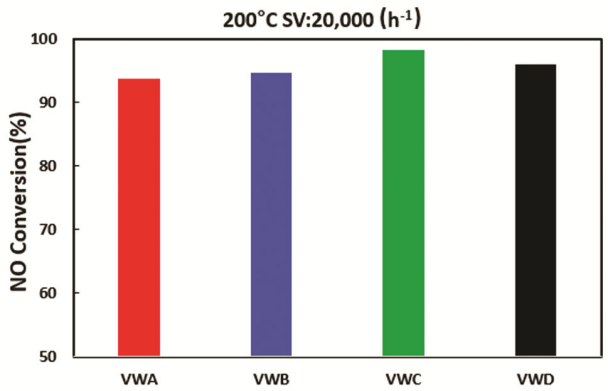

Fig. 2 — Conversion of NO over VWA~VWD

$$NO\ conversion\ reduction(\%) = \left(\frac{[NO]_{no\ SO_2} - [NO]_{after\ 10\ h}}{[NO]_{no\ SO_2}}\right) \times 100 \quad \ldots(2)$$

Eq. (2) was used to calculate the reduction of the NO conversion. Compared with the initial NO removal performance, the NO conversion of VWA decreased by13.2%, VWB by13%, VWC by9.5%, and VWD by10.8%. All catalysts showed the reduction in the NO removal performance of more than 9.5%. It can be seen that VWC has better sulfur resistance and NO removal performance than other catalysts. Therefore, a further experiment of the degradation of the NO removal performance was conducted over catalysts which were prepared by varying the mixing ratio of VWC catalyst and HY-Zeolite.

Effect of HY-Zeolite mixing on the NO removal performance

The initial NO removal performance of catalysts mixed with HY-Zeolite was measured without SO_2. The results are shown in Fig. 4 and were 96.5% for

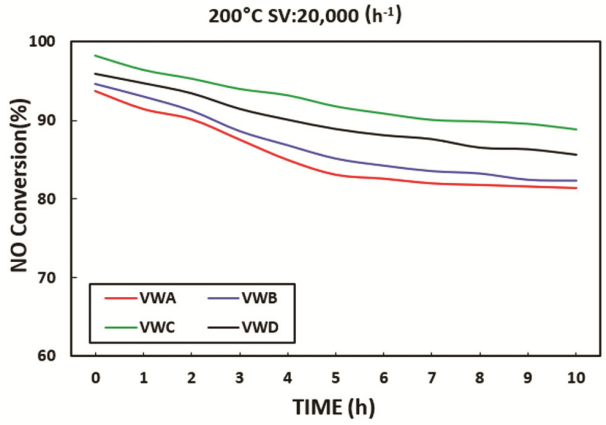

Fig. 3 — Conversion of NO over VWA~VWD for 10 hours under SO_2 exposure

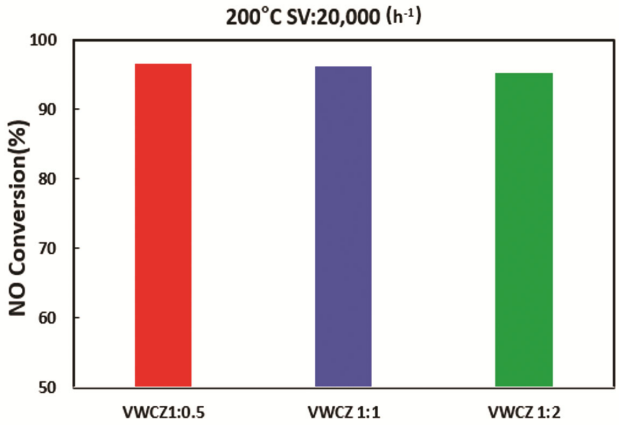

Fig. 4 — Conversion of NO over VWCZ1:0.5~VWCZ1:2

VWCZ-1:0.5, 96.2% for VWCZ-1:1 and 95.2% for VWCZ-1:2. All catalysts prepared by mixing HY-Zeolite had lower NO removal performance than VWC, which is believed to be due to the lower ratio of active components compared with VWC.

To confirm the degradation of the NO removal performance, the experiment was conducted for 10 h under 200 ppm SO_2 exposure. The results are shown in Fig. 5. Compared to the initial NO removal performance without SO_2 exposure, VWCZ-1:0.5 is reduced by 5.41%, VWCZ-1:1 by 1.04%, and VWCZ-1:2 by 1.16%. As the zeolite mixing ratio increased, the specific surface area decreased (Table 3) and the NO removal performance also decreased. Meanwhile, the content of Al_2O and SiO_2, which are the main components of zeolite, increased (Table 4), and the sulfur resistance effect also increased. However, there was little difference between the results of zeolite mixing ratios of 1:1 and 1:2, so it was confirmed that mixing equal amounts of zeolite and catalyst was the optimal mixing ratio under these experimental conditions.

Specific surface area analysis of catalysts

The specific surface area of catalysts mixed with HY-Zeolite measured by BET are shown in Table 3. The result of VWCZ-1:0.5 was 204.4 m^2/g, VWCZ-1:1 was 161.8 m^2/g, and VWCZ-1:2 was 134.6 m^2/g. It was observed that the specific surface area of decreased as the ratio of HY-Zeolite increased. The average pore width of VWCZ-1:0.5 was 5.1 nm, VWCZ-1:1 was 6.2 nm, and VWCZ-1:2 was 7.1 nm. Unlike this, the average pore width increased as the ratio of HY-Zeolite increased. These results are likely due to the mixing of HY-Zeolite with relatively large pores and small specific surface area.

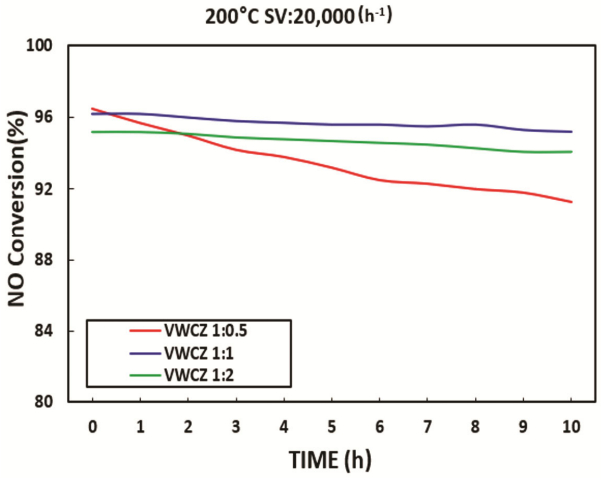

Fig. 5 — Conversion of NO over VWCZ for 10 h under SO_2 exposure

Composition analysis of catalysts

To determine the component content of the prepared catalysts, XRF analysis results are shown in Table 4. After coating on the substrate, the remaining catalyst slurry was calcined for analysis. It was found that the content of active components like V, W and TiO_2 decreased as the percentage of HY-Zeolite increased.

Surface analysis of catalysts

Specific surface area, impurity content, particle size, pore size distribution, and density are known to affect the activity of the catalysts[17]. SEM analysis reveals the particle size and distribution.To observe the surfaces of the prepared catalysts, the magnification was varied to 50 µm and 10 µm. The results are shown in Fig. 6. It can be seen that VWCZ-1:0.5 with more active component has more small particles compared to VWCZ-1:2.

Measurement of abrasion resistance

Particulate matter such as fly ash is generated in steel mills. When the particulate matter collides with the catalyst, the coated slurry is desorbed. It may cause the decrease in the NO removal performance. Therefore, the adhesion of the slurry to the substrate is a major factor in catalyst activity and long-term stability[17]. The erosion rates of the VWCZ-1:0.5, VWCZ-1:1 and VWCZ-1:2 catalysts were measured using the instrument shown in Fig. 7. The

Table 3 — The result of BET analysis

Catalyst	BET Surface area (m^2/g)	Average pore width (nm)
VWCZ-1:0.5	204.4	5.1
VWCZ-1:1	161.8	6.2
VWCZ-1:2	134.6	7.1

Table 4 — XRF analysis results of the prepared catalysts

	VWCZ-1:0.5	VWCZ-1:1	VWCZ-2:1
	wt%	wt%	wt%
Na_2O	0.0767	0.0275	0.0259
Al_2O_3	3.32	2.48	1.97
SiO_2	22.7	17.1	13.4
SO_3	0.105	0.121	0.124
V_2O_5	9.65	10.1	11.6
SnO_2	0.0483	0.0265	0.0358
WO_3	5.23	5.6	6.06
Nb_2O_5	0.133	0.155	0.158
TiO_2	58.4	64.2	66.4

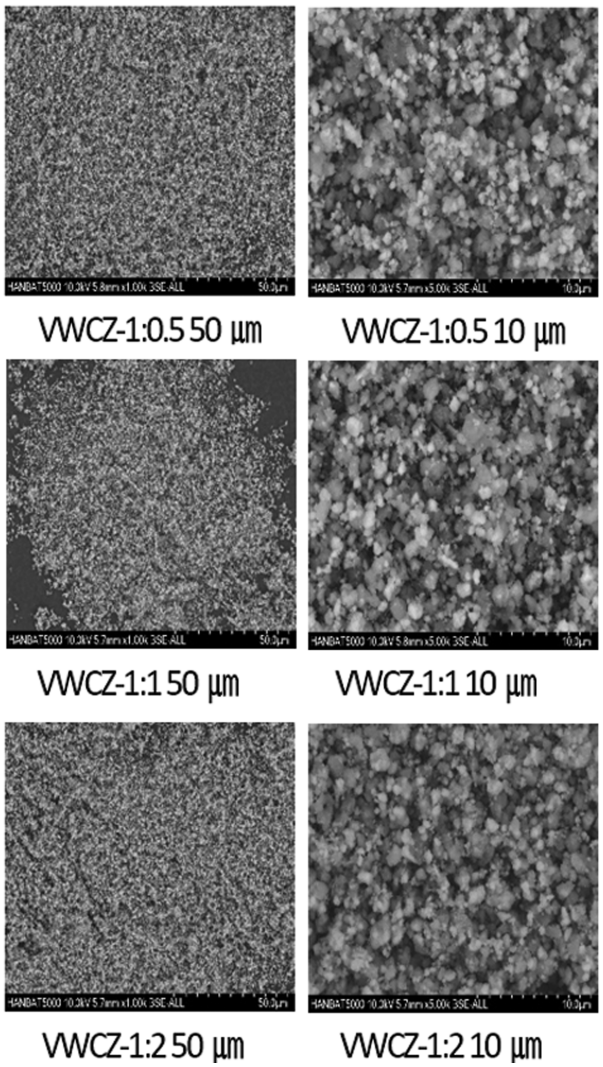

Fig. 6 —SEM images of the prepared catalysts

Fig. 7 — Air jet erosion instrument

Table 5 — Experimental conditions

Abrasive	SiO_2 #6
Linear Velocity	25 m/s
Discharge amount of abrasive	3 kg/h
Test Time	30 min

Table 6 —The result of air jet erosion test

Catalyst	Before weight (g)	After weight (g)	Erosion rate (%)
VWCZ-1:0.5	160.03	156.96	1.92
VWCZ-1:1	159.98	157.42	1.60
VWCZ-1:2	160.09	157.82	1.42

experimental conditions and results are shown in Table 5 and Table 6, respectively. From the calculated erosion rate, it was confirmed that there was almost no difference in adhesion depending on the HY-Zeolite content, and therefore, the amount of binder used when mixing slurry was found to be optimal.

Conclusion

In this study, the catalysts were prepared by physically mixing with HY-Zeolite to improve the sulfur resistance of SCR catalysts in the low temperature region. The initial NO removal performance without SO_2 exposure of VWA was 93.8%, VWB was 94.6%, VWC was 98.2% and VWD was 96%. Compared to this performance, the NOx conversion of VWA decreased by13.2%, VWB by 13%, VWC by 9.5%, and VWD by 10.8%.VWC has the best NO removal performance and sulfur resistance. The catalysts were prepared with different ratio of 14% V and HY-Zeolite, and the experiments were conducted for 10 h with SO_2 exposure. Compared to the NO removal performance without SO_2 exposure, VWCZ-1:0.5 is reduced by 5.41%, VWCZ-1:1 by 1.04%, and VWCZ-1:2 by 1.16%.The degradation of the NO removal performance of the VWC was about 9.5% after 10 h, but the catalysts with HY-Zeolite all showed degradation under 5.41%. It was confirmed that HY-Zeolite improves sulfur resistance. From these results, it was confirmed that it is necessary to select an appropriate mixing ratio in consideration of the sulfur resistance and material cost. BET analysis confirmed that the higher the ratio of HY-Zeolite, the lower the specific surface area and the average pore width increased as the ratio of HY-Zeolite increased. Comparing the initial NO removal performance with the specific surface area, the catalyst with larger specific surface area showed better NO removal performance.VWCZ-1:1 and VWCZ-1:2 had lower initial NO removal

performance than VWCZ-1:0.5, however due to smaller specific area, the sulfur contact area was also small, so the degradation was smaller than VWCZ-1:0.5. XRF analysis confirmed that the catalyst with a high ratio of HY-Zeolite had a relatively low amount of active ingredients. SEM analysis showed that the catalyst with a lower percentage of HY-Zeolite had more small particles. Air jet erosion results showed that there is no difference depending on the content of HY-Zeolite.

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