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Low Temperature Performance and Compressive Strength Characteristics of an Extruded Homogeneous SCR

Choong-Kil Seo*, Kwang-Chul Oh**† and Shin-Han Kim***

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Abstract: The purpose of this study is to identify the low temperature performance and strength characteristics of V-based extruded homogeneous SCR. The extruded catalyst and the coated catalyst showed 50% and 27% of NOx conversion performance respectively at about 210℃ of catalyst temperature, so the extruded SCR was higher in de-NOx performance than the coated SCR especially at a low temperature zone. The compressive strength of the Enhanced Extrusion #1, in which the content of promoters such as silica, clay, glass fiber and binder was optimized, was a 120% improvement compared to the Extrusion#1 catalyst, higher than the coated SCR.

Key Words : Diesel engine, NOx, SCR, Extrusion, Coating, V_2O_5, Strength

1. Introduction

The emission regulations for diesel automobiles are becoming still stricter. For a diesel engine, there is some difficulty in reducing both PM and NOx simultaneously due to its combustion method, and various post-treatment technologies for each exhaust gas have been developed and applied. For a PM (Particulate Matter), a DPF (Diesel Particulate Filter) device has been already installed after Euro-4 to meet the emission regulations. However, for a nitrogen oxide (NOx), various technologies, such as EGR (Exhaust Gas Recirculation), LNT (Lean NOx Trap)[1)], SCR (Selective Catalytic Reaction)[2)] and a combination of the mentioned technologies, are being applied. A strong technology to reduce the NOx emitted from a car is urea-SCR. For SCR catalysts, the vanadium (V_2O_5) SCR catalyst, which is excellent in sulfur resistance and is low in price, was most generally used for an initial stationary purpose. The SCR shows a difference in de-NOx performance depending on the temperature of exhaust gas, which is decreasing according to development in regulation modes and engine performances. Accordingly, the demand for the low temperature activity of a nitrogen oxide reducing device is strongly rising[3)].

For SCR catalysts for vehicles, coated catalysts are generally being used, but recently the R&D and commercialization of extruded SCR catalysts are under way because of the demand for enhancement of low temperature activity and the advantage of simplifying the catalyst manufacturing process. The extruded catalyst has an advantage of reducing the volume of SCR catalysts due to an increase in surface area of the reaction according to an increase in the structure or porosity of the wall flow such as

**† Kwang-Chul Oh(corresponding author) : Korea Automotive Technology Institute
E-mail : kcoh@katech.re.kr, Tel : 041-559-3089
* Choong-Kil Seo : Howon university
*** Shin-Han Kim : Ceracom

DPF as well as the reaction on the existing wall surface because the whole substrate is composed of catalysts without inactive parts[4-6]. As kinds of extruded SCR, zeolite and vanadium SCRs have been used, of which the vanadium SCR has an advantage of a high NOx conversion rate at a low temperature but has a disadvantage that vanadium melts at 690℃. Therefore, the calcination temperature for production of extruded SCR is low to reduce its strength, so the research to improve the low temperature performance and strength of extruded SCR catalysts is important and meaningful.

The purpose of this study is to investigate the low temperature performance and compressive strength characteristics of extruded SCR.

2. Experimental setup and method

2.1 Catalyst preparation and characteristics

The extruded SCR manufactured in this study is a vanadium-based V_2O_5-WO_3/TiO_2 catalyst for diesel engines. The coated catalyst should go through complicated processes such as a process to make a substrate, a process to coat a substrate with catalysts and a process to calcinate it finally. On the contrary, the process to produce a extruded SCR catalyst gone through a process of mixing, extruding, drying and calcinating the raw material store in force the strength of substrates for the raw material of catalysts, to be economical.

The extruded SCR used for this study was manufactured as follows: Put a support TiO_2 into an aqueous solution, stir it, put the designated precursor NH_4VO_3 and ammonium paratungstate into it, and mix it. The SCR was manufactured through drying (110℃, 12h) and calcination (400℃, 5.5h), and the details of catalyst manufacturing cannot be provided due to the security for the company. The Brunauer-Emmett-Teller (BET) method was used to measure the specific surface areas, pore volumes and pore size distributions of the catalyst samples (ASAP 2020, Micromeritics). Before the measurements, all of the samples were degassed to 1×10^{-4} Torr. The adsorption isotherms were obtained after degassing the pre-adsorbed hydrogen at 300℃ at 1×10^{-6}Torr for 0.5h. For the catalyst strength test, tester to measure the bending and compressive strength at 3points was used Tinius Olsen(H50K-SUTM).

Table 1 shows the analytical results of SCR samples. The coated and extruded catalysts #1 are vanadium SCR catalysts, and are different in the manufacturing process. The extruded catalysts #1 and #2 are catalysts manufactured through a extrusion process, but are a vanadium SCR manufactured by an impregnation method and a Fe-zeolite catalyst manufactured by a ion exchange method, whose compositions are different.

Table 1 Analysis conditions

SCR sample	Type	BET	CPSI
Comm. extrusion	Vanadia	-	360
Prepared coating	Vanadia	-	320
Comm. coating	Vanadia	89	400
Prepared coating	Vanadia	73.07	240
Extrusion #1	Vanadia	64.80	200
Extrusion #2	Fe-zeolite	248.2	200

2.2 Compression test method

Table 2 shows the specification of SCR catalysts to evaluate the strength of catalysts. In general, the extrusion #2 is larger in size (W*L*H) and thicker in wall thickness than the 2 kinds of SCR catalysts. The calculation of bending strength can be represented with the Equation (1) below, and the SCR catalysts used for this experiment are hollow cores, not solid cores, so it was converted into the area of the red part in figure of Fig. 1, and calculated. The converted cross-sectional area of the compressive strength used the area cut in the longitudinal direction.

$$\sigma_b = \frac{3pl}{2bt^2} \quad (1)$$

Bending strength σ_b, load P (kgf), width b (mm), thickness t (mm), distance between nodes l (mm)

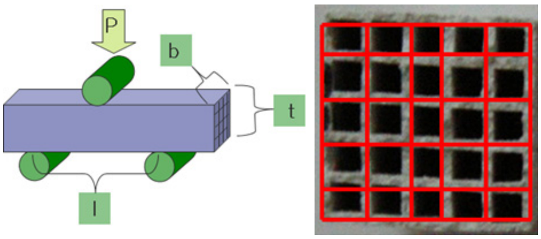

Fig. 1 Calculation of the three-point bending strength

Table 2 Catalyst specification for evaluating strength

SCR	Comm. coating	Coating	Extrusion #1	Extrusion #2
W*L*H (mm)	4.35*4.35*6.3	5.3*5.3*6.1	5.5*5.5*6.62	6.5*6.5*6.28
Wall thick. (mm)	0.212	0.336	0.305	0.462
Sectional area(mm^2)	5.34	8.20	8.08	11.61

Fig. 2 shows the shape and cross section of the 3*3 cells of SCR catalysts to measure the strength of extruded catalysts compared to coated catalysts. The cell density and wall thickness of each sample are different from each other, but an average value of 5 measurements at different locations was used to minimize errors in measurements. In Fig. 2, it can be seen that the wall of the coated SCR was coated with washcoat, and that the corner part of the wall was coated a little thicker. It can be seen that the extruded #1 and 2 were manufactured in an extrusion type, so the wall was not coated. The thicknesses of the wall was in the order of Extruded #2 > Coating > Extruded #1 > Commercial coating.

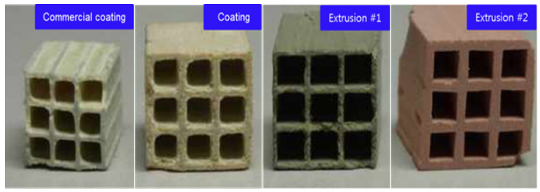

Fig. 2 Photo of SCR catalyst for evaluating strength (three type of SCR (3*3 cell)

3. Experimental results and discussion

3.1 Enhancement of low temperature performance of an extruded SCR

Fig. 3 shows the de-NOx performance depending on a change in the space velocity of the commercial extruded (vanadium) and coated SCR catalyst (vanadium) whose surface area ratios are relatively similar. For SV 20,000 h^{-1}, the extruded and the coated SCR catalysts show 50% and 27% of NOx conversion performance respectively at an about 210℃ of catalyst temperature. They show 87% and 76% respectively at 350℃ of catalyst temperature, and the extruded SCR was higher in the de-NOx performance than the coated SCR especially at a low temperature zone. The NOx conversion performance dropped more as the SV increased

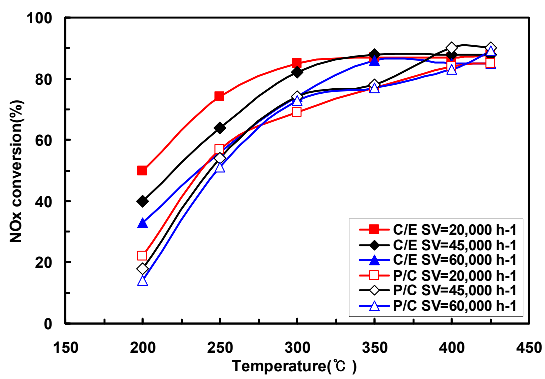

Fig. 3 Enhanced low temperature performance of extrusion SCR compared to coating SCR (NH3/NOx=1.0)

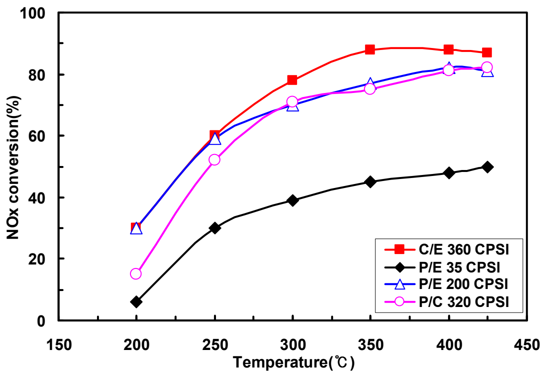

Fig. 4 NOx conversion according to CPSI of extrusion SCR compared to coating SCR

more, because the reaction time shortened according to an increase in flow speed in a catalyst during a series of processes such as adsorption, reaction and desorption of NOx.

Fig. 4 shows the NOx conversion rate depending on CPSI of an extruded SCR compared to a coated SCR. Extrusion #1 (35 CPSI) shows the lowest NOx conversion rate compared to other SCR, because a less amount of catalysts are extruded due to a small CPSI. Extrusion #1 (200 CPSI) shows 10-13% higher NOx conversion rate at below 250℃ of catalyst temperature compared to the coated catalyst (320 CPSI), and the same level of NOx conversion performance at higher than 250℃. The overall trend, the NOx conversion of commercial extrusion SCR (360 CPSI) was higher than the prepared coating SCR (320 CPSI) of the same level. The reason is because the substrate itself of extrusion SCR was composed of the catalyst materials with higher active area.

3.2 Compressive strength characteristics of a extruded SCR catalyst

The vehicles should also secure the strength of post-treatment catalysts due to the rotations and vibrations in many directions that occur during a drive. The extruded catalysts were weak in mechanical strength in the past to be less frequently used in vehicles, but have recently overcome the weakness in mechanical strength due to development in the canning and material technology to be commercialized in cars, so a research on this should be continued. The calcination temperature for a vanadium-based extruded SCR is less than the substrate calcination temperature for a coated SCR because vanadium melts at about 690℃. Accordingly, the compressive strength of an extruded SCR can be lower than the existing SCR coated on a ceramic structure.

Fig. 5 shows a photograph after a 3point bending strength test of SCR catalysts. For every SCR catalyst, fracture and destruction are realized at the central point to which bending was applied. The Fe-zeolite SCR of Extrusion #2 was highest in bending strength.

Fig. 6 shows the behavior of the 3point bending strength of the Extrusion #1 SCR. When a bending load was applied to a SCR catalyst, 1st fracture happened about 85 seconds later and 2nd fracture happened about 116 seconds later. When a 2.5kg_f load was applied, 3rd fracture happened about 128 seconds later, and the catalyst samples was destroyed at 150 seconds.

Fig. 7 shows the loads depending on the displacement of catalyst samples for 3 kinds of SCR. The commercial coating and Extrusion #1 SCR catalysts was destroyed at a 0.3mm displacement, and when a 17 and 4 kg_f load is applied, a 0.3mm displacement happens, so the commercial coating is larger in bending strength. On the contrary, the Extrusion#1 catalyst is destroyed when a 4kg_f bending load is applied, and is weakest in bending strength. The coated SCR samples was destroyed at a 0.4mm displacement when a about 7kg_f bending load was applied, and was better in expansion property compared to other catalyst samples.

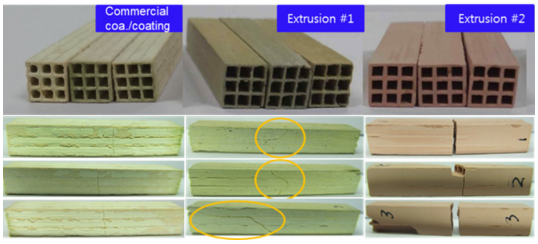

Fig. 5 Photo after the three-point bending strength test

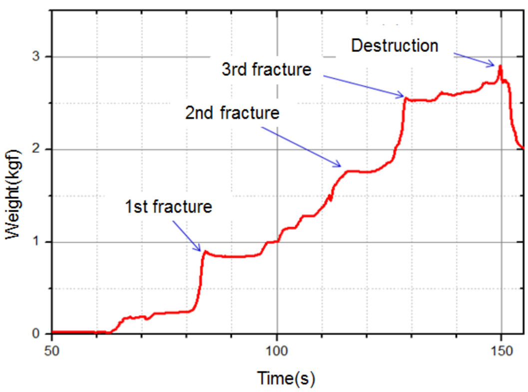

Fig. 6 Behavior of the 3 point bending strength of Extrusion #1

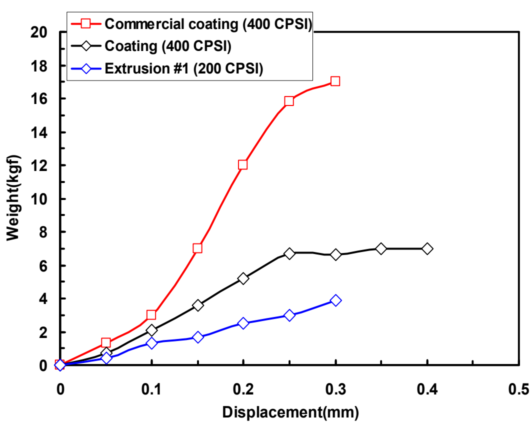

Fig. 7 Displacement according to load changes (displacement 5mm/min)

Fig. 8 shows the compressive strength of various kinds of SCR catalysts at the peak load where the material is destroyed, and for the size of specimens

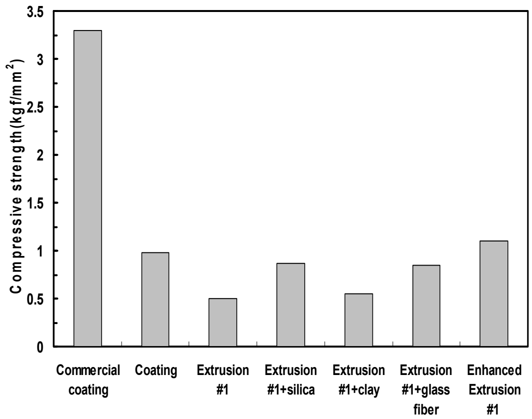

Fig. 8 Compressive strength of several type of SCR at maximum load

used in the test, the displacement of a compressive strength tester was set to 5mm/min. The compressive strength of the commercial coating (400 CPSI) SCR was about 3.3 kgf/mm^2, the biggest, and the compressive strength of the Coating (240CPSI) and Extrusion #1 (200CPSI) SCR catalyst was 1 and 0.5kg$_f$/mm^2 respectively. In general, the compressive strengths are in the order of Commercial coating>Coating>Extrusion #1, and the Extrusion #1 is about 6.5 times smaller than the commercial coating SCR actually applied to cars, and about 2 times smaller than the Coating SCR. This is because since vanadium melts at about 690℃, the vanadium extruded SCR is calcinated at a temperature lower than this for manufacturing. The coated SCR, in which a substrate is calcinated and manufactured and then the surface of the substrate is coated with a catalyst, can raise the strength of the substrate by raising the firing temperature of the substrate. On the contrary, the extruded SCR was made by a simple process in which a catalyst substance plays two roles of a substrate and a catalyst, and the thickness of the substance composing a catalyst was relatively thin, so its compressive strength was lower than the coated SCR. The compressive strength of the Extrusion #1 was about 6.5 times smaller than the commercial coating SCR actually applied to vehicles, and about 2 times smaller than the coated SCR. The Extrusion #1+silica SCR, changing the content of silica in the Extrusion #1 to overcome this, was improved to 0.87 kg_f/mm^2 74% in compressive strength. The compressive strength of Extrusion #1+clay was insignificantly improved depending on a change in content of clay. The Extrusion #1+glass fiber SCR catalyst, in which a glass fiber was added to the Extrusion #1, was also improved 70% in compressive strength, and less than 1mm length of glass fiber was used. The compressive strength of the Enhanced Extrusion#1, in which the content of promoters such as silica, clay, glass fiber and binder was optimized, was 1.1kg_f/mm^2, which was improved 120% compared to the Extrusion #1 catalyst, which was higher than the coated SCR. The extruded catalysts have many advantages in economic efficiency and performance if the number of cells (CPSI), catalyst composition, promoters and binders are optimized, to have a bright prospective of commercialization into a catalyst for vehicles, ships and industry in the future.

4. Conclusions

The results of a study on the low temperature performance and compressive strength characteristics of the extruded homogenous SCR catalyst are as follows:

1. The extruded catalyst and the coated catalyst showed 50% and 27% of NOx conversion performance respectively at about 210℃ of catalyst temperature, and 87% and 76% respectively at 350℃ of catalyst temperature.

2. The extruded SCR was higher in de-NOx performance than the coated SCR especially at a low temperature zone.

3. The compressive strength of the Enhanced Extrusion #1, in which the content of promoters such as silica, clay, glass fiber and binder was optimized, was a 120% improvement compared to the Extrusion #1 catalyst, higher than the coated SCR.

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