

Optimum chemical composition of raw catalytic materials for a De-NO_x SCR honeycomb

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The chemical composition of raw materials for a TiO₂- based honeycomb extruded for De-NO_x via selective catalytic reduction (SCR) was optimized in terms of catalytic activity and extrusion formability. The catalytic activity of powder mixtures containing TiO₂, 10 w/o of WO₃, 1-2 w/o of V₂O₅ and 1, 3 and 5 w/o of SO₃ were examined. Various combinations of catalytic materials in the form of either oxide power or precursor dissolvable in an oxalic acid solution were attempted in order to differentiate the effect of homogeneity of catalytic materials while mixing with TiO₂ powder. V₂O₅ powder or ammonium metavanadate (AMV), and WO₃ powder or ammonium metatungstate hydrate (AMT) dissolved in an oxalic acid solution were used as sources of V₂O₅ and WO₃, respectively. The powder mixture containing 1 w/o V₂O₅ and 10 w/o WO₃ obtained from AMV and AMT dissolved in an oxalic acid solution, exhibited more than 90% of De-NO_x activity at temperatures above 300 °C, attributed to the homogeneous dispersion of V₂O₅ in TiO₂ particles due to the complete solubility of AMV in oxalic acid. Increasing the V₂O₅ content from 1 w/o to 2 w/o, and adding 1 w/o of SO₃ in the form of H₂SO₄, while maintaining the WO₃ content at 10 w/o, consequently with a chemical composition of TiO₂/10 w/o WO₃/2 w/o V₂O₅/1 w/o SO₃, showed nearly 100% NO_x reduction in the temperature range of 250 °C to 400 °C. Based on this composition of a catalytic powder mixture, the additives for extrusion forming such as inorganic binder, water, MC, and PEG were also optimized as 8, 40, 3.5 and 3.5 parts, respectively, with respect to the weight of the catalytic powder mixture. The processing developed in this study was applied in manufacturing a large scale commercial SCR honeycomb catalyst with 150 mm × 150 mm × 1,000 mm dimensions.

Key words: De-NO_x SCR, Honeycomb extrusion, Catalytic activity, Optimum SCR composition.

Introduction

The nitrogen oxides (NO_x) contained in the flue gas discharged from coal-fired power plant, chemical plants and municipal incinerators etc. causes a photochemical smog and depletion of ozone layer, and thus has been considered as major air pollutants [1]. Various techniques for reducing NO_x such as direct decomposition, selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) have been developed. However, a lower efficiency and a narrower operation temperature of methods of direct decomposition and SNCR in comparison with SCR resulted in more attention to the SCR technique in the last decades [2, 3].

The De-NO_x process of the SCR technique comprises the direct reaction of NO_x gas with ammonia (NH₃) on the surface of the SCR catalyst at temperature between 250 and 450 °C, producing non-toxic resultants, N₂ and water. The De-NO_x efficiency of SCR is influenced significantly by the type and amount of raw catalytic powder materials

[4]. V₂O₅ and WO₃, MoO₃ and mixtures of V₂O₅/WO₃ have been used as major raw catalytic materials for SCR [4-8]. Amongst many different types of SCR catalysts such as plate type and corrugated shape where the catalytic powder was coated on a metal or fibrous inorganic sheet and a ceramic honeycomb, the monolithic ceramic honeycomb extruded using a raw powder of TiO₂ in which the catalytic materials V₂O₅ and WO₃ were dispersed homogeneously showed a higher activity and chemical stability, and has been most widely commercialized.

In the TiO₂/V₂O₅/WO₃ system, the anatase crystalline TiO₂ powder containing sulfate could show high activity [9]. The acidic properties of TiO₂ strongly depend on the amount of sulfate addition. Lewis acid sites on metal cations generated by sulfation have been confirmed as playing an important role in enhancing the catalytic De-NO_x activity of SCR [14].

It is also necessary to evaluate the effect of the SO₃ content on the formability during extrusion process. This requires to measure the plasticity of the plasticized dough in a quantitative manner. Although some testing methods were previously introduced by authors of this paper [10-13], the techniques have not been yet standardized. Bae and Shin developed a new simple technique which was proved from a scientific point-of-view [15]. Thus the degree of

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Table 1. Properties of TiO₂ for SCR catalyst

Crystalline	Surface area	Mean particle size	SO ₃ content
Anatase	90 m ² /g	1.1 μm	< 2.0 w/o

plasticity for the doughs containing various amount of SO₃ was measured here using the method suggested by Bae and Shin [15] in order to examine the effect of the SO₃ content on the formability of the dough for honeycomb extrusion.

Besides the optimum amounts of V₂O₅ and WO₃ in terms of catalytic activity at various temperatures from 250 °C to 500 °C, the dispersion method of these two catalytic materials into TiO₂ was also examined to confirm whether a better homogeneity in dispersing the materials in TiO₂ could give a higher De-NO_x activity. Thus powder forms of V₂O₅ and WO₃ together with the precursors of V₂O₅ and WO₃ in the form of both ammonium metavanadate (AMV) and ammonium metatungstate hydrate (AMT) dissolved completely in 10% oxalic acid solution were used to alter the dispersion homogeneity.

In this study, the optimum ratio and the method of dispersion of the raw catalytic materials were determined in SCRs containing V₂O₅/WO₃/SO₃/TiO₂ to provide an ideal composition for a commercialized SCR honeycomb.

Experimental

The De-NO_x efficiency was measured in the TiO₂/V₂O₅/WO₃ system depending on the different methods of adding the raw catalytic materials. The characteristics of TiO₂ powder used for this study are presented in Table 1.

Either 1 w/o V₂O₅ powder (Samchun Chem., 99%, Korea) or ammonium metavanadate (AMV: Aldrich Chem. 99%)

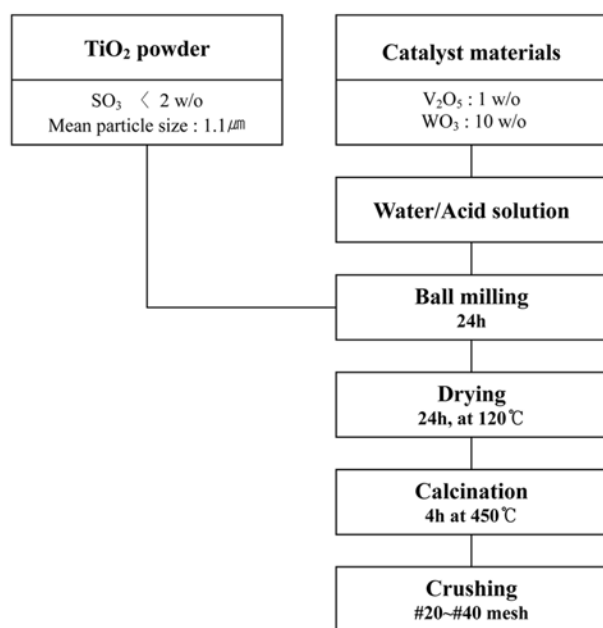
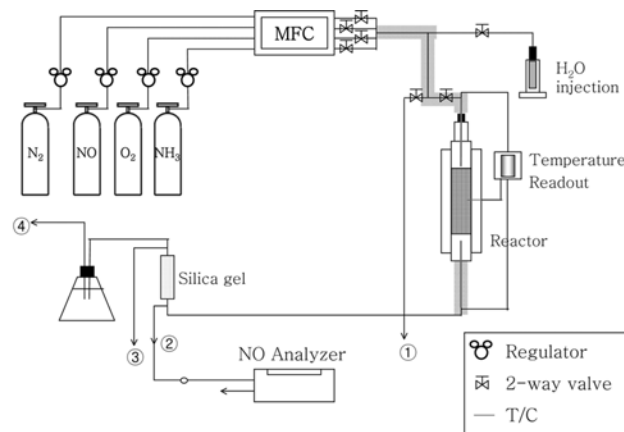
Table 2. Combination of raw materials for SCR catalyst

Catalyst Sample	V ₂ O ₅	AMV	WO ₃	AMT	Oxalic acid
AM-O		○		○	○
AM-W		○		○	
AW-O		○	○		○
AW-W		○	○		
VM-O	○			○	○
VM-W	○			○	
VW-O	○		○		○
VW-W	○		○		

solution was mixed with TiO₂. For the addition of WO₃, either 10 w/o WO₃ powder (Kanto chem. 99%, Japan) or the equivalent amount of ammonium metatungstate hydrate (AMT: Aldrich Chem. 99.99%) solution was mixed with TiO₂. All the weight percentages (w/o) described in this study represent a relative weight of a particular raw material in the resultant oxide form with respect to the total weight of the catalytic powder mixture.

The raw catalytic materials were first dispersed into either water or 10 w/o oxalic acid (Deajung Chem., 99.5%, Korea) solution, then mixed with TiO₂ powder prior to ball milling for 24 hours. The slurry was dried for 24 hours at 120 °C before calcination at 450 °C for 4 hours. The calcined powder was then sieved to produce the catalytic powder mixture (Fig. 1). The addition of catalytic raw materials in the form of either oxide powder or precursor was attempted in various combinations shown in Table 2. In fact, V₂O₅, and AMV were not dissolved in water but dissolved in oxalic acid solution whereas AMT can be dissolved well both in water and the oxalic acid solution, but WO₃ was not dissolved in both solvents. Considering these tendencies of dissolution of raw catalytic materials, the various combinations shown Table 2 were chosen to examine the effect of the degree of homogeneity in the dispersion of raw catalytic materials on the De-NO_x catalytic activity.

Each designation of sample name means that A: ammonium metavanadate (AMV), M: ammonium

**Fig. 1.** Preparation of raw powder mixture for the SCR catalyst.**Fig. 2.** Schematics of micro-reactor for measuring the NO_x removal activity of the catalyst powder.

metatungstate hydrate (AMT), O: oxalic acid solution and W: water. Thus sample AM-O means a slurry of AMV as source of 1 w/o of V_2O_5 and AMT as 10 w/o of WO_3 in the water solution with 10 w/o of oxalic acid, and VW-W means 1 w/o of V_2O_5 , and 10 w/o WO_3 in pure water.

Crushed catalytic powder after calcining was collected from the sieve in between #20 and #40 mesh sieves and then the relative surface areas and the amount of oxides were measured by BET (micromeritics, ASAP 2010) and XRF (Philips, Venus 200), respectively. The De-NOx activity of the resultant powder mixture was measured using the micro-reactor assembled in this study as schematically shown in Fig. 2 under the conditions of a space velocity of $200,000\text{ h}^{-1}$ at a temperature from $250\text{ }^{\circ}\text{C}$ to $450\text{ }^{\circ}\text{C}$ with $50\text{ }^{\circ}\text{C}$ intervals. The rather higher space velocity $200,000\text{ h}^{-1}$ was chosen for ready differentiability of catalytic activity. The input concentration of NO gas was 300 ppm, the ratio of NH_3/NO was 1.0, and the concentration of O_2 was 4%.

H_2SO_4 was used as a source of sulfite in preparing the catalytic powder with SO_3 contents of 1, 3 and 5 w/o. H_2SO_4 solution was added to the WO_3/TiO_2 mixture and then wet ball-milled for 24 hours before drying for 24 hours at $120\text{ }^{\circ}\text{C}$ to yield the $TiO_2/WO_3/SO_3$ system. Again, the ammonium metavanadate dissolved in the oxalic acid solution would be 1 and 2 w/o V_2O_5 prior to ball-milling for 24 hours and subsequent drying at $120\text{ }^{\circ}\text{C}$ for 24 hours. Consequently, the systems of $TiO_2/10\text{ w/o } WO_3/1$ and $2\text{ w/o } V_2O_5/1$, 3 and 5 w/o SO_3 were studied in this investigation.

Figure 3 shows the flow chart for honeycomb extrusion using the raw SCR powder mixture with different sulfite contents. The sulfite-containing raw powder mixture was mixed with 3.5 parts of methyl cellulose as organic binder and 8 parts of glass-fiber as inorganic binder for 40 minutes in the dry state. Then water, PEG and lubricant were added to produce the dough for extrusion in the wet mixer. After twice of kneading using a laboratory scale extruder, the dough was extruded into a honeycomb structure of 35 cell per square inch (cpsi) with $25 \times 25 \times 200\text{ mm}$ dimensions. The green bodies were dried at $70\text{ }^{\circ}\text{C}$ in an oven prior to heat treating at $500\text{ }^{\circ}\text{C}$ for 4 hours.

A modified vicat needle was adopted to evaluate the degree of plasticity of doughs containing 3 different sulfite contents [15]. The catalytic activity for NOx reduction was measured in a micro-reactor for the honeycomb sample with $25 \times 25 \times 100\text{ mm}$ dimensions. The space velocity and reaction temperatures were $5,000\text{ h}^{-1}$ and $200\text{--}450\text{ }^{\circ}\text{C}$, respectively. The concentrations of reactants were 500 ppm NO, 500 ppm NH_3 and 10% O_2 .

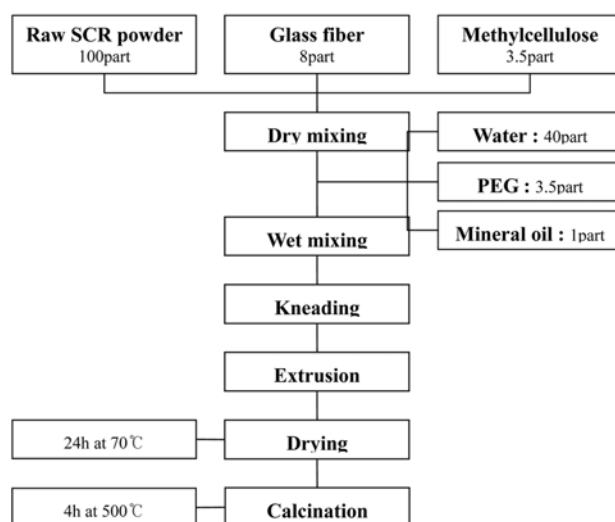


Fig. 3. Flow chart showing the extrusion of honeycomb using the raw SCR powder mixture with various sulfite contents of 1, 3 and 5 w/o.

Results and Discussions

The variation of surface area depending on the dispersion method of the raw catalytic materials is presented in Table 3.

Compared to the surface area of TiO_2 powder, $90\text{ m}^2/\text{g}$, the smaller surface areas of catalytic powder mixtures shown in Table 3 could be attributed to the filling of catalytic materials into the micro-pores existing in the TiO_2 powder. The mixing of catalytic materials dissolved in the oxalic acid solution resulted in a larger surface area in comparison with the mixture obtained from the catalytic materials dispersed in water, representing a more homogeneous dispersion of the oxalic acid solution with the TiO_2 powder. The content of WO_3 in the resultant SCR catalyst powder remained near to 10 w/o. The De-NOx activity of the SCR catalyst powder depending on the dispersion method is presented in Fig. 4.

The difference in the activity depending on the degree of homogeneous dispersion ability of catalytic materials could be more clearly distinguished at lower temperatures such as low as $250\text{ }^{\circ}\text{C}$. For instance in AM-O, the catalytic precursors of AMV and AMT can be completely dissolved in oxalic acid solution whereas V_2O_5 powder remained as particles in the water solution in the VW-O sample. Since the catalytic activity at low temperatures was mainly determined by V_2O_5 , the more homogeneous dispersion of V_2O_5 using the AMV dissolved in the oxalic acid solution for the AM-O sample could contribute to the higher activity at low temperature in comparison with the SCR powder obtained from the V_2O_5 powder dispersed in the water

Table 3. Variation of surface area of SCR catalyst powders

Sample	AM-O	AM-W	AW-O	AW-W	VM-O	VM-W	VW-O	VW-W
Surface area(m^2/g)	82.0	75.9	79.8	77.5	79.2	76.1	81.1	77.9
WO_3 contents(w/o)	9.6	9.7	9.8	9.9	9.7	9.6	9.8	9.9

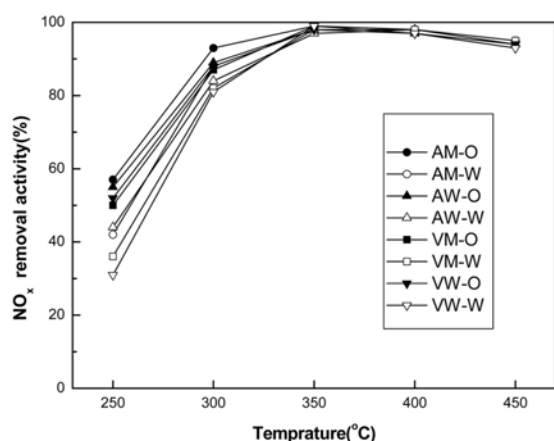


Fig. 4. NO_x removal activity of SCR catalyst powders of the 1 w/o V₂O₅/10 w/o WO₃/TiO₂ system.

solution which consequently led to a less homogeneous dispersion of V₂O₅ when mixed with the TiO₂ powder. On the other hand, the role of WO₃ in preventing oxidation of ammonia and increasing the De-NO_x activity at a high temperature from 300 °C has been reported [16]. All of the samples studied in this investigation showed a De-NO_x activity higher than 90% at temperatures higher than 350 °C, regardless of the types of catalytic materials and solutions. This could be due to the high content of WO₃ controlling the activity at high temperature. In particular, the AM-O sample showed higher than 90% activity at a temperature even at 300 °C, attributed to the better dispersion using the AMT dissolved in the oxalic acid solution. From these results, we assume that the higher the content of V₂O₅ the higher the activity at lower temperature, however, a higher content of V₂O₅ could also lead to the reverse effect of a higher conversion rate of SO₂ to SO₃. Thus, the amount of V₂O₅ was determined as 2 w/o after many trial and error experimentals in terms of high activity at low temperature and less than 1% conversion rate of SO₂ to SO₃. Also 10 w/o of WO₃ could be enough to show activity at high temperature. Thus, 2 w/o V₂O₅/10 w/o WO₃/TiO₂/1, 3 and 5 w/o SO₃ systems were prepared for the final SCR catalyst powder.

The compositions of the three sulfite containing SCR

Table 4. Chemical compositions of sulfite containing SCR catalyst powder and the calcined honeycomb

	Catalyst			Honeycomb		
	AC-1	AC-3	AC-5	AH-1	AH-3	AH-5
TiO ₂	86.62	84.79	83.27	80.92	80.14	79.40
WO ₃	9.61	9.54	9.27	9.17	9.03	8.84
V ₂ O ₅	1.98	1.96	1.98	1.78	1.67	1.60
SO ₃	1.11	3.08	4.92	0.90	2.20	3.39
Others	0.68	0.63	0.56	7.23	6.96	6.77

Designation of sample names, AC-1, 3, and 5 originates from aiming the sulfite contents at 1, 3 and 5 w/o, respectively, and accordingly the calcined honeycomb using the three different catalytic powders have the names AH-1, 3 and 5.

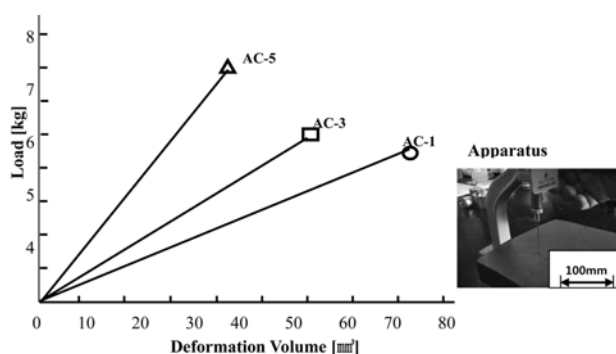


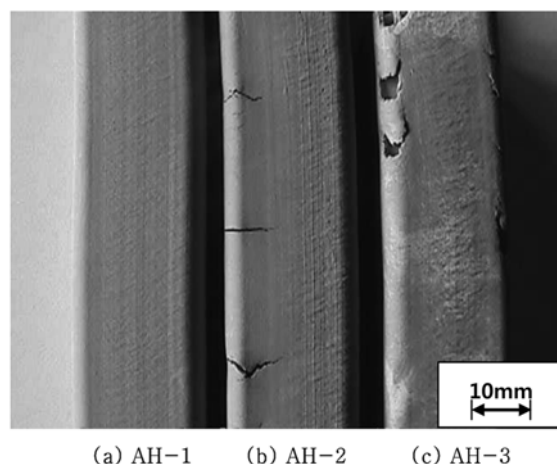
Fig. 5. Effect of the sulfite contents on plasticity of the dough measured by a modified vicat needle [15].

powder and the sintered honeycomb were characterized by XRF as shown in Table 4. The amount of sulfite, SO₃, for the sulfite-containing catalyst powder mixtures were 1.11, 3.08 and 4.92 w/o, respectively, and after calcining the honeycomb, the sulfite contents were reduced to 0.90, 2.20 and 3.40 w/o, respectively. The relative amounts of other chemicals including Al₂O₃, SiO₂ and MgO were increased in the calcined honeycomb. This could be attributed to evaporation of SO₃ during calcining, and the addition of extrusion additives such as the inorganic binder.

The degree of plasticity of the dough depending on the sulfite content is shown in Fig. 5. The higher the sulfite content, the poorer the formability (Fig. 5). The steeper the slope the larger the stress required for extrusion forming. AC-1 exhibited the lowest slope amongst the 3 doughs and consequently better plasticity.

The formability of dried honeycombs extruded from the 3 doughs containing different SO₃ contents are presented in Fig. 6. As expected from the previous plasticity results, both the AH-3 and AH-5 compositions required a higher load for the same depth of deformation in comparison with that of the AH-1 honeycomb. Thus, these two compositions were failed in extruding defect-free 35 cpsi green bodies.

The De-NO_x catalytic activity was measured for the calcined honeycomb samples with different sulfite contents



(a) AH-1 (b) AH-2 (c) AH-3

Fig. 6. Photograph of dried honeycomb samples with different sulfite contents.

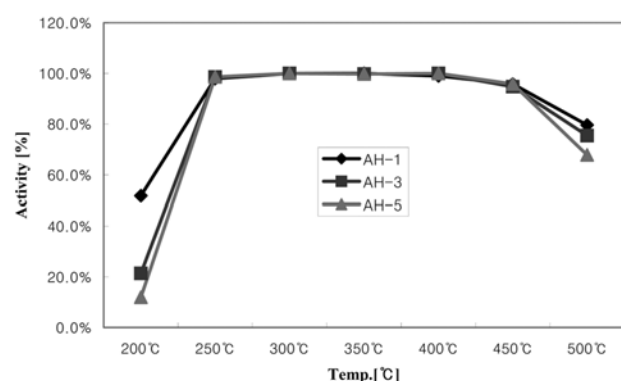


Fig. 7. De-NOx catalytic activities of $\text{TiO}_2/\text{WO}_3/\text{V}_2\text{O}_5/\text{SO}_3$ system as a function of sulfite contents.

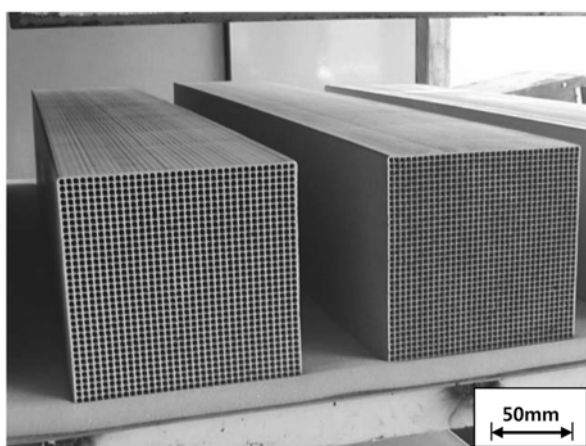


Fig. 8. Large-scale 35 cpsi SCR honeycomb with dimensions of $150 \times 150 \times 1,000$ mm extruded using the catalytic raw powder mixture of $\text{TiO}_2/10 \text{ w/o } \text{WO}_3/2 \text{ w/o } \text{V}_2\text{O}_5/1 \text{ w/o } \text{SO}_3$ determined in this study.

as shown Fig. 7. All of the samples showed a nearly 97% catalytic activity in a wide temperature range from 250 °C to 450 °C. At temperatures lower than 250 °C and higher than 450 °C, the activities dropped remarkably.

Based on the experimental results on the optimum contents of catalytic materials, the system of $\text{TiO}_2/10 \text{ w/o } \text{WO}_3/2 \text{ w/o } \text{V}_2\text{O}_5/1 \text{ w/o } \text{SO}_3$ was chosen for the SCR raw powder mixture using AMV and AMT dissolved in the oxalic acid solution and H_2SO_4 as source of SO_3 . The dispersion technique and the composition determined in this study have successfully been applied to the extrusion of a commercial 35 cpsi SCR honeycomb catalyst with high De-NOx activity of nearly 100% over a wide temperature range of 250 °C to 450 °C as presented in Fig. 8.

Conclusions

The optimum SCR catalytic composition in terms of De-NOx activities higher than 90% at a temperature as low as 250 °C and with high extrusion formability yielding large scale 35 cpsi honeycomb was studied. Two sources of raw materials were used for each catalytic material, i.e., for V_2O_5 , V_2O_5 powder and AMV precursor, and for

WO_3 , WO_3 powder and AMT precursor. In addition, 10 w/o oxalic acid solution and water were used as solvents of the raw catalytic materials. V_2O_5 and AMV were not dissolved in water but dissolved in oxalic acid solution whereas AMT could be dissolved well both in water and oxalic acid solution, but WO_3 was not dissolved in both solvents. Various combinations of catalytic raw materials were examined in the light of a homogeneous dispersion of catalytic raw materials. The powder mixture obtained from AMV dissolved in oxalic acid solution showed higher activities at lower temperature in comparison with the mixture obtained from V_2O_5 powder dispersed in water. It was also confirmed that the De-NOx catalytic activity at a temperature as low as 250 °C was mainly controlled by the content of V_2O_5 since the activity increased from less than 60% to nearly 100% by increasing the V_2O_5 content from 1 w/o to 2 w/o while other ingredients remained constant. The De-NOx activity at a temperature higher than 300 °C could be controlled mainly by WO_3 . In addition, sulfite in the form of SO_3 could increase the activity, but significantly reduced the extrusion formability when more than 1 w/o was added. Taking all these effects into consideration, the raw catalytic material system aimed at $\text{TiO}_2/10 \text{ w/o } \text{WO}_3/2 \text{ w/o } \text{V}_2\text{O}_5/1 \text{ w/o } \text{SO}_3$ were prepared using AMV and AMT dissolved in oxalic acid solution and H_2SO_4 as the source of SO_3 . Then a 35 cpsi honeycomb SCR catalyst with dimensions of $150 \times 150 \times 1,000$ mm showing a De-NOx activity of nearly 100% in the temperature range of 250 °C to 400 °C was successfully commercialized.

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