A Study on the de-NOx Activity of V$_2$O$_5$-Sb$_2$O$_3$/TiO$_2$ SCR Catalyst at Low Temperature According to the Wash Coating Conditions

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Abstract
To develop a high performance SCR catalyst which has better catalyst volume, price, temperature response than existing commercial SCR catalyst, V$_2$O$_5$-Sb$_2$O$_3$/TiO$_2$ catalysts were prepared by washcoating of catalyst materials on metal foam as a substrate at various washcoating conditions. In this study, de-NOx performance of prepared catalysts and the deactivating effect of SO$_2$ on the catalyst were evaluated in a laboratory scale atmospheric micro-reactor and the physical and chemical properties of them by analyzers such as Porosimeter, SEM(scanning electron microscope), EDX(energy dispersive x-ray spectrometer), ICP(inductively coupled plasma) were also characterized. It was found that de-NOx performance was excellent with decrease of binder contents as used for coating without dispersive reagent. This result was considered that active sites of catalyst with low content binder were less occupied by the binder than those of catalyst with high content binder. And also, it was found that there was no difference in NOx conversion of prepared catalysts when SO$_2$ was present or not over low temperature range of this study. De-NOx durability of prepared catalysts to SO$_2$ was pretty good judge from the result that initial NOx conversion was maintained at high concentration of 400ppm SO$_2$ for 5 hours. Therefore it was recommended that metal foam V$_2$O$_5$-Sb$_2$O$_3$/TiO$_2$ SCR catalyst will be able to be applicable as commercial catalyst in the relevant industrial field.

Keywords: De-NOx, Metal foam, SCR catalyst, Wash coating

INTRODUCTION
The NOx emission from fossil fuel is considered as a major component to air pollution and contributes health problem to human nature. Thus NOx emission is regulated and controlled by stringent regulation in the worldwide.

The most fossil fuels except LNG contain sulfur which transforms SOx during the combustion. The facility, especially for power plant, using fossil fuel power has problems of corrosion and deactivation of SCR catalyst by SOx in the exhaust gas.[1-5]

As environmental regulations are more and more stringently enforced by authority, NOx emission regulation in Korea has been changed from volumetric(ppm) concentration to total mass amount (ton/yr). For city and its vicinity at present time in Korea, the total mass amount regulation of air pollution imply to allocation of quota system. In modern technology for NOx elimination, SCR(Selective Catalytic Reduction) using NH$_3$ or Urea as reducing agent is well known, proven and efficient technology.[6-8]

The types of catalyst used in SCR are categorized as extrusion-honeycomb type, plate type and corrugated type. Those three types are the most commonly used in worldwide.[9]

The extrude-honeycomb catalyst is used in combined cycle power plant(CCPP), incineration plant, coal fired power plant. But its weight is heavy and low respond to rapid operation temperature. For plate catalyst, it can be used in coal fired power plant of which contains a large amount of dust, but this type of application require large volume of catalyst and large installation space due to its low specific surface area. For corrugated catalyst, it can be used in combined cycle power plant due to light weight and less volume of catalyst to be installed but it may make a fire in catalyst bed. Therefore, in this study, to resolve disadvantages described the above, metal substrate known as metal foam was used to take advantage of its mechanical strength and superior thermal conductivity with high specific surface area. The advantage of metal foam is that this type of SCR catalyst requires less installation area and less weight compare to extruded and plate catalyst.[10-11]

Also due to nature of raw material as metal, the metal foam SCR catalyst has economic advantage because it can be easily regenerated or remanufactured in several times for reuse.

In this study, to overcome disadvantages of commonly commercialized catalyst, metal foam substrate was used and coated with slurry specified as V$_2$O$_5$-Sb$_2$O$_3$/TiO$_2$ and various binders(33.3, 50, 66.7, 100wt%).[12-13]

The NOx reduction efficiency of prepared catalyst has been confirmed by using laboratory scale atmospheric pressure micro-reactor, and the durability of catalyst also has been studied at low temperature range(150~220℃) with the presence of SO$_2$.

TEST AND ANALYSIS
Catalyst preparation
The metal foam substrate used in this study was a size of 3,000㎛ supplied by Alantum Inc. in Korea, and coating slurry was consists of TiO$_2$(99%, Cristal Global Co., Ltd. in Saudi Arabia), V$_2$O$_5$(99%, Daejung Chemical CO., Ltd. in Korea), Sb$_2$O$_3$(98.5%, Daejung Chemical CO., Ltd in Korea), Silicasol 20% solution(99%, REMtech. in Korea) as binder, DispexA40(83%, BASF CO., Ltd. in Germany) as dispersive
agent, and DI water. For the process of making catalyst slurry, V$_2$O$_5$ and Sb$_2$O$_3$ were mixed with DI water, dissolved it at 45~50°C and put this solution into TiO$_2$. And then agitating this solution for 15min then coated on the surface of metal substrate through dip-sipping method.

The samples for NOx reduction efficiency test were prepared in size of metal foam (2.8cm × 2.8cm × 0.45cm) for 6 pieces each, total of 30 pieces. The coating slurry were controlled to V$_2$O$_5$11wt%, Sb$_2$O$_3$3wt% with respect to TiO$_2$. Based on TiO$_2$ 76wt%, binder 100%, 66.7%, 50%, 33.3% added dispexA40 100%. And samples of binder 50% added dispexA40 0%. The coating quantity was set at 210g/L, and the samples were coated in 6 pieces. The notation of sample is shown in Table 1.

### Table 1. Notation of prepared catalysts

<table>
<thead>
<tr>
<th>Catalyst notation</th>
<th>Binder Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>MFB1</td>
<td>100%</td>
</tr>
<tr>
<td>MFB2/3</td>
<td>66.7%</td>
</tr>
<tr>
<td>MFB1/2</td>
<td>50%</td>
</tr>
<tr>
<td>MFB1/3</td>
<td>33.3%</td>
</tr>
<tr>
<td>MFB1/2non</td>
<td>50% non-dispex A40</td>
</tr>
</tbody>
</table>

**Physical characteristics analysis**

For specific surface area analysis, incinerated slurry prior to coating has been measured by using Porosimeter(Auto Pore IV 9520, Micromeritics, in USA). And for surface composition analysis of Ti, V and Sb, SEM-EDX(MIRA3, TESCAN, in Czech), ICP(Inductively coupled plasma optical emission spectrometer: ICP-OES, 5300DV, PerkinElmer, in USA) were used. Also porosity was measured in range of 0~60,000psia.

**Test condition and apparatus**

The schematic of NOx reduction efficiency test unit is shown in Fig. 1. The apparatus used in this study was continuous atmospheric pressure micro-reactor, and the catalyst volume was 14 cm$^3$. All gases were controlled and injected by MFC (Mass Flow Controller, F-100C, Bronkhorst Co., Ltd. in UK). The temperature was controlled by PID controller, and operating temperature was selected based on commercial incinerator’s operating range(150~220℃) required from incinerator field. The NOx was analyzed by Gas analyzer(Greenline D max. II, 9000, Eurotron Co., Ltd. in UK). For catalyst performance test, NO gas(10% in N$_2$, Sungkang specialty gas, in Korea) 350ppm (v/v) was injected continuously and NH$_3$ gas(10% in N$_2$, Sungkang specialty gas, in Korea) was injected as 0ppm, 200ppm and 400ppm respectively. The total flow for the test was maintained and balanced with N$_2$ gas(99.9%, Sungkang specialty gas, in Korea). The space velocity (SV) was selected from 5,000hr$^{-1}$~10,000hr$^{-1}$. The simulated gas was heated and raised up to operation temperature and stayed for 30min for maintaining operating temperature with appropriate flow rate. The test condition is shown in Table 2 and the test sample is shown in Fig. 2.

**RESULT AND DISCUSSION**

**The evaluation of catalytic de-NOx activity**

The samples of metal foam catalyst were prepared as MFB1, MFB2/3, MFB1/2, MFB1/3 and MFB1/2non. The efficiency of catalyst were tested with respect to Space Velocity(SV) in the presence of SO$_2$ in the simulation gas.
The result is shown in Fig. 3-16. The NOx reduction efficiency with respect to SV 5,000-10,000hr\(^{-1}\) and presence of SO\(_2\) is shown in Fig. 3-6. From the result, as the quantity of binder decreases, NOx reduction efficiency increases in the low temperature operating range. Fig. 7-16 shows the result of catalyst performance in the presence of SOx in the simulated gas to find out influence of SOx on the catalyst reduction efficiency. The result shows that there are no significant differences among the catalyst samples, which is the same result of Ha et al. who reported that addition of Sb\(_2\)O\(_3\) as promoter to catalyst make SCR catalyst resistant to SOx.[14]

The NOx reduction efficiency with respect to binder based on SV 5,000hr\(^{-1}\) showed similar result in MFB1 and MFB2/3. Also MFB1/2 and MFB1/3 were similar. However in case of S.V 10,000hr\(^{-1}\), those sample showed different NOx reduction efficiency. In comparison of MFB1/2non and MFB1/2, the NOx reduction efficiency was the highest when dispersive agent was not added.

Figure 2. Picture of prepared catalysts.

Figure 3. Conversion of NOx at different amount of binder over prepared catalyst. (SO\(_2\) 0ppm, S.V : 5,000hr\(^{-1}\))
Figure 4. Conversion of NOx at different amount of binder over prepared catalyst. (SO$_2$ 200ppm, S.V : 5,000hr$^{-1}$)

Figure 5. Conversion of NOx at different amount of binder over prepared catalyst. (SO$_2$ 0ppm, S.V : 10,000hr$^{-1}$)
Figure 6. Conversion of NOx at different amount of binder over prepared catalyst. (SO$_2$ 200ppm, S.V : 10,000hr$^{-1}$)

Figure 7. Conversion of NOx over MFB1 catalyst at different SO$_2$ concentrations. (S.V : 5,000hr$^{-1}$)
Figure 8. Conversion of NO over MFB2/3 catalyst at different SO$_2$ concentrations. (S.V : 5,000hr$^{-1}$)

Figure 9. Conversion of NOx over MFB1/2 catalyst at different SO$_2$ concentrations. (S.V : 5,000hr$^{-1}$)
Figure 10. Conversion of NOx over MFB1/3 catalyst at different \( \text{SO}_2 \) concentrations. (S.V : 5,000hr\(^{-1} \))

Figure 11. Conversion of NO over MFB1/2non catalyst at different \( \text{SO}_2 \) concentrations. (S.V : 5,000hr\(^{-1} \))
Figure 12. Conversion of NOx over MFB1 catalyst at different SO\textsubscript{2} concentrations. (S.V : 10,000hr\textsuperscript{-1})

Figure 13. Conversion of NOx over MFB2/3 catalyst at different SO\textsubscript{2} concentrations. (S.V : 10,000hr\textsuperscript{-1})
Figure 14. Conversion of NOx over MFB1/2 catalyst at different SO$_2$ concentrations. (S.V : 10,000hr$^{-1}$)

Figure 15. Conversion of NOx over MFB1/3 catalyst at different SO$_2$ concentrations. (S.V : 10,000hr$^{-1}$)
The analysis of porosity of catalyst

The porosity of catalyst was analyzed by Porosimeter, and result is shown in Table 3. From the result, the porosity of catalyst increased as less quantity of binder was added. Based on sample MFB1, the porosity range of sample MFB1/2non have changed significantly. This means that the pore size of catalyst will be narrowed as the quantity of binder is increased. And this result is correspond to the result of reduction efficiency found in this study.

<table>
<thead>
<tr>
<th>Items</th>
<th>MFB1</th>
<th>MFB2/3</th>
<th>MFB1/2</th>
<th>MFB1/3</th>
<th>MFB1/2non</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity(%)</td>
<td>66.98</td>
<td>70.70</td>
<td>74.51</td>
<td>74.13</td>
<td>74.38</td>
</tr>
</tbody>
</table>

Table 3. Porosimeter analysis result of catalyst sample
The analysis of specific surface area composition

The specific surface was observed by SEM for the samples prepared with respect to various quantity of binders, and the result is shown in Fig. 18. For analysis of composition of surface of catalyst, the slurry has been incinerated prior to coating, and those sample was analyzed by EDX and ICP. The result is shown in Table 4~5. The amount of impregnation of vanadium as main active component of catalyst was high in sample MFB1 and MFB1/2, but NOx reduction efficiency increased as additional amount of binder decreased despite of vanadium impregnation amount. This means that as the amount of binder increased, it may contribute reduction of active sites on the catalyst surface, but the durability of catalyst with respect to presence of SOx shows no significant difference.

### Table 4. EDX analysis results of the prepared catalyst (unit : wt%)

<table>
<thead>
<tr>
<th>Items</th>
<th>MFB1</th>
<th>MFB2/3</th>
<th>MFB1/2</th>
<th>MFB1/3</th>
<th>MFB1/2non</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>51.93~63.70</td>
<td>35.10~52.95</td>
<td>50.13~56.84</td>
<td>54.77~62.39</td>
<td>26.87~67.47</td>
</tr>
<tr>
<td>Si</td>
<td>1.12~1.62</td>
<td>1.56~2.61</td>
<td>0.92~9.49</td>
<td>0.99~1.29</td>
<td>0.25~1.04</td>
</tr>
<tr>
<td>Ti</td>
<td>27.66~35.73</td>
<td>33.21~40.25</td>
<td>23.80~32.40</td>
<td>31.08~35.33</td>
<td>24.94~38.48</td>
</tr>
<tr>
<td>V</td>
<td>2.18~4.10</td>
<td>1.54~1.94</td>
<td>2.47~5.09</td>
<td>1.46~2.98</td>
<td>1.84~2.33</td>
</tr>
<tr>
<td>Sb</td>
<td>2.07~3.60</td>
<td>1.52~2.64</td>
<td>1.56~2.44</td>
<td>1.52~2.12</td>
<td>1.39~1.84</td>
</tr>
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</table>

### Table 5. ICP analysis results of the prepared catalyst (unit : ppm)

<table>
<thead>
<tr>
<th>Items</th>
<th>MFB1</th>
<th>MFB2/3</th>
<th>MFB1/2</th>
<th>MFB1/3</th>
<th>MFB1/2non</th>
</tr>
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<tbody>
<tr>
<td>Sb</td>
<td>20,640</td>
<td>19768</td>
<td>22,825</td>
<td>16,994</td>
<td>16,325</td>
</tr>
<tr>
<td>Ti</td>
<td>393,339</td>
<td>398,306</td>
<td>406,495</td>
<td>375,500</td>
<td>410,493</td>
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<tr>
<td>V</td>
<td>36,642</td>
<td>27,583</td>
<td>38,453</td>
<td>34,629</td>
<td>27,870</td>
</tr>
<tr>
<td>Si</td>
<td>16,938</td>
<td>23,763</td>
<td>8,194</td>
<td>11,504</td>
<td>9,816</td>
</tr>
</tbody>
</table>
CONCLUSION

In this study, catalyst activity tests had been done for prepared catalyst using metal foam as substrate with respect to various wash coating conditions. And NOx reduction efficiency was also studied and analyzed physical characteristics as follows:

1) In spite of high vanadium(main active component of SCR catalyst) impregnation analyzed by ICP and EDX in the sample MFB1 and MFB1/2 EDX, NOx reduction efficiency increased as the amount of binder was decreased. This means that as the amount of binder increased, it may contribute to loose of active sites on the catalyst surface. Also in comparison of NOx reduction efficiency with respect to amount of binder, the result between MFB1 and MFB2/3 is similar. And MFB1/2 and MFB1/3 are also similar. Thus these results were represent a reduction efficiency is not proportional to the amount of binder, but certain amount of binder may contribute to a similar result.

2) The presence of SO2 in the simulated gas stream at low temperature range is almost not affect to the reduction efficiency of catalyst. This may happen due to addition of Sb in the catalyst. The NOx reduction of MFB1/2non is higher than MFB1/2 at low operating temperature range. At the temperature as low as 200℃, the conversion rate of catalyst is more than 90%. Also for the influence of SO2 0ppm and 400ppm in 5 hours, there is no effect on de-NOx activity of catalyst and maintain its performance as much as fresh catalyst with respect to durability against SOx at low temperature.

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REFERENCES


