

A Study on the de-NO_x Activity of V₂O₅-Sb₂O₃/TiO₂ 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, V₂O₅-Sb₂O₃/TiO₂ catalysts were prepared by washcoating of catalyst materials on metal foam as a substrate at various washcoating conditions. In this study, de-NO_x performance of prepared catalysts and the deactivating effect of SO₂ 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-NO_x 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 NO_x conversion of prepared catalysts when SO₂ was present or not over low temperature range of this study. De-NO_x durability of prepared catalysts to SO₂ was pretty good judge from the result that initial NO_x conversion was maintained at high concentration of 400ppm SO₂ for 5 hours. Therefore it was recommended that metal foam V₂O₅-Sb₂O₃/TiO₂ SCR catalyst will be able to be applicable as commercial catalyst in the relevant industrial field.

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

INTRODUCTION

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

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

As environmental regulations are more and more stringently enforced by authority, NO_x 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

NO_x elimination, SCR(Selective Catalytic Reduction) using NH₃ 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 V₂O₅-Sb₂O₃/TiO₂ and various binders(33.3, 50, 66.7, 100wt%).[12-13]

The NO_x 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°C) with the presence of SO₂.

TEST AND ANALYSIS

Catalyst preparation

The metal foam substrate used in this study was a size of 3,000 μ m supplied by Alantum Inc. in Korea, and coating slurry was consists of TiO₂(99%, Cristal Global Co., Ltd. in Saudi Arabia), V₂O₅(99%, Daejung Chemical CO., Ltd. in Korea), Sb₂O₃(98.5%, Daejung Chemical CO., Ltd. in Korea), Silicasol 20% solution(99%, REMtech. in Korea) as binder, DisplexA40(83%, BASF CO., Ltd. in Germany) as dispersive

agent, and DI water. For the process of making catalyst slurry, V_2O_5 and Sb_2O_3 were mixed with DI water, dissolved it at $45\sim 50^\circ\text{C}$ 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 NO_x reduction efficiency test were prepared in size of metal foam ($2.8\text{cm} \times 2.8\text{cm} \times 0.45\text{cm}$) for 6 pieces each, total of 30 pieces. The coating slurry were controlled to V_2O_5 11wt%, Sb_2O_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

Catalyst notation	Binder Content
MFB1	100%
MFB2/3	66.7%
MFB1/2	50%
MFB1/3	33.3%
MFB1/2non	50% non-dispex A40

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 $0\sim 60,000\text{psia}$.

Test condition and apparatus

The schematic of NO_x 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($150\sim 220^\circ\text{C}$) required from incinerator field. The NO_x 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 based on NO concentration by MFC. The concentration of O_2 gas(99.9%, Sungkang specialty gas, in Korea) was maintained at 15% (v/v), and SO_2 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 $5,000\text{hr}^{-1} \sim 10,000\text{hr}^{-1}$. 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.

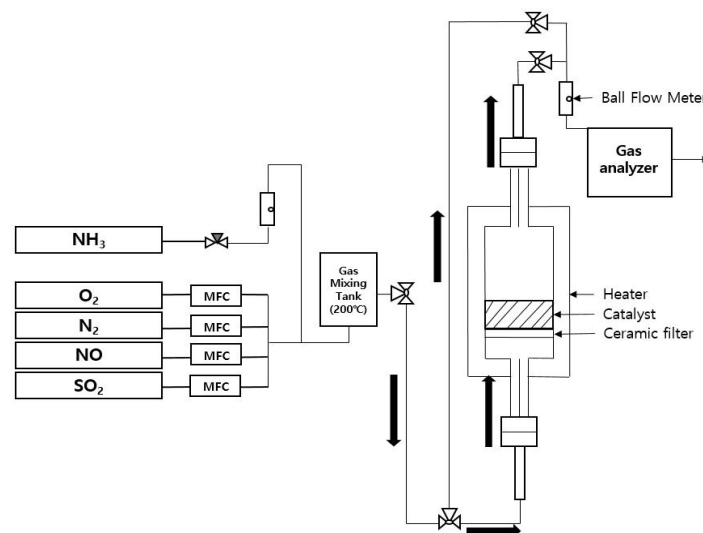


Figure 1. Process flow diagram of catalyst performance test unit.

Table 2. Catalyst performance test conditions

Item	Condition
Space velocity (hr^{-1})	5,000, 10,000
catalyst volume (cm^3)	14
Temperature ($^\circ\text{C}$)	$150\sim 220$ (at an interval of 10°C)
O_2 (%)	15
NO (ppm)	350
SO_2 (ppm)	0, 200
NH_3 (ppm)	350

RESULT AND DISCUSSION

The evaluation of catalytic de- NO_x 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.

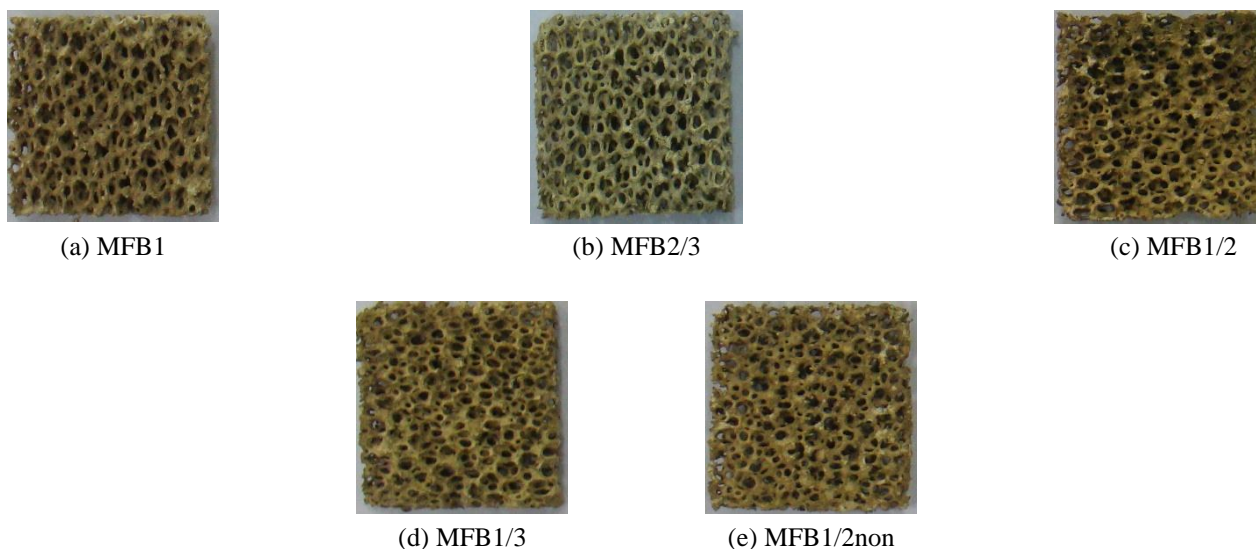


Figure 2. Picture of prepared catalysts.

The result is shown in Fig. 3~16. The NO_x reduction efficiency with respect to SV 5,000~10,000hr⁻¹ and presence of SO₂ is shown in Fig. 3~6. From the result, as the quantity of binder decreases, NO_x reduction efficiency increases in the low temperature operating range. Fig. 7~16 shows the result of catalyst performance in the presence of SO_x in the simulated gas to find out influence of SO_x on the catalyst reduction efficiency. The result shows there are no significant differences among the catalyst samples, which is same result of Ha et.al

who reported that addition of Sb₂O₃ as promotor to catalyst make SCR catalyst resistant to SO_x. [14]

The NO_x 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 NO_x reduction efficiency. In comparison of MFB1/2non and MFB1/2, the NO_x reduction efficiency was the highest when dispersive agent was not added.

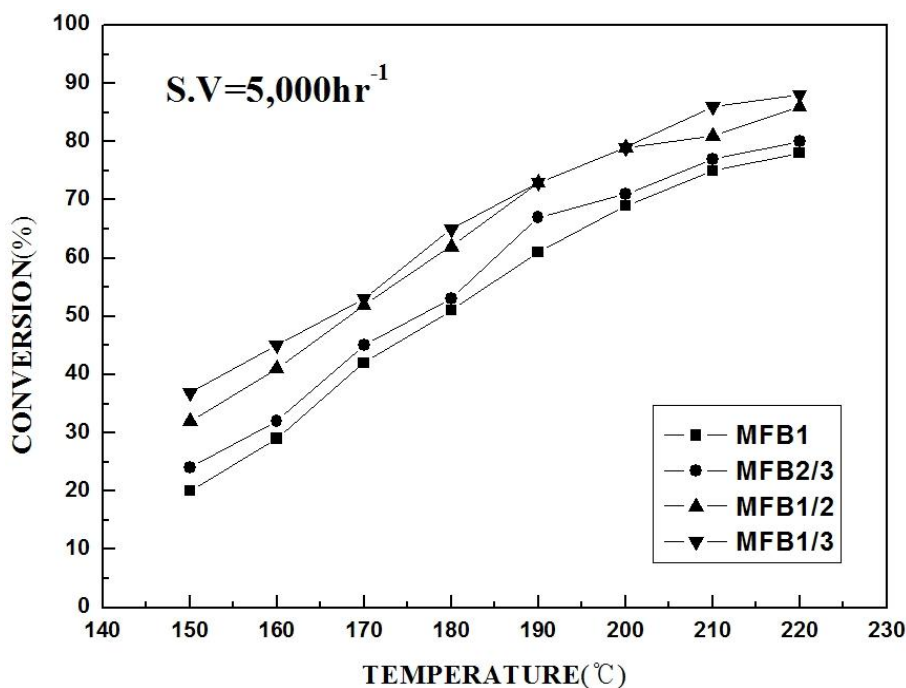


Figure 3. Conversion of NO_x at different amount of binder over prepared catalyst. (SO₂ 0ppm, S.V : 5,000hr⁻¹)

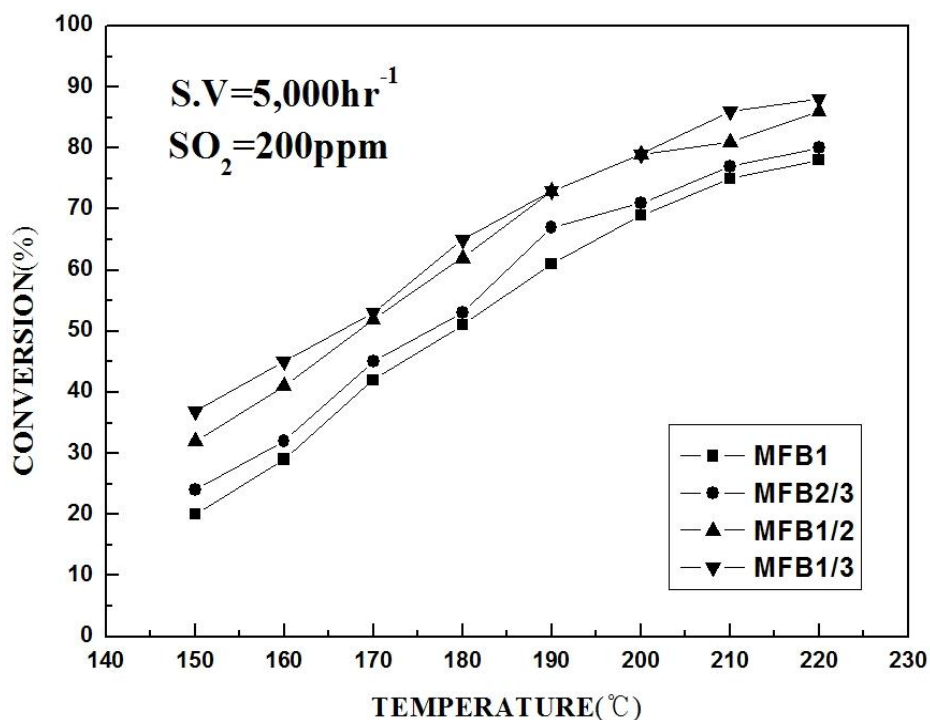


Figure 4. Conversion of NOx at different amount of binder over prepared catalyst. (SO₂ 200ppm, S.V : 5,000hr⁻¹)

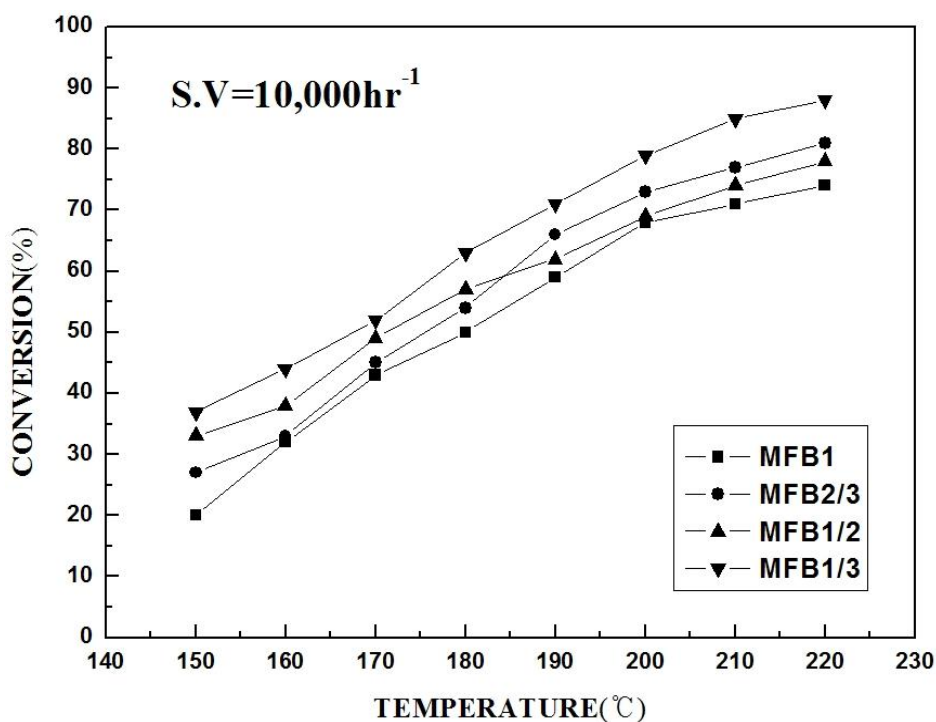


Figure 5. Conversion of NOx at different amount of binder over prepared catalyst. (SO₂ 0ppm, S.V : 10,000hr⁻¹)

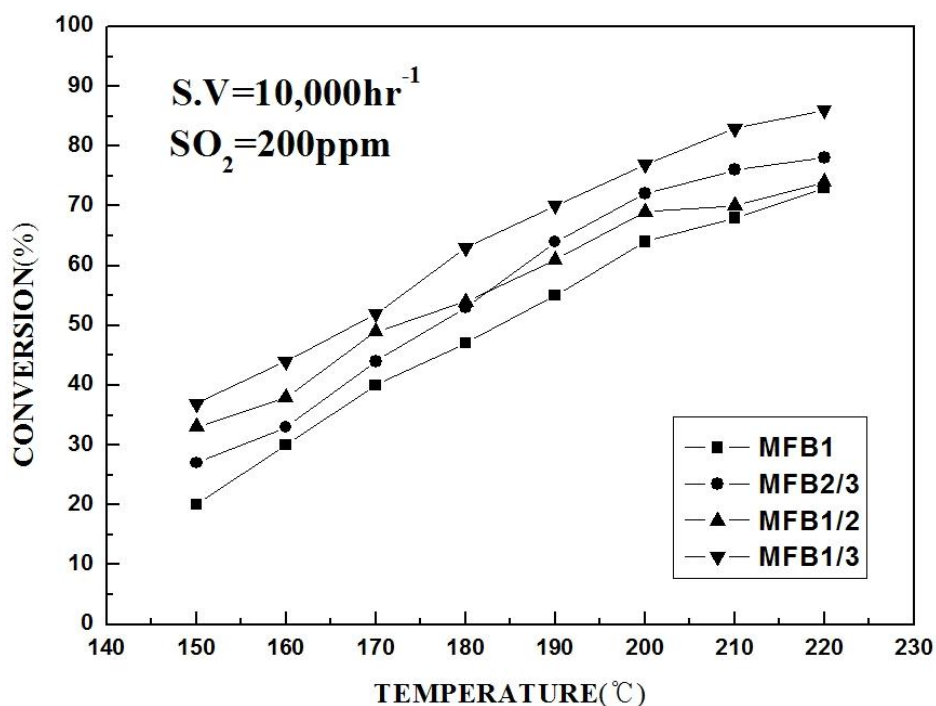


Figure 6. Conversion of NOx at different amount of binder over prepared catalyst. (SO₂ 200ppm, S.V : 10,000hr⁻¹)

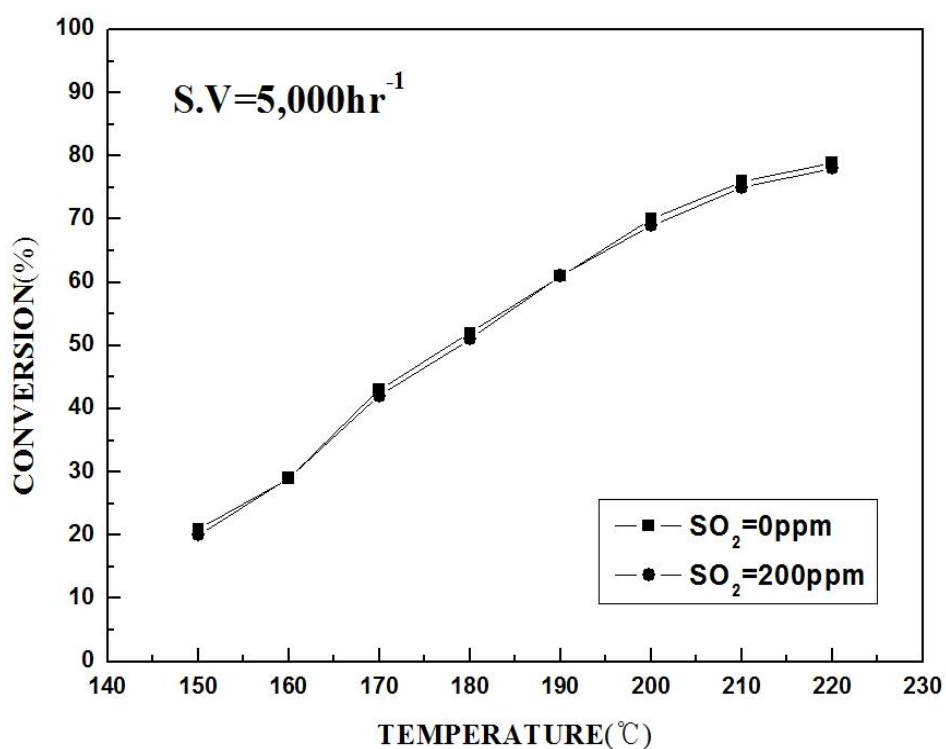


Figure 7. Conversion of NOx over MFB1 catalyst at different SO₂ concentrations. (S.V : 5,000hr⁻¹)

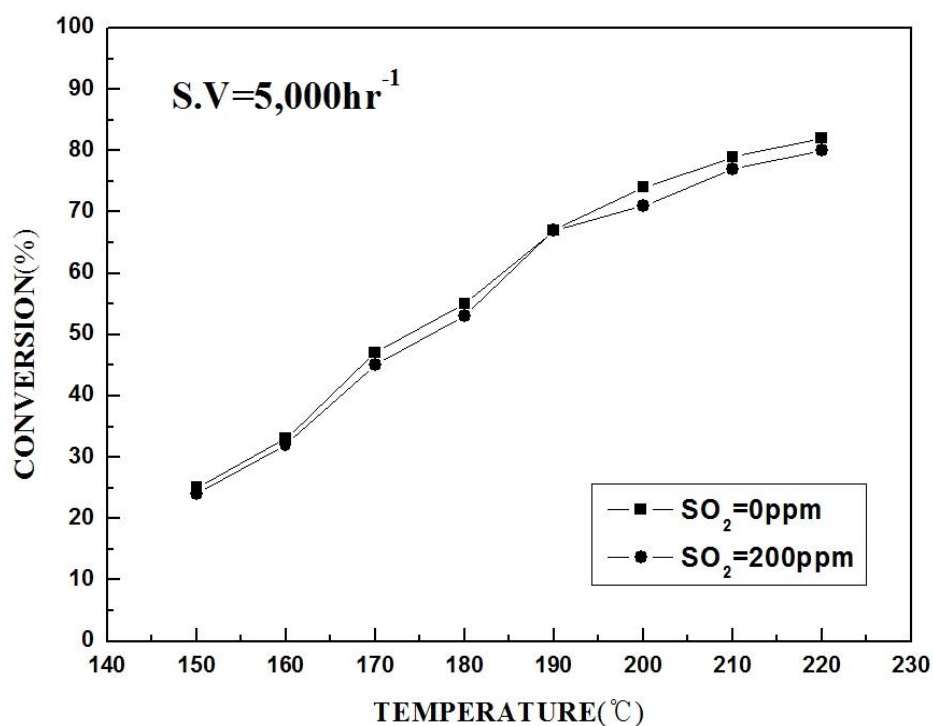


Figure 8. Conversion of NO over MFB2/3 catalyst at different SO₂ concentrations. (S.V : 5,000hr⁻¹)

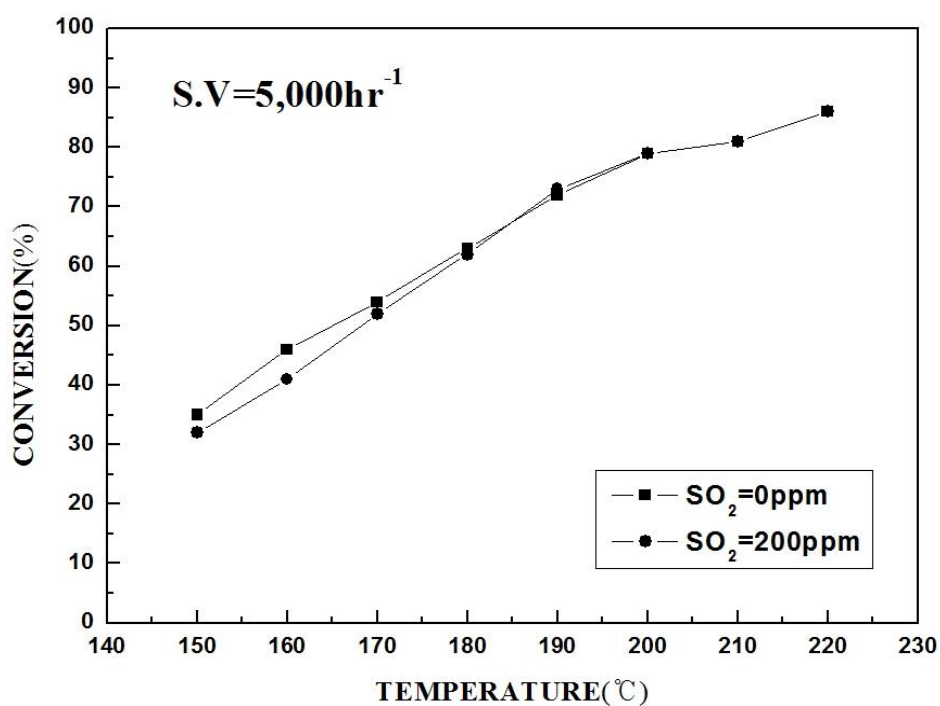


Figure 9. Conversion of NO_x over MFB1/2 catalyst at different SO₂ concentrations. (S.V : 5,000hr⁻¹)

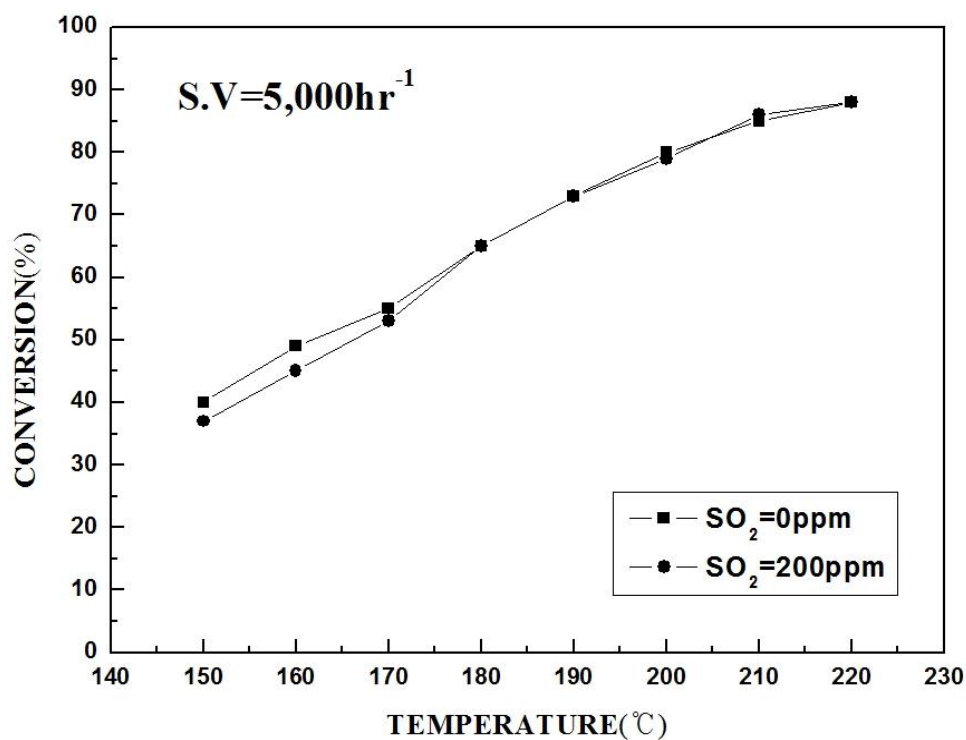


Figure 10. Conversion of NOx over MFB1/3 catalyst at different SO₂ concentrations. (S.V : 5,000hr⁻¹)

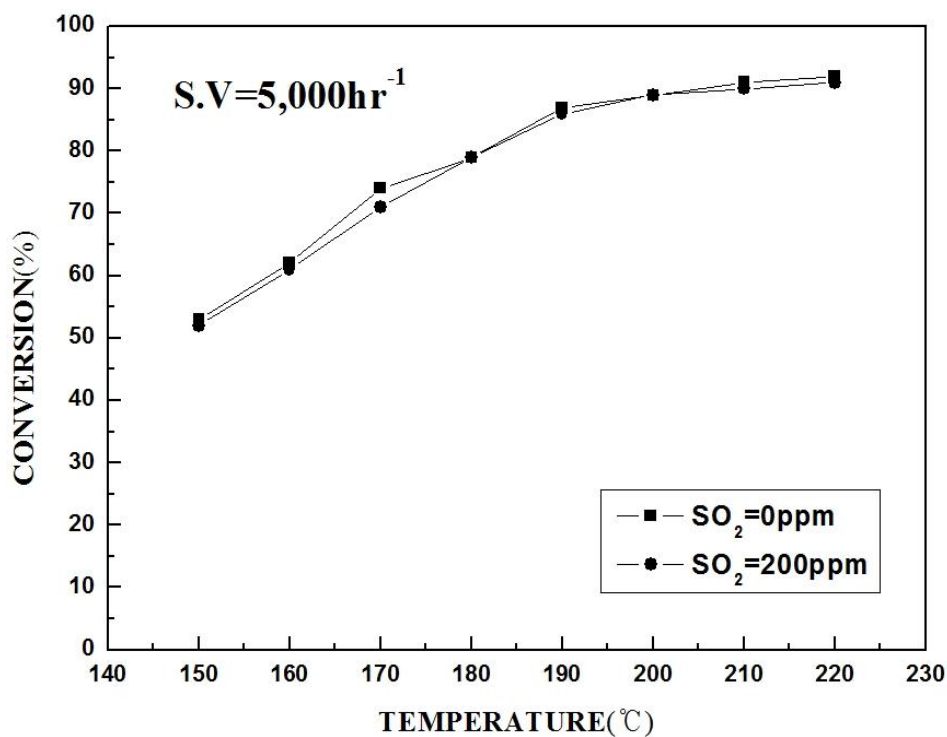


Figure 11. Conversion of NO over MFB1/2non catalyst at different SO₂ concentrations. (S.V : 5,000hr⁻¹)

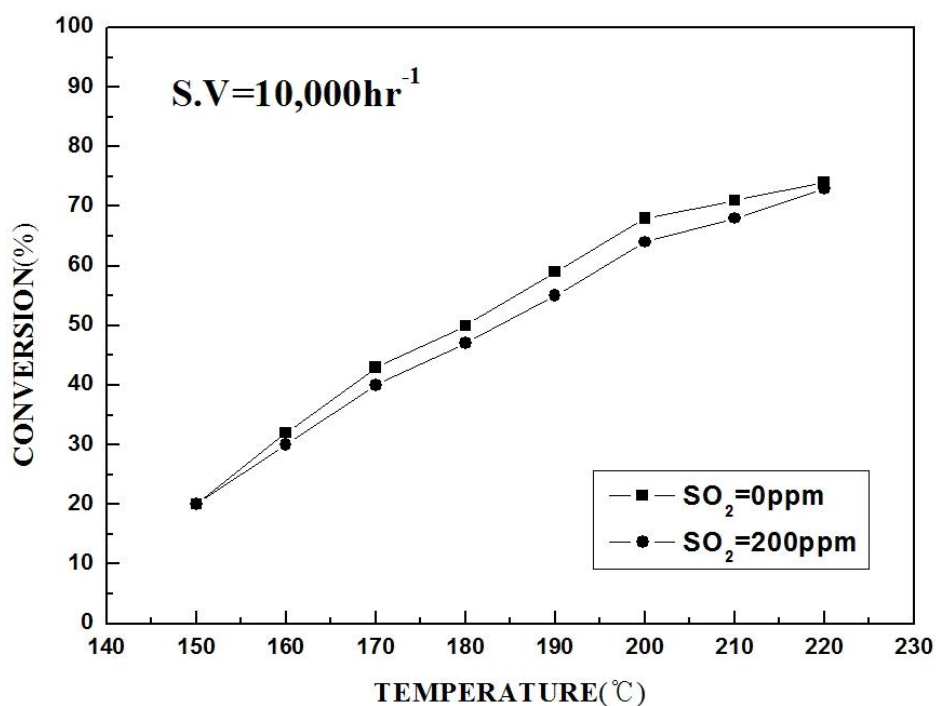


Figure 12. Conversion of NOx over MFB1 catalyst at different SO₂ concentrations. (S.V : 10,000hr⁻¹)

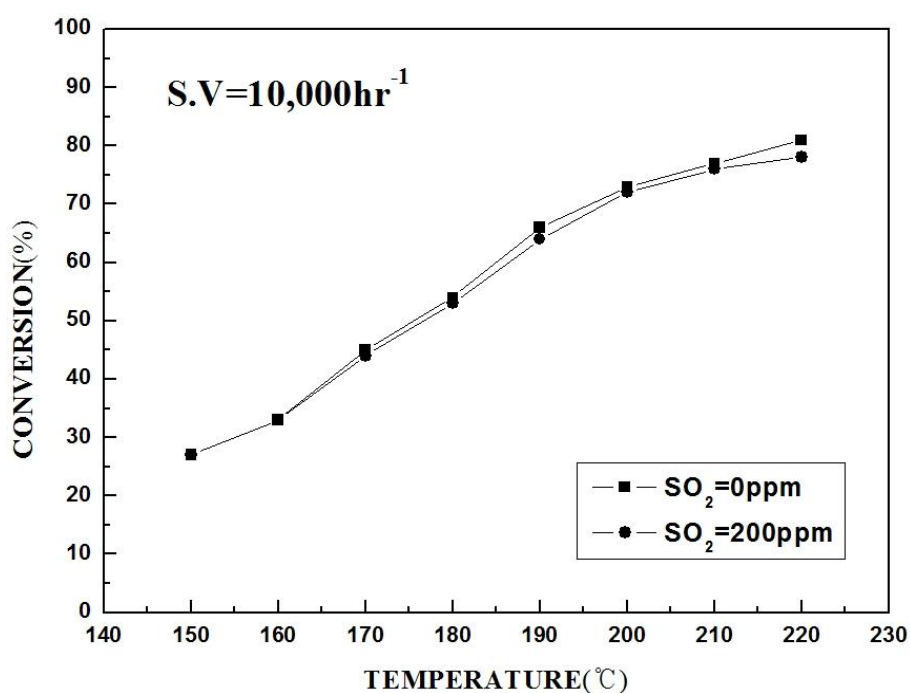


Figure 13. Conversion of NOx over MFB2/3 catalyst at different SO₂ concentrations. (S.V : 10,000hr⁻¹)

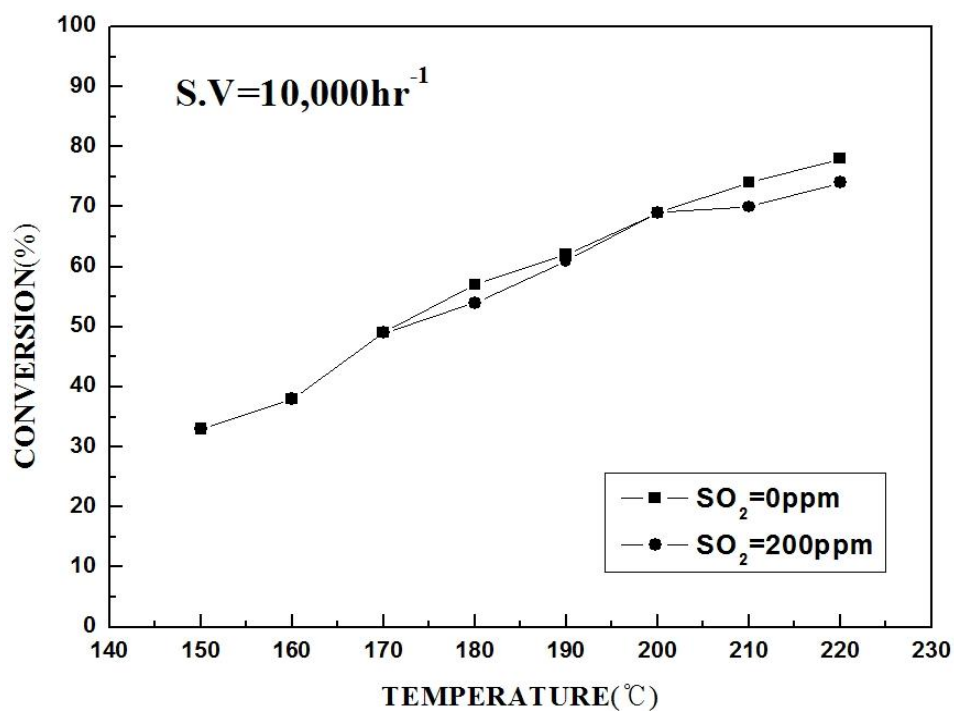


Figure 14. Conversion of NOx over MFB1/2 catalyst at different SO₂ concentrations. (S.V : 10,000hr⁻¹)

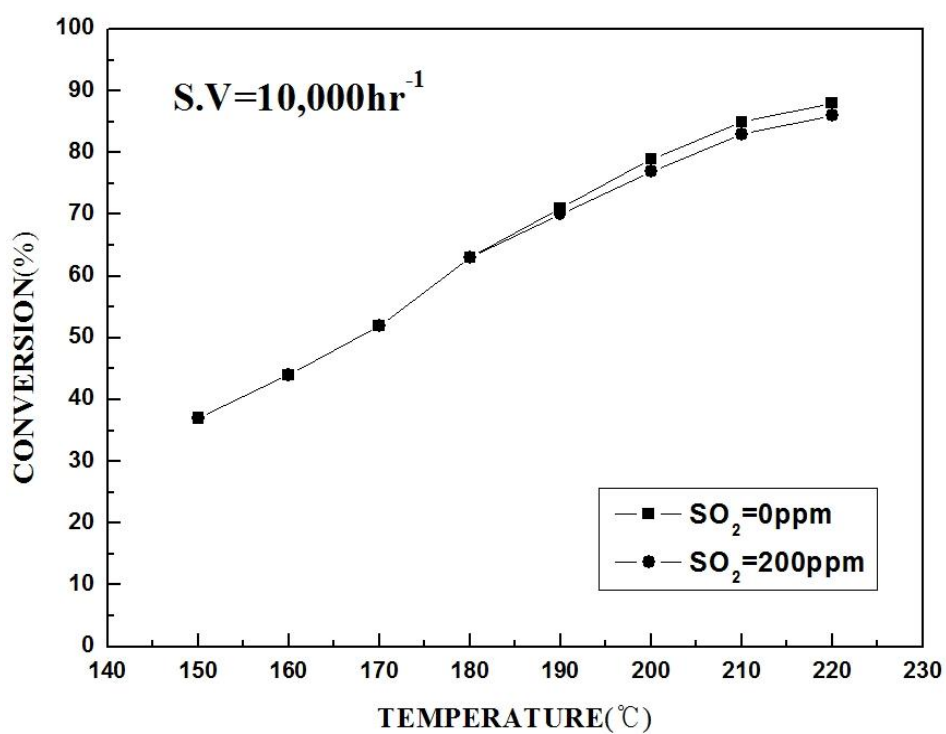


Figure 15. Conversion of NOx over MFB1/3 catalyst at different SO₂ concentrations. (S.V : 10,000hr⁻¹)

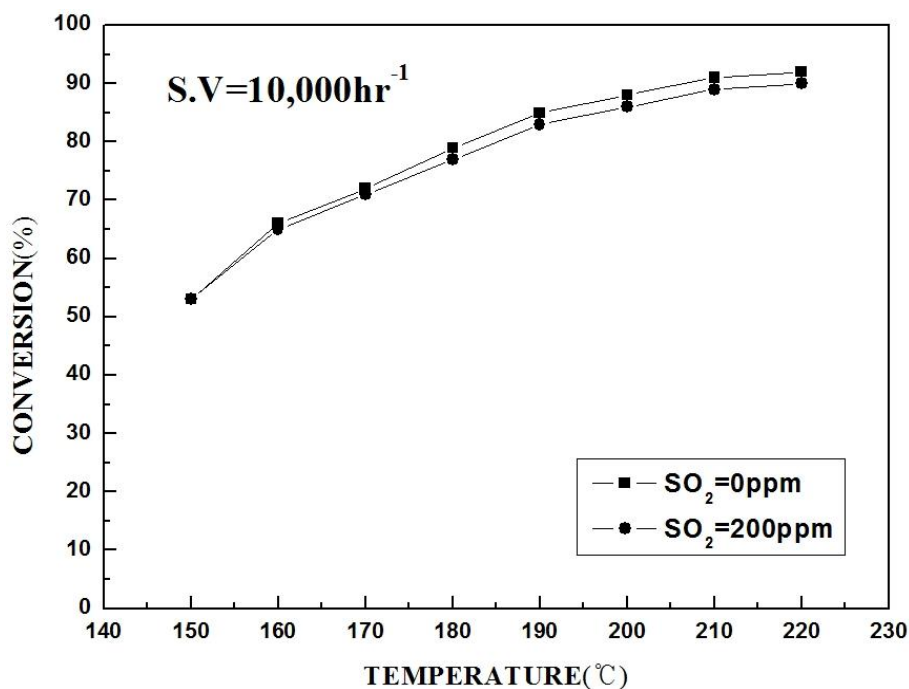


Figure 16. Conversion of NOx over MFB1/2non catalyst at different SO₂ concentrations. (S.V : 10,000hr⁻¹)

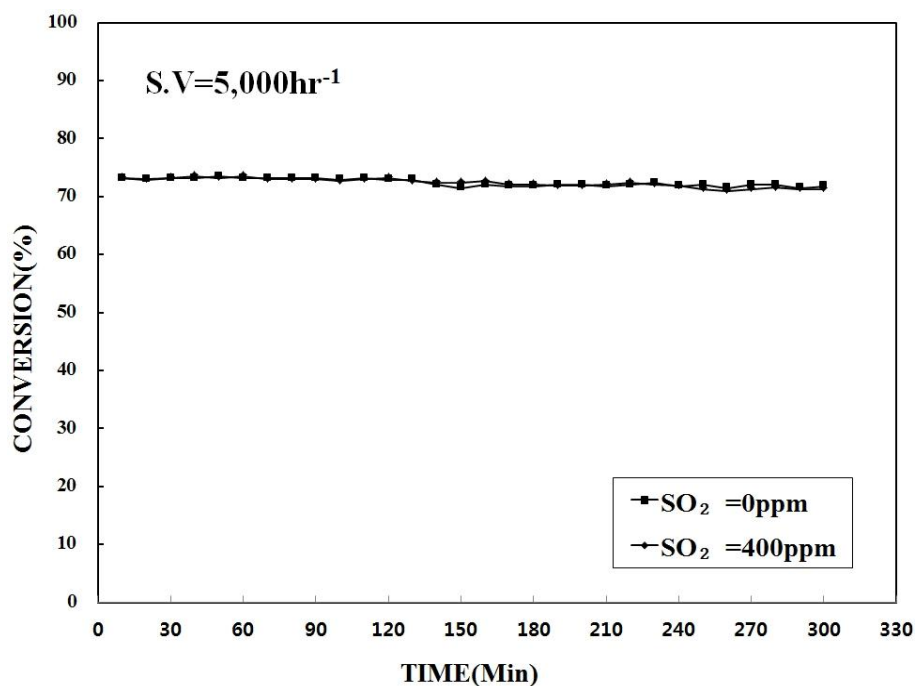


Figure 17. NOx conversion at different SO₂ concentrations for 5 hours. (MFB1/3)

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 3. Porosimeter analysis result of catalyst sample

Items	MFB1	MFB2/3	MFB1/2	MFB1/3	MFB1/2non
Porosity(%)	66.98	70.70	74.51	74.13	74.38

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

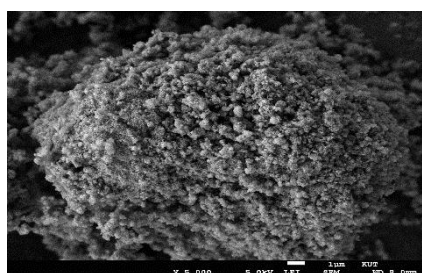
vanadium as main active component of catalyst was high in sample MFB1 and MFB1/2, but NO_x reduction efficiency increased as additional amount of binder decreased despite of vanadium impregnation amount. This means that as the amount of binder increased, it may contribute reduction of active sites on the catalyst surface, but the durability of catalyst with respect to presence of SO_x shows no significant difference.

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

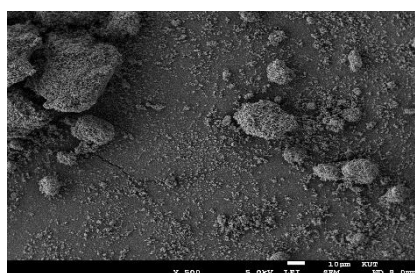
Items	MFB1	MFB2/3	MFB1/2	MFB1/3	MFB1/2non
O	51.93~63.70	35.10~52.95	50.13~56.84	54.77~62.39	26.87~67.47
Si	1.12~1.62	1.56~2.61	0.92~9.49	0.99~1.29	0.25~1.04
Ti	27.66~35.73	33.21~40.25	23.80~32.40	31.08~35.33	24.94~38.48
V	2.18~4.10	1.54~1.94	2.47~5.09	1.46~2.98	1.84~2.33
Sb	2.07~3.60	1.52~2.64	1.56~2.44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

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

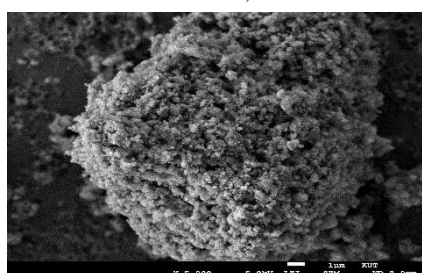
Items	MFB1	MFB2/3	MFB1/2	MFB1/3	MFB1/2non
Sb	20,640	19768	22,825	16,994	16,325
Ti	393,339	398,306	406,495	375,500	410,493
V	36,642	27,583	38,453	34,629	27,870
Si	16,938	23,763	8,194	11,504	9,816



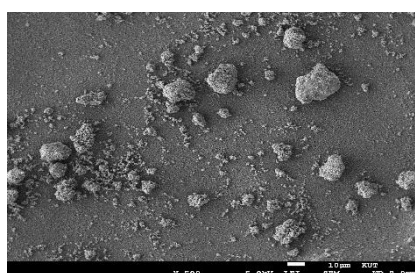
MFB1 ×5,000



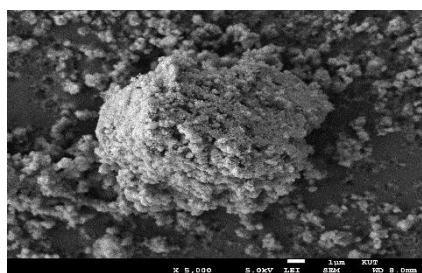
MFB1 ×500



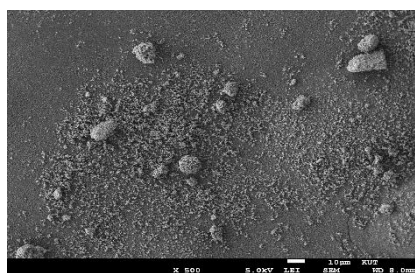
MFB2/3 ×5,000



MFB2/3 ×500



MFB1/2 ×5,000



MFB1/2 ×500

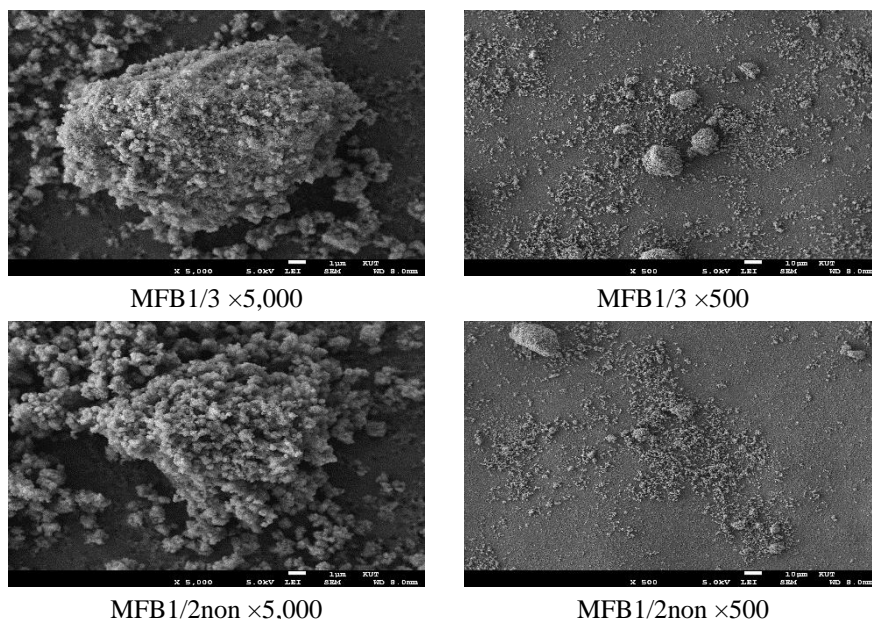


Figure 18. SEM analysis results of the prepared catalysts.

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 NO_x 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, NO_x 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 NO_x 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 NO_x reduction of MFB1/2non is higher than MFB1/2 at low operating temperature range. At the temperature as low as 200°C, 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-NO_x activity of catalyst and maintain its performance as much as fresh catalyst with respect to durability against SO_x at low temperature.

ACKNOWLEDGMENTS

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