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A practical scale evaluation of sulfated V_2O_5/TiO_2 catalyst from metatitanic acid for selective catalytic reduction of NO by NH_3

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Abstract

The characteristics of sulfated V_2O_5/TiO_2 honeycomb catalyst from metatitanic acid (MTA) were studied in the practical conditions of pilot plant using high dust flue gas from coal fired utility boiler. The effects of reaction temperature, NH_3/NO mole ratio, space velocity and operation time on the reduction of nitric oxide (NO) were mainly investigated for engineering application. The catalyst showed high NO reduction of about 90% at a space velocity of $4000\,h^{-1}$, NH_3/NO mole ratio of 1.0 and reaction temperature of 300–400 °C. The efficiency of this catalyst remained constant during the present experiment of 2400 h and the erosion by fly ash was lower than that of the commercial catalysts. These results clearly demonstrate the high potential for this catalyst to be applied commercially for the control of NO_x emissions from coal fired utility boiler.

Keywords: Selective catalytic reduction; Sulfated TiO_2; Nitric oxide; Extruded catalyst; High dust

1. Introduction

Selective catalytic reduction (SCR) with ammonia is presently the most effective technique for removing the NO_x from utility boiler flue gas because of its high efficiency and stability [1,2]. Various types of SCR catalysts including noble metal, Cu/zeolite and V_2O_5/TiO_2 have been proposed and examined for the reduction of NO_x [3–6]. Especially, V_2O_5/TiO_2 catalyst has been most commercially used due to its high activity and its high resistance to poisoning by SO_2 [7,8]. Recently, the surface sulfate species on V_2O_5/TiO_2 catalysts have been known as a promoter for SCR of NO_x by NH_3 [9]. The sulfate species on the support interact with adsorbed water to form Brönsted acid sites on the catalyst surface under SCR reaction conditions, promoting the adsorption of ammonia [10]. The physico-chemical characteristics of V_2O_5/TiO_2 from metatitanic acid (MTA) containing sulfur was examined for the use of SCR catalyst by Choo et al. [11]. It shows that the surface sulfate species enhance the formation of the polymeric vanadate by reducing the available surface area of the catalyst and the polymeric vanadate species on the catalyst surface is the active reaction site for SCR system. Although the sulfate catalysts show excellent physico-chemical properties as SCR catalyst, the characteristics of the catalysts have been tested under model gas mixtures, and the performance test under actual flue gas conditions is still unknown.

In this study, V_2O_5/TiO_2 catalyst from MTA containing sulfur was extruded in the shape of honeycomb. The activity and endurance were compared with commercial catalysts in the pilot plant handling 3000 Nm^3/h of actual flue gas from a coal fired utility boiler. The effects of reaction temperature, NH_3/NO mole ratio and space velocity on NO reduction were examined for engineering application. Also, its erosion was investigated to evaluate the mechanical strength.

2. Experimental

2.1. Catalyst preparation

Sulfated titania (TiO_2) as a catalyst support was prepared from MTA ($TiO(OH)_2$) containing sulfur following the same method reported elsewhere [11] and their properties are shown in Table 1. The paste of the TiO_2 powder was first mixed with binder and extruded into TiO_2 honeycomb monolith with a square cell shape. It was dried at 120 °C, calcined at 500 °C and impregnated with NH_4VO_3 diluted in oxalic acid, and calcined to the finished sulfate V_2O_5/TiO_2 catalyst. The amount of the vanadia was

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Table 1
Characteristics of MTA and sulfated TiO_2

MTA ($TiO(OH)_2$)	
Supplier	Hankook Titanium
Preparation	Sulfate route
Concentration	ca. 40 g/l
pH	1.0–1.2
Sulfated TiO_2[a]	
BET surface area	98 m^2/g
Phase	Anatase
Sulfur content	1.72 wt.%

[a] The sample was dried at 120 °C over 10 h and calcined at 500 °C over 5 h.

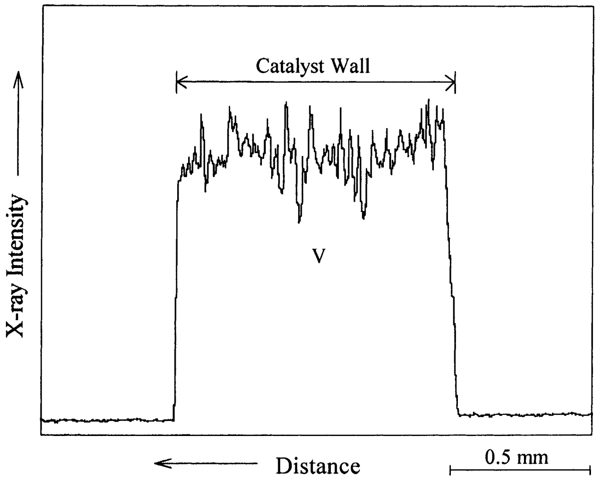

Fig. 1. EPMA (electron probe microanalysis) line profile for vanadium over a cross-section of the catalyst wall.

2.0 wt.% and it was well impregnated in the extruded TiO_2 monolith as shown in Fig. 1. The size of the catalyst element is 76 mm × 76 mm × 100 mm and the other physical properties are listed in Table 2. The catalyst module (500 mm × 500 mm × 500 mm) which consists of the catalyst elements was prepared for pilot plant test and compared with commercial catalysts listed in Table 3.

2.2. The pilot plant

The pilot plant consisting of four catalytic reactors in order to compare NO reductions of the prepared catalysts in the same flue gas condition is shown in Fig. 2. The flue gas was extracted from coal fired utility boiler and the composition is listed in Table 4. The flue gas was introduced into the catalytic reactors by the blower with capacity of 3000 Nm^3/h and controlled to desired flow rate and reaction temperature by by-pass damper and electric heater, respectively. Each catalytic reactor was normally operated in the range of 300–700 Nm^3/h and 260–400 °C. Anhydrous NH_3 was injected into the flue gas between the electric heater and the reactor. For the complete mixing of NH_3 with the flue gas, injection nozzles and baffles were installed before the catalytic reactor. The quantity of NH_3 was determined on the basis of the NO concentration at reactor inlet. The concentration of NO, SO_2 and NH_3 was measured by the NDIR type analyzer (Rosemount, Model 880A) and O_2 was measured by the analyzer zirconium oxide sensor (Rosemount, OXA 1000). In addition to the direct measurement, NH_3 slip was measured by manual gas sampling method [12]. All the data from this system such as concentration of flue gases, temperature, flow rate and pressure drop were monitored by the computer-interfaced automatic system. In order to investigate the erosion of the catalyst by fly ash, the three sample catalysts (sulfated catalyst, commercial B and commercial C) were installed in the probe inserted into the upstream of the pilot plant. The sample catalysts were of honeycomb type and the size of each catalyst was 25 mm × 25 mm × 25 mm. The stream velocity at the probe was speeded up to 15 m/s in order to accelerate their erosion.

3. Result and discussion

3.1. Effect of reaction temperature on NO reduction

The effect of the reaction temperature on NO reduction was determined at a space velocity of 4000 h^{-1} and NH_3/NO

Table 2
Physical properties of sulfated catalyst element

Type	Open frontal area (%)	Cell density (cell/in.^{2})	Cell size (mm)	Wall thickness (mm)	Hydraulic diameter (mm)	Geometric surface area (m^2/m^3)	V_2O_5 contents (wt.%)
Honeycomb	62	20	4.3	1.15	1.86	580	2.0

Table 3
Commercial catalyst for comparison

Catalyst	Type	Cell density (cell/in.^{2})	Composition	Application	Geometry (mm^3)
Commercial A	Plate	–	TiO_2, V oxide, Mo oxide	High dust	500 × 500 × 500
Commercial B	Honeycomb	20	TiO_2, V_2O_5, WO_3, MoO_3	High dust	500 × 500 × 500
Commercial C	Honeycomb	20	TiO_2, V_2O_5, WO_3	High dust	500 × 500 × 500

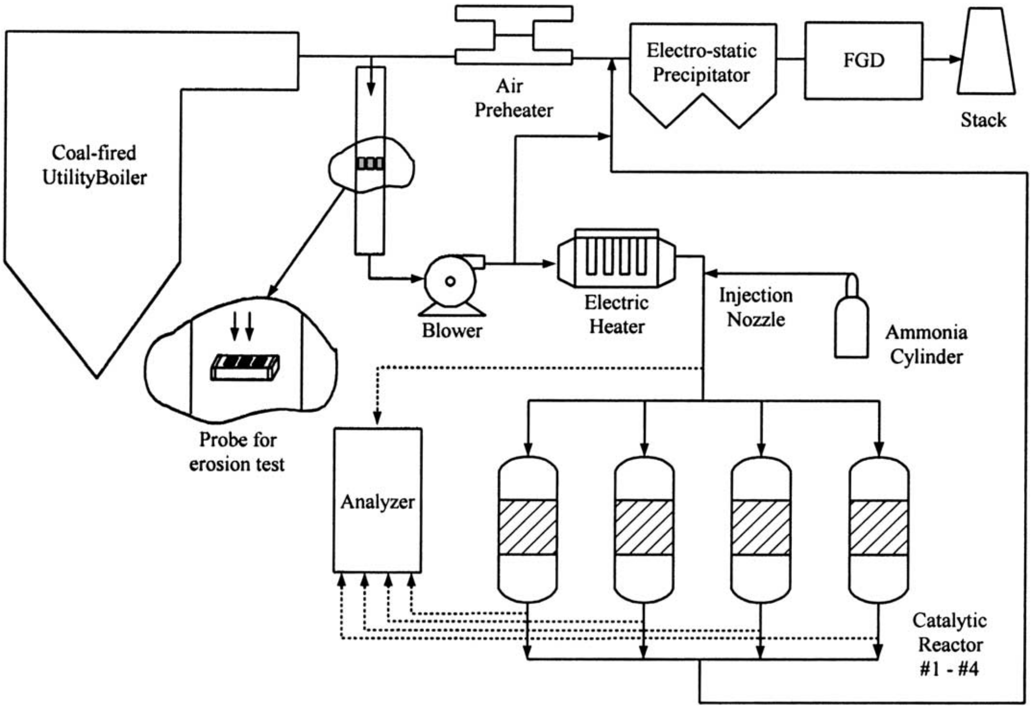

Fig. 2. Schematic flow diagram of SCR pilot plant.

mole ratio of 1.0. As shown in Fig. 3, the reduction of NO increased with increasing reaction temperature and reached a maximum value at approximately 350 °C. The reaction temperature windows for effective NO reduction was similar to those of the commercial catalysts showing a maximum value at approximately 350 °C.

3.2. *Effect of the mole ratio of NH_3/NO on NO reduction*

The mole ratio of NH_3/NO is one of the critical variables, because it can affect the removal of NO and ammonia slip which can lead to secondary impacts such as the formation of ammonia sulfates in the presence of SO_3. Fig. 4 shows NO reduction and ammonia slip of sulfated catalyst and commercial A catalyst according to the mole ratio of NH_3/NO at a reaction temperature of 350 °C and a space velocity of $4000\,h^{-1}$. The reduction of NO increased linearly with the mole ratio of NH_3/NO up to the mole ratio of 1.0. However, ammonia slip also increased with increasing mole ratio of NH_3/NO. It was the same as the commercial A catalyst showing a high efficiency. It is recommended that ammonia slip is kept below 5 ppm to prevent the formation of ammonia sulfates [13]. Therefore, NH_3/NO mole ratio should be 0.9–1.0 in order to keep the ammonia slip below 5 ppm and more than 85% reduction of NO.

Table 4
Flue gas composition

	N_2 (%)	O_2 (%)	CO_2 (%)	H_2O (%)	NO (ppm)	SO (ppm)	Fly ash (g/Nm^3)
Composition	75.5	3.5	14.0	7.0	200	300	17.4

3.3. *Effect of space velocity on NO reduction*

One of the most important parameters for catalytic reactor design and performance evaluation is the space velocity

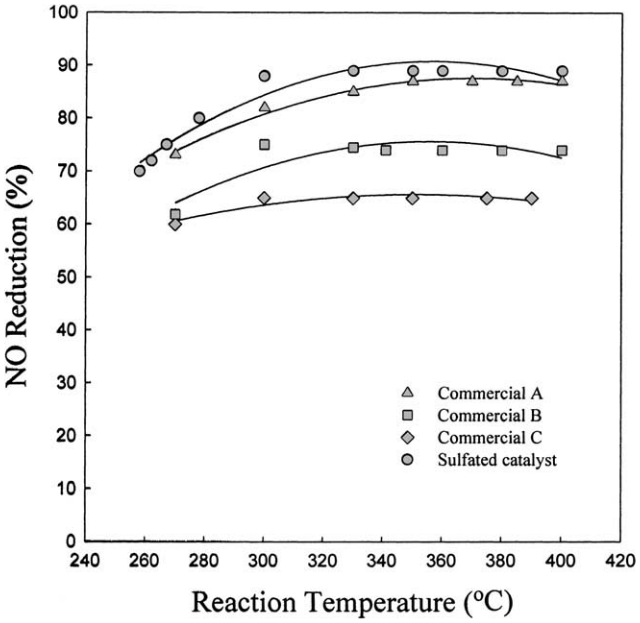

Fig. 3. Effect of reaction temperature on NO reduction.

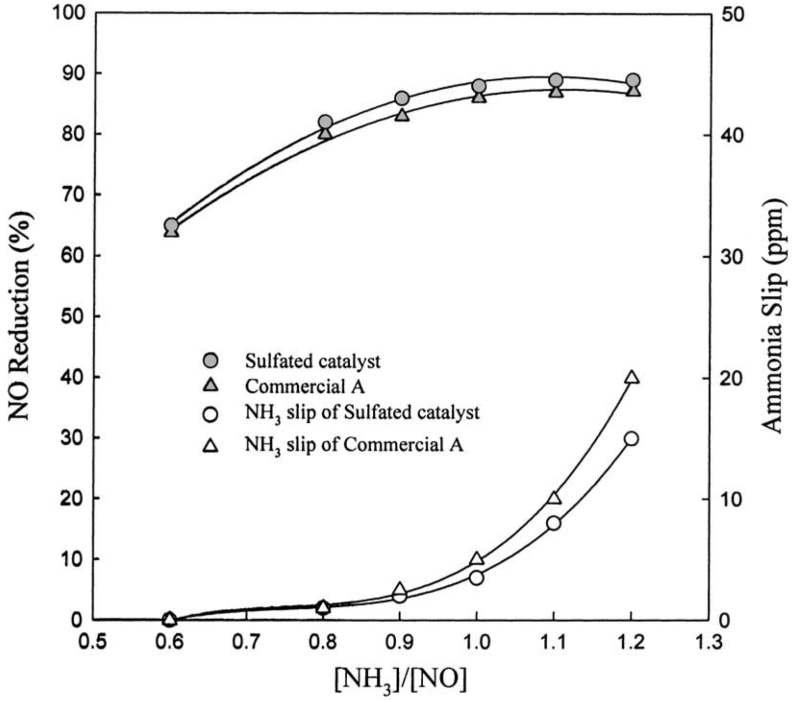

Fig. 4. Effect of NH_3/NO mole ratio on NO reduction and ammonia slip.

which is defined as the volumetric gas flow rate divided by the superficial volume of catalyst [1]. The effect of space velocity on NO reduction over sulfate catalyst was determined at reaction temperature of 350 °C and NH_3/NO mole ratio of 1.0. As shown in Fig. 5, NO reduction of about 90% was not changed with increasing space velocity up to 4000 h^{-1} and then it slightly decreased to about 85% with further increase of space velocity. From this result, the space velocity should be 4000 h^{-1} for ensuring good efficiency and avoiding excessive catalyst expense.

3.4. *Effect of operation time on NO reduction*

The reduction of NO was measured as a function of operation time in order to examine the endurance of sulfated

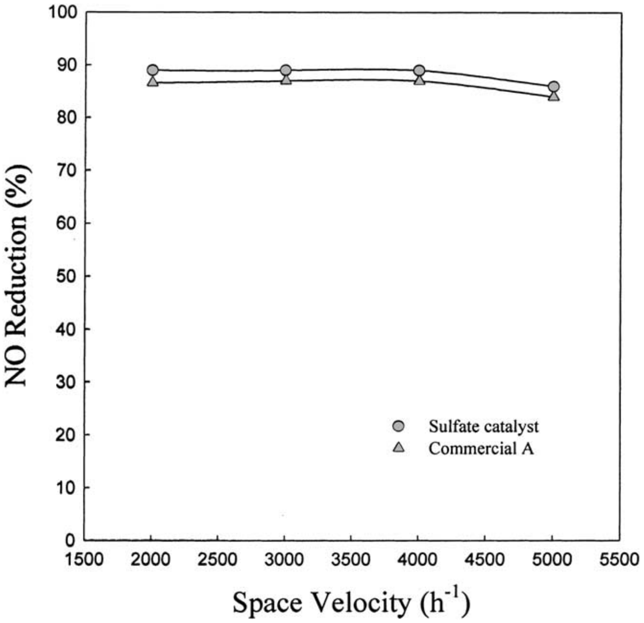

Fig. 5. Effect of space velocity on NO reduction.

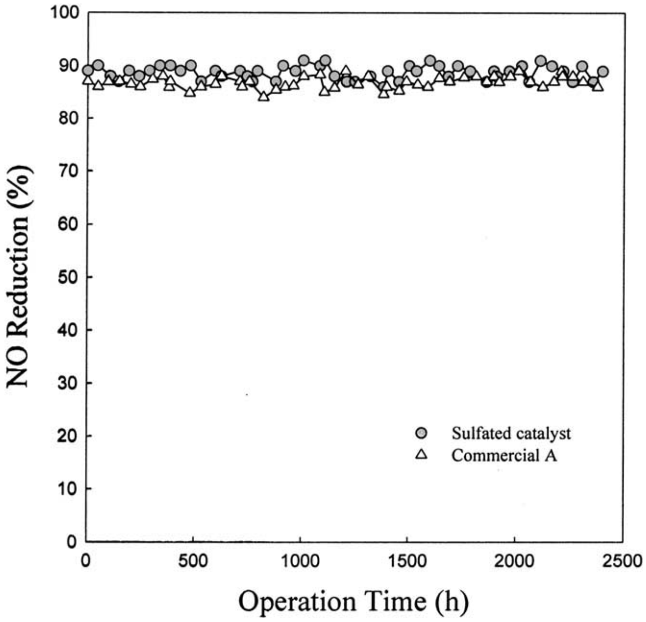

Fig. 6. Effect of operation time on NO reduction.

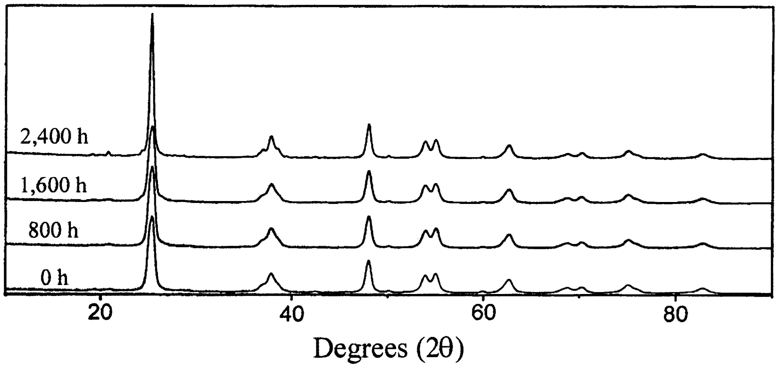

Fig. 7. XRD spectroscopy results of catalyst support TiO_2 with exposed time.

catalyst. The operation of catalytic reactor had been continued for 2400 h at a reaction temperature of 350 °C, space velocity of 4000 h^{-1} and NH_3/NO mole ratio of 1.0. As shown in Fig. 6, about 90% reduction of NO remained constant during the operation time as commercial A catalyst. However, considering the commercial catalyst life of 2–3 years, the long-term life test should be continued.

3.5. *Physical change of catalyst*

The X-ray diffraction (XRD) spectroscopy results of catalyst support TiO_2 after various periods of exposure are shown in Fig. 7. From the XRD patterns of the exposed catalyst, it is concluded that no important variations in the nature of phases of TiO_2 (anatase) were produced during the operation time. As shown in Table 5, the surface area of the catalyst decreased slightly and the mean pore diameter increased with increasing operation time. It could be attributed to masking of the micropore of the catalyst by fly ash. However, there was no change of catalytic activity as shown in Fig. 6.

3.6. *Erosion of catalyst*

In high dust SCR system, the strength of the catalyst is very important because of the catalyst erosion by fly ash, so that the linear velocity of the gas stream in commercial reactor is limited to approximately 6 m/s to prevent erosion [1]. The sample probe containing three catalyst samples was inserted into the upstream of the pilot plant in order to investigate the erosion of the honeycomb catalysts in the severe condition. As shown in Fig. 8, the erosion occurred severely for all catalysts because of high stream velocity of 15 m/s. However, the erosion rate of sulfated catalyst was about 17% after 2400 h of exposure time and lower than that of the commercial catalysts. It shows a good mechanical strength in comparison with commercial ones.

Table 5
Variation in surface area and mean pore diameter with exposed time

Exposed time (h)	Surface area (m^2/g)	Mean pore diameter ($\times 10^{-10}$ m)
0	53	392
800	53	404
1600	48	438
2400	47	439

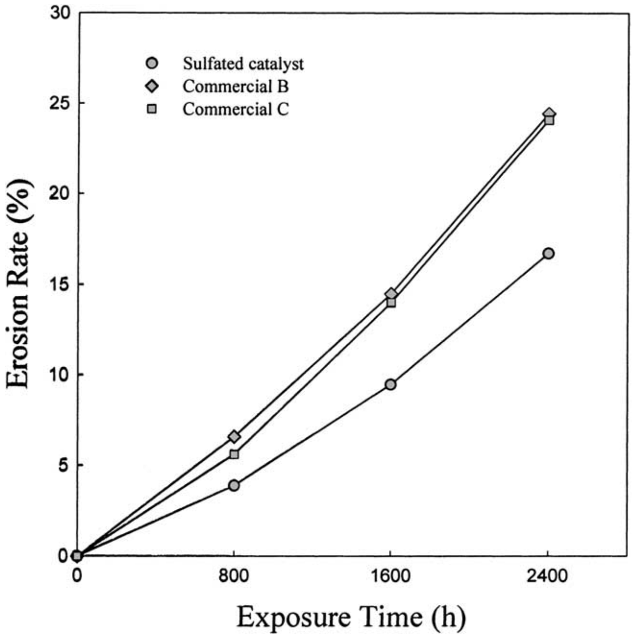

Fig. 8. Erosion rate of the honeycomb catalysts by fly ash.

4. Conclusion

Sulfated V_2O_5/TiO_2 catalyst from MTA was extruded in the shape of honeycomb in order to test under practical conditions. The activity and endurance of the catalyst were examined and compared with commercial catalysts in a pilot plant using actual flue gas from a coal fired utility boiler. The catalyst showed high NO reduction of about 90% at a space velocity of 4000 h^{-1}, NH_3/NO mole ratio of 1.0 and reaction temperature of 300–400 °C. The NO reduction remained constant during the present experiment of 2400 h. The erosion rate of the catalyst by fly ash was lower than that of the commercial catalysts. The results clearly demonstrate the high potential for this sulfated catalyst to be used commercially for the control of NO_x emissions from coal fired power plant.

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