

The Preparation of V_2O_5/TiO_2 Catalyst Supported on the Ceramic Filter Candle for Selective Reduction of NO

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Abstract—In order to prepare the catalytic filters based on V_2O_5/TiO_2 for the removal of NO_x and particulate simultaneously from the flue gas stream, the experimental study was carried out. The effective method to support TiO_2 layer in the pore of the commercial ceramic filter element was developed. TiO_2 layer was supported on the filter element by three methods; impregnation with Ti solution, sol-gel dip coating and sol-gel centrifugal coating. As the model test to check the catalytic activity, NO reduction in the oxidizing stream was investigated. The catalytic filter prepared by applying the centrifugal force showed the best NO conversion more than 90% when the face velocity was 0.02 m/sec. This was a very promising result for the application of catalytic filter for the flue gas control at high temperature. The supporting methods by the impregnation and dip coating were not recommended because the TiO_2 layer was concentrated in the exterior layer of the filter element.

Key words: Preparation, Catalytic Filter, NO Reduction, Ceramic Filter, V_2O_5/TiO_2

INTRODUCTION

Recently, many interests have been focused on the development of the catalytic filter in order to control the particulate and NO_x simultaneously. The concept of catalytic filter is adding the catalytic function to the high temperature filter element. The advanced ceramic filter element is composed of two layers; interior support and exterior membrane layer [Choi et al., 1999a]. Most of the filtration is carried out through the membrane layer that is the very thin thickness of about 100 μm . And the support layer is less useful for the function of the filtration but for a rigid supporter. The catalytic filter utilizes this large pores of the support layer of which pore size is about 100 μm for the room of the catalyst support.

Nitrous oxides are reduced by ammonia into nitrogen on the SCR catalyst. The utilization of catalytic filter for the effluent gas treatment was first introduced by B&W [Kudlac et al., 1992] and called SNBR. In this process, acidic gases like sulfuric oxides and hydrogen chloride are absorbed preliminary. And then particle and nitrous oxides are removed simultaneously through the catalytic filter. It has been pointed out this compact process is very attractive because it reduce the load for the heat recovery system by the pre-treatment of particulate, keeping the temperature high enough to convert the chemical pollutants into useful materials. It is also advantageous to construct in the various size and circumstance effectively and economically.

SCR catalysts have been widely developed in their forms and compositions [Nam et al., 1995; Amiridis et al., 1996; Saracco et al., 1995]. Among them, vanadium oxide/titanium oxide is proven

catalyst and very popular owing to its high activity and the poison resistance in sulfuric oxides and water [Amiridis et al., 1996; Terabe et al., 1994]. The strong poison property of this catalyst by alkali metal and the SCR performance are highly improved by the promotion effects by tungsten oxide. The advantage of the catalytic filter in the form of rigid filter elements like ceramic filter candle is to enable the lower pressure drop system as well as its dual function for control the particulate and nitrous oxides. So it allows the energy saving and a compact system to treat the effluent gases. Catalysts of honeycomb or plate types have advantages in their compact and successfully commercialized for gasoline engines and incinerators. However, it needs the pre-cleaning system for particulate because its particle path is too narrow to be plugged in the stream of high particulate concentration. Otherwise, the catalytic filters meet well for the streams of high concentration of particulate. However, the potential tasks for application this in an advanced system is to increase the catalytic activity by increasing the catalyst distribution.

It is reported that the SCR performance of the catalytic filter was successfully demonstrated in the pilot plants in EERC at university of North Dakota and Ohio Edisons R. E. Burger plant [Weber et al., 1994]. These tests showed the removal percent of nitrous oxides, sulfuric oxides, and particles are more than 90, 80, and 99.9%, respectively. However, the potential task is how to overcome the ammonia slip from the low conversion of NO_x . In order to solve the problem, the effective catalytic filter should be developed. Increasing the dispersion of TiO_2 particles is one of the solutions. The aim of this study is to develop an effective method to increase the dispersion of TiO_2 particles supporting on the ceramic filter elements which have been widely developed for the high temperature application like the advanced coal gasification and combustion.

EXPERIMENTAL

1. Preparation of Catalytic Filter

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The catalytic filters were prepared with the methods of impregnation, sol-gel coating, and sol-gel centrifuging coating. The commercial ceramic filter elements, PRD-66 (PRD) from AlliedSignal and alumina based-Kermidur (KRM) from USFilter were utilized as received form and compositions. PRD is prepared by spin weaving the textile glass yarn and is composite of corundum, cordierite, and mullite after high temperature treatment. It has high porosity of 60% with its pore size of the support layer is larger than 100 μm while it has effective membrane layer of its median pore size about 10 μm . KERM is fabricated by the sintering of alumina granule and has a mono-support layer of about 100 μm median pore size. The original dimension of the filter candles is 1.5 m length, 0.04 and 0.06 m of inner and outer diameter, respectively. It was cut in the tube form of 0.02 m length in order to fix in a small reactor. The filter tube was washed in an ultrasonic water bath and treated in 0.05 mole NaOH aqueous solution and then dried for 2 hr at 110 $^{\circ}\text{C}$ before being used.

In the method of impregnation, the filter tube was impregnated for 6 hr with the co-solution of tetra isopropyl ortho titanate (TIPO) and vanadium (III) acetyl acetonate (VAA) in benzene. The weight percent of TIPO and VAA was 5% and 0.5 or 1.0% with respect to benzene, respectively. The impregnated filter tube was vacuum dried at 2 $^{\circ}\text{C}$ for 1 hr and on-line calcinated in the air stream for 2 hr at 450 $^{\circ}\text{C}$ in the reactor.

The filter tube was wet coated for 20 minute with the colloidal TiO_2 solution prepared with a sol-gel method [Terabe et al., 1994; Choi et al., 1999b] in the sol-gel coating method. The colloidal TiO_2 was prepared by the procedure to dose TIPO in 35% HCl aqueous solution, cool to room temperature, gradually add water, and stabilize for 2 hr at 80 $^{\circ}\text{C}$. The catalytic filters were prepared at different mole ratio of HCl/TIPO (H/T) and dipping number. The dipped-filter tube was dried for one day at room temperature and 1 hr at 100 $^{\circ}\text{C}$ and then calcinated in the air stream for 2 hr. After then it was impregnated with 0.2 or 0.5 wt% VAA in benzene for 6 hr and was dried and calcinated with the same procedure as the impregnation method. The catalytic filters fabricated with the sol-gel coating method were classified in Table 1.

In the sol-gel centrifugal coating method, centrifugal force was applied in order to enhance the particle penetration into the inner layer of the filter element. The rotation speed was exactly controlled and measured by a tachometer. Colloidal TiO_2 was introduced into the rotating filter element as shown at Fig. 1. This method is expected to increase the mobility of TiO_2 particles into the inner pore of the filter element.

2. The Performance Test

The activity of the catalytic filter was tested in an experimental unit using mixture gas of NO, NH_3 , O_2 , and N_2 [Choi and Ahn, 1999b]. 0.2% NH_3 in N_2 , 0.15% NO in N_2 , and air were used as the source of the mixture gas. In the normal test run, the concentrations of NO, NH_3 , and O_2 were 300 (or 500) ppm, 300 (or 500) ppm, and 2 vol%

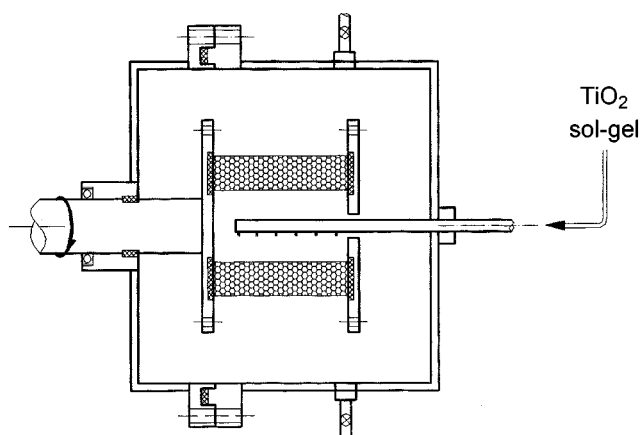


Fig. 1. The apparatus for TiO_2 coating by catalytic the centrifugal method.

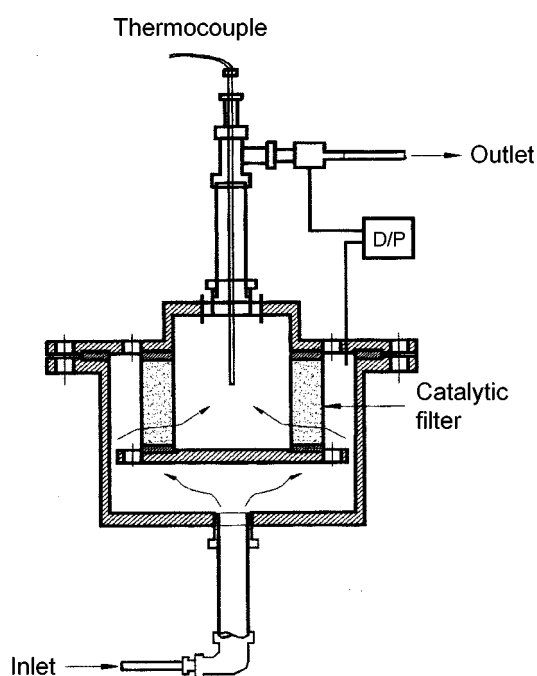


Fig. 2. The detail drawing of catalytic filter reactor.

in N_2 balanced, respectively. The total gas flow rate was controlled at the value that the actual face velocity was 0.01 (or 0.02) m/sec. The catalytic filter was mounted using flanges as shown at Fig. 2. It was first fixed between top and middle flanges with long bolts. And the reaction part was sealed with the top and bottom flanges. The reaction gases were introduced from bottom inlet of the reactor and passed out through the catalytic filter. So this gas pass mode (inward from the outer surface) is the same as that of industrial filtration using ceramic filter element. The differential pressure through

Table 1. Description of PRD-66 catalytic filters prepared by sol-gel dip method

Name	VAA wt% in Bz	Wt% of V_2O_5 over TiO_2	Name	VAA wt% in Bz	Wt% of V_2O_5 over TiO_2
PRDC1	0.5	1.45	PRDC4	3.0	8.10
PRDC2	1.0	2.40	PRDC5	4.0	10.71
PRDC3	2.0	4.94	PRDC6	10.0	-

the catalytic filter was measured with a differential pressure transducer.

The concentrations of NO, NO₂, and NH₃ were continuously analyzed by an on-line ammonia analyzer using a chemiluminescence method (TEI model 17, Thermo Environmental Instruments Inc.). And O₂ was analyzed by an off-line TCD using GS-Q capillary column.

RESULTS AND DISCUSSIONS

1. Supporting Characteristics of TiO₂

As previously reported [Choi et al., 1999c], one of the problems in the impregnation method is the ill distribution of the TiO₂ particles along the radial pore position. Most of the titanium oxides are concentrated in the exterior layer of the filter element and form patches having the low surface areas as shown at Fig. 3. TiO₂ particles showing the SEM images in the Fig. 3 were formed on KERM by the impregnation with 5% TIPOT solution in benzene. It seems that this result is due to the high vaporization rate of benzene. Benzene gas vaporizing at high speed entrains the impregnated TIPOT into the exterior layer during the drying time and concentrates the particles in the layer. This apt of ill distribution of titanium particle was

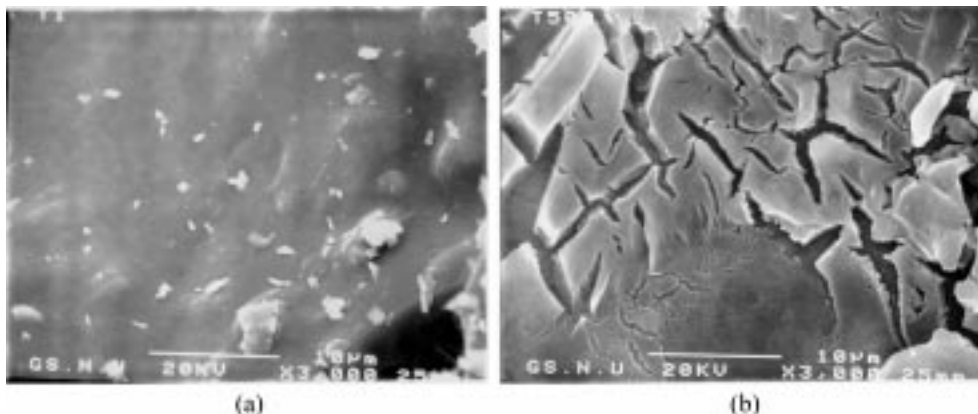


Fig. 3. The SEM images of TiO₂ coated on the interior (a) and exterior (b) position of KERM.

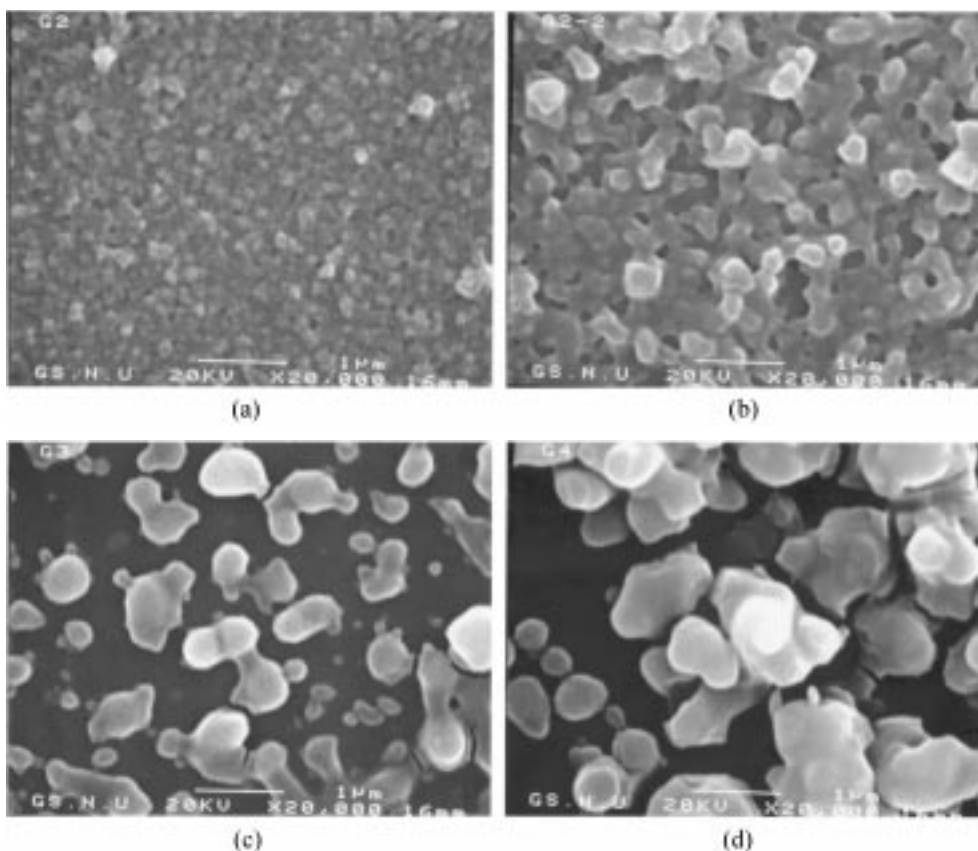


Fig. 4. The SEM images of TiO₂ particles supported on slide glass: dried sample (a) of H/T=2 and calcinated sample of H/T is 2(b), 3(c), and 4(d), respectively.

slightly improved when the drying temperature reduced to 2 °C [Choi and Ahn, 1999b]. In ordinary drying condition, it was very difficult to distribute TiO_2 particles well in the whole range of the filter element pore by the impregnation in benzene solution.

The method of sol-gel dip coating was tried to improve the distribution by using the formed- TiO_2 particles. The particle size of titanium sol-gel was effectively controlled by the change of HCl/TIPOT mole ratio (H/T). The particle size of TiO_2 was about 200 nm when H/T was 2 and increased with the increase of HCl concentration as shown at Fig. 4. TiO_2 particles showing the SEM images in the Fig. 4 were coated on the slide glass and dried at 120 °C and calcinated at 450 °C. From the analysis of the images of the dried (a) and calcinated (b) sample, it is evident that the fine TiO_2 particles are annealed during the calcination process. The particle was apparently crystallized when H/T is higher than 3. The photograph in Fig. 5 shows that a part of TiO_2 particle was well distributed on the surface of the filter element and other parts are freely segregated in the pore. However, it was difficult to find the TiO_2 particles distributed in the interior layer of the filter element when the filter element was coated by the simple dipping method. This result is because that it is difficult for TiO_2 to diffuse through the pores of the filter element by the method. Table 1 shows that the surface area of the catalytic filter was slightly increased after then

the coating number were 3.

As one of the effective method to penetrate TiO_2 particles into the inner pores of the filter element, the centrifugal force was applied by rotating the filter element while the colloidal TiO_2 solution was fed as shown at Fig. 1. Fig. 6 shows TiO_2 particles were also embedded at the interior layer of the filter element. It shows PRD pore was filled with TiO_2 particles stacked by the several times of coating. It is certain that the applying the centrifugal force during the wet coating is effective to penetrate the TiO_2 particles into the inner pore of the support layer of the filter element. The sol-gel solution for the centrifugal coating was prepared at the acid concentration (H/T) of 3. About 50 ml of the sol-gel solution was centrifugally circulated 10 times through the filter element (PRD) of the length of 0.02 m. According to the results showing in Fig. 6(b) and Fig. 7, the rotation speed is a sensitive factor on the supporting behavior of TiO_2 particles. We think this is because that the gel particles of TiO_2 form a flexible structure enough to be softened by any strength of force. It can be flatted with the impact force during the centrifugal penetrating at high speed. Otherwise, long resident time of the sol-gel solution on the filter surface should lead the segregation when the rotation speed is too low. We choose the optimum speed at 580 rpm when the supporting amount of TiO_2 particle is maximum. The weight percent of TiO_2 particles supported was 2.745

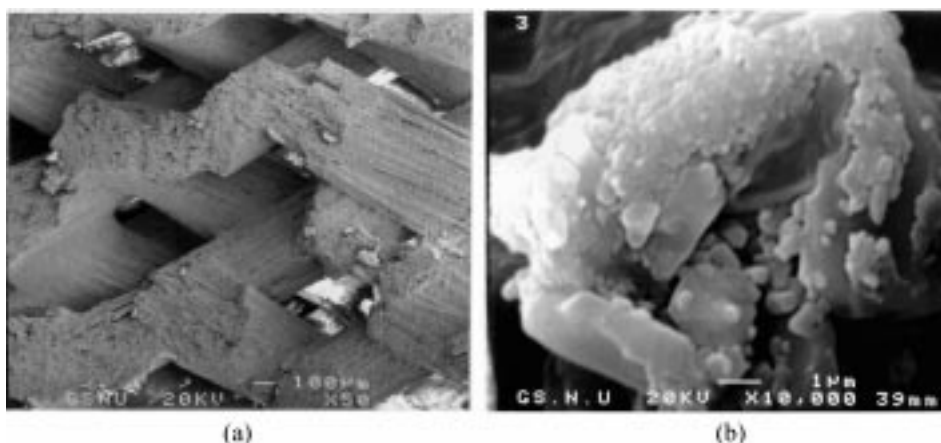


Fig. 5. The SEM morphology of the fresh PRD (a) and supported-titania (b) on PRD by the sol-gel dip coating.

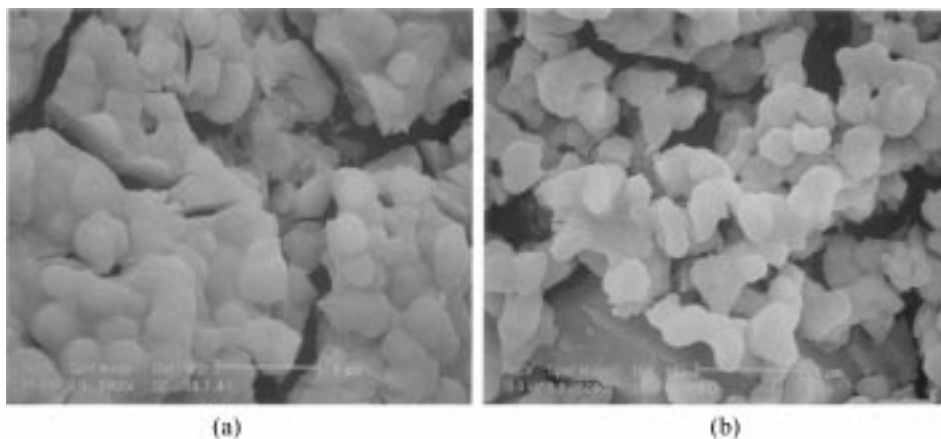


Fig. 6. SEM images of TiO_2 particles supported on the interior (a) and the exterior (b) PRD pore by the centrifugal coating method when the rotation speed is 740 rpm.

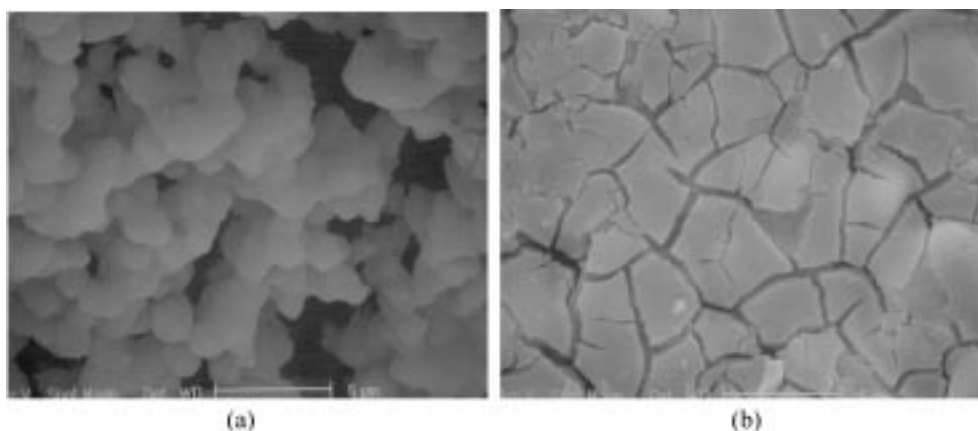


Fig. 7. SEM images of TiO_2 particles supported on the exterior PRD pore by the centrifugal coating method when the rotation speed is 580 (a) and 430 (b) rpm.

Table 2. The description of catalytic filter prepared by sol-gel centrifugal method

Name	H/T	VAA wt% in Bz	Surface area (m^2/g)	Name	H/T	VAA wt% in Bz	Surface area (m^2/g)
PRDS1	1	0.2	1.25	PRDS5	1	0.5	2.53
PRDS2	2	0.2	1.56	PRDN2	2	0.2	4.19
PRDS (PRDN)	3	0.2	2.53	PRDN3	3	0.2	5.16
PRDS4	4	0.2	2.55	PRDN4	4	0.2	5.62

with respect to the filter element. The weight percent of VAA respect to TiO_2 was shown in Table 2.

2. Performance of the Catalytic Filter

Fig. 8 shows the NO conversion of the catalytic filters prepared by the sol-gel dip coating with the change of H/T when the face velocity is 0.01 m/sec and concentrations of ammonia and NO are 300 ppm. This figure shows that NO conversion over the catalytic filters prepared by sol-gel dip coating has a limit performance which do not meets the industrial goal even though the activity was slightly increased as H/T increases. PRDI1 in the figure denotes the catalytic filter prepared by co-impregnation method with the 0.5 and 5.0 wt% of the concentration of VAA and TIPOT, respectively, in benzene. And PRDS5 is the catalytic filter prepared by the sol-gel dip coating method with the concentration of VAA of 0.5%. NO

conversions over these two catalytic filters are about 80%, which are not satisfactory for the industrial application. The reason of this result is likely due to the ill penetration of titanium gels into the inner pores of the filter candle by a simple dipping method.

In order to increase the coating amount of TiO_2 particles, catalytic filters were fabricated with several times of dip coating. Fig. 9 shows the pressure drop though the catalytic filter is significantly increases after the coating number is 3 times. And the catalytic activity was also invariant after the dip coating times was twice as shown at Fig. 10. So the optimum number for the dip coating was selected as 3 times.

Fig. 11 shows that NO conversion over the catalytic filter prepared by applying centrifugal force. It is apparently high compared

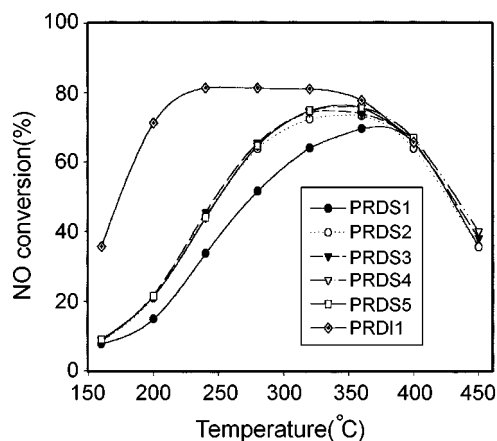


Fig. 8. NO conversion over the catalytic filter prepared according to H/T.

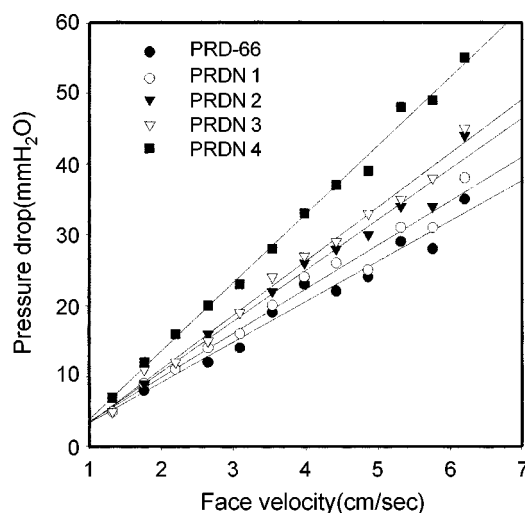


Fig. 9. Effect of coating times on the pressure of the catalytic filters.

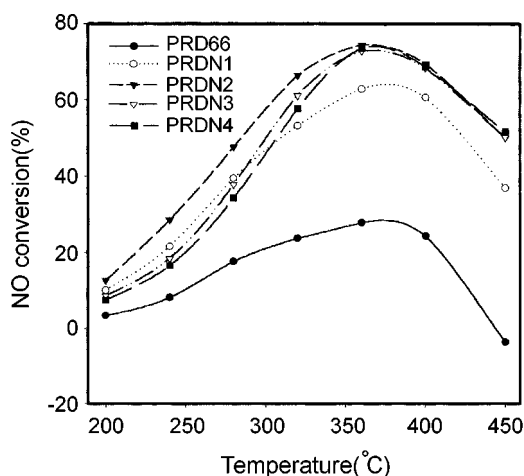


Fig. 10. Effect of coating number on the catalytic activity of PRDN'S.

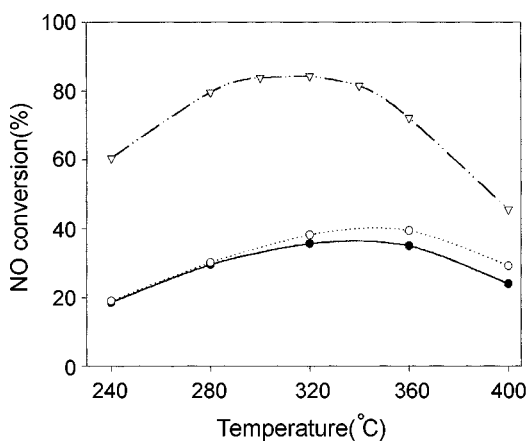


Fig. 11. NO conversion over catalytic filters: PRDC2 (▽) and co-impregnated one with VAA/TIPOT=0.5/5.0 (●) and 1.0/5.0 (○).

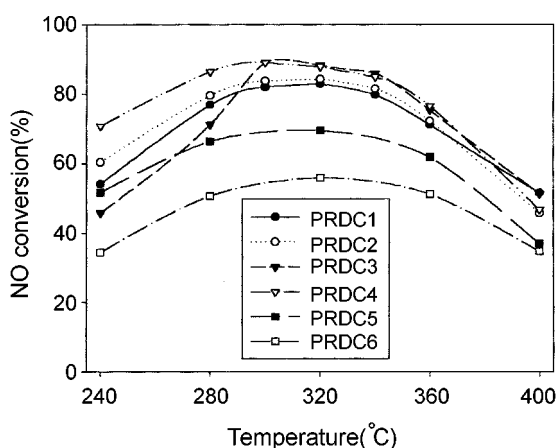


Fig. 12. The effect of VAA concentration on according the NO conversion over PRDC series.

to the impregnated- one when the face velocity is 0.02 m/sec for the case of ammonia concentration is 500 ppm. The catalytic activity was further improved up to 90% by the increase of VAA con-

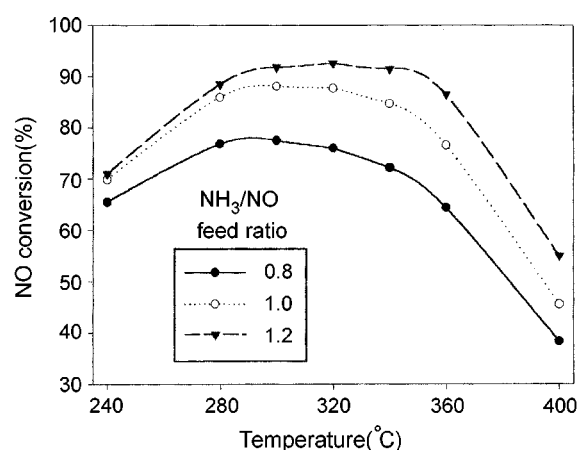


Fig. 13. NO conversion over PRDC4 according to ammonia feed rate.

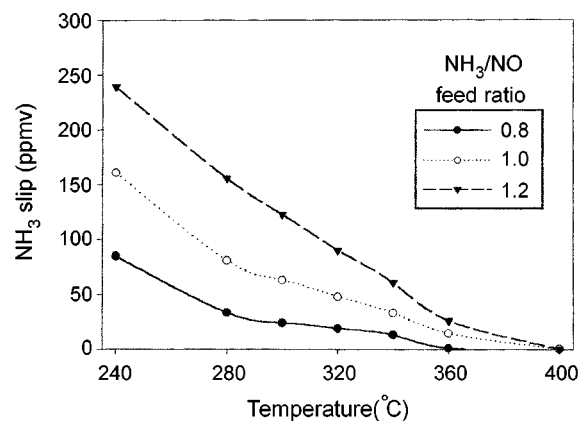


Fig. 14. Ammonia slip over PRDC4 according to ammonia feed rate.

centration as shown at Fig. 12. It was optimized at VAA concentration of 3.0 wt% with respect to benzene. Even though the result is well satisfactory for the regulation of NO, it still does not meet successfully the recommending limit for ammonia slip which is less than 10 ppm for the commercialization of SCR unit. using this catalytic filter because the ammonia slip is more than 50 ppm for the control of effluent gas containing ammonia concentration of 500 ppm with 90% of conversion efficiency. Fig. 13 and Fig. 14 show the NO conversion and ammonia slip with respect to the change of ammonia feed rate. These figures denote there is rare choice to select the optimum operation condition to fit the ammonia slip less than 10 ppm. So we need further more trials to improve the catalytic activity up to 99.8 % with using the catalytic promoters.

CONCLUSIONS

In order to preparation the catalytic filters based on V_2O_5/TiO_2 , the supporting methods of TiO_2 layer in the pore of the commercial ceramic filter element were compared and the catalytic activity was measured in an experimental unit using the simulated gas.

The NO reduction activities of the catalytic filter prepared by the impregnation and sol-gel dip coating methods were very low

because that TiO_2 particles supported were concentrated in the exterior layer of the ceramic filters.

TiO_2 particles supported on PRD-66 by the sol-gel centrifugal coating were well distributed. And the catalytic filter prepared this method shows NO conversion more than 90% for the NO concentration of 500 ppm at the face velocity of 0.02 m/sec, which was very promising in order to develop the commercial catalytic filter for the flue gas control at high temperature. The result is well satisfactory for the regulation of NO. However, it still does not meet successfully the recommend limit for ammonia slip that should be less than 10 ppm for the commercialization of SCR unit using this catalytic filter because the ammonia slip is more than 50 ppm for the control of ammonia concentration of 500 ppm with 90% of conversion efficiency. So there is further task to improve the catalytic activity up to 99.8% with using the catalytic promoters.

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