

NO REDUCTION PROPERTY OF Pt-V₂O₅-WO₃/TiO₂ CATALYST SUPPORTED ON PRD-66 CERAMIC FILTER

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Abstract : The effect of Pt addition over V₂O₅-WO₃-TiO₂ catalyst supported on PRD-66 was investigated for NO reduction in order to develop the catalytic filter working at low temperature. Catalytic filters, Pt-V₂O₅-WO₃-TiO₂/PRD, were prepared by co-impregnation of Pt, V, and W precursors on TiO₂-coated ceramic filter named PRD (PRD-66). Titania was coated onto the pore surface of the ceramic filter using a vacuum aided-dip coating method. The Pt-loaded catalytic filter shifted the optimum working temperature from 260-320°C (for the catalytic filter without Pt addition) to 190-240°C, reducing 700 ppm NO to achieve the N_x slip concentration (N_x = NO+N₂O+NO₂+NH₃) less than 20 ppm at the face velocity of 2 cm/s. Pt-V₂O₅-WO₃-TiO₂ supported on PRD showed the similar catalytic activity for NO reduction with that supported on SiC filter as reported in a previous study,¹⁾ which implies the ceramic filter itself has no considerable interaction for the catalytic activity.

Key Words : Catalytic filter, Low temperature, Ammonia, NO reduction, Platinum effect, Ceramic filter

INTRODUCTION

Catalysts based on vanadia-titania have been widely developed and are most successfully commercialized ones for the reduction of NO_x with ammonia.²⁻⁹⁾ Recently, a key issue regarding commercial Selective Catalytic Reduction (SCR) catalysts is SO₃ formation by SO₂ oxidation whereby the SO₃ can subsequently form alkali sulphates. Although there is interesting report that a monolayer of sulphate species stabilizes the anatase phase of vanadia by inhibiting phase transition,¹⁰⁾ alkali sulphates have known as the elements inhibiting SCR activity by plugging the monolith gaps. Plugging the gaps of a monolith catalyst leads to serious operational problems, especially when dust con-

centration is high. Catalytic filter using a rigid filter element such as ceramic filter candle is one of solutions to solve the plugging problem as it has large space as well as having the filtration function. So it provides a low pressure drop system while treating particulate and nitrogen oxides simultaneously. Recently, it has been successfully developed to coat the pore surface of ceramic filters with TiO₂ using a centrifugal coating process.¹¹⁾ V₂O₅-WO₃-TiO₂ based-catalytic filters prepared by this method provided NO conversion efficiencies greater than 99% (for the initial NO concentration 700 ppm) at the face velocities of 2 cm/s over the temperature range of 290 to 350°C.¹²⁾

In order to extend the application, the development of catalytic filter working at low temperature is attractive to treat the ordinary flue gas streams preferably working at 150~250°C. Recently, Choi et al.¹⁾ reported that the optimum working temperature of NO reduction

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over V_2O_5 - WO_3 - TiO_2 catalyst supported SiC filter shifted to 180-230°C from 260-320°C by the addition of Pt. In the previous study,¹⁾ SiC filter was considered as the catalyst carrier which supplies the room for catalysts in its pore surface. However, SiC filter has known as an expensive and heavy material although it keeps a good filtration performance at high temperature over 700°C. Regarding the catalytic filter working at low temperature below 300°C, the cheap and light filter has more benefits. As an alternative material replacing SiC filter, PRD was selected in this study as it is inexpensive and light as well as friendly with the catalyst materials composed of metal oxides. The study was carried out at the same experimental conditions to investigate the relative properties with the case of SiC filter already reported in previous study.¹⁾

EXPERIMENTAL

TiO_2 powder (in the form of $TiO(OH)^2$) was purchased from Grand Chemical Industries and used as received. Its particle size is ranged from 5 to 10 nm. The TiO_2 particles were dispersed in a 0.05 M HCl aqueous solution and stabilized for 1 hr under agitation. The cylindrical ceramic filter elements, PRD-66 (PRD) from AlliedSignal Composite Inc.,¹³⁾ was used as received. PRD has known to be prepared by spin-weaving of the textile glass yarn and is composed of corundum ($\alpha-Al_2O_3$), cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$), and mullite ($3Al_2O_3 \cdot 2SiO_2$). It has the porosity of 60% with the pore size larger than 150 μm in the support layer also with the membrane layer of the median pore size around 10 μm . The original dimensions of the candle-type filter elements are 1.5 m in length and 4/6 cm in inner/outer diameter. The filter was cut into 1 cm in length in order to mount the tubular slice in a small experimental reactor. The slice was cleaned in an ultrasonic water bath, washed with the aqueous solution of 0.05 M NaOH and dried at 110°C for 2 hrs, in order, prior to loading TiO_2 . TiO_2 loading amount was adjusted by the

Table 1. The composition of the catalytic filters prepared with the variation of Pt and TiO_2 concentrations

Catalytic filter	TiO_2 in solution (wt.%)	TiO_2 /filter (wt.%)	Pt/ V_2O_5 (wt.%)
PRDT1	5	2.01	-
PRDT2	8	2.98	-
PRDT3	10	3.96	-
PRDT4	12	4.02	-
PRDPt1	8	2.98	5
PRDPt2	8	2.98	10
PRDPt3	8	2.98	15

change of TiO_2 concentration in the aqueous coating solution and measured by weighing the mass of the filter element before and after the coating process. The TiO_2 loading of each catalytic filter is shown in Table 1.

TiO_2 particles as the catalyst support were coated on the pore surface of the ceramic filter elements by a vacuum aided-dip coating method. The filter element was first evacuated for 30 min at a vacuum container to maintain the pressure at approximately 10^{-2} Pa. And then the corresponding aqueous coating solution was introduced from the bottom of the vacuum chamber. After being stabilized for 2 hrs in the coating solution at room temperature, the TiO_2 loaded-filter element was taken out from the solution, kept overnight at room condition, followed by drying for 1hr at 110°C, and then treated in the air stream of 450°C for 2 hrs. In order to support the catalyst, the TiO_2 loaded-ceramic filter element was impregnated in an oxalic acid solution containing ammonium metavanadate (NH_4VO_3) and ammonium para-tungstate ($(NH_4)_{10}W_{12}O_{41}$) in their desired-compositions. Platinum, in the precursor of ammonium tetrachloroplatinate(II) ($(NH_4)_2PtCl_4$), was added to the impregnation solution when required. The solution was slowly evaporated at 40°C until the filter element absorbed all of the solution, followed by drying overnight at room temperature, 1hr at 110°C and then treated in the air stream at 450°C for 2 hrs.

The compositions of Pt in the fabricated catalytic filters, based on the mass of V_2O_5 , are

shown in Table 1. The TiO₂ composition of the catalytic filters in Table 1 denotes the weight percent based on the mass of the filter element. And all the catalytic filters contain the same compositions for V₂O₅ and WO₃ (1 wt.% and 8 wt.%, based on TiO₂, respectively) as the compositions are chosen as the optimal composition in the previous study.¹⁾

The morphology and elemental compositions of catalyst supported on the filter elements were examined using scanning electron microscopy (SEM) (accelerating voltage 20 KV) and energy-dispersive X-ray analysis (EDX) (JEOL JSM-6300), respectively, after coating the samples with a thin layer of gold.

The catalytic activity was measured by the same experimental unit used in the previous study.¹⁾ The experimental unit, conditions, and procedures were described in detail previously. As the standard run, the concentrations of NO,

NH₃, and O₂ were 700 ppm, 700 ppm, and 2 vol. %, respectively, the remainder being N₂ to adjust the actual face velocity of 2 cm/s. The catalytic activity of the filter was measured at a series of steady state temperatures.

The concentrations of NO, N₂O+NO₂, and NH₃ were continuously analyzed by a chemiluminescence method (TEI model 17, Thermo Environmental Instruments Inc.). Oxygen concentration was analyzed by an off-line GC with TCD using a GS-Q capillary column.

RESULTS AND DISCUSSION

TiO₂ Coating on the Pore Surface of PRD

Figure 1(a) is the typical SEM image of fresh PRD, presenting the pores, developed in the interior supporting layer and formed by the intersectional spaces between the ceramic fibers crossing each other. The distance of a large

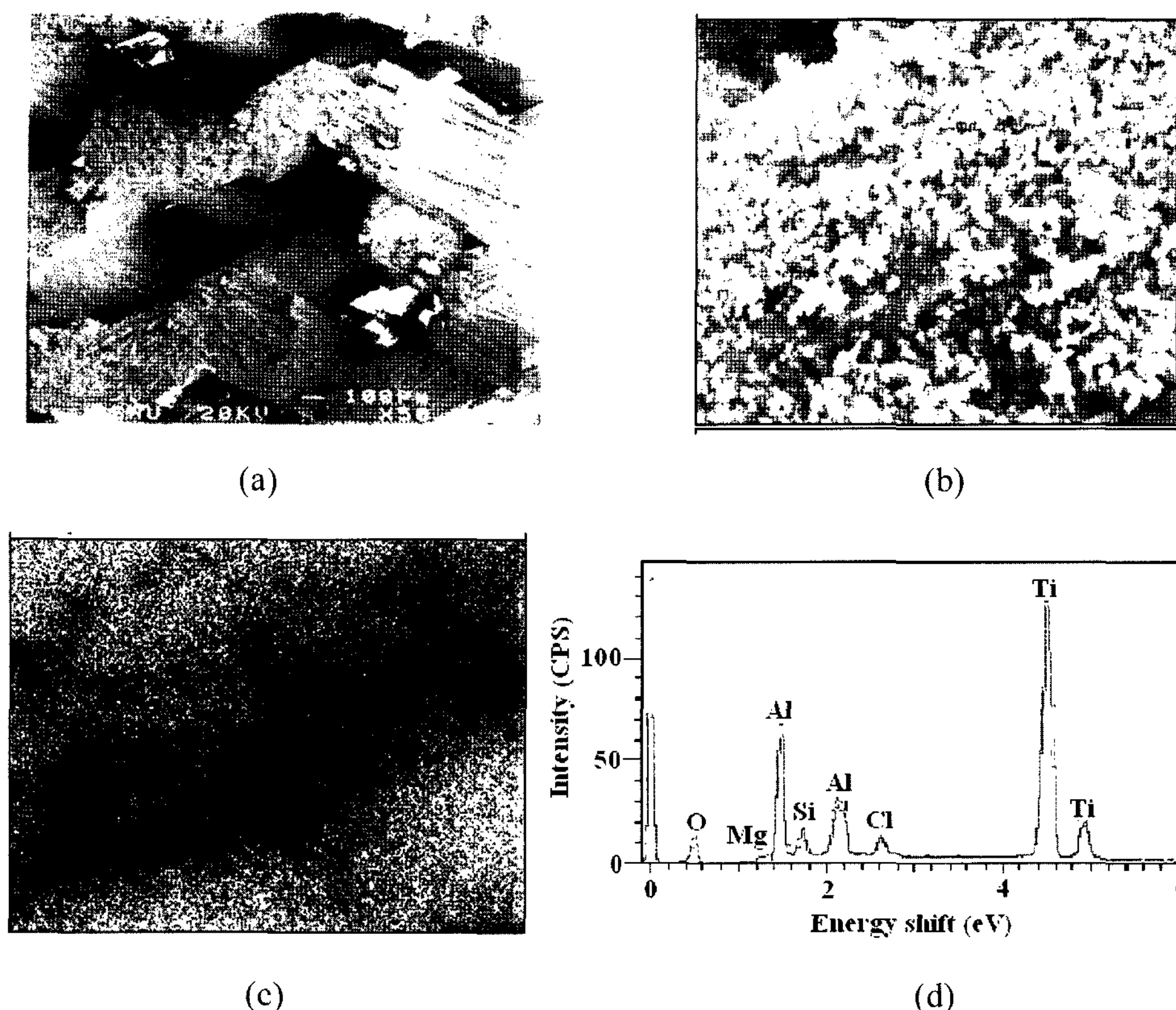


Figure 1. SEM images of: (a) fresh PRD; (b) TiO₂ coated on PRD; (c) Ti mapping image of section b; (d) EDS analysis of section b.

space is greater than 150 μm . Figure 1(b) represents the typical SEM image of TiO_2 particles coated on the ceramic fiber, and indicates the small TiO_2 particles (less than 1 μm diameter) were well distributed on the surface, forming multiple layers. The results of both the Ti mapping images (in Figure 1(c)) and the EDS analysis (in Figure 1(d)) show the particles in Figure 1(b) represent TiO_2 supported on the free surface of the fibers composing of the filter element.

The BET surface area of the fresh PRD is 0.1 m^2/g .¹³⁾ In previous work,¹²⁾ the surface area of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2/\text{PRD}$ was observed as 1.33 m^2/g for TiO_2 loading of 3.1 wt.%. The surface area of $\text{Pt-V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2/\text{PRD}$ was measured as 1.30 m^2/g for TiO_2 loading of 2.98 wt.%. So it was considered there was no considerable diminish in the surface area by Pt adding in the catalytic filter.

Pt- $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2/\text{PRD}$ Catalytic Filter

Figure 2 shows NO conversion of the catalytic filters $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2/\text{PRD}$ prepared with different concentrations of TiO_2 in the coating solution. The result shows that PRDT2, prepared by 8 wt.% TiO_2 solution, exhibits the best catalytic activity with the highest NO conversion and the broadest temperature window for NO conversion greater than 99.5%. PRDT2 is

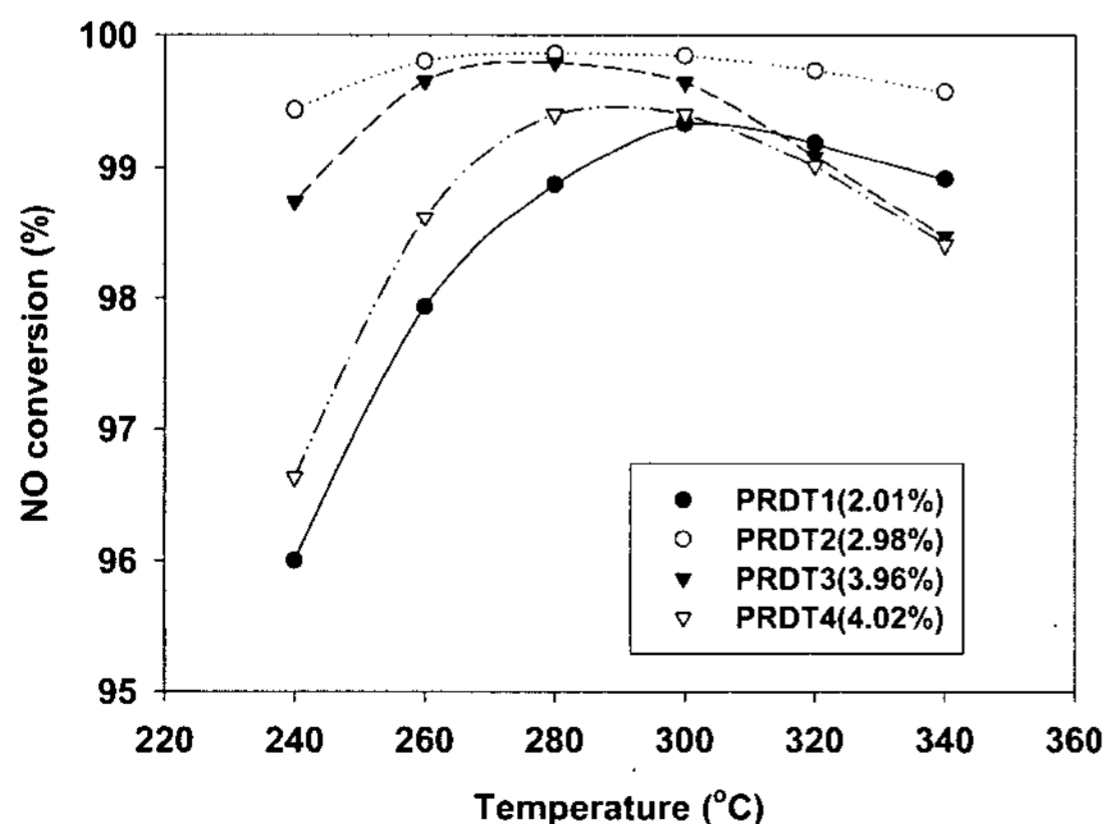


Figure 2. NO conversions in the NO SCR by NH_3 on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2/\text{PRD}$ catalytic filters prepared with different TiO_2 loadings.

expected to have the most N_2 selectivity as can be estimated by the results of N_x slip concentration (in Figure 3). Figure 3 presents the N_x slip concentration in the discharge gas from the catalytic filter reactor for the same samples denoted in Figure 2. N_x concentration indicates the summation of NH_3 , NO , N_2O , and NO_2 concentrations and represents the concentration of total pollution sourced by N-components included in the SCR reaction. Substitution of N_2 selectivity with the N_x slip concentration is in order to judge the catalytic activity showing the least amount of total pollutants. It is hard to set the environmentally acceptable N_x slip concentration value as it is different from system to system as well as dependant on the national policy. In Korean Permissible Air Discharge Standards, the discharge limits of ammonia and nitrogen oxides are 50 ppm for the each case in the strictest case. In this study, the tolerable limit of N_x slip concentration is specified arbitrary as 20 ppm just in order to compare the catalytic performance carried out in the laboratory scale unit. $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2/\text{PRD}$ catalytic filter meet this specification over the temperature range of 260 to 320°C. The most active catalytic filter, PRDT2, provides the optimum temperature window of 60°C (showing an N_x slip less than 20 ppm), ranging from 260 to 320°C, with an NO conversion greater than

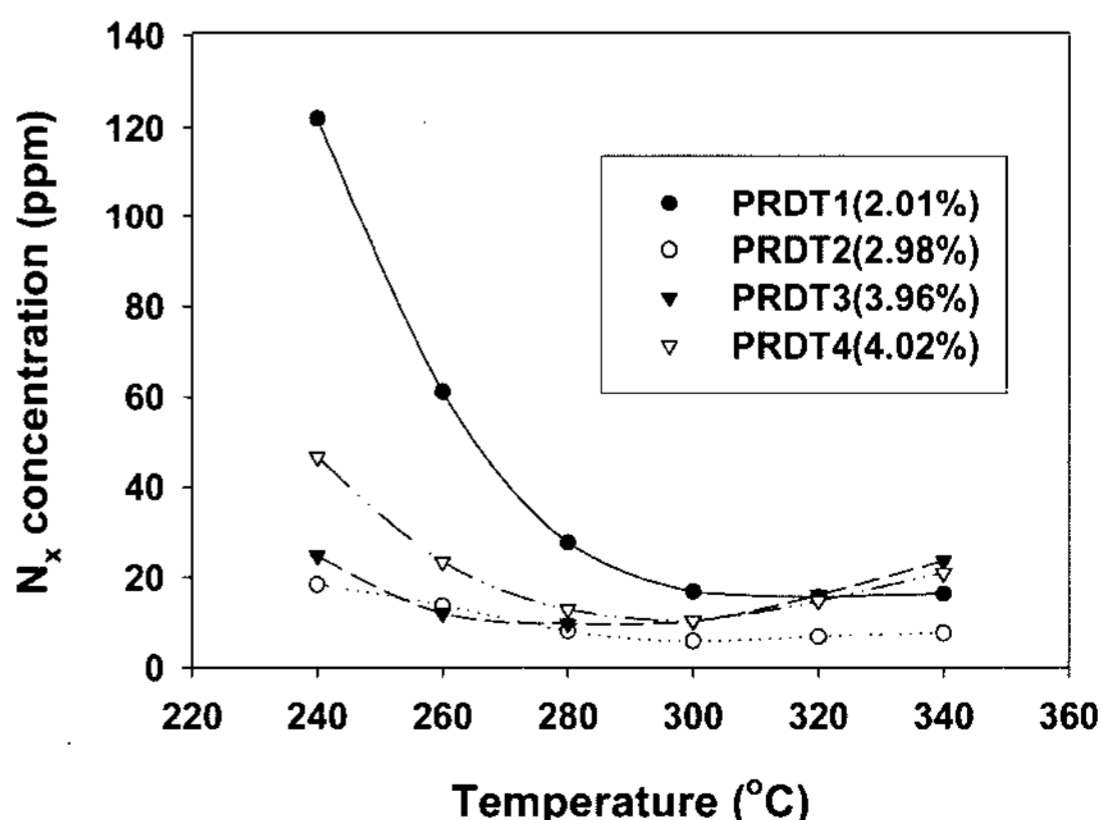


Figure 3. N_x slip concentrations in the NO SCR by NH_3 on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2/\text{PRD}$ catalytic filters prepared with different TiO_2 loadings.

99.8% for the treatment of 700 ppm NO at the face velocity of 2 cm/s. It is apparent that the catalytic filter developed in this study is a suitable replacement for the current commercial SCR catalyst and possesses the additional advantage of dust removal for in the effluent gas treatment, which is especially valuable for systems that are operated at high temperatures.

The TiO₂ loading (2.98 wt.%) of PRDT2 is less than that of PRDT3 (3.96 wt.%) and PRDT4 (4.02 wt.%) which were prepared using 10 and 12 wt.% TiO₂ solutions, respectively. Despite the higher loadings, the catalytic performances of PRDT3 and PRDT4 were lower than that of PRDT2. This may be an effect of the increased presence of TiO₂ reducing the surface area of the TiO₂-coated film via the clogging of the pores in the coating layer (not shown here). This outcome highlights a limitation of the vacuum coating method, and indicates an alternative method is required in order to obtain a high TiO₂ surface area in the pores of the ceramic filter. Among the samples considered, TiO₂ loading condition for PRDT2 provided the best catalyst for NO_x removal and therefore was used for further studies on catalytic filters containing platinum.

Figure 4 shows the effect of Pt addition to V₂O₅-WO₃/TiO₂/PRD catalytic filters on the NO conversion. Pt addition consistently shifts the active temperature towards a lower temperature range (190-240°C) with respect to catalytic filter without Pt (260-320°C for PRDT2). The maximum Pt loading of the catalytic filters in this study was 15% based on the V₂O₅ loading. Therefore, on the basis of TiO₂ present, the maximum Pt loading is 0.15 wt.% (as the V₂O₅ loading is 1% based on TiO₂). It is apparent such a small loading of Pt will cover only a minute percentage of the TiO₂ surface when we guess from the report that a Pt dose of 10 wt.% covers 6% of the titania surface.¹⁴⁾ However, catalytic activity of the V₂O₅-WO₃/TiO₂/PRD catalytic filters at low temperature is dramatically promoted by the addition of these small amounts of Pt.

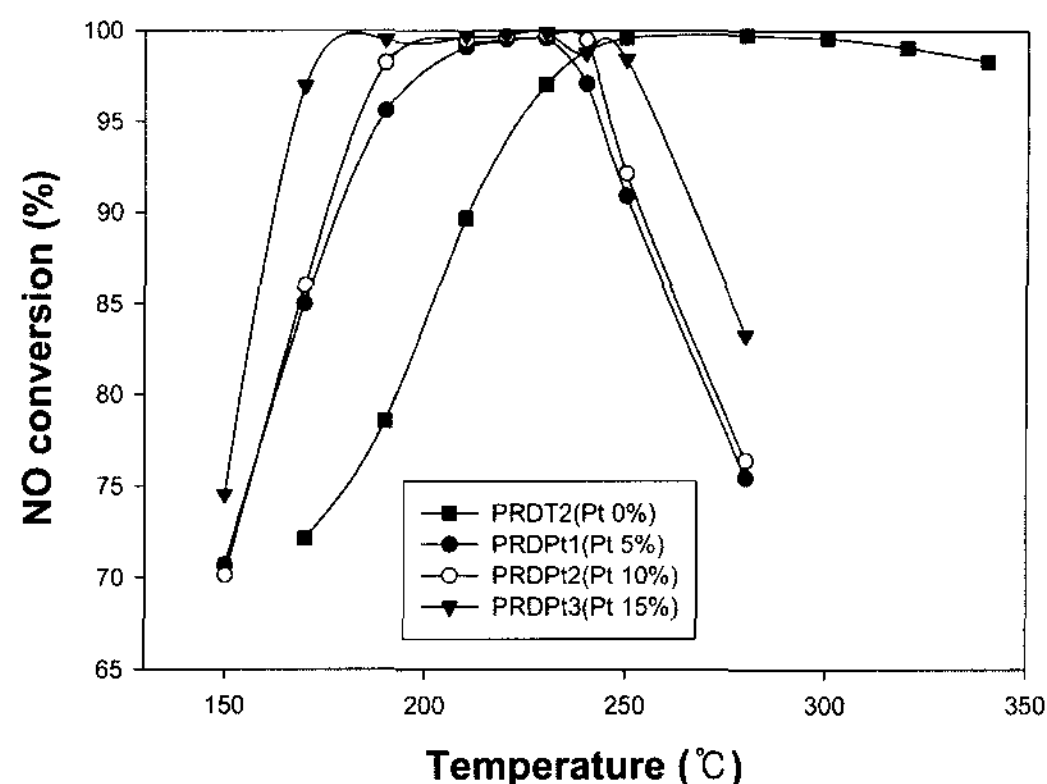


Figure 4. NO conversion of Pt-V₂O₅-WO₃/TiO₂/PRD catalytic filters containing different Pt loadings.

In the context of electronic modification, the effect of tungsten oxide on the system is relatively small because the energy band gap and band position are similar for TiO₂ and WO₃.¹⁵⁻¹⁶⁾ Paganini¹⁶⁾ reported that WO₃/TiO₂ (for a WO₃ dose up to 9 wt.%) displays similar electronic properties with pure TiO₂. However, the inclusion of V₂O₅ (even at 1 wt.% based on TiO₂) has enough impact to reduce the electron transfer energy with respect to TiO₂. Linsebigler et al.¹⁵⁾ reported that a small amount (0.3 - 1.3 wt.%) of vanadium present in V₂O₅/TiO₂ systems was preferentially reduced the electron transfer energy with respect to TiO₂. In the case of dosing with Pt, the TiO₂ surface is strongly modified by the formation of a Schottky junction between Pt and TiO₂,¹⁷⁻¹⁸⁾ where the electrons are trapped in Pt particle, resulting in a reduction of the band gap energy and promotion of electron transfer between the reactants and surface sites. This kind of Pt promotion effect has been well described in Pt/TiO₂ catalysts using as photo catalytic reaction systems, which has been understood as being carried out by the redox process.¹⁷⁾ It is understood that the temperature shift toward low one by the addition Pt in the catalytic filter is due to the similar effect of the formation of a Schottky junction between Pt and TiO₂ even though SCR is carried out by thermal energy as SCR has the same reduction mechanism with

the photo catalytic reduction.

Regarding the NO reduction mechanism with NH_3 , there are a number of mechanistic proposals,⁹⁾ which in some instances contradict each other. Almost all authors agree that the SCR involves a strongly adsorbed activated NH_3 species and a gas-phase or weakly adsorbed NO species. Moreover, there is little doubt on the reaction proceeds via a "redox" process and requires "acid" sites where the adsorbed ammonia is activated. There remains debate on whether the acid sites are Brönsted and/or Lewis types or single or multiple sites. Irrespective of the type of active sites, it is evident that they are deeply related to electron transfer or oxygen mobility for NO reduction with ammonia. The electron transfer properties seem to be strongly promoted by the presence of Pt on the catalysts.

In terms of SCR selectivity, It seems that the primary reason for the decrease in NO conversion (or alternatively the increase in N_x slip concentration (shown in Figure 5) for Pt addition is due to the stimulating of the oxidation properties by Pt addition at high temperature such as the increase of NH_3 oxidation to N_2O , NO or NO_2 . There are several reports describing that ammonia oxidation competes with NO reduction in the SCR system. In the case of V_2O_5 crystallites, ammonia oxidation occurs above 400°C when the vanadium reoxidation

rate increases¹⁹⁾ in the normal SCR gas composition. At low temperature ($< 200^\circ\text{C}$) platinum has known as a good catalyst for the selective oxidation of ammonia to N_2 .²⁰⁾ On Pt sponge,²¹⁾ N_2O was the dominant product during ammonia oxidation between 50 and 100°C , without NO formation. NO was only observed at temperatures greater than 300°C . Pt/ TiO_2 (P-25) decomposes ammonia at 170°C to N_2 in an environment containing water and oxygen with the slight formation of NO_2^- and NO_3^- (3-4 ppm for an initial 1000 ppm concentration and 95% conversion).²²⁾ On the basis of these results, for SCR catalyst acting at low temperatures, Pt in particular displays a higher activity towards oxidation than V_2O_5 . Similarly, for the catalytic filter containing Pt, NO conversion and N_2 selectivity dramatically decrease after 250°C as illustrated in Figure 6. This occurs as oxygen mobility increases by the presence of metals on the catalyst, resulting in a shift of ammonia oxidation temperatures towards lower values.

The trends of N_x slip concentration over the catalytic filter prepared with SiC and PRD filters were compared according to temperature change in Figure 7. Both of the two catalytic filters have the same catalyst composition based on the corresponding filter. And the experimental conditions are the same. The temperature region for the optimal reaction of NO reduction

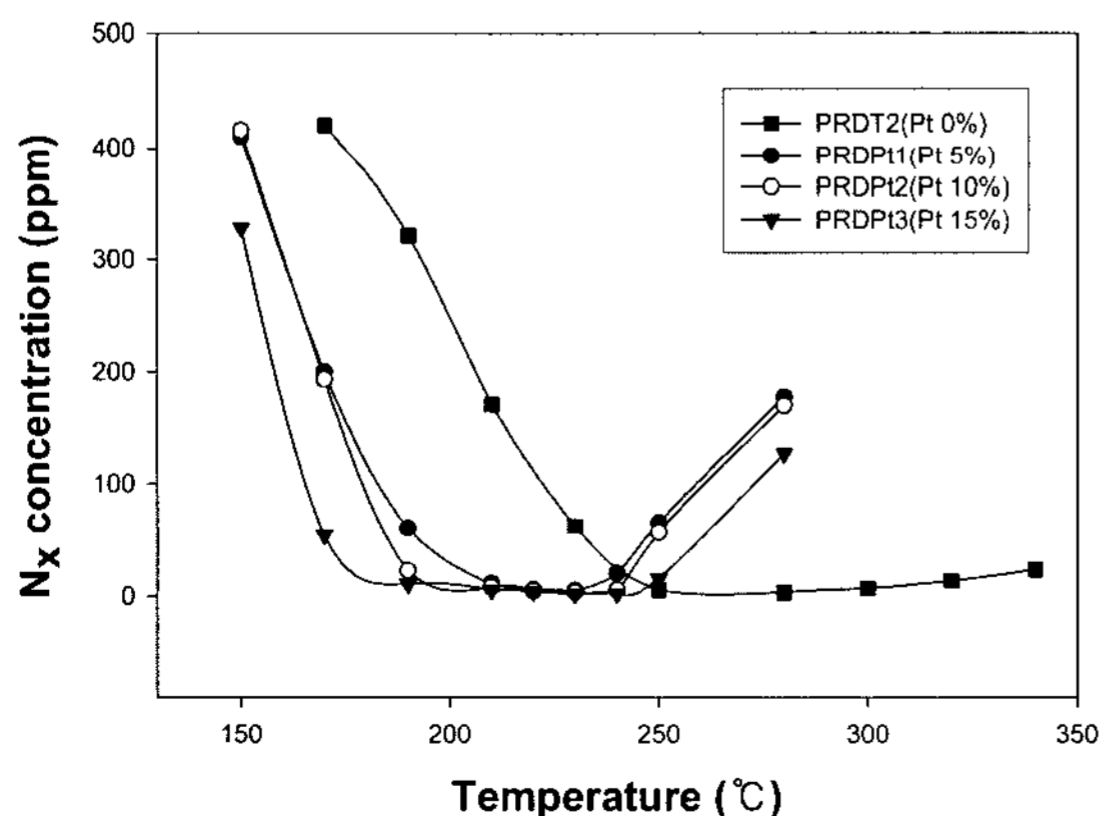


Figure 5. N_x slip concentration of Pt- V_2O_5 - WO_3 / TiO_2 /PRD catalytic filters containing different Pt loadings.

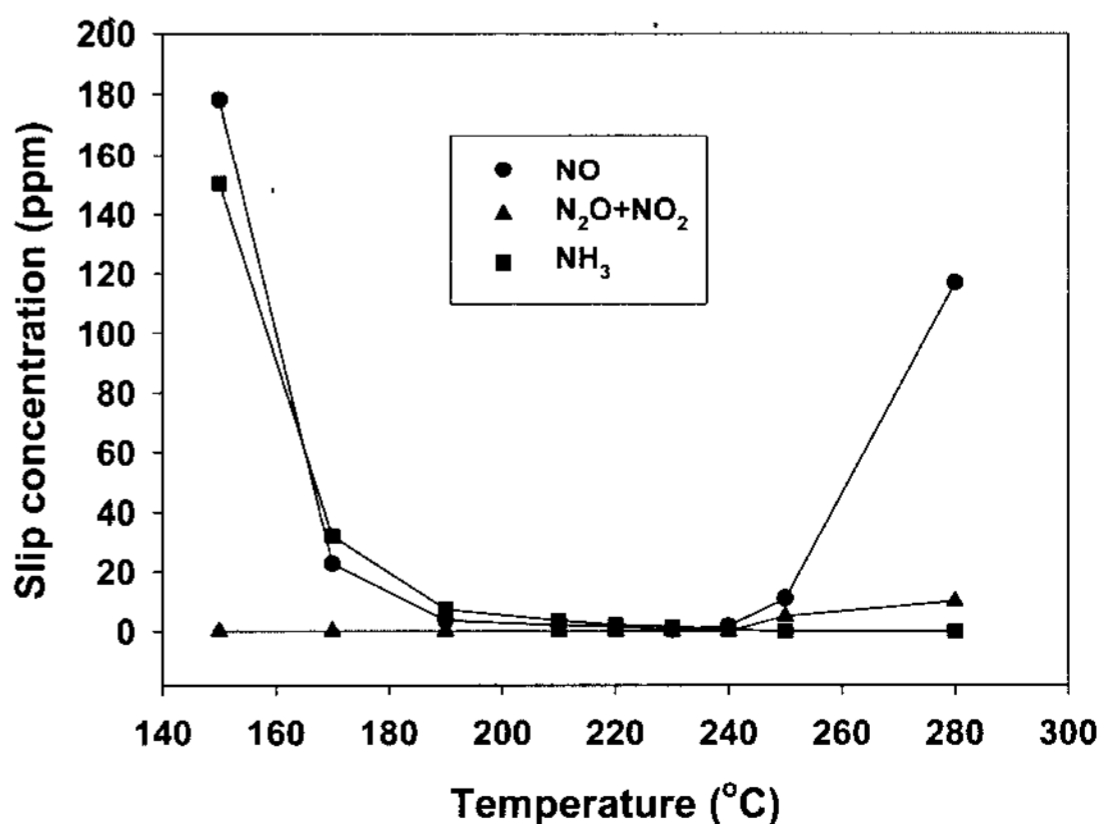


Figure 6. Slip concentrations of hazardous components involved in the NO SCR over PRDPt3.

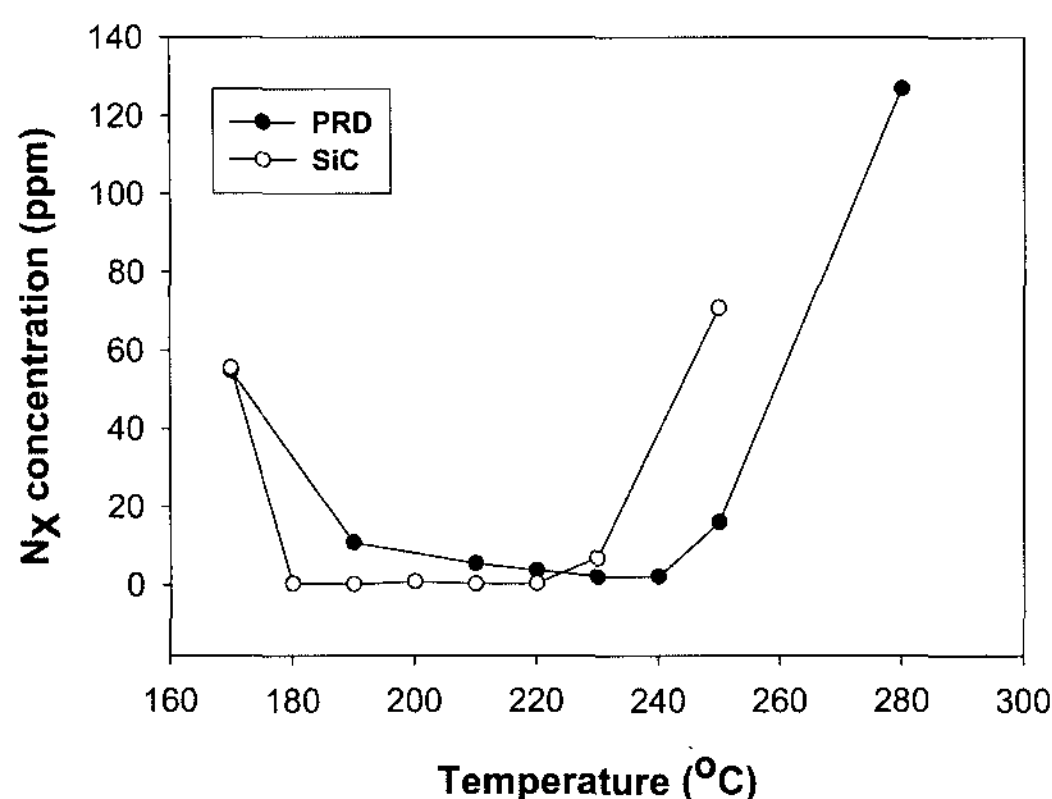


Figure 7. Comparison of N_x slip concentration for Pt-V₂O₅-WO₃/TiO₂ catalysts over PRD and SiC filter.

is similar with slight different. This result indicates that the filter as the catalyst supporter has no significant interaction with the catalyst components. So PRD filter is one of the valuable filter elements for the catalytic filter working at low temperature as it is cheap and light.

CONCLUSION

The promotion effect of Pt addition on V₂O₅-WO₃/TiO₂/PRD catalytic filters for NO reduction with ammonia was observed. The catalytic filters were prepared by impregnation of a TiO₂ vacuum coated-ceramic filter using a solution of V, W, and Pt precursors. TiO₂ was effectively coated on the pore surfaces of the ceramic filter (PRD) using the vacuum method. The optimal TiO₂ loadings on PRD were identified as 2.98 wt.%. The optimum loading of Pt was found to be 15 wt.% based on V₂O₅ which corresponded to a composition of 1.0 wt.% based on TiO₂ mass.

The presence of Pt in the catalytic filter acted to shift the optimum working temperature (giving an N_x slip concentration below 20 ppm at a face velocity of 2 cm/s) towards lower one: 190-240°C compared to 260-320°C for the catalytic filter without Pt. The behavior of Pt promotion effect of the catalytic filter over PRD filter is very similar in the case using SiC,¹⁾ which means PRD-66 filter is one of the

commendable catalyst supporters as it is cheap and light.

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