

Improvement of V₂O₅-WO₃/TiO₂ Supported Catalytic Sheet Filter for Simultaneous Reduction of NO_x and Particulates

Phule A. D., Choi J. H., and Kim J. H.

Abstract—Improvement of V₂O₅-WO₃/TiO₂ (VWT) supported catalytic sheet filter (SF) has been achieved by using a simple dip coating method with varied concentration of ball milled catalyst coating solution (10-30 wt%) and discussed their NO conversion performances at different reaction temperature (220-380 °C). Increase in the catalyst concentration more than 15 wt% it observed the bimodal particle size distribution with the particle size of ~1 micron and >2 micron, which leads to increase in pressure loss of catalyst filter as result to improve the NO conversion performance from 50% (BM10SF) to more than 90% (BM25SF and BM30SF) at reaction temperature range of 260-360 °C with N_x leakage less than 50 ppm in the reaction temperature range of 280-340 °C. Microstructural study with the help of an optical images explained the surface morphology of the SF with empty and buried (with VWT catalyst) pores. The filtration rate was less than 0.01 m / s, the NO conversion rate of 90% or more was achieved.

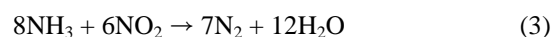
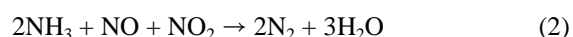
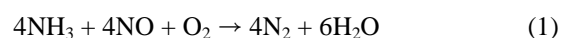
Index Terms—Ball milling, dip coating, NO_x and particulates reduction, SCR catalyst, V₂O₅-WO₃/TiO₂ catalytic sheet filter.

I. INTRODUCTION

Emission of nitrogen oxides in fuel from the stationary sources primarily from power stations, industrial heaters and cogeneration plants, diesel engines represents a major worldwide environmental problem. NO_x is blamed for the formation of ozone in troposphere, the production of acid rains, and respiratory problems to mankind [1]. Also the fine dust emission which negatively affects the human body has intended to increase every year in a world. One of the most efficient technologies for the reduction of NO_x emission as well as particulates is the selective catalytic reduction (SCR) with NH₃ over catalyst based on V₂O₅-WO₃/TiO₂ (VWT) [2], [3]. These catalysts are utilized in the rigid forms supported on the surface of ceramic filter elements in the industrial fields. However, plugging of their gas flow path is one of the serious operational problems which leads to the limited-application of SCR catalyst working at the dust-free stream only [4]. In order to overcome the problems pointed above, highly effective catalyst supported in the pores of the ceramic sheet

filter elements is one of the solutions to prevent the plugging problem and to provide a low pressure drop of the system as well as keeping an important advantage owing to the simultaneous treatment of particulates and NO_x.

The schematic of SCR process is as showed in Fig. 1 and which is based mainly on the following reactions:



Reaction (1) proceeds very rapidly over the catalyst in the temperature range of 250-450 °C with excess O₂ and the accounts of overall stoichiometry of the process (NH₃/NO = 1:1), since NO_x typically consists of >90% NO. The selective term refers to the ability of ammonia to react selectively with NO_x instead of being oxidized by oxygen to form N₂, N₂O, and NO; this ability has not been observed in the case of other simple reagents such as carbon monoxide and hydrocarbons and is thus unique of ammonia [1].

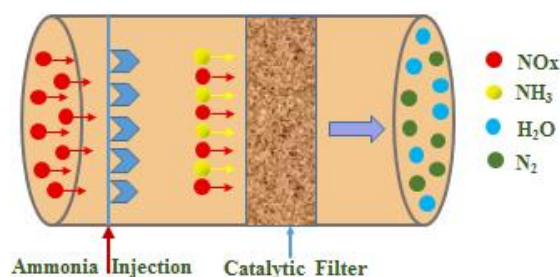


Fig. 1. Schematic of the selective catalytic reduction system.

In our study, we are using the simple solution (which has been prepared by using ball milling process to receive the catalyst particles with particular size distributions) dip coating technique to fabricate the V₂O₅-WO₃/TiO₂-supported ceramic catalytic sheet filters for simultaneous reduction of NO_x and particulates with NH₃. We observed the effect of coating solution concentration on NO_x reduction performance of the prepared VWT supported ceramic catalytic sheet filter. Particle size distribution of catalyst has been analyzed by using the ball milled coating solution. As the reaction time is a very important factor for completion of the reaction which performs at the surface of the catalytic filters, we studied the effect of face velocity on the NO_x reduction reaction. Microstructure of the coated and virgin

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sheet filters has been characterized by optical microscope to make sure that the pores of the ceramic sheet filters has been buried/filled with the VWT catalyst.

II. EXPERIMENTAL

A. Preparation of Catalyst Powder

Powder catalysts of V_2O_5 - WO_3 / TiO_2 was initially prepared by the wet impregnation method [5]. The composition 6 wt% V_2O_5 and 9 wt% WO_3 has been calculated on the basis of TiO_2 . First Ammonium meta-tungstate hydrate $[(NH_4)_{10}W_{12}O_{41}]$ (from Aldrich) was slowly added into the oxalic acid solution at 60-70 °C temperature with magnetic stirring then Ammonium vanadate NH_4VO_3 (from Junsei chemical Co. Ltd.) has been added slowly to above solution with magnetic stirring in their desired compositions. TiO_2 (P25) powder (Degussa Ltd.) was added slowly to above obtained green colored solution. The VWT catalyst solution was heated at 60-70 °C with magnetic stirring with agitation and then slowly evaporated until the liquid phase disappeared. The paste formation with the color change from green to blue has been observed. The catalyst paste was then treated in an air stream at 450 °C for 5 hr. The calcined VWT catalyst powder was used to prepare the coating solution of different concentration. The crystallinity of the VWT catalyst powder was investigated using X-ray diffractometer (XRD). XRD patterns were captured with X-ray diffractometer D8 Advanced (Bruker) operated at 40 kV and 200 mA employing Cu K α radiation.

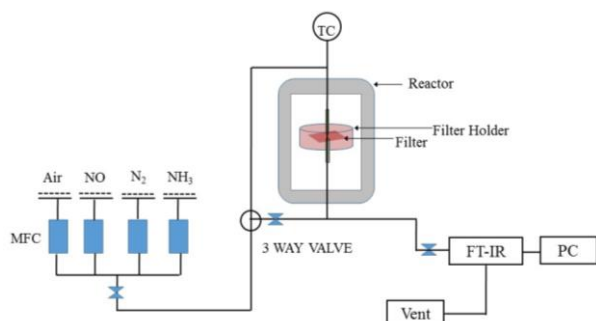


Fig. 2. Schematic representation of the reactor set up with FTIR.

B. Catalyst Coating Solution Preparation

The coating solution of the VWT catalyst has been prepared by using high energy ball milling machine with the speed of 1000 rpm for the duration of 7 min. to obtain a particular sized VWT catalyst particles. Catalyst particle size of the coating solution was measured during its ball milling process with the help of a particle size and shape analyzer (1090LD Shape Analyzer from SCINCO). To observe the effect of catalyst loading on the NO_x performance of the catalytic sheet filter, we have prepared the different weight percentage of coating solutions like 10, 15, 20, 25, and 30 wt% (which has been named as BM10CS, BM15CS, BM20CS, BM25CS, and BM30CS respectively, see Table I) with distilled water as a solvent. These coating solutions has further used to prepare the coated catalytic SF.

C. Catalytic Sheet Filter Coating Method

The ceramic sheet filter with 4X4 cm dimension and 4-5 mm thickness has been coated with the VWT catalyst by using simple dip coating method. First the sheet filter has been cleaned with the ultrasonication process for 30 min. at room temperature in distilled water then dried at 120 °C for 2 hrs in an electric oven. The dried SF has been dipped into the coating solutions (prepared by ball milling) for 2 min. and dried at 120 °C for 2 hrs to evaporate the solvent followed by the calcination at 450 °C in an electric furnace for 5 hrs to obtain the VWT coated SF. The specific surface area and porosity of the virgin and VWT coated SF has been measured by Hg porosimetry. The surface morphology of the virgin and VWT coated ceramic SF has been studied by using Optical microscope (HiMax Tech. Co. Ltd., Model HT004).

TABLE I: COMPOSITION OF CATALYST SUPPORTED ON SHEET FILTER USING THE DIFFERENT CATALYST COATING SOLUTION CONCENTRATION

Catalytic coating solution	Catalyst concentration (wt%)	V_2O_5 (wt%)	WO_3 (wt%)
BM10CS	10	6.05	9.0
BM15CS	15	6.05	9.0
BM20CS	20	6.05	9.0
BM25CS	25	6.05	9.0
BM30CS	30	6.05	9.0

TABLE II: MERCURY POROSIMETRY RESULTS FOR THE VIRGIN SHEET FILTER AND BM25SF

Sr. No.	Properties	Virgin Sheet Filter	BM25SF
1	Total Intrusion volume (mL/g)	0.3239	0.2444
2	Total pore area (m ² /g)	0.032	3.351
3	Median pore diameter (volume) (micron)	54.1161	24.8857
4	Median pore diameter (Area) (micron)	24.8998	0.0403
5	Average pore diameter (4V/A) (micron)	40.1107	0.2917
6	Bulk Density at 0.45 psia (g/mL)	1.7105	1.8958
7	Apparent (skeletal) density (g/mL)	3.8351	3.5326
8	Porosity (%)	55.4004	46.3355

D. Catalytic Activity Measurement

The catalytic activity of the catalytic filters was measured in an experimental unit shown in Fig. 2, where a special reactor designed to mount the sheet type ceramic catalytic filter by keeping the commercial operation mode of the filtration in such a way that the reacting gas passes from outside into inside of the filter element. The typical reaction gas was composed of 700 ppm NO , 700 ppm NH_3 , 7 vol. % O_2 , with balanced N_2 . A mass flow controller has been used to control the total gas flow rate to adjust the actual face velocity of 0.02 m/s. The catalytic activity was measured at a series of steady state temperature condition.

FT-IR spectrometer (MIDAC Prospect-IR) with a heated gas cell (Permanently Aligned 10 meter gas cell from GEMINI Scientific Instruments) and DTGS detectors were

used to analyze simultaneously the concentrations of NO, N₂O, NO₂, and NH₃. To avoid the condensation in the system all gas line tubes were heated at 120 °C. Background spectra has been recorded by using dry air. Each component's concentration was calculated by integration of the specific absorption frequencies (cm⁻¹) based on ethylene 938-962: NO 1873-1881, N₂O 2188-2190, NO₂ 1610-1614, NH₃ 951-989, and H₂O 1987-1994. N_x slip concentration (the summation of outlet concentrations of [NO]_{out} + [N₂O]_{out} + [NO₂]_{out} + [NH₃]_{out}) was used to estimate the catalytic performance which are the ultimate pollutants in the SCR unit. This simple formula, $([NO]_{in} - [NO]_{out}) / [NO]_{in}$ was used to calculate NO. Where, [X]_{in} and [X]_{out} means the concentration of component X (ppm) in the inlet and outlet, respectively.

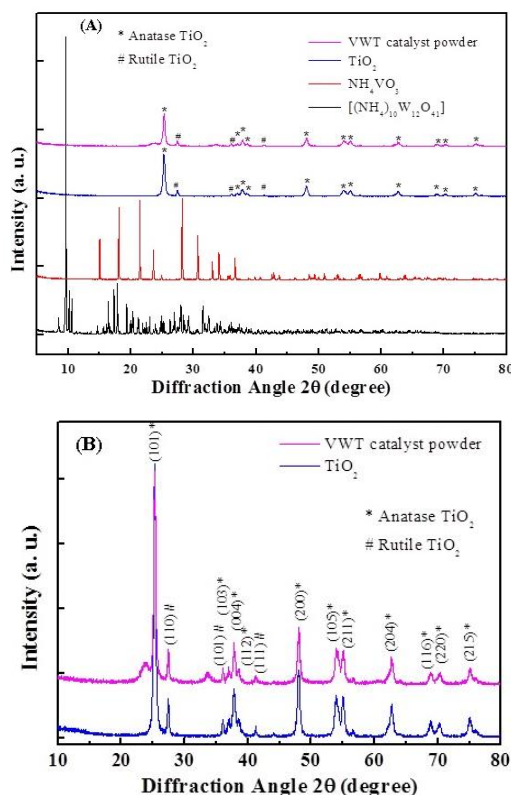


Fig. 3. XRD pattern in (A) ammonium meta-tungstate hydrate, ammonium vanadate, TiO₂, and VWT catalyst powder and (B) XRD pattern in TiO₂ and VWT for more clarity.

III. RESULTS AND DISCUSSIONS

Fig. 3A shows the different XRD pattern of the fresh NH₄VO₃, [(NH₄)₁₀W₁₂O₄₁], TiO₂ and VWT catalyst powder. The diffraction peaks for TiO₂ and VWT catalyst were mainly anatase phase (marked with *) (PDF-ICDD21-1272) of TiO₂ with a little of rutile phase (marked with #) (PDF-ICDD21-1276) of TiO₂. To make XRD peak intensities in TiO₂ and VWT much more visible a separate plots has been showed in Fig. 3B. It is worthy to note that the diffraction peaks ascribed to crystalline V₂O₅ and WO₃ phase was absent in the XRD pattern of VWT catalyst powder. It suggested that V and W be well dispersed, which support and improve the catalytic activity because it was favorable for an increased number of active sites [6], [7].

Fig. 4A, B shows optical images of the virgin SF the front and back side of SF at lower magnification and Figure 5C,D

shows the front and back side of the SF at higher magnification. It clearly observed that SF contains very big pores. Fig. 5A-H showed the optical images of VWT catalytic SF with 10 wt% (BM10SF) and 30 wt% (BM30SF) catalyst concentration for both sides of the SF. It can be seen that the pores are largely buried by catalyst, but still some pore remained (see magnified images Fig. 5B,D,F,H) open.

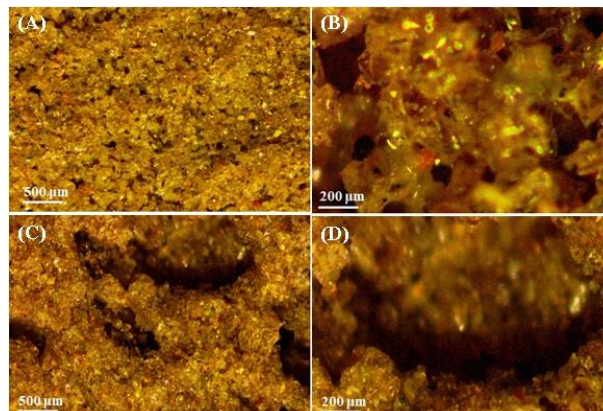


Fig. 4. Optical images of virgin sheet filter, (A, B) front side with lower and higher magnification and (C, D) of back side with low and high magnification.

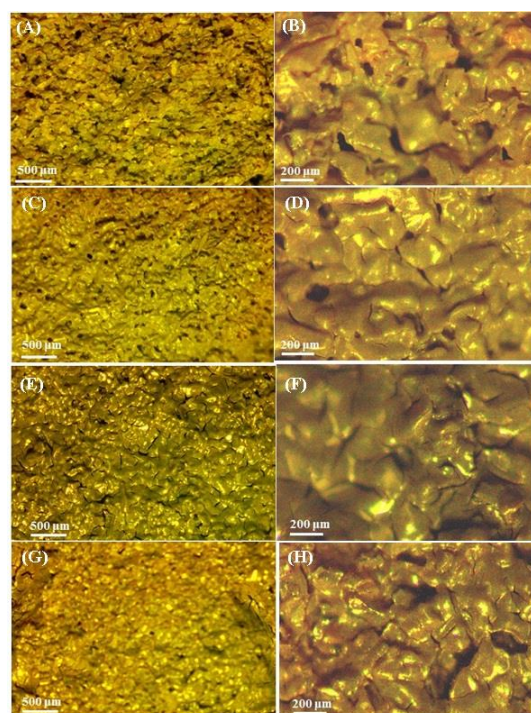


Fig. 5. Optical images of catalyst coated SF: (A, B) front side and (C, D) of back side for BM10SF and (E, F) front side and (G, H) of back side for BM30SF. All left side images with lower and right side images with higher magnification.

The particle size distribution of the catalyst in the different coating solution has been showed in Fig. 6, when the concentration of the catalyst solution is low. It shows the single distribution with an average particle size of 1 micron, but as we increase the concentration more than 15 wt% it observed the bimodal distribution with the particle size of ~1 micron and >2 micron. As the amount of catalyst coating increases the pressure loss of catalyst filter increases (see Fig. 7). For BM10SF, the pressure loss was 10 mmH₂O or less even at a filtration rate of 0.01 m / s, but increased to 40 mmH₂O for BM30SF. Therefore, it can be seen that when the

concentration of the catalyst is high, the pores of the filter are filled in a large amount. However, when the concentration of catalyst was 15 ~ 25 wt% the pressure loss was almost similar.

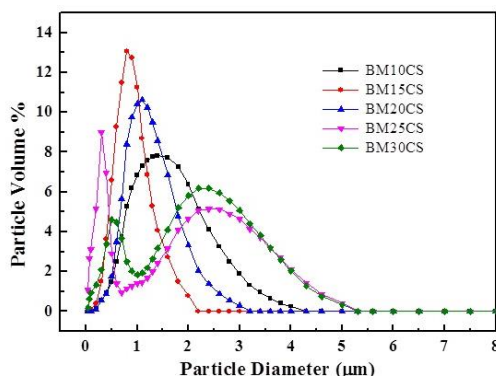


Fig. 6. Particle size distribution in BM10CS, BM15CS, BM20CS, BM25CS and BM30CS.

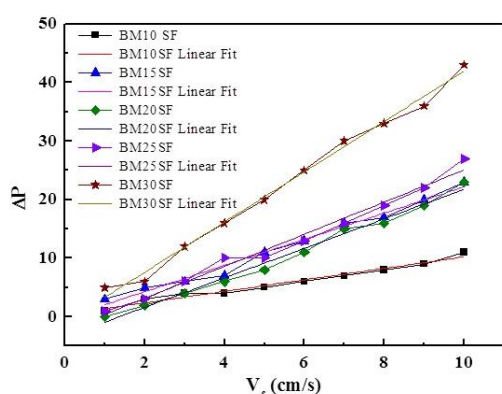


Fig. 7. Plot for pressure drop at different face velocity (V_f) for sheet filter coated with 10, 15, 20, 25 and 30 wt% coating solution of $V_2O_5-WO_3/TiO_2$ catalyst powder with air pressure 0.1 kgf/cm².

Fig. 8 shows the NO conversion rate as a performance test of the catalytic sheet filter. BM10SF showed very poor performance with a maximum conversion rate of less than 50%. However, NO conversion rate increased with the increased amount of catalyst coating, and NO conversion rate was more than 90% at reaction temperature range of 260-360 °C for the case of BM25SF and BM30SF. In this case N_x leakage is less than 50 ppm in the reaction temperature range of 280-340 °C. Fig. 9 shows the N_2O formation during NO reduction reaction, which is less than 35 ppm in all case of catalytic SF.

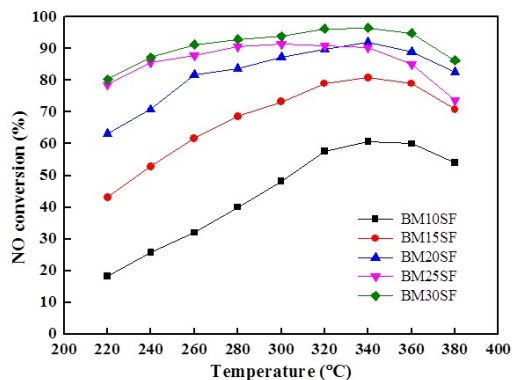


Fig. 8. Plot of NO conversion at different temperature (220-380 °C) for BM10SF, BM15SF, BM20SF, BM25SF and BM30SF with reaction condition; NO and NH_3 = 700 ppm, O_2 = 5 vol. %, Face velocity = 2 cm/s.

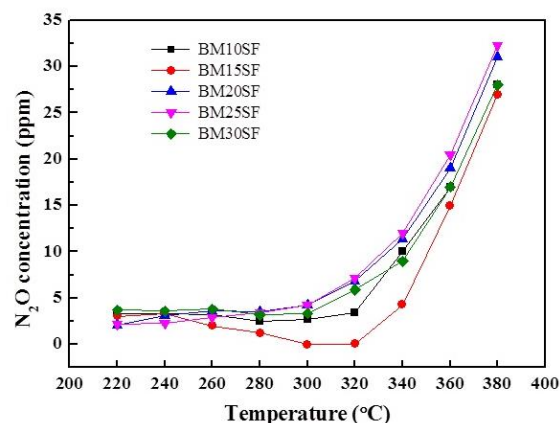


Fig. 9. Plot of N_2O concentration at different temperature (220-380 °C) for BM10SF, BM15SF, BM20SF, BM25SF and BM30SF with reaction condition; NO and NH_3 = 700ppm, O_2 = 5 vol. %, Face velocity = 2 cm/s.

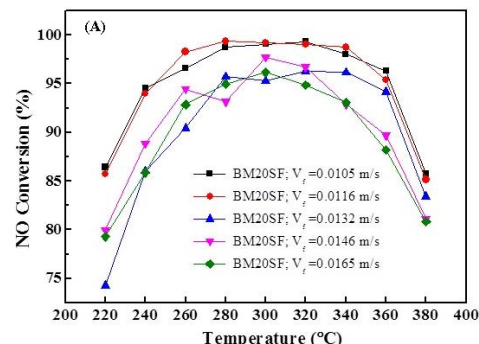
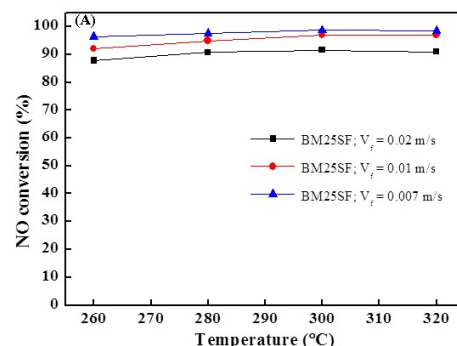


Fig. 10. (A) NO conversion rate and (B) N_x leakage concentration with varied filtration rate for NO conc. = 700 ppm for BM25SF.

The filtration rate is related to the reaction residence time, and as the filtration rate is lower, the reaction contact time is increased and the reactant conversion of the catalyst is increased. It is therefore an important reaction factor to determine the amount of catalyst required to process a given reactant. Fig. 10 (A), (B) shows the activity of the BM25SF catalytic filter with varying filtration rate, i.e. reactant flow rate, without changing the composition of the reactants. When

the filtration rate was less than 0.01 m/s, the NO conversion rate of 90% or more was obtained. However, at 0.02 m/s, the NO conversion rate was 87% and the N_x leak rate was more than 70 ppm. This may be the result of the lack of the absolute amount of catalyst, but the presence of non-ideal large pores in the filter is considered to be a major cause. This is because, as shown in Fig. 11A and Fig. 11B, even in the case of BM20SF having a small catalyst coating amount, NO conversion of 97% or more and N_x leakage of less than 20 ppm can be achieved at a filtration rate of less than 0.0116 m/s.

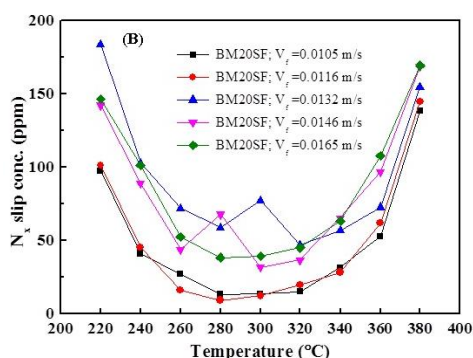


Fig. 11. (A) NO conversion rate and (B) N_x leakage concentration with varied filtration rate for NO conc. = 700 ppm for BM20SF.

It is presumed that the main reason that the sheet-like catalytic filter does not show high performance is leakage of the reaction gas through non-ideal pores existing in the filter. In order to observe how the pore size of the catalyst filter changes when the catalyst is coated, the results of Mercury porosity measurement are compared in Table II (also see the Fig. 12). The mean pore size of the crude filter without catalyst was reduced to 54 μ m, while that of BM25SF decreased to 24 μ m and the average pore size decreased from 40 μ m to 0.34 μ m. Therefore, it can be seen that the balls are significantly buried by coating the catalyst.

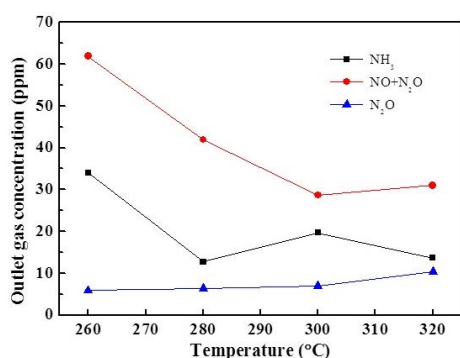


Fig. 12. Plot of outlet gas (NH_3 , $NO+N_2O$ and NO) concentration at different temperature (260–320 °C) for BM25SF with reaction condition; NO and NH_3 = 700ppm, O_2 = 5 vol. %, Face velocity = 0.01 m/s.

IV. CONCLUSION

The XRD study reveals that V and W are well dispersed, which support and improve the catalytic activity because it was favorable for an increased number of active sites. Mercury porosimetry result proves that the pores in the virgin SF has been filled up with the VWT catalyst by dip coating method successfully, as the average pore size decreased from

40 μ m in virgin SF to 0.34 μ m in BM25SF. Microstructural study also supports this. Improved NO conversion has been achieved with the increase in the concentration of catalytic coating solution. NO conversion rate was more than 90% at reaction temperature range of 260–360 °C for the case of BM25SF and BM30SF with N_2O formation less than 35 ppm. But the pressure loss for BM30SF is quite more compare to others, the plausible reason is the failure of absolute catalyst loading amount; however the non-ideal large pores present in the SF is the main cause for this. Because in the case of BM20SF even with small catalyst coating amount compare to BM25SF and BM30SSF, NO conversion of more than 97% and N_x leakage less than 20 ppm achieved at filtration rate of 0.116 m/s. BM25SF shows the more than 90% NO conversion at 0.01 m/s filtration rate and 87% for 0.02 m/s filtration rate. Modification of the TiO_2 with polymer to prepare the catalyst and to develop a good catalytic sheet filter has a wide scope in the future.

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