Influencing factors on low-temperature deNO\textsubscript{x} performance of foamed metal based catalytic filter

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Abstract. A series of supported vanadium-titanium denitrification catalysts were prepared by impregnation method with foam metal as carrier for NH\textsubscript{3}-SCR of NO\textsubscript{x} at low temperature. Effects of pH, slurry concentration, catalyst loading rate, face velocity and O\textsubscript{2} concentration on catalytic performance were studied. The results showed that when immersion concentration was 30g/100mL and filtration speed was 0.7m/min, the pressure drop was 300Pa and NO\textsubscript{x} removal efficiency was 98\% at 200\degree C. The foam catalytic filter was put into the bag dust collector, which had the function of simultaneous removing particulate and NO\textsubscript{x}. When filtration velocity was 0.7m/min, NO\textsubscript{x} removal efficiency reached 95.5\% at 200\degree C and it had good water resistance. The results provided the basis for further pilot experiment.

1. Introduction
According to the report "emission characteristics and control technology of multi-pollutant emission from iron and steel sintering", dust emission from iron and steel sintering process accounts for about 20\% of the total emission from iron and steel production, SO\textsubscript{2} accounts for up to 60\%, and NO\textsubscript{x} emission is about 48\% [1,2]. Sintering flue gas has become the main emission source of waste gas pollutants in the iron and steel industry. The bag dust collection had been widely used in the iron and steel industry due to its high dust removal efficiency, stable operation, low initial investment and other advantages. SCR method with high denitrification rate (>90\%), mature technology and no harmful products, has become the main method (96\%) for denitrification in power plants[3]. However, the catalysts are easy poisoning and clogging when used in sintering flue gas, because of complex composition of flue gas, dust content and large variation of nitrogen oxide concentration in the exhaust gas. To improve the activity of the SCR catalyst and render its resistant against SO\textsubscript{2} poisoning, WO\textsubscript{3} or MoO\textsubscript{3} are often added to the SCR catalyst[4].

At present, the research on integration of dust removal and denitrification has attracted extensive attention in various fields. Dvorak et al.[5] reported a catalytic bag filter with V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} as catalyst of selective NO reduction with NH\textsubscript{3}. When gas flow amounted to 1000m\textsuperscript{3}/h, the deNO\textsubscript{x} efficiency was 33.2\% in 220\degree C. Wu et al.[6] prepared filter cloth supported by MnO\textsubscript{x}-CeO\textsubscript{2}/TiO\textsubscript{2} catalytic material with liquid phase deposition-impregnated method to achieve removal of dust and NO\textsubscript{x} simultaneously. By optimizing the preparation process and reaction conditions, the denitrification efficiency could reach 93.1\% at 180\degree C. Manfred et al.[7] designed a porous ceramic tube wall that could remove particulate matter, NO\textsubscript{x} and VOC simultaneously. On the one hand, collaborative purification device could simplify the process, reduce equipment investment and operating costs; on the other hand, the low sulfur flue gas after dust removal also reduces the poisoning of SCR catalyst.
which extends the life of the catalyst. Therefore, collaborative purification technology has become a new development trend of removing NO\textsubscript{x}[8-9].

Foam metal has unique three-dimensional irregular channel and large specific surface area, which can obviously promote the effective contact between fluid and active components of the catalyst. Therefore, foam metal has a very broad application prospects. Our research team developed a vanadium-titanium denitrification catalyst which has been put into industrial application[10]. In this study, vanadium-titanium denitrification catalyst was supported to the foam metal to prepare denitrification filter. The effects of preparation technology and reaction conditions were investigated. It is expected to achieve the cooperative removal of particulate and NO\textsubscript{x} by putting it into the filter bag of bag dust remover for the integrated performance test.

2. Experimental

2.1 Preparation of foam metal supported catalysts

Vanadium-titanium based denitrification catalysts were prepared by dipping method. In the experiment, the powder catalyst were mixed with a certain amount of dispersant, binder and deionized water, and then kept a continuous stirring for 30min at room temperature until the slurry was dispersed evenly. The clean foam metal was immersed in the stirred slurry for 5min, then dried at 110°C for 2 h in an oven. The above procedure was repeated by immersing it in equal concentration slurry and then roasting it in muffer furnace at 300°C for 3h to produce integral catalysts (as shown in figure 1). The catalyst was simply called V-Ti/FM, and the foam metal was called FM. As shown in figure 2, The foam metal was made into a cylindrical filter cage with one end closed. Figure 3 shows a scanning electron microscopy (SEM) image of FM and V-Ti/FM magnified 300 times and 10000 times. As shown in figure 3 (a), the surface of the foam metal was three-dimensional porous without any impurities attached. As seen in figure 3 (b), a large number of V-Ti catalyst particles were attached to the surface of the foam metal and the particles were evenly distributed.

2.2 Characterization of foam metal supported catalysts

The sample morphology was observed by jsm-6490lv scanning electron microscope (Host: tungsten filament lighting; point resolution: 3nm; acceleration voltage: 0.5~30 kV). The sample was sprayed with gold and demagnetized before test. Rotational viscometer was used to test the viscosity of catalyst slurry. Mastersizer 3000 laser particle size analyzer from Malvern was used to test the particle size distribution of slurry, and average particle size of samples was analyzed with intensity mode.

![Figure 1](image1.png)  
Figure 1. Sample of denitrification catalyst.  
(a) (b)

![Figure 2](image2.png)  
Figure 2. Foam filter element (a) without catalyst supported (b) supported catalyst.  
(a) (b)

![Figure 3](image3.png)  
Figure 3. SEM images of FM (a) without supported catalyst (b) supported catalyst.  
(a) 300x (b) 300x (c) 10000x
2.3 Activity measurement
Denitrification test: the catalytic activity was evaluated in a stainless steel tube reactor. Foam metal was fixed in a small reactor with a diameter of 50 mm. The sample was heated in a tubular furnace and temperature was measured by a thermocouple (type K), as shown in figure 4. The inlet gas composition was controlled by mass flow controllers, and the test temperature was 140°C ~ 240°C. The flue gas composition (volume fraction): filtering wind speed of 0.70 m/min, 0.07% NO, 0.07% NH₃, 5% O₂ and N₂ for balance. The gas pressure drop was monitored by a U-shaped manometer. The concentrations of NO at the inlet and outlet were determined using a Testo 350 flue gas analyzer. The NO conversion (η,%) was calculated as equation (1):

\[ \eta = 1 - \frac{\varphi(NO_{\text{out}})}{\varphi(NO_{\text{in}})} \times 100\% \]  

(1)

Where \( \varphi(NO_{\text{in}}) \) is the inlet concentration of NO, and \( \varphi(NO_{\text{out}}) \) is the outlet concentration of NO, volume fractions.

Integrated performance test of denitrification and dust removal: in order to simulate the conditions of industrial application, it was put into the external filter bag dust collector to carry out the integrated experiment of denitrification and dust removal. Schematic diagram of integrated apparatus for denitrification and dust removal was shown in figure 5. Four filter bags and catalytic foam filter were installed in bag dust collector with 840mm in length, respectively. Flue gas entered from outside of the filter bag and passed out through the catalyst layer. The evaluation temperature was 150°C ~ 210°C with filtering wind speed of 0.70 m/min. The concentrations of NO at the inlet and outlet were measured using MGA5 flue gas analyzer in real time.

3. Results and discussion
3.1 The effect of pH on slurry stability
By adjusting the pH value of the suspension, the particle size of the catalysts will change to characterize the dispersion of the slurry[11]. In order to investigate the effect of pH on slurry stability,
C$_2$H$_7$NO was added to slurry to regulate pH. Figure 6 was the curve of slurry viscosity and the relative height of supernatant liquid with pH value when slurry concentration was 30g/100mL. When pH was 4, the viscosity and the relative height of supernatant liquid were both high. As can be seen from figure 7, the particle size of catalysts were large and the agglomeration was serious. The attraction between particles is greater than the repulsive force between the electrical double layer. When pH was 8~10, the viscosity and relative height of supernatant liquid significantly decreased, the curve tended to be stable. Particles were easily suspended in the water and keep a good dispersion state.

### 3.2 Determination of catalyst loading process

The V-Ti/FM catalysts were tested for the NO conversion from 140°C~240°C. The face velocity was 0.7m/min and the inlet concentrations of NO and NH$_3$ were 0.07%.

Figure 8 shows the catalyst load rate and pressure drop increased with the increase of slurry concentration. When the loading rate increased from 130% to about 170%, the agglomeration of catalyst particle gradually strengthened, and the foam metal channels were covered and blocked by catalysts. So the pressure drop rapidly increased from 300Pa to 1100Pa. Pressure drop was closely related to the back blowing frequency and operating cost of catalytic filters in industrial applications. Therefore, the actual load rate of foam metal cannot be too large in industrial application.

Figure 9 shows the effect of reaction temperature on NO conversion. Interestingly, all samples varied with a similar trend that the catalytic activity increased rapidly with the elevation of temperature firstly, the increase rate became gently from 200°C. With the increase of slurry concentration, the catalyst load rate increased gradually. In general, when the amount of catalyst is large, more active sites can be provided for NH$_3$ adsorption, thus achieving a higher NO removal efficiency[12]. When the concentration of the impregnation solution increased from 10g/100mL to
30g/100mL, NO conversion increased from 89.4% to 98.0% at 200°C. When slurry concentration increased to 40g/100mL, the catalyst activity decreased slightly. This is mainly due to the overloading of catalysts, which leads to the failure of the active components to disperse on the surface of catalyst carrier [13].

3.3 Face velocity
As the gas velocity increases, the contact time between the reaction gas decreases, resulting in incomplete reaction and reducing NO removal efficiency. Figure 10 showed the effect of face velocity on NO conversion with NH₃:NO=1:1 and 5% O₂. With the increase of face velocity, NO conversion decreased gradually. When the face velocity increased from 0.6m/min to 1.1m/min, the NO conversion decreased by about 21.0% at 160°C and 8.2% at 240°C. The reason is that when the inlet gas flow increases, the contact time between the reaction gas and the catalyst becomes shorter, so the removal efficiency of NO is bound to decrease.

3.4 Integrated testing
For industrial application, the experiment should be enlarged and simulated. The selective catalytic reduction of NO with V-Ti/FM catalyst was studied on the experiment platform of dust removal and denitrification. Figure 11 showed the effect of temperature on catalytic activity under dry and wet flue gas conditions (i.e.(H₂O)=10%,15%,20%). The filtration gas velocity was 0.7m/min and the inlet concentration of NO was 0.07%. With the increase of reaction temperature, the NO conversion increased gradually. Under the condition of dry flue gas, NO conversion was 95.5% at 200°C after SCR reaction was stable. When 10%, 15%, 20% H₂O was added in the reaction atmosphere, the NO conversion decreased to 93.0%, 89.9%, 83.6%, respectively. It can be seen that the presence of water vapor has a certain inhibitory effect on the SCR activity. The possible reason is that the presence of large amount of water vapor inhibits the reaction of NH₃ and NO adsorbed on Bronsted acidic position[14]. As the temperature increases, the inhibition of water vapor diminishes[15]. It is an encouraging result that catalytic filters have such a high NO conversion.

![Figure 10. The effect of face velocity on NO conversion](image1)

![Figure 11. The effect of H₂O volume reaction on NO conversion](image2)

4. Conclusion
1) Increasing the slurry pH can change the particle size of the catalyst, thereby affecting the slurry stability and the catalyst load uniformity. When pH was 8~10, the slurry dispersion was good and the catalyst coating was more evenly distributed.

2) When concentration was 30g/100mL, the NO conversion was 98% at 200°C and the pressure loss maintained at 300Pa. Besides, gas velocity range was wide.

3) Water resistance test was carried out on the integrated experiment platform of dust removal and denitrification, and it was found that NO removal efficiency could exceed 80% after 20% water vapor was injected. This is a promising catalytic filtration system for commercial application.
Comments
At present, desulfurization, dust removal and denitrification equipment are relatively independent in industrial flue gas treatment technology. Therefore, there is a large occupancy area and high investment on infrastructure. Foam metal was used as support material for selective catalytic reduction of NO. Denitrification was carried out after desulfurization and dust removal, which greatly reduced the toxic effect of dust on the catalyst. In order to meet the national emission standards and reduce the cost of enterprises, multi-pollutant joint removal is the future development direction.

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