Catalytic filter for the removal of dust and NO$_x$ at low temperature

Lei Zhao, Kun Li, Ruian Wu, Hua Zhang and Jiang Jin

College of Materials Science and Engineering, Nanjing Tech University, Nanjing, 210009, People’s Republic of China

E-mail: jinjiang@njtech.edu.cn

Keywords: dust removal, regeneration performance, catalytic filter, NO$_x$ removal

Abstract

The catalytic filter was fabricated by selecting a selective catalytic reduction (SCR) catalyst on the low-density ceramic (LDC) for the removal of dust and nitrogen oxides (NO$_x$) in the flue gases at a low temperature. MnO$_x$–ZrO$_2$–TiO$_2$ catalyst was selected as the SCR catalyst. The NO$_x$ and dust removal efficiency, filter resistance, regeneration performance, and anti-sulfur performance were investigated. The result showed that the NO$_x$ removal efficiency at 180°C reached 98.4% (1 m/min filtration velocity) for 6 wt% MnO$_x$–ZrO$_2$–TiO$_2$ catalytic filter with Mn/Zr molar ratio of 2. Furthermore, MnO$_x$–ZrO$_2$–TiO$_2$ catalytic filter performed good anti-sulfur performance. In the presence of 10 vol% water vapor and 100 ppm SO$_2$ at 180°C, the NO$_x$ removal efficiency for MnO$_x$–ZrO$_2$–TiO$_2$ catalytic filter could retain up to 83.2% and could recover to 91.8% when the water vapor and SO$_2$ were cut off. MnO$_x$–ZrO$_2$–TiO$_2$ catalytic filter showed high dust removal efficiency of 99.99% and the low filter resistance of less than 200 Pa. The filter resistance of MnO$_x$–ZrO$_2$–TiO$_2$ catalytic filter could maintain 235.7 Pa after 200 times pulse blowback. The result illustrated that MnO$_x$–ZrO$_2$–TiO$_2$ catalytic filter showed good regeneration performance.

1. Introduction

Air pollution has been recognized as one of the most important health issues in recent years. The emission of dust and nitrogen oxides gives rise to human’s focus. Dust (especially particulate matter ≤ 10 μm) could float in the air and fine dust comprises toxic components to human health [1, 2]. In industry plants, the electrostatic precipitators and fabric filters are the main facilities to control the particulate matter [3, 4]. Moreover, the application of LDC filter fabricated by ceramic fibers has proved the improvement in the gas-solid separation in recent years [5, 6].

Nitrogen oxides are one of the main causes of haze, acid rain, and greenhouse. Removal of NO$_x$ is essential to accord with the environmental emission requirement. Selective catalytic reduction (SCR) process performs high efficiency and reliability, and it becomes the most common technology to eliminate NO$_x$ in industry plants [7]. The common commercial catalyst for SCR process is V$_2$O$_5$–WO$_3$(MoO$_3$)–TiO$_2$, which is highly active in the temperature range of 300 °C–400 °C [8, 9]. The constitution of flue gas in industry plants is more complex and the fine particles in flue gas can produce physical or chemical poisoning effects on SCR catalysts. The dust removal apparatus is usually installed with the denitrification unit in the industrial application. But these two units occupy a lot of space and consume enormous amounts of energy. A new technique to remove dust and NO$_x$ simultaneously has been developed. Kim developed V$_2$O$_5$–WO$_3$/TiO$_2$ supported–SiC catalytic filters by using rotational coating [10]. The catalytic filter element showed high SCR activity leading to 99% NO$_x$ conversion efficiency at 300°C. But the filter resistance of V$_2$O$_5$–WO$_3$/TiO$_2$ supported–SiC catalytic filters was very high (over 1000 Pa). On the other hand, the temperature of exhaust gas emitted from some industry boilers is lower than 300 °C. The catalytic activity of V$_2$O$_5$–WO$_3$ (MoO$_3$)–TiO$_2$ reduced at relative low temperature and cannot meet the requirement for exhaust gas treatment. Abubakar et al. reported a catalytic bag filter using V$_2$O$_5$-MoO$_3$–TiO$_2$ as catalyst [11]. The catalytic bag filter showed only 60% NO$_x$ conversion efficiency at 200 °C. Furthermore, vanadium pentoxide is toxic to environment and human health. Thus, it is necessary to develop a new catalytic filter for the application at lower temperature. Mn-based complex oxides have been exhibited an
excellent performance for the NOx removal at low temperature [12–16]. Kang et al prepared a catalytic filter with MnOx catalyst coating on P84 bag filter [17]. The NOx conversion efficiency of catalytic filter was over 90% at 150 °C. A catalytic filter with Mn–Ce–Nb–Ox catalyst coated on P84 felts was also studied for the removal of particulates and NOx [18]. The NOx removal efficiency and PM2.5 removal efficiency at 200 °C reached 95.3% and 99.98%, respectively. For the above studies, the bag filter or P84 felts used as filter materials and catalysts support is nonrigid, which deformed during the pulse blowback operation. The most staple problem for these catalytic filters is the peeling of catalysts during the operation of gas-solid separation and NOx removal, which caused the decline of NOx conversion efficiency. Polytetrafluoroethylene (PTFE) was used as binder in the catalyst coating emulsion for fixing the catalysts on the bag filter or P84 filter. But it could increase the filter resistance and decrease the NOx removal efficiency. The solution to solve these problems is using the rigid ceramic filter as the catalysts support for avoiding the degradation of catalytic performance caused by catalyst falling off. The low-density ceramic (LDC) filter composed of short ceramic fibers (mullite fiber, Al2O3 fiber and aluminum silicate fiber) possesses the high porosity, good thermal shock resistance and low filter resistance. Furthermore, LDC displays better resistance to acids and alkalis [19]. Therefore, LDC filter was used as the catalyst support in this work.

The objective of this study is to develop an integration technology for the removal of dust and NOx in the flue gases at relative low temperature and improve the service life of catalytic filter. The MnOx–ZrO2/TiO2 catalyst was loaded on the pore surface of LDC filter and dispersed throughout the filter by introducing TiO2 using homogeneous precipitation method. The effect of Mn/Zr molar ratio, catalyst loading, filtration velocity and anti-poison ability on the NOx removal was discussed. The dust removal efficiency, filter resistance and regeneration performance of the MnOx–ZrO2/TiO2 catalytic filter were also studied to provide a reference for the industrial applications of catalytic filters.

2. Experimental methods

2.1. Preparation of LDC catalytic filter element

The LDC filter element for gas-solid separation was prepared by following process. Firstly, the mullite fiber (Zhejiang Hongda Crystal Fiber Co., Ltd, China), glass powder (Nanjing Sanle Co., Ltd, China), activated carbon powder (200 mesh, Shanghai Xitan Environmental Protection Technology Co., Ltd, China) and carboxymethyl cellulose (Sinopharm Chemical Group Co., Ltd) was mixed in a certain mass ratio. Then, the appropriate amount of water was added to green mud with stirring. The mixture was aged at room temperature for 24 h and pressed into a circular pellet (d = 20 mm, h = 10 mm). The specimens were dried at 60°C for 12 h and sintered at 1100 °C for 1 h to obtain the LDC filter element. The TiO2 was loaded on the LDC filter element by the homogeneous precipitation method [20]. Then, TiO2-loaded filter element was immersed in the mixed solution of Mn(NO3)2 (50 wt%, Sinopharm Chemical Group Co., Ltd) and ZrO(NO3)2 (AR, Aladdin Reagent Co., Ltd, China). The LDC filter element with catalyst solution was dried at room temperature for 24 h, followed by calcining at 500 °C for 2 h. The catalyst loading was controlled by changing the concentration of solution or immersion times.
2.2. Catalyst characterization
The micromorphology of LDC catalytic filter element was analyzed using field-emission scanning electron microscopy (FESEM, ZEISS Ultra 55) with energy dispersive x-ray spectrometry (EDX). The pore size distribution was measured using Mercury Porosimeter (GT-60, Quantachrome, America).

2.3. Catalytic activity and dust removal efficiency
SCR catalytic activity was determined on a fixed-bed flow reactor. The reactor was composed of two quartz tubes and a tubular programmable temperature control furnace (figure 1). The basic composition of flow gas was composed of 600 ppm NOx, 600 ppm NH3, 6 vol% O2, with balanced N2. A mass flow controller has been used to control the total gas flow rate. The total flow rate of flue gas was 314 ml min\(^{-1}\) (corresponding to the filtration velocity of 1 m min\(^{-1}\)). The NOx concentration was detected by flow gas analyzer (ECOM-D, RBR, Germany). The NOx removal efficiency was calculated as follows:

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\eta = \frac{\text{NOx}_{\text{in}} - \text{NOx}_{\text{out}}}{\text{NOx}_{\text{in}}} \times 100\%
\]

The dust removal test was performed with an air filter efficiency instrument (CW-HAT2100). The filter resistance was characterized by the Chinese standard ‘test method of the performance of high efficiency particulate air filter’ (GB/T 6165–2008). Song et al\cite[21] presented the details on how to test the filter resistance. The fly-ash was used as pollution dust (\(\Phi = 2–3 \mu m\)). The procedures of regeneration performance measurement were mentioned in our previous work\cite[19].
Figure 3. EDX mapping images of MnOx–ZrO2/TiO2 catalytic filter element.

Figure 4. The pore size distributions of (a) LDC filter element. (b) MnOx–ZrO2/TiO2 catalytic filter element.
3. Result and discussion

3.1. Micromorphology and pore size distribution of catalytic filter
The micromorphology of LDC catalytic filter element was showed in figure 2. It could be observed that the mullite fibers were interconnected with each other to build three dimensional connected channels, which separate the gases and particulates effectively (figure 2(a)). The catalysts showed ball-like and distributed on the fibers (figure 2(b)). Figure 3 showed the EDX mapping images of catalyst distribution for MnOx-ZrO2/TiO2 catalytic filter. Mn and Zr were coated on the surface of TiO2 and mullite fibers. No accumulation of catalysts was founded at the intersection of the fibers. The catalysts highly dispersed and adhered firmly on the fibers throughout the filter. The pore size distribution for LDC filter element with and without MnOx-ZrO2/TiO2 catalyst was also studied (figure 4). Both filter elements have a narrow pore size distribution. The predominant pore size was distributed in the range of 15–60 μm for LDC filter element and 10–50 μm for MnOx-ZrO2/TiO2 catalytic filter element. The change of pore size distribution was contributed from the catalyst loading on the fiber.

3.2. Effect of molar ratio and catalyst loading on NOx removal
The effect of Mn/Zr molar ratio on the NOx removal efficiency was studied to obtain the optimum catalytic activity for SCR. The results showed that the highest catalytic activities were obtained at Mn/Zr molar ratio of 2 (figure 5(a)). The NOx removal efficiency was more than 90% in the temperature range of 140 °C–240 °C and reached 98.4% at 180 °C especially. The MnOx-ZrO2/TiO2 catalyst showed excellent NOx removal efficiency.
and it could be attributed to an intimated interaction between Mn, Ti and Zr, which allowed more electron transfer between Mn, Ti and Zr. Figure 5(b) showed the redox mechanism of NOx reduction via the Eley-Rideal mechanism over the MnOx–ZrO2/TiO2 catalyst. Ti4+ and Zr4+ could restore the Mn3+ to Mn4+. The intimate interaction facilitated the electron transfer and accelerated the circulation of Mn4+ and Mn3+ redox couple, which promotes the NH3-SCR process [22–26].

The filtration and NOx removal principle of LDC catalytic filter were illustrated in figure 6. The fine particles in the flue gas could be intercepted by the filter and accumulated on the surface of LDC catalytic filter element, while the gases could infiltrate into the pores of LDC catalytic filter. The NH3, NOx in the flue gas were sufficiently absorbed by the SCR catalyst dispersed throughout the filter and converted into N2 and H2O in the presence of O2.

The catalyst loading could influence the performance of NOx removal. As can be seen in figure 7, the NOx removal efficiency exhibited a growing trend with the catalyst loading increasing within 6 wt%. The higher catalyst loading means the more acid active sites for the adsorption of NH3, which makes the improvement of NOx removal efficiency. The NOx removal efficiency for MnOx–ZrO2 loading of 6 wt% was over 90% in the temperature range of 140–200 °C. When the MnOx–ZrO2 catalyst loading increased to 8 wt%, the NOx removal
efficiency remained flat. Considering the cost and the NO\textsubscript{x} removal efficiency, the MnO\textsubscript{x}–ZrO\textsubscript{2} catalyst loading of 6 wt\% is selected for later experiment.

3.3. Effect of the filtration velocity, SO\textsubscript{2} and H\textsubscript{2}O on NO\textsubscript{x} removal efficiency
The filtration velocity is an important factor for the filter. The filtration velocity is inversely proportion to the reaction time. The higher filtration velocity would result in the decline of NO\textsubscript{x} removal efficiency. Figure 8 showed the effect of filtration velocity on the NO\textsubscript{x} removal efficiency. With filtration velocity increasing every 0.2 m min\textsuperscript{-1}, the NO\textsubscript{x} removal efficiency for MnO\textsubscript{x}–ZrO\textsubscript{2}/TiO\textsubscript{2} catalytic filter diminished about 3\%. When the filtration velocity was 1 m min\textsuperscript{-1}, MnO\textsubscript{x}–ZrO\textsubscript{2}/TiO\textsubscript{2} catalytic filter showed more than 92\% NO\textsubscript{x} removal efficiency in the temperature range of 140 °C–200 °C. Even when the filtration velocity increased to 1.4 m min\textsuperscript{-1}, the NO\textsubscript{x} removal efficiency for MnO\textsubscript{x}–ZrO\textsubscript{2}/TiO\textsubscript{2} catalytic filter was over 90\% in the temperature range of 160 °C–200 °C. It could dispose more amount of flue gas and decrease the cost at the same time. The results showed that the MnO\textsubscript{x}–ZrO\textsubscript{2}/TiO\textsubscript{2} catalytic filter could meet the requirement of various industrial applications.
Usually, the industrial flue gas contains 3–10 vol% water vapor and small amount SO2, which makes catalysts poisoning. The NOx removal efficiency declines with the deterioration of catalyst. Figure 9 illustrated the effect of 10 vol% water vapor and 100 ppm SO2 on the NOx removal efficiency. The NOx removal efficiency for MnOx–ZrO2/TiO2 catalytic filter decreased significantly in first two hours when the water vapor and SO2 were injected into the flue gas. There is the competitive adsorption of water vapor, SO2 and NH3 on the acid active sites, which had an inhibiting effect on the NH3–SCR process [27, 28]. Moreover, water vapor and SO2 reacts with NH3 to produce sulfur ammonium salt (NH4HSO4, (NH4)2SO4), which occupied the acid active sites. Thus, the NOx removal efficiency decreases with the reduction of acid active sites. The consumption of NH3 would weaken the SCR process too. The NOx removal efficiency for MnOx–ZrO2/TiO2 catalytic filter could retain up to 83.2% in the presence of 10 vol% water vapor and 100 ppm SO2 and it returned to 91.8% when the water vapor and SO2 were cut off.

3.4. Dust removal efficiency and regeneration performance

During the filtration process, the filter resistance increases with the dust entering the pores of filter elements or with the cake accumulating on the surface of filter elements. The pulse blowback was used to clean the filter elements, which resulted in an instant decrease of the filter resistance. The filter resistance observed after pulse blowback is named residual filter resistance. The residual filter resistance increases continuously and eventually stabilize to a value, defined as baseline filter resistance. The baseline filter resistance is one of the important criteria for evaluating regeneration performance of filters [19].

The filter resistance for MnOx–ZrO2/TiO2 catalytic filter with catalyst loading of 6 wt% was measured as 198 Pa. As shown in figure 10, the residual filter resistance of LDC filter and MnOx–ZrO2/TiO2 catalytic filter increased at first, and then reached a balance with the increase of cycle times. The baseline filter resistance of MnOx–ZrO2/TiO2 catalytic filter was 236 Pa. The filter resistance of MnOx–ZrO2/TiO2 catalytic filter just increased 38 Pa after 200 times pulse blowback compared with the initial filter resistance. The result indicated that the MnOx–ZrO2/TiO2 catalytic filter had good regeneration performance. The dust removal efficiency for the MnOx–ZrO2/TiO2 catalytic filter reached 99.99%.

4. Conclusion

The MnOx–ZrO2/TiO2 catalytic filter with the higher NOx conversion efficiency and the lower filter resistance was successfully fabricated for the removal of dust and nitrogen oxide simultaneously. The NOx removal efficiency (1 m min⁻¹ filtration velocity) at 180 °C with Mn/Zr molar ratio of 2 and catalyst loading of 6 wt% reached 98.4%. Furthermore, MnOx–ZrO2/TiO2 catalytic filter exhibited good anti-sulfur performance and regeneration performance. In addition, the dust (PM2.5) removal efficiency for MnOx–ZrO2/TiO2 catalytic filter reached 99.99% and the filter resistance was less than 200 Pa. The filter resistance of MnOx–ZrO2/TiO2 catalytic filters just increased 38 Pa after 200 times pulse blowback, which implied that the service life of catalytic filter could be improved.

Acknowledgments

We would thank the project Funded by the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions and we also thank Postgraduate Research & Practice Innovation Program of Jiangsu Province (KYCX19_0841).

ORCID iDs

Jiang Jin https://orcid.org/0000-0002-0100-4703

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