Fe-Mn based catalytic ceramic filters with SO\textsubscript{2} resistance for NH\textsubscript{3}-SCR at low temperature

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Abstract

The Fe-Mn based catalyst was loaded on porous ceramic filter with impregnation method to prepare a catalytic ceramic filter which integrates the denitrification and dust removal at low temperature. The effect of the Fe/Mn ratio and doping Sm on the catalytic performance of Fe-Mn based catalyst were studied. In the temperature range of 120 °C–220 °C, the Fe\textsubscript{2}Mn\textsubscript{1}Sm\textsubscript{0.2}O\textsubscript{x} catalytic filter exhibited over 90% NO removal efficiency. When 100 ppm SO\textsubscript{2} and 7 vol.% H\textsubscript{2}O in the flue gas, the NO removal efficiency still maintained above 89% at 200 °C. These results proved that the Fe\textsubscript{2}Mn\textsubscript{1}Sm\textsubscript{0.2}O\textsubscript{x} catalytic filter has excellent catalytic performance and excellent H\textsubscript{2}O and SO\textsubscript{2} resistance at low temperature. In addition, the dust collection efficiency reached 99.99%. The NH\textsubscript{3}-TPD, H\textsubscript{2}-TPR and XPS confirmed that the Fe\textsubscript{2}Mn\textsubscript{1}O\textsubscript{x} catalysts doped with Sm have stronger surface acid, more surface absorbed oxygen and more oxygen vacancy, which lead to higher NH\textsubscript{3}-SCR activity and better SO\textsubscript{2} and H\textsubscript{2}O resistance.

1. Introduction

Nitrogen oxides caused serious air pollution problems, such as acid rain, photochemical smog and ozone depletion [1]. The removal of nitrogen oxides has been an important issue. Selective catalytic reduction of NO\textsubscript{x} with NH\textsubscript{3} (NH\textsubscript{3}-SCR) is the most efficient and economical method to remove NO\textsubscript{x}. It is well known that the commercial catalysts for NH\textsubscript{3}-SCR are V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} or V\textsubscript{2}O\textsubscript{5}-MoO\textsubscript{3}/TiO\textsubscript{2} [1], which exhibit excellent catalytic performance between 300 °C–400 °C, but some drawbacks are unavoidable, such as the toxicity of vanadium, the narrow operating temperature range and specific temperature conditions (above 300 °C) [2]. Therefore, it is meaningful to develop environmentally friendly catalysts which applied at low temperature, around 200 °C or even lower and wider temperature range.

Many investigations for low-temperature SCR catalysts have been performed recently. MnO\textsubscript{x} and FeO\textsubscript{x} has attracted wide attention because of the low cost and high catalytic performance at low temperature [3–5]. It was proved that Mn\textsubscript{0.5}Fe\textsubscript{2.5}O\textsubscript{4} catalyst with spinel structure exhibited excellent low-temperature denitrification performance (90 °C–300 °C for ≥90% NO\textsubscript{x} conversion) and a wide operating temperature window [6]. Zhang et al studied Fe-W catalyst and found that the crystallinity of Fe-W catalyst calcined at 400 °C was low, which contributed to the formation of abundant surface oxygen vacancies [7]. The catalytic activity of Fe-W was improved due to the surface defect and acidity of catalyst were optimized by adjusting calcination temperature. It was reported that the lower calcination temperature led to more Mn species for Mn-based catalysts. Calcining at 400 °C contributed to the formation of Mn\textsubscript{3}O\textsubscript{4} and amorphous MnO\textsubscript{2} species which were able to act together in NO reduction process and the catalytic performance was improved [8]. Tan et al prepared three-dimensionally ordered macroporous (3DOM) Fe–Mn oxide catalysts by the colloidal crystal template method. The NO conversion for 3DOM-Fe\textsubscript{1}Mn\textsubscript{3}O\textsubscript{8} catalyst stays above 90% in the temperature range of 300 °C–450 °C. However, 3DOM-Fe\textsubscript{1}Mn\textsubscript{3}O\textsubscript{8} is not suitable for low temperature environment. The NO conversion dropped sharply with the temperature decrease and it is only 35% at 250 °C [9].

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It has been reported that there was a competitive adsorption between H$_2$O and NO when the catalyst was exposed to H$_2$O. The competitive adsorption would limit the reaction between NH$_3$ and NO. Moreover, SO$_2$ in the flue gas would form sulfates on the catalyst surface which leaded to catalyst deactivated. Therefore, it is meaningful to enhance the H$_2$O and SO$_2$ resistance of the catalysts. Rare earth elements have become increasingly important in catalytic processes largely due to their incompletely filled 4f orbital structure. Lanthanide-containing catalysts additionally offer the opportunity to tune the catalytic performance. La$^{12}$, Pr$^{13}$, Ce$^{14–17}$ and Sm$^{18, 19}$ had been used as addition to enhance the SO$_2$ resistance of the catalysts. From these reports, the catalyst doped by the rare earth element could generate more chemisorbed oxygen species, enhance NH$_3$ adsorption and inhibit the formation of ammonium sulfate species. For the catalysts contained rare earth element, SO$_2$ is more likely to react with the rare earth element to produce sulfate, which protects the active sites. Therefore, adding rare earth element into catalyst is an effective way to improve the SO$_2$ resistance of the catalysts.

Particulates in the flue gas may cause respiratory diseases to people. Dust collection treatment must be carried out before emission of industrial flue. The dust collection equipment consumes enormous amounts of energy and occupies much space. To solve the problem of energy consumption and space occupation, the catalysts were loaded on the filter to integrate the denitration and dust collection. Abubakar et al prepared V$_2$O$_5$-MoO$_3$/TiO$_2$ based catalytic bag filters by coating the corresponding catalytic slurry. However, the coating strength of the catalyst and the denitration performance at low temperature (denitration efficiency was only 70% at 180$^\circ$C) were not satisfied. The problem for the bag filter was the peeling of catalyst during the pulse blowback, which caused the decline of denitrification efficiency. Rigid porous ceramic as a catalyst support is an effective way to prevent the peeling of catalyst. Wang et al reported that the V$_2$O$_5$-WO$_3$-TiO$_2$ ceramic catalytic filter for denitration and particulates separation had 80% NO removal efficiency in the wide temperature range (240 $^\circ$C–340 $^\circ$C). MnO$_x$-ZrO$_2$/TiO$_2$ ceramic catalytic filter applied for relative low temperature was prepared by impregnation method. The catalytic filter showed 98.4% NO conversion at 180 $^\circ$C and performed a certain anti-sulfur performance. When the flue gas contained H$_2$O and SO$_2$, the NO conversion for the catalytic filter dropped to 83% in 3 h. The resistance of H$_2$O and SO$_2$ was not satisfied for industrial application. The catalytic performance under flue gas containing H$_2$O and SO$_2$ needs to be improved further.

In this paper, the Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ catalyst was loaded on porous ceramic filter for industrial application by impregnation method. The catalyst performance was evaluated comprehensively. A series of characterizations about structure, reduction property and surface acid of the catalysts were performed. In addition, the effect of Sm on the catalytic performance and the resistance of H$_2$O and SO$_2$ was analyzed.

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**Figure 1.** Schematic diagram of catalytic filter test unit: 1. Stream generator, 2. Mass flow controller, 3. Flue gas mixer, 4. Glass tubes ($\Phi = 22$ mm/$\Phi = 38$ mm), 5. Tube furnace, 6. Flue gas analyzer.
2. Experimental

2.1. Preparation of catalysts

The specific preparation method of porous ceramic filter (pretreated PCF) was described in detail in our previous study [24, 25]. The Fe-Mn based catalysts (Fe/Mn = 1, 2, 4) were loaded on PCF matrix by the impregnation method. Appropriate amounts of ferric nitrate and manganese nitrate were dissolved in appropriate deionized water to obtain precursor solution. Then, the disc of PCF with the diameter of 22 mm and thickness of 10 mm was put into the precursor solution to load the catalyst. Before and after impregnation, the PCF volume did not change (as shown in figure 1 illustration). The impregnation was operated at a vacuum of approximately 0.8–1.0 MPa to ensure that the solution well penetrated into the fiber matrix inside. The PCF was dried at 70 °C for 6 h and then calcined at 400 °C for 5 h.

2.2. Characterization of catalysts

The crystal phase of the catalysts was determined by x-ray diffraction (XRD) using a Rigaku Smartlab diffractometer equipped with Cu Kα monochromator. The data of 2θ from 20° to 70° were collected with the step 0.02° at a scanning rate of 10° min⁻¹. The morphology of the samples was observed by scanning electron microscope (SEM, JSM-6510).

X-ray Photoelectron Spectroscopy (XPS) was implemented on KRATOS AXIS SUPRATM surface analysis system using Al Kα radiation (1486.6 eV, 150 W) to analyze the surface atomic concentration and indicate the chemical states of the elements. The XPS spectra were calibrated based on the binding energy of C1s (BE = 284.6 eV).

The H₂-temperature programmed reduction (H₂-TPR) experiments and the NH₃-temperature-programmed desorption (NH₃-TPD) experiments were carried out on AutoChem I II 2920. Before H₂-TPR, the sample (100 mg) was pretreated in the highly purified Ar (50 ml min⁻¹) at 400 °C for 1h and cooled to 50 °C. Then the sample was heated in a mixed gas (5% H₂/Ar, 50 ml min⁻¹) from 50 to 800 °C at a rate of 10 °C min⁻¹. At the same time, the signal was monitored by a thermal conductivity detector (TCD). In the part of NH₃-TPD, samples (100mg) were...
pretreated with highly purified He (50 ml min \(^{-1}\)) at 400 °C for 1 h. Then, the catalyst was saturated with a mixed gas (10% NH\(_3\)/He, 50 ml min \(^{-1}\)) at 50 °C for 1 h, and washed with highly purified He (50 ml min \(^{-1}\)) at the same temperature for 1 h to remove the gaseous NH\(_3\). Finally, the experiment was conducted from 50 to 700 °C at a rate of 10 °C min \(^{-1}\) in He (50 ml min \(^{-1}\)) and the signal for ammonia was monitored on-line by the TCD. The BET surface area was tested by N\(_2\) adsorption/desorption surface-area analyzer (ASAP 2020 V3.00 H).

Table 1. Comparison of SCR performance and dust collection efficiency.

| Catalysts            | Reaction condition | NO conversion | Dust collection efficiency | References |
|----------------------|--------------------|---------------|---------------------------|------------|
| Fe\(_2\)Mn\(_2\)O\(_4\) | [NO] = [NH\(_3\)] = 700 ppm, [O\(_2\)] = 6 vol.% | >90% (120 °C–180 °C) | 99.99% | this work |
| Fe\(_2\)Mn\(_2\)O\(_4\) | [NO] = [NH\(_3\)] = 700 ppm, [O\(_2\)] = 6 vol.% | >90% (120 °C–220 °C) | 99.99% | this work |
| Fe\(_2\)Mn\(_3\)Sm\(_2\)O\(_4\) | [NO] = [NH\(_3\)] = 700 ppm, [O\(_2\)] = 6 vol.% | >97% (140 °C–200 °C) | 99.99% | this work |
| Mn\(_2\)Fe\(_4\)Al\(_{27}\)O\(_4\) | [NO] = [NH\(_3\)] = 500 ppm, [O\(_2\)] = 5 vol.% | >99% (100 °C–225 °C) | none | [26] |
| MnO\(_2\)/TiO\(_2\)/SiC | [NO] = [NH\(_3\)] = 300 ppm, [O\(_2\)] = 5 vol.% | >80% (120 °C–180 °C) | 99.97% | [21] |

2.3. Catalytic activity measurement

The catalytic activity of catalyst for NO reduction was measured in a tube furnace reactor (figure 1). The reactor consisted of a programmable temperature control furnace and two glass tubes (inner diameter, 38 mm and 22 mm). The cylindrical catalytic filter (diameter was 22 mm) was fixed at the end of the glass tube (diameter was 22 mm). The filtration velocity was 1 m min \(^{-1}\) and total flue gas processing capacity was 18.841 h \(^{-1}\). The simulated flue gas was a mixture of 700 ppm NO, 700 ppm NH\(_3\), 6 vol.% O\(_2\), balanced with N\(_2\). And 7 vol.% H\(_2\)O and 100 ppm SO\(_2\) were introduced into simulated flue gas according to the requirements of the experimental conditions. The NO concentrations were detected by a flue gas analyzer (ECOM-D, RBR, Germany) after the reaction was stabilized.

The main equation of SCR reactions was displayed as follows:

\[
4\text{NO} + 4\text{NH}_3 + 2\text{O}_2 = 6\text{H}_2\text{O} + 4\text{N}_2
\]  

The catalytic activity of the catalysts was expressed by the following equation:

\[
\frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100\%
\]  

NO\(_{\text{in}}\) means the NO concentration before the reaction, and NO\(_{\text{out}}\) means the NO concentration after the reaction.

The catalytic filter resistance was evaluated according to the Chinese standard (GB/T 6165–2008) [24].

3. Results and discussion

3.1. Catalytic performance

The NH\(_3\)-SCR activity of Fe–Mn based catalysts in the temperature range of 100 °C–260 °C were shown in figure 2(a). The Fe\(_2\)Mn\(_2\)O\(_4\) and Fe\(_2\)Mn\(_3\)O\(_4\) catalytic filter showed the satisfactory catalytic performance (over 90%) in the temperature range of 120 °C–220 °C and the Fe\(_2\)Mn\(_3\)Sm\(_2\)O\(_4\) catalytic filter showed the higher catalytic performance (over 98%) in the temperature range of 140 °C–200 °C. The SCR performance of this work compared with literature was listed in table 1. It can be clearly seen that the NO conversion is significantly improved with the addition of Sm. Therefore, the addition of Sm is benefit to NO conversion in NH\(_3\)-SCR. The Fe\(_2\)Mn\(_3\)Sm\(_2\)O\(_4\) catalytic filter owned wider operating temperature range and higher dust collection efficiency compared with MnO\(_2\)/TiO\(_2\)/SiC catalytic filter. The Fe\(_2\)Mn\(_3\)Sm\(_2\)O\(_4\) catalytic filter showed higher catalytic performance than Mn\(_2\)Fe\(_4\)Al\(_{27}\)O\(_4\) catalytic filter under similar condition.

In order to study the effect of water steam on the catalytic performance, a water on-off test was carried out at 200 °C. As shown in figure 2(b), the NO conversion changed when turning the water steam on and off. The NO conversion for Fe\(_2\)Mn\(_3\)O\(_4\) and Fe\(_2\)Mn\(_3\)O\(_4\) only dropped by 5% when 7vol.% water steam was introduced into the gas flow. While, the catalytic performance of Fe\(_2\)Mn\(_3\)O\(_4\) was greatly affected by water steam. The NO conversion for Fe\(_2\)Mn\(_3\)O\(_4\) dropped by 17% when the water steam flow was truing on. The NO conversion for Fe\(_2\)Mn\(_3\)Sm\(_2\)O\(_4\) just dropped by 1% compared with Fe\(_2\)Mn\(_3\)O\(_4\) when 7vol.% water steam was introduced into the gas flow. In addition, the NO conversion was recovered to original values when the water steam was cut off. The water molecules covered the acid sites and reduce the contacting chance of NO and NH\(_3\) molecules with the acid sites. When the water steam was cut off, water molecules could be desorbed from the acid sites and the acid sites were released [10]. Thus, NO and NH\(_3\) molecules could react on the acid sites and the NO conversion was recovered. Considering the effect of H\(_2\)O on the NO conversion, the Fe\(_2\)Mn\(_3\)O\(_4\) and Fe\(_2\)Mn\(_3\)Sm\(_2\)O\(_4\) were selected for the later study.
Oxygen concentration in the flue gas is an important factor in NH3-SCR reaction. Figure 2(c) showed the effect of different oxygen concentrations on the NO conversion at 200 °C. The NO conversion for all samples was less than 75% when the flue gas did not contain the oxygen. The NO conversion was obviously improved when there was 1% oxygen in the flue gas. Especially Fe2Mn1Sm0.2Ox showed the satisfactory catalytic performance in low oxygen environment. When oxygen concentrations achieved 1%, the NO conversion for Fe2Mn1Sm0.2Ox reached 96%. It indicated that Fe2Mn1Sm0.2Ox can apply to low-oxygen flue gas. In the special flue gas environment, the concentration of O2 is extreme low. Therefore, Fe2Mn1Sm0.2Ox is acceptable for industrial applications.

Usually, the SO2 and H2O in the flue gas will poison the catalyst and reduce the NO removal efficiency [11]. As shown in figure 2(d), the tolerance to H2O and SO2 of the Fe2Mn1Ox and Fe2Mn1Sm0.2Ox were evaluated at 200 °C. The SCR reaction had been maintained for 1h at 200 °C before the introduction of 7vol.% H2O and 100 ppm SO2. The NO conversion for Fe2Mn1Ox decreased to 64% gradually in 7 h after SO2 and H2O were introduced. The decrease of NO conversion was due to the formation of (NH4)2SO4 or NH4HSO4, which covered on the surface of the catalyst and occupied on the partial active sites [27]. For Fe2Mn1Sm0.2Ox catalyst, the NO conversion decreased to 89% in 7 h after SO2 and H2O were introduced. This phenomenon suggested that the addition of Sm to Fe2Mn1Ox catalyst significantly improves the SO2 resistance of the catalyst. The increase of tolerance to H2O and SO2 for Fe2Mn1Sm0.2Ox could be thought that Sm restrain the formation of (NH4)2SO4 or NH4HSO4. In addition, part of Sm act as a sacrificial agent to react with SO2 to prevent catalyst deactivating [13].

Figure 3. XRD patterns of catalysts. (Illustration: XRD partial enlarged view).

Figure 4. H2-TPR profiles of Fe2Mn1Ox and Fe2Mn1Sm0.2Ox.
3.2. Crystal structure of catalyst

The XRD patterns for catalysts were presented in figure 3. The diffraction peaks at 2θ of 33.15°, 35.61° and 54.09° were assigned to the (104), (110), and (116) crystallographic planes of hematite Fe₂O₃ (PDF # 33–0664). The peaks at 2θ of 28.68°, 37.33° and 56.65° were assigned to the (110), (101), and (211) crystallographic planes of pyrolusite MnO₂ (PDF # 24–0735). As the ratio of Fe/Mn increased, the peaks of hematite Fe₂O₃ became more and more obvious and the peaks of pyrolusite MnO₂ disappeared gradually. In addition, it was clearly observed that the peaks of hematite Fe₂O₃ shifted to lower angles (figure 3 illustration). The noticeable shifts of Fe₂O₃ reflections to lower angles indicated a lattice expansion caused by the substitution of larger manganese cation (Mn⁴⁺: 0.65Å) for smaller iron cation (Fe³⁺: 0.55Å). For Fe₂Mn₁Sm₀.₂Oₓ, no peaks corresponding to MnOₓ were observed in the XRD patterns, which suggested that Sm restrained the crystallization of manganese oxides. It was reported that the catalyst with low crystallinity had better catalytic performance [28, 29]. The increase of NO conversion for Fe₂Mn₁Sm₀.₂Oₓ is related to the poor crystallization of manganese oxide. Therefore, adding Sm to Fe₂Mn₁Oₓ is beneficial to improving the SCR performance.

3.3. Reduction property and surface acidity

The redox ability is an important factor in the NH₃-SCR reaction. The redox ability of the samples were characterized by H₂-TPR (figure 4). It could be seen that there were three reduction peaks in the range of 350 °C–600 °C. The peak of region I was attributed to the reduction of MnO₂ → Mn₂O₃ and Fe₂O₃ → Fe₃O₄, the peak of region II was attributed to the reduction of Mn₂O₃ → Mn₃O₄ and Fe₃O₄ → FeO, the peak of region III was attributed to the reduction of Mn₃O₄ → MnO and FeO → Fe [12, 13]. The relative area of the peak is proportional to the redox ability of the catalyst and the moderate redox ability is beneficial to catalytic performance. The peaks of Fe₂Mn₁Sm₀.₂Oₓ in the region I and region II shifted to higher temperature and the relative area decreased compared with Fe₂Mn₁Oₓ. However, the peak in the region III shifted to lower temperature and its relative area increased. Considering the high catalytic performance of Fe₂Mn₁Sm₀.₂Oₓ, adding Sm adjusted the redox ability of the Fe₂Mn₁Oₓ and the moderate redox ability improved the catalytic performance.

The surface acidity of catalyst is a significant factor affecting the catalytic performance. NH₃-TPD was conducted for understanding the relationship between surface acidity and catalytic performance. As shown in figure 5, the samples exhibited two broad desorption peaks centered at 175 °C and 375 °C respectively and a sharp desorption peak at 550 °C. The relative area of each peak represents the sum of the amount of desorbed ammonia in the temperature range. The peak at 175 °C corresponds to weak acid site and the peak at 375 °C corresponds to strong acid site. The sharp desorption peak at 550 °C may correspond to H₂O evolution [30]. It is well known that the overall area of the desorption peaks represents the numbers of acid sites and the temperature of desorption peak is related to the acid strength. For Fe₂Mn₁Sm₀.₂Oₓ, the peaks at 375 °C shifted to higher temperature and its relative area increased. This indicated that the acid strength and acid content of the catalyst increased with adding Sm. Therefore, the enhancement of de-NOₓ performance at low temperature is related to the increase in surface acid sites induced by the addition of Sm.
3.4. Surface physical and chemical states of catalysts

Table 2 showed SBET, Pore volume and Pore diameter for Fe2Mn1Ox and Fe2Mn1Sm0.2Ox catalysts. Fe2Mn1Sm0.2Ox catalyst owned larger SBET and pore volume compared with Fe2Mn1Ox catalyst. For Fe2Mn1Sm0.2Ox catalyst, larger SBET and pore volume were beneficial to the diffusion of SCR reactive gas.

In order to investigate the surface chemical states of the catalysts, the XPS of O1s, Mn2p and Fe2p were recorded (Figure 6) and the corresponding results were listed in Table 3.

As shown in Figure 6(b), the XPS profiles of O1s peak was fitted into three peaks: O\(_{\alpha}\) (529.4 eV), O\(_{\beta}\) (531.0 eV), and O\(_{\gamma}\) (532.20 eV), corresponding to lattice oxygen (O\(^2-\)) and chemical adsorbed oxygen (O\(^-\), O\(^2-\)), respectively [31]. According to calculation, the ratio of (O\(^-\) + O\(_{\gamma}\)) / O\(^2-\) in Fe2Mn1Ox was 23.5%, and the ratio of (O\(^-\) + O\(_{\gamma}\)) / O\(^2-\) in Fe2Mn1Sm0.2Ox was 64.2%. The chemical adsorbed oxygen is the primary active oxygen species which maintains the balance in oxidation reaction. The surface adsorbed oxygen species is more reactive in oxidation reactions due to its higher mobility than lattice oxygen [32, 33]. As a result, high ratio of chemical adsorbed oxygen promote the catalytic activity.

Figure 6(c) shows the XPS profiles of Mn2p for the catalysts. Two main peaks belonged to Mn 2p1/2 and Mn 2p3/2 were found. Each peak was fitted into two peaks: Mn\(^{4+}\) (653.8 eV), Mn\(^{3+}\) (652.7 eV), Mn\(^{4+}\) (642.3 eV) and Mn\(^{3+}\) (641.2 eV) [9, 31]. The content of Mn\(^{4+}\) in Fe2Mn1Ox and Fe2Mn1Sm0.2Ox was 54.3% and 52%.

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Table 2. Physicochemical properties for different catalyst.

| Catalysts      | SBET (m\(^2\) g\(^{-1}\)) | Pore volume (cm\(^3\) g\(^{-1}\)) | Pore diameter (nm) |
|----------------|---------------------------|-----------------------------------|-------------------|
| Fe2Mn1Ox       | 11.53                     | 0.038                             | 10.64             |
| Fe2Mn1Sm0.2Ox  | 24.71                     | 0.069                             | 7.28              |

\(^{a}\) BET surface area.  
\(^{b}\) BJH desorption pore volume.  
\(^{c}\) BJH desorption pore diameter.
respectively. Although Mn$^{4+}$ was a key factor in SCR reaction, the 2.3% content change did not influence the catalytic activity decisively.

In figure 6(d), the XPS profiles of Fe 2p3/2 peak was fitted into two peaks: 709.6 eV and 710.8 eV corresponding to Fe$^{2+}$ and Fe$^{3+}$, respectively [31]. According to calculations, the ratio of Fe$^{2+}$/Fe$^{3+}$ in Fe$_2$Mn$_1$O$_x$ was 32%, and the ratio of Fe$^{2+}$/Fe$^{3+}$ in Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ was 56%. It means that the introduction of Sm is beneficial to the formation of Fe$^{2+}$. It was reported that the high ratio of Fe$^{2+}$/Fe$^{3+}$ was conducive to the generation of oxygen vacancy, which could lead to better electronic conductivity and better oxygen mobility of catalysts [9]. These results made Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ present better catalytic performance.

### 3.5. Filtration and dust collection performance

The microstructure and morphology of catalytic filter was explored by SEM. Figure 7(a) showed the porous structure of the catalytic filter and figure 7(b) showed the ceramic matrix without catalyst loading. The matrix with connecting pore channel was constructed by ceramic fiber interconnecting. Connected pore channel

*Table 3. XPS results of Fe$_2$Mn$_1$O$_x$ and Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ catalysts.*

| Catalyst                | Fe species | Mn species | Absorbed oxygen | Lattice oxygen |
|-------------------------|------------|------------|-----------------|----------------|
|                         | Fe$^{2+}$  | Fe$^{3+}$  | R$^a$          |                |
| Fe$_2$Mn$_1$O$_x$       | 24.3       | 75.7       | 0.32           |                |
| Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ | 36.0       | 64.0       | 0.36           |                |
|                         | Mn$^{4+}$  | Mn$^{3+}$  | R$^b$          |                |
| Fe$_2$Mn$_1$O$_x$       | 54.3       | 45.7       | 1.19           |                |
| Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ | 52         | 48         | 1.08           |                |
|                         | O$^{2-}$   | O$_2$      | O$^{2-}$       | R$^d$          |
| Fe$_2$Mn$_1$O$_x$       | 12.4       | 6.6        | 81             | 0.23           |
| Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ | 34.3       | 4.8        | 60.9           | 0.64           |

$^a$ Calculated by the area of each peak in the XPS spectra.

$^b$ R: Calculated by the ratio of Fe$^{2+}$/Fe$^{3+}$.

$^c$ R: Calculated by the ratio of Mn$^{4+}$/Mn$^{3+}$.

$^d$ R: Calculated by the ratio of ($O^2- + O_2^-$)/($O^2- + O_2^-$).
structure can effectively filter dust and ensure lower filtration resistance. The Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ was loaded on the fibers of filter as presented in figure 7(c). It can be observed that catalyst occupied part of the space of the channel. The catalyst in the channel was conducive to the contact of gas molecules to react. As shown in figure 7(d), the dust was accumulated on the surface of catalytic filter and the gas go through the pores of catalytic
filter to achieve the purpose of dust removal. The NO molecules reacted with NH3 molecules on the surface of catalyst to generate N2 and H2O.

Figures 8(a) and (b) showed the EDX mapping images of catalysts distribution for Fe2Mn1Sm0.2Ox catalytic filter (35 times and 1000 times respectively). The distribution of oxygen, aluminum and silicon elements overlapped and showed the fiber matrix. Fe and Mn uniformly distributed around the fiber, which indicated that Fe2Mn1Sm0.2Ox catalyst was support on the fibers.

The filtration resistance increased by about 80 Pa after catalysts were loaded (table 4). This increment in filtration resistance of catalytic filter is acceptable in industrial applications.

The filtration performance of the Fe2Mn1Sm0.2Ox catalytic filter was tested using dusty gas with dust concentration of 2 g m\(^{-3}\). After filtration, the dust concentration decreased obviously and the value was only 0.2 mg m\(^{-3}\).

The dust collection efficiency of the catalyst filter was expressed by the following equation:

\[
\text{Efficiency} = \left( \frac{C_{\text{in}} - C_{\text{out}}}{C_{\text{in}}} \right) \times 100\%
\]

\(C_{\text{in}}\) means the dust concentration before the filtration process, and \(C_{\text{out}}\) means the dust concentration after the filtration process. The dust collection efficiency for the Fe2Mn1Sm0.2Ox catalyst filter reached up to 99.99%.

The filter resistance increases because dust accumulated on the surface of the filter during the filtration process. The pulse blowback was used to decrease the filter resistance. With the increase of the times of the pulse blowback, the filter resistance finally increases to a stable value, which is defined as baseline filter resistance. The lower baseline filter resistance indicates the better regeneration performance of filters [34]. As shown in figure 9, the resistance of Fe2Mn1Sm0.2Ox catalytic filter increased with the times of repeated blowback and reached to the baseline filter resistance (262 Pa) eventually. Compared with the resistance of the clean filter, the resistance of Fe2Mn1Sm0.2Ox catalytic filter only increased 60 Pa after 250 times pulse blowback. As shown in figure 9 illustration, the results proved that dust removal will not affect the SCR activity of the Fe2Mn1Sm0.2Ox catalytic filter after 120 times and 240 times pulse blowback. The result proved that the Fe2Mn1Sm0.2Ox catalytic filter has low resistance and excellent regeneration performance.

### Table 4. Resistance of different catalytic filters.

| Catalytic filter | Catalyst loading(wt%) | Filter resistance(Pa) |
|------------------|------------------------|-----------------------|
| PCF              | 0                      | 129                   |
| Fe2Mn1Ox-PCF     | 8                      | 206                   |
| Fe2Mn1Sm0.2Ox-PCF| 8                      | 208                   |

Figure 9. The regeneration performance of Fe2Mn1Sm0.2Ox catalytic filter. (Illustration: the effect of dust remove on SCR activity of Fe2Mn1Sm0.2Ox catalytic filter).
4. Conclusion

In summary, a novel catalytic filter applied to low temperature industrial flue gas was prepared. It was demonstrated that the Fe$_2$Mn$_1$O$_x$ catalyst showed better performance at low temperature than Fe$_1$Mn$_1$O$_x$ and Fe$_2$Mn$_1$O$_x$. Doping Sm enhanced the performance of Fe$_2$Mn$_1$O$_x$. Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ showed the great H$_2$O and SO$_2$ resistance and the NO removal efficiency remains above 89% after 100 ppm SO$_2$ and 7vol.% H$_2$O were introduced. The NO conversion was over 90% in a low temperature range (120°C–220°C) and low oxygen concentration (oxygen concentration ≥1%). The role of Sm on the catalytic performance was summarized as follows. Sm restrained the formation of (NH$_4$)$_2$SO$_4$ or NH$_4$HSO$_4$, thereby improved the SO$_2$ resistance of the catalysts. The crystallinity of catalyst was decreased with adding Sm. The acid strength and acid content of the catalyst increased because of adding Sm. The addition of Sm led to more chemical adsorbed oxygen and increased the ratio of Fe$^{2+}$/Fe$^{3+}$ which could result in higher electronic conductivity and oxygen mobility. Fe$_2$Mn$_1$Sm$_{0.2}$O$_x$ catalyst filter had the satisfactory dust collection efficiency (99.99%) and excellent regeneration performance.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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