1. Introduction

$\text{NO}_x$ (NO, $\text{NO}_2$) is a harmful air pollutant that causes many environmental issues, such as photochemical smog, acid rain, and the greenhouse effect. In addition, it can also cause harm to human health such as through respiratory and pulmonary disease. The large-scale application of the middle-temperature selective catalytic reduction (SCR) technology in coal-fired power plants has led to a sharp drop in their $\text{NO}_x$ emissions. On the other hand, $\text{NO}_x$ emissions of the iron and steel industry are still huge as an energy and pollution intensive manufacturing sector. The sinter plants are the main source of most gaseous pollutants ($\text{NO}_x$, $\text{SO}_2$, etc.). According to a China annual report on environment statistics in 2015, the $\text{NO}_x$ emissions of the iron and steel industry are still as high as 1.043 million tons each year, and $\text{NO}_x$ emissions are increasing year by year. The existing denitration technology for sintering flue gas is the circulating fluidized bed desulfurization–denitration technology and the activated carbon denitration technology. Although the fluidized bed desulfurization–denitration technology has a high $\text{SO}_2$ removal efficiency, the $\text{NO}_x$ removal efficiency is low. And the activated carbon technology has high operating costs by consuming a large amount of activated carbon during the desorption of activated carbon. Based on the modification list of air pollutants emission standard for sintering and pelletizing of iron and steel industry (GB 28662-2012) in China, the demand of $\text{NO}_x$ emission standard will be raised to 100 mg m$^{-3}$ in metallurgical sintering process. However, many sintering plants have not yet reached the emission standard. According to the National environmental statistics bulletin in 2015 in China, there are only 63 sets of de$\text{NO}_x$ equipment in 1522 sets of sintered pellets process of China. Therefore, studying a new de$\text{NO}_x$ method in metallurgical sintering flue gas is imperative. Sintering flue gas has the characteristics of low-temperature exhaust gas (120–180 °C), high oxygen concentration (15–18 vol%) and large flue gas volume. The method of low-temperature selective catalytic reduction of $\text{NO}_x$ with $\text{NH}_3$ ($\text{NH}_3$-SCR) is a heterogeneous catalytic reaction. Therefore, it can adapt the high smoke flow and complex smoke constituents of metallurgical sintering flue gas. This method can selectively convert $\text{NO}_x$ into non-polluting nitrogen in low temperature flue gas. Compared to the vanadium-based medium-temperature $\text{NH}_3$-SCR method, it does not need to...
reheat a lot of low temperature flue gas to the temperature of 300–400 °C, which is energy efficient and economical. Therefore, the low temperature NH₃-SCR method is believed to be the most promising denitration method in the future.

The low temperature SCR catalyst is the focus of research in low temperature NH₃-SCR method. High performance SCR catalysts attract the attention of many researchers. Transition metals and rare earth metals are called research hotspots due to the characteristic of high performance and low cost. Manganese oxides have the best low temperature catalytic activity, but pure manganese oxides have disadvantages such as poor N₂ selectivity and poor thermal stability. Some researchers aim to optimize and select high performance carrier (TiO₂, Al₂O₃, SiO₂, mesoporous silicon, activated carbon, semi-coke, titania nanotubes, Fe–Ti spinel, Mn–Ni–Ti tube) because of their high specific surface area can facilitate uniform dispersion of manganese oxides and improve their thermal stability. In addition, the doping of the transition metal (Mn–Fe, Mn–Zr, Mn–Ni) and the rare earth metal (Mn–Ce) by the active component promotes the formation of more defects in the catalyst. And these defects will form various acid sites and weak linkages, which are beneficial to ammonia adsorption and activation in both Eley–Rideal and Langmuir–Hinselwood mechanism. This study used the prepared zirconium and iron polymeric pillared interlayered montmorillonite as an acidic carrier which has the both a large specific surface area and a large amount of acid sites. Due to its unique physicochemical properties, it has been applied in many ways, such as Fisher–Tropsch, VOCs purification, photocatalysis Fenton, etc. And this is beneficial to improve the low temperature catalytic activity. This study used the high performance catalyst carrier to support the active components of Mn and Sm with different ratio (20 : 0, 18 : 2, 15 : 5, 10 : 10, 5 : 15, 0 : 20) to improve the catalytic activity. The characterization methods of XRD, SEM–EDS, NH₃–TPD, H₂–TPR, and liquid nitrogen adsorption method were used to investigate the structure and physicochemical properties of these catalysts.

2. Experimental

2.1 Catalyst preparation

The 98% pure Na montmorillonite (NaMt) was used as raw material for preparing metal pillared interlayered montmorillonite carrier. The ZrOCl₂·8H₂O (AR, Sinopharm), Fe(NO₃)₃·9H₂O (AR, Sinopharm), and Na₂CO₃ (AR, Sinopharm) were used as precursors preparation material to hydrolyze to form metal oligomers for the montmorillonite pillared process. The Sm(NO₃)₃·6H₂O and Mn(NO₃)₂ (50 wt% Mn(NO₃)₂ solution) were used as active component precursors. The NaMt chemical composition included SiO₂ (60.28%), Al₂O₃ (20.97%), MgO (3.46%), Na₂O (7.63%), CaO (0.38%), Fe₂O₃ (4.62%), K₂O (0.63%), and TiO₂ (0.51%). The NaMt ion exchange capacity was 120 meq/100 g.

Yamanaka S and Ilse Heylen studied the preparation method of Zr–PILM. This study had been improved on the basis of previous studies. The detailed preparation method of acidic carrier ZrFe–PILM can refer to the previous research. First, the zirconium pillaring agent and iron pillaring agent were prepared separately. The zirconium cations in 0.1 M ZrOCl₂ precursor solution was hydrolyzed to zirconium oligomers at 80 °C and stirred for another 2 h. The 0.1 M Na₂CO₃ alkaline solution was added to the 0.1 M Fe(NO₃)₃ solution to promote hydrolysis of iron cations to iron oligomer cations and stirred for 4 h at room temperature. The molar ratio of Na₂CO₃ and Fe(NO₃)₃ was 1 : 1 and the stirred solution continues to age for 24 h at room temperature to form iron pillaring agent. After that, the mixed pillaring agent of zirconium and iron was prepared by the molar ratio of Zr/Fe = 1 : 3 and stirred vigorously at room temperature for another 3 h. Then, the zirconium iron mixed pillaring agent were added to the 1 wt% NaMt slurry. The metal cations and NaMt molar ratio was (Zr + Fe)/NaMt = 10 mmol g⁻¹. Then the mixed suspensions were stirred at 60 °C for another 3 h. The mixed suspension was centrifuged and washed for five times. At last, the ZrFe–PILM carrier was obtained by dried at 90 °C for 24 h and calcined at 400 °C for 3 h.

Different molar ratios of Mn and Sm (Mn/Sm = 20 : 0, 18 : 2, 15 : 5, 10 : 10, 5 : 15, 0 : 20) were impregnated into the ZrFe–PILM carrier with 10 wt% of the catalyst. Then the impregnated wet samples were dried at 90 °C for 24 h and calcined at 400 °C for 3 h with 5 °C min⁻¹ heating rate under air condition. The catalyst expression form was Mn–Sm/ZrFe–PILM (A : B) and the A : B represents the molar ratio of Mn to Sm. The catalyst preparation process visualization flow chart is shown in Fig. 1.

2.2 Catalyst characterization

The Shimadzu XRD 7000 diffractometer was used to detect the X-ray spectrum of these catalysts with the Cu Kα radiation. The XRD scan speed was 2 deg min⁻¹, and the scanning angles was from 10 to 70°.

Element content was recorded by a Rigaku ZSX100E analyzer with a Pd anode as the X-ray source and F-PC and SC detector. The surface morphology and surface element distribution of Mn–Sm/ZrFe–PILM catalysts were detected by scanning electron microscope and energy dispersive spectrometer (SEM–EDS) (Ultra Plus, Carl Zeiss AG).

The Quantachrome physical adsorption instrument was used to record N₂ adsorption–desorption isotherm curve at −196 °C. The specific surface area, total pore volume and pore size distribution of the sample can be calculated from the N₂ adsorption–desorption isotherm. The catalyst samples need to be dried at 200 °C for 3 h before testing. The specific surface area of these catalysts was calculated by Brunauer–Emmett–Teller (BET) method at the relative pressure P/P₀ between 0.05 to 0.2. The total pore volume (Vₚₒ) was obtained from the N₂ adsorption capacity at the relative pressure P/P₀ = 0.98. The average pore sizes (D) of these catalysts can be calculated by the formula below: D = 4Vₚₒ/S_RO. And the pore size distribution can be calculated by the Barrett–Joyner–Halenda (BJH) method.

The curves of ammonia temperature-programmed desorption (NH₃–TPD) can be recorded by a thermal conductivity detector (TCD) of Tianjin XQ TP5080 automatic adsorption instrument. First, a quartz tube was added with 100 mg of catalyst sample and purged at 30 mL min⁻¹ at 200 °C for 30 min.
in a helium atmosphere to remove catalyst adsorbed impurity. The heating rate from room temperature to 200 °C is 10 °C min⁻¹. Then the quartz tube heating furnace was cooled down to 50 °C and begins to pass pure ammonia for 30 min with the flow of 30 mL min⁻¹. The catalyst was purged with 30 mL min⁻¹ of helium for 1 h to 2 h to remove the physically adsorbed ammonia. Finally, the catalyst was heated to 550 °C with the heating rate of 5 °C min⁻¹ and the catalyst NH₃-TPD curves was obtained.

The curves of temperature-programmed reduction by H₂ (H₂-TPR) can be recorded by a Tianjin XQ TP5080 chemisorption analyzer instrument. First, a 20 mg sample catalyst was placed in a quartz tube furnace and heated from room temperature to 200 °C with rate of 10 °C min⁻¹ for pretreatment. And the catalyst sample was purged at 50 mL min⁻¹ helium for 30 min at 200 °C. The sample was then cooled to 50 °C and passed through a mixture of 5% H₂ + He at 50 mL min⁻¹ for 30 min to be stabilized at baseline. The sample was desorbed to a temperature of 800 °C at a heating rate of 5 °C min⁻¹ in a 5% H₂ + He gas stream, and the evolved gas was detected by a thermal conductivity detector (TCD).

2.3 Catalytic activity test

The catalytic detection system was divided into a gas distribution system, a catalytic activity detection system and a gas detection system. The simulated flue gas was composed of NO (500 ppm), NH₃ (500 ppm), O₂ (15 vol%) and balance gas argon. The gas flow rate and volumetric space velocity were 300 mL min⁻¹ and 20 000 h⁻¹ respectively. The formulated NH₃ and NO were standard gases of 5% NH₃ in Ar and 5% NO in Ar, respectively. In addition, both Ar and O₂ were high purity gases. These gases were supplied by Dalian Airichem Specialty Gases & Chemicals Co. Ltd. Use a heating belt to heat from the premixed gas tank and keep it at 120 °C to prevent precipitation of ammonium nitrate precipitation. Catalytic activity was measured in a steady flow mode in a quartz tube fixed bed reactor (i.d. = 10 mm). Catalytic reaction temperature increased from 120–200 °C at intervals 20 °C. Each temperature point was kept for 30 min to achieve a balanced reaction gas concentration. In the detection system, Gasmet DX4000 FT-IR gas analyzer (Gasmet Technologies Inc.) was used to detect the gas concentrations of NO, NO₂, NH₃ and N₂O in the outlet gas. The evaluation index of catalytic activity was NOx conversion and N₂ selectivity. Then its calculation equation was as follows:

\[
\text{NOx conversion} (\%) = \left(1 - \frac{[\text{NOx}]_{\text{out}}}{[\text{NOx}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_2]_{\text{out}} - [\text{NH}_3]_{\text{out}}} \right) \times 100\% 
\]

(1)

\[
\text{N}_2 \text{ selective (%) } = \left(1 - \frac{2[N_2O]_{\text{out}}}{[\text{NOx}]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_2]_{\text{out}} - [\text{NH}_3]_{\text{out}}} \right) \times 100\% 
\]

(2)

where \([\text{NOx}]_{\text{in}}\) was the sum of \([\text{NO}]\) and \([\text{NO}_2]\), and \([\text{NOx}]_{\text{out}}, [\text{NH}_3]_{\text{out}}, [\text{NO}_2]_{\text{out}}, [\text{NH}_3]_{\text{out}}\) were the corresponding outlet and inlet gas concentrations.

3. Results and discussion

3.1 Catalyst phase composition and active component distribution

In order to accurately understand the content of Mn and Sm in the Mn–Sm/ZrFe-PILM catalysts and its ratios are shown in Table 1. It can be seen that the actual molar ratio of Mn : Sm is similar to the molar ratio at the time of preparation. The actual molar ratio of Mn : Sm were 8.31, 3.06, 1.14, and 0.37. In order to better observe the dispersibility of the catalyst, XRD and SEM-EDS were used to observe the dispersibility of the active components Mn and Sm on the catalyst surface.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Mn content (wt%)</th>
<th>Sm content (wt%)</th>
<th>Mn : Sm molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn/ZrFe-PILM</td>
<td>6.65</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mn–Sm/ZrFe-PILM (18 : 2)</td>
<td>6.25</td>
<td>2.09</td>
<td>8.31</td>
</tr>
<tr>
<td>Mn–Sm/ZrFe-PILM (15 : 5)</td>
<td>4.84</td>
<td>4.40</td>
<td>3.06</td>
</tr>
<tr>
<td>Mn–Sm/ZrFe-PILM (10 : 10)</td>
<td>3.21</td>
<td>7.82</td>
<td>1.14</td>
</tr>
<tr>
<td>Mn–Sm/ZrFe-PILM (5 : 15)</td>
<td>1.56</td>
<td>11.6</td>
<td>0.37</td>
</tr>
<tr>
<td>Sm/ZrFe-PILM</td>
<td>—</td>
<td>13.7</td>
<td>—</td>
</tr>
</tbody>
</table>
The XRD patterns of Mn–Sm/ZrFe-PILM catalysts with different Mn/Sm molar ratio (20 : 0, 18 : 2, 15 : 5, 10 : 10, 5 : 15, 0 : 20) are shown in Fig. 2. The NaMt crystalline phase peaks were shown at 20.2°/C14°, 26.8°/C14°, 35.5°/C14°, and 50.6°/C14°, which correspond to NaMt phase. These catalysts all had NaMt characteristic peaks. But the crystalline phase peaks of intercalated ZrO2 and Fe2O3 were not found. This was because that the iron and zirconium polymerized oligomers were exchanged to the pillared interlayered montmorillonite layer with suitable molar ratio of Zr/Fe = 1 : 3. The polymerized pillared montmorillonite not only enhanced the pore size structure of the catalyst, but also promoted uniform dispersion of ZrO2 and Fe2O3. And the ZrO2 and Fe2O3 had a low crystallinity in pillared montmorillonite. And the detailed reasons can refer to the previous study.28 Similarly, the crystalline spectra peaks of manganese oxides and samarium oxides were also not found. It was because that manganese oxides and samarium oxides were highly dispersed into the Zr–Fe polymeric pillared interlayered montmorillonite carrier. And this was also consistent with the results of SEM-EDS results in Fig. 3.

3.2 Morphology and texture

The surface morphology of ZrFe-PILM (A) carrier and Mn–Sm/ZrFe-PILM (18 : 2) (B) catalyst are shown in the Fig. 4. Scanning electron microscopy images of the catalysts were magnified at 10 000 times. The ZrFe-PILM carrier and Mn–Sm/ZrFe-PILM catalyst had a rough surface and a porous surface structure. The carrier of ZrFe-PILM had a specific surface area of 176.2 m² g⁻¹, and the specific surface area was greatly improved compared to the raw materials Na montmorillonite (13.69 m² g⁻¹). The specific surface area of Mn–Sm/ZrFe-PILM (18 : 2) drops to 102.5 m² g⁻¹ compared to carrier ZrFe-PILM. This may be due to the fact that the active components Mn and Sm carry the carrier and occupy some of the pore size of the support.
Therefore, a large number of pore structures facilitated the loading and uniform dispersion of the active components.

The detailed aperture type and pore size distribution can be seen from Fig. 5. The ZrFe-PILM carrier and Mn–Sm/ZrFe-PILM (18 : 2) catalyst had a similar N₂ adsorption desorption isotherm shapes. And based on the International Union of Pure and Applied Chemistry (IUPAC), the adsorption and desorption curves of ZrFe-PILM and Mn–Sm/ZrFe-PILM (18 : 2) belonged to the type of IV. It indicated that the aperture type of ZrFe-PILM and Mn–Sm/ZrFe-PILM (18 : 2) were mainly mesoporous. The hysteresis loop of the N₂ adsorption desorption isotherm belonged to the H3 type. This type of hysteresis loop represented the mesopores of the slits or crack shape pores. This is because the mixed oligomer of zirconium and iron entered the montmorillonite layer and supported the montmorillonite layer. Since the carrier and catalyst were mesoporous structure, the BJH method was used to calculate the pore size distribution. As can be seen from the pore size distribution of Fig. 4, the pore sizes of ZrFe-PILM and Mn–Sm/ZrFe-PILM were concentrated at 1.91 nm and 1.92 nm, respectively. The higher specific surface area and smaller pore structure provided more reaction and adsorption platforms for the reactants in the SCR reaction.

3.3 Catalyst surface acidity

The nature of acidic sites of the Mn–Sm/ZrFe-PILM catalysts with different Mn/Sm molar ratio were determined by ammonia temperature programmed desorption (NH₃-TPD) technique. The NH₃-TPD patterns collected are illustrated in Fig. 6. These catalysts exhibited primarily two ammonia desorption peaks in the temperature range from 80 °C to 550 °C. The peaks that appeared at low temperatures were ascribed to ammonia bound to weak acidic sites. And the peaks at higher temperatures attributed to strong acidic sites for ammonia adsorption. When the molar ratio of Mn/Sm was 20 : 0, 18 : 2, and 15 : 5, the ammonia desorption peaks were at a lower temperature around 120 °C and 300 °C. When the ratio of Mn/Sm was 10 : 10, 15 : 5, and 20 : 0, the ammonia desorption peaks were at a higher temperature around 200 °C and 400 °C. It was established that the acidic site distribution can broaden by the addition of small amount of Sm. The Mn–Sm/ZrFe-PILM (18 : 2) had the most acidic sites, especially the weak acidic sites. And it exhibited a larger peak centered at 117 °C which can be attributed to the desorption of ammonia coordinated on weak acid sites. In general, the weak acid sites belonged to the Lewis acid sites on the surface of the catalyst. A large amount of Lewis acid sites was beneficial to the adsorption of ammonia. Based on the principle of Langmuir–Hinshelwood and Eley–Rideal mechanism, this enhancement in ammonia adsorption or activation will increase reaction rate and promote selective catalytic reduction activity. This was also in good agreement with the activity experiments in the catalytic activity.

3.4 Catalyst reduction property

In the low temperature SCR reaction, the redox properties of the catalyst played an important role in the activity of the catalyst. The reduction profiles for carrier ZrFe-PILM and Mn–Sm/ZrFe-PILM catalysts with various ratio Mn/Sm (Mn/Sm = 20 : 0, 18 : 2, 15 : 5, 10 : 10, 5 : 15, and 0 : 20) were determined by...
3.5 Catalyst activity

The NO\textsubscript{x} conversion of Mn–Sm/ZrFe-PILM catalysts with different molar ratios of Mn and Sm and carrier ZrFe-PILM are shown in Fig. 8. The NO\textsubscript{x} conversion of these catalysts was increased with increasing temperature from 120 °C to 200 °C. The active component Sm loaded onto the ZrFe-PILM carrier and the carrier ZrFe-PILM had the lowest NO\textsubscript{x} conversion with around 14% from 120–200 °C reaction temperature. The NO\textsubscript{x} conversion of Mn/ZrFe-PILM was increased from 52.0% to 91.1% in the temperature range from 120 °C to 200 °C. Interestingly, when a small amount of Sm doped into the active component Mn (Mn : Sm = 18 : 2), its catalytic activity was improved from 120 °C to 200 °C. It had the largest NO\textsubscript{x} conversion with 95.5% NO\textsubscript{x} conversion at 200 °C. However, when the molar ratio of Sm increased, the catalytic activity decreased. This may be due to the fact that a small amount of samarium oxides doped into manganese oxides can increase a large number of defect sites. These defect sites form more acidic sites and a large amount of active oxygen. The ammonia adsorption and activation were increased in the SCR reaction. It was an important step in the reaction mechanism of Eley–Rideal and Langmuir–Hinshelwood mechanism. This was also the root cause of the increase in catalytic activity. However, the increase in catalytic activity of the trace Sm-doped Mn also reduced the N\textsubscript{2} selectivity of the catalyst, as it is shown in Fig. 9. This was because the introduction of the samarium does not inhibit the excessive activation of ammonia, resulting in an increase in side reactions that produce N\textsubscript{2}O. Although the Mn–Sm/ZrFe-PILM (18 : 2) catalyst had the lowest N\textsubscript{2} selectivity compared to other catalysts. However, its N\textsubscript{2} selectivity was greater than 85% between 120 and 200 °C. This was because ZrFe-PILM acts as an acidic carrier for the active component, inhibiting partial ammonia overactivation, thereby increasing the N\textsubscript{2} selectivity of the catalyst.\textsuperscript{29} Then, the catalyst Mn–Sm/ZrFe-PILM (18 : 2) was tested at 180 °C in the activity detection system for 720 min to assess whether the catalyst would be deactivated for a long time. The activity test results were shown in Fig. 10. It can be seen from the test data in the figure that the activity of the catalyst was stable above 91% after a test of up to 720 min. This means that the Mn–Sm/ZrFe-PILM not only had good catalytic activity, but also had long activity stability. This
Conclusions

A series of Mn–Sm/ZrFe-PILM catalysts with different molar ratios of Mn/Sm (Mn : Sm = 20 : 0, 18 : 2, 15 : 5, 10 : 10, 5 : 15, 0 : 20) were prepared and studied. The results showed that a small amount of samarium doping (Mn : Sm = 18 : 2) was beneficial to improve the low temperature catalytic activity of the catalyst Mn–Sm/ZrFe-PILM. The NO\textsubscript{x} conversion rate reached 95.5% at 200 °C. XRD and SEM results showed that the active components manganese and samarium oxides were highly dispersed on the surface of the mesoporous support ZrFe-PILM. Highly dispersed active components provided more reaction platform for catalytic reactions. The NH\textsubscript{3}-TPD results indicated that the Mn–Sm/ZrFe-PILM (18 : 2) catalyst had the most weakly Lewis acid sites. Lewis acid promoted the adsorption of ammonia in the Langmuir–Hinshelwood and Eley–Rideal mechanisms. Therefore, the low temperature catalytic activity of the catalyst was promoted. In addition, the addition of samarium reduced the bond energy of the Mn/ZrFe-PILM catalyst, and Mn–Sm/ZrFe-PILM (18 : 2) had the lowest bond energy according to the H\textsubscript{2}-TPR pattern. Therefore, when trace amount of samarium was doped with Mn/ZrFe-PILM, the low-temperature catalytic activity of the catalyst was improved. Compared with other catalytic systems, this study mainly used the prepared high specific surface area acidic carrier to promote the adsorption of ammonia and nitrogen oxides. The active component loading and doping facilitates the redox reaction between the support and the active component, thereby promoting the activity of the catalyst.

Conflicts of interest

There are no conflicts to declare.

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References