Thulium oxides supported on MnCeTiO\textsubscript{X} catalysts for low-temperature NH\textsubscript{3}-SCR of NO\textsubscript{X}

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Abstract

In this work, the MnCeTiO\textsubscript{X} catalyst was prepared by sol-gel method and doped with thulium (Tm), which improved its low-temperature selective catalytic reduction (SCR) activity and resistance to SO\textsubscript{2} poisoning. In this paper, the surface properties of Tm-doped MnCeTiO\textsubscript{X} catalysts were studied and analysed by means of BET, XRD, SEM, NH\textsubscript{3}-TPD, H\textsubscript{2}-TPR and XPS. The catalyst performance was tested by using simulated flue gas. The results show that Tm doping can effectively inhibit the crystallization degree of TiO\textsubscript{2}, increase the catalyst specific surface area, and make the elements distribute more uniformly on the catalyst surface. Meanwhile, the amount of Brønsted acid sites could be increased by Tm doping. It also increased the concentration of surface adsorbed oxygen and the ratio of Mn\textsuperscript{4+}/Mn and Ce\textsuperscript{4+}/Ce. Therefore, the activity of the catalyst was improved by Tm doping in the temperature range of 90 ºC to 270 ºC, the catalyst activity remained above 97% in the temperature range of 180 ºC to 270 ºC. And the catalyst activity remained above 88% after a 10 h-SO\textsubscript{2} poisoning test. Tm doping could effectively inhibit SO\textsubscript{2} poisoning of the catalyst and reduce the adsorption of SO\textsubscript{2} on the catalyst surface.

1. Introduction

Generally, Nitrogen oxides (NO\textsubscript{X}) are main concerns of environmental governance due to severe atmospheric problems, such as greenhouse impacts, particulate matter and acid rain [1]. NH\textsubscript{3}-SCR is the most mature denitrification method used in industry. Currently, the most widely used SCR catalyst is V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}(MoO\textsubscript{3})/TiO\textsubscript{2} [2], which could achieve the best catalytic efficiency at 300 ºC–400 ºC. Thus, the catalyst needs to be installed near the flue gas outlet in the whole flue gas purification to reduce the loss of flue gas temperature. It means that the dust and SO\textsubscript{2} cannot be removed in flue gas when it reacts on SCR catalysts. This would shorten the catalyst usage time due to the dust washout and SO\textsubscript{2} poisoning. At the same time, the use of vanadium would be toxic to human body and threaten human health. Therefore, it is necessary to develop a non-toxic catalyst that can adapt to the low-temperature environment in order to remove the dust and SO\textsubscript{2} first in flue gas.

Low temperature SCR denitrification technology has been widely researched by scholars. The outstanding performance of many metal oxides have facilitated them to be applied as promoters. Manganese oxide has labile lattice oxygens and multivalent Mn species [3–5]. Meanwhile, manganese oxides have the advantages of being environmentally friendly, abundant in resources and low in cost [6]. Thus, the manganese oxide has been always applied to the preparation for low-temperature SCR denitrification catalysts. Rare earth elements are widely used as catalyst promoters due to incompletely occupied 4f and empty 5d orbitals [7]. According to several academic reports, many rare earth elements have been shown to promote the catalytic activity of low temperature NH\textsubscript{3}-SCR catalyst, such as Sm, Eu, Ho, Nd, Ce [8–11]. Cerium oxide has a glorious ability to store and release oxygen, and it also exhibits outstanding performance in low-temperature SCR reactions [12]. Additionally, SO\textsubscript{2} would be more likely to react with rare earth elements, which would protect the other active sites on the catalyst surface [13]. The thermostability of sulfates could be reduced by Ce on the catalyst surface to
improve the SO₂ resistance of the catalyst [14]. In the preparation of catalysts, the choice of a suitable carrier is also crucial. TiO₂ could provide a large specific surface area, chemical stability and have abundant acid sites on the surface [15]. Smirniotis et al reported the manganese oxides supported on different carriers, and concluded that the decreasing order of SCR performance of catalysts is as follows: TiO₂ (anatase, high surface area) > TiO₂ (rutile) > TiO₂ (anatase, rutile) > γ-Al₂O₃ > SiO₂ > TiO₂ (anatase, low surface area) [16]. In summary, the preparation and modification of MnCeTiOX catalyst has become one of the most important research projects [17–19]. However, the reported MnCeTiOX catalysts still face challenges in suppressing SO₂ poisoning, because SO₂ in flue gas still remains even after being cleaned. SO₂ would form (NH₄)₂SO₄/NH₄HSO₄ with NH₃. And (NH₄)₂SO₄/NH₄HSO₄ could stick to the catalyst surface, covering active sites of the catalyst [20]. SO₂ also reacts with the metal active sites to form metal sulfATES, which would reduce the active sites [21]. Therefore, it is essential to modify the catalyst to improve its resistance to SO₂ poisoning.

Although rare earth element Tm is widely used in the preparation of optical nanodevices, it is less used in denitification. Niu et al found that the low-temperature SCR activity of the Mn/TiO₂ catalyst was enhanced after Tm modification [22]. Jin et al modified the CeO₂/Al₂O₃ catalyst with rare earth elements (La, Nd, Sm, Gd, Tm), and found that Tm and Ce synergized to promote the enhancement of catalyst performance [23]. In addition, there is no clear and specific academic results about the effect of the activity of MnCeTiOX catalysts modified with Tm and the toxic influence of the SO₂ on SCR catalysts doped with Tm. Therefore, in order to further study the effect of Tm on the low temperature SCR catalyst, Tm-doped MnCeTiOX catalysts were prepared by sol-gel method in this study. The synthesized catalysts were tested for NH₃-SCR denitification activity in temperature range of 90 °C to 270 °C and also tested for SO₂ poisoning at 180 °C for 10 h. The morphology, structure, surface acid strength and element valence state of the catalyst surface were then analyzed.

2. Experimental

2.1. Catalysts fabrication

The Tm-doped MnCeTiOX catalysts that were prepared by sol-gel method. Initially, solution A was obtained by mixing 5 ml tetrabutyl titanate and 2.5 ml ethanol and stirred for 30 min. Secondly, 1.4 ml Mn(NO₃)₂·6H₂O, Tm(NO₃)₂·5H₂O were dissolved in a solution containing 2.5 ml ethanol, 2.5 ml acetic acid and 0.7 ml deionized water, marked it as solution B. Then solution B was slowly dropped into solution A and stirred at room temperature for 4 h to form a sol. The sol was allowed to stand for 24 h to form a gel, and the gel was dried at 105 °C for 6 h. Finally, the gel would be calcined at 2 °C min⁻¹ to 500 °C for 3 h in air atmosphere to obtain catalyst Tₐₙ-MnCeTiOX (denoted as Tₐₙ-MCT hereafter, n is the molar ratio of Tm:Ti). The molar ratio of components used for preparing the catalyst was Mn:Ce:Ti = 0.4:0.1:1. The MnCeTiOX (denoted as MCT hereafter) catalyst was prepared by the similar procedure without adding Tm(NO₃)₂·5H₂O in solution B. The catalysts were labeled S-MCT and S-Tₐₙ-MCT after the SO₂ poisoning tests.

2.2. Characterization

X-ray powder diffractometer (XRD, D/max2550VB/PC) with 2θ range from 10° to 80° to characterize crystals. Scanning electron microscope (SEM, S-3400N) characterized the surface morphology. X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi) characterized the composition and valence of surface elements. The Quantachrome Autosorb iQ had an N₂ adsorption-desorption isotherm at 77K. Calculated the final specific surface area and corresponding pore size distribution in Brunauer–Emmett–Teller (BET) equation and BJH model. H₂-TPR and NH₃-TPD were carried out in conventional equipment equipped with TCD. Among them, the amount of test sample was 50 mg. For the H₂-TPR test, the sample was first pretreated with N₂ flow (30 ml min⁻¹) at 200 °C for 2 h, and then cooled to room temperature. Afterwards, the sample was tested from 100 °C to 800 °C through the 5% H₂/N₂ flow (30 ml min⁻¹) at a heating rate of 10 °C min⁻¹. In the NH₃-TPD test, each sample was pretreated with N₂ at 400 °C for 1 h, cooled to 50 °C, saturated with 5% NH₃/Ar, and finally purged with N₂ to remove physically adsorbed NH₃.

2.3. Catalytic activity measurement

The performance of catalysts were tested in a fixed bed reactor. The reaction gas was composed of 500 ppm NO, 500 ppm NH₃, 5% O₂, 100 ppm SO₂ (if used) and balanced N₂ to simulate flue gas. The total mass flow rate was 200 ml min⁻¹ and the gas hourly space velocity was 50,000 h⁻¹, and each test used 0.200 g catalyst. Additionally, used Thermo Fisher 42i to continuously detect NOₓ concentration. After reaching the predetermined temperature point, waiting for 30 min-60 min to ensure the data stable and record it.
The catalytic activity of the catalyst was calculated using the following equation:

\[
\text{NO conversion}(\%) = \frac{\text{NO}_{\text{in}} - \text{NO}_{\text{out}}}{\text{NO}_{\text{in}}} \times 100\%
\]

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

3. Results and discussion

3.1. Catalytic performance

Figure 1 illustrates the relationship between NO conversion of the catalysts and the temperature. It could be seen that the catalyst has the best activity when the molar ratio of Tm:Ti = 0.06:1. With the increase of Tm doping in the MCT catalyst, the activity of the catalysts increases first and then decreases. It indicates that suitable Tm doping is beneficial to the performance of the MCT catalyst. Compared with the MCT catalyst, the T0.06MCT catalyst significantly improves the NO conversion rate. It shows that the Tm modified catalyst can improve the activity of the catalyst in lower temperature region. Thus, MCT catalyst and T0.06MCT catalyst are used for the later study.

As mentioned above, SO2 would have a side reaction on the catalyst surface to form deposited \((\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4\) on the catalyst surface to reduce the catalytic activity. In order to study the poisoning effect of SO2 on the catalyst, SO2 poisoning test is carried out at 180 °C as shown in figure 1(b). It could be seen that the NO conversion rate changed when SO2 is switched on and off. When SO2 is added, the catalysts activity
has a rapid decline at first and then tends to decline slowly. When SO2 is switched off, the catalysts activity remain unchanged, indicating that SO2 poisoning is irreversible. The NO conversion rate of T0.06MCT catalyst is only be reduced 12% by 10 h, which is better than MCT catalyst. Thus, doping Tm is beneficial to improving its resistance to SO2 poisoning.

3.2. Structural and morphological analysis of catalysts

Figure 2 shows the N2 adsorption-desorption curve of the catalysts. It seems that all catalysts present the typical ‘type IV’ adsorption-desorption curves with H2 (b) hysteresis loops [24], which are typical mesoporous structure characteristics in figure 2. According to the research, it is clear that the mesoporous channel can more easily promote the dynamic balance between the formation and decomposition of \((\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4\) [25, 26]. Meanwhile, the modification of Tm do not change the mesoporous structure of the catalyst. It could improve the anti-SO2 poisoning ability of the catalyst. The specific surface area and pore volume of each catalyst are shown in table 1. According to the data in table 1, it could be seen that the specific surface area of the T0.06MCT is significantly increased, and a larger specific surface area can provide more active sites. After SO2 poisoning tests, the specific surface area of catalysts is decreased, and the pore volume also be decreased. This is attributed to the fact that SO2 reacts with NH3 on the catalysts surface to form \((\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4\). The specific surface area of the S-T0.06MCT catalyst is still larger than that of S-MCT catalyst, indicating that the large specific surface area is one of the reasons for performance improvement of the catalyst.

XRD results of samples have been clearly shown in figure 3. The peaks at 25.7°, 48.8°, 54.8°, 55.9°, 63.1° and 63.7° could be attributed to the anatase phase of TiO2. The corresponding lattice plane are (101), (200), (105), (211), (213) and (204), respectively (PDF#75–1537). The catalysts all show obvious characteristic peaks of anatase TiO2, indicating that the catalysts do not change the TiO2 crystal phase due to the modification. Anatase TiO2 has abundant active sites which can improve the activity performance of the catalysts [27]. It can be seen that the position of the peak shifts slightly to the low-angle direction after MCT catalyst doped with Tm, which indicates that Ti4+ (68 pm) may be replaced by large-sized Tm3+ (86.9 pm) [28]. The weakened and broadened peaks of TiO2 in T0.06MCT catalysts indicate that Tm-O-Ti bonds are formed at the grain boundaries, which could inhibit the crystal growth of TiO2 [29, 30]. This can also be confirmed from the SEM results. Meanwhile, there are no peaks of other oxides are discovered. The broad peak at 31° is characterized as an amorphous

| Samples        | BET surface area (m² g⁻¹) | Total pore volume (cm³ g⁻¹) | Average pore diameter (nm) |
|----------------|---------------------------|-----------------------------|---------------------------|
| MCT            | 102.8                     | 0.1432                      | 3.860                     |
| T0.06MCT       | 155.2                     | 0.1642                      | 3.449                     |
| S-MCT          | 89.1                      | 0.1257                      | 3.858                     |
| S-T0.06MCT     | 129.1                     | 0.1360                      | 3.864                     |

Figure 3. XRD patterns of the different catalysts.
structure. This result indicates that active ingredients are dispersed evenly on the catalyst surface with an amorphous structure [31]. A weak peak at 20.5° can be found in the S-MCT catalyst XRD results, which can be attributed to (NH₄)₂SO₄ (PDF#40–0660) [32]. It can’t be found in the S-T₀.₀₆MCT catalyst XRD results, indicating that Tm-doped can effectively inhibit the adsorption of SO₂ on the catalyst surface.

In order to explore the morphological change of the catalyst surface, SEM is used to achieve this test as shown in figures 4(a)–(d). Based on the result, the agglomeration degree of active components is obviously reduced by Tm doping, which can be attributed to the fact that Tm can suppress the degree of crystallization of the catalyst. This is consistent with the results described in XRD. With decreasing crystallinity, it also increases the specific surface area of the catalyst. After the SO₂ poisoning tests, the degree of agglomeration of S-MCT is obviously larger than S-T₀.₀₆MCT, which would reduce the number of active sites on the catalyst surface and decrease the activity of the catalyst. It is proved that Tm can effectively inhibit the agglomeration of active components. In summary, Tm plays an essential role in catalyst. Therefore, in order to further understand the reduction property and surface acidity of the catalyst surface, we carried out relevant test analysis.

### 3.3. Reduction property and surface acidity

NH₃-TPD is used to detect the acid strength of catalysts surface, and the results are shown in the figure 5. There is a broad peak corresponding to the weak acid sites between 180 °C and 300 °C, which are attributed to the desorption of NH₄⁺ at the Brønsted acid sites [33, 34]. The peak at 370 °C corresponds to the strong acid sites that are owing to the desorption of NH₃ at the Lewis acid sites. Brønsted acid sites can not only strengthen the adsorption of NH₃, but also suppress the adsorption of SO₂. And SO₂ can compete with NH₃ for adsorption at Lewis acid sites [35]. Obviously, based on the change of peak area, it can be inferred that the Lewis acid sites are significantly reduced and the Brønsted acid sites are increased after the catalyst doped with Tm. Thus, the adsorption of NH₃ on the catalyst is enhanced in the low temperature region and the adsorption of SO₂ on the catalyst surface will be reduced. This can be attributed to the synergistic effect of Tm and other elements to change the distribution of acid sites on the catalyst surface. After the SO₂ poisoning tests, the Lewis acid sites are...
reduced compared with the fresh catalysts, and the Brønsted acid sites are increased. The increase of Brønsted acid sites is due to the thermal decomposition of $(\text{NH}_4)_2\text{SO}_4/\text{NH}_4\text{HSO}_4$.

The figure 6 has shown the $\text{H}_2$-TPR curve of each sample between the 100 °C and 800 °C. The MCT catalyst and $\text{T}_{0.06}\text{MCT}$ catalyst have three peaks at 334.5 °C, 390 °C and 505.5 °C. These reduction peaks could be attributed to the continuous reduction process of $\text{MnO}_2 \rightarrow \text{Mn}_2\text{O}_3 \rightarrow \text{Mn}_3\text{O}_4 \rightarrow \text{MnO}$ [36]. The reduction peak of cerium oxide and thulium oxide could not be found because of the overlap with the reduction peak of cerium oxide and thulium oxide.

Figure 6. $\text{H}_2$-TPR patterns of the different catalysts.

Figure 7. XPS spectra of the different catalysts: (a) Mn 2p, (b) Ce 3d, (c) O 1s and (d) S 2p.
manganese oxide [37]. The area of the reduction peak at 334.5 °C is significantly increased after the catalyst modified with Tm. It indicates that the content of Mn⁴⁺ increases. Mn⁴⁺ is beneficial to improve the catalytic activity of the catalyst [38]. It can be attributed to the synergistic effect Tm³⁺ + Mn⁵⁺ → Tm²⁺ + Mn⁴⁺. After SO₂ poisoning tests, there is a new peak attributed to the reduction of sulfates at 533 °C and 548 °C. The peak area at 533 °C is smaller than the peak area at 548 °C, illustrating that the T₀.₀₆MCT catalyst has lower metal sulfation and less sulfate substance [28].

### 3.4. Surface elements and valence states

In figure 7, the XPS test is used to further determine the valence states and elements species of catalyst surface and the element ratios are presented in table 2. As shown in figure 7(a), it illustrates that Mn 2p consists of two peaks. One is Mn 2p₃/₂ which binding energy (BE) is 641.25 eV, and the other is Mn 2p₁/₂ which binding energy (BE) is 653.5 eV [39]. The peaks at 640.1 eV, 642.1 eV, 645.2 eV could be assigned to Mn²⁺, Mn³⁺ and Mn⁴⁺. Mn⁴⁺ is generally considered to be the main functional element for the low-temperature SCR reaction. The ratio of Mn⁴⁺/Mn in T₀.₀₆MCT catalyst is increased, it is consistent with the previous results measured by H₂-TPR. It shows that Tm modified catalyst could increase the amount of Mn⁴⁺. The ratio of Mn⁴⁺/Mn decreases in catalysts after the SO₂ poisoning tests, but the degree of Mn⁴⁺ decreased in T₀.₀₆MCT (7%) is lower than that in MCT (12.3%), showing that Tm could suppress the SO₂ poisoning of the catalyst.

The XPS result of Ce 3d is composed of two partial peaks that belong to the spin–orbit split of the 3d₅/₂ and 3d₃/₂ core holes. Ce³⁺ consists of two peaks at 885.4 eV and 903.4 eV which corresponds to Ce³⁺ 3d₅/₂ and Ce³⁺ 3d₃/₂ [40]. The peaks at 882.7 eV, 889.4 eV and 898.0 eV are characteristics to Ce⁴⁺ 3d₅/₂, and the peaks at 901.3 eV, 907.3 eV, 916.4 eV are assigned to Ce⁴⁺ 3d₃/₂. The increase of Ce³⁺ content could improve the redox process between Ce³⁺ and Ce⁴⁺, and it generates more oxygen vacancies to improve the activity of the catalyst [41]. The doping of Tm could promote the conversion of Ce⁴⁺ to Ce³⁺. After SO₂ poisoning tests, the Ce³⁺ content increases due to the Ce⁴⁺ could be reduced by SO₂ [42]. Thus, Tm could inhibit the electron transfer of SO₂ to Ce that reduce SO₂ adsorption on the catalyst surface.

O 1s spectra can be divided into two types: lattice oxygen (O₃) at 529.7 eV and surface adsorbed oxygen (O₅) at 531.3 eV [43]; the test indicates that Tm doped would increase the O₃ content in catalysts. O₃ has a higher mobility than O₅, and it facilitates the conversion of NO to NO₂ [44]. Therefore, the increase of O₃ ratio helps to enhance the activity of catalyst at low temperatures.

The figure 7(d) shows the S 2p spectra of catalysts S-MCT and S-T₀.₀₆MCT. S 2p consists of two peaks, one is SO₂⁻ at 168.5 eV and the other one is SO₄²⁻ at 169.7 eV [45, 46]. According to the comparison of the area, there is more sulfur in T₀.₀₆MCT catalyst. It indicates that Tm can inhibit the adsorption of SO₂ on the catalyst surface by producing a synergistic effect with Mn and Ce, which could protect the active sites on the catalyst surface. In addition, it can be found that the proportion of SO₄²⁻ decreases, indicating that the doping of Tm can inhibit the formation of sulfate.

### 4. Conclusion

In conclusion, Tm-modified MnCeTiO₅ catalyst prepared by sol-gel method could change the strength of acid sites and the element valence on the catalyst surface. The modification of MCT catalyst with Tm can effectively enhance its catalytic activity. When Tm:Ti = 0.06, the activity of T₀.₀₆MCT catalyst is the best. Meanwhile, the catalytic activity of the T₀.₀₆MCT catalyst only decreased by 12% in 10 h SO₂ poisoning test at 180 °C, which is obviously better than MCT catalyst. It indicates that Tm can alleviate SO₂ poisoning of catalyst. The addition of Tm to the catalyst can inhibit the crystallization of TiO₂ and facilitate the active components to be distributed evenly on the catalyst surface. Tm can also increase the specific surface area of the catalyst that would provide more active sites for catalyst to obtain efficient catalytic performance. Tm doping can increase the amount of weak acid sites on the catalyst surface, make the catalyst to adsorb more NH₃ in the low temperature region. Based on the element valence analysis, it is clear that the content of Mn⁴⁺ and Ce³⁺ on the catalyst surface increases, which can be attributed to the electron transfer between Tm and other elements, which reduces the
formation of \((\text{NH}_3)_2\text{SO}_4/\text{NH}_4\text{HSO}_4\) on the catalyst surface. The content of \(\text{O}_3\) also increased because of the addition of Tm. In general, Tm doping can improve the low-temperature SCR denitrification activity of the catalyst, and inhibit the formation of ammonium sulfate on the surface of the catalyst to enhance its resistance to \(\text{SO}_2\) poisoning.

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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).

**Conflict of interest**

The authors declare no conflict of interest.

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