Composite catalytic systems: A strategy for developing the low temperature NH₃-SCR catalysts with satisfactory SO₂ and H₂O tolerance

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1. Introduction

Low temperature selective catalytic reduction of NO with NH₃ (low temperature NH₃-SCR), as promoting technology to treat exhaust gas from stationary sources, has been paid more and more attention in the past decades [1–4]. Comparing with typical NH₃-SCR catalysts, low temperature NH₃-SCR catalysts could be located downstream of the electrostatic precipitator and even desulfurizer where most of SO₂ and dust have been removed for the advantage of low activity temperature. Transition metal oxides based catalysts such as Mn oxides [5,6], Fe oxides [7,8], V oxides [9,10] have been reported to exhibit excellent low temperature NH₃-SCR activity, whereas their poor SO₂ and H₂O tolerance inhibited their applications. In this work, utilizing transition metal sulfates, the poisoning effects caused by transition metal sulfates, the poisoning effects caused by transition metal sulfation are irreversible [13–15]. Moreover, the formation of ammonium sulfates from SO₂, O₂, and NH₃ was universal in low temperature NH₃-SCR. The formed ammonium sulfates deposit on the surface of catalyst, which induces the coverage of active sites and the blockage of catalysts pores, and therefore, the deactivation of NH₃-SCR catalysts [13–15]. Ammonium sulfates decompose at 280 °C. It is effective to regenerate the deactivated NH₃-SCR catalysts through a thermal treatment.

Water vapor, as a product of organics containing hydrogen combustion, often exists in stack gas, which could cause the deactivation of NH₃-SCR catalysts by decreasing the available active sites [16]. Due to the competitive adsorption on catalysts surface between H₂O and reactants, the adsorption of reacting agents decreased, such as NH₃ and NO, leading to the deactivation of NH₃-SCR catalysts [17–19]. Besides, the dissociative adsorption of H₂O on catalysts usually resulted in the formation of surface hydroxyls on active sites of the catalysts. Owing to the high decomposition temperature of transition metal sulfates, the poisoning effects caused by transition metal sulfation are irreversible [13–15]. Moreover, the formation of ammonium sulfates from SO₂, O₂, and NH₃ was universal in low temperature NH₃-SCR. The formed ammonium sulfates deposit on the surface of catalyst, which induces the coverage of active sites and the blockage of catalysts pores, and therefore, the deactivation of NH₃-SCR catalysts [13–15]. Ammonium sulfates decompose at 280 °C. It is effective to regenerate the deactivated NH₃-SCR catalysts through a thermal treatment.

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sulfates formation from NH₃ and sulfur oxides. Hence, H₂O promote the formation of ammonium sulfates, which amplified the SO₂ poisoning effects on SCR catalysts.

Doping elements [22–24], sacrificial agents [25], stable supporters immune to sulfating [26–28] were employed to increase SO₂ and H₂O tolerance of NH₃-SCR catalysts, according to literature. Fe dopant is capable to decrease the formation rate of sulfate species [3, 29], while Ce is able to restrain the formation of ammonia sulfate on catalysts surface [22, 23]. Chen et al. [30] found that the SO₂ tolerance and catalytic activity of MnOₓ could be dramatically enhanced by the introduction of Cr due to the formation of CrMn₁.₅O₄. Zhang et al. [31] found the MnₓCo₃₋ₓO₄ catalyst exhibited decent SO₂ tolerance due to its hierarchically porous structure, abundant active sites and strong interaction between Mn and Co oxides. Because of the alkalinity, SO₂ prefer to react with alkaline earth metal oxide, such as CaO, which was reported as a sacrificial agent protecting transition metal oxides catalysts from SO₂ [25]. Chen et al. [30] found the MnₓCo₃₋ₓO₄ catalyst exhibited decent SO₂ tolerance due to its hierarchically porous structure, abundant active sites and strong interaction between Mn and Co oxides.

Mn oxides, which were widely studied as low temperature NH₃-SCR catalysts, usually exhibited excellent NH₃-SCR activity for its unique redox ability whereas terrible SO₂ and H₂O tolerance [32–34]. It is noticed that no matter SO₂ poisoned Mn oxides catalyst via metal oxide sulfation or forming ammonium sulfates on catalysts surfaces, SO₂ was consumed from feed gas. The serious deactivation of Mn oxides catalysts in the presence of small amount of SO₂ indicated that Mn oxide was sensitive to SO₂. Therefore, it seems a promoting strategy to employ Mn oxides as deSOₓ materials to protect SCR catalysts from SO₂. In this work, composite catalytic systems (CC systems) including Mn oxides as deSOₓ catalyst, γ-Al₂O₃ as a buffer layer, and NH₃-SCR catalyst was designed and prepared. CC systems exhibited superb NH₃-SCR performance in the presence of SO₂ and H₂O. The deSOₓ mechanism of Mn oxides in the co-existence of SO₂ and H₂O was investigated. SO₂ can be oxidized to SO₃ on Mn oxides surface. The oxidized SO₃ could further react with Mn oxides forming MnSO₄ or desorb from Mn oxides flowing away through feed gas. The flowing away SO₃ reacted with NH₃ and H₂O and deposited as NH₄HSO₄ which inhibited the formation of MnSO₄. When H₂O and NH₃ were excessive, SO₃ could completely transform to NH₄HSO₄ moving away from the feed gas, whereas Mn oxides were not consumed. Thus, Mn oxides played a role of deSOₓ catalyst and provided a non-SO₂ atmosphere for NH₃-SCR catalysts, which resulted in superb NH₃-SCR performance in the presence of SO₂ and H₂O. This work provided promoting strategy to design NH₃-SCR catalyst with SO₂ and H₂O resistance.

2. Experimental section

2.1. Materials

Mn oxides and γ-Al₂O₃ were purchased from Aladdin, and were used without further purifying.
Table 1: NH₃-SCR performances of representative catalysts in the presence of SO₂ and H₂O.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalysts</th>
<th>Reaction condition</th>
<th>NH₃-SCR performance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ni-Mn-Ti composite oxides</td>
<td>240 °C, GHSV = 40,000 h⁻¹, H₂O</td>
<td>NO conversion reduced to 80% within 15 h</td>
</tr>
<tr>
<td>2</td>
<td>Mn-Ce/CeSAPO-34</td>
<td>180 °C, GHSV = 40,000 h⁻¹, H₂O</td>
<td>NO conversion reduced to 80% within 20 h</td>
</tr>
<tr>
<td>3</td>
<td>MnFe₀.₁Oₓ nanorods</td>
<td>250 °C, GHSV = 28,000 h⁻¹, N₂</td>
<td>NO conversion reduced to 60% within 20 h</td>
</tr>
<tr>
<td>4</td>
<td>Cu₂Mn₀.₅Al₀.₅Oₓ</td>
<td>150 °C, GHSV = 80,000 h⁻¹, H₂O</td>
<td>NO conversion reduced to 90% within 15 h</td>
</tr>
<tr>
<td>5</td>
<td>Sm-Mn composite oxides</td>
<td>100 °C, GHSV = 49,000 h⁻¹, H₂O</td>
<td>NO conversion maintained over 95% for 72 h</td>
</tr>
</tbody>
</table>

a MnOₓ/CeO₂ catalysts synthesized in oxalic acid solution.

b V₂O₅-decorated Mn-Fe composite oxides supported on attapulgite.

designed as Scheme 1b. Along the direction of feed gas flow, 4 γ-Al₂O₃ beds located after Mn oxides bed. Each γ-Al₂O₃ bed was 1 cm thick, and was separated by silica wool. When the "flowing away" sulfur species reacted with NH₃, it would transform to ammonium salt captured on γ-Al₂O₃ bed, which could conversely be used to investigate the "flowing away" sulfur species.

2.2. Design of composite catalytic systems

The designed CC systems have 3 parts as showed in Scheme 1a. Mn oxides were employed as deSox catalyst located in the 1st part of CC systems. γ-Al₂O₃ buffer layer (0.2 g) as 2nd part, and the low temperature NH₃-SCR (0.2 g) catalyst as 3rd part were put after Mn oxides, respectively.

2.3. Preparation of catalysts used as the 3rd part of composite catalytic systems

Mn-Ti oxide catalyst was synthesized via hydrothermal method. Mn (Ac)₂-H₂O (1.00 g), ethyl alcohol (28 mL), and tetrabutyl titanate (5 mL) were mixed and stirred for 30 min. The obtained clear solution was transferred into a Teflon-lined autoclave and heated at 180 °C for 24 h. The resulting powders were centrifuged at 10,000 rpm for 10 min, washed twice with deionized water and twice with ethanol. The black powders were obtained by drying at 80 °C over night, following by calcining at 450 °C for 3 h under air, where the heating rate was 10 °C/min. The synthesized Mn-Ti oxide catalyst was denoted as Mn-Ti.

Mn-Ce and Mn-Fe oxide catalysts were prepared by coprecipitation method. Mn(AC)₂-H₂O (1.00 g) and Ce(NO₃)₃·9H₂O (5.31 g, for Mn-Ce oxide catalyst) or Fe(NO₃)₃·9H₂O (4.95 g, for Mn-Fe oxide catalyst) were dissolved in 100 ml deionized water, and the solutions were stirred for 30 min. Adding ammonium hydroxide dropwise under vigorous stirring until pH = 7. Keep stir for 24 h, and the turbid solution was filtered and washed by deionized water for 3 times. The obtained powders were dried at 80 °C in oven over night, following by calcining at 450 °C for 3 h under air, where the heating rate was 10 °C/min. The synthesized Mn-Ce and Mn-Fe oxide catalyst was denoted as Mn-Ce and Mn-Fe, respectively.

2.4. NH₃-SCR tests in the presence of SO₂ and H₂O

The NH₃-SCR activity tests were performed in a fixed-bed reactor with 0.2 g metal oxide catalyst or CC systems with 0.2 g NH₃-SCR catalyst. CC systems containing different catalysts were denoted as CC-X, where X represented abbreviation of certain NH₃-SCR catalysts. The feed gas contained 500 ppm NO, 600 ppm NH₃, 5 vol.% O₂, 100 ppm SO₂, 5 vol.% H₂O with N₂ as the balance gas. The total flow rate of the feed gas was 100 ml/min, corresponding to a space velocity approximately 30,000 h⁻¹. Including SO₂, NO, NH₃, NO₂, and N₂O, the effluent gases were continuously analyzed at 160 °C by an online Thermofisher IS10 FTIR spectrometer equipped with a 2 m path-length gas cell (250 ml volume).

2.5. SO₂ break-through experiments

The SO₂ break-through experiments were investigated in a fixed-bed reactor with 0.2 g Mn oxides. The feed gas contained 500 ppm NH₃ (when used), 5 vol.% O₂ (when used), 5 vol.% H₂O (when used), and 15 ppm SO₂, with N₂ as the balance gas. The total flow rate of the feed gas was 100 ml/min, corresponding to a space velocity approximately 30,000 h⁻¹. The concentrations of SO₂ were continuously analyzed at 160 °C by an online Thermofisher IS10 FTIR spectrometer equipped with a 2 m path-length gas cell (250 ml volume).

2.6. Capture of "flowing away" sulfur species

Because of the acidity of sulfur oxide, NH₃ was employed to capture the "flowing away" sulfur species, and the experimental facility was designed as Scheme 1b. Along the direction of feed gas flow, 4 γ-Al₂O₃ beds located after Mn oxides bed. Each γ-Al₂O₃ bed was 1 cm thick, and was separated by silica wool. When the "flowing away" sulfur species reacted with NH₃, it would transform to ammonium salt captured on γ-Al₂O₃ bed, which could conversely be used to investigate the "flowing away" sulfur species.
away sulfur species.

2.7. Characterizations

X-ray powder diffraction (XRD) data were collected on a XRD-6000 X-ray diffractometer (Shimadzu) with Cu Kα radiation (λ = 0.15418 nm). N2 adsorption–desorption measurements were conducted on an ASAP2020 physical adsorption instrument (Micromeritics) at liquid N2 temperature (−196 °C). The element contents were tested by X-ray fluorescence spectrometry (XRF), which was collected on an ARL-9800 instrument.

The total converted SO2 was calculated by the integral of the SO2 breakthrough curves.

The mass of SO2 located on Mn oxides as MnSO4 was obtained via inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis. For the solubility of MnSO4, the Mn oxides samples treated by SO2 were washed by deionized water. The eluate were collected and diluted with deionized water to 50 mL. The concentration of Mn2+ in eluate was obtained via ICP analysis on an Optima 5300DV inductively coupled plasma-atomic emission spectrometer. The mass of SO2 participated in Mn oxide sulfating process was calculated as bellow.

\[ n(\text{SO}_2) = n(\text{MnSO}_4) = n(\text{Mn}^{2+}) \]

\[ m(\text{SO}_2) = m(\text{Mn}^{2+})/M(\text{Mn}) \times V \times M(\text{SO}_2) \]

Where \( n \) is the mole number of different materials. \( m(\text{SO}_2) \) is the mass of SO2 participating in Mn oxide sulfating process. \( m(\text{Mn}^{2+}) \) is the mass concentration of Mn2+, which could be obtained by ICP-AES analysis. \( V \) is the volume of diluted eluate. \( M(\text{Mn}) \) and \( M(\text{SO}_2) \) are molar mass of Mn and SO2, respectively.

X-ray photoelectron spectroscopy (XPS) and fourier transform infrared spectroscopy (FT-IR) analyses were employed to investigate the surface species on Mn oxides and γ-Al2O3 beds after treatments in different atmosphere. XPS analyses were performed on a PHI 5000 VersaProbe spectrophotometer with Al Kα radiation. Binding energies were calibrated by using the containment carbon (C1s = 284.8 eV).

FT-IR analyses were carried out on a NICOLET NEXUS870 FTIR spectrometric analyzer using KBr pellets.

3. Results and discussion

3.1. NH3-SCR performance in the presence of SO2 and H2O

Owing to serious SO2 poisoning effect in the presence of SO2 and H2O, Mn oxides were expected to have deSOx ability in NH3-SCR atmosphere. Here a CC system employing Mn oxides as deSOx instrument to protect NH3-SCR catalysts located after Mn oxides from SO2 (Scheme 1a) has been designed. Mn-Ti, Mn-Fe, and Mn-Ce catalysts were used as the third part of the CC systems, and the NH3-SCR performances in the presence of SO2 and H2O were represented in Fig. 1a. The NO
provide a non-SO2 environment for NH3-SCR catalysts. Therefore, CC system has exhibited a general strategy for enhancing low-temperature NH3-SCR performances in the presence of SO2 and H2O.

3.2. Properties of catalysts before and after NH3-SCR test

Catalysts properties before and after NH3-SCR test in the presence of SO2 and H2O were investigated by XRD and BET analysis. According to the XRD result (Figure S1a), XRD peaks contributing to Akhtenskite phase MnO2 (30-0820) and Ramsdellite phase MnO2 (39-0375) were observed, which indicated that Mn oxides we used was a mixture of Akhtenskite phase and Ramsdellite phase. After the SO2 and H2O tolerance test, the used Mn oxides exhibited no phase change than the fresh one. As showed in Table S1, the results of BET analysis showed that Mn oxides had a low surface area of 30 m²/g, and the surface area of the used Mn oxides slightly decreased to 26 m²/g. It was indicated that Mn oxides maintained unchanged during the SO2 and H2O tolerance test.

In addition, in order to further understand the nature of the catalyst used in the 3rd part of CC systems, XRD, BET, and XRF analysis of Mn-Ti, Mn-Fe, Mn-Ce catalysts were carried out. As showed in Figure S1, XRD peaks of anatase TiO2 (Figure S1b), Hematite and Fe3O4 (Figure S1c), and CeO2 (Figure S1d) were detected in XRD patterns of Mn-Ti, Mn-Fe, Mn-Ce catalysts, respectively. Catalysts after SO2 and H2O tolerance test exhibited same XRD patterns with the fresh catalysts. BET and XRF results of Mn-Ti, Mn-Fe, Mn-Ce catalysts were listed in Table S1. Fresh and used catalysts exhibited similar surface areas and element contents. Considering the maintained high NH3-SCR performances in SO2 and H2O tolerance test, it was believed that Mn-Ti, Mn-Fe, Mn-Ce catalysts located in the 3rd part of CC system were protected from SO2 poisoning by MnOx bed and Al2O3 bed.

3.3. The role of O2 in deSOx process

The reaction behavior between SO2 and Mn oxides under certain atmosphere was investigated in order to understand the deSOx process on Mn oxides bed. Firstly, O2 was introduced, and the SO2 absorption results were represented in Fig. 2a. In the absence of O2, SO2 broke through Mn oxides bed after it was introduced into the feed gas for 2 h, and saturated absorbed on Mn oxides at 6 h with absorption capacity of 0.013 mg. With the assistance of O2, the breakthrough point of SO2 on Mn oxides prolonged to 4.5 h, the absorption capacity of SO2 on Mn oxides increased to 0.027 mg. It is demonstrated that the presence of O2 is beneficial to the SO2 capture on Mn oxides. The product of SO2 captured on Mn oxides was studied via XPS analysis. In the Mn2p spectra of fresh Mn oxides (Fig. 2c), the Mn2p3/2 peak was divided to two peaks at 641.33 and 642.85 eV, which contributed to Mn3+ and Mn4+ ions, respectively [35]. It is indicated that both Mn(III) and Mn(IV) oxide existed on the surface of fresh Mn oxides. When Mn oxides sample was treated by SO2, a new peak at 645.02 eV appeared in Mn2p spectra, belonging to MnSO4 [35], which illustrated that SO2 was oxidized by Mn oxides.

Interestingly, when O2 was introduced into feed gas, the kinds of Mn species and S species on the treated Mn oxides surface consisted with that in the absence of O2, whereas the content of Mn3+ ions increased (Table 2). O2 hardly influenced the kind of reaction product between SO2 and Mn oxides, yet could be beneficial to the oxidation of Mn species. According to Fig. 2b, the mass of SO2 located on Mn oxides as...
MnSO₄ was lower than the total SO₂ consumption. It is indicated that a part of sulfur species flowed away with feed gas flow, instead of being captured by Mn oxides as MnSO₄. It is reasonable to deduce that SO₂ could be oxidized to SO₃ intermediate on the surface of Mn oxides, for the oxidation ability of Mn oxides. The generated SO₃ can either flow away through feed gas or react with Mn oxides forming MnSO₄. Thus a possible mechanism was provided (Scheme 2a). Where SO₃(a) represents SO₃ absorbed on Mn oxides surface, and SO₃(g) represents SO₃ in the gas phase.

\[
\begin{align*}
Mn(III) + O &\rightarrow Mn(II) + SO₃(a) \\
Mn(IV) + O &\rightarrow Mn(IV) + SO₃(g) \\
SO₃(a) + O &\rightarrow SO₃(g)
\end{align*}
\]

The absorbed SO₂ can be oxidized by Mn oxides, transforming to SO₃ absorbed on Mn oxides surface (Eqs. (1) and (2)). In the meanwhile, Mn species with high valence state on the surface of Mn oxides were reduced to Mn(II) species. The absorbed SO₃ can further react with Mn(II) species, producing MnSO₄ (Eq. (3)). The absorbed SO₃ can also desorb and flow away with feed gas flow (Eq. (4)). O₂ did not participate in the sulfating process, hence the kind of sulfating products is independent on O₂. However, Mn(II) species is unstable and can be oxidized to high valence state by O₂ (Eqs. (5) and (6)). The regenerated Mn species can react with SO₂ through Eqs. (1) and (2) again, resulting in the increasing capacity of SO₂ on Mn oxides.

**Table 3**

<table>
<thead>
<tr>
<th>Distance between Mn oxides and γ-Al₂O₃ beds</th>
<th>Feed gas containing SO₂, NH₃, and O₂</th>
<th>Feed gas containing SO₂, NH₃, O₂, and H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 cm</td>
<td>S(%) 2.57 N(%) 2.68</td>
<td>S(%) 1.00 N(%) 1.08</td>
</tr>
<tr>
<td>2 cm</td>
<td>S(%) 2.08 N(%) 2.13</td>
<td>S(%) 0 N(%) 0</td>
</tr>
<tr>
<td>3 cm</td>
<td>S(%) 1.52 N(%) 1.62</td>
<td>S(%) 0 N(%) 0</td>
</tr>
<tr>
<td>4 cm</td>
<td>S(%) 0.67 N(%) 0.73</td>
<td>S(%) 0 N(%) 0</td>
</tr>
</tbody>
</table>

MnSO₄ was lower than the total SO₂ consumption. It is indicated that a part of sulfur species flowed away with feed gas flow, instead of being captured by Mn oxides as MnSO₄. It is reasonable to deduce that SO₂ could be oxidized to SO₃ intermediate on the surface of Mn oxides, for the oxidation ability of Mn oxides. The generated SO₃ can either flow away through feed gas or react with Mn oxides forming MnSO₄. Thus a possible mechanism was provided (Scheme 2a). Where SO₃(a) represents SO₃ absorbed on Mn oxides surface, and SO₃(g) represents SO₃ in the gas phase.

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**3.4. The role of NH₃ in deSOₓ process**

It is noted that though O₂ was beneficial to SO₂ transforming, the rapid SO₂ breaking-through on Mn oxides (Fig. 2a) is definitely inconsistent with the excellent deSOₓ ability of Mn oxides in the presence of NH₃ and H₂O (Fig. 1b). To further simulate the actual atmosphere where NH₃-SCR catalysts worked, deSOₓ ability of Mn oxides in the presence of NH₃ was investigated. As illustrated in Fig. 3a, when NH₃ was introduced into the feed gas, the break-through time of SO₂ was dramatically delayed and the SO₂ conversion on Mn oxides kept near 100% within 24 h, which demonstrated that NH₃ in feed gas is beneficial to deSOₓ process on Mn oxides. Interestingly, according to the SO₂ consumption results showed in Fig. 3b, total SO₂ consumption on Mn oxides in the presence of NH₃ exceeded that in the absence of NH₃, whereas the amount of SO₂ forming MnSO₄ was greatly decreased after NH₃ addition. It is indicated that NH₃ inhibited the sulfating of Mn oxides. However, the mass of sulfur oxides flowing away from Mn oxides was believed to increase in the presence of NH₃, which resulted
in enhanced deSOx ability of Mn oxides. For the acidity of sulfur oxides and the alkalinity of NH3, it is inferred that there is neutralization reaction between them (Eq. (7)), which accelerated the desorption of SO3 (Eq. (4)) and thus promoted the oxidation of SO2 on Mn oxides (Eqs. (1) and (2)) by consuming the products. Hence, the deSOx ability of Mn oxides in the presence of NH3 was enhanced. Besides, the accelerating effect of Eq. (4) inhibited its competing reaction (Eq. (3)), leading to the decrease of MnSO4 formation. To ensure this speculation, as illustrated in Scheme 1b, γ-Al2O3 beds was located after Mn oxides bed to accept the products generated from the reaction between NH3 and sulfur oxides. XPS and FT-IR analyses were employed to identify the deposit on γ-Al2O3 beds. As displayed in Fig. 3c, the XPS spectra of γ-Al2O3 exhibited 2 fined peaks centered at 169.7 eV and 168.5 eV, which belonged to S2p1/2 and S2p3/2 peaks of sulfate species [35]. No peak of impurity was detected in S2p spectra of γ-Al2O3 located at different distances to Mn oxides bed. For N1s spectra of γ-Al2O3 (Fig. 3d), peaks contributed to NH4+ were observed at 401.3 eV [35]. For the similar contents of N and S elements on γ-Al2O3 surface listed in Table 3, it was believed that the deposit on γ-Al2O3 was mainly formed by NH4HSO4. In FT-IR results (Figure S2), peaks at 3400 cm−1 (O–H groups) [36,37], 1634 cm−1 (NH3) [36,37], 1406 cm−1 (NH+4) [36,37], 1125 cm−1 (SO42−) [38] were detected in spectra of γ-Al2O3, which further confirmed the formation of NH4HSO4 on γ-Al2O3. In the presence of SO2 and NH3, NH4HSO4 could be formed and deposited on the surface of Mn oxide, which was a widely accepted SO2 poisoning pathway of Mn based NH3-SCR catalysts according to literature [15,39,40]. For the unstability of ammonium salt, it seems possible that NH4HSO4 on Mn oxides sublimated and condensed on γ-Al2O3 bed. To confirm the original source of NH4HSO4 detected on γ-Al2O3 bed, pure NH4HSO4 was treated under N2 flow at 160 °C, and γ-Al2O3 after NH4HSO4 bed was analyzed by XPS. As showed in Figure S3, there was no peaks of S and N species detected in the XPS spectra of γ-Al2O3 after NH4HSO4 bed, demonstrating the stability of NH4HSO4 at 160 °C. Hence, it was believed that the NH4HSO4 located on γ-Al2O3 after Mn oxides bed was completely from the flowing away sulfur species and NH3 in feed gas. It was evidently pointed that NH3 could react with the flowing away sulfur species to form NH4HSO4 deposit, and the flowing away sulfur species is SO3, which further confirmed the SO3 desorption in Eq. (4). Thus, a possible mechanism of SO2 reacting with Mn oxides in the presence of NH3 was provided (Scheme 2b). NH3 could react with the flowing away SO3 and H2O in environment (Eq. (7)), which decreased the SO3 concentration in air. The decrease of product concentration resulted in more absorbed SO3 desorbing through Eq. (4), and thus more SO2 was oxidized to SO3 on Mn oxides (Eqs. (1),(2)). Therefore, NH3 is beneficial to SO2 conversion on Mn oxides. Besides, formation of MnSO4 (Eq. (3)) and desorption of SO3 (Eq. (4)) are two competing reactions. When NH3 was introduced, the increasing SO3 desorption restrained the Mn oxide sulfiting process.

\[ \text{NH}_3 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4 \]  

(7)

3.5. The role of H2O in deSOx process

H2O, which has negative effect on NH3-SCR catalysts, usually exist in exhaust gas of stationary sources. The effect of H2O was investigated to further understand the de-SOx behavior of Mn oxides in the actual atmosphere. As showed in Fig. 4a, when 5% H2O was injected into the feed gas, the SO2 concentration kept near 0% for 24 h, which presented that H2O was beneficial to SO2 conversion on Mn oxides. The mass of formed MnSO4 in the presence of H2O surpasses that in the absence of H2O (Fig. 4b). It is widely accepted that SO3 can react with H2O forming H2SO4 with strong corrosivity to metal oxide (Eq. (8)), which improved the sulfiting process of Mn oxides.

\[ \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 \]  

(8)

With the addition of NH3 (Fig. 5a), the SO2 concentration after Mn oxides bed still kept near 0 ppm for 24 h, whereas MnSO4 never generated (Fig. 5b). NH3 and H2O are necessary reactants for NH4HSO4 formation (Eq. (7)). Therefore, it is reasonable to infer that when NH3 and H2O are both excessive, the transformation from SO3 to NH4HSO4 through Eq. (7) can operate completely. This conjecture was supported by FT-IR (Figure S4) and XPS (Fig. 5c and d) results. In the FT-IR spectrum of the first γ-Al2O3 bed after Mn oxides, peaks at 3400 cm−1 (O–H groups) [36,37], 1634 cm−1 (NH3) [36,37], 1406 cm−1 (NH+4) [36,37], 1125 cm−1 (SO42−) [38] were detected, indicating NH4HSO4 depositing on the first γ-Al2O3 bed. However, IR peak at 1125 cm−1 disappeared in the FT-IR spectra of other γ-Al2O3 beds, which evidently pointed that there were no sulfate species on other γ-Al2O3 beds except the first one. This deduction was also supported by XPS results. Sulfate species (169.7 eV and 168.5 eV) and NH4+ (401.0 eV) [35] were detected in S2p and N1s spectra of the first γ-Al2O3 bed after Mn oxides bed (Fig. 5c and d). No XPS peaks of S and N elements were observed in XPS spectra of other γ-Al2O3 bed located more far away from Mn oxides bed. According to the surface elements contents listed in Table 3, there is more N element on the surface of Mn oxides in SO2 + O2 + H2O + NH3 than that in SO2 + O2 + NH3. It is believed that, as illustrated in Scheme 2c, the transformation from SO3 to NH4HSO4 was accelerated.

Fig. 4. When NH3 was excluded from feed gas, (a) break-through curves of SO2 on Mn oxides in the presence and the absence of H2O, and (b) contents of total SO2 and SO4 located on Mn oxides as MnSO4.
by excessive NH3 and H2O, leading to an increasing amount of NH4HSO4 depositing on Mn oxides. And this reaction operated so fast that the flowing away SO3 totally deposited as NH4HSO4 before the feed gas flow through the first γ-Al2O3 bed after Mn oxides bed.

It is extensively acknowledged that NH3 can react with MnSO4 aqueous, forming Mn hydroxide sediment (Eq. (9)). To confirm whether this aqueous reaction could occur in gas-solid interface, pure MnSO4 was treated under NH3 + H2O + O2 flow at 160 °C for 6 h. The treated MnSO4 and fresh Mn oxides were analyzed via XPS analysis, and the results were displayed in Fig. 6. In the O1s spectra of Mn oxides, the O1s peak could be fitted as the overlay of two peaks at 529.9 eV (surface OH groups) [35] and 531.6 eV (lattice oxygen) [35]; whereas in that of MnSO4 treated by NH3 and H2O, the O1s peak was divided as an increasing peak at 529.9 eV (surface OH groups), a decreasing peak at 531.6 eV (lattice oxygen), and a new appearing peak at 532.7 eV (SO42−) [35], comparing with that of Mn oxides. According to the relative contents of surface oxygen species listed in Table 4, the surface oxygen species of treated MnSO4 was formed by dominant amount of surface OH groups, small amount of lattice oxygen and SO42−, which indicated the formation of hydroxides on MnSO4 surface. The Mn2p3/2 peak of Mn oxides could be divided as two peaks centered at 641.3 and 642.8 eV, belonging to Mn3+ and Mn4+ in Mn oxides, respectively [35]. In the spectra of MnSO4 treated by NH3 and H2O, the Mn2p3/2 peak was divided as two main peaks at 641.3 and 642.8 eV contributing to Mn3+ and Mn4+ in Mn oxides, respectively [35]. As shown in Table 4, Mn oxides or hydroxides are the main Mn species on the treated MnSO4 sample, which indicated that MnSO4 could react with NH3 and H2O forming sediment (Eq. (9)). The values of Mn ions on the surface of the treated MnSO4 sample were +3 (major) and +4 (minor), rather than +2, which indicated Mn species were oxidized during the treatment (Eq. (10)). The transformation from MnSO4 to Mn hydroxide during the treatment of NH3 and H2O (Eqs. (9) and (10)) consumed the formed MnSO4 through Eq. (4), which caused the non-occurrence of Mn oxides sulfating in the presence of NH3 and H2O (Scheme 2c).

\[
\text{MnSO}_4 + \text{NH}_4 + 2\text{H}_2\text{O} \rightarrow \text{Mn(II) hydroxide} + \text{NH}_4\text{HSO}_4
\]

(9)

\[
\text{Mn(II) hydroxide} + \text{O}_2 \rightarrow \text{Mn(III, IV) hydroxide}
\]

(10)

Furthermore, the SO2 transforming ability of the Mn hydroxide sediment in the co-existence of SO2 and H2O was investigated and the result was displayed in Figure S5. The sediment exhibited excellent SO2 transforming ability as Mn oxides for 24 h, which indicated the sediment can play the same role as Mn oxides.

3.6. DeSOx mechanism of Mn oxides in composite catalytic systems

The possible deSOx mechanism of Mn oxides in the presence of NH3 and H2O was showed in Fig. 7. SO2 could be oxidized to absorbed SO3 by the high valence state Mn species on the surface of Mn oxides (Eqs. (1) and (2)). Simultaneously, Mn oxides lost lattice oxygen and were reduced. The lost lattice oxygen could be supplied by O2 in air (Eqs. (5) and (6)). Destiny of absorbed SO3 had divergences. One part of absorbed SO3 desorbed from Mn oxides surface and flowed away with feed gas (Eq. (4)). The flowing away SO3 could further react with NH3 and H2O in air, generating NH4HSO4 and depositing from the gas phase (Eq. (7)). Another part of absorbed SO3 entered Mn oxides lattice forming MnSO4 (Eq. (3)). This reaction was accelerated in the presence of H2O (Eq. (8)), whereas decelerated via NH3 for the generation of NH4HSO4 (Eq. (7)). The formed MnSO4 reacted with NH3 and H2O in
feed gas forming Mn(II) hydroxide sediment as it occurred in aqueous solution (Eq. (9)). Mn(II) hydroxide was unstable in air, and could be further oxidized to Mn hydroxide with high valence state by O$_2$ (Eq. (10)). The oxidized Mn hydroxide exhibited the same behavior as Mn oxides in NH$_3$ + H$_2$O + O$_2$ + SO$_2$ atmosphere, which represented the completing of the Mn species transforming cycle under NH$_3$-SCR atmosphere in the presence of SO$_2$ and H$_2$O.

As the first part of the CC systems, Mn oxides play the role of catalyst for SO$_2$ oxidation. The oxidized SO$_3$ further react with NH$_3$ and H$_2$O in feed gas depositing as NH$_4$HSO$_4$. Due to SO$_3$ desorbing from Mn oxides, NH$_4$HSO$_4$ can deposit on not only the Mn oxides but also the tailing buffer layer. The buffer layer can be any stable material with a large surface area for NH$_4$HSO$_4$ capacity. In this work, γ-Al$_2$O$_3$ was employed as a buffer layer. After the deSOx process in the former two parts of CC systems, SO$_2$ was completely removed from the feed gas, hence NH$_3$-SCR catalysts could work in a non-SO$_2$ environment and maintain their inherent catalytic activity, which makes CC systems a general strategy for enhancing the SO$_2$ and H$_2$O tolerances of low-temperature NH$_3$-SCR catalysts.

### 4. Conclusions

In this work, CC systems including Mn oxides as deSOx catalyst, γ-Al$_2$O$_3$ as a buffer layer, and NH$_3$-SCR catalyst was designed and prepared. CC systems exhibited excellent NH$_3$-SCR performance in presence of SO$_2$ and H$_2$O. The deSOx mechanism of Mn oxides in CC systems was clearly revealed. SO$_2$ could be oxidized to SO$_3$ on Mn oxides surface. A part of SO$_3$ entered into Mn oxides lattice forming MnSO$_4$, which could be accelerated by H$_2$O whereas decelerated by NH$_3$. The other part of SO$_3$ desorbed from Mn oxides surface and formed NH$_4$HSO$_4$ deposit with NH$_3$ and H$_2$O in feed gas. When NH$_3$ and H$_2$O were excessive, SO$_3$ could be completely removed as NH$_4$HSO$_4$ and Mn oxides itself was not consumed. Therefore, Mn oxides could be used as

**Fig. 6.** XPS results of Mn2p (a) and O1s (b) over fresh Mn oxides and MnSO$_4$ treated by NH$_3$ and H$_2$O at 160 °C for 6 h.

| Surface species contents of Mn oxides and MnSO$_4$ treated by NH$_3$ and H$_2$O according to XPS results. |
|------------------|------------------|
|                  | Fresh Mn oxides  | MnSO$_4$ treated by NH$_3$ and H$_2$O |
| Peak areas of surface Mn species | Mn$^{3+}$ in metal oxide | 8151 | 8585 |
|                  | Mn$^{4+}$ in metal oxide | 6107 | 6025 |
|                  | Mn$^{2+}$ in sulfate | – | 2444 |
|                  | High valence state Mn in sulfate | – | 641 |
| Contents of surface Mn species (%) | Mn$^{3+}$ in metal oxide | 57.13 | 48.52 |
|                  | Mn$^{4+}$ in metal oxide | 42.83 | 34.05 |
| Peak areas of surface O species | Lattice oxygen | 8653 | 2384 |
|                  | Surface OH groups | 1909 | 23491 |
|                  | Sulfate | – | 8158 |
| Contents of surface O species (%) | Lattice oxygen | 81.92 | 7.00 |
|                  | Surface OH groups | 18.08 | 69.02 |
The formation of NH4HSO4 occurred in feed gas flow, which resulted in NH4HSO4 depositing in places beyond Mn oxides through feed gas flow. A-Al2O3 buffer layer is necessary to capture all the NH4HSO4. Owing to the non-SO2 atmosphere after Mn oxides and A-Al2O3 buffer layer, NH3-SCR catalyst can be protected from SO2 poisoning. This work provided a general catalytic desOx method utilizing NH3 and H2O which usually existed in exhaust gas from stationary sources, successfully designed and synthesized CC systems as a general strategy for enhancing the SO2 and H2O tolerance of low-temperature NH3-SCR catalysts.

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Appendix A. Supplementary data

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References


