Improvement of SO$_2$ Resistance of Low-Temperature Mn-Based Denitration Catalysts by Fe Doping

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ABSTRACT: The influence of vapor and SO$_2$ in coal firing flue gas on the selective catalytic reduction activity of Mn/γ-Al$_2$O$_3$ and Mn–Fe/γ-Al$_2$O$_3$ catalysts was investigated at 150–275 °C. Denitration experiments and detailed characterization of catalysts were conducted. Vapor had no chemical effects on denitration, and the mechanism of SO$_2$ deactivating the Mn/γ-Al$_2$O$_3$ catalysts was investigated in detail. This is due to the reaction between MnO$_2$ and SO$_2$ and the ammonium sulfate deposits forming on the surface. Sulfation of the Mn-active component was significantly reduced by doping the Mn/γ-Al$_2$O$_3$ catalyst with Fe. Iron doping also lowered the stability of the ammonium sulfate surface deposits, forcing them to rapidly decompose. Thus, iron doping significantly improved SO$_2$ resistance and the denitration efficiency of Mn–Fe/γ-Al$_2$O$_3$ catalysts was not clearly decreased.

1. INTRODUCTION

Gas emissions from industries related to power production, steel and nonferrous metals metallurgy, building materials, petrochemical, and so forth, are the main sources of nitrogen oxides (NO$_x$), which can cause severe human poisoning and plant damage as well as photochemical pollution. Nitrogen oxides similar with sulfur oxides contribute to acid rains and cause acid corrosion damages. Therefore, nitrogen oxide emission is an environmental problem worldwide and now an emergency in China that needs to be solved. Selective catalytic reduction (SCR) technology is the current industrial denitration technology around the world, and it uses vanadium–tungsten–titanium catalysts. However, its operation temperature is ~350 °C, and it is active only upon contact with the hot flue gas. Therefore, the SCR reactor is usually placed behind the economizer, in front of the precipitator of high efficiency, and the flue gas desulphurization system; the alkaline metals from the dust and dust itself as well as heavy metals and SO$_2$-laden atmosphere poison and deactivate the catalyst, significantly reducing its service life. However, if the processing associated with denitration is placed after dedusting, the flue gas is the cleaner and the catalyst maintains longer life. However, in this case, the temperature of the flue gas is lower to about 160 °C, for the conventional SCR temperature window is 350–420 °C, new efficient SCR denitration catalysts suitable for the low temperature conditions are essential for these processes.

Currently, research on low-temperature SCR catalysts is mostly concentrated around transition metals (e.g., Cu, Fe, Cu, Ce). Catalysts based on manganese oxides also received a lot of attention because of their excellent low-temperature performance. However, activity of manganese oxide catalysts is easily affected by vapor and SO$_2$, which is often part of the flue gas even after it was dedusted and desulfurized after circulating fluidized bed combustion. Therefore, it is necessary to develop the sulfur-resistant and vapor-resistant Mn-based catalyst. Doping Mn-based catalysts with Fe is a way to improve the sulfur and vapor resistance of the Mn/γ-Al$_2$O$_3$ catalysts. The mechanisms of improving sulfur and vapor resistance by Fe addition are focused on in this paper.

2. EXPERIMENTAL SECTION

2.1. Catalyst Preparation. The Mn–Fe/γ-Al$_2$O$_3$ catalyst was prepared by a wet impregnation method using γ-Al$_2$O$_3$ as the carrier and MnO$_2$ and FeO$_x$ as active components. γ-Al$_2$O$_3$ powder was heated at 110 °C for 2 h to remove weakly adsorbed water, after which it was placed in a drying dish to cool and then sealed in a sample plastic bag for storage. We prepared four different catalysts using the procedures described below. Table 1 shows synthesis details.

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Table 1. Mn Amounts Used To Prepare the Mn/γ-Al2O3 Catalyst #1−#4

| catalyst numbers/Mn/γ-Al2O3 | 1 | 2 | 3 | 4 |
|-----------------------------|---|---|---|---|
| Mn/ mmol · g−1             | 0.2| 0.4| 0.8| 0.12|
| Mn(NO3)2/mL                | 12.1| 26.2| 38.3| 41.0|

“Amount of γ-Al2O3 used to prepare these catalysts was 120 g.

(1) Mn(NO3)2 solution (analytical grade, the mass fraction was 50%) was placed in a 1 L beaker, and 400 mL of deionized water was added under constant stirring.

(2) Four different amounts of Fe(NO3)3 · 9H2O (analytical grade) were placed in a beaker and dissolved in deionized water under constant stirring (see Table 2). These solutions were then used to prepare Mn−Fe/γ-Al2O3 catalysts.

Table 2. Initial Fe(NO3)3 · 9H2O Amounts Used To Prepare Catalysts #1−#4

| catalyst numbers/Mn−Fe/γ-Al2O3 | 1 | 2 | 3 | 4 |
|---------------------------------|---|---|---|---|
| Fe/ mmol · g−1                 | 0.02| 0.04| 0.06| 0.08|
| Fe(NO3)3 · 9H2O/g              | 1.25| 2.12| 3.29| 4.65|

“Amounts of Mn(NO3)2 and γ-Al2O3 used to prepare these catalysts were 38.3 mL and 120 g, respectively.

(3) γ-Al2O3 powder was placed into the above solution under constant stirring for 2 h, after which water was evaporated in a bath at 100 °C.

(4) After evaporation, products were additionally dried at 110 °C for 12 h and then calcined at 500 °C for 5 h. After cooling to room temperature, Mn−Fe/γ-Al2O3 powder catalysts were obtained.

(5) To prepare the pellets, the powders were mixed with clay and sesbania gum powder and then compacted using a press machine and dried at 110 °C for 12 h.

2.2. Characterization of the Catalytic Activity and Sulfur Resistance. The experimental setup system for low-temperature SCR denitration using Mn-based catalysts is shown in Figure 1. The gas used was from the coal-fired boiler tail flue. Catalyst pellets (3 mm in diameter and 3 mm long) were placed at around 100 mm height upstream in the distributor bed in a tube furnace (20 mm in diameter). Gas absorption and reduction reactions were performed in a fixed bed. The inlet flue gas flow rate was adjusted in such a way that the catalyst and the flue gas were in contact for ~1 s.

To compare the NOx removal performance and resistance of the catalysts to SO2, layers consisting of sodium lime and allochroic silica gel were used to absorb SO2 and to dry the flue gas prior to its contact with the catalyst first. The flue gas passing through enough soda lime was introduced into the flue gas analyzer, and if the SO2 concentration was not observed, the SO2 was completely removed, and then the allochroic silica gel was controlled and no color change at its top to ensure H2O was completely removed. Then, the soda lime and allochroic silica gel were shorting switch for the SO2-resistance experiments.

Gas flow rates were controlled by flow meters. Initial volume fractions of each component in the mixed flue gas were the following: 0.03% NO, 0.033% NH3, 6 v/v % vapor, 250 mg/m3 of SO2, and 6% O2 and N2 by balance. Gas superficial velocity was 6000−14 000 h−1, while the SCR catalyst layer height was varied corresponding to the 1 s contact time. At each temperature, NOx from the flue gas was absorbed by the catalyst and reacted with the active component. Gas composition before and after the contact with the catalysts were analyzed using the flue gas analyzer. The vapor content in the flue gas was measured by a humidor of EXTECH-RH101. Then, the NOx removal efficiency (ηNOx) was calculated using the following formula 1

$$\eta_{NOX} = \frac{c_{NOx,in} - c_{NOx,out}}{c_{NOx,in}} \times 100\%$$

(1)

$c_{NOx,in}$: the volume concentration of NOX at the inlet of the flue gas; $c_{NOx,out}$: the volume concentration of NOX at the outlet of the flue gas.

2.3. Characterization. The as-prepared catalyst (1 g) was ground up to 200-mesh particles for further X-ray diffraction (XRD) analysis, which was performed by an Ultima IV X-ray diffractometer (Japan) using Cu Kα radiation at 40 kV and 40 mA with 2°/min scanning speed over the 10−80° 2θ range.

Sample morphology was analyzed using a JEOL JSM-6390LV scanning electron microscope. The specific surface area was determined using Quantachrome Autosorb iQ3 (USA).

3. RESULTS AND DISCUSSION

3.1. Denitration Performance of Mn/γ-Al2O3 and Mn−Fe/γ-Al2O3 Catalysts. Results of denitration experiments obtained using Mn/γ-Al2O3 catalysts with different loadings of Mn/γ-Al2O3 and Mn−Fe/γ-Al2O3 catalysts with different Fe additions are shown in Figures 2 and 3, respectively.

The popular reaction mechanism of the NH3 reaction with NOx under the action of catalyst follows the E−R or L−H mechanism, as described by the following reactions.

The E−R model

$$NH_3(g) \rightarrow NH_3(ad) \quad (over \ Lewis \ acid \ sites)$$

Figure 1. Schematics of the flue gas denitrification setup.
O(g) → 2O(ad)

NH(ad) + O(ad) → NH₂(ad) + OH(ad)

NH₂(ad) + NO(g) → NH₂NO(ad) → N₂(g) + H₂O

After NH₃ was adsorbed on the Lewis acid sites of the Mn catalyst, it was easily oxidized to NH₂(ad) and OH(ad) by the O(ad). NH₂(ad) reacted with NO to form an intermediate product NH₂NO(ad), which was finally decomposed into N₂ and H₂O.

The L–H model

O(g) → 2O(ad)

NO(g) + O(ad) → NO₂(ad)

NH₃(g) → NH₂(ad)

NO₂(ad) + NH₂(ad) + H⁺ → NH₄NO₂

NH₄NO₂ → NH₂NO(ad) + H₂O(g) → N₂(g) + H₂O

Unlike the E–R model, NO was first oxidized to NO₂(ad) by O(ad) and then reacted with NH₃(ad) and H⁺ to form NH₄NO₂(ad), which was reduced to NH₃NO(ad) and then to nitrogen. For there was a large quantity of oxygen in flue gas, O₂(g) absorption was easily in advance of NO(g) and NH₃(g) to form the chemical adsorption oxygen. Therefore, the L–H mechanism was more corresponding to the denitration reaction in the low-temperature flue gas.

Denitration efficiency of Mn/γ-Al₂O₃ series of the catalyst reached 84% at ~175 °C (see Figure 2). When Fe was added to the catalyst, NO₃ denitration efficiency reached 93% at ~150 °C (see Figure 3), and it is similar to the DeNOₓ efficiency of the complex catalyst of Ce–Cu–V₂O₅/TiO₂ in the flue gas temperature range of 150–200 °C. Thus, Fe presence in the Mn/γ-Al₂O₃ catalysts significantly improved their SCR activity and lowered SCR temperature.

The most active low-temperature SCR catalysts were Mn-3/γ-Al₂O₃ and Mn–Fe-2/γ-Al₂O₃. Thus, these two catalysts were used for the consequent experiments and analyses.

3.2. Vapor and SO₂ Influence on SCR Activity of Mn/γ-Al₂O₃ and Mn–Fe/γ-Al₂O₃ Catalysts. The effect of vapor and SO₂ on the SCR activity of Mn-3/γ-Al₂O₃ and Mn–Fe-2/γ-Al₂O₃ catalysts is shown in Figure 4. Experiments were performed at 150 °C, 6 vt % vapor, and 250 mg/cm³ SO₂ concentration. For a more accurate comparison, the catalysts were prepared using the same amount of initial Mn(NO₃)₂ (see Tables 1 and 2), which were also the most efficient SCR low-temperature catalysts tested in this work. As shown in Figure 4, the vapor introduction in flue gas decreased the denitration efficiency, about 8% for the Mn–Fe-2/γ-Al₂O₃ catalyst and 10% for the Mn-3/γ-Al₂O₃ catalyst. After 10 h, the vapor supply was closed, and the denitration efficiency of these two catalysts were all recovered closely to the original performance. Therefore, the vapor adsorbed on catalysts caused competitive physical absorption against the NH₃ absorption over Lewis acid sites and prohibited the NH₂NO(ad) reduction.

However, the presence of SO₂ had a severe poisoning effect on NO₃ removal efficiency using the Mn-3/γ-Al₂O₃ catalyst: it
The catalyst was not purely physical adsorption. Rodlike crystals on the catalyst surface increased as the Fe amount was increased. Spherical crystals on the catalyst surface may improve upon Fe incorporation into the Mn−γ-Al2O3 catalysts. SEM micrographs of unmodified (a) Mn−3/γ-Al2O3 and (b) Mn−4/γ-Al2O3 as well as Fe-doped [(c) Mn−Fe−2/γ-Al2O3 and (d) Mn−Fe−4/γ-Al2O3] catalysts. Before the reaction with SO2-containing flue gas, Mn−3/γ-Al2O3 and Mn−Fe−2/γ-Al2O3 catalysts were evenly distributed (see Figure 6a,c). After the reaction with sulfur-containing flue gas, Mn−3/γ-Al2O3 and Mn−Fe−2/γ-Al2O3 catalysts were analyzed using SEM (see Figure 6).

Figure 6. SEM micrographs of unmodified [(a) Mn−3/γ-Al2O3 and (b) Mn−4/γ-Al2O3] as well as Fe-doped [(c) Mn−Fe−2/γ-Al2O3 and (d) Mn−Fe−4/γ-Al2O3] catalysts.

The mechanism of SO2−resistance improvement when Fe doping in the manganese catalyst was investigated by varied characterization means.

3.3. SO2 Influence on Physicochemical Properties of Mn/γ-Al2O3 and Mn−Fe/γ-Al2O3 Catalysts. 3.3.1. SEM Analysis. To understand the changes of catalyst efficiency and activity after Fe was introduced, Mn−3/γ-Al2O3 and Mn−Fe−2/γ-Al2O3 as well as Mn−4/γ-Al2O3 and Mn−Fe−4/γ-Al2O3 were analyzed using SEM (see Figure 6).

Two types of crystals were observed that were identified as spherical α-MnO2 and rodlike β-MnO2. Spherical α-MnO2 was observed in both Mn−3/γ-Al2O3 and Mn−Fe−2/γ-Al2O3, as well as Mn−4/γ-Al2O3 and Mn−Fe−4/γ-Al2O3. The dispersion of the spherical crystals on the catalyst surface may be improved upon Fe incorporation into the Mn/γ-Al2O3 catalysts. As the amount of added Fe increased, spherical crystals on the catalyst surface started to agglomerate and some fine rodlike crystals started to appear eventually becoming larger as the Fe amount was further increased. The amount of rodlike crystals on the surface of the catalyst increased, its denitration efficiency decreased.

Thus, the amount of added Fe affected morphology of the catalyst as well as the dispersion degree of the active components, both of which contributed to its low-temperature denitration performance.

The catalyst variation was analyzed before and after denitration of SO2-containing flue gas to understand morphology and catalytic activity changes of Mn−3/γ-Al2O3 catalysts. When Fe was present on the catalyst surface, the MnO2 active component was more uniform and not clearly detectible by XRD. XRD analysis of Mn−3/γ-Al2O3 after the reaction showed only the diffraction peaks of γ-Al2O3. MnO2 was formed in the Mn−4/γ-Al2O3 catalysts. As the amount of added Fe increased, spherical crystals on the catalyst surface increased, its denitration efficiency decreased. XRD analysis of Mn−3/γ-Al2O3 catalysts showed only the diffraction peaks of γ-Al2O3. When Fe was present on the catalyst surface, distribution of the MnO2 active component was more uniform and not clearly detectible by XRD. XRD analysis of Mn−3/γ-Al2O3 after the reaction showed only the diffraction peaks of γ-Al2O3. MnO2 was formed in the Mn−4/γ-Al2O3 catalysts.
comparison, the Mn−Fe-2/γ-Al2O3 catalyst decreased after the reaction from 129 m²g⁻¹ and 0.21 mLg⁻¹ to 87 m²g⁻¹ and 0.15 mLg⁻¹, respectively (see Table 3). Thus, addition of Fe suppressed specific surface area loss and pore volume decrease upon reaction with SO2-containing flue gas.

The number of mesopores with diameters 2−7 nm significantly decreased for the Mn-3/γ-Al2O3 catalyst after its reaction with the SO2-containing flue gas, as shown in Figure 9.

Figure 9. Pore size distribution of (a) Mn-3/γ-Al2O3 and (b) Mn−Fe-2/γ-Al2O3 catalysts before and after reaction with SO2-containing flue gas.

The main reason for the surface area decrease was compared to the surface area prior to this reaction.

Surface area decrease reduced denitration efficiency of the catalyst.22 However, after SO2 poisoning of the Mn−Fe-2/γ-Al2O3 catalysts, mesopores with pore diameters of 2−7 nm were still abundant and continued to provide active reaction sites maintaining high catalytic activity.

3.4. Mechanism of SO2 Poisoning of Mn/γ-Al2O3 and Mn−Fe/γ-Al2O3 Catalysts. Deactivation of the Mn/γ-Al2O3 catalyst by SO2 occurs because of the following reactions and processes. First, SO2 reacts with NH4-forming NH4HSO4, which has a decomposition temperature of ~200 °C. Therefore, during the low-temperature SCR, NH4HSO4 continuously deposits on the catalyst surface gradually blocking the surface pores and reactive sites causing catalytic activity degradation. MnSO4 formed upon reaction between SO2 causing active component loss, which also significantly decreases catalyst activity.

The presence of Fe reduces sulfating of the active component on the catalyst surface, thereby minimizing loss of Lewis acid sites. At the same time, addition of Fe reduces stability of ammonium sulfate, preventing catalyst pore blockage and coverage of the active sites. All these factors play a significant role in improving anti-SO2 poisoning performance of the Fe-doped Mn/γ-Al2O3 catalysts.

4. CONCLUSIONS

(1) Fe addition improves denitrization performance of the Mn/γ-Al2O3 catalyst to 93%, especially at a low temperature of 150 °C of flue gas.

(2) At low temperatures, vapor effects the denitrization for its competitive adsorption and prohibition of reduction, no poisons the catalyst; but the presence of SO2 during SCR reaction poisons Mn-3/γ-Al2O3 catalyst and decreasing its NOx removal rate from 84 to 57.6%. Fe addition forms the Mn−Fe-2/γ-Al2O3 catalyst, which is able to maintain NOx removal efficiency close to 84.3% under the same experimental conditions.

(3) A certain amount of ammonium sulfate deposits on the surface of the Mn/γ-Al2O3 catalyst in a SO2-containing atmosphere decreasing the specific surface area of the catalyst. Additionally, SO2 reacts with the most important active component (MnO2) of the Mn/γ-Al2O3 catalyst forming manganese sulfate, which significantly decreases denitrification efficiency of the catalyst.

(4) Upon Fe doping, reaction of MnO2 on the catalyst surface with SO2 is minimized. Additionally, ammonium sulfate deposits on the surface of the Mn−Fe/γ-Al2O3
catalyst decrease significantly as well. Overall decrease of the specific surface area of the Fe-doped catalyst after reaction with SO₂-containing gas is not as significant as for the undoped catalyst. Thus, Fe addition improves anti-SO₂ poisoning performance of Mn/γ-Al₂O₃ catalysts.

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**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

SCR, selective catalytic reduction; FGD, flue gas desulfurization; CFB, circulating fluidized bed; SEM, scanning electron microscope; XRD, X-ray diffraction; BET, Brunner–Emmet–Teller

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