

Review



Sulfur and Water Resistance of Mn-Based Catalysts for Low-Temperature Selective Catalytic Reduction of NO_x: A Review

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Abstract: Selective catalytic reduction (SCR) with NH₃ is the most efficient and economic flue gas denitrification technology developed to date. Due to its high low-temperature catalytic activity, Mn-based catalysts present a great prospect for application in SCR de-NO_x at low temperatures. However, overcoming the poor resistance of Mn-based catalysts to H₂O and SO₂ poison is still a challenge. This paper reviews the recent progress on the H₂O and SO₂ resistance of Mn-based catalysts for the low-temperature SCR of NO_x. Firstly, the poison mechanisms of H₂O and SO₂ are introduced in detail, respectively. Secondly, Mn-based catalysts, and Mn-based supported catalysts—to review the research progress of Mn-based catalysts for H₂O and SO₂ resistance. Thirdly, several strategies to reduce the poisonous effects of H₂O and SO₂, such as metal modification, proper support, the combination of metal modification and support, the rational design of structure and morphology, are summarized. Finally, perspectives and future directions of Mn-based catalysts for the low-temperature SCR of NO_x are proposed.

Keywords: selective catalytic reduction; Mn-based catalysts; H_2O and SO_2 resistance; low-temperature; de-NO_x

1. Introduction

Nitrogen oxides (NO_x, x = 1,2) emitted from power plants and diesel engines are major air pollutants that can cause acid rain, photochemical smog, ozone depletion, and other severe environmental problems [1–5]. Selective catalytic reduction (SCR) with NH₃ is the most efficient and economic method for post-NO_x abatement, and V₂O₅–WO₃(MoO₃)/TiO₂ has been the most popular commercial SCR catalyst since the 1970s [6,7]. However, V₂O₅-based catalysts have drawbacks, such as the toxicity of vanadium, SO₂ oxidation to SO₃, over-oxidation of NH₃ to N₂O, and a high working temperature [8]. Because of the high working temperature window (300–400 °C), V₂O₅-based catalysts have to be placed upstream of the dust removal system and desulfurization units to avoid costly heating of the flue gas, where the catalysts are susceptible to deactivation by dust accumulation and SO₂ poison. Therefore, SCR catalysts that are environmentally friendly and can work at low temperatures (around 250 °C or even lower) urgently need to be developed [9–11].

Due to its high low-temperature catalytic activity, manganese oxide (MnO_x) has been intensively studied in recent decades [4,12–14]. Recently, our research group has also made a series of progress in the low-temperature SCR of NO with NH₃ over Mn-based catalysts [15–21]. However, several problems, including thermal instability, narrow operation window, and poor resistance to H₂O and SO₂ poison, remain. Among these drawbacks, the poor tolerance to H₂O and

 SO_2 is one of the most significant disadvantages, which limits the practical application of Mn-based catalysts [22]. Researchers have done numerous studies to develop Mn-based catalysts with good tolerance to water and sulfur and to uncover the deactivation mechanism of Mn-based catalysts in the presence of water and sulfur. In this review, we focused on the recent progress on the water and sulfur resistance of Mn-based catalysts. To make the organization clear, catalysts were introduced by the following three categories, single MnO_x catalysts, Mn-based multi-metal oxide catalysts and Mn-based supported catalysts. Table 1 summarizes Mn-based catalysts reported in the literature that have exhibited good performance in the presence of water and sulfur.

Catalyst	Reaction Conditions	T/°C	X _{NO}	X _{NO} -U	X _{NO} -A	References
MnO _x	500 ppm NH ₃ , 500 ppm NO, 3% O ₂ , 10% H ₂ O, 100 ppm SO ₂ GHSV at 47,000 h^{-1}	80	98%	70%	90%	[13]
MnO _x	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 11% H ₂ O, 100 ppm SO ₂ GHSV at 50,000 h ⁻¹	120	100%	94%	100%	[23]
Mn–Ce	1000 ppm NH ₃ , 1000 ppm NO, 2% O ₂ , 2.5% H ₂ O, 100 ppm SO ₂ GHSV at 42,000 h ⁻¹	120	100%	95%	100%	[24]
Mn–Ce	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 5% H ₂ O, 50 ppm SO ₂ GHSV at 64,000 h ⁻¹	150	~98%	~95%	/	[25]
Mn–Ce	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 5% H ₂ O, 100 ppm SO ₂ 60,000 mL g^{-1} h ⁻¹	200	~97%	~70%	~85%	[26]
Mn–Fe	1000 ppm NH ₃ , 1000 ppm NO, 2% O ₂ , 2.5% H ₂ O, 37.5 ppm SO ₂ GHSV at 15,000 h ⁻¹	160	100%	~98%	/	[27]
Mn–Fe	1000 ppm NH ₃ , 1000 ppm NO, 3% O ₂ , 5% H ₂ O, 100 ppm SO ₂ GHSV at 30,000 h ⁻¹	120	100%	87%	93%	[28]
Mn–Co	500 ppm NH ₃ , 500 ppm NO, 3% O ₂ , 8% H ₂ O, 200 ppm SO ₂ GHSV at 38,000 h ⁻¹	175	100%	90%	100%	[29]
Mn–Co	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 5% H ₂ O, 100 ppm SO ₂ GHSV at 50,000 h ⁻¹	200	100%	80%	90%	[30,31]
Mn–Cu	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 11% H ₂ O, 100 ppm SO ₂ GHSV at 50,000 h ⁻¹	125	95%	64%	~90%	[32]
Mn–Sm	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 2% H ₂ O, 100 ppm SO ₂ GHSV at 49,000 h ⁻¹	100	100%	91%	97%	[33]
Mn–Eu	600 ppm NH ₃ , 600 ppm NO, 5% O ₂ , 5% H ₂ O, 100 ppm SO ₂ GHSV at 108,000 h ⁻¹	350	100%	90%	95%	[34]
Mn–Fe–Ce	1000 ppm NH ₃ , 1000 ppm NO, 2% O ₂ , 2.5% H ₂ O, 100 ppm SO ₂ GHSV at 42,000 h ⁻¹	150	98%	95%	98%	[35]
Mn–Ce–Fe	1000 ppm NH ₃ , 1000 ppm NO, 3% O ₂ , 10% H ₂ O, 100 ppm SO ₂ GHSV at 30,000 h ⁻¹	120	100%	75%	95%	[36]
Mn–Sn–Ce	1000 ppm NH ₃ , 1000 ppm NO, 2% O ₂ , 12% H ₂ O, 100 ppm SO ₂ GHSV at 35,000 h ⁻¹	110	100%	70%	90%	[37,38]
Mn–Ce–Ni	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 10% H ₂ O, 150 ppm SO ₂ GHSV at 48,000 h ⁻¹	175	~90%	~78%	~90%	[39]
Mn–Ce–Co	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 10% H ₂ O, 150 ppm SO ₂ GHSV at 48,000 h ⁻¹	175	~90%	~72%	~90%	[39]
Mn-W-Zr	500 ppm NH ₃ , 500 ppm NO 5% O ₂ , 5% H ₂ O, 50 ppm SO ₂ GHSV at 128,000 h ⁻¹	300	100%	~90%	100%	[40]
Mn–Fe/TiO ₂	1000 ppm NH ₃ , 1000 ppm NO, 2% O ₂ , 2.5% H ₂ O, 100 ppm SO ₂ GHSV at 15,000 h ⁻¹	150	100%	90%	100%	[41]
Mn/Fe-TiO ₂	500 ppm NH ₃ , 500 ppm NO, 2% O ₂ , 8% H ₂ O, 60 ppm SO ₂ GHSV at 12,000 h ⁻¹	200	100%	83%	100%	[42]
Mn–Ce/TiO ₂	1000 ppm NH ₃ , 1000 ppm NO, 3% O ₂ , 3% H ₂ O, 100 ppm SO ₂ GHSV at 30,000 h ⁻¹	150	100%	84%	/	[9]
Mn-Fe-Ce/TiO ₂	600 ppm NH ₃ , 600 ppm NO, 3% O ₂ , 3% H ₂ O, 100 ppm SO ₂ GHSV at 50,000 h ⁻¹	180	100%	84%	90%	[43]
Mn-Ce/Ti-PILC	600 ppm NH ₃ , 600 ppm NO, 3% O ₂ , 3% H ₂ O, 100 ppm SO ₂ GHSV at 50,000 h ⁻¹	200	~95%	~90%	~90%	[44]
Mn–Ce/TiO ₂	220 ppm NH ₃ , 200 ppm NO, 8% O ₂ , 6% H ₂ O, 100 ppm SO ₂ GHSV at 60,000 h ⁻¹	180	100%	62%	70%	[45]
Mn–Ce/TiO ₂	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 5% H ₂ O, 50 ppm SO ₂ GHSV at 64,000 h^{-1}	200	~95%	~90%	~93%	[46]
Ni-Mn/TiO ₂	1000 ppm NH ₃ , 1000 ppm NO, 3% O ₂ , 15% H ₂ O, 100 ppm SO ₂ GHSV at 40,000 h ⁻¹	240	100%	~95%	100%	[47]
MnCe@CNTs	500 ppm NH ₃ , 500 ppm NO, 3% O ₂ , 4% H ₂ O, 100 ppm SO ₂ GHSV at 10,000 h ⁻¹	300	100%	87%	90%	[48]
Fe2O3@MnOx@CNTs	550 ppm NH ₃ , 550 ppm NO, 5% O ₂ , 10% H ₂ O, 100 ppm SO ₂ GHSV at 20,000 h ⁻¹	240	97%	91%	95%	[49]
Mn–Ce/TiO ₂ –graphene	500 ppm NH ₃ , 500 ppm NO, 7% O ₂ , 10% H ₂ O, 200 ppm SO ₂ GHSV at 67,000 h ⁻¹	180	95%	95%	100%	[50,51]
$MnO_x(0.6)/Ce_{0.5}Zr_{0.5}O$	600 ppm NH ₃ , 600 ppm NO, 3% O ₂ , 3% H ₂ O, 200 ppm SO ₂ GHSV at 30,000 h ⁻¹	180	100%	~92%	~98%	[52]
W _y SnMnCeO _x	500 ppm NH ₃ , 500 ppm NO, 5% O ₂ , 5% H ₂ O, 100 ppm SO ₂ 60,000 mL $g^{-1} h^{-1}$	200	~97%	~90%	~95%	[53]
MnO _x /3DOMC	1000 ppm NH ₃ , 1000 ppm NO, 5% O ₂ , 5% H ₂ O, 200 ppm SO ₂ GHSV at 36,000 h ⁻¹	190	100%	~87%	~95%	[54]
W _{0.25} -Mn _{0.25} -Ti _{0.5}	1000 ppm NH ₃ , 1000 ppm NO, 5% O ₂ , 10% H ₂ O, 100 ppm SO ₂ GHSV at 25,000 h ⁻¹	/	~100%	~100%	/	[55]

Table 1. Summary of the current status of H₂O and SO₂ tolerance study on Mn-based catalysts in the literature.

X_{NO}, X_{NO}-U, and X_{NO}-A represent NO_x conversion of regular SCR reaction, NO_x conversion under tolerance test and after tolerance test, respectively.

2. The Poisoning Mechanism of Mn-Based Catalysts

2.1. The Poisoning Mechanism of H_2O

Water vapor has a negative effect on SCR reaction mainly because of the loss of available active sites on the surface of catalysts [43,56–58]. Even under dry conditions, the catalysts can be affected by the water vapor produced in the SCR reaction [56,59]. It is believed that the poisonous effects of H₂O can be generally divided into two aspects: reversible and irreversible deactivation. As shown in Figure 1, the competitive adsorption between H₂O and NH₃ (or NO) is generally considered as the cause of reversible deactivation. Less adsorption of reacting agents on the surface leads to a decrease in NO_x conversion. Fortunately, this effect generally disappears if H₂O vapors are removed [60]. The formation of additional surface hydroxyls (–OH) caused by dissociative adsorption and decomposition of H₂O on the catalyst surface is likely to be the reason of irreversible deactivation, and this effect can occur at a relatively low temperature (below 200 °C) [61]. Because of the good thermal stability of hydroxyls (in the 250–500 °C range), the NO_x conversion cannot be recovered even shutting the H₂O stream down at such a low temperature, thus resulting in an irreversible deactivation [62].



Figure 1. Scheme of the regular selective catalytic reduction (SCR) reaction, the H₂O poisoning effect, and the SO₂ poisoning effect.

2.2. The Poisoning Mechanism of SO₂

The presence of a significant amount of SO_2 in flue gas has a critical influence on the catalyst for SCR reaction at low temperatures. The poisonous effects of SO₂ can be generally classified in two categories: reversible and irreversible deactivation. For reversible deactivation, as displayed in Figure 1, SO₂ is easily oxidized to SO₃, which will easily react with NH₃ to generate ammonia sulfate. The ammonia sulfates (NH₄HSO₄ and (NH₄)₂SO₄) could cover on the active sites of catalysts and lead to a decrease in NO_x conversion [63–65]. In addition, the competitive adsorption between SO_2 and NO on the active sites of the catalysts also contributes to the poisoning effect of SO_2 on the SCR reaction [66]. However, the reversible effect can be eliminated by washing with water or acid solution, or high temperature treatment of catalyst. For the irreversible case, as illustrated in Figure 1, SO_2 (or SO_3) can directly react with active components and form metallic sulfate, which leads to surface active site loss. Hence, the conversion decreases. Due to the high thermal stability of metallic sulfate, washing with water or high temperature treatment cannot bring much recovery of NO_x conversion. When H₂O and SO₂ are introduced simultaneously, water will make the poisoning effect of SO₂ severer, leading to a great decrease in the NO_x conversion. Mn-based catalysts can work at low temperatures, which means that the SCR unit can be installed downstream of the dust removal system and desulfurization units. According to the Chinese Standard (GB13233-2011) and the EU Standard (BREF), residual SO2 in flue gas after desulfurization (35–150 ppm depending on different fuels and desulfurization methods) is allowed. The remaining SO_2 and H_2O in flue gas still have inevitable effects [59,67]. Thus, developing Mn-based catalysts with good tolerance to water and sulfur is crucial for commercial applications.

2.3. The Effect on N_2 Selectivity

The N₂ selectivity is another indicator for the evaluation of SCR catalysts, which is closely related to the yield of N₂O. During NH₃–SCR reaction, N₂O can be produced together with N₂, especially at high temperatures. However, for Mn-based catalysts, some N₂O can also be formed even at low temperatures due to side reactions resulting from the oxidative properties of manganese oxides, whether the NH₃–SCR reaction follows the Eley–Rideal (E–R) mechanism or the Langmuir–Hinshelwood (L–H) mechanism. It has been reported that H₂O presents a positive effect on N₂ selectivity. Xiong et al. found that the formation of N₂O over the Mn–Fe spinel and MnO_x–CeO₂ catalysts following the E-R mechanism was notably restrained by H₂O due to the decrease in the oxidation ability of MnO_x, the suppression of NH₃ adsorption and the inhibition of the interface reaction. Furthermore, the generation of N₂O through the L–H mechanism was completely suppressed by H₂O due to the fact that the formation of NH₄NO₃ was inhibited or the decomposition of generated NH₄NO₃ was promoted [68,69]. As regards the effect of SO₂ on N₂ selectivity, there is a lack of research in this area at the moment.

3. Research Progress of Mn-Based Catalysts for Water and Sulfur Resistance

3.1. Single MnO_x Catalysts

It has been proven that pure MnO_x has terrific catalytic activity for the SCR of NO_x with NH_3 but poor resistance to the poison of water and sulfur at low temperatures [4,70–72]. It has been reported that several factors, such as the preparation method and the specific surface area, have a great influence on the tolerance of MnO_x . Tang et al. prepared a series of amorphous MnO_x catalysts using three methods, the solid phase reaction method (SP), the co-precipitation method (CP), and the rheological phase reaction method (RP) [13], and they found that the MnO_x (CP) exhibited the best sulfur and water resistance, but the MnO_x (SP) presented a larger surface area (150 m^2g^{-1} for MnO_x (SP) and 96 m²g⁻¹ for MnO_x (CP)). As shown in Figure 2, the NO_x conversion at 80 $^{\circ}$ C over MnO_x (CP) decreased from 98 to 73% in 3 h. After turning off SO₂ and H_2O , the NO_x conversion was quickly restored to 90%. After the MnO_x (CP) was heated for 1–2 h in N₂ at 280 °C, its activity was restored to the initial level. Kang et al. prepared two MnO_x catalysts using sodium carbonate (SC) and ammonia (AH) as precipitants [23]. They found that an MnO_x-SC catalyst showed better SCR activity and great sulfur and water tolerance, and they ascribed this to the larger surface area (173.3 m^2/g for MnO_x-SC and 18.7 m^2/g for MnO_x-AH). As displayed in Figure 3, the NO_x conversion over the MnO_x-SC catalyst was decreased from 100 to 94% after both SO₂ (100 ppm) and H₂O (11 vol %) were fed into the reaction system with aspace velocity of 50,000 h⁻¹, which is still very high de-NO_x activity at 120 $^{\circ}$ C. Moreover, its activity was rapidly recovered to 100% after the supply of SO_2 and H_2O was cut off.



Figure 2. The effect of SO₂ and H₂O on NO_x conversion over MnO_x (CP) and MnO_x (SP) (dotted line: only added 10% H₂O; solid line: added 10% H₂O + 100 ppm SO₂). (Reproduced with permission from Reference [13], Copyright 2007, Elsevier).



Figure 3. The effects of H_2O and SO_2 on NO_x conversions over MnO_x -SC catalyst at 120 °C. Reactants: 500 ppm NO, 500 ppm NH₃, 5 vol % O_2 in N_2 . The gas hourly space velocity (GHSV) was 50,000 h⁻¹. (Reproduced with permission from Reference [23], Copyright 2006, Springer).

3.2. Mn-Based Multi-Metal Oxide Catalysts

It has been widely demonstrated that mixing or doping MnO_x with other metal oxides can greatly improve the water and sulfur resistance of single MnO_x catalysts because of the synergistic effect between them [73]. For Mn-based binary metal oxide catalysts, it has been reported that different dopants have different effects on the improvement of the tolerance to water and sulfur [74,75]. For Mn-based ternary metal oxide catalysts, the modification of a small amount of a third element can enhance the synergistic effect resulted from the changes in both electronic and structural properties.

3.2.1. Mn-Based Binary Metal Oxide Catalysts

Among the metal elements, cerium [24,25], chromium [10], iron [27,28,76], cobalt [29,30], copper [52], nickel [77], and several other elements have drawn the most attention as the mixture or dopant to construct binary metal oxide catalysts with MnO_x. CeO₂ has been studied extensively due to its good characteristics, such as increasing surface acidity after SO₂ poisoning [78,79], high surface area [80,81], good dispersion of MnO_x on the surface [45], and the redox shift between Ce^{4+} and Ce^{3+} . It should be noted that the shift between Ce⁴⁺ and Ce³⁺ can result in the formation of oxygen vacancies and anincrease in the chemisorbed oxygen on the surface of Mn-Ce binary metal oxide catalysts, which are helpful for the enhancement of water and sulfur resistance [25,82]. Qi and Yang [24] reported that the Mn–Ce catalyst with a proper mole ratio (Mn/(Mn+Ce) = 0.3) showed great tolerance to water and sulfur. As illustrated in Figure 4, the NO conversion over an Mn–Ce catalyst gradually decreased from 100 to 95% within 4 h after 100 ppm SO₂ and 2.5% H₂O were added to the reaction gas at 120 °C. Moreover, the NO conversion was restored after $SO_2 + H_2O$ was stopped. Liu et al. prepared an Mn–Ce catalyst by the surfactant-template method using hexadecyltrimethyl ammonium bromide (CTAB) as the template. The obtained Mn₅Ce₅(ST) catalyst presented a noticeable decrease in the catalytic activity for the NO_x conversion at 100 $^{\circ}$ C in the presence of H₂O and SO₂ (Figure 5), a slight inhibiting effect was observed from 150 to 200 °C, and the promoting effect was exhibited above 200 °C [25]. Yao et al. successfully prepared a series of Mn/CeO₂ catalysts via impregnation using deionized water, anhydrous ethanol, acetic acid, and oxalic acid as a solvent and found that Mn/Ce–OA (oxalic acid) exhibited the best water and sulfur tolerance among all catalysts (Figure 6) [26]. Chen et al. [10] found that the SO_2 tolerance of MnO_x was dramatically enhanced by the introduction of Cr due to the formation of $CrMn_{1.5}O_4$.



Figure 4. The effect of on-stream time on SCR activity with $H_2O + SO_2$ and without $H_2O + SO_2$ (Reaction conditions: 120 °C, $[NH_3] = [NO] = 1000$ ppm, $[O_2] = 2\%$, GHSV = 42,000 h⁻¹. Catalyst: MnO_x(0.3)–CeO₂). (Reproduced with permission from Reference [24], Copyright 2003, The Royal Society of Chemistry).



Figure 5. Catalytic performance of $Mn_5Ce_5(ST)$ catalysts in the presence of H_2O and SO_2 (Reaction conditions: NO = 500 ppm, NH₃ = 500 ppm, $O_2 = 5\%$, $H_2O = 5\%$, $SO_2 = 50$ ppm, GHSV = 64,000 h⁻¹). (Reproduced with permission from Reference [25], Copyright 2013, Elsevier).



Figure 6. The effect of H₂O and SO₂ on NO conversion for Mn/CeO₂ catalysts (Reaction conditions: $[NO] = [NH_3] = 500 \text{ ppm}, [O_2] = 5 \text{ vol }\%, [SO_2] = 100 \text{ ppm}, [H_2O] = 5 \text{ vol }\%, N_2 \text{ balance, } T = 200 ^{\circ}C, 60,000 \text{ mL } g^{-1} \text{ h}^{-1}$). (Reproduced with permission from Reference [26], Copyright 2017, Elsevier).

Iron is another potential element that has been demonstrated to play a positive role in the sulfur and water tolerance of Mn-based catalysts. Long et al. [27] observed that Fe–Mn-based transition metal oxides were resistant to H_2O and SO_2 at 140–180 °C (Figure 7). Chen et al. [28] found that the NO conversion over an Fe–Mn mixed oxide catalyst decreased slightly from 100 to 87% in 4 h at 120 °C in the presence of 5% H_2O and 100 ppm SO_2 , which could be restored to 93% after the stopping of both SO_2 and H_2O (Figure 8). They attributed the enhanced resistance to the formed Fe₃Mn₃O₈ phase in Fe–Mn mixed oxides. Yang et al. [76] prepared an Mn–Fe spinel catalyst and found that the NO conversion over Mn–Fe spinel catalyst decreased from 100 to about 60% after the addition of H_2O and SO_2 for 100 min, and the NO conversion could be recovered to the original level after washing catalyst with water.



Figure 7. SCR activities on the Fe–Mn-based transition metal oxides in the presence of SO₂ + H₂O (Reaction conditions: 0.5 g catalyst, [NO] = [NH₃] = 1000 ppm, [O₂] = 2%, [SO₂] = 37.5 ppm and [H₂O] = 2.5% (when used), He = balance, total flow rate = 100 mL/min, and GHSV = 15,000 h⁻¹). (Reproduced with permission from Reference [27], Copyright 2002, The Royal Society of Chemistry.).



Figure 8. Lifetime, SO₂ tolerance, and water resistance of Fe-(0.4)MnO_x(CA-500) catalyst (Reaction conditions: 120 °C, [NO] = [NH₃] = 1000 ppm, $[O_2] = 3\%$, $[SO_2] = 100$ ppm, $[H_2O] = 5\%$, N₂ as balance, and GHSV = 30,000 h⁻¹; Plasma treatment conditions: 10 MHz, 25 °C, pure oxygen with 50 mL/min under 2.4 s of residence time, and duration of 6 h): (**a**) Lifetime testing; (**b**) regeneration property; (**c**) SO₂ tolerance; (**d**) water resistance; (**e**) the combined effect of SO₂ and H₂O. (Reproduced with permission from Reference [28], Copyright 2012, American Chemical Society.).

It has been reported that cobalt also presents a positive role on the tolerance of Mn-based catalysts to sulfur and water. Zhang et al. [29] found that the $Mn_xCo_{3-x}O_4$ nanocage catalyst exhibited decent SO_2 tolerance due to its hierarchically porous structure, abundant active sites, and strong interaction between Mn and Co oxides (Figure 9). Qiu et al. prepared a mesoporous 3D-MnCo₂O₄ catalyst, which exhibited great SCR activity and good tolerance to sulfur and water [30,31]. As illustrated in Figure 10, the NO conversion over $MnCo_2O_4$ was maintained at 86% in the presence of 5 vol % H₂O and 100 ppm SO_2 . Futhermore, the NO conversion could be recovered to 93% after the supply of H₂O and SO_2 was cut off.



Figure 9. (a) H_2O resistance, (b) SO_2 tolerance, and (c) H_2O and SO_2 synergetic effect study of the catalysts at 175 °C (Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 3 vol %, [H₂O] = 8 vol % (when used), [SO₂] = 200 ppm (when used), N₂ balance, and GHSV = 38,000 h⁻¹). (Reproduced with permission from Reference [29], Copyright 2014, American Chemical Society.).



Figure 10. H₂O resistance, SO₂ tolerance, and H₂O and SO₂ synergetic effect study of the MnCo₂O₄ catalyst at 200 °C (Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = [H₂O] = 5 vol %, [SO₂] = 100 ppm, N₂ balance, and GHSV = 50,000 h⁻¹). (Reproduced with permission from Reference [30], Copyright 2015, Elsevier).

Copper also presents a positive effect on the tolerance of MnO_x -based catalysts to water and sulfur. Kang et al. reported a Cu–Mn mixed oxide catalyst, which exhibited good tolerance to water and sulfur [32]. When 100 ppm SO₂ and 11 vol % H₂O were added to the reaction gas, the NO_x conversion over Cu–Mn oxides decreased from 95 to 64% at 125 °C after 4 h, and the NO_x conversion was gradually recovered after stopping the supply of SO₂ and H₂O.

Recently, several rare earth elements have been demonstrated to promote the enhanced tolerance to sulfur and water. For instance, Meng et al. developed a Sm-modified MnO_x catalyst [33], and found that a proper Sm modification (Sm/Mn = 1:10) enhanced the sulfur and water tolerance of MnO_x. As shown in Figure 11, the NO_x conversion over the Sm–Mn-0.1 catalyst could be maintained at about 91% at 100 °C when 2% H₂O and 100 ppm SO₂ were added into the feed gas, and the NO_x conversion was recovered to 97% after both H₂O and SO₂ were removed from the feed gas. Sun et al. prepared a Eu-modified MnO_x catalyst [34]. They tested the sulfur and water resistance of this catalyst at a higher temperature (350 °C), instead of a low temperature, such as 100 °C. The deactivation effect of SO₂ and H₂O on MnEuO_x-0.1 was weak, and the NO_x conversion over MnEuO_x-0.1 kept over 90% in the presence of 100 ppm SO₂ and 5% H₂O. Furthermore, the NO_x conversion nearly recovered its original level after the supply of SO₂ and H₂O was cut off (Figure 12).



Figure 11. The effect of H_2O and SO_2 on the catalytic activities of the MnO_x and Sm-Mn-0.1 catalysts for the SCR reaction at 100 °C (Reaction conditions: 0.3 g catalyst, 500 ppm NO, 500 ppm NH₃, 5% O_2 , Ar to balance, GHSV = 49,000 h⁻¹). (Reproduced with permission from Reference [33], Copyright 2016, American Chemical Society).



Figure 12. Effect of SO₂ and H₂O on the SCR activities of MnO_x and MnEuO_x-0.1 catalysts (Reaction conditions: [NO] = [NH₃] = 600 ppm, [SO₂] = 100 ppm, [H₂O] = [O₂] = 5%, balance Ar, GHSV = 108,000 h⁻¹, reaction temperature = 350 °C). (Reproduced with permission from Reference [34], Copyright 2017, Elsevier).

3.2.2. Mn-Based Ternary Metal Oxide Catalysts

It has been reported that the introduction of a small amount of a third element can enhance the tolerance of Mn-based binary metal oxide catalysts to H₂O and SO₂. Qi et al. successfully prepared Mn–Fe–Ce mixed oxides that performed well under 100 ppm SO₂ and 2.5% H₂O condition (Figure 13) [35]. The NO conversion over Mn–Fe–Ce decreased from 98 to 95% in 3 h in the presence of SO₂ and H₂O and then restored quickly to its original level after the supply of SO₂ and H₂O was cut off. France et al. developed a CeFeMnO_x catalyst that exhibited excellent sulfur and water resistance at a low temperature [36]. As presented in Figure 14, the NO conversion over this catalyst only decreased from 100 to 75% when water and sulfur were introduced, and then recovered to 95% after the supply of H₂O and SO₂ was cut off. Chang et al. found that Sn doping could enhance the sulfur resistance of Mn–Ce catalysts because SO₂ was easier to react with Ce on the surface instead of forming ammonia sulfate; meanwhile, more surface acid sites were introduced due to Sn doping [37,38]. As shown in Figure 15, the NO conversion was kept at around 70% in the presence of SO_2 and H_2O and recovered to almost the original level within less than 3 hafter SO₂ and H₂O were removed. Gao et al. [39] found that the SCR pathways over MnO_x–CeO₂ catalyst are based on the adsorption, activation, and reaction of monodentate nitrite species and coordinated NH₃ species, and these species are significantly inhibited by SO₂ through competitive adsorption. In contrast, over Co- and Ni-doped MnO_x–CeO₂ catalysts, the primary NO_x adsorbed species are in the form of bidentate nitrate without the influence by SO_2 . The NO conversion over Co- and Ni-doped MnO_x-CeO₂ catalysts decreased 20% after 150 ppm SO₂ and 10% H₂O were introduced, and recovered after the supply of SO₂ and H₂O was cut off (Figure 16). Liu et al. successfully prepared WO_3 promoted Mn–Zr mixed oxide catalyst [40]. As shown in Figure 17, the NO_x conversion over MnWZr catalyst was maintained above 90% in the presence of 50 ppm SO₂ and 5% H_2O , and the conversion quickly recovered after the supply of SO₂ and H_2O was cut off.



Figure 13. The effects of SO₂ and H₂O on the SCR activities of MnO_x(0.4)–CeO₂(500)-based catalysts (Reaction conditions: 0.2 g catalyst, $[NH_3] = [NO] = 1000$ ppm, $[O_2] = 2\%$, He = balance and total flow rate = 100 mL/min, T = 150 °C). (Reproduced with permission from Reference [35], Copyright 2004, Elsevier).



Figure 14. Influence of H₂O and combined H₂O and SO₂ on NO_x conversion of FeMnO_x and Ce(12.5) (Reaction conditions: [NO] = [NH₃] = 0.1%, [H₂O] = 5% or 10%, [SO₂] = 100 ppm, [O₂] = 3%, N₂ balance, GHSV = 30,000 h⁻¹; reaction temperature = 120 °C). (Reproduced with permission from Reference [36], Copyright 2017, Elsevier).



Figure 15. (a) NO conversion in the presence of 100 ppm SO₂ and 12% H₂O at 110 °C; (b) NO conversion in the presence of 100 ppm SO₂ at 250 °C (Reaction conditions: 0.2 g samples, 1000 ppm NO, 1000 ppm NH₃, 2% O₂, N₂ balance, GHSV = 35,000 h⁻¹). (Reproduced with permission from Reference [37], Copyright 2012, Elsevier).



Figure 16. The resistance to H_2O and/or SO_2 over $Co_1Mn_4Ce_5O_x$ and $Ni_1Mn_4Ce_5O_x$ (Reaction conditions: $[NO] = [NH_3] = 500$ ppm, $[O_2] = 5$ vol %, $[SO_2] = 150$ ppm, $[H_2O] = 10$ vol %, N_2 to balance, total flow rate = 200 mL/min, GHSV = 48,000 h⁻¹). (Reproduced with permission from Reference [39], Copyright 2017, Elsevier).



Figure 17. Response of NO_x conversion over MnZr and 15WMnZr catalysts at 300 °C to intermittent feed of H₂O and SO₂ (Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5%, [H₂O] = 5%, [SO₂] = 50 ppm, GHSV = 128,000 h⁻¹). (Reproduced with permission from Reference [40], Copyright 2016, Elsevier).

3.3. Supported Mn-Based Catalysts

Supports play an important role in NH_3 –SCR reaction. Proper supports not only can provide a huge surface to disperse the active components and prevent the formation of large crystalline particles but can also affect the sulfur and water tolerance. To date, various materials, such as TiO₂, carbon materials, and Al_2O_3 , have been explored as supports to load Mn-based catalysts.

3.3.1. TiO₂ Supported Mn-Based Catalysts

 TiO_2 is known to be more resistant to sulfur poisoning because of the stability of sulfates on the TiO_2 surface is weaker than that on other oxides [59], which made TiO_2 an ideal support for the loading of Mn-based catalysts.

Qi and Yang [41] prepared a series of MnTi and FeMnTi catalysts. As shown in Figure 18, the NO conversion over Fe–Mn/TiO₂ was decreased from 100 to 90% within 5 h at 150 °C after 100 ppm SO₂ and 2.5% H₂O were added. After the supply of SO₂ and H₂O was cut off, the NO

conversion recovered to 100% again quickly. Yang et al. investigated the sulfur and water tolerance of Fe–Ti spinel supported MnO_x catalyst [42]. As shown in Figure 19, the NO_x conversion at 200 $^{\circ}$ C gradually decreased from 100 to 83% and then kept unchanged after 8% of H_2O and 60 ppm of SO_2 were introduced. After the supply H_2O and SO_2 was shut off, the NO_x conversion rapidly recovered to 100%. Wu et al. found that the sulfur resistance of Mn/TiO_2 can be greatly improved by Ce addition [9]. As displayed in Figure 20, SO₂ presented an obvious poisonous effect on SCR activity of Mn/TiO_2 at low temperatures because the NO conversion over the MnTi catalyst decreased from 93 to 30% in the presence of SO₂ within 6.5 h, while the NO conversion over MnCeTi still maintained at about 84% under the same conditions. As shown in Figure 21, the surface of fresh catalysts was smooth and uniform (Figure 21A,C). After the catalyst was poisoned with 100 ppm SO_2 for 24 h, the significant agglomeration and deposition could be observed from the surface of MnTi–S (Figure 21B), while only a few deposited particles (no agglomeration) appeared on the surface of MnCeTi-S (Figure 21D). Yu et al. [80] developed a mesoporous MnO₂-Fe₂O₃-CeO₂/TiO₂ catalyst. The NO conversion over this catalyst was stable at 80% under astream of SO_2 . Shen et al. [43] found that the addition of proper iron enhanced the tolerance of TiO₂-supported Mn–Ce catalyst to water and sulfur. As exhibited in Figure 22, Fe(0.15)–Mn–Ce/TiO₂ showed higher resistance under 3 vol % H₂O and 0.01 vol % SO₂ and still provided 83.8% NO conversion over afurther 5 h, an improvement over the Mn–Ce/TiO₂ catalyst. Shen et al. found that titanium-pillared clays (Ti-PILCs) presented advantages in sulfur tolerance over traditional TiO₂ supports [44]. It can be seen from Figure 23 that the NO conversion was stable at around 90% without any obvious decrease in the presence of 3 vol % H_2O and 0.01 vol % SO_2 , suggesting that Mn–CeO_x/Ti–PILC(S) possessed good resistance to H₂O and SO₂. Lee et al. prepared a series of Mn/Ce–TiO₂ catalysts and found that Mn(20)/Ce(4)–TiO₂ showed good H₂O and SO₂ tolerance [45]. As shown in Figure 24, the NO conversion decreased to 60% and it recovered to almost the original level when the SO₂ supply was shut off. Park et al. [83] prepared Mn/Ti catalysts via chemical vapor condensation (CVC) method and claimed that this Mn/Ti not only showed higher activity at low temperature but also exhibited better tolerance to water and sulfur. Only a small NO conversion decrease from 70 to 58% was found under 200 ppm of SO₂ in 250 min at 100 °C. Liu et al. [46] prepared an Mn–Ce–Ti catalyst using the hydrothermal method, and the NO_x conversion over the $Mn_{0.2}Ce_{0.1}Ti_{0.7}O_x$ catalyst under H_2O and SO_2 was further investigated at 200 °C. As shown in Figure 25, the introduction of H₂O and SO₂ induced a slight decrease in NO_x conversion. After H₂O and SO₂ were excluded from the reactant feed, the NO_x conversion completely recovered.



Figure 18. NO conversion on the various Fe–Mn-based catalyst in the presence of SO₂ + H₂O (Reaction conditions: temperature = 150 °C, [NO] = [NH₃] = 1000 ppm, [O₂] = 2%, [SO₂] = 100 ppm, [H₂O] = 2.5%, balance He, total flow rate 100 mL/min, catalyst 0.5 g). (Reproduced with permission from Reference [41], Copyright 2003, Elsevier).



Figure 19. Stability of NO reduction over 10% Mn/Fe–Ti spinel in the presence of H₂O and SO₂ (Reaction conditions: $[NH_3] = [NO] = 500 \text{ ppm}$, $[SO_2] = 60 \text{ ppm}$, $[H_2O] = 8\%$, catalyst mass = 500 mg, the total flow rate = 100 mL and GHSV = 12000 cm³ g⁻¹ h⁻¹). (Reproduced with permission from Reference [42], Copyright 2016, Elsevier).



Figure 20. SCR activities of Mn/TiO₂ and Ce-doped Mn/TiO₂ in the presence of SO₂ (Reaction conditions: $[NH_3] = [NO] = 1000 \text{ ppm}$, $[O_2] = 3\%$, $[SO_2] = 100 \text{ ppm}$, $[H_2O] = 3 \text{ vol }\%$, N₂ balance, GHSV = 40,000 h⁻¹, reaction temperature = 150 °C; hollow symbols for MnTi and solid symbols for MnCeTi).



Figure 21. Scanning electron microscope (SEM) micrographs of fresh and SO₂-poisoned catalysts. (**A**) MnTi, (**B**) MnTi-S, (**C**) MnCeTi, and (**D**) MnCeTi-S. (Reproduced with permission from Reference [9], Copyright 2009, Elsevier).



Figure 22. Effect of H₂O and SO₂ on NO conversion over Mn–Ce/TiO₂ and Fe–Mn–Ce/TiO₂ catalysts (Reaction conditions: 0.06 vol % NO, 0.06 vol % NH₃, 3 vol % O₂, 3 vol % H₂O (when used), 0.01 vol % SO₂ (when used), balance N₂, GHSV 50,000 h⁻¹, total flow rate 300 mL/min, tested at 180 °C). (Reproduced with permission from Reference [43], Copyright 2010, Science Direct).



Figure 23. Effect of H_2O and SO_2 on NO conversion over Mn– CeO_x /TiPILC(S) at 200 °C (Reaction conditions: 0.06 vol % NO, 0.06 vol % NH₃, 3 vol % O_2 , 3 vol % H_2O (when used), 0.01 vol % SO_2 (when used), balance N_2 , GHSV 50,000 h⁻¹, total flow rate 300 mL/min). (Reproduced with permission from Reference [44], Copyright 2012, Science Direct).



Figure 24. The effects of the H₂O and SO₂ in the Mn/Ce(4)–TiO₂ catalysts with different ratio of Ce/Ti (Reaction condition: 200 ppm NO, 8% O₂, 6% H₂O, 100 ppm SO₂, 0.28 g of sample and 500 cc/min total flow rate, tested at 180 °C). (Reproduced with permission from Reference [45], Copyright 2012, Elsevier).



Figure 25. Response of the NO_x conversion over $Mn_{0.2}Ce_{0.1}Ti_{0.7}O_x$ catalyst at 200 °C to the intermittent feed of H₂O and SO₂ (Reaction condition: 500 ppm of NO, 500 ppm of NH₃, 5% O₂, 5% H₂O, 50 ppm of SO₂, balance He, GHSV = 64,000 h⁻¹). (Reproduced with permission from Reference [46], Copyright 2014, American Chemical Society).

3.3.2. Carbon Materials Supported Mn-Based Catalysts

Carbon materials, such as activated carbon (AC), activated carbon fiber (ACF), carbon nanotube (CNT), and graphene (GE), have been widely studied as substrates for supporting low-temperature SCR catalysts due to their high specific surface area, unique pore structure, excellent dispersion of active components, and chemical stability [70,84–86]. Among these carbon materials, CNT and GE have been considered as good supports that can enhance the tolerance of H₂O and SO₂.

Zhang et al. prepared a novel MnCe@CNTs-R catalyst, which exhibited great tolerance to 100 ppm SO₂ and 4 vol % H₂O due to the good dispersion degree of the active components on the surface of CNTs [48]. The coexistence of SO₂ and H₂O induced a 13% NO conversion decrease and the NO conversion was recovered to 90% after the supply of SO₂ and H₂O was cut off. Cai et al. designed a multi-shell Fe₂O₃@MnO_x@CNTs catalyst and found that the Fe₂O₃ shell effectively suppressed the formation of the surface sulfate species, which led to a good tolerance to H₂O and SO₂ (Figure 26) [49]. Lu et al. successfully synthesized a series of TiO₂–graphene-supported Mn and Mn–Ce catalysts with good tolerance to H₂O and SO₂ due to the well dispersed Mn component (Figure 27) [50,51]. Wang et al. investigated the effect of SO₂ on activated carbon honeycomb (ACH)-supported MnO_x and CeO₂–MnO_x catalysts, and the S 2p XPS results are displayed in Figure 28. The peak intensity of Mn/ACH was much higher than that of CeMn/ACH, indicating that Ce doping on ACH had an inhibition of sulfates loading [81].



Figure 26. SO₂ + H₂O tolerance test at 240 °C (Reaction conditions: $[NH_3] = [NO] = 550$ ppm, $[O_2] = 5$ vol %, $[SO_2] = 100$ ppm, $[H_2O] = 10$ vol % (when used), N₂ as balance gas, GHSV = 20,000 h⁻¹). (Reproduced with permission from Reference [49], Copyright 2016, The Royal Society of Chemistry).



Figure 27. SO₂ + H₂O tolerance test at 180 °C (Reaction conditions: $[NH_3] = [NO] = 500 \text{ ppm}$, $[O_2] = 7 \text{ vol }\%$, $[SO_2] = 200 \text{ ppm}$, $[H_2O] = 10 \text{ vol }\%$ (when used), N₂ as balance gas, GHSV = 67,000 h⁻¹). (Reproduced with permission from Reference [51], Copyright 2015, Elsevier).



Figure 28. X-ray photoelectron spectroscopy (XPS) spectra of S 2p for poisoned Mn/ACH and CeMn/ACH catalysts. (Reproduced with permission from Reference [81], Copyright 2015, American Chemical Society).

3.3.3. Other Supported Mn-Based Catalysts

Mixed metal oxides and SiO₂ have also been studied as substrates for supporting SCR catalysts. Yao et al. prepared MnO_x/SiO_2 , MnO_x/Al_2O_3 , MnO_x/TiO_2 , and MnO_x/CeO_2 catalysts and found that the catalytic activity in the presence of H₂O and SO₂ was in the order of $MnO_x/SiO_2 < MnO_x/TiO_2 < MnO_x/CeO_2 < MnO_x/Al_2O_3$ (Figure 29) [87]. Shen et al. also compared the tolerance to H₂O and SO₂ of MnO_x -supported on various substrates including Al₂O₃, TiO₂, CeO₂, ZrO₂, and Ce_{0.5}Zr_{0.5}O₂. Their results showed that the resistance ability was decreased in the following order: $MnO_x/Ce_{0.5}Zr_{0.5}O_2 > MnO_x/Al_2O_3 > MnO_x/CeO_2 > MnO_x/TiO_2 > MnO_x/ZrO_2$, and they ascribed the excellent toleranceof $MnO_x/Ce_{0.5}Zr_{0.5}O_2$ to the combination of the advantages of the two supports (ZrO₂ and CeO₂) (Figure 30) [52]. Huang et al. prepared a mesoporous silica-supported Mn–Fe catalyst and found that its SCR activity was suppressed gradually in the presence of SO₂ and H₂O, and the inhibitory effect was relieved after heating treatment [88].



Figure 29. The results of $H_2O + SO_2$ resistance at 200 °C of these supported Mn-based catalysts with different supports. (Reproduced with permission from Reference [87], Copyright 2017, Elsevier).



Figure 30. The effect of H_2O and SO_2 on NO conversion for $MnO_x(0.6)/Ce_{0.5}Zr_{0.5}O_2$ (Reaction conditions: [NO] = [NH₃] = 600 ppm, [O₂] = 3 vol %, N₂ balance, T = 180°C, catalyst 0.5 g, GHSV 30,000 h⁻¹). (Reproduced with permission from Reference [52], Copyright 2014, Elsevier).

4. Strategies to Reduce the Poisoning Effect

Although there are many factors that affect the water and sulfur tolerance of Mn-based catalysts, such as the preparation method, the reaction temperature, the gas hourly space velocity (GHSV), and the morphology, structure, and surface area of the catalyst, deactivation can be attributed to three main causes: (1) the competitive adsorption between SO₂ and NO, H₂O, and NH₃ on the active sites, (2) the blocking effect of the NH₄HSO₄ and (NH₄)₂SO₄ formed on the surface active sites, and (3) the formation of metallic sulfate, which reduces the active sites on the surface. Hence, suppressing the three negative effects is the key to enhancing resistance against H₂O and SO₂. To date, many strategies have been taken to reduce the poisoning effect on Mn-based catalysts.

4.1. Metal Modification

Metal modification or doping is a common solution to the problem. Most transition metals have been used as dopants to modify Mn-based catalysts for good resistance to SO_2 and H_2O . Cerium has been fully studied, and the mechanism has been uncovered. Cerium reacts more sensitively with SO_2 , so the formation of NH_4HSO_4 and $(NH_4)_2SO_4$ is reduced on the surface of Ce-modified Mn-based catalysts [36,79,89]. Furthermore, metallic sulfates formed by cerium and SO_2 are relatively stable and can provide surface acid sites to enhance the adsorption of NH₃ and to inhibit the catalytic oxidization of NH₃ at the same time, thus promoting SCR reactions in the presence of SO₂ and H₂O [68,78,90]. Liu et al. confirmed, using density functional theory, that Ce isable to inhibit the formation of ammonia sulfate on the surface of catalysts, which is believed to be a key factor in improving tolerance [79]. It was also reported that iron is capable of decreasing the formation rate of sulfate species, thus promoting tolerance [41,91]. Furthermore, several reports have shown that the doping of a third metal, such as Sn and W, into Mn-based catalysts can further improve resistance to SO₂ and H₂O [38,92,93]. Zhang et al. found that resistance to SO₂ and H₂O over the W-modified SnMnCeO_x catalysts, in comparison with unmodified SnMnCeO_x, was further improved (Figure 31) [53]. They attributed this improvement to the introduction of WO_x species, which prevented the formation of (NH₄)₂SO₄ on the catalyst and blocked the interactions between Mnⁿ⁺, SO₄²⁻, and gaseous SO₃ [37]. Rare earths have drawn an increasing amount of attention recently, and Sm and Eu doping have been shown to have a positive influence on the tolerance of SO₂ and H₂O [33,34]. However, the mechanism of SO₂ and H₂O resistance still needs to be uncovered.



Figure 31. NH₃–SCR activity over W_ySnMnCeO_x catalysts in the presence of SO₂/H₂O at 200 °C (Reaction conditions: [NO] = [NH₃] = 500 ppm, [O₂] = 5%, [SO₂] = 100 ppm (when used), [H₂O] = 5% (when used), N₂ balance, total flow rate 100 mL min⁻¹ and GHSV = 60,000 mLg⁻¹h⁻¹). (Reproduced with permission from Reference [53], Copyright 2017, Elsevier).

4.2. Proper Support

It is well believed that loading Mn-based SCR catalysts on a suitable support is an effective measure to enhance the tolerance to SO_2 and H_2O [60,94] because of the high thermal and mechanical stability, large surface area, and highly dispersed active sites. Furthermore, the interaction between support and active components exhibits positive effects on the tolerance to SO_2 and H_2O [95]. Therefore, it is very important for Mn-based catalysts to choose an appropriate support. Among several supports, TiO₂, porous carbon material, and CNTs are considered to be good options. It has been widely reported that TiO₂ can provide a higher specific surface area [58], a higher surface acidity [96], and a good dispersion of active components, all of which effectively enhance SO_2 and H_2O resistance [97]. Gao et al. reported a novel nanocomposite of MnO_x nanoparticles supported on three-dimensionally ordered macroporous carbon (MnO_x/3DOMC). They found that this novel catalyst exhibited good water and sulfur tolerance (Figure 32) [54]. As a special ordered carbon material with unique nanostructure and electronic properties, carbon nanotubes (CNTs) have been reported to be an interesting support for SCR catalysts [98,99]. Zhang et al. proved that active components were well dispersed on the surface of the support such that the blocking effect caused by NH₄HSO₄ and (NH₄)₂SO₄ was reduced [48].



Figure 32. Effect of water vapor and SO₂ on NO conversion over the $MnO_x/3DOMC$ (black), MnO_x/NAC (red), and MnO_x/TiO_2 (blue) catalysts (Reaction conditions: 190 °C, 1000 ppm of NO, 1000 ppm of NH₃, 5% of O₂, 5% of water vapor, and/or 200 ppm of SO₂, He balance). (Reproduced with permission from Reference [54] Copyright 2015, The Royal Society of Chemistry).

4.3. Combination of Metal Modification and Support

The combination of metal modification and support is considered to be a good way of enhancing the water and sulfur tolerance of Mn-based catalysts due to the advantages of both strategies. Compared with non-supported mixed metal oxides, supported catalysts often possess a larger specific surface area and a better dispersion of active components, which facilitates tolerance to water and sulfur. On the other hand, compared with supported single MnO_x catalysts, the synergistic effect introduced by one or more modifiers can reduce the poisonous effect and protect the surface active components. Thus, combining two measures, mixing (or doping) MnOx with suitable metal oxides and loading active components on a suitable support, is the best way to enhance the tolerance to water and sulfur. Chen et al. prepared an NiMn/Ti catalyst and investigated the effects of H₂O and SO_2 on its SCR performance (Figure 33) [47]. They found that the coexistence of 100 ppm SO_2 and 15 vol % H_2O led to an apparent decrease in NO_x conversion, and the NO_x conversion recovered quickly to 100% after stopping the addition of H_2O . Chen et al. found that W-modified MnO_x/TiO_2 exhibited better tolerance to SO_2 than MnO_x/TiO_2 catalyst due to the fact that W addition inhibited the formation of sulfate species [93]. Wang et al. reported a series of W-modified MnO_x/TiO_2 and found that a W(0.25)–Mn(0.25)–Ti(0.5) catalyst showed the best SCR activity and good tolerance to water and sulfur. As illustrated in Figure 34, the W(0.25)–Mn(0.25)–Ti(0.5) catalyst presented a 100% NO_x conversion from 140 to 260 °C [55]. Our group successfully prepared a europium-modified TiO₂-supported Mn-based catalyst and found that this catalyst showed better tolerance than the Mn–TiO₂ catalyst due to the highly dispersed MnO_x and Eu_2O_3 on the surface of TiO₂ [18]. Zhao et al. synthesized an Nb-modified Mn/Ce/Ti catalyst and tested the water and sulfur tolerance at a high GHSV of 180,000 h⁻¹ at 175 °C [100]. They found that the catalyst was deactivated with a decreased NO conversion from 100 to 10% within 4 h, which recovered to almost the original level after regeneration by washing.



Figure 33. Effects of H_2O and SO_2 on NO_x conversion over the $Ni_{0.4}Mn_{0.6}Ti_{10}$ catalyst. (Reproduced with permission from Reference [47], Copyright 2017, The Royal Society of Chemistry).



Figure 34. Effects of SO₂ and H₂O on the NO_x conversion of W(0.25)–Mn(0.25)–Ti(0.5) at GHSV of 25,000 h⁻¹ (Reaction conditions: [NO] = [NH₃] = 1000 ppm, [O₂] = 5 vol %, [SO₂] = 100 ppm, [H₂O] = 10 vol %, in He as balance). (Reproduced with permission from Reference [55], Copyright 2016, Elsevier).

4.4. Rational Design of Structure and Morphology

The rational design of catalyst structure and morphology is another method of reducing the poisoning effect of SO₂ and H₂O. Shen et al. developed a hollow MnO_x –CeO₂ mixed oxide catalyst, which exhibited good SCR performance under water and sulfur poison at a high GHSV of 120,000 h⁻¹ due to the hollow structure [101]. Zhang et al. [28] found that an $Mn_xCo_{3-x}O_4$ catalyst with a nanocage structure exhibited much better SO₂ and H₂O tolerance than $Mn_xCo_{3-x}O_4$ without a nanocage structure. Qiu et al. synthesized a mesoporous 3D-MnCo₂O₄ catalyst that exhibited great SCR activity and good tolerance to sulfur and water [30,31], and the mesoporous structure enabled a dynamic balance between the formation and decomposition of ammonium sulfate, and thus suppressed the blocking effect during the SCR reaction. Li et al. prepared Mn_2O_3 -doped Fe₂O₃ hexagonal microsheet catalyst [102] and found the single H₂O resistance (15%) and the single SO₂ resistance (100 ppm) over this catalyst were good and stable with the NO conversion at around 92% and 85% for 100 h, respectively, because of this special structure.

4.5. Monolithic Catalysts

Preparing monolithic catalysts may be an option to promote the tolerance of Mn-based SCR catalysts to SO₂ and H₂O. As well known, the commercial catalysts (V_2O_5 -WO₃(or MoO₃)/TiO₂) used in thermal power plant are in the monolithic form because the honeycomb monoliths are suitable for a high gas flow rate, reduce pressure drop problems, exhibit high tolerance to dust and attrition, and are easy to regenerate [103–106]. Recently, metal foam and wire mesh as novel monolithic support for Mn-based and other vanadium-free SCR catalysts are drawing an increasing amount of attention due to their high porosity, stability, thermal conductivity, and mass transfer ability [107,108]. Xu et al. prepared porous MnCo_xO_y nanocubes on a Ti mesh as a novel monolithic catalyst for SCR [109]. They found that this monolithic catalyst exhibited better SCR activity than MnCo_xO_y@honeycomb ceramics. Meanwhile, the water resistance test results of this novel monolithic catalysts that showed good tolerance to water and sulfur [110].

5. Conclusions and Perspectives

Recent progress on the sulfur and water resistance of Mn-based catalysts for the low-temperature selective catalytic reduction of NO_x has been reviewed comprehensively in this work. Although much progress has been made, many questions still need to be answered, and many problems need to be solved:

- (1) The exploration of novel Mn-based catalysts with excellent resistance to SO₂ and H₂O is still worthwhile. Resistance to SO₂ and H₂O directly decides whether this catalyst can be commercialized. Up to now, mixing (or doping) MnO_x with suitable metal oxides and loading Mn-based active components on a suitable support are considered an efficient strategy. Discovering new doping elements and novel supports may be promising research directions.
- (2) The actual effect of every specific doping element on tolerance promotion needs to be explained. To date, many works have been done to test the tolerance of Mn-based catalysts to H₂O and SO₂. However, the reasons why the tolerance of Mn-based catalysts to H₂O and SO₂ can be enhanced by mixing (or doping) them with other suitable elements need to be further explored in detail.
- (3) The role of support ought to be further analyzed. Does support only provide a higher specific surface area and a good dispersion of Mn? Is the support involved in SCR reaction? Such questions need to be answered.
- (4) Long-term tolerance tests need to be conducted. Most tests only last for several hours, and it is hard to predict the long-term performance of the catalyst under H₂O and SO₂ poison.
- (5) N₂ selectivity is an important indicator for the commercialization of SCR catalysts, which is closely related to the yield of N₂O. However, there is currently a lack of research on the effect of SO₂ on N₂ selectivity over Mn-based catalysts. Therefore, it is necessary to carry out this research in the near future.
- (6) Most studies focus on powder catalysts. From a commercial perspective, monolithic catalysts should be given more consideration.

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