

Review

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

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Abstract: Low-temperature NH₃-SCR is an efficient technology for NO_x removal from flue gas. The carbon-based catalyst designed by using porous carbon material with great specific surface area and interconnected pores as the support to load the active components shows excellent NH₃-SCR performance and has a broad application prospect. However, overcoming the poor resistance of H₂O and SO₂ poisoning for carbon-based catalysts remains a great challenge. Notably, reviews on the sulfur and water resistance of carbon-based low-temperature NH₃-SCR catalysts have not been previously reported to the best of our knowledge. This review introduces the reaction mechanism of the NH₃-SCR process and the poisoning mechanism of SO₂ and H₂O to carbon-based catalysts. Strategies to improve the SO₂ and H₂O resistance of carbon-based catalysts in recent years are summarized through the effect of support, modification, structure control, preparation methods and reaction conditions. Perspective for the further development of carbon-based catalysts in NO_x low-temperature SCR is proposed. This study provides a new insight and guidance into the design of low-temperature SCR catalysts resistant to SO₂ and H₂O in the future.

Keywords: low-temperature SCR; carbon-based catalysts; SO₂ and H₂O resistance; NO_x



Citation: Shen, Z.; Ren, S.; Zhang, B.; Bian, W.; Xing, X.; Zheng, Z. Sulfur and Water Resistance of Carbon-Based Catalysts for Low-Temperature Selective Catalytic Reduction of NO_x: A Review. *Catalysts* **2023**, *13*, 1434. <https://doi.org/10.3390/catal13111434>

Academic Editor: Maria J. Sabater

Received: 23 September 2023

Revised: 3 November 2023

Accepted: 9 November 2023

Published: 13 November 2023



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1. Introduction

Nitrogen oxide (NO_x) mainly comes from iron and steel enterprises, electric power enterprises, and other fixed sources [1]. As one of the air pollutants, it not only reacts with hydrocarbons to form photochemical smog through ultraviolet irradiation, but it also reacts with water in the air to generate the main component of acid rain, causing a series of serious environmental problems [2–4]. This poses a serious threat to the human respiratory system. Therefore, it is an increasingly urgent task to remove NO_x. Currently, several denitration technologies, including selective non-catalytic reduction (SNCR) [5–7], selective catalytic reduction (SCR) [8,9], and non-selective catalytic reduction (NSCR) [10,11], can be used to reduce NO_x. Among them, selective catalytic reduction (SCR) for the removal of NO_x is considered to be one of the most promising technologies which has been commercialized for both stationary and mobile NO_x sources. The choice of catalyst is crucial for the application of SCR denitration technology. Depending on the efficiency of NO_x removal, primarily the operating temperatures, process parameters, and catalyst regeneration, various catalysts including metal (titanium, vanadium, and iron, etc.) oxides [12], noble metals [13], zeolites [14], and activated carbon [15,16] have been developed for the NH₃-SCR process. At present, V₂O₅/TiO₂ [17,18] and V₂O₅-WO₃/TiO₂ [19] catalysts with high activity and sulfur resistance have been widely used in industrial denitration [20,21]. However, the traditional V-based catalyst temperature is 300–400 °C [22], which does not apply for most industrial flue gas cleaning with lower practical temperature. For example, in the iron

and steel industry, the temperature of the sintering flue gas is generally 120–180 °C. It needs to be heated to the application temperature to satisfy the high temperature catalyst, a process that consumes a lot of energy. The supports, such as TiO₂, Al₂O₃, ZrO₂, SiO₂, and carbon-based materials [23–25], have important influence on the denitration performance. Among them, carbon-based materials have gradually become a promising support for low-temperature SCR catalysts due to their large specific surface area, developed pore structure, and broad resources [26]. Compared with titanium, iron, aluminum, and other metal oxide catalysts, the surface of carbon-based catalysts is abundant in oxygen functional groups that can well adsorb NO_x. In addition, the larger specific surface area can provide a place for the active metal to be highly dispersed. The catalysts with rare earth oxides and transition metal oxides as active components have excellent catalytic performance at low temperature, such as MnO_x/ACs [23,27], CeO_x/ACs [28,29], FeO_x/ACs [30], etc. In the flue gas, these carbon-based catalysts display high low-temperature SCR activity in atmospheres free of SO₂ and H₂O. In particular, the valence state of Mn-based catalysts is variable and the redox ability is superb, which display good denitration ability. However, when the flue gas contains SO₂ and H₂O, the denitration activity of catalysts decreases greatly [31–33]. For example, the actual sintering flue gas contains about 10–13% water vapor and 300–1500 mg/Nm³ SO₂ [34]. Under the conditions, the catalyst is prone to inactivate, which limits the practical application [35,36]. Therefore, it is necessary to develop the carbon-based catalysts with high SO₂ and H₂O resistance for low-temperature SCR technology.

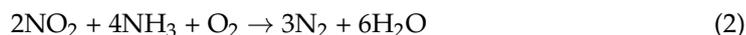
Over time, the related scholars have conducted a lot of work on the sulfur and water resistance of low-temperature NH₃-SCR catalysts and achieved remarkable results. In addition, the reviews in this area have been widely reported. A review by Zhang et al. comprehensively overviewed the progress of Mn-based catalysts in sulfur and water resistance and focused on analyzing the challenges and opportunities faced in the development of Mn-based catalysts [37]. A review by Xu et al. provided the reaction mechanism of Ce-based catalysts for low-temperature NH₃-SCR, and the technology to improve the resistance to sulfur and water was emphasized [38]. The recent review by Tang et al. also summarized the research progress of Mn-based catalysts in improving the denitrification activity of NH₃-SCR at low temperature and the resistance to sulfur and water, and the challenges and possible solutions for designing catalyst systems with high sulfur and water resistance were discussed in detail [39]. However, a review of sulfur and water resistance performance of carbon-based catalysts for low-temperature NH₃-SCR is rarely reported. This paper has reviewed the research findings on carbon-based catalysts in sulfur and water resistance in recent years. The reaction behavior of the low-temperature SCR catalyst and the poisoning mechanism in the flue gas containing SO₂ and H₂O are summarized. For carbon-based catalysts, strategies to enhance the SO₂ and H₂O resistance performance are systematically introduced from the aspects of catalyst support, modification, structure control, and preparation methods. In addition, the application of theoretical calculation in the development of low-temperature SCR carbon-based catalysts resistant to SO₂ and H₂O is introduced. Finally, the possible development direction in this field is proposed, which plays a certain reference and guidance role for the design of low-temperature carbon-based catalysts resistant to SO₂ and H₂O in the future.

2. Reaction Mechanisms of Carbon-Based Catalysts for SCR Denitration

2.1. Reaction Mechanisms of Carbon-Based Catalysts

NO oxidation on carbon-based catalysts is a micropore filling process with NO as the adsorbate. NH₃-SCR mainly uses NH₃ as the reducing agent, which selectively reduces NO_x to N₂ and H₂O at a temperature of 80–400 °C. The catalytic process lowers the activation energy of the chemical reactions [36]. Typical NH₃-SCR reaction equations are shown in Equations (1) and (2).



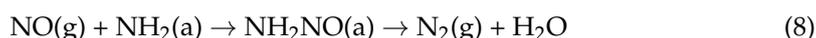


If the O_2 is absent, the reaction equations are shown as Equations (3)–(5).



At present, there are two generally recognized mechanisms of the NH_3 -SCR reaction, Eley–Rideal (E-R) [40] and Langmuir–Hinshelwood (L-H) [41,42] mechanisms.

For the E-R mechanism, NH_3 -SCR of NO_x occurs through Equations (6)–(8). NH_3 is adsorbed and oxidized to NH_2 by acid sites. Then, NH_2 active intermediates react with the gas phase NO to form N_2 and H_2O .



The NH_3 -SCR of NO_x according to the L-H mechanism occurs via Equations (6), (9) and (10). NO reacts with O_2 to generate adsorbed NO_2 , which reacts with coordinating NH_3 to form N_2 and H_2O .



Carbon-based materials show larger specific surface area and abundant pore structure, which provide more active sites for the reaction. More gas phases NO and O_2 are captured on the empty active sites. NO adsorbed on the carbon surface is oxidized to adsorbed NO_2 . The adsorbed NO_2 further reacts with NH_3 and NO to generate N_2 and releases the active vacancies so that the whole reaction continues. Among them, the adsorption of NO_2 on the AC surface involves the participation of NO, and the adsorbed NO_2 oxidizes the AC surface, thereby promoting the subsequent NO_2 adsorption.

For carbon-based catalysts, at a temperature of 80–200 °C, the NH_3 -SCR reaction mainly follows the L-H mechanism, or the two mechanisms cooperate. At a higher temperature above 200 °C, it mainly follows the E-R mechanism.

2.2. Poisoning Mechanisms of Carbon-Based Catalysts

The active temperature range of carbon-based NH_3 -SCR catalysts is rather low, about 100–150 °C, which avoids the clogging of pores on the surface of the catalyst due to excessive temperature. However, they are easily poisoned by H_2O and SO_2 , leading to catalyst deactivation, which seriously affects their application and development in industry. Therefore, in order to improve H_2O and SO_2 tolerance, relevant scholars have conducted a lot of research on the mechanism of SO_2 and H_2O poisoning in the process of carbon-based catalyst denitration.

2.2.1. Poisoning of SO_2

The catalytic performance of carbon-based catalysts is severely affected by SO_2 [43–46]. The effects of SO_2 poisoning can be divided into reversible inactivation and irreversible

inactivation. The competitive adsorption of SO_2 and NO on carbon-based catalysts is a reversible deactivation. In an irreversible situation, when the adsorbed SO_2 reacts with the active components on the carbon-based catalysts' surface, it generates sulfate, which occupies the active center, resulting in a decrease in available active sites and NO_x conversion (Figure 1). For $\text{CeO}_2\text{-WO}_3/\text{TiO}_2$ catalysts shown in Figure 2, the introduction of SO_2 prevents the generation of active intermediates, such as NH_2NO . In addition, SO_2 reacts with NH_3 or CeO_2 to form $(\text{NH}_4)_2\text{SO}_4$ and $\text{Ce}_2(\text{SO}_4)_3$, respectively, which cover the active sites and inhibit the redox performance. This results in the irreversible inactivation. In addition, industrial flue gas usually contains other metals such as Cd , and SO_2 binding with it also produces CdSO_4 to cover the active sites, causing further deactivation of the catalyst. The production of sulfate on carbon-based catalysts' surface covering the active sites and the vulcanization of the active metal are the two main forms of permanent deactivation. As shown in Figure 3, the addition of SO_2 to a MnFeO_x catalyst results in the production of MnSO_4 , FeSO_4 , and $(\text{NH}_4)_2\text{SO}_4$, which inhibit both L-H and E-R mechanisms. Thus, the catalysts display poor SCR activity. When Sm is dropped, SO_2 is preferred to combine with it. As a result, the active sites could be protected. The addition of another metal that preferentially reacts with SO_2 is the main method to enhance the SO_2 resistance of carbon-based $\text{NH}_3\text{-SCR}$ catalysts.

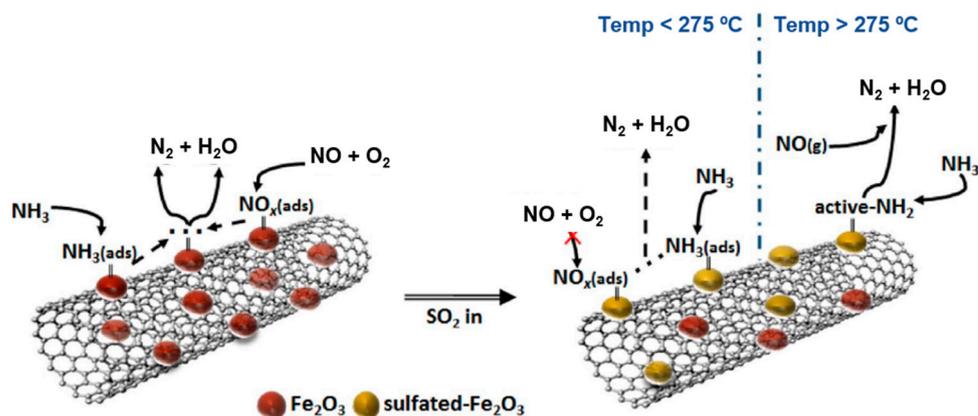


Figure 1. Reaction routes for fresh Fe/CNTs and $\text{SO}_2\text{-Fe/CNTs}$ catalysts. (Reproduced with permission from reference [43], Copyright 2018, MDPI (Basel, Switzerland)).

2.2.2. Poisoning of H_2O

Water vapor deprives the catalyst surface of available active sites, thereby negatively affecting the SCR reaction [43,47]. Generally, the poisoning mechanism of H_2O includes both reversible inactivation and irreversible inactivation. Among them, the competitive adsorption between H_2O and NH_3 (or NO) is the main reason for the reversible deactivation (Figure 4). When the adsorption of reactive gas molecules is lower, the NO_x conversion rate also decreases. At a lower temperature, the thermal stability of hydroxyl groups is poor, and water has a significant effect on the catalyst activity, resulting in irreversible deactivation. However, when the temperature is higher than $200\text{ }^\circ\text{C}$, water vapor is not easily adsorbed on the catalyst surface, and the effect of water on the catalyst activity can be ignored. Water vapor affects the crystal shape, grain size, and specific surface area of carbon-based catalysts to a certain extent, which results in a reduction in catalytic activity. The adsorption of water molecules on a carbon-based catalyst surface competes with reaction gases for the active sites, reducing the active centers available and thus decreasing the activity of the catalyst.

2.2.3. Poisoning of SO_2 and H_2O

So far, the poisoning mechanism of H_2O and SO_2 of low-temperature SCR catalysts has been widely recognized, and the study of the mechanism of carbon-based catalysts resisting SO_2 and H_2O has made some progress [48,49]. It needs to be emphasized that some catalysts have good resistance to single SO_2 or H_2O , and the denitration rate could be

maintained at a relatively high level. However, when SO_2 and H_2O coexist, the denitration rate decreases sharply. The main reason is that the reaction of H_2O and SO_2 produces H_2SO_4 , which accelerates the sulfation of the active metal oxides. Therefore, we still need to conduct in-depth research on carbon-based catalysts with both sulfur and water resistance. As shown in Figure 5, when SO_2 is introduced, it is absorbed on the MnO_x surface and oxidized to SO_3 . When the sulphates accumulate to a certain amount, the formation of SO_4^{2-} polymers result in a reduction in the surface area and the inhibition of redox property. Washing with water can remove SO_4^{2-} polymers and restore the catalytic activity of active components.

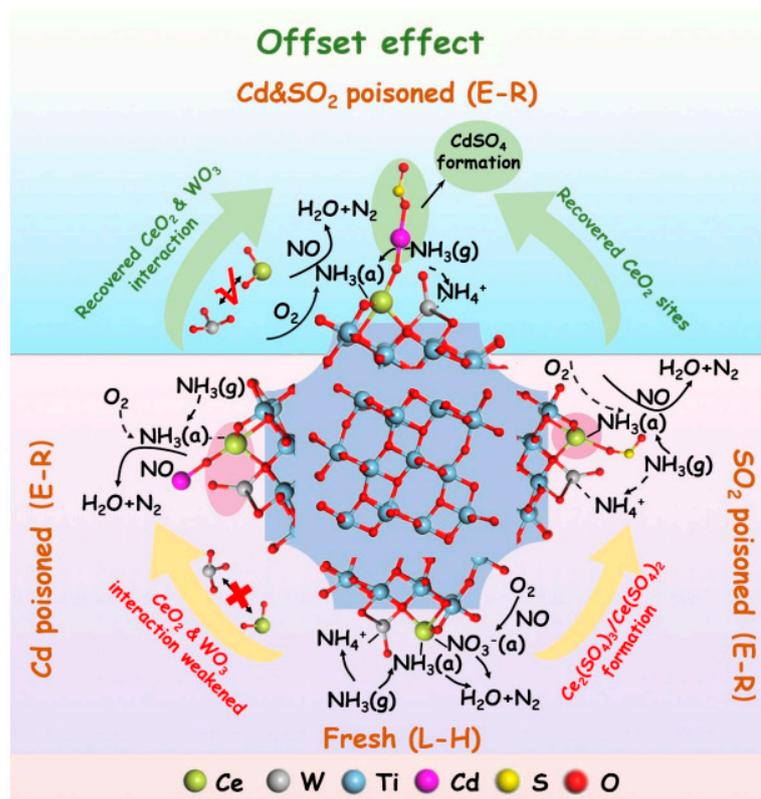


Figure 2. Offset effects between Cd and SO_2 over $\text{CeO}_2\text{-WO}_3/\text{TiO}_2$ catalysts. (Reproduced with permission from reference [44], Copyright 2020, American Chemical Society (Washington, DC, USA)).

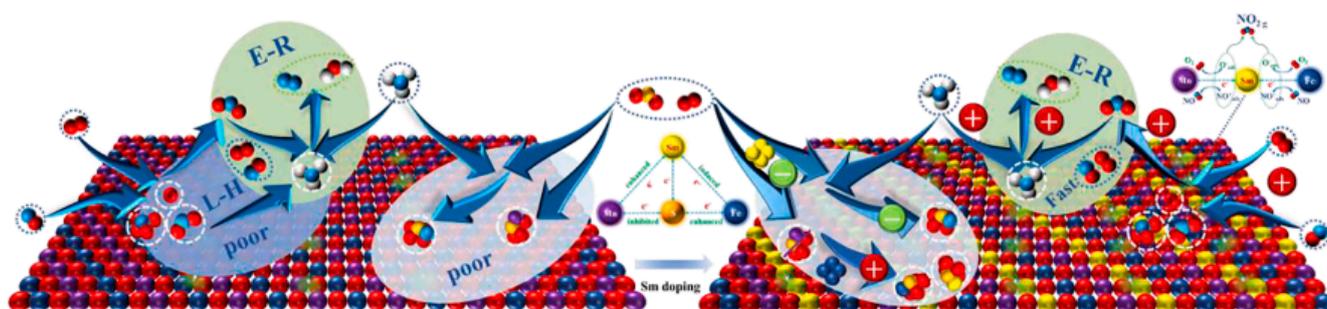


Figure 3. Mechanism model of Sm promoting SCR activity and SO_2 resistance over MnFeO_x catalysts. (Reproduced with permission from reference [46], Copyright 2022, Elsevier (Amsterdam, The Netherlands)).

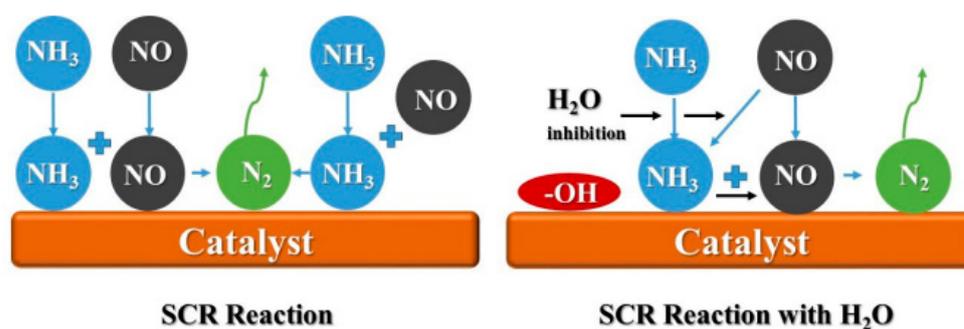


Figure 4. Scheme of regular SCR reaction and H₂O poisoning effect. (Reproduced with permission from reference [43], Copyright 2018, MDPI (Basel, Switzerland)).

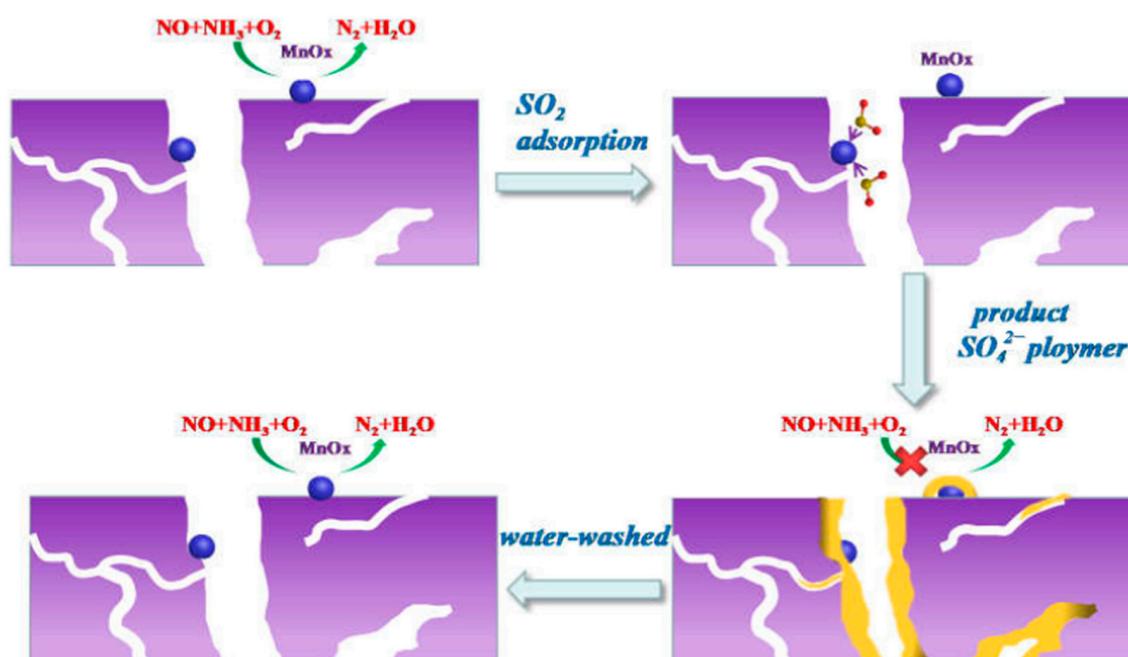


Figure 5. Proposed sulfur-treated poisoning and water-washed regeneration mechanism model. (Reproduced with permission from reference [48], Copyright 2021, MDPI (Basel, Switzerland)).

3. Research Progresses of Carbon-Based Catalysts for SO₂ and H₂O Resistance

In order to improve the denitration activity and enhance the anti-toxic ability of the catalysts, the finding of suitable supports and active components is necessary [50]. The research progress of SO₂ and H₂O resistant carbon-based catalysts was introduced as follows [51,52].

3.1. Effects of Support

In industrial applications, in terms of thermal stability, mechanical strength, and large specific surface area, the supported catalyst is superior to the non-supported oxide catalyst. Selecting a suitable support is an important way to improve the anti-poisoning ability of carbon-based catalysts. In the presence of O₂, SO₂ will react with NH₃ to form (NH₄)₂SO₄, leading to the blockage of the pores of the catalyst, and H₂O is adsorbed on the surface of the support to inhibit the adsorption of reaction gas. It is noted that the number of acid centers affects the adsorption performance of SO₂. Therefore, an important method to enhance the resistance of SO₂ and H₂O is to improve the surface acidity of the support [53–55]. At present, the commonly used carbon support mainly includes activated carbon, carbon nanotubes, activated carbon fiber, and graphene. The carbon-based catalysts for SCR described above are summarized in Table 1.

Table 1. The carbon-based catalysts for SCR.

Catalysts	Active Test Reaction Conditions	NO _x Conversion/ Temperature	N ₂ Selectivity/ Temperature	SO ₂ Tolerance/ Water-Resistance	Ref.
Activated carbon/coke	[NH ₃] = 550 ppm [NO] = 500 ppm [O ₂] = 5 vol% [SO ₂] = 50 ppm [H ₂ O] = 10 vol% balance of N ₂ GHSV = 50,000 h ⁻¹	>40%/ (150 °C)	-	>38%/ >32%	[51]
Carbon nanotubes	[NH ₃] = 500 ppm [NO] = 500 ppm [O ₂] = 5 vol% [H ₂ O] = 3 vol% balance of N ₂ GHSV = 60,000 h ⁻¹	>80%/ (200 °C)	>60%	-	[56]
Activated carbon fiber	[NH ₃] = 500 ppm [NO] = 500 ppm [O ₂] = 5 vol% balance of N ₂ GHSV = 40,000 h ⁻¹	>75%/ (150 °C)	-	-	[57]
Graphene	[NH ₃] = 500 ppm [NO] = 500 ppm [O ₂] = 7 vol% [H ₂ O] = 10 vol% balance of N ₂ GHSV = 67,000 h ⁻¹	>90%/ (150 °C)	>90%	>80%/ >95%	[58]

3.1.1. Activated Carbon/Coke

Due to the advantages of abundant surface groups, large specific surface area, high porosity, and strong adsorption capacity, activated carbon/coke (AC) has attracted extensive attention and is widely used as catalyst support [51]. As shown in Figure 6, the reaction of NO on MnO_x-Cu/AC catalysts follows both L-H and E-R mechanisms. For the E-R mechanism, NO in the gas phase reacts with NH₃ activated by the acidic sites on the catalyst surface. For the L-H mechanism, NO and O₂ in the gas phase interact and are oxidized to nitrate or nitrite intermediates by the catalyst, which then react with activated NH₃. It is worth noting that regardless of the mechanism, the activation of NH₃ at the acidic site is a key step for the reaction to proceed. The adsorption properties of AC are impacted by changing the polarity and/or acidity of surface functional groups. The main active sites on activated carbon are different kinds of oxygen-containing groups. Some researchers believe that for the V₂O₅/AC catalyst, in the presence of H₂O, SO₂ will react with NH₃ and O₂ to form ammonium sulfate, causing the pores of the catalyst to be blocked. As shown in Figure 7, after the introduction of SO₂, the activity of the V₂O₅/AC catalyst decreased rapidly, then had a weak rise, and finally declined slowly to remain a stable value [53]. However, when the SO₂-poisoned V₂O₅/AC catalyst was characterized, it is observed that only a small part of the pores on surface are blocked by sulfate. The generation of VOSO₄ via the reaction of V₂O₅ and SO₂ caused the NO conversion to drop sharply, which is the main reason for the deactivation of the catalyst. The sulfurization of active metal oxides by SO₂ is the main cause of the irreversible inactivation of most carbon-based catalysts in sulfur-containing flue gas. For Mn-Ce/AC catalysts shown in Figure 8, SO₂ reacted with NH₃ to inhibit the reaction of NO and NH₃ [54]. On the other hand, SO₂ combined with manganese oxide and cerium oxide to form MnSO₄ and (Ce)₂(SO₄)₃, which caused permanent inactivation. The addition of V could improve the acidity of the catalyst surface and inhibit the combination of SO₂ and NH₃. In addition, the vulcanization of Mn-Ce solid solution is also prevented. Therefore, the sulfur resistance of the catalyst could be enhanced.

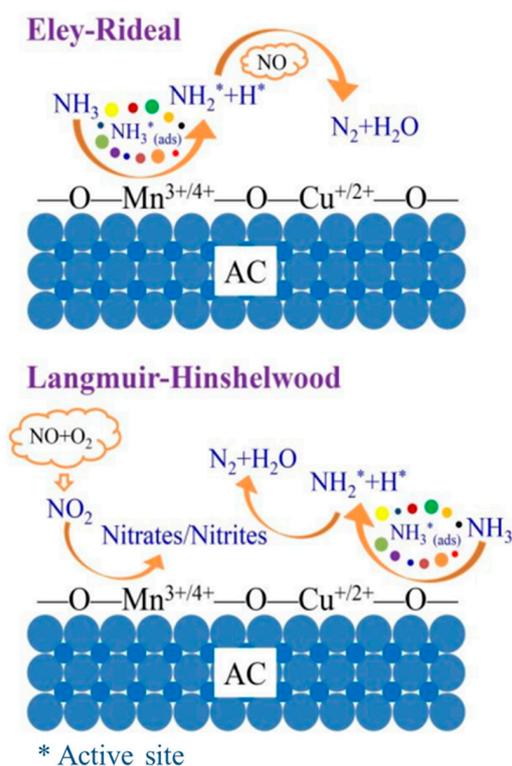


Figure 6. NO removal mechanism of the $\text{MnO}_x\text{-Cu}/\text{AC}$ catalyst. (Reproduced with permission from reference [51], Copyright 2020, MDPI (Basel, Switzerland)).

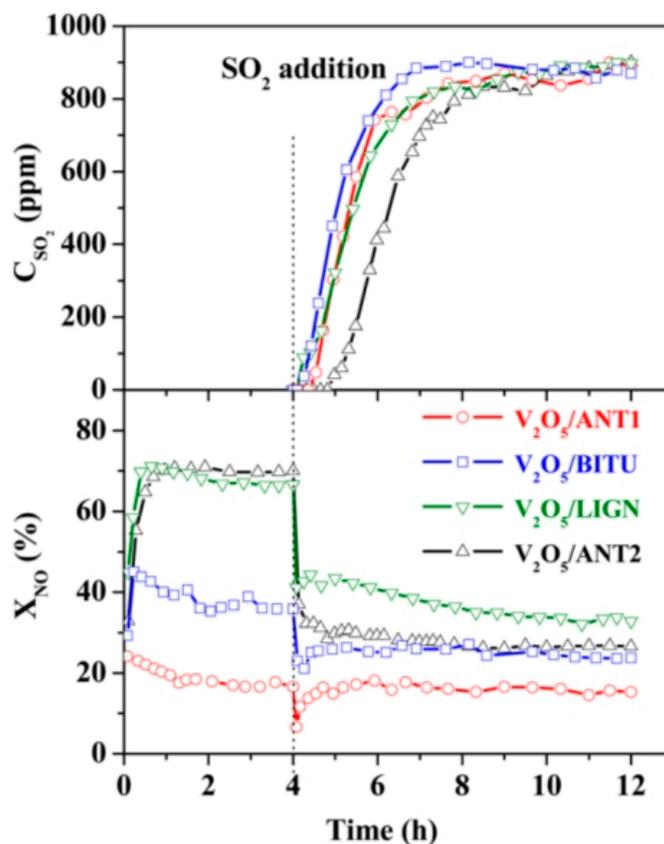


Figure 7. NO conversions and SO_2 release concentrations during the SCR of NO over various $\text{V}_2\text{O}_5/\text{AC}$ catalysts at 200 °C. (Reproduced with permission from reference [53], Copyright 2014, American Chemical Society (Washington, DC, USA)).

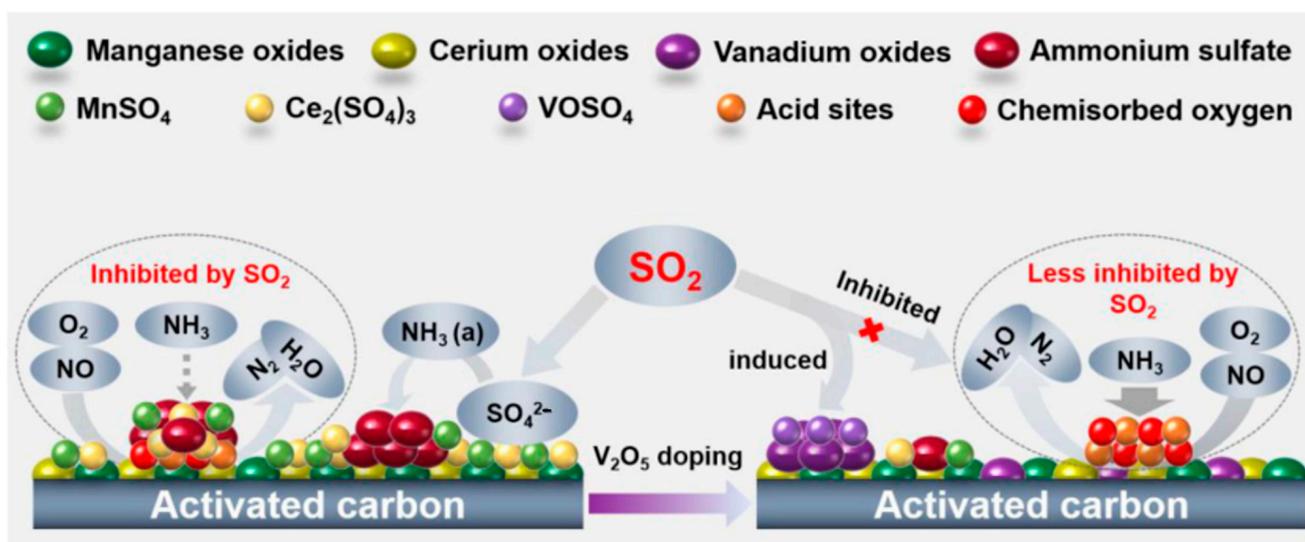


Figure 8. Mechanism of SO_2 tolerance over Mn–Ce(0.4)–V/AC catalysts. (Reproduced with permission from reference [54], Copyright 2019, Elsevier (Amsterdam, The Netherlands)).

In addition, different types of activated carbons have different specific surface areas and pore volumes. Among them, Mn–Ce catalysts supported by charcoal and coal exhibit a large specific surface area and strong surface acidity, which leads to an increase in adsorbed oxygen and high dispersibility of metal oxides with high catalytic activity. Meanwhile, the surface properties of AC have an obvious influence on the structure and performance of the supported catalysts. Nitric acid treatment can enhance the surface acidity of activated carbon and the dispersibility of active components and can significantly improve the NO conversion and SO_2 resistance of the catalyst [56]. However, AC catalysts are still prone to deactivation when SO_2 reaches a certain level. Therefore, further efforts should be made to strengthen the SO_2 resistance of SCR catalysts.

3.1.2. Carbon Nanotubes

As an allotrope of carbon, the pore size of carbon nanotubes (CNTs) can range from several nanometers to 100 nm. CNTs have adjustable nano hollow tubular structures, with a specific surface area of generally about 50–1300 m^2/g and a tensile strength of 50–200 GPa [59,60]. CNTs are used as supports for NH_3 -SCR catalysts due to their high adsorption capacity of NO_x and NH_3 as well as good SO_2 and H_2O resistance (Figure 9). At present, the research on CNT supports mainly focuses on the morphology of CNTs and the direction of CNTs composite supports. Wang et al. [61] elucidated the effects of SO_2 and water vapor on Ce/AC-CNTs catalysts. Obviously, when adding 50 ppm of SO_2 , the Ce/AC-CNTs catalyst had a small inhibition on NO conversion, which was only reduced by 4.8%. In addition, when H_2O was introduced, the activity of Ce/AC-CNTs reduced by 21.7%, while the NO conversion of Ce/AC declined by 30.6%. CNTs can not only change the oxidation state of surface oxygen and active components but also increase the concentration of chemically adsorbed oxygen species. CNTs have a certain resistance to SO_2 and H_2O [62]. The morphology of CNTs is also related to the performance of the catalyst. When SO_2 and H_2O coexist, the denitration rate of multi-shell CNT catalysts is nearly 60% higher than that of ordinary CNT catalysts. Multi-shell CNTs can effectively inhibit the generation of surface sulfate species [63]. However, due to the limitations of the preparation process and scale of CNTs, the cost of CNTs is very high, which is known as “black gold”. The use of CNTs as catalyst supports is still in the stage of laboratory research and has not been industrialized.

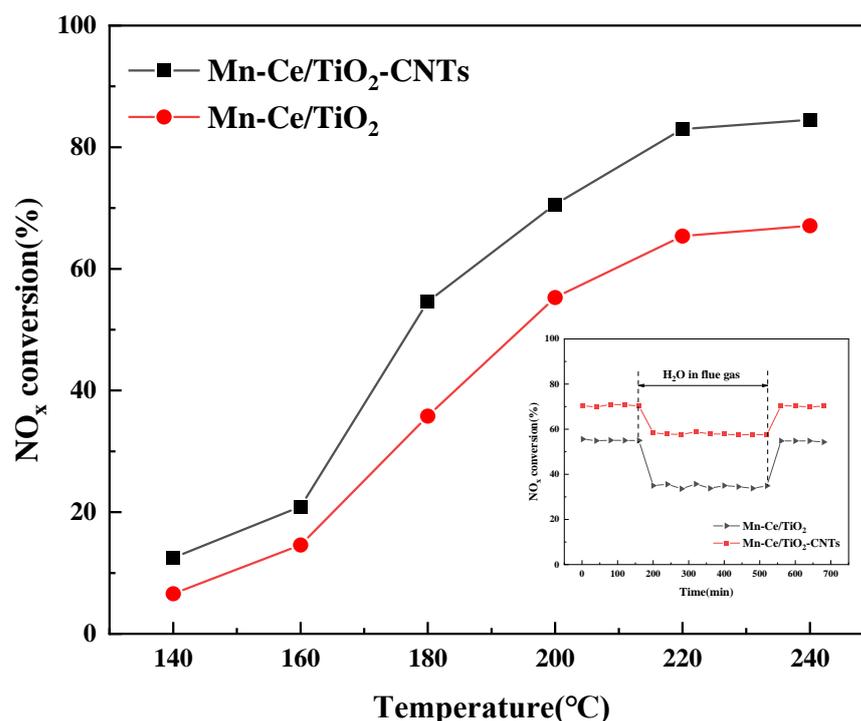


Figure 9. NO_x conversion over Mn–Ce/TiO₂ and Mn–Ce/TiO₂–CNTs catalysts. (Reproduced with permission from reference [59], Copyright 2021, Elsevier (Amsterdam, The Netherlands)).

3.1.3. Activated Carbon Fiber

Activated carbon fiber (ACF) is usually a porous fiber material that is activated by carbon fiber or various carbon-containing materials at high temperature. ACF has a large specific surface area which can reach 1000–1500 m²/g or even more than 2000 m²/g. Among the pores of ACF, the proportion of micropores accounts for more than 90%, most of which are distributed on the fiber surface with narrow pore size, uniform distribution, easy contact with adsorbates, and strong adsorption capacity for low-concentration adsorbates. Hence, it has a fast adsorption and desorption rate and excellent adsorption and separation performance.

ACF has a certain catalytic activity and strong adsorption capacity for NO, and the adsorbed NO and O₂ in micropores can be converted into NO₂. However, the removal efficiency of NO using ACF as a catalyst alone is low. The highest NO conversion of ACF in the range of 150–310 °C is only about 15%. When 10% CeO₂ is added to ACF, the denitration activity is greatly improved. In the temperature range of 140–240 °C, more than 85% of the denitration rate can be achieved, which is higher than that of the same amount of the MnO_x catalyst [64]. The catalytic activity of ACF can be greatly increased by modifying it with active components (Figure 10). However, the cost of catalysts supported by activated carbon fiber is also very high, and it has not been applied in industry at present.

3.1.4. Graphene

Compared with other carbonaceous supports, Graphene (GE), as a novel type of carbon nanomaterial, has a unique planar extension structure with a specific surface area of 100–2600 m²/g and conductivity of 10⁶–10⁸ S/m [65]. The excellent electronic properties can promote electron transfer in the redox process, which accelerates the catalytic reaction. The special structure of GE can disperse active components to improve the interaction, which produces more active oxygen species and active sites to enhance the low-temperature catalytic activity. TiO₂-GE nanocomposite support shows uniform components, which is conducive to increasing the specific surface area of the carrier, changing its pore structure characteristics, and promoting the uniform loading of active ingredients. At 180 °C, the NO

conversion of the $\text{CeO}_x\text{-MnO}_x/\text{TiO}_2\text{-GE}$ catalyst reaches 95% [66]. As a catalyst support, GE can also inhibit the sulfation of active components. Compared with the unsupported catalyst [67], the GE catalyst has a strong resistance ability for H_2O and SO_2 (Figure 11). The NO_x conversion is restored from 73% to 79% at 180 °C after the H_2O and SO_2 is stopped. However, the existing graphene preparation process is immature, which limits the large-scale application.

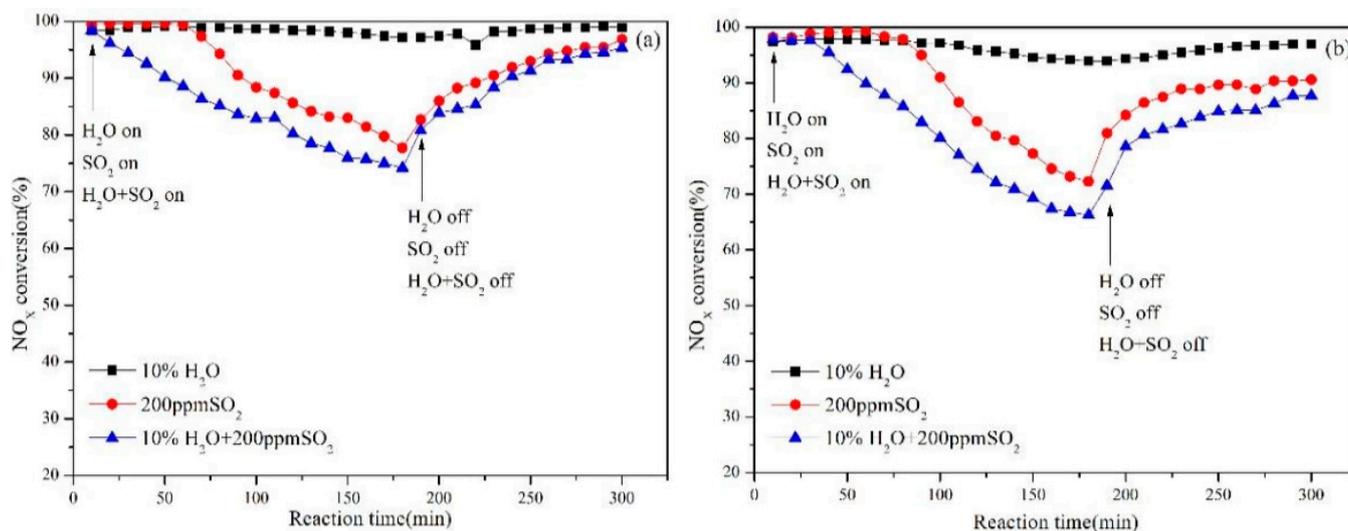


Figure 10. Effects of H_2O or/and SO_2 on NO_x conversion of (a) $\text{MnO}_x\text{-CeO}_2$ (8:1)/GR and (b) $\text{MnO}_x\text{-CeO}_2$ (2:1)/GR at 140 °C. (Reproduced with permission from reference [64], Copyright 2017, Elsevier (Amsterdam, The Netherlands)).

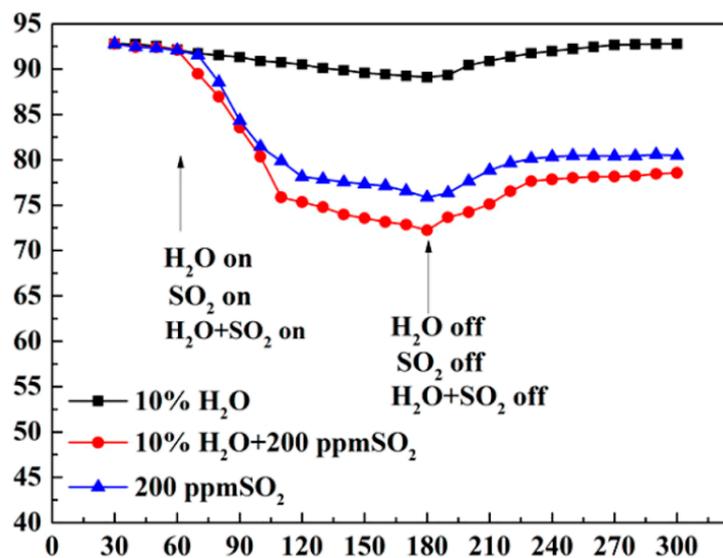


Figure 11. Effect of H_2O and SO_2 on NO_x conversion over $7\%\text{MnO}_x/\text{TiO}_2\text{-0.8\%GE}$ catalysts. (Reproduced with permission from reference [67], Copyright 2014, American Chemical Society (Washington, DC, USA)).

3.2. Effects of Modification

Many scholars have studied the influence of active components on the anti-toxicity and denitration performance of the catalysts [68,69]. At present, more research is focused on Mn-based catalysts [70] and Ce-based catalysts [71]. Additionally, there are other metal oxide catalysts such as V and Fe catalysts. This section mainly introduces the related

research on the single modification, bimetallic modification, and polymetallic modification of metal oxides.

3.2.1. Single Metal Oxide-Modified Catalysts

Single metal-modified catalysts mainly include Mn-modified catalysts, Ce-modified catalysts, Fe-modified catalysts, V-modified catalysts, and other modified catalysts.

Single Mn-Modified Catalysts

Mn-based catalysts, as a research hotspot, have a variety of valence states and excellent redox ability, easily carry out the oxidation reaction, and have higher catalytic performance at low temperatures.

Generally, the higher valence state shows the better catalytic effect for Mn-based catalysts. The SCR activity decreases as follows: $\text{MnO}_2 > \text{Mn}_5\text{O}_8 > \text{Mn}_2\text{O}_3 > \text{Mn}_3\text{O}_4$ [72]. MnO_x -modified catalysts can increase the dispersity of amorphous states, the ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$, and the surface area and pore volume, which improves the NO conversion [73]. The performance of the catalyst is enhanced by adding Mn in an amount in the range of 10–20 wt.%. When the content of Mn increases to 25 wt.%, MnO_x particles gather on the catalyst surface and the NO conversion decreases (Figure 12). However, SO_2 has a serious toxicity to single Mn-based catalysts. The active Mn atoms are sulfated after the introduction of SO_2 , which leads to rapid deactivation. It is usually difficult to regenerate for the deactivated Mn-based catalysts.

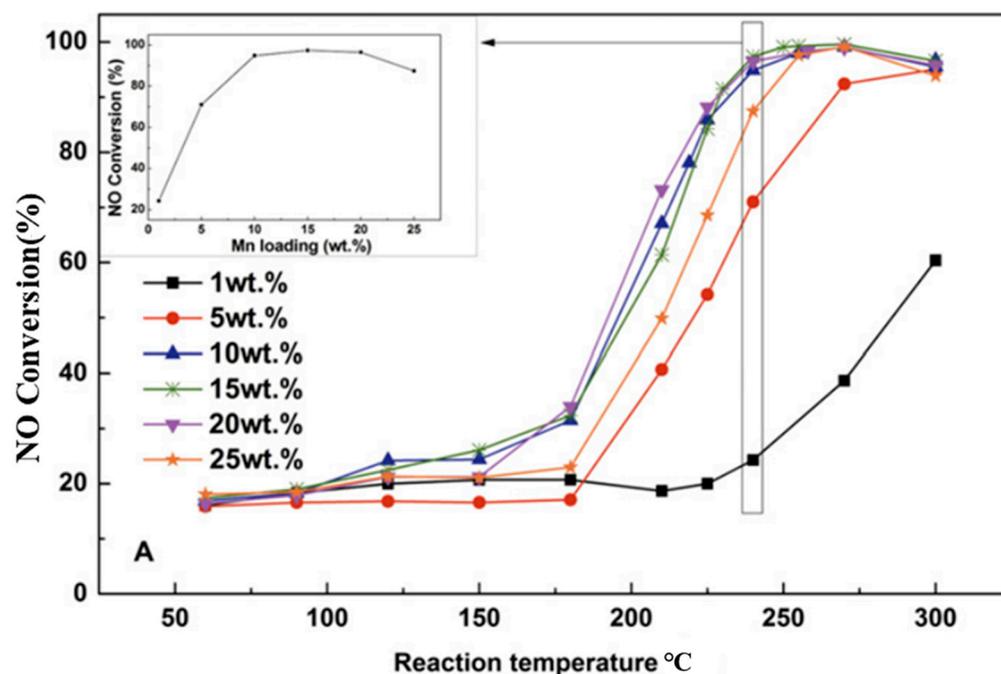


Figure 12. Effect of Mn loading of $\text{MnO}_x/\text{MWCNTs}$ (60–100, 500) catalysts on catalytic activity. (Reproduced with permission from reference [68], Copyright 2021, Elsevier (Amsterdam, The Netherlands)).

Single Ce-Modified Catalysts

As an important rare earth metal oxide, CeO_2 has strong redox performance and excellent oxygen storage/release ability. Between Ce^{4+} and Ce^{3+} , the electron transfer promotes an increase in active oxygen species and accelerates the conversion of NO to NO_2 , thereby improving the activity of SCR. Therefore, CeO_2 is usually used as an active component to improve NH_3 -SCR activity. Doping the rare earth element Ce effectively facilitates the generation of oxygen vacancies. The high concentration of oxygen vacancy is favorable for the adsorption of O_2 and the further oxidation of NO, which is conducive to the subsequent

reduction reaction [38]. In all temperature ranges, the maximum NO conversion of CeO₂ nanoparticles is only 50%. The NO conversion on pure carbon nanotubes is extremely low. While carbon nanotubes are introduced as supports for CeO₂, the NO conversion rate is increased significantly for all catalysts. In the temperature range of 250 °C to 370 °C, the CeO₂/CNTs platinum catalysts display the best activity, corresponding to above 90% NO conversion. For CeO₂/CNTs-PM catalysts, the maximum conversion of NO can only reach 80% below 380 °C [74]. The catalysts with a lower addition have less dispersed active sites, an incomplete catalytic reduction reaction, and low denitration efficiency. Appropriate CeO₂ content can enhance the active sites on the catalyst surface and improve the catalytic performance. Excessive CeO₂ loading causes the CeO₂ particles to aggregate on the surface, which leads to a reduction in active sites. Compared with CeO₂ nanoparticles, CeO₂ nanotubes on the catalyst surface have more Ce and O atoms, more acidic centers, and stronger acidity, which is conducive to improve SCR performance [75]. The SO₂ can preferentially bind with CeO₂ to form Ce₂(SO₄)₃, thereby reducing the generation of (NH₄)₂SO₄ and NH₄HSO₄ to suppress catalyst deactivation (Figure 13) [76]. Therefore, CeO₂-modified catalysts have broad prospects.

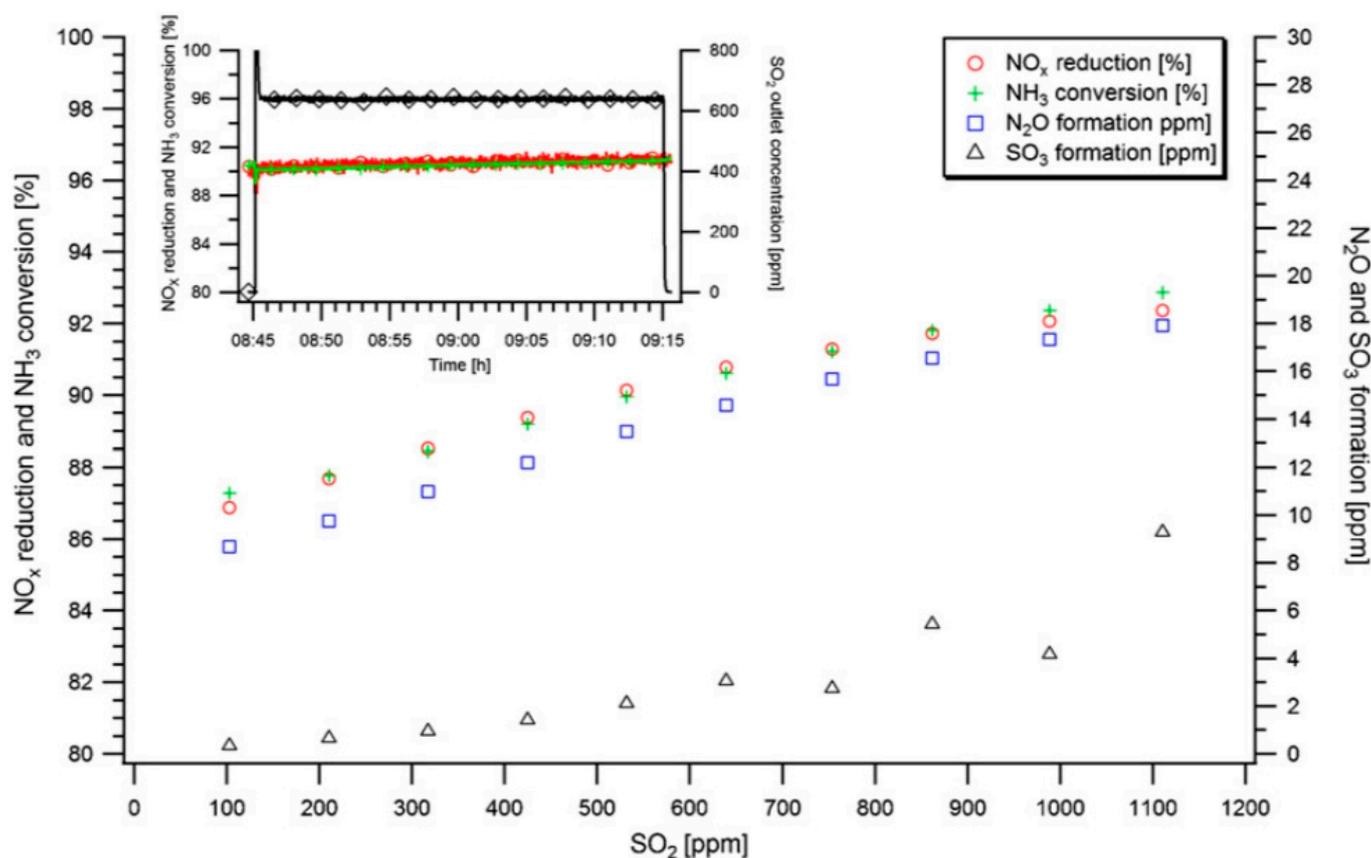


Figure 13. Influence of the SO₂ concentration on the NO_x reduction performance over sample of V₂O₅-WO₃/TiO₂. (Reproduced with permission from reference [76], Copyright 2012, Elsevier (Amsterdam, The Netherlands)).

Single Fe-Modified Catalysts

Iron in Fe₂O₃ has a variety of valence states such as +2 and +3, which shows good redox properties. In addition, it has the characteristics of non-toxic and harmless, wide source, and low price. The mutual conversion between Fe²⁺ and Fe³⁺ can form unstable oxygen vacancies and lattice oxygen species with high transfer ability. Therefore, Fe is often used as the active component and support of catalysts and has attracted extensive attention among scholars [77–79]. For Fe-modified AC catalysts, when the molar ratio of

Fe to AC was 0.10 [80], the performance was optimal, exhibiting 83.9% NO conversion at 240 °C. However, when the ratio was 0.15, the Fe₂O₃/AC catalyst displayed poor NO conversion. The influences of SO₂, H₂O, or SO₂ + H₂O on the NO_x conversions of 8Mn6Fe/AC catalysts were investigated in [81]. The NO_x conversion decreased by 12% when H₂O was introduced into the reactor, due to a competitive adsorption between NH₃ and H₂O, and then, the activity remained stable. Fe was mainly dispersed in the form of γ-Fe₂O₃. After the introduction of Mn, the ratio of Fe³⁺/Fe²⁺ + Fe³⁺ changed only a little, and the value of O_β/(O_β + O_α) increased significantly. The doping of Mn increased the amount of chemisorbed oxygen with higher migration ability, which could oxidize NO to NO₂ to form a “fast SCR” reaction, thus promoting the denitration performance and SO₂ resistance of the catalysts (Figure 14).

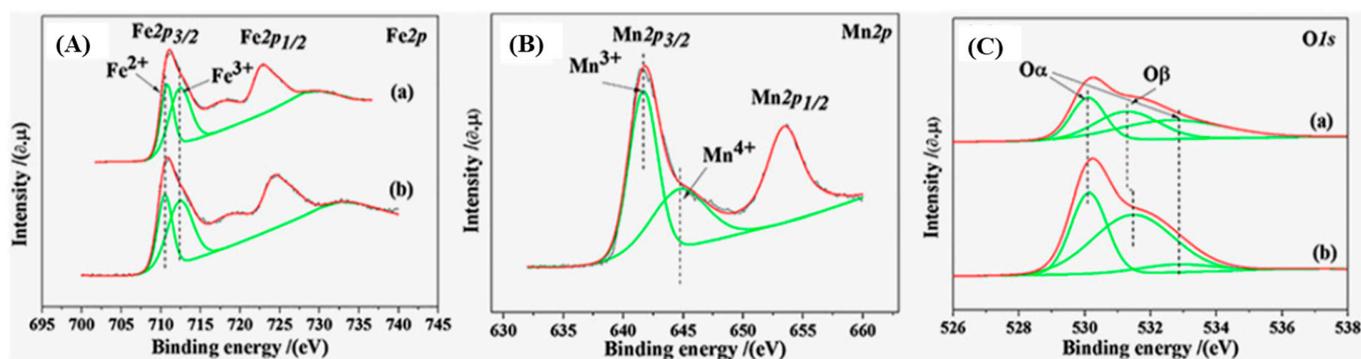


Figure 14. XPS spectra for (A) Fe 2p, (B) Mn 2p, and (C) O 1s of Fe₂O₃/AC (a) and Mn-Fe₂O₃/AC (b) catalysts. (Reproduced with permission from reference [81], Copyright 2018, Wiley-Blackwell (Hoboken, NJ, USA)).

Single V-Modified Catalysts

Vanadium is a rich material with low cost and high energy efficiency which can be loaded on the support to increase the activity and anti-poisoning ability of catalysts. In the field of NH₃-SCR [82,83], traditional vanadium-titanium catalysts are widely applied, which makes more researchers explore vanadium-titanium catalysts that meet the anti-poisoning performance and low-temperature denitration performance.

V₂O₅/AC catalysts have a high SO_x absorption capacity at 120–200 °C [84]. When the V addition is 5%, the NO conversion can reach 80% at 250 °C. After adding SO₂, the NO conversion increases to more than 90%. For the abnormal phenomenon of increasing NO conversion, it is found that the interaction of AC with vanadium oxide activates the ammonium sulfate on the low-loaded V₂O₅/AC catalyst. The activated species react with NO, increase the acidity on the surface, and enhance the catalytic activity. Catalysts with V₂O₅ as the active component do not perform as well as Mn-based catalysts in low-temperature SCR reactions, but its sulfur resistance is obviously higher than Mn-based catalysts.

Other Single-Modified Catalysts

In addition to MnO_x, CeO₂, FeO_x, and V₂O₅ modification, there are also some other modified catalysts which can also improve the denitration performance and poisoning resistance [85–87]. For nickel-supported carbon-based catalysts, appropriate pore structure and surface area can improve the SO₂ resistance. Doping the transition metal oxide CrO₃ on activated carbon can increase the formation of acid sites. Due to the valence change between Cr⁶⁺ and its low oxidation states, such as Cr⁵⁺, Cr³⁺, and Cr²⁺, the reaction rate of SCR is increased. When the mass ratio of Cr/AC is 2%, the NO removal efficiency is optimal, and the NO conversion rate is more than 90% at 125–150 °C. The NO conversion on the catalyst decreases after the addition of 100 ppm SO₂. When 300 ppm SO₂ is added, the NO conversion reduces to only about 5%. When 5% H₂O is added, the NO conversion

decreases by about 15%. The NO conversion decreases to 71.5% within a few minutes under the conditions of 100 ppm SO₂ and 5% H₂O [88]. The coexistence of H₂O and SO₂ leads to the formation and deposition of ammonium sulfate, which blocks active sites on the catalysts and inactivates the catalysts.

However, single-modified catalysts show weak surface acidity, relatively low activity, a narrow working temperature window, and poor resistance of SO₂ under high temperature, which limit their practical application.

3.2.2. Bimetallic-Modified Catalysts

Bimetallic-modified catalysts mainly introduce Mn–Ce catalysts, Fe–Mn catalysts, V–Mn catalysts, and other bimetallic-modified catalysts.

Mn–Ce Catalyst

Manganese-containing catalysts show excellent catalytic activity, while SO₂ resistance ability is poor. CeO₂ has excellent redox properties and certain sulfur resistance. The addition of Ce can enhance the oxygen storage capacity of the catalyst and the capacity of NO oxidation to NO₂. The NO conversion of MnO_x–CeO₂/AC catalysts is maintained at 92% at 210 °C after adding SO₂, which has excellent resistance to SO₂ toxicity [89]. The sulfation of active components is not obvious within a short time at 210 °C, and there is no obvious accumulation of NH₄HSO₄ in the reaction process. CeO₂ could reduce the bond energy of NH₄⁺ and SO₄²⁻ and lower the decomposition temperature of NH₄HSO₄ to enhance the SO₂ resistance. When the support is carbon nanotubes, the Mn–CeCNTs-R catalyst has good dispersibility of active components on its surface [90]. Under the conditions of 4 vol% H₂O and 100 ppm SO₂, it shows strong tolerance. With the coexistence of H₂O and SO₂, the NO conversion of the catalyst decreases by 13%. The NO conversion rate returns to 90% after stopping the addition of SO₂ and H₂O (Figure 15). Compared with the single metal-modified catalysts, the resistance to SO₂ of Mn–Ce bimetallic catalysts is significantly improved.

Fe–Mn Catalyst

At low temperatures, Fe–Mn bimetallic oxides have high NO conversion and SO₂ resistance. The NO conversion of Mn–FeO_x/CNTs catalysts is close to 98% at 180 °C and decreases by 20% after adding SO₂ [91]. By being in the form of amorphous oxides, Fe and Mn are highly dispersed on the support surface so that the catalyst has good redox performance. The NO conversion of Fe₂O₃@MnO_x/CNTs catalysts decreases from 95% to 91% and recovers to 95% after SO₂ and H₂O removal, while MnO_x/CNTs catalysts only recovered to 36% and could not be restored to the initial level [60]. The resistance of Fe–Mn bimetallic catalysts to SO₂ and H₂O is better than Mn–Ce bimetallic catalysts.

Other Bimetallic-Modified Catalysts

In addition to the above bimetallic catalysts, other bimetallic catalysts can also enhance resistance to H₂O and SO₂ performance. For instance, CeMo(0.3) hollow microsphere catalysts prepared with carbon microspheres as a template not only have the best low-temperature SCR performance [92] but have good stability and H₂O resistance as well (Figure 16). For Fe₂O₃/AC catalysts, doping Ce can make γ-Fe₂O₃ evenly disperse on the AC surface, and the denitrification efficiency is significantly improved. Moreover, the sulfur resistance can be enhanced. The catalysts with a Ce/Fe mass ratio of 0.5:6 can achieve 94.1% NO conversion when 100 × 10⁻⁶ (vol) SO₂ is added at 240 °C. When H₂O is 5 wt.%, the NO conversion is stable at 86%. The introducing of slight vanadium oxide can enhance the dispersity of Fe species on Fe₂O₃/AC catalysts [93]. Whether it is V-modified or non-V-modified, in the presence of H₂O and SO₂, catalysts are severely deactivated. But at low space velocities, the inhibition caused by H₂O and SO₂ is reversible for 3%Fe-0.5%V catalysts. The addition of V species prevents the generation of sulfate by increasing the surface acidity, thereby enhancing the resistance to SO₂.

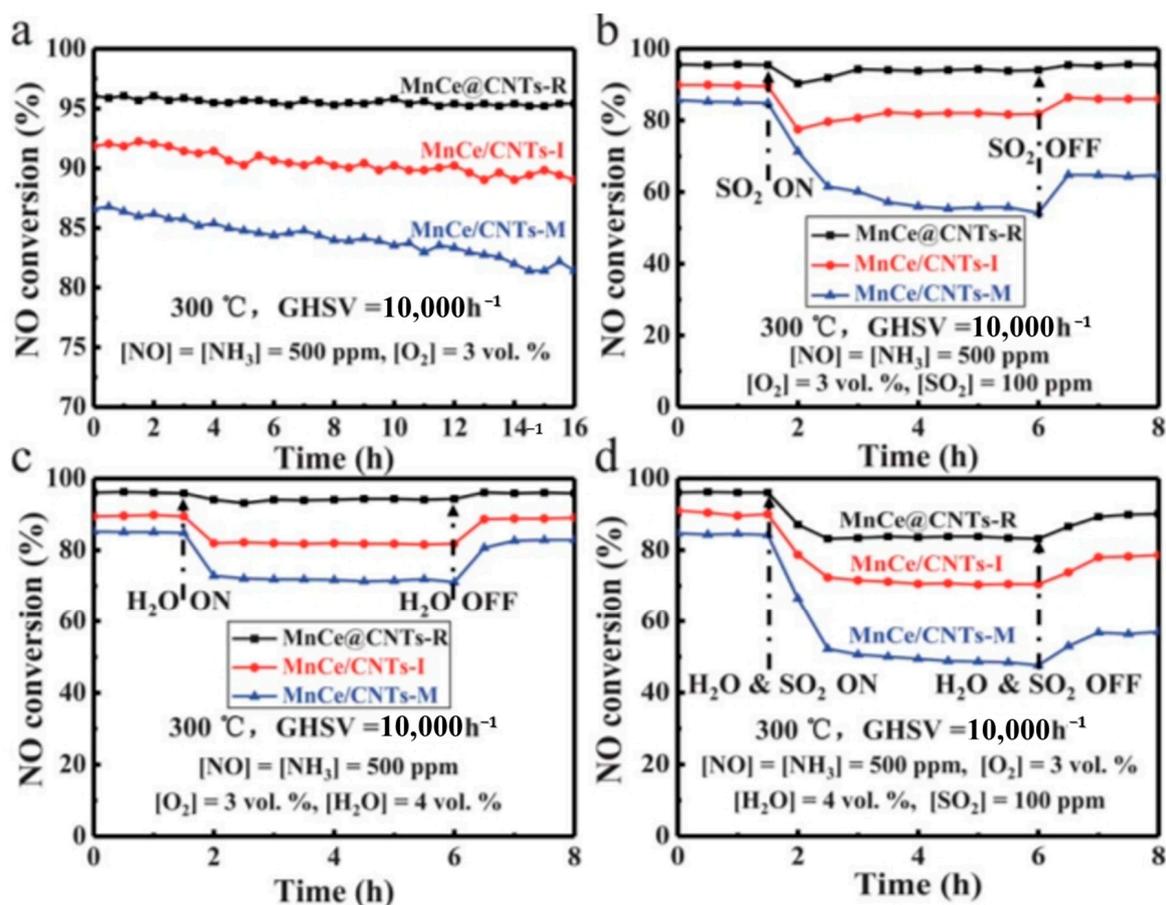


Figure 15. NH_3 -SCR performance of Mn–Ce@CNTs–R catalysts. (a) Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 3 \text{ vol}\%$, N_2 balance, and $\text{GHSV} = 10,000 \text{ h}^{-1}$. (b) Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 3 \text{ vol}\%$, N_2 balance, and $\text{GHSV} = 10,000 \text{ h}^{-1}$, $[\text{SO}_2] = 500 \text{ ppm}$. (c) Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 3 \text{ vol}\%$, N_2 balance, and $\text{GHSV} = 10,000 \text{ h}^{-1}$, $[\text{H}_2\text{O}] = 4 \text{ vol}\%$. (d) Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 3 \text{ vol}\%$, N_2 balance, and $\text{GHSV} = 10,000 \text{ h}^{-1}$, $[\text{H}_2\text{O}] = 4 \text{ vol}\%$, $[\text{SO}_2] = 500 \text{ ppm}$. (Reproduced with permission from reference [90], Copyright 2018, Royal Society of Chemistry (London, UK)).

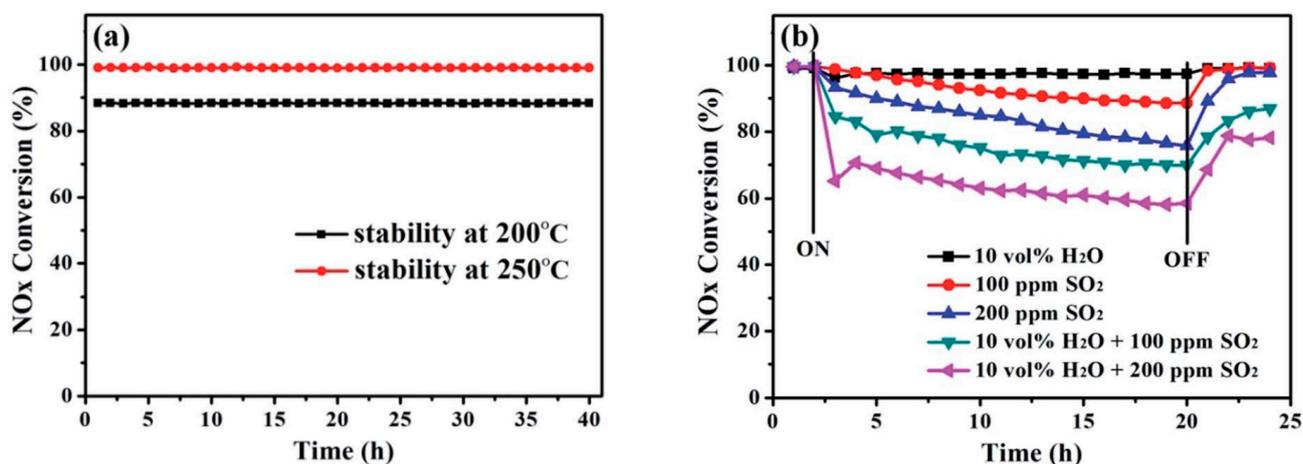


Figure 16. (a) The study of thermal stability and (b) H_2O resistance and SO_2 tolerance at $250 \text{ }^\circ\text{C}$ on CeMo(0.3) hollow microspheres. Reaction conditions: $[\text{NO}] = [\text{NH}_3] = 500 \text{ ppm}$, $[\text{O}_2] = 5\%$, balanced in N_2 . (Reproduced with permission from reference [92], Copyright 2016, Royal Society of Chemistry (London, UK)).

3.2.3. Polymetallic-Modified Catalyst

Polymetallic-modified catalysts mainly introduce Fe–Mn–Ce catalysts, V–Mn–Ce catalysts, and other polymetallic-modified catalysts.

Fe–Mn–Ce Catalysts

Fe is often used as an additive to modify the catalyst. The effect of doping Fe on AC-supported Mn–Ce oxide catalysts are investigated for NH₃-SCR. When the content of Fe is 5%, the NO conversion of Mn–Ce–Fe/AC is 90% at 125 °C and 12,000 h^{−1} space velocity [94]. As shown in Figure 17, the metal ions can enter the graphite crystal structure of AC and divide it into smaller graphene fragments. The doping of Fe can inhibit the decrease in surface area in the calcining process of the catalyst. In addition, the ratios of Mn⁴⁺/Mnⁿ⁺ and Ce³⁺/Ceⁿ⁺ and the amount of adsorbed oxygen and acid increase significantly after Fe doping. The main reason is that the Fe species expose the active sites of the acid or influence the chemical state of Mn/Ce species. The performance and SO₂ resistance of Mn–Fe–Ce/ACN catalysts is better than that of Mn/ACN catalysts. As shown in Figure 18, the surface acidity, reducibility, and surface chemisorbed oxygen are improved due to the addition of FeO_x and CeO₂, which promote the NH₃-SCR performance [95]. In addition, the stronger surface acidity inhibits the adsorption of SO₂ and the consumption of SO₂ to adsorbed NH₃. Moreover, a small amount of SO₂ adsorbed on the catalyst surface reacts preferentially with CeO₂ to protect the main active components MnO_x and FeO_x from sulfation.

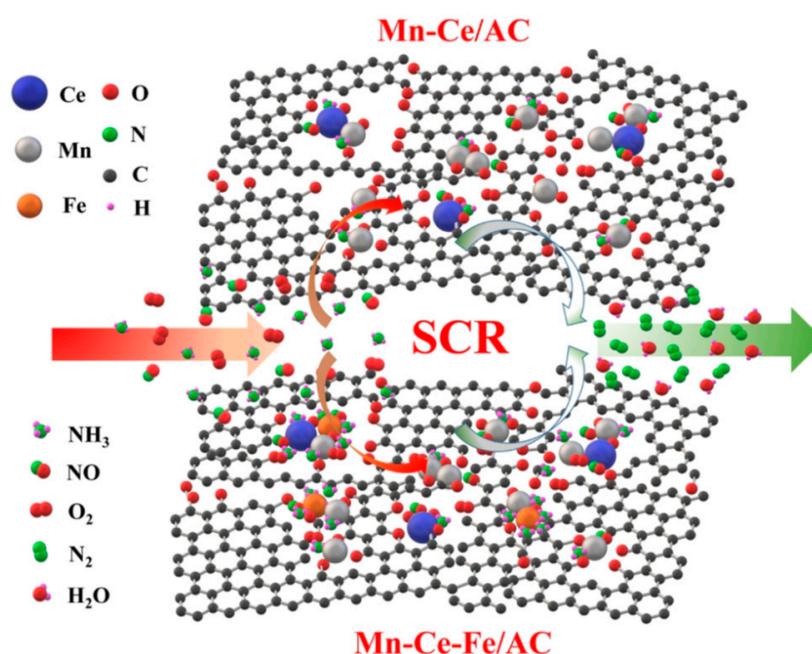


Figure 17. Reaction diagram of Mn–Ce/AC and Mn–Ce–Fe/AC catalysts for NO removing. (Reproduced with permission from reference [94], Copyright 2020, Elsevier (Amsterdam, The Netherlands)).

V–Mn–Ce Catalyst

For Mn–Ce/AC catalysts, doping V₂O₅ can obviously increase the NO conversion and improve SO₂ resistance. Whether it is V–Mn–Ce/AC or Mn–Ce/AC catalysts, their NO conversions are close to 98% at 200 °C. After adding SO₂, the NO conversion decreases slightly to about 90% for V–Mn–Ce/AC catalysts, and there is little change after SO₂ removal. For Mn–Ce/AC catalysts, the NO conversion drops significantly to around 68%, and it hardly restores after SO₂ removal. In the coexistence of SO₂ and H₂O, the deactivation of V–Mn–Ce/AC is more pronounced and the inhibition is irreversible, compared to the presence of SO₂ alone (Figure 19) [54]. Doping V₂O₅ enriches the chemically adsorbed oxygen and

enhances the surface acidity, which accelerates the reaction of SCR. To some extent, the V_2O_5 clusters prevent SO_2 forming and sulfating the dispersed Mn–Ce solid solution.



Figure 18. Mechanism of better SO_2 tolerance by doping FeO_x and CeO_x to Mn/CAN. (Reproduced with permission from reference [95], Copyright 2021, Elsevier (Amsterdam, The Netherlands)).

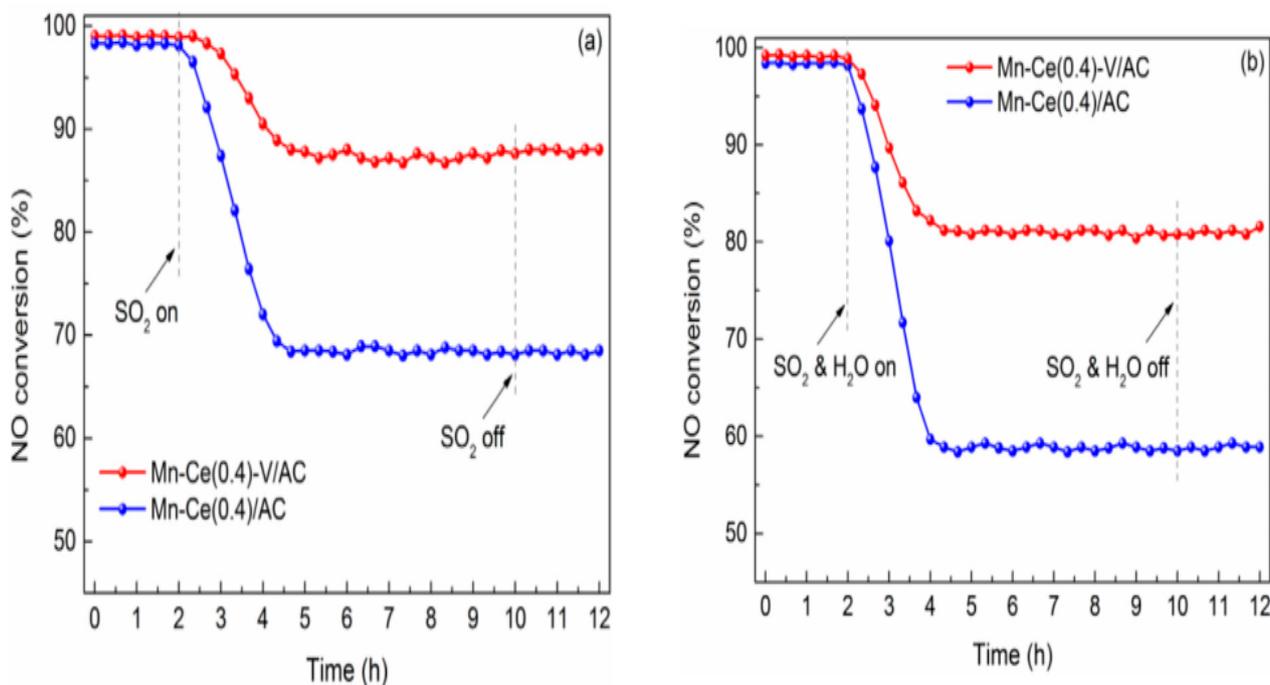


Figure 19. NO conversion over (a) Mn–Ce/AC and V–Mn–Ce/AC in the presence of SO_2 and (b) combined SO_2/H_2O at 200 °C. (Reproduced with permission from reference [54], Copyright 2019, Elsevier (Amsterdam, The Netherlands)).

Other Polymetallic-Modified Catalysts

Novel core-shell structure $\text{SiO}_2@\text{FeO}_x\text{-CeO}_x/\text{CNTs}$ catalysts have good SO_2 resistance and high stability. The introduction of 500 ppm SO_2 shows little influence on the catalytic activity, and the NO removal rate is about 90% [96]. $\text{Fe-V}_2\text{O}_5/\text{TiO}_2\text{-CNT}$ catalysts also show excellent SCR performance. The NO conversion of the $\text{Fe}_3\text{-V}/\text{Ti-C}$ catalyst decreases from 96% to 91% after the addition of SO_2 [97]. When SO_2 is stopped, the activity recovered to 94% (Figure 20). In the coexistence of oxygen, water vapor, and sulfur dioxide, the NO conversion of the $\text{Cu-Ce-Fe-Co}/\text{AC}$ catalyst remains at 100% for 240 min [98].

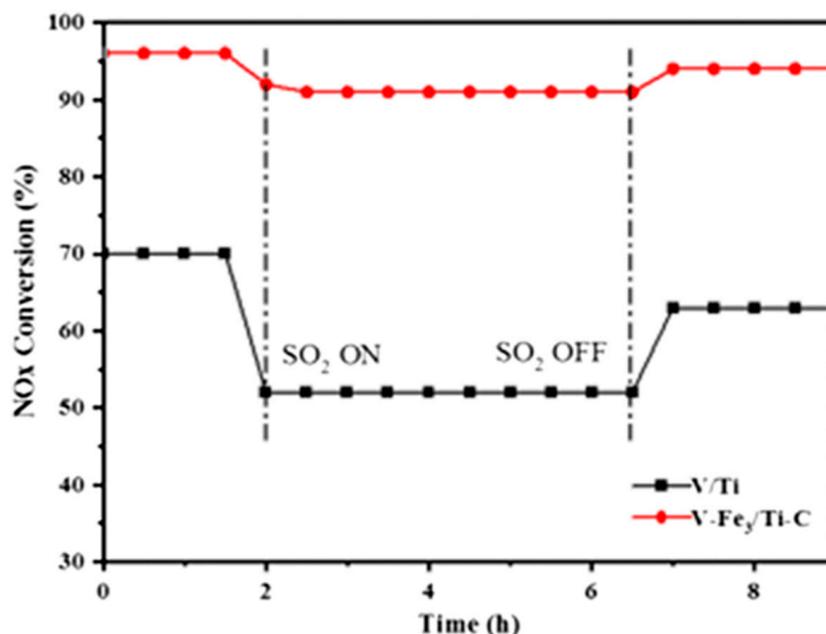


Figure 20. Catalytic reduction of NO_x over V/Ti and $\text{V-Fe}_3/\text{Ti-C}$ catalysts. (Reproduced with permission from reference [97], Copyright 2020, Springer Netherlands (Berlin, Germany)).

3.3. Application of Theoretical Calculation

As one of the most commonly used methods in computational chemistry, density functional theory (DFT) takes electron density instead of wave function as the research object. For DFT calculations [99–102], it can establish that quantity a SCR catalytic reaction is a fast process which cannot be understood by experimental characterization. The structure–activity relationships are revealed by simulating the adsorption process of active molecules and toxic molecules on the catalyst surface. The adsorption behavior of NO , NH_3 , and O_2 on the $\text{Fe}_x\text{O}_y/\text{AC}$ surface is investigated by DFT. On vacancies of the AC surface, Fe_xO_y clusters are stably adsorbed with accompanying charge redistribution. These are nitroso, nitro, and nitrite when NO is adsorbed on the surface of $\text{Fe}_x\text{O}_y/\text{AC}$ (Figure 21) [103]. Through DFT analysis and calculation, the adsorption process of reaction gases on the Mn-MOF-74 metal-organic framework catalyst system can be obtained. It was found that the molecules had competitive adsorption at the Mn metal sites. Compared with H_2O , SO_2 can displace NH_3 more easily, which explains the poisoning difference between H_2O and SO_2 [104]. In addition, DFT calculations have shown that the SCR activity of the $\text{Fe}_x\text{O}_y/\text{AC}$ catalyst is 28% higher than that of the corresponding oxide catalyst. Carbon deposition increases both the amount of intermediate/strong acid centers and the reducibility of catalytic centers.

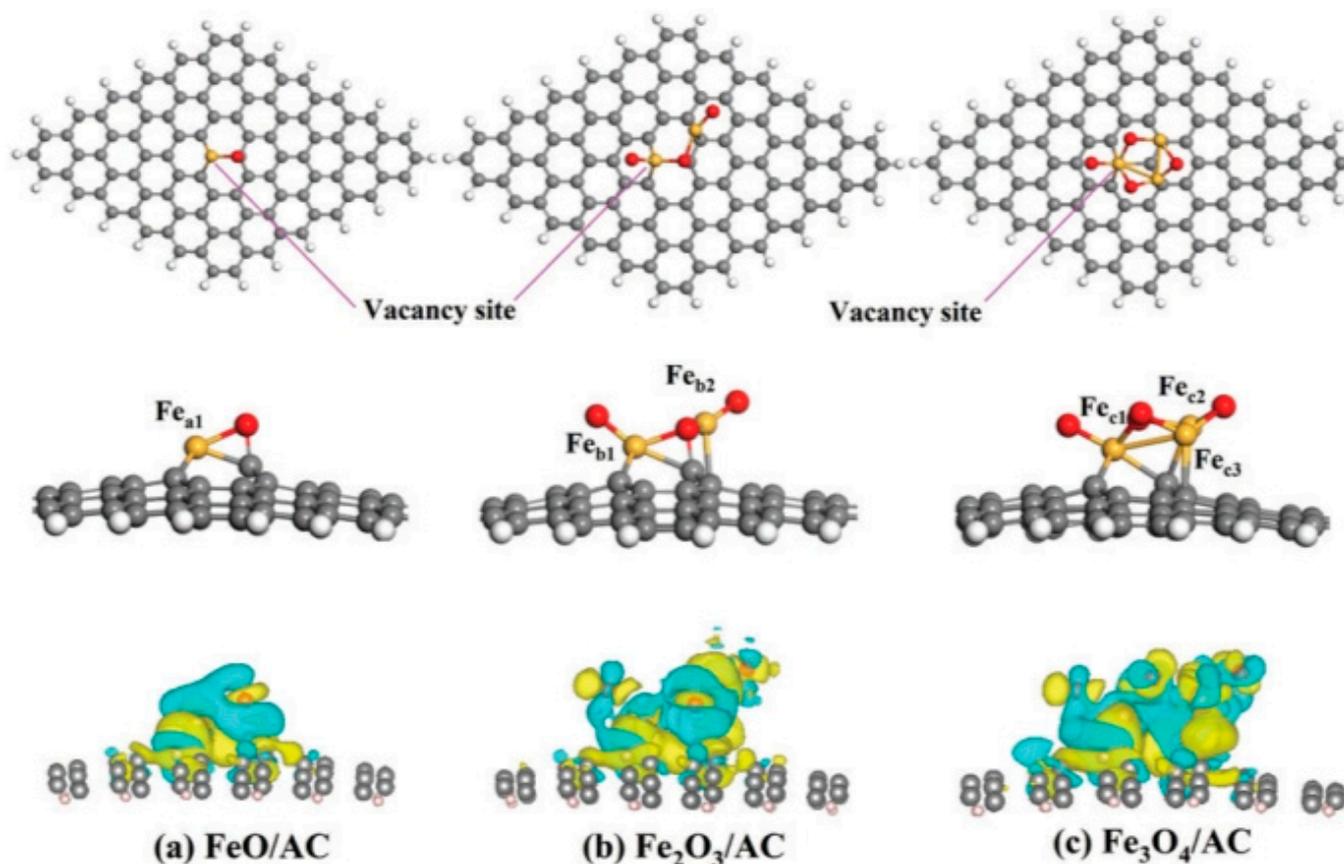


Figure 21. Configurations of $\text{Fe}_x\text{O}_y/\text{AC}$ surface (Fe: golden, O: red, C: gray, H: white) and the electron density difference plots of Fe_xO_y supported on the AC surface (cyan: loose electron, yellow: obtained electron). (Reproduced with permission from reference [103], Copyright 2021, Royal Society of Chemistry (London, UK)).

4. Other Strategies for Improving Sulfur and Water Resistance

In addition to selecting appropriate supports and active components for modification, it can also be improved by controlling the preparation method and reaction conditions of the catalyst for the SO_2 and H_2O resistance.

4.1. Preparation Methods

The successful support of metal oxide catalysts on adsorbents can be achieved by a variety of synthetic methods. So far, the preparation methods of denitration catalysts include the sol-gel method, citric acid method, precipitation method, ion exchange method, and impregnation method. The preparation method mainly affects the physical properties of the catalyst, including surface oxygen vacancy, pore volume, and specific surface area [105–107]. At present, the most common synthetic methods are impregnation and deposition precipitation. The enrichment of carbon support by completely immersing and mixing it with a metal precursor (i.e., copper nitrate solution) is called wet pore volume impregnation [108]. The $\text{MnO}_x\text{-CeO}_2/\text{P-CA}$ catalysts were prepared via incipient wetness impregnation using $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ as precursors on phosphorus-doped carbon aerogels (P-CA) for $\text{NH}_3\text{-SCR}$ of NO . The hydrophilicity of the carbon carrier for the $\text{MnO}_x\text{-CeO}_2/\text{P-CA}$ catalyst was improved, which was conducive to the dispersity of active components and enhanced the electronic interaction between MnO_x and CeO_2 . Even with the presence of SO_2 , the catalyst can still adsorb and oxidize more NO , forming more NO complexes. And the suppression of SO_2 to the SCR reaction is reduced through the L-H mechanism, which enhances the anti- SO_2 ability (Figure 22).

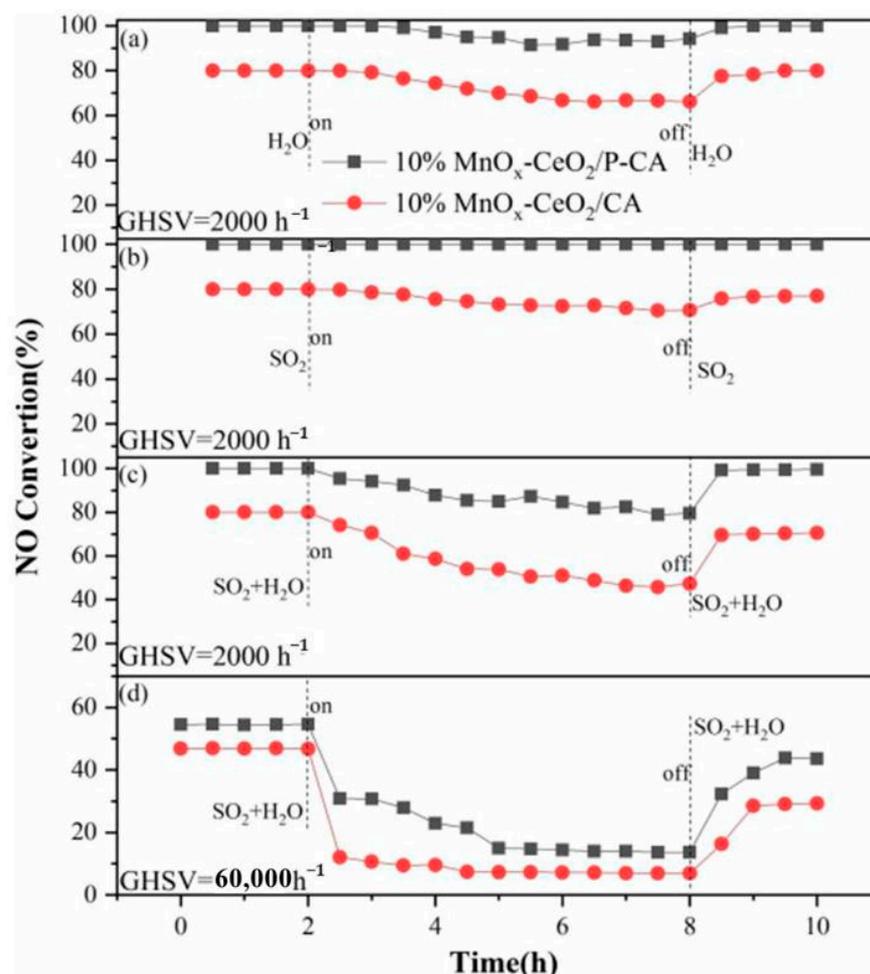


Figure 22. The influence of (a) H₂O, (b) SO₂, and (c) SO₂ + H₂O on the NO conversion of 10%MnO_x-CeO₂/CA and 10%MnO_x-CeO₂/P-CA catalysts under GHSV of 2000 h⁻¹ at 160 °C, and (d) SO₂ + H₂O resistance of 10%MnO_x-CeO₂/CA and 10%MnO_x CeO₂/P-CA catalysts under GHSV of 60,000 h⁻¹ at 200 °C. (Reproduced with permission from reference [108], Copyright 2021, Wiley-Blackwell Publishing Ltd. (Weinheim, Germany)).

Deposition precipitation means that the metal precursor (i.e., nitric acid) is dissolved with the precipitant, and the carbon support (bulk) is completely mixed and heated. The precipitation method could make the distribution of active components more uniform so they have better adsorption and oxidation properties for NO. However, the precipitation method generates more impurities, which affects the performance of the catalyst. The operation of the impregnation method is simple, while the dispersity of the obtained catalyst's metal active particles is low.

4.2. Preparation and Reaction Conditions

The catalytic performance of catalysts is affected by reaction temperature, space velocity, initial NO concentration, O₂ concentration, NH₃ concentration, and SO₂ concentration [98]. The NO_x conversion of Mn-Ce/AC catalysts calcined in a N₂, O₂, and air atmosphere is 94%, 75.6%, and 85.6%, respectively [109]. The catalyst calcined under the N₂ atmosphere could increase the dispersity of metallic oxides and enhance the surface acidity, reducing the oxidation and crystal formation of MnO₂ which positively impacts the catalytic oxidation performance and sulfur tolerance on catalysts. In addition, the impacts of loadings and precursors on the activity of MnO_x/ACs catalysts have been studied [110]. Mn₃O₄ using manganese acetate tetrahydrate as a precursor with a loading of 8% shows the best removal effect on NO, and the removal rate is 97% at 180 °C (Figure 23).

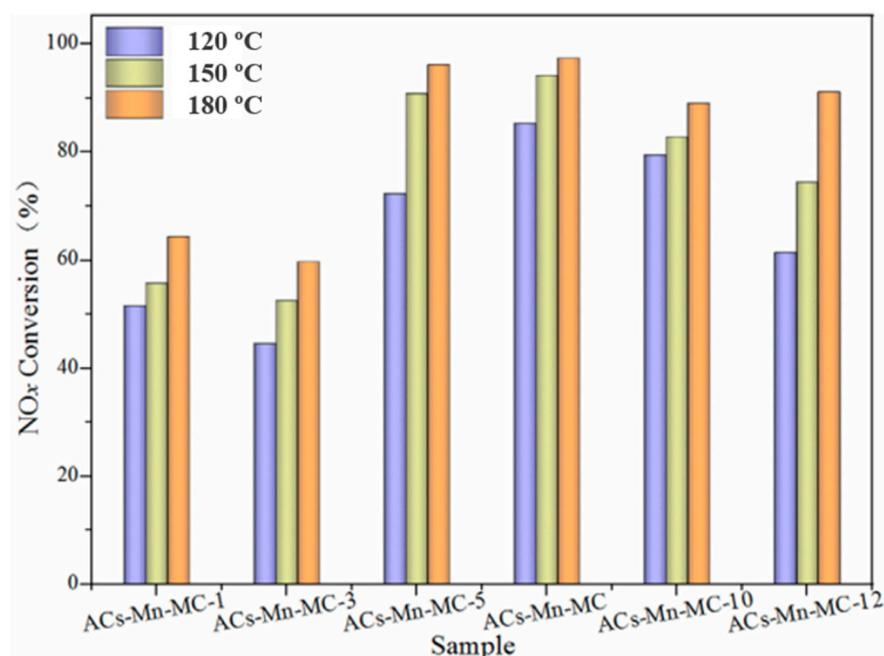


Figure 23. NO_x conversion of samples with different loading amounts of Mn in the testing conditions: T = 120–180 °C, v(O₂) = 3.0%, c(NO) = c(NH₃) = 800 ppm, and GHSV = 10,000 h⁻¹ [110]. (Reproduced with permission from reference [110], Copyright 2020, Elsevier (Amsterdam, The Netherlands)).

5. Conclusions and Perspectives

Low-temperature SCR technology is one of the most effective technologies for removing NO_x from flue gas. Carbon-based catalysts show excellent low-temperature activity and are a promising SCR catalyst. However, the presence of SO₂ and H₂O in the flue gas can easily lead to catalyst poisoning and deactivation. This paper reviews the research progress of low-temperature SCR for NO_x removal against SO₂ and H₂O of carbon-based catalysts. The low-temperature NH₃-SCR reaction mechanism and SO₂ or/and H₂O poisoning mechanism are discussed, and the main strategies to enhance the SO₂ and H₂O resistance are summarized. In addition, the characteristics of common carbon-based materials are introduced. Moreover, the advantages and disadvantages of main low-temperature carbon-based SCR catalysts are evaluated comprehensively, and the application of DFT theoretical calculation in catalyst design and improvement of sulfur and water resistance is analyzed. Although great progress has been made in recent years, many catalysts can only be used under laboratory conditions and do not meet practical industrial application needs, so more in-depth research is needed.

- (1) At present, the mixing or doping of metal oxides to carbon-based catalysts has been extensively studied to enhance H₂O and SO₂ resistance. However, the mechanism of anti-sulfur and anti-water reactions of carbon-based catalysts has not been thoroughly explored.
- (2) When the carbon-based material is used as the carrier of the catalyst reaction, in addition to providing a larger specific surface area, the active site is increased and the activity is improved. In this process, whether the carbon-based materials participate in the reaction process or have a certain influence on the active components needs further study.
- (3) Many studies have focused on the effect of supports on the activity of carbon-based catalysts and their resistance to sulfur and water. However, the influences of different preparation processes on the catalytic performance and sulfur resistance of carbon-based material have not been fully considered and studied. The influence of various factors on the anti-sulfur and water-resistance of carbon-based catalysts needs to be further studied.

- (4) Mn–Ce carbon-based catalysts have excellent low-temperature NH₃-SCR activity and certain resistance to sulfur and water, and are considered as the most promising denitrification catalysts. However, the research of Mn–Ce carbon-based catalysts is mainly in the laboratory stage, and its original poisoning mechanism needs to be further explored.
- (5) In the actual industrial flue gas, in addition to SO₂ and H₂O, it also contains heavy metals, alkali metals, and dust. Therefore, the influence mechanisms of SO₂/H₂O and other harmful substances on carbon-based catalysts need to be studied. Moreover, corresponding anti-poisoning strategies should also be proposed.
- (6) Noble metal catalysts have excellent catalytic performance, but they cannot be used in large scale due to the high cost. The use of non-noble metal catalysts instead of noble metal has become the focus and general trend of research. However, most of the non-noble metal carbon-based catalysts possess poor stability and general sulfur and water resistance and are only used in the laboratory. It is necessary to develop non-precious metal carbon-based catalysts with excellent sulfur and water resistance under industrial conditions.
- (7) Each industrial flue gas containing NO_x has its own characteristics, and a single catalyst is difficult to meet the needs of NO_x removal in all flue gases. Therefore, high-performance NH₃-SCR catalysts should be designed and developed according to the characteristics of the actual flue gas.
- (8) At present, carbon-based SCR catalysts have achieved corresponding results in improving sulfur and water resistance, but most catalysts are still inactivated after use for a period of time. In my opinion, the rapid and low-cost regeneration methods of deactivated catalysts and corresponding mechanisms are another topic for future research.

Author Contributions: Z.S.: Conceptualization, writing the original draft, and formal analysis; S.R.: writing, review, and editing, funding acquisition, and supervision; B.Z.: conceptualization; W.B.: formal analysis and investigation; X.X.: writing, review, and editing, funding acquisition, and supervision; Z.Z.: review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Natural Science Basic foundation of China (No. 52174325), the Shaanxi Province key research and development plan project (2019TSLGY05-05), the Shaanxi Province innovation ability support plan (2023-CX-TD-53), and the Shaanxi Provincial Department of Education Key Laboratory Scientific Research Project (20JS072). And The APC was funded by 20JS072. The authors gratefully acknowledge their support.

Data Availability Statement: Not applicable.

Conflicts of Interest: Authors Baoting Zhang and Weixin Bian were employed by the company Hanzhong Iron and Steel Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest. There are no conflict of interest.

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