Recent advances in heighten sulfur resistance of SCR catalysts: A review

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ABSTRACT

NO_x removal by selective catalytic reduction (SCR) technology is a research hotspot in the field of environmental catalysis, and this method is dominated by catalysts. However, denitrification catalyst is easy to be polluted by the presence of SO₂, which seriously restricts its practical industrial application. This review focuses on the latest domestic and foreign research results and advancement in improving sulfur resistance of deNO_x catalysts, reveals the sulfur poisoning mechanism and regeneration process, as well as introduces the positive role of quantum chemistry in the field of sulfur resistance. In view of the questions set forth in this review, the future development direction of deNO_x catalysts is prospected, which provides valuable scientific guidance for the design and development of efficient and practical sulfur resistant deNO_x catalysts.

Keywords: deNO_x catalyst, DFT, Regeneration, Selective catalytic reduction, Sulfur poisoning

1. Introduction

China's rapid economic growth has caused severe air pollution, and people are increasingly concerned about its negative impact on health, environment and sustainable economic development. Similar to most industrialized countries, China is currently changing from SO₂-based air pollution to NO_x and O₃-based air pollution [1]. It is well known that nitric oxide (NO) and nitrogen dioxide (NO₂) are the main types of nitrogen oxides (NO_x) in China. The combustion of fossil fuels and vehicle exhaust emissions are the main sources of pollution [2]. According to official statistics released by the Chinese government, China's NO_x emissions are expected to reach 42.96 million tons in 2030 without reasonable measures to control NO_x emissions. The Outline of the National 13th Five-Year Plan has clearly stated that NO_x emission will be reduced by 15% within 5 years. In the 2019 government work report, Premier Li Keqiang clearly pointed out that NO_x emissions should be reduced by 3% [3]. In the face of increasingly stringent pollutant emission standards, the elimination of NO_x has become a hot spot in the environmental protection field.

Post-combustion flue gas purification technologies mainly include solid adsorption, liquid absorption, selective catalytic reduction, catalytic decomposition, plasma catalysis, and microbial meth-

od [4]. Among them, selective catalytic reduction (SCR) is considered as the mainstream method for NO_x removal due to its high deNO_x efficiency, excellent selectivity and practicability. The catalyst is the core part of the technology, and its performance will directly affect the deNO_x effect of SCR system. In addition, the catalyst cost accounts for a large proportion of the total cost of the SCR system. At present, due to the tremendous progress in material preparation science and technology, academic researchers and engineers have developed a number of SCR catalysts with high NO_x removal efficiency in SO₂-free flue gas. However, the SO₂ contained in the actual flue gas will inevitably lead to catalyst poisoning and deactivation, reducing catalytic efficiency and service life, which has become a major obstacle restricting the practical industrial application of the catalyst. Therefore, it is urgent to develop catalytic materials with excellent activity, high stability, good SO₂ tolerance and environmental friendliness that can be operated in low temperature and complex environment.

Research scholars at home and abroad have conducted in-depth and meticulous research on the deactivation research of SCR catalysts and found that the sulfur poisoning mechanism of the catalysts is different. At present, catalyst poisoning in an SO₂ atmosphere is mainly carried out in three different ways. One thing is that SO₂ in the flue gas has a competitive adsorption relationship with

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NO_x under the action of van der Waals force. The presence of SO_2 will inhibit the adsorption of NO_x , which further hinders the occurrence of SCR reaction. This reaction is reversible inactivation, and the catalyst activity can be restored after the removal of adsorbed SO_2 by means of thermal regeneration. In addition, the reaction of SO_2 with the active component of the catalyst leads to the sulfation of the active center atom, thereby cutting off the redox cycle of the active phase, causing the catalyst to be poisoned and irreversible. Last but not least, SO_2 reacts with NH_3 to form ammonium sulfate salts, which are deposited on the surface of the catalyst, could block the adsorption site, catalytic active sites and pore structure on the surface of the catalyst, and result in irreversible inactivation of the catalyst.

So far, researchers have been using surface modification or cocatalyst doping to obtain more practical and cost-effective SCR catalysts, and have achieved encouraging results. Many scholars have reviewed the newly developed high-activity de NO_x catalysts, but there is a lack of research progress on the sulfur resistance of catalysts. Based on the SCR technology, this article focuses on the latest research progress in the strategy of improving the sulfur resistance of the catalyst during the de NO_x process, reveals the sulfur poisoning mechanism, and explains the regeneration process of the sulfur poisoning catalysts and the quantum chemistry in the field of sulfur resistance application. We hope this article will provide a reference for the optimization of existing catalysts and the development of SCR catalysts with excellent sulfur resistance in the future.

2. Strategies to Enhance The Sulfur Resistance of Catalysts

2.1. Adding Functional Promoters

2.1.1. Fe modification

Iron is usually used as an active ingredient or additive in catalysts [5, 6], due to its cheap raw materials, higher abundance, good reactivity and environmental friendliness. The d-orbital electrons of iron-based oxide are not saturated and can capture electrons, which has the potential of catalytic reduction of NO .

Kang et al. [5] prepared Fe_2O_3 modified CeW/H catalyst and found that Fe_2O_3 doping can effectively suppress the irreversible combination of SO_2 and active components. When the Fe-Ce molar ratio is 4, the catalyst achieves the best NO_x conversion rate and SO_2 tolerance. After the material was continuously reacted in a 100 ppm SO_2 atmosphere for 8 hours, the NO_x conversion rate decreased by only 5%. It is worth noting that the catalyst without Fe doping has a 50% reduction in catalytic activity. The author used in situ Fourier transform spectroscopy to reveal the mechanism of action between SO_2 and catalyst, as shown in Fig. 1. The results showed that there was competitive adsorption between SO_2 and NO on the surface of CeW/H sample. SO_2 could react with the active component CeO_2 to generate stable sulfate ($\text{Ce}_2(\text{SO}_4)_3$) species, thus reducing the number of active sites and further inhibiting the reduction reaction. For Fe-modified catalysts, SO_2 reacts with Fe_2O_3 to produce $\text{Fe}_2(\text{SO}_4)_3$, which can protect the active component $\text{CeO}_2\text{-WO}_3$ from being affected. Furthermore, the team [7] recently

Fig. 1. The mechanism of NO_x reduction in the presence of SO_2 over Fe@CeW/H and CeW/H catalysts [5].

claimed that Fe-doped CeVO_4 catalyst can significantly inhibit the adsorption of SO_2 and sulfate species deposition for operating temperatures at 240°C compared to CeVO_4 ones. Zeng et al. [8] explored the promotion of Fe^{3+} ions on NH_3 -SCR activity of CePO_4 catalyst, and found that Fe^{3+} doping can induce $\text{Fe}^{3+} + \text{Ce}^{3+} \rightleftharpoons \text{Fe}^{2+} + \text{Ce}^{4+}$ redox balance, thereby significantly improving the redox performance of CePO_4 catalyst. For $\text{Fe}_{0.3}\text{Ce}_{0.7}$ sample, after exposing to 5vol% H_2O and 100 ppm SO_2 for 10 h, the de NO_x efficiency remained at 35.5%, but the activity of CePO_4 sample almost completely disappeared after 4 h.

Jia et al. [9] synthesized a novel Fe-Sb binary metal oxide catalyst by ethylene glycol assisted co-precipitation technique. The $\text{Fe}_{0.7}\text{Sb}_{0.3}\text{O}_x$ catalyst showed good NH_3 -SCR activity with 100% conversion of NO_x from 175°C to 250°C and high $\text{SO}_2/\text{H}_2\text{O}$ durability at 250°C . Wang et al. [10] developed iron-tungsten catalysts, which obtained above 90% NO removal efficiency within a wide operating temperature window. Results also showed pronounced stability and relatively high NO_x conversion in the presence of H_2O , SO_2 and CO_2 .

Li et al. [11] confirmed that the main reasons for the deactivation of $\text{Fe}_{10-x}\text{V}_x$ binary metal oxides in 3DOM structures were the deposition of NH_4HSO_4 on the catalyst surface and the weakening or destruction of Brønsted acid potential. Zhu et al. [12] showed that after injecting SO_2 and H_2O into the reaction system for 24 hours, Fe-V-Ti catalyst remained above 93% NO_x conversion rate at 250°C , and the catalytic efficiency restored to 100% after removal.

Dong et al. [13] showed that the Brønsted and Lewis acid content in Ti-PILC catalyst increased after Fe loading, and $\text{H}_2\text{O}(\text{g})$ and SO_2 had little influence on C_3H_6 -SCR reaction. Qian et al. [14] also confirmed that Fe doping could improve the conversion rate of NO and C_3H_6 and the selectivity of N_2 . Sulfur dioxide and water vapor had little effect on the catalytic activity of Fe/Al-PILC. Wang et al. [15] pointed out that an increase in Fe content is beneficial to the conversion of CO and NO adsorbed on the catalyst surface ($\text{NO} \rightarrow \text{M-NO}_2 \rightarrow \text{NO}_2^- \rightarrow \text{M-N}_2\text{O}/\text{NO}_3^- \rightarrow \text{N}_2\text{O}/\text{N}_2$; $\text{CO} \rightarrow \text{COO}^- \rightarrow \text{CO}_3^{2-} \rightarrow \text{CO}_2$). The H_2O and SO_2 resistance test results showed that an appropriate increase in the proportion of Fe will promote the resistance of $\text{SO}_2/\text{H}_2\text{O}$. The mechanism is that Fe inhibited the formation of sulfate and generates more water adsorption sites, as well as Fe optimized the pore structure. Fang et al. [16] found that calcination temperature would affect the sulfur resistance of Fe-Mn-Zr catalyst, and FMZ-500 had better tolerance to 100 and

200 ppm SO_2 than other samples (Fig. S1). Wang et al. [17] reported by doping with Fe on $\text{Mn}/\gamma\text{-Al}_2\text{O}_3$ catalyst, the sulfate formation of Mn active component can be dramatically reduced and lower the stability of surface sediments (NH_4SO_4), forcing them to decompose rapidly. Xie et al. [18] fabricated mesoporous $\gamma\text{-Fe}_2\text{O}_3$ -modified nanoflower- MnO_2 /attapulgite catalyst through a facile hydrothermal method, which can effectively inhibit SO_2 and H_2O poisoning.

2.1.2. Ce modification

CeO_2 has attracted much attention in the field of heterogeneous catalysis due to its excellent redox properties and oxygen storage capacity. It stores and releases oxygen through oxidation-reduction changes between $\text{Ce}^{4+}/\text{Ce}^{3+}$ under oxidation and reduction conditions, so that the catalyst can obtain more chemisorbed oxygen under oxygen-rich or oxygen-depleted conditions, further improving the dispersion of active ingredients on the catalyst surface [19]. In addition, the anti- SO_2 poisoning ability improved after adding additive Ce. There are two main reasons. On the one hand, the cerium element will form a M-O-Ce solid solution with other metal elements on the surface of the catalyst, enhancing the Lewis acidity of the catalyst, thereby inhibiting the adsorption of acid gas SO_2 . On the other hand, the addition of cerium reduces the stability of sulfate species and weakens its deposition on the catalyst surface.

In research has been done by Chen et al. [20], a high-performance denitrification catalyst was synthesized based on Mn-Ce mixed oxide derived from a specific Mn/Ce precursor. Compared to MnO_x , the new Mn-Ce mixed oxides delivered a much better SO_2 tolerance, the NO_x conversion increased from 92.6% to 97.8% at 150°C when pouring into 200 ppm SO_2 . Wang et al. [21] carefully designed and synthesized CeO_2 modified MnCoCeO_x catalysts for NH_3 -SCR reaction, and found that the modified catalyst has significantly enhanced low temperature de NO_x activity and SO_2 tolerance. The results showed that MnCoO_x samples after NH_3 -SCR reaction for 12 hours in the presence of 50 ppm SO_2 and 5vol% H_2O contained more metal sulfate substances than MnCoCeO_x , which proved that the former was more likely to be sulfurized as metal sulfate. In other words, the added CeO_2 acts as a protective layer on the surface of the MnCoO_x catalyst, which can prevent the active site of the MnCoO_x material from being poisoned by SO_2 . Fan et al. [22] also proved that the addition of cerium oxide can inhibit the deposition of NH_4HSO_4 and preferentially react with SO_2 to protect the active center.

Zhang et al. [23] reported that the effect of SO_2 on NO conversion is greatly dependent on the reaction temperature over the Ce-TiO₂ catalyst. With the increase of reaction temperature, the tolerance of SO_2 is gradually improved. Using catalyst performance measurements, after 8 hours of SO_2 poisoning at 300°C, the NO conversion rate decreased from 96.9% to 91.1%, and remained unchanged after SO_2 was cut off. The superior SCR activity of Ce-TiO₂ catalyst in the presence of SO_2 at a higher reaction temperature may be attributed to the synergistic effect of cerium sulfate and bulk CeO_2 . Cerium sulfate acts as the acidic site for NH_3 adsorption and CeO_2 acts as the redox site. The DRIFT study has found that the formation of sulfate/cerium sulfite on the catalyst surface will inhibit the E-R and L-H pathways of the SCR reaction (as shown in Fig. 2).

Fig. 2. The reaction mechanism for SO_2 poisoning at low and middle temperatures [23].

Kwon et al. [24] investigated the influence of SO_2 on the SCR process of Ce modified V/Sb/Ce/Ti catalyst, and observed that NH_4HSO_4 could be formed on the surface of V/Sb/Ti (or V/W/Ti) catalyst due to SO_2 in the flue gas being oxidized to SO_3 , which would result in the blockage of catalyst pore. However, Ce in the modified catalyst reacts with SO_2 and O_2 to form $\text{Ce}_2(\text{SO}_4)_3$, which consumes SO_2 and thus inhibits the formation of NH_4HSO_4 . Therefore, the incorporation of Ce can improve the sulfur resistance of the catalyst. This study further confirmed the protective effect of Ce.

Shu et al. [25] developed a Ce-Fe/TiO₂ supported metal honeycomb monolithic catalyst, which exhibited good anti-sulfur performance within 100 h. In addition, sulfation can lead to the enrichment of Ce^{3+} on the surface of the catalyst and generate a large number of Brønsted acid sites. The mechanism study showed that the NH_3 -SCR reaction follows the Eley-Rideal (E-R) mechanism in the case of the sulfated catalysts. Ma et al. [26] also concluded that the $\text{Cu}_{0.02}\text{Fe}_{0.2}\text{-Ce}_{0.2}\text{Ti}_{0.8}\text{O}_x$ catalyst has excellent H_2O and SO_2 resistance after modifying with appropriate cerium.

2.2. Choosing Suitable Carriers

Numerous studies have shown that a suitable carrier both provide a surface for dispersing active ingredients, and a space for catalytic reactions. In addition, optimizing the interaction between the carrier and active components may improve the SO_2 poisoning in SCR reaction.

Yao et al. [27] studied the denitrification performance of CeO_2 -TiO₂ catalysts supported by TiO₂ with different crystal structures. It was observed that the catalysts supported on rutile TiO₂ had better denitrification performance than those supported on anatase or brookite TiO₂, which were ascribed to the rich acid site, Ce^{3+} ions, adsorbed oxygen species and improved redox capacity. In addition, CeO_2 -TiO₂ catalyst with CeO_2 as the carrier has superior SO_2 tolerance than only TiO₂ carrier. The reasonable reason for this result is loading of TiO₂ on the surface of CeO_2 can restrain the sulfation of bulk CeO_2 , thus maintaining the redox ability. NH_3 -SCR reaction can take place through the synergistic effect of bulk CeO_2 and surface sulfates. Liu et al. [28] put forward

that the NO_x conversion and SO_2 resistance was well enhanced when TiO_2 supporter adding to ZrO_2 . Researchers found that the surface area of the supporter would be enormously increased by introducing TiO_2 , thus the active components (Fe_2O_3 and SO_4^{2-}) are highly dispersed on the support of binary metal oxides (TiO_2 - ZrO_2). Compared with single TiO_2 or ZrO_2 , the interaction between Ti and Zr will significantly improve the conversion of Fe^{3+} to Fe^{2+} on Ti1Zr4 carrier.

Li et al. [29] found that the catalyst ($\text{MnCeO}_x/\text{TiO}_2\text{-Al}_2\text{O}_3$) adding Al_2O_3 supporter presents higher SCR performance and SO_2 poisoning tolerance than $\text{MnCeO}_x/\text{TiO}_2$ alone. Wang et al. [30] advocated that the sulfur tolerance of the NbOPO_4 supported Cu-Ce sample was greatly improved compared to TiO_2 and Ti-Nb supported samples. Cu-Ce/Nb-P sample has shown above 80% NO removal efficiency after reaction for 10 h (250°C, 100 ppm SO_2). The excellent properties were owing to the increase of acidity and the strong interaction between Cu-Ce oxides and NbOPO_4 support, which avoided the surface oxygen species from being sulfurized by SO_2 . Wu et al. [31] proposed that the introduction of carbon nanotubes will be helpful to the improvement of sulfur resistance of catalysts.

2.3. Regulation of Structure and Morphology

Different synthesis methods of the catalysts will form different structures and morphologies, which will directly affect the inherent characteristics, the specific surface area, pore structure as well as the activity of the catalysts, and so on. The reasonable design of the catalysts with unique structure and morphology is an important method to protect the active substances from SO_2 poisoning.

Han et al. [32] compared the influence of the micromorphologies of CeO_2 supports on the NH_3 -SCR reaction. The $\text{Fe}_2\text{O}_3/\text{CeO}_2$ nanorods achieving higher catalytic activity than the $\text{Fe}_2\text{O}_3/\text{CeO}_2$ nanopolyhedra and the NO conversion value still maintain 94% during the whole test period whether inlet or cease SO_2 . Gao et al. [33] fabricated novel Mn-Ni spinel nanosheets and attained 85–90% NO_x conversion after introducing 10 vol% H_2O + 150 ppm SO_2 in the temperature regime between 150 and 300°C. The higher SCR activity was attributed to two reasons: (1) the tetrahedral structure of spinel containing Ni avoids the sulfurization of Mn active sites wrapped in inner octahedron. (2) The morphology of the nanosheets hinders the adhesion of the sulfur ammonia component, thereby alleviating the deposition/inhibition effects.

CeTiO_x catalysts with nanotube structure and high activity was reported by Zhang et al. [34], in which more than 98% NO conversion can be got in the temperature range between 180°C and 390°C. Moreover, after introducing 100 ppm SO_2 and 6% H_2O at 240°C, the NO conversion rate remained at about 96% within 8 hours. After closing H_2O and SO_2 , the NO conversion rate can quickly return to the initial value. Huang et al. [35] developed a $\text{V}_2\text{O}_5/\text{HWO}$ catalyst by support V_2O_5 on a hexagonal WO_3 (HWO), which possess exceptional resistance simultaneously to alkalis and SO_2 poisoning in the SCR reactions owing to the hexagonal structure of the HWO. Guo et al. [36] reported an interesting finding that regulating the pore size of the material contribute to decompose the deposited NH_4HSO_4 . This team also found that the $\text{Fe}_2\text{O}_3/\text{SBA-15}$ catalyst with larger mesopores exhibited much improved sulfur resistance, and quantitative analysis results demonstrated that the deposited sulfates was significantly relieved.

Fig. 3. The SO_2 deactivation mechanism over MnO_x - $\text{CeO}_2/\text{TiO}_2$ and MnO_x - $\text{CeO}_2@/\text{TiO}_2$ catalysts [39].

Sheng et al. [37] found that the core-shell structure can protect the catalytic active sites from the effects of H_2O and SO_2 poisoning. The SO_2 tolerance of $\text{MnO}_x@/\text{TiO}_2$ core-shell nanorods is higher than that of MnO_x and $\text{MnO}_x/\text{TiO}_2$ catalysts, which is due to SO_2 can be effectively isolated on the TiO_2 shell. Gan et al. [38] explored the $\alpha\text{-MnO}_2@/\text{CeO}_2$ catalyst with a core-shell structure and found that the CeO_2 shell can bind to SO_2 firmly in preference to MnO_2 , and protect the active sites on the $\alpha\text{-MnO}_2$ core from SO_2 poisoning. Ma et al. [39] also proved that $\text{MnO}_x\text{-CeO}_2@/\text{TiO}_2$ core-shell composites showing the excellent SCR activity in the presence of SO_2 than conventional $\text{MnO}_x\text{-CeO}_2/\text{TiO}_2$ catalysts. The SO_2 deactivation mechanism over above catalysts are as follows (Fig. 3). Zhang et al. [40] proved that for the $\text{SiO}_2@/\text{FeCeO}_3/\text{CNTs}$ core-shell catalyst, the coated SiO_2 shell establish an available barrier to hinder the generation of FeSO_4 and restrain the reduction of chemisorbed oxygen, improving its stability and SO_2 tolerance.

Yu et al. [41] designed and fabricated a novel $\text{MnO}_x@/\text{Eu-CeO}_x$ catalyst with composite-shell structure and attained more than 95% NO_x conversion at low temperature (100°C). The formation of the composite-shell structure enhanced the surface acidity and redox performance of catalyst, resulting in outstanding catalytic activity. When SO_2 was introduced into the reaction for 4 h, the NO_x removal rate only declined from 93.7% to 91.0%. Notably, when the SO_2 flow in the simulated flue gas was cut off, the denitrification activity of the catalyst was almost completely recovered, this means that the major active components in the catalyst may not be irreversibly affected. The author drawn a conclusion that the protection of the $\text{EuO}_x\text{-CeO}_x$ composite-shell can reduce the toxicity of SO_2 to Mn active sites and the strong interaction between the Ce and Mn can effectively limited the deposition of the surface sulphates (as shown in Fig. S2) Cai et al. [42] designed multi-shell $\text{Fe}_2\text{O}_3@/\text{MnO}_x@/\text{CNTs}$ catalysts, which also proved that the Fe_2O_3 shell could effectively suppress the formation of the surface sulfate species.

2.4. Establishing a Dynamic Equilibrium between Sulfate Formation and Decomposition

Lately, the research team of Zhejiang University [43] proposed new countermeasures to enhance the sulfur dioxide tolerance of

Fig. 4. The deposition and decomposition of surface sulfate are in a dynamic equilibrium over catalysts [43].

SCR catalyst - by establishing a dynamic equilibrium between sulfates formation and decomposition. This team designed a novel $\text{MnO}_x/\text{CeO}_2$ nanorod catalyst with the assistance of key information obtained from TEM experiments and first-principles calculations. The catalysts showed almost no activity loss with an apparent NO_x reaction rate of $1,800 \mu\text{mol g}^{-1} \text{h}^{-1}$ for 1000 h test at 250°C in the presence of 200 ppm SO_2 . They found that the deposition and decomposition of surface sulfate are in a dynamic equilibrium over $\text{CeO}_2(\text{NR})$ and $\text{MnO}_x/\text{CeO}_2(\text{NR})$, which can suppress the accumulation of sulfate and keep the exceedingly good activity at low temperature, the reactions involved in the establishment of surface formation and decomposition as shown below (Fig. 4): $2\text{CeO}_2 + 3\text{SO}_2 + \text{O}_2 \rightarrow \text{Ce}_2(\text{SO}_4)_3$, $\text{Ce}_2(\text{SO}_4)_3 + 4\text{NH}_3 + 3\text{H}_2\text{O} \rightarrow \text{Ce}_2\text{O}_3 + (\text{NH}_4)_2\text{SO}_4 + 2\text{NH}_4\text{HSO}_4$, $\text{Ce}_2\text{O}_3 + 1/2\text{O}_2 \rightarrow 2\text{CeO}_2$, $(\text{NH}_4)_2\text{SO}_4 + 2\text{NH}_4\text{HSO}_4 + 2\text{NO} + 1/2\text{O}_2 \rightarrow 3\text{N}_2 + 9\text{H}_2\text{O} + 3\text{SO}_2$.

2.5. The Improvement Strategy of Several Classic Catalysts

2.5.1. Vanadium-based catalysts

Vanadium-based catalysts have been predominantly used as commercial catalysts with the operating temperature concentrated at $300\text{--}400^\circ\text{C}$. However, some drawbacks of this type of catalysts including narrow working temperature window ($300\text{--}400^\circ\text{C}$) and susceptible to deactivation by residual SO_2 in the exhaust. The characteristics of actual flue gas are low temperatures and high SO_2 content which conventional vanadium-based catalysts cannot handle. Therefore, the resistance to sulfur poisoning of the catalyst need to be further improved to satisfy the practical application.

Liang et al. [44] put forward that adding moderate F ions would erode the surface morphology of the catalyst and reduce its particle size, so as to improve the NO conversion rate at low temperature and the sulfur and water resistance of $\text{V}_2\text{O}_5\text{--}\text{WO}_3/\text{TiO}_2$ catalyst. Kang et al. [45] reveals the reason for sample obtained after the physical mixing of $\text{V}_2\text{O}_5\text{--}\text{WO}_3/\text{TiO}_2$ with several Fe_2O_3 has superior performance through a series of representational means ($\text{SO}_2\text{-TPD}$, $\text{NH}_3\text{-TPD}$ and in situ FT-IR), which attributable to the following two reasons: (1) Fe_2O_3 adjacent to $\text{V}_2\text{O}_5\text{--}\text{WO}_3/\text{TiO}_2$ inhibited the formation of NH_4SO_4 by generating FeSO_4 (2) The formation of FeSO_4 provides additional Brønsted acid sites, which promotes

the conversion of NO_x . The mechanism of sulfate species formation over catalysts was illustrated in Fig. S3.

Team of Professor Li from Dalian University of Technology [46] proposed that the sulfation tends to have a negative effect on the low-temperature reaction of FeVO_x catalyst, but actively promotes high-temperature activity by inhibiting harmful NH_3 oxidation. Li et al. [47] found that $\text{V-W/Ce/Ti-5\%}$ presented better $\text{NH}_3\text{-SCR}$ activity and higher NH_4HSO_4 resistance at 280°C when 5% WO_3 was loaded. The result is due to WO_3 doping suppresses the formation of NH_4HSO_4 and metal sulfate species over active sites by lowering the alkalinity of $\text{V-W/Ce/Ti-5\%}$.

2.5.2. Manganese-based catalysts

Manganese-based catalysts have been widely used in recent years on account of their variable valence, remarkable redox capabilities, rich Lewis acid sites, and excellent low-temperature catalytic activity. However, for a single MnO_x catalyst, poor resistance to SO_2 is the main challenge that hinders its further industrial application [48]. The Li Junhua team [49] reported that exposing to 150 ppm SO_2 at 150°C , the NO conversion rate of pure MnO_x decreased from 92% to 23%, and only recovered to 45% after cutting off SO_2 . Due to the strong oxidation ability of Mn oxide, SO_2 is easily oxidized to SO_3 at low temperature, and the formed SO_3 reacts with NH_3 or active components to form sulfate, which can cover the surface of the catalyst, block the pore of the catalyst, and inhibit the contact between the catalyst and reaction molecules, thus causing the catalyst deactivation. Therefore, preventing or reducing SO_2 poisoning of Mn-based catalyst has become the focus of academic and industrial attention. More and more studies show that introducing another phase as sacrificial agent to capture SO_2 in priority can improve the anti-sulfur performance of Mn-based catalyst.

Jiang et al. [50] synthesized some $\alpha\text{-MnO}_2$ catalysts doped with Fe, Ce, Cr, Zr or Co as metal co-catalysts by hydrothermal method, and found that the catalysts doped with Co showed the best low temperature $\text{NH}_3\text{-SCR}$ activity and excellent $\text{H}_2\text{O}/\text{SO}_2$ tolerance. NO conversion activity remained at 100% at 200°C when H_2O and SO_2 exists in the flue gas. Sun et al. [51] prepared a series of MnNb/TiO_2 catalyst samples with different Nb/Mn molar ratios using the sol-gel method, and studied the effect of SO_2 on the denitrification process. The experimental results show that introducing Nb into the Mn/TiO_2 catalyst can increase the specific surface area, enhance the reducibility and surface acidity, promote the formation of more Mn^{4+} and chemically adsorbed oxygen on its surface, and produce more NO_2 . Liu et al. [52] found that MnEu/TiO_2 catalyst also had excellent SO_2 resistance performance. Through in-situ infrared technology, it was found that SO_2 could promote the adsorption of NH_3 and inhibit the adsorption of NO_x . Eu modification could partially offset the inhibition effect of SO_2 on the adsorption of NO_x on Mn/TiO_2 catalyst.

The research team of Huazhong University of Science and Technology [53] found that the presence of Sm promotes the anti- SO_2 performance of the Mn/TiO_2 catalyst. The electron transfer between Sm and Mn ions inhibits the oxidation of SO_2 , thereby inhibiting the formation of sulfate (Fig. S4). Wang et al. [54] also demonstrated the superiority of the Sm modified catalyst. Compared with catalysts without Sm, mesoporous MnCeSmTiO_x mixed oxides maintained higher catalytic performance after H_2O and SO_2 were added by

suppressing the oxidation of SO₂ by Mn⁴⁺ and Ce⁴⁺. Zhang et al. [55] found that when 200 ppmV SO₂ was introduced into the feed gas, the catalytic activity of Sb modified Mn/PG catalyst was reduced by only 1%, while the NO conversion rate of unmodified catalyst was reduced by nearly 60%.

Liu et al. [56] claimed that graphite carbon has a positive role in improving the anti-SO₂ performance of Mn-based catalysts, thanks to its assembly structure, small grain crystals, high specific surface area and appropriate oxidation capacity. The Mn₃O₄-A catalyst was reduced from 98% conversion rate to 13% within 8 hours, while the Mn₃O₄@GA catalyst was able to maintain 80% catalytic activity under H₂O and SO₂ atmosphere. XPS and He-TPD characterization results show that the sulfate species on the surface of Mn₃O₄-A are mainly formed by the reaction between Mn₃O₄ and SO₃ and the decomposition products of NH₄HSO₄, but no obvious sulfates were found on the surface of the Mn₃O₄@GA catalyst. It is proved that the weakening of the oxidation ability of Mn₃O₄@GA can inhibit the oxidation of SO₂ to SO₃ and avoid the formation of NH₄HSO₄, thereby further improving the performance of anti-SO₂. Fan et al. [57] found that Al₂O₃ is a promoter to enhance the sulfur resistance of MnO_x. The result indicates that Al₂O₃ can decrease the thermal stability of NH₄HSO₄ and the adsorbed SO₂ species to some extent.

Gao et al. [58] prepared novel hydroxyl containing Co-Mn and Ni-Mn binary oxides by the combined complexation-esterification method to eliminate NO_x. The study found that the addition of Co and Ni elements increased the concentration of chemically adsorbed oxygen on the catalyst surface and the effective electron conversion of cations, which delayed the SO₂ poisoning process. In addition, this team [59] also explored the influence of SO₂ on the surface of Mn₂NiO₄ spinel catalyst on the reaction path, and further proved that the Ni modified MnO_x catalyst had an extremely significant enhancement effect on the tolerance of SO₂, which may be attributed to the special spinel structure. Xiong et al. [60] investigated the role of low-valent copper dopants in Mn₃O₄ spinel SCR catalysts. The study pointed out that the doping of copper element increases the specific surface area, active Mn⁴⁺ species and surface acid content of the spinel catalyst, thereby greatly improving the low-temperature SCR activity and SO₂ tolerance. Under the combined action of SO₂ and H₂O (200°C), the NO_x conversion rate only dropped by about 4% and remained at 87%.

Yan et al. [61] prepared a new low-temperature NH₃-SCR catalyst Cu_xMn_yTi_{1-y}O_x from layered double hydroxides (LDHs) precursor. The study found that Cu₁Mn_{0.5}Ti_{0.5}O_x showed the optimal SCR performance, with a NO_x conversion rate of 90% and N₂ selectivity of 99.4% at 200°C, which were much higher than the control catalyst

Table 1. Summary of SCR Catalysts with Strong Resistance to SO₂

Catalyst	Reaction condition	Catalytic activity	Ref.
Fe@CeW/H	[NO] = [NH ₃] = 500 ppm, [SO ₂] = 100 ppm, [O ₂] = 5vol%, N ₂ balance, total gas flow rate = 250 mL/min, GHSV = 40,000 h ⁻¹	93% (200°C)	[5]
Fe _{0.1} V _{0.1} TiO _x	[NO] = [NH ₃] = 500 ppm, [SO ₂] = 100 ppm [O ₂] = 5vol.%, [H ₂ O] = 5vol.%, N ₂ balance, total gas flow rate = 500 mL/min, GHSV = 200,000 h ⁻¹	93% (250°C)	[12]
Mn-Fe-2/γ-Al ₂ O ₃	[NO _x] = 0.03%, [NH ₃] = 0.033%, [SO ₂] = 250 mg/cm ³ , [O ₂] = 6vol.%, [H ₂ O] = 6vol.%, N ₂ balance, GHSV = 6,000 -14,000 h ⁻¹ .	84% (150°C)	[17]
γ-Fe ₂ O ₃ /nf-MnO ₂ -ATP	[NO] = [NH ₃] = 1000 ppm, [SO ₂] = 200 ppm [O ₂] = 3vol.%, N ₂ balance, total gas flow rate = 2 L/min, GHSV = 45,000 h ⁻¹ .	89% (200°C)	[18]
Mn/Ce-400-Air	[NO] = [NH ₃] = 500 ppm, [SO ₂] = 200 ppm, [O ₂] = 3vol%, N ₂ balance, GHSV = 52,500 h ⁻¹	97.8% (150°C)	[20]
Ce-TiO ₂	[NO] = [NH ₃] = 600 ppm, [SO ₂] = 1000 ppm, [O ₂] = 3vol%, N ₂ balance, GHSV = 40,000 h ⁻¹	91.1% (300°C)	[23]
FeS/(Ti1Zr4)	[NO] = [NH ₃] = 500 ppm, [SO ₂] = 200 ppm, [O ₂] = 3vol%, N ₂ balance, total gas flow rate = 300 mL/min, GHSV = 47,000 h ⁻¹	96% (300°C)	[28]
Fe ₂ O ₃ /CeO ₂ -NR	[NO] = [NH ₃] = 500 ppm, [SO ₂] = 100 ppm, [O ₂] = 3vol%, N ₂ balance, total gas flow rate = 250 mL/min, GHSV = 20,000 h ⁻¹	94% (275°C)	[32]
NiMn ₂ O ₄ -UHHs	[NO] = [NH ₃] = 500 ppm, [SO ₂] = 150 ppm, [O ₂] = 5vol%, [H ₂ O] = 10vol.%, N ₂ balance, total gas flow rate = 100 mL/min, GHSV = 32,000 h ⁻¹	85–90% (150–300°C)	[33]
CeTiO _x -T	[NO] = [NH ₃] = 1000 ppm, [SO ₂] = 100 ppm, [O ₂] = 3vol%, [H ₂ O] = 6vol.%, N ₂ balance, total gas flow rate = 200 mL/min, GHSV = 40,000 h ⁻¹	96% (240°C)	[34]
MnO _x @Eu-CeO _x	[NO] = [NH ₃] = 600 ppm, [SO ₂] = 100 ppm, [O ₂] = 2.5vol%, Ar balance, GHSV = 90,000 h ⁻¹	91% (200°C)	[41]
MnO ₂ -Co-0.8	[NO] = [NH ₃] = 500 ppm, [SO ₂] = 100 ppm, [O ₂] = 5vol%, [H ₂ O] = 5vol.%, Ar balance, total gas flow rate = 100 mL/min, GHSV = 50,000 h ⁻¹	100% (200°C)	[50]
Cu-Ce/SP-0.75	[NO] = [NH ₃] = 500 ppm, [SO ₂] = 100 ppm, [O ₂] = 5vol%, N ₂ balance, total gas flow rate = 100 mL/min, GHSV = 20,000 h ⁻¹	90% (200–450°C)	[65]

Mn/TiO₂ (80.7%, 88%) and Cu-Mn/TiO₂ (86.1%, 95%) prepared by the traditional immersion method. The outstanding catalytic activity is closely related to its large specific surface area and surface acidity as well as abundant active substances (MnO₂ and CuO). The addition of copper can increase the number of acid groups and strengthen SO₂-resistance of Mn-based catalysts. By comparing the in-situ DRIFT spectra obtained by the catalyst exposed to NO_x and SO₂, the results show that there is a competitive relationship between SO₂ and NO_x on the surface adsorption sites. Significantly, the intensity of the peak attributable to the sulfur species on Cu₁Mn_{0.5}Ti_{0.5}O_x is higher than that of Cu-Mn/TiO₂. It is much weaker than Mn/TiO₂, and the intensity attributable to the NO_x peak is the opposite, further proving the former's stronger sulfur resistance. Chen et al. [62] reported that a Mn₁Fe_{0.25}Al_{0.75}O_x catalyst obtained by calcining the LDH precursor also has excellent SO₂ resistance. Zhou et al. [63] found that two-dimensional layered double oxide (LDO) catalyst MnFeCo obtained 100% deNO_x efficiency at 100°C, and MnFeCo-LDO catalyst at 120°C had better water resistance (rehydroxylation) and sulfur dioxide resistance than MnCo-LDO and MnFe-LDO samples.

2.5.3. Zeolite catalysts

Recently, ion-exchanged zeolites catalysts have aroused people's special attention for its outstanding catalytic performance with wide operation temperature window. Nevertheless, the deposition of (NH₄)₂SO₄ or NH₄NO₃ can block the pore/channel of the conventional microporous zeolites, resulting in the deactivation of the catalyst at low reaction temperature. Based on this, it is urgent to improve the zeolite catalyst.

Peng and his team [64] successfully developed hierarchical Cu-ZSM-5 zeolite with different structures (meso- and micro-pore). The study found that, compared with the conventional Cu-ZSM-5 catalyst (73% NO conversion), the hierarchical Cu-ZSM-5 catalyst exhibits better denitrification efficiency with 93% NO conversion at 250°C. The better performance on Cu-ZSM-5-meso can be attributed to its rich mesoporous structure, which can greatly promote the mass transfer process of reactants or products at low temperature. Furthermore, the NO_x conversion rate of the new Cu-ZSM-5-meso catalyst below 350°C is higher than that of the conventional Cu-ZSM-5 samples after introducing 100 ppm SO₂ into reaction system, which may be due to the hierarchical structure of Cu-ZSM-5-meso can weaken the negative effect of sulfate species. Ma et al. [65] came up with a series of Cu-Ce co-doped SAPO-5/34 catalyst and discovered Cu-Ce/SP-0.75 can maintain more than

90% SCR activity at 200–450°C after adding 100 ppm of SO₂.

Wan et al. [66] synthesized a series of Fe/Cu-SSZ-13 catalysts with different Fe loading content by simple one-pot method. compared with Cu-SSZ-13, Fe_{0.63}/Cu_{1.50}-SSZ-13 catalyst with proper Fe content present typical chabazite (CHA) structure and exhibit extraordinary catalytic activity from 160–580°C, excellent hydrothermal stability as well as good resistance to sulfur toxicity. Yu et al. [67] prepared Cu-SSZ-13 molecular sieve complexes with different metal oxide components (Mn, Co, Ni, Zn) via sol-dispersion method. The results showed that ZnTi₁₀O_x in the hybrid catalyst could be used as a sacrificial component to preferentially react with SO₂, thus preventing the Cu²⁺ active site from sulfur inactivation.

According to the above contents, we can find that doping other substances to protect the active centers from sulfur poisoning is a promising method to strengthen the sulfur resistance of catalysts.

3. Regeneration of Sulfur Poisoning Catalyst

The development of deNO_x technology is accompanied by the problem of disposal of waste catalysts. At present, deactivated deNO_x catalysts are included in the field of hazardous waste in China. Therefore, how to dispose of waste catalysts rationally is a major problem. The regeneration of deNO_x catalysts is the only way for the development of deNO_x industry. Catalyst regeneration is an important way to recover the activity of deactivated catalyst, and the use of regenerated catalyst is conducive to saving raw materials, realizing the recycling of limited resources, and greatly reducing the cost of SCR technology. In addition, it can avoid secondary pollution of the environment, protect the environment and implement the concept of sustainable development.

3.1. Thermal Regeneration Method

Thermal regeneration refers to the roasting of the catalyst at a certain temperature. The regeneration of the catalyst depends upon whether the heat treatment can eliminate NH₄HSO₄ and M_x(SO₄)_y formed on the surface of the toxic catalyst. Since the thermal decomposition temperature of (NH₄)₂SO₄ and NH₄HSO₄ compounds generated on the surface of the catalyst is 200–400°C [68], thermal regeneration can decompose the ammonium sulfate salt deposited on the surface of the catalyst to restore the catalytic active site.

Xu et al. [69] heated the deactivated catalyst to 400°C in a fixed-bed

Table 2. Summary of Regeneration of Sulfur Poisoning Catalyst

Catalyst	Regeneration method	Regeneration conditions	Performance	Ref.
1%VWTi-r	Thermal regeneration	400°C, 30 min, in N ₂	85%	[69]
Ce _{0.75} Zr _{0.25} O ₂ -PO ₄ ³⁻	Thermal regeneration	650°C, under air	over 80%	[70]
FeW/Ti	Thermal regeneration	400°C, 30 min	over 90%	[71]
In/H-BEA	Thermal reduction regeneration	400°C, 60min, in 5vol.% H ₂ /95 vol.%Ar	over 90%	[72]
2% Ag/-Al ₂ O ₃	Thermal reduction regeneration	670 °C, 40 min, in H ₂	over 90%	[73]
MnFe/TiO ₂	Thermal regeneration	350°C, 3 h, under air	35%	[77]
MnFe/TiO ₂	Water washing regeneration	1.2g/50 mL DI water, 30 s	88%	[77]

quartz reactor and kept it for 30 minutes. The deposited NH_4HSO_4 species were decomposed on the surface of the catalyst, and the catalytic ability of the catalyst was recovered. Si et al. [70] regenerated the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2\text{-PO}_4^{3-}$ catalyst in 650°C air for 3 h, which could completely regenerate the sulfur aged catalyst. Yu et al. [67] heated the sulfurized $\text{ZnTi}_{10}\text{O}_x\text{-Cu-SSZ-13}$ and Cu-SSZ-13 catalysts at 650°C for 3 h in an air atmosphere to regenerate them. Wang et al. [71] found that compared with other catalysts (FeW/Ti , MnW/Ti and CuW/Ti), VW/Ti possessed good regeneration performance and catalytic activity. After thermal regeneration at 400°C for 30 minutes, the catalytic activity returned to its original level.

3.2. Thermal Reduction and Regeneration Method

Thermal reduction and regeneration method are to mix the inert gas with reducing gas (ammonia gas, hydrogen gas, etc.). Under high temperature, the reducing gas can reduce the ammonium sulfide compound covering the catalyst surface to SO_2 and/or H_2S to achieve desulfurization and regeneration of the catalyst.

The catalyst showed similar activity with fresh catalyst when the In/H-BEA-S catalyst sulfated for 45 h at 450°C in the $\text{CH}_4\text{-SCR}$ reaction was reduced in 5vol% H_2/Ar for 1 h [72]. The regeneration mechanisms as shown in Fig. 5. Doronkin et al. [73] heated the 2% $\text{Ag/-Al}_2\text{O}_3$ catalyst used for H_2 assisted $\text{NH}_3\text{-SCR}$ in the SCR feed gas at $650\text{-}700^\circ\text{C}$ and kept for 10-20 min, and surprisingly detected that the catalyst had exceptional regeneration ability. Chang et al. [74] put forward that the sulfated $(\text{Ce}_3\text{W}_2)_{0.9}\text{Ge}_{0.1}\text{O}_x$ catalysts could be easily regenerated via heating at 300°C in H_2 atmosphere and the regenerated catalyst showed better activity.

Fig. 5. The mechanisms of regenerated In/H-BEA catalysts [72].

3.3. Washing Regeneration Method

Water washing treatment is one of the auxiliary regeneration methods commonly used in industrial catalysts. It can dissolve the soluble sulfate or nitrate generated on the surface of the sulfur poisoning catalyst and the derivative substances produced by SO_2 adsorption, so that the active center covered on the catalyst surface can be exposed again. The combination of agitation, ultrasound

and other means can enhance the washing effect.

Zhao et al. [75] continuously stirred the deactivated sample in an aqueous solution for 2 h, and then dried it at 105°C . The results showed that washing regeneration can remove the sulfate species on the catalyst surface, exposing more active sites. After washing and regeneration, the Brønsted acid sites in the catalyst are restored to almost the same level as the fresh catalyst. Hu et al. [76] soaked the sulfur poisoning catalyst in deionized water for 30min, and continuously oscillated it with ultrasonic waves, and then filtered and dried the washed sample. After regeneration, the catalyst activity returned to the initial level. Lee et al. [77] reported that water washing was capable to remove both ammonium salts and metal sulfates on the MnFe/TiO_2 catalysts, and the NO_x conversion could be recovered to 88% (compared to 99% for the fresh catalyst).

Comparing the above regeneration methods, it can be found that the washing regeneration method is simple to operate, low energy consumption, and the regeneration effect is obvious.

4. Application of Quantum Chemistry in the Field of Sulfur Resistance Research

With the progress of quantum chemistry technology and the significant improvement of computer computing power, the first-principle calculation based on density functional theory (DFT) has been applied in the field of SCR, which can provide useful help to clarify the mechanism of catalyst sulfur poisoning.

Han et al. [78] used DFT theory to study the SO_2 adsorption energy of $\text{m-TiO}_2\text{@Fe}_2\text{O}_3$ complex on TiO_2 -shell and Fe_2O_3 -nucleus to explain the reason why the composite inhibited sulfate deposition. It was found that the adsorption energy of SO_2 on the surface of $\text{TiO}_2(101)$, $(\text{Fe}_2\text{O}_3)_2/\text{TiO}_2(101)$ was smaller (0.21eV and 0.86eV, respectively), thus it was easy to be replaced by NO (1.65 eV) and NH_3 (1.90 eV) with higher adsorption energy. Fan et al. [22] found that for Ce doped Mn based catalyst, the SO_2 adsorption capacity at Ce site was greater than Mn site, which prevented the acidification of manganese active site to a certain extent.

Yang et al. [79] used the generalized gradient approximation method (GGA) for periodic density functional theory calculations. The adsorption behavior and sulfation process of copper species (Cu^+ , Cu^{2+} , Cu^+/H^+ , $[\text{Cu}^{\text{II}}\text{OH}]^+$) in Cu-SAPO-34 catalyst to SO_2 were studied by calculating adsorption energy, energy barrier, charge density, etc. It was found that the electronic and structural properties of copper in the catalyst had great influence on SO_2 adsorption, as well as copper with low oxidation state was the main site for SO_2 adsorption. Cu^{2+} is not conducive to SO_2 adsorption, but SO_2 tends to be adsorbed on Cu^+ and Cu^+/H^+ . The authors believed copper species with high oxidation state have difficulty in providing electrons to SO_2 . SO_2 forms copper sulfate at the Cu^+/H^+ site, which seriously affects the redox cycle of the SCR reaction ($\text{Cu}^+ \rightarrow \text{Cu}^{2+}$). As a result, the concentration of Cu^{2+} decreases, which significantly hinders the SCR reaction rate. Hammershøi et al. [80] also confirmed this similar conclusion.

Fig. 6. Model structures of SO_2 adsorbed on Mn_3O_4 (a), and $\text{Cu}_{1.0}\text{Mn}_{2.01-\delta}\text{O}_4$ (c), (e) as " $-\text{Mn}-\text{SO}_2$ ". Model structures of SO_2 adsorbed on Mn_3O_4 (b), and $\text{Cu}_{1.0}\text{Mn}_{2.01-\delta}\text{O}_4$ (d), (f) as " $-\text{Mn}-\text{O}-\text{S}-\text{O}-\text{Mn}-$ " [30].

Xiong et al. [60] determined the adsorption energy and corresponding bond length of Mn_3O_4 and SO_2 on the $(\text{Cu}_{1.0}\text{Mn}_{2.01-\delta}\text{O}_4)$ catalyst by DFT calculation (as shown in Fig. 6). It was found that SO_2 could hardly be adsorbed on the two model catalysts in the form of " $-\text{Mn}-\text{SO}_2$ ", and their adsorption energy is close to 0. However, it is easy to adsorb in the form of " $-\text{Mn}-\text{O}-\text{S}-\text{O}-\text{Mn}-$ ", one O in SO_2 combines with Mn, as well as one S in SO_2 is combined with the terminal O in " $\text{O}-\text{Mn}-$ ", while the " $-\text{Mn}-\text{O}-\text{S}-\text{O}-\text{Cu}-$ " structure is very unstable. The " $\text{O}-\text{Cu}$ " bond in this structure is easily broken, and the residual O combines with another Mn to form " $-\text{Mn}-\text{O}-\text{S}-\text{O}-\text{Mn}-$ ". This shows that SO_2 cannot be adsorbed on the copper ions in $(\text{Cu}_{1.0}\text{Mn}_{2.01-\delta}\text{O}_4)$ spinel. SO_2 is easier to use " $-\text{Mn}-\text{O}-\text{S}-\text{O}-\text{Mn}-$ " form adsorption, doping Cu in Mn_3O_4 reduces the content of adjacent Mn, thus preventing the formation of MnSO_4 on the spinel. Wei et al. [49] found that Cr can convert sulfur to Brønsted acid sites by comparing the dissociation energy barrier of NH_3 on doped catalysts of different elements and analyzing the projected density of state (PDOS) of SO_2 adsorption, and this element can be used as a potential dopant for modified manganese catalysts.

5. Conclusions and Outlook

Selective catalytic reduction technology is an effective method to eliminate NO_x in flue gas, but the residual SO_2 in flue gas will inevitably affect the activity of the catalyst, reduce the catalytic efficiency, and shorten the catalytic life. Therefore, exploring the effect of sulfur on the activity of the catalytic system and the mechanism of sulfur poisoning of the catalyst is crucial to the development of a deNO_x catalyst that combines high efficiency and long life. At present, the potential causes of sulfur poisoning mechanism of catalysts can be classified as follows: competitive adsorption between SO_2 and NO_x ; sulfation of active center atoms, formation and deposition of ammonium sulfate on the catalyst surface, resulting in blockage of catalyst channels. From the point of existing achievements, reducing/avoiding the sulfation of catalyst active

sites is an effective strategy to improve the sulfur resistance of the catalyst, which can be achieved by adding components, improving the support, and regulating the structure and morphology of the catalyst.

Nowadays, tremendous efforts have been devoted to focuses on the denitrification efficiency and deactivation mechanism of catalyst in the presence of single sulfur toxicity factor, there are few studies on the deactivation mechanism of the catalyst and the regeneration of the deactivated catalyst in the presence of multiple toxic factors, so future research on the SCR catalyst can be considered from the following aspects:

- (1) Deactivation of catalysts has always been a key problem in selective catalytic reduction of nitrogen oxides. The deactivation of most denitration catalysts is not affected by a single factor, and the deactivation reasons are complex. The fly ash particles in the flue gas, alkali metals (K, Na), alkaline earth metals (Ca, Mg), heavy metals (Pb, As), etc. all have a toxic effect on the catalyst. The deactivation mechanism of catalyst is worthy of further study. It is also necessary to develop catalyst with excellent resistance to various poisons according to the deactivation mechanism of different toxic factors, which provides beneficial attempt and exploration for industrial application.
- (2) The deactivation of the catalyst is not caused by a single factor, and the effect of a single regeneration method is limited. Therefore, it is necessary to explore the combined regeneration method to achieve the ideal regeneration effect.
- (3) Theoretical calculation is an important research method in the field of environmental catalysis, which helps to clarify the reaction mechanism that is difficult to obtain only through experimental research. At present, the research on the application of quantum chemistry in SCR field is very limited. The theoretical calculation and experiment can be further combined to develop efficient, stable, long service life and environment-friendly deNO_x catalyst materials.

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Author Contributions

L.Z. (Associate Professor) wrote and revised the manuscript. Y.Z. (Master student) wrote and revised the manuscript. M.D.K (Master student) revised the manuscript.

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