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

Ling Zhao†, Yu Zhang, Mengdi Kang

School of Ecology and Environment, Inner Mongolia University, China

ABSTRACT

NOx 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 deNOx 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 deNOx catalysts is prospected, which provides valuable scientific guidance for the design and development of efficient and practical sulfur resistant deNOx catalysts.

Keywords: deNOx 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 NOx 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 (NOx) 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 NOx emissions are expected to reach 42.96 million tons in 2030 without reasonable measures to control NOx emissions. The Outline of the National 13th Five-Year Plan has clearly stated that NOx emission will be reduced by 15% within 5 years. In the 2019 government work report, Premier Li Keqiang clearly pointed out that NOx emission will be reduced by 3% [3]. In the face of increasingly stringent pollutant emission standards, the elimination of NOx 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 method [4]. Among them, selective catalytic reduction (SCR) is considered as the mainstream method for NOx removal due to its high deNOx efficiency, excellent selectivity and practicability. The catalyst is the core part of the technology, and its performance will directly affect the deNOx 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 NOx 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, due to the tremendous progress in material preparation science and technology, academic researchers and engineers have developed a number of SCR catalysts with high NOx 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.
NOx under the action of van der Waals force. The presence of SO2 will inhibit the adsorption of NOx, 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 SO2 by means of thermal regeneration. In addition, the reaction of SO2 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, SO2 reacts with NH3 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 deNOx 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 deNOx 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 Fe2O3 modified CeW/H catalyst and found that Fe2O3 doping can effectively suppress the irreversible combination of SO2 and active components. When the Fe:Ce molar ratio is 4, the catalyst achieves the best NOx conversion rate and SO2 tolerance. After the material was continuously reacted in a 100 ppm SO2 atmosphere for 8 hours, the NOx 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 SO2 and catalyst, as shown in Fig. 1. The results showed that there was competitive adsorption between SO2 and NO on the surface of CeW/H sample. SO2 could react with the active component CeO2 to generate stable sulfate (Ce2(SO4)3) species, thus reducing the number of active sites and further inhibiting the reduction reaction. For Fe-modified catalysts, SO2 reacts with Fe2O3 to produce Fe3(SO4)2, which can protect the active component CeO2-WO3 from being affected. Furthermore, the team [7] recently claimed that Fe-doped CeVO4 catalyst can significantly inhibit the adsorption of SO2 and sulfate species deposition for operating temperatures at 240°C compared to CeVO4 ones. Zeng et al. [8] explored the promotion of Fe3+ ions on NH3-SCR activity of CoFe catalyst, and found that Fe3+ doping can induce Fe3++Ce3+→Fe3++Ce4+ redox balance, thereby significantly improving the redox performance of CoFe catalyst. For Fe0,Co0.7 sample, after exposing to 5vol% H2O and 100 ppm SO2 for 10 h, the deNOx efficiency remained at 35.5%, but the activity of CePO4 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 Fe0.5Sb0.5O3 catalyst showed good NH3-SCR activity with 100% conversion of NOx from 175°C to 250°C and high SO2/H2O 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 NOx conversion in the presence of H2O, SO2 and CO2.

Li et al. [11] confirmed that the main reasons for the deactivation of Fe0,Co,V binary metal oxides in 3DOM structures were the deposition of NH4HSO4 on the catalyst surface and the weakening or destruction of Brønsted acid potential. Zhu et al. [12] showed that after injecting SO2 and H2O into the reaction system for 24 hours, Fe-V-Ti catalyst remained above 93% NOx 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 H2O(g) and SO2 had little influence on C3H6-SCR reaction. Qian et al. [14] also confirmed that Fe doping could improve the conversion rate of NO and C3H6 and the selectivity of N2. 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 (NO→M–NO2→NO3→M–NO2+M–NO3→N2O4+M; CO→CO3→CO32→CO2). The H2O and SO2 resistance test results showed that an appropriate increase in the proportion of Fe will promote the resistance of SO2/H2O. 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 calculation temperature would affect the sulfur resistance of Fe-Mn-Zr catalyst, and FMZ-500 had better tolerance to 100 and
200 ppm SO2 than other samples (Fig. S1). Wang et al. [17] reported by doping with Fe on Mn/γ-Al2O3 catalyst, the sulfate formation of Mn active component can be dramatically reduced and lower the stability of surface sediments (NH4SO4), forcing them to decompose rapidly. Xie et al. [18] fabricated mesoporous γ-Fe2O3-modified nanoflower-MnO2/attapulgite catalyst through a facile hydrothermal method, which can effectively inhibit SO2 and H2O poisoning.

2.1.2. Ce modification

CeO2 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 Ce4+/Ce3+ 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-SO2 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 SO2. 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 MnOx, the new Mn-Ce mixed oxides delivered a much better SO2 tolerance, the NO conversion increased from 92.6% to 97.8% at 150°C when pouring into 200 ppm SO2. Wang et al. [21] carefully designed and synthesized CoOx modified MnCoOx catalysts for NH3-SCR reaction, and found that the modified catalyst has significantly enhanced low temperature dNOx activity and SO2 tolerance. The results showed that MnCoOx samples after NH3-SCR reaction for 12 hours in the presence of 50 ppm SO2 and 5% H2O contained more metal sulfate substances than MnCoOx, which proved that the former was more likely to be sulfurized as metal sulfate. In other words, the added CeO2 acts as a protective layer on the surface of the MnCoOx catalyst, which can prevent the active site of the MnCoOx material from being poisoned by SO2. Fan et al. [22] also proved that the addition of cerium oxide can inhibit the deposition of NH4HSO4 and preferentially react with SO2 to protect the active center.

Zhang et al. [23] reported that the effect of SO2 on NO conversion is greatly dependent on the reaction temperature over the Ce-TiO2 catalyst. With the increase of reaction temperature, the tolerance of SO2 is gradually improved. Using catalyst performance measurements, after 8 hours of SO2 poisoning at 300°C, the NO conversion rate decreased from 96.9% to 91.1%, and remained unchanged after SO2 was cut off. The superior SCR activity of Ce-TiO2 catalyst in the presence of SO2 at a higher reaction temperature may be attributed to the synergistic effect of cerium sulfate and bulk CeO2. Cerium sulfate acts as the acidic site for NH4 adsorption and CeO2 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).

Kwon et al. [24] investigated the influence of SO2 on the SCR process of Ce modified V/Slb/Ge/Ti catalyst, and observed that NH4HSO4 could be formed on the surface of V/Slb/Ti (or V/W/Ti) catalyst due to SO2 in the flue gas being oxidized to SO3, which would result in the blockage of catalyst pore. However, Ce in the modified catalyst reacts with SO2 and O2 to form Ce2(SO4)3, which consumes SO2 and thus inhibits the formation of NH4HSO4. 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 Ce3+ on the surface of the catalyst and generate a large number of Brønsted acid sites. The mechanism study showed that the NH3-SCR reaction follows the Eley-Rideal (E-R) mechanism in the case of the sulfated catalysts. Ma et al. [26] also concluded that the Cu0.02Fe0.2-Ce0.1Ti0.8Ox catalyst has excellent H2O and SO2 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 SO2 poisoning in SCR reaction.

Yao et al. [27] studied the denitrification performance of CeO2-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, Ce3+ ions, adsorbed oxygen species and improved redox capacity. In addition, CeO2-TiO2 catalyst with CeO2 as the carrier has superior SO2 tolerance than only TiO2 carrier. The reasonable reason for this result is loading of TiO2 on the surface of CeO2 can restrain the sulfation of bulk CeO2, thus maintaining the redox ability. NH3-SCR reaction can take place through the synergistic effect of bulk CeO2 and surface sulfates. Liu et al. [28] put forward...
that the NOx conversion and SO2 resistance was well enhanced when TiO2 supporter adding to ZrO2. Researchers found that the surface area of the supporter would be enormously increased by introducing TiO2, thus the active components (Fe2O3 and SO2+2) are highly dispersed on the support of binary metal oxides (TiO2–ZrO2). Compared with single TiO2 or ZrO2, the interaction between Ti and Zr will significantly improve the conversion of Fe3+ to Fe2+ on TiZr4 carrier. Li et al. [29] found that the catalyst (MnCeOx/TiO2-Al2O3) adding Al2O3 supporter presents higher SCR performance and SO2 poisoning tolerance than MnCeOx/TiO2 alone. Wang et al. [30] advocated that the sulfur tolerance of the NbOPo4 supported Cu–Ce sample was greatly improved compared to TiO2 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 SO2). The excellent properties were owing to the increase of acidity and the strong interaction between Cu–Ce oxides and NbOPo4 support, which avoided the surface oxygen species from being sulfurized by SO2. 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 SO2 poisoning. Han et al. [32] compared the influence of the micromorphologies of CeO2 supports on the NH3–SCR reaction. The Fe2O3/CoO nanorods achieving higher catalytic activity than the Fe2O3/CoO nanopolyhedra and the NO conversion value still maintain 94% during the whole test period whether inlet or cease SO2. Gao et al. [33] fabricated novel Mn–Ni spinel nanosheets and attained 85–90% NOx conversion after introducing 10 vol% H2O + 150 ppm SO2 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 ammonium component, thereby alleviating the deposition/inhibition effects.

CeTiOx 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 SO2 and 6% H2O at 240°C, the NO conversion rate remained at about 96% within 8 hours. After closing H2O and SO2, the NO conversion rate can quickly return to the initial value. Huang et al. [35] developed a V2O5/HWO catalyst by support V2O5 on a hexagonal WO3 (HWO), which possess exceptional resistance simultaneously to alkalis and SO2 poisoning in the SCR reactions owning 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 NH4HSO4. This team also found that the Fe2O3/SBA-15 catalyst with larger mesopores exhibited much improved sulfur resistance, and quantitative analysis results demonstrated that the deposited sulfates was significantly relieved.

Sheng et al. [37] found that the core-shell structure can protect the catalytic active sites from the effects of H2O and SO2 poisoning. The SO2 tolerance of MnOx@TiO2 core-shell nanorods is higher than that of MnOx and MnOx/TiO2 catalysts, which is due to SO2 can be effectively isolated on the TiO2 shell. Gan et al. [38] explored the α-MnOx@CeO2 catalyst with a core-shell structure and found that the CeO2 shell can bind to SO2 firmly in preference to MnOx, and protect the active sites on the α-MnOx core from SO2 poisoning. Ma et al. [39] also proved that MnOx–CoO/α-TiO2 core–shell composites showing the excellent SCR activity in the presence of SO2 than conventional MnOx–CoO/α-TiO2 catalysts. The SO2 deactivation mechanism over above catalysts are as follows (Fig. 3), Zhang et al. [40] proved that for the SiO2@FeCeOx/CNTs core-shell catalyst, the coated SiO2 shell establish an available barrier to hinder the generation of FeSO4 and restrain the reduction of chemisorbed oxygen, improving its stability and SO2 tolerance. Yu et al. [41] designed and fabricated a novel MnOx@Eu–CeO2 catalyst with composite-shell structure and attained more than 95% NOx 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 SO2 was introduced into the reaction for 4 h, the NOx removal rate only declined from 93.7% to 91.0%. Notably, when the SO2 flow in the simulated flue gas was cut off, the desulfurification 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 EuOx–CeO2 composite-shell can reduce the toxicity of SO2 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 Fe2O3/MnOx@CNTs catalysts, which also proved that the Fe2O3 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
SCR catalyst - by establishing a dynamic equilibrium between sulfates formation and decomposition. This team designed a novel MnOx/CeO2 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 NOx reaction rate of 1,800 μmol g⁻¹ h⁻¹ for 1000 h test at 250°C in the presence of 200 ppm SO2. They found that the deposition and decomposition of surface sulfate are in a dynamic equilibrium over CeO2(NR) and MnOx/CeO2(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):

\[ \text{Ce}^{4+} + \text{O}_2 \rightarrow \text{Ce}^{3+} \text{SO}_4 \]

\[ \text{Ce}^{2+} \text{SO}_4 + 4\text{NH}_3 + 3\text{H}_2\text{O} \rightarrow \text{Ce}_2\text{O}_3 + (\text{NH}_4)_2\text{SO}_4 + 2\text{NH}_4\text{HSO}_4 \]

\[ \text{Ce}_2\text{O}_3 + 1/2\text{O}_2 \rightarrow \text{Ce}_2\text{O}_3 + \text{NH}_4\text{SO}_4 + 2\text{NH}_4\text{HSO}_4 + 2\text{NO} + 1/2\text{O}_2 \rightarrow 3\text{N}_2 + 4\text{H}_2\text{O} + 3\text{SO}_2 \]

2.5.1. Vanadium-based catalysts

Vanadium-based catalysts have been predominantly used as commercial catalysts with the operating temperature concentrated at 300–400°C. However, some drawbacks of this type of catalysts including narrow working temperature window (300–400°C) and susceptible to deactivation by residual SO2 in the exhaust. 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 FeVOx catalyst, but actively promotes high-temperature activity by inhibiting harmful NH3 oxidation. Li et al. [47] found that V-W/Co/Ti-5% presented better NH3-SCR activity and higher NH4HSO4 resistance at 280°C when 5% WO3 was loaded. The result is due to WO3 doping suppresses the formation of NH4HSO4 and metal sulfate species over active sites by lowering the alkalinity of V-W/Co/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 MnOx catalyst, poor resistance to SO2 is the main challenge that hinders its further industrial application [48]. The Li Junhua team [49] reported that exposing to 150 ppm SO2 at 150°C, the NO conversion rate of pure MnOx decreased from 92% to 23%, and only recovered to 45% after cutting off SO2. Due to the strong oxidation ability of Mn oxide, SO2 is easily oxidized to SO3 at low temperature, and the formed SO3 reacts with NH3 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 SO2 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 SO2 in priority can improve the anti-sulfur performance of Mn-based catalyst.

Jiang et al. [50] synthesized some α-MnO2 catalysts doped with Fe, Co, Cr, Zr or Co as metal co-catalysts by hydrothermal method, and found that the catalysts doped with Co showed the best low temperature NH3-SCR activity and excellent H2O/SO2 tolerance. NO conversion activity remained at 100% at 200°C when H2O and SO2 exist in the flue gas. Sun et al. [51] prepared a series of MnNb/TiO2 catalyst samples with different Nb/Mn molar ratios using the sol-gel method, and studied the effect of SO2 on the denitrification process. The experimental results show that introducing Nb into the Mn/TiO2 catalyst can increase the specific surface area, enhance the reducibility and surface acidity, promote the formation of more Mn4+ and chemically adsorbed oxygen on its surface, and produce more NO2. Liu et al. [52] found that MnEu/TiO2 catalyst also had excellent SO2 resistance performance. Through in-situ infrared technology, it was found that SO2 could promote the adsorption of NH3 and inhibit the adsorption of NOx. Eu modification could partially offset the inhibition effect of SO2 on the adsorption of NOx on Mn/TiO2 catalyst.

The research team of Huazhong University of Science and Technology [53] found that the presence of Sm promotes the anti-SO2 performance of the Mn/TiO2 catalyst. The electron transfer between Sm and Mn ions inhibits the oxidation of SO2, 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 MnCoSm/TiO2 mixed oxides maintained higher catalytic performance after H2O and SO2 were added by
suppressing the oxidation of SO2 by Mn4+ and Co4+. Zhang et al. [55] found that when 200 ppmv SO2 was introduced into the feed gas, the catalytic activity of Sb modified MnPG 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 MnO2-A catalyst was reduced from 98% conversion rate to 13% within 8 hours, while the MnO2@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 MnO2-A are mainly formed by the reaction between MnO2 and SO2 and the decomposition products of NH4HSO4, but no obvious sulfates were found on the surface of the MnO2@GA catalyst. It is proved that the weakening of the oxidation ability of MnO2@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 MnOx. 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 NOx. 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 Mn3NiO4 spinel catalyst on the reaction path, and further proved that the Ni modified MnOx 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 MnO2 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 NOx conversion rate only dropped by about 4% and remained at 87%.

Yan et al. [61] prepared a new low-temperature NH3-SCR catalyst Cu1Mn0.5Ti0.5Ox from layered double hydroxides (LDHs) precursor. The study found that Cu1Mn0.5Ti0.5Ox showed the optimal SCR performance, with a NOx 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] = [NH3] = 500 ppm, [SO2] = 100 ppm, [O2] = 5vol%, N2 balance, total gas flow rate = 250 mL/min, GHSV=40,000 h⁻¹ | 93% (200°C) | [5] |
| Fe3V0.1TiO4 | [NO] = [NH3] = 500 ppm, [SO2] = 100 ppm, [O2] = 5vol%, [H2O] = 5vol%, N2 balance, total gas flow rate = 500 mL/min, GHSV=200,000 h⁻¹ | 93% (250°C) | [12] |
| Mn-Fe-2γ-Al2O3 | [NO] = 0.03%, [NH3] = 0.03%, [SO2] = 250 mg/cm², [O2] = 6vol%, [H2O] = 6vol%, N2 balance, GHSV = 6,000–14,000 h⁻¹ | 84% (150°C) | [17] |
| γ-Fe2O3/nf-MnO2–ATP | [NO] = [NH3] = 1000 ppm, [SO2] = 200 ppm, [O2] = 3vol%, N2 balance, total gas flow rate = 2 L/min, GHSV=45,000 h⁻¹ | 89% (200°C) | [5] |
| Mn/Ce-400-Air | [NO] = [NH3] = 500 ppm, [SO2] = 200 ppm, [O2] = 3vol%, N2 balance, GHSV = 52,500 h⁻¹ | 97.8% (150°C) | [20] |
| Ge-TiO2 | [NO] = [NH3] = 600 ppm, [SO2] = 1000 ppm, [O2] = 3vol%, N2 balance, GHSV = 40,000 h⁻¹ | 91.1% (300°C) | [23] |
| FeS/(Tit1Zr4) | [NO] = [NH3] = 500 ppm, [SO2] = 200 ppm, [O2] = 3vol%, N2 balance, total gas flow rate = 300 mL/min, GHSV = 47,000 h⁻¹ | 96% (300°C) | [28] |
| Fe2O3/GeO2–NR | [NO] = [NH3] = 500 ppm, [SO2] = 100 ppm, [O2] = 3vol%, N2 balance, total gas flow rate = 250 mL/min, GHSV = 20,000 h⁻¹ | 94% (275°C) | [32] |
| NiMn2O4–UHHS | [NO] = [NH3] = 500 ppm, [SO2] = 150 ppm, [O2] = 5vol%, [H2O] = 10vol%, N2 balance, total gas flow rate = 100 mL/min, GHSV = 32,000 h⁻¹ | 85–90% (150–300°C) | [33] |
| CeTiO3–T | [NO] = [NH3] = 1000 ppm, [SO2] = 100 ppm, [O2] = 3vol%, [H2O] = 6vol%, N2 balance, total gas flow rate = 200 mL/min, GHSV = 40,000 h⁻¹ | 96% (240°C) | [34] |
| MnOx@Eu–CeOx | [NO] = [NH3] = 600 ppm, [SO2] = 100 ppm, [O2] = 2.5vol%, Ar balance, GHSV = 90,000 h⁻¹ | 91% (200°C) | [41] |
| MnO2–Co–0.8 | [NO] = [NH3] = 500 ppm, [SO2] = 100 ppm, [O2] = 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] = [NH3] = 500 ppm, [SO2] = 100 ppm, [O2] = 5vol%, N2 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 (MnO, 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 NOx and SO2, the results show that there is a competitive relationship between SO2 and NOx on the surface adsorption sites. Significantly, the intensity of the peak attributable to the sulfur species on Cu2Mn0.93Ti0.07O5 is higher than that of Cu-Mn/TiO2. It is much weaker than Mn/TiO2, and the intensity attributable to the NOX peak is the opposite, further proving the former’s stronger sulfur resistance. Chen et al. [62] reported that a Mn2Fe0.5Al0.5Ox 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% deNOx 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 NH4HSO4 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 denitification 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 NOx 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/Co/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, Fe0.12/Cu1.50-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 ZnTiOx 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 deNOx technology is accompanied by the problem of disposal of waste catalysts. At present, deactivated deNOx 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 deNOx catalysts is the only way for the development of deNOx 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 Mn(SO4)2 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 N2 | 85%          | [69] |
| Ce0.75Zr0.25O2–PO4| Thermal regeneration | 650°C, under air | over 80% | [70] |
| FoW/Ti         | Thermal regeneration | 400°C, 30 min | over 90% | [71] |
| In/H-BEA       | Thermal reduction regeneration | 400°C, 60 min, in 5vol.% H2/95 vol.%Ar | over 90% | [72] |
| 2% Ag2–Al2O3   | Thermal reduction regeneration | 670 °C, 40 min, in H2 | over 90% | [73] |
| MnFe/TiO2      | Thermal regeneration | 350°C, 3 h, under air | 35%          | [77] |
| MnFe/TiO2      | Water washing regeneration | 1.2g/50 mL DI water, 30 s | 88%          | [77] |
quartz reactor and kept it for 30 minutes. The deposited NH\(_4\)HSO\(_4\) species were decomposed on the surface of the catalyst, and the catalytic ability of the catalyst was recovered. Si et al. [70] regenerated the Ce\(_0.75\)Zr\(_0.25\)O\(_2\)-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 ZnTiO\(_x\)-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\(_2\)S 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 CH\(_4\)-SCR reaction was reduced in 5vol% H\(_2\)/Ar for 1 h [72]. The regeneration mechanisms as shown in Fig. 5. Dorenkin et al. [73] heated the 2\%\(\text{Al}_2\text{O}_3\) catalyst used for H\(_2\) assisted NH\(_3\)-SCR in the SCR feed gas at 650-700°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 (Ce\(_0\)W\(_{0.9}\)Ge\(_{0.1}\)O\(_x\)) catalysts could be easily regenerated via heating at 300°C in H\(_2\) atmosphere and the regenerated catalyst showed better activity.

### 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 Bronsted 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 m-TiO\(_2@\text{Fe}_2\text{O}_3\) complex on TiO\(_2\)-shell and Fe\(_2\text{O}_3\)-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 TiO\(_2\)(101), (Fe\(_2\text{O}_3@\text{TiO}_2\) (101) was smaller (0.21eV and 0.86eV, respectively), thus it was easy to be replaced by NO\(_x\) (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\(^{+}/\text{H}^+\), [Cu\(^{6+}\text{OH}^-\)]) 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\(^{+}/\text{H}^+\). 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\(^{+}/\text{H}^+\) site, which seriously affects the redox cycle of the SCR reaction (Cu\(^{+}\)→Cu\(^{2+}\)). As a result, the concentration of Cu\(^{+}\) decreases, which significantly hinders the SCR reaction rate. Hammershøi et al. [80] also confirmed this similar conclusion.

Fig. 5. The mechanisms of regenerated In/H-BEA catalysts [72].
Xiong et al. [60] determined the adsorption energy and corresponding bond length of Mn$_3$O$_4$ and SO$_2$ on the (Cu$^{1.0}$Mn$^{2.01-}$) 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 “–Mn–SO$_2$”, and their adsorption energy is close to 0. However, it is easy to adsorb in the form of “–Mn–O–S–O–Mn–”, one O in SO$_2$ combines with Mn, as well as one S in SO$_2$ is combined with the terminal O in “O–Mn–”, while the “–Mn–O–S–O–Cu” structure is very unstable. The “O–Cu” bond in this structure is easily broken, and the residual O combines with another Mn to form “–Mn–O–S–O–Mn–”. This shows that SO$_2$ cannot be adsorbed on the copper ions in (Cu$_{1.0}$Mn$_{2.01-}$) spinel. SO$_2$ is easier to use “–Mn–O–S–O–Mn–” form adsorption, doping Cu in Mn$_3$O$_4$ 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 Brunsted 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. The theoretical calculation and experiment can be further combined to develop efficient, stable, long service life and environment-friendly deNO$_x$ catalyst materials.

Acknowledgments

We acknowledge the financial support of the National Natural Science Foundation of China (Nos. 21866022, 21567018).

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.

References

1. Zeng YY, Gao YC, Qiao X, Seyler BC, Tang Y. Air pollution reduction in China: Recent success but great challenge for the future. Sci. Total Environ. 2019;663:329-337.
2. Liu MH, Liu T, Xiao CL. Research progress of low temperature selective catalytic reduction (SCR) catalysts for denitrification.
17. Wang JY, Nie ZG, An ZW, et al. Improvement of SO2 resistance of MnO/γ-Al2O3 catalysts. *Industrial Catalysis* 2019;27:1-23.

18. Xie AJ, Tao YY, Jin X, et al. A γ-Fe2O3-modified nanoflower-MnO2/attapulgite catalyst for low temperature SCR of NOx with NH3. *New J. Chem.* 2019;43:2490-2500.

19. Chen JJ, Zhao WT, Wu Q, Mi JX, Wang XY, Ma L. Effects of anaerobic SO2 treatment on nano-Co3O4 of different morphologies for selective catalytic reduction of NOx with NH3. *Chem. Eng. J.* 2020;382:122910.

20. Chen JY, Fu P, Lv DF, et al. Unusual positive effect of SO2 on Mn-Co mixed-oxide catalyst for the SCR reaction of NOx with NH3. *Chem. Eng. J.* 2021;407:127071.

21. Wang XB, Duan RB, Liu W, Wang DW, Wang BR, Xu YR. The insight into the role of Co2+ in improving low-temperature catalytic performance and SO2 tolerance of MnCo2O4 microflowers for the NH3-SCR of NOx. *Appl. Surf. Sci.* 2020;510:145517.

22. Fan YM, Ling W, Huang BC, Dong LF, Yu CL, Xi HX. The synergistic effects of cerium presence in the framework and the surface resistance to SO2 and H2O in NH3-SCR. *J. Ind. Eng. Chem.* 2017;56:108-119.

23. Zhang VJ, Liu GF, Jiang J, et al. Temperature sensitivity of the selective catalytic reduction (SCR) performance of Ce-TiO2 in the presence of SO2. *Chemosphere* 2020;243:125419.

24. Kwon DW, Nam KB, Hong SC. The role of ceria on the activity and SO2 resistance of catalysts for the selective catalytic reduction of NOx by NH3. *Appl. Catal., B* 2015;156:167-177.

25. Shu Y, Akebair T, Quan X, Chen S, Yu HT. Selective catalytic reaction of NOx with NH3 over Co-Fe2O3-loaded wire-mesh honeycomb: Resistance to SO2 poisoning. *Appl. Catal., B* 2014;150-151:629-635.

26. Ma SB, Tan HS, Li YS, et al. Excellent low-temperature NH3-SCR NO removal performance and enhanced H2O resistance by Ce addition over the Cu0.3Fe2O3Ce0.7Ti0.5O3 (y = 0.1, 0.2, 0.3) catalysts. *Chemosphere* 2020;243:125309.

27. Yao XJ, Kang KK, Cao J, et al. Enhancing the denitration performance and anti-K poisoning ability of CeO2-TiO2/P25 catalyst by H2SO4 pretreatment: Structure-activity relationship and mechanism study. *Appl. Catal., B* 2020;269:118808.

28. Liu CX, Bi YL, Li JH. Activity enhancement of sulphated Fe2O3 supported on TiO2-ZrO2 for the selective catalytic reduction of NO by NH3. *Appl. Surf. Sci.* 2020;528:146695.

29. Li G, Mao DS, Chao MX, Li GH, Yu J, Guo XM. Low-temperature NH3-SCR of NO over MnCo2O4/TiO2 catalyst: Enhanced activity and SO2 tolerance by modifying TiO2 with AlO3. *J. Rare Earths.*

30. Wang XQ, Liu Y, Wu ZB. Highly active NbOPO4 supported Cu-Co catalyst for NH3-SCR reaction with superior sulfur resistance. *Chem. Eng. J.* 2020;382:122941.

31. Wu X, Meng H, Du YL, Liu JN, Hou BH, Xie XM. Fabrication of highly dispersed Cu-based Oxides as desirable NH3-SCR catalysts via employing CNTs To decorate the CuAl-layered double hydroxides. *ACS Appl. Mater. Interfaces* 2019;11:32917–32927.

32. Han J, Meeprasert J, Maitarad P, Nammuangrak S, Shi LY, Zhang DS. Investigation of the facet-dependent catalytic performance of FeOx/CoOx for the selective catalytic reduction of NO with NH3. *J. Phys. Chem. C* 2016;120:1523–1533.

33. Gao FY, TangXJ, Sani Z, et al. Spinel-structured Mn-Ni nanosheets for NH3-SCR of NO with good H2O and SO2 resistance.
at low temperature. *Catal. Sci. Technol.* 2020;22(10):7486-7501.
34. Zhang ZP, Li RM, Wang M, et al. Two steps synthesis of Co$_3$TiO$_4$ oxides nanotube catalyst: Enhanced activity, resistance of SO$_2$ and H$_2$O for low temperature NH$_3$-SCR of NO. *Appl. Catal., B* 2021;282:119542.
35. Huang ZW, Li H, Gao JY, et al. Alkali- and sulfur-resistant tungsten-based catalysts for NO$_x$ emissions control. *Environ. Sci. Technol.* 2015;49:14460-14465.
36. Guo K, Fan GF, Gu D, et al. Pore size expansion accelerates ammonium bisulfate decomposition for improved sulfur resistance in low-temperature NH$_3$-SCR. *ACS Appl. Mater. Interfaces* 2019;11:4900-4907.
37. Sheng ZY, Ma DR, Yu DQ. Synthesis of novel MnO$_x$@TiO$_2$ core-shell nanorod catalyst for low-temperature NH$_3$-selective catalytic reduction of NO with enhanced SO$_2$ tolerance. *Chin. J. Catal.* 2018;39:821-830.
38. Gan LN, Li KZ, Yang WN, Chen JJ. Core-shell-like structured α-MnO$_2$-CeO$_2$ catalyst for selective catalytic reduction of NO: Promoted activity and SO$_2$ tolerance. *Chem. Eng. J.* 2020;391:123473.
39. Ma DR, Yang L, Huang BJ, et al. MnO$_x$–CeO$_2$@TiO$_2$ core-shell composites for low temperature SCR of NO. *New J. Chem.* 2019;43:15161-15168.
40. Zhang HW, Zhang MZ, Hao LF, et al. Enhanced SO$_2$ tolerance of FeCoO$_x$@CNTs catalyst for NO and Hg$^+$ removal by coating shell SiO$_2$. *Fuel Process. Technol.* 2020;201:106342.
41. Yu CL, Hou D, Huang BC, Lu MJ, Peng RS, Zhong ZY. A MnO$_x$@Eu-CeO$_2$ nanorod catalyst with multiple protective effects: Strong SO$_2$-tolerance for low temperature DeNOx processes. *J. Hazard. Mater.* 2020;399:123011.
42. Cai SX, Hu H, Li HR, Shi LY, Zhang DS. Design of multi-shell Fe$_2$O$_3$@Mn$_x$O$_y$@CNTs for the selective catalytic reduction of NO with NH$_3$: improvement of catalytic activity and SO$_2$ tolerance. *Nanoscale* 2016;8:3588-3598.
43. Ma ZX, Sheng LP, Wang XW, et al. Oxide catalysts with ultrastrong resistance to SO$_2$ deactivation for removing nitric oxide at low temperature. *Adv. Mater.* 2019;31:1903719.
44. Liang QM, Li J, He H, Yue Tao, Tong Li. Effects of SO$_2$ and H$_2$O on low-temperature NO conversion over F-V$_2$O$_5$-WO$_3$/TiO$_2$ catalysts. *J. Environ. Sci.* 2020;90:253-261.
45. Kang TH, Yoon S, Kim DH. Improved catalytic performance and resistance to SO$_2$ over V$_2$O$_5$-WO$_3$/TiO$_2$ catalyst physically mixed with Fe$_2$O$_3$ for low-temperature NH$_3$-SCR. *Catal. Today.* 2020. (In Press, Corrected Proof)
46. Mu JC, Li XY, Wang XY, et al. New insight into the effects of NH$_3$ on SO$_2$ poisoning for in situ removal of metal sulfates in low-temperature NH$_3$-SCR over an Fe–V catalyst. *J. Phys. Chem. C* 2020;124:21396–21406.
47. Li CX, Shen MQ, Wang JQ, Wang J, Zhai YP. New insights into the role of WO$_3$ in improved activity and ammonium bisulfite resistance for NO reduction with NH$_3$ over W–V/CoTi catalyst. *Ind. Eng. Chem. Res.* 2018;57:8424–8435.
48. Gao FY, Tang XL, Yi HH, Li JY, Zhao SZ, Wang JG. Promotional mechanisms of activity and SO$_2$ tolerance of Co or Ni-doped MnO$_x$–CeO$_2$ catalysts for SCR of NO$_x$ with NH$_3$ at low temperature. *Chem. Eng. J.* 2017;317:20-31.
49. Wei L, Cui SP, Guo HX. Study the low-temperature SCR property of M-doped (M=Ni, Cr, Co, Se, Sn) MnO$_x$(100) through density functional theory (DFT): Improvement of sulfur poisoning resistance. *Mol. Catal* 2018;459:31-37.
50. Jiang HX, Wang J, Zhou JL, Chen YF, Zhang MH. Effect of promoters on the catalytic performance and SO$_2$/H$_2$O resistance of α-MnO$_2$ catalysts for low temperature NH$_3$-SCR. *Ind. Eng. Chem. Res.* 2019;58:1760–1768.
51. Sun P, Huang SX, Guo RT, Li MY, Liu, SM. The enhanced SCR performance and SO$_2$ resistance of Mn/TiO$_2$ catalyst by the modification with Nb: A mechanistic study. *Appl. Surf. Sci.* 2018;447:479-488.
52. Liu J, Guo RT, Li MY, Sun P, Liu SM. Enhancement of the SO$_2$ resistance of Mn/TiO$_2$ SCR catalyst by Eu modification: A mechanism study. *Fuel* 2018;223:385-393.
53. Liu L, Xu K, Su S. Efficient Sm modified Mn/TiO$_2$ catalysts for selective catalytic reduction of NO with NH$_3$ at low temperature. *Appl. Catal., A* 2020;592:117413.
54. Wang B, Wang MX, Han LN, et al. Improved activity and SO$_2$ resistance by Sm-modulated redox of MnCeSmTiO$_5$ mesoporous amorphous oxides for low-temperature NH$_3$-SCR of NO. *ACS Catal* 2020;10:9694-9695.
55. Zhang XL, Lv SS, Zhang X, Xiao KS, Wu XP. Improvement of the activity and SO$_2$ tolerance of Sm-modified Mn/PG catalysts for NH$_3$-SCR at a low temperature. *J. Environ. Sci.* 2020;101:1-15.
56. Liu Z, Wang MM, Liu SJ, Chen Z, Yang LZ. Design of assembled composite of Mn$_x$O$_y$@Graphitic carbon porous nano-dandelions: A catalyst for low-temperature selective catalytic reduction of NO with remarkable SO$_2$ resistance. *Appl. Catal., B* 2020;269:118731.
57. Fan ZY, Shi JW, Niu CH, Wang BR, He C, Cheng YH. The insight into the role of Al$_2$O$_3$ in promoting the SO$_2$ tolerance of MnO$_x$ for low-temperature selective catalytic reduction of NO with NH$_3$. *Chem. Eng. J.* 2020;398:125572.
58. Gao FY, Tang XL, Yi HH. Novel Co- or Ni-Mn binary oxide catalysts with hydroxyl groups for NH$_3$-SCR of NO$_x$ at low temperature. *Appl. Surf. Sci.* 2018;443:103-113.
59. Gao FY, Tang XL, Yi HH, Zhao SZ, Zhu JW, Shi YR. MnNiO$_x$ spinel catalyst for high-efficiency selective catalytic reduction of nitrogen oxides with good resistance to H$_2$O and SO$_2$ at low temperature. *J. Environ. Sci.* 2020;89:145-155.
60. Xiong SC, Peng Y, Wang D, Huang N, Zhang QF. The role of the Cu dopant on a Mn$_x$O$_y$ spinel SCR catalyst: Improvement of low-temperature activity and sulfur resistance *J. Chem. Eng. J.* 2020;387:124090.
61. Yan QH, Chen SN, Zhang C, Wang Q, Louis B. Synthesis and catalytic performance of Cu$_3$Mn$_8$Te$_6$O$_{18}$ mixed oxide as low-temperature NH$_3$-SCR catalyst with enhanced SO$_2$ resistance. *Appl. Catal., B* 2018;238:236-247.
62. Chen SN, Yan QH, Zhang C, Wang Q. A novel highly active and sulfur resistant catalyst from Mn–Fe–Al layered double hydroxide for low temperature NH$_3$-SCR. *Catal Today* 2019;327:81-89.
63. Zhou X, Yu F, Sun RB, Tian JQ, Wang Q, Dai B. Two-dimensional MnFeCo layered double oxide as catalyst for enhanced selective catalytic reduction of NO$_x$ with NH$_3$ at low temperature (25-150°C). *Appl. Catal., A* 2020;592:117432.
64. Peng C, Yan N, Peng HG, et al. One-pot synthesis of layered
mesoporous ZSM-5 plus Cu ion-exchange: Enhanced NH3-SCR performance on Cu-ZSM-5 with hierarchical pore structures. J. Hazard. Mater. 2020;385:121593.

65. Ma YY, Li ZF, Zhao N, Teng YL. One-pot synthesis of Cu-Co co-doped SAPO-5/34 hybrid crystal structure catalysts for NH3-SCR reaction with SO2 resistance. J. Rare Earths. 2020. (In press)

66. Wan J, Chen JW, Zhao R, Zhou RX. One-pot synthesis of Fe/Cu-SSZ-13 catalyst and its highly efficient performance for the selective catalytic reduction of nitrogen oxide with ammonia. J. Environ. Sci. 2021;100:306–316.

67. Yu R, Zhao ZC, Huang SJ, Zhang WP. Cu-SSZ-13 zeolite-metal oxide hybrid catalysts with enhanced SO2-tolerance in the NH3-SCR of NOx. Appl. Catal., B 2020;269:118825.

68. Zhou JL, Wang BD, Ma J, Li G. SO2 and H2O poisoning resistance of manganese oxide-based catalysts for low-temperature selective catalytic reduction of NOx. Environ. Chem. 2018;37:782-791.

69. Xu LW, Wang CZ, Chang HZ, Wu QR, Zhang T, Li JH. New insight into SO2 poisoning and regeneration of CoO2-WO3/TiO2 and V2O5-WO3/TiO2 catalysts for low-temperature NH3-SCR. Environ. Sci. Technol. 2018;52:7064-7071.

70. Si ZC, Weng D, Wu XD, Wu XD. NH3-SCR activity, hydrothermal stability, sulfur resistance and regeneration of Ce0.75Zr0.25O2-P2O5 catalyst. Catal. Commun. 2012;17:146-149.

71. Wang YZ, Yi W, Yu J, Zeng J, Chang HZ. Novel methods for assessing the SO2 poisoning effect and thermal regeneration possibility of MoO3-WO3/TiO2 (M = Fe, Mn, Cu, and V) catalysts for NH3-SCR. Environ. Sci. Technol. 2020;54:12612–12620.

72. Pan H, Jian YF, Yu YK, He C, Shen ZX. Regeneration and sulfur poisoning behavior of In/H-ZSM catalyst for NOx reduction by CH4. Appl. Surf. Sci. 2017;401:120-126.

73. Korotkin DE, Khan TS, Bligaard T, Fogle S, Bligaard T, Dahl S. Sulfur poisoning and regeneration of the Ag/γ-Al2O3 catalyst for H2-assisted SCR of NOx. J. Appl. Catal., B 2012;117:118-49-58.

74. Chang HZ, Li JH, Yuan J, et al. Mn-doped CoO2-WO3 catalysts for NH3-SCR of NOx: Effects of SO2 and H2 regeneration. Catal. Today. 2013;201:139–144.

75. Zhao L, Yang SW, Duan J, Liu QF. Improved NO reduction in the presence of SO2 by using Zr-promoted calcined NiAl hydrotalcite-like compounds and the regeneration of deactivated catalysts. Fuel 2020;263:116668.

76. Hu YF, Xue JM, Wang XM, Sheng CY, Liao WP. Research on characteristics of SO2-poison and regeneration of Mn-Ce/TiO2 catalyst for low temperature selective catalytic reduction. Industrial Catalysis 2013;21:27-33.

77. Lee T, Bai H. Metal sulfate poisoning effects over MnFe/TiO2 for selective catalytic reduction of NO by NH3 at low temperature. Ind. Eng. Chem. Res. 2018;57:4848-4858.

78. Han LP, Gao M, Hasegawa JY, Li SX. SO2-tolerant selective catalytic reduction of NOx over Meso-TiO2@Fe2O3@Al2O3 metal-based monolith catalysts. Environ. Sci. Technol. 2019;53:6462-6473.

79. Yang GP, Du XS, Ran JY, Wang XM, Chen YR, Zhang L. Understanding SO2 poisoning over different copper species of Cu-SAPO-34 catalyst: A periodic DFT study. J. Phys. Chem. C 2018;122:21468-21477.

80. Hammershøi PS, Vennestrom PNR, Falsig H, Jensen AD. Importance of the Cu oxidation state for the SO2-poisoning of a Cu-SAPO-34 catalyst in the NH3-SCR reaction. Appl. Catal., B 2018;236:377-383.