SO2 Poisoning Mechanism

Subjects: Others

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The selective catalytic reduction (SCR) has been widely used in industrial denitrification owing to its high denitrification efficiency, low operating costs, and simple operating procedures. However, coal containing a large amount of sulfur will produce SO_2 during combustion, which makes the catalyst easy to be deactivated, thus limiting the application of this technology. This review summarizes the latest NH_3-SCR reaction mechanisms and the deactivation mechanism of catalyst in SO_2-containing flue gas. Some strategies are summarized for enhancing the poison-resistance through modification, improvement of support, the preparation of complex oxide catalyst, optimizing the preparation methods, and acidification. The mechanism of improving sulfur resistance of catalysts at low temperatures is summarized, and the further development of the catalyst is also prospected. This paper could provide a reference and guidance for the development of SO_2 resistance of the catalyst at low temperatures.

selective catalytic reduction SO2 resistance at low temperature catalyst modification NOx NH3-SCR

1. Introduction

Nitrogen oxide (NO_x) is a general term composed of nitrogen, oxygen, and other compounds. It is one of the major pollutants from the exhaust gas of thermal power plants, industrial furnaces, motor vehicles, ship exhaust emissions, and includes N_2O, NO, NO_2, etc.—among which NO and NO_2 account for the largest proportion[1]. A large amount of NO_x emitted into the air will cause a series of environmental concerns. Therefore, exploring and developing efficient exhaust gas deNO_x technology has been an area of intense investigation. Among all flue gas denitrification technologies, selective catalytic reduction (SCR) is an extensively applied technology due to its low reaction temperature and high denitrification efficiency[2][3]. Selective catalytic reduction (SCR) mainly refers to the reaction of NO_x using NH_3 as a reducing agent in the presence of O_2 to produce pollution-free N_2 and H_2O, whose core is the catalyst.

2. SO_2 Poisoning Mechanism of Low-Temperature Catalyst

At present, some power plants adopt wet desulfurization to remove SO_2 with lower flue gas temperature, failing to meet the reaction requirements of V_2O_5/TiO_2 catalyst. Therefore, there are many drawbacks such as low denitrification efficiency and catalyst waste. After desulfurization, tiny amounts of SO_2 still exist in the exhaust gas, bringing about the deactivation of SCR catalyst. Therefore, developing a vanadium-free catalyst with great denitrification performance and sulfur and water resistance at low temperatures is extremely necessary[4]. To solve the sulfur poisoning of catalysts, many scholars have done a lot of research and elaborated on the poisoning mechanism in detail.

From the above studies, the SO_2 deactivation mechanism on the catalyst at low temperatures can be observed mainly in the following three aspects. (1) The ammonium sulfate and ammonium bisulfate are formed by the reaction of SO_2 and NH_3 in the presence of O_2 and attach to the catalyst surface, which can decrease the surface area, pore volume, and pore size of the catalyst, and then reduce the reaction rate. However, ammonium sulfate and ammonium bicarbonate will self-decompose when the NH_3-SCR reaction is carried out above 280 °C and 350 °C, respectively, so the catalytic activity is able to be restored by the washing method at low temperatures[5]. (2) In the presence of O_2, SO_2 will react with the active component (mainly transition metal) on the catalyst surface to generate metal sulfate salt, which will cause irreversible deactivation of the catalyst. (3) SO_2 will compete with NO at the adsorption sites on the catalyst surface when these acidic gases are present in the reaction system, which would reduce the formation of SCR intermediate products and the catalytic efficiency of catalyst. Figure 1-3 show the mechanism of catalyst sulfur poisoning.

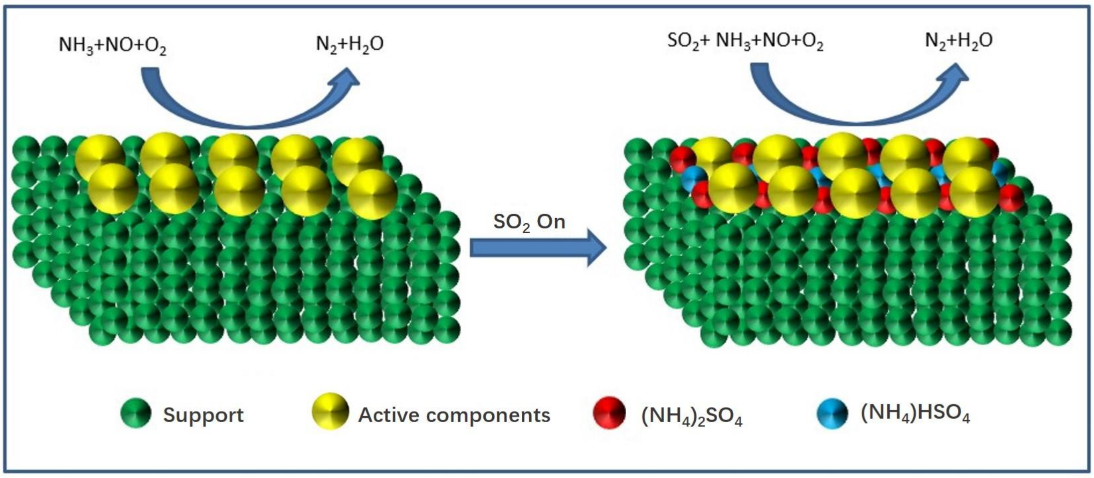

Figure 1. The formation process of $(NH_4)_2SO_4$ and NH_4HSO_4.

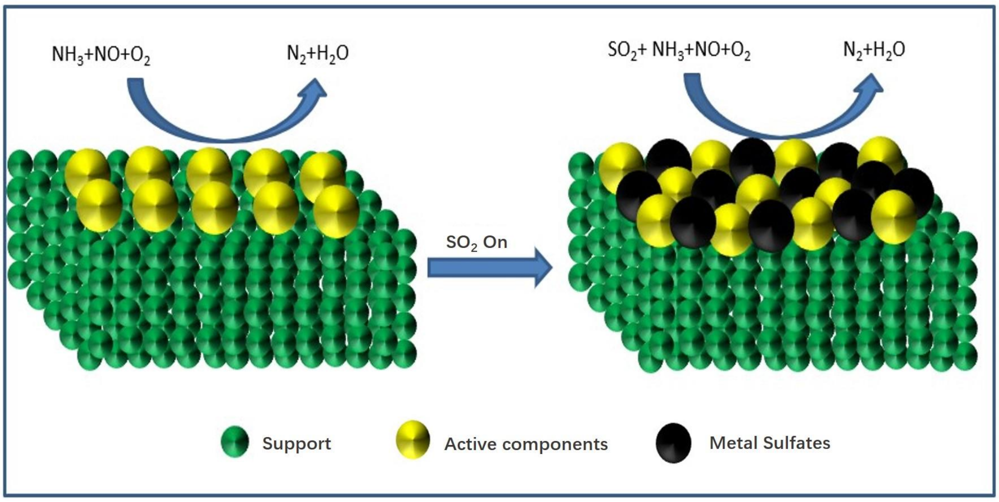

Figure 2. Sulfation of active components.

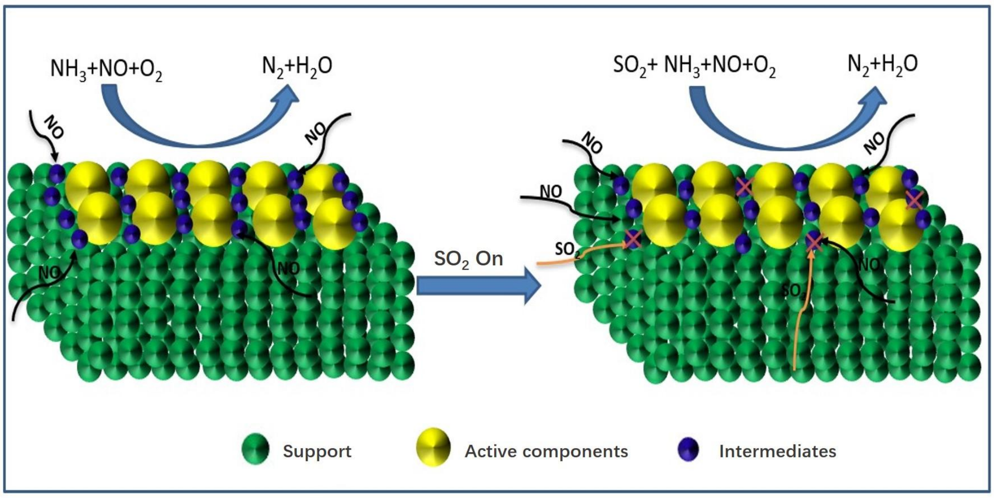

Figure 3. Competitive adsorption of NO and SO_2.

3. Research Progress of SO_2 Resistance Catalyst at Low Temperatures

Catalyst is usually composed of active component and support, and there are other forms of catalysts such as composite oxide catalysts. To enhance the low-temperature sulfur resistance of catalysts, many scholars have focused their attention on the improvement of active components and supports. In addition, some scholars have found that the preparation method—the handling catalyst by acidification and reaction conditions—can make a difference in the SO_2 resistance of catalyst.

3.1. Effects of Active Components

The active component, which is composed of one or more substances, is the main unit of catalyst and affects the NH_3-SCR reaction significantly. Using rare earth metals as well as transition metal oxides to improve active components is one of the most effective methods to improve sulfur resistance at low temperatures. We mainly summarized the SCR performance and/or SO_2 resistance mechanism of catalysts modified with Ce, Fe, Cu, W and other metal elements, as shown in Figure 4-9.

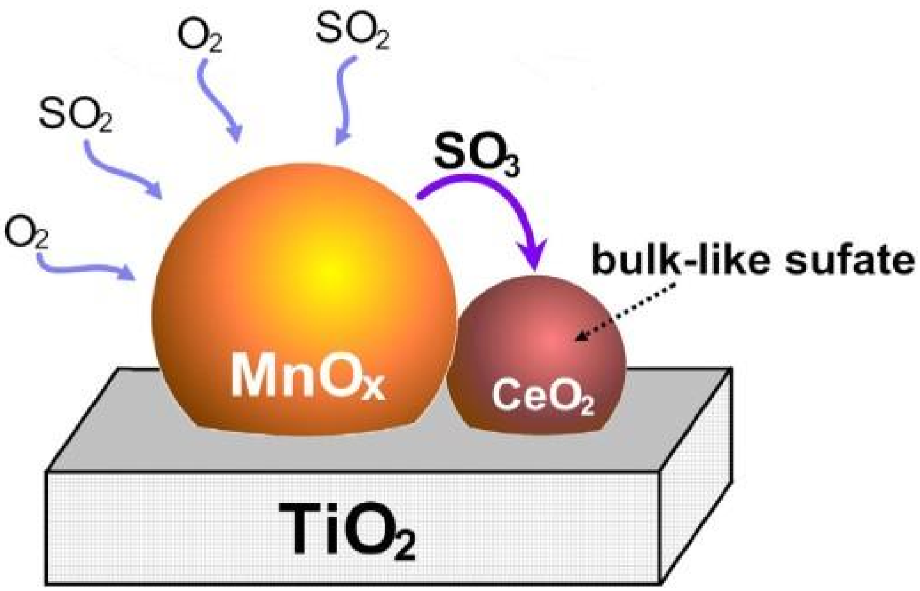

Figure 4. The sulfation mechanism of Ce-modified Mn–Ce/TiO_2 catalyst[6].

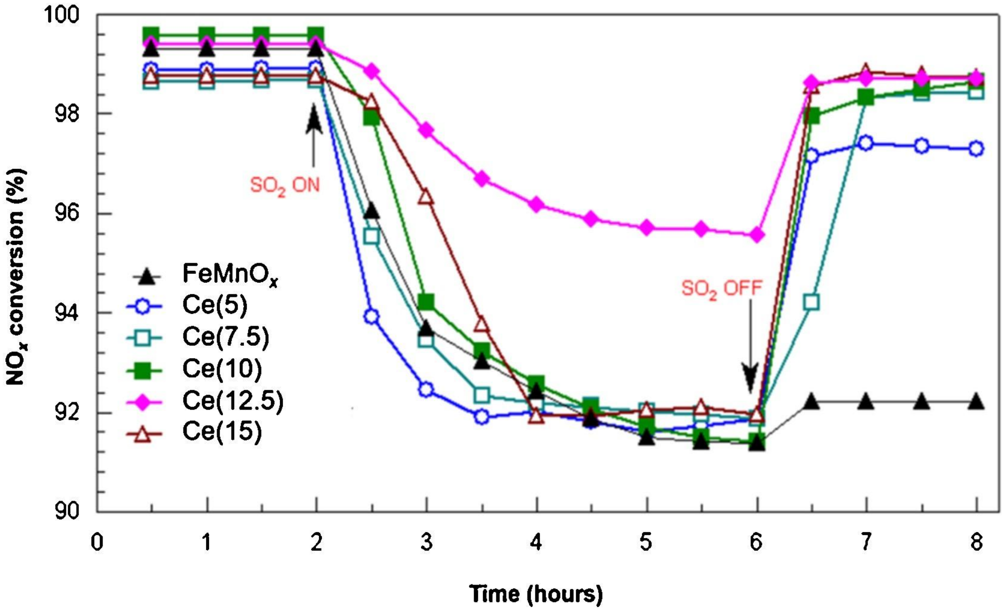

Figure 5. Influence of SO_2 on NO_x conversion of $FeMnO_x$ and Ce(y) catalysts. Reaction conditions: [NO] = [NH_3] = 0.1%; [SO_2] = 100 ppm; [O_2] = 3%; N_2 balance, GHSV = 30,000 h^{-1}; reaction temperature = 120 °C[7].

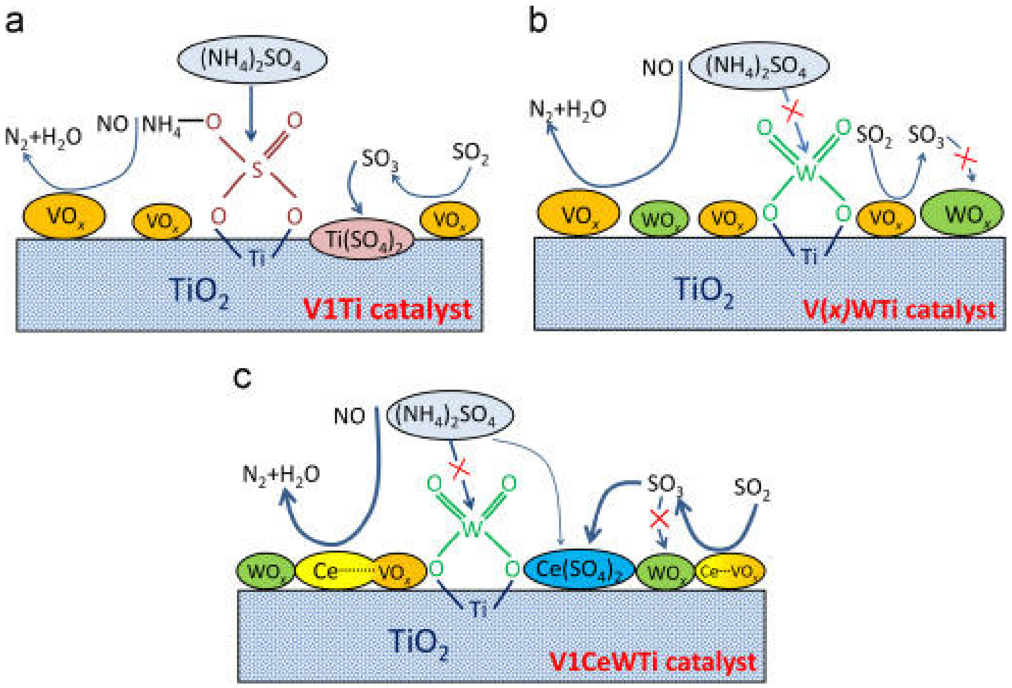

Figure 6. The mechanism of sulfur poisoning at low temperatures of catalysts (a) V1Ti; (b) V(x)WTi; (c) V1CeWTi[8].

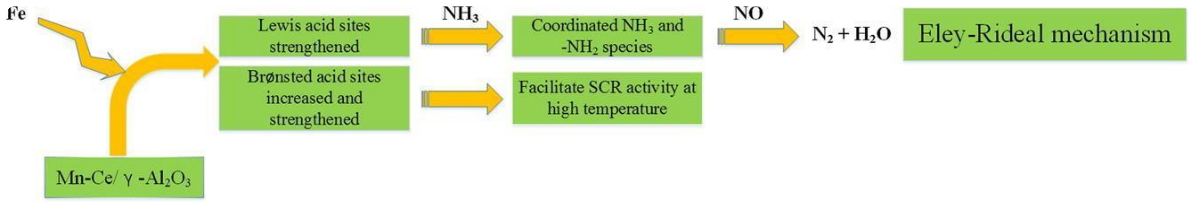

Figure 7. The reaction flow chart of Fe–Mn–Ce/γ-Al_2O_3 catalyst[9].

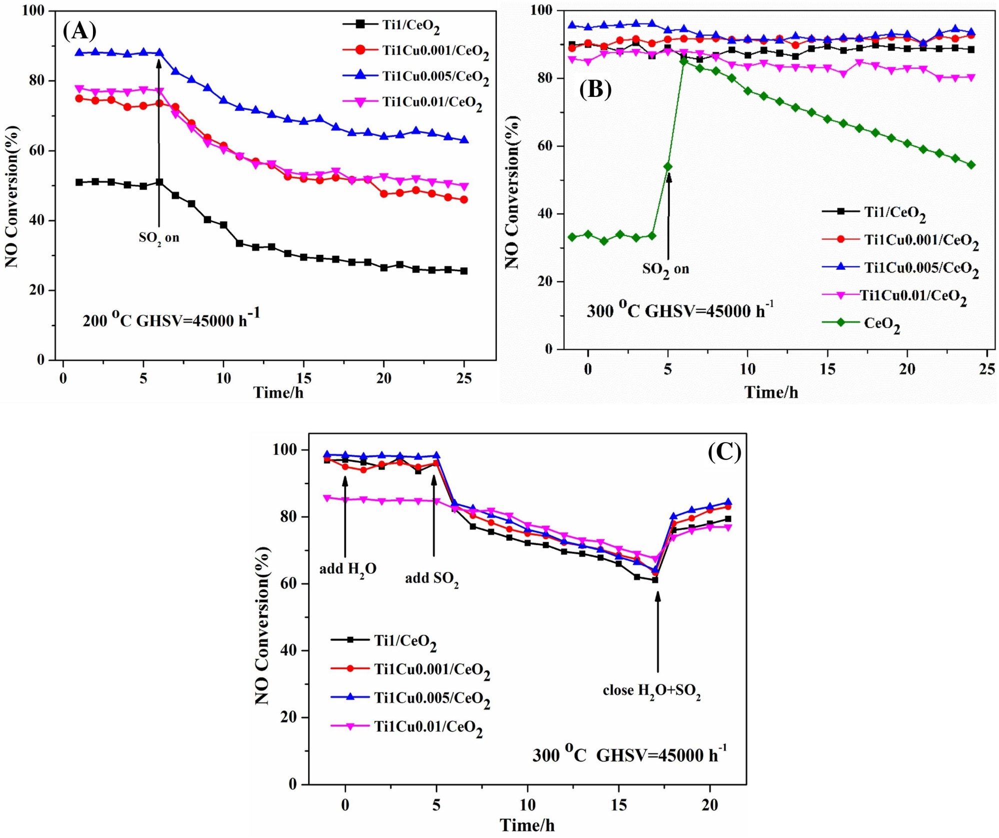

Figure 8. SO_2 durability of catalysts (A) SO_2 durability over Ti1/CeO_2 and Ti1Cuy/CeO_2 catalysts at 200 °C (B) SO_2 durability over Ti1/CeO_2 and Ti1Cuy/CeO_2 catalysts at 300 °C. (C) H_2O/H_2O + SO_2 durability over Ti1/CeO_2 and Ti1Cuy/CeO_2 at 300 °C[10].

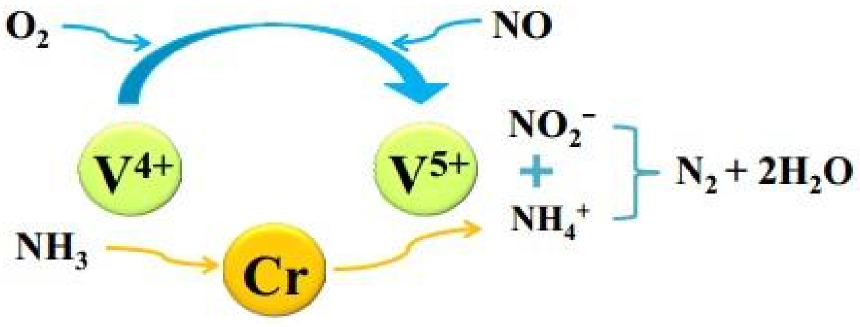

Figure 9. Mechanism of Cr doping improving sulfur resistance of Cr–V/TiO_2 catalyst[11].

Above all, the content of oxygen adsorbed on the active material and catalyst surface—and even the number of acid sites—could be increased by adding Ce, Fe, Cu, W, and others to the active components, which would accelerate the rapid reaction of SCR and increase the catalytic performance of catalyst. Under the reaction conditions containing SO_2, these additives can preferentially react with SO_2 as the SO_2 catchers to avoid the sulfation of active substances. Besides, the stability of NH_4HSO_4 and $(NH4)_2SO_4$ on the surface was reduced, and the low-temperature sulfur tolerance of catalyst was effectively improved. It is believed that transition metals and rare earth elements will have promising applications in improving sulfur resistance of catalyst at low temperatures.

Figure 10 shows the typical SO_2-tolerant modified catalyst at low temperatures for selective catalytic reduction (SCR) reaction.

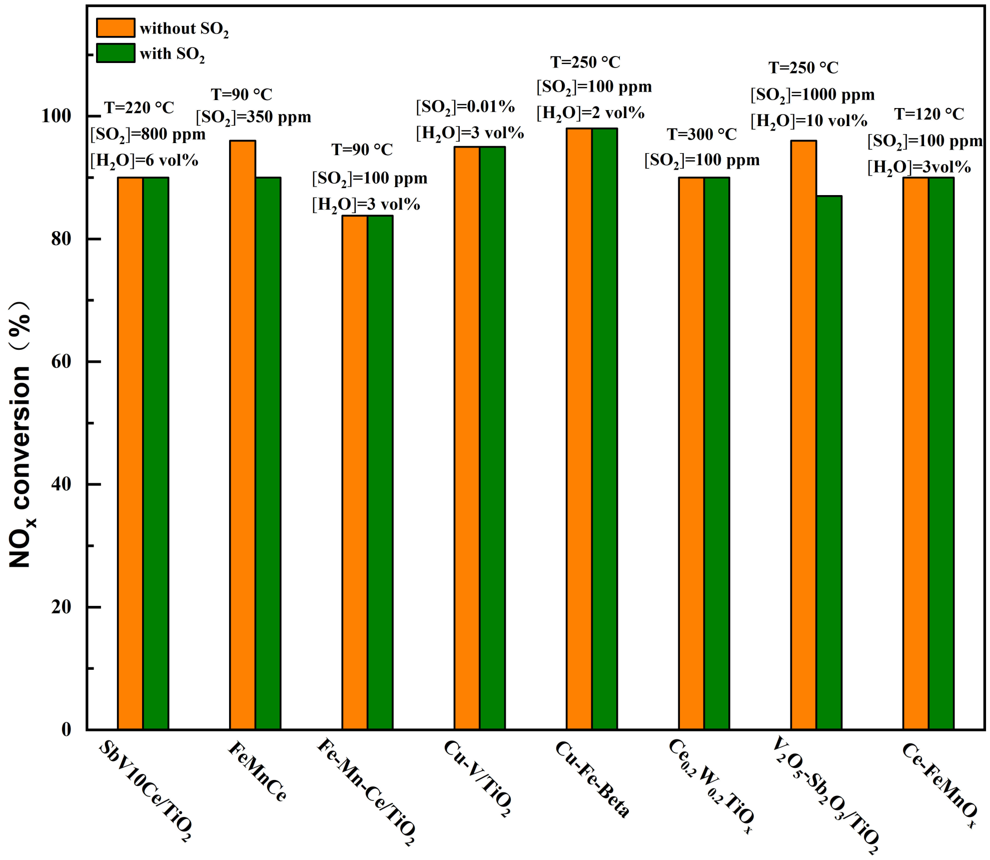

Figure 10. Typical SO_2-tolerant modified catalyst at low temperatures for selective catalytic reduction (SCR) reaction[7][12][9][13][14][15][16][17].

3.2. Effects of Supports

The support of catalyst is of vital importance in the catalytic activity. Loading the active components onto the support contributes to improving the specific surface area, thermal resistance, and mechanical strength of catalyst. Especially, the supports can slow down SO_2 poisoning on the catalytic activity of catalyst. As of now, there are TiO_2, Al_2O_3, activated carbon and zeolites, and other conventional supports in practical application, as shown in Figure 11 and Figure 12. However, different supports show different catalytic activity and sulfur resistance, which makes the research and improvement of the support become a part of the emphasis of research to improve the low-temperature SO_2 resistance of catalyst. Figure 13 shows the typical SO_2-tolerant catalysts with different supports at low temperatures for SCR reaction.

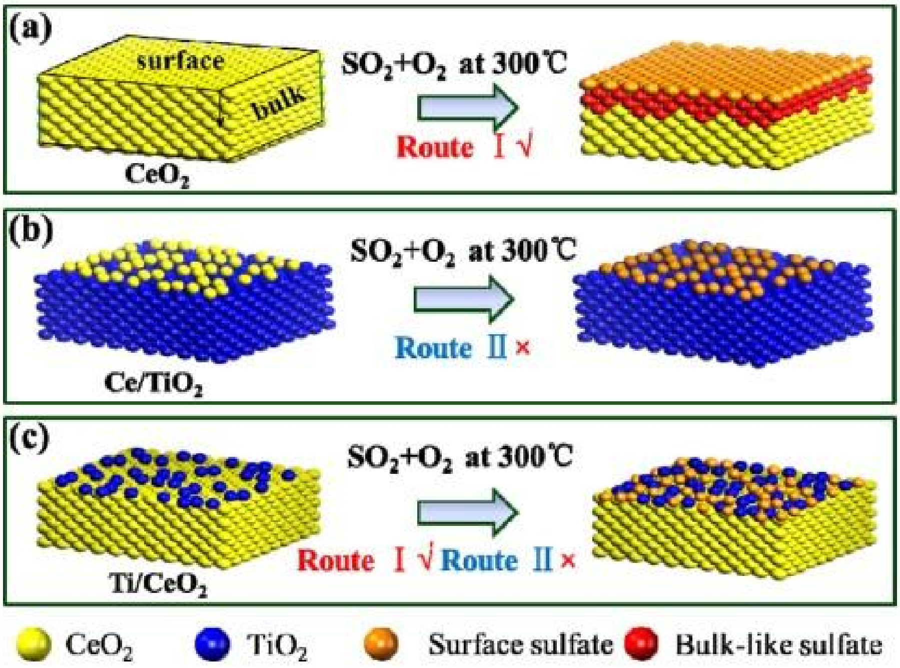

Figure 11. Sulfur resistance mechanism of (a) CeO_2, (b) Ce/Ti and (c) Ti/Ce catalyst[18].

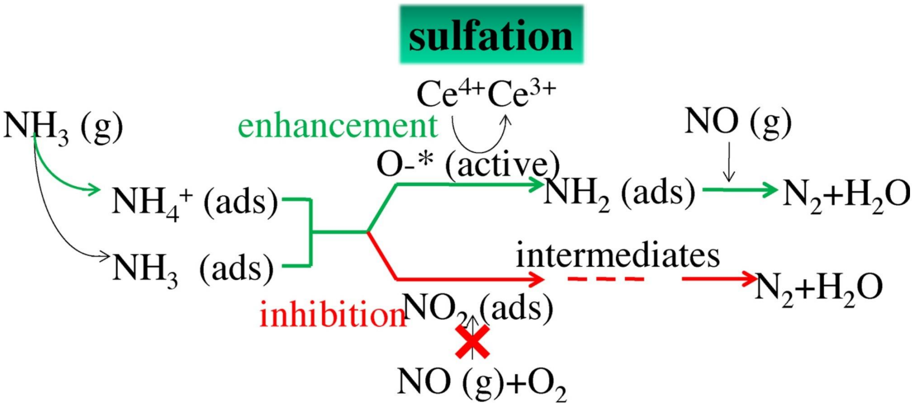

Figure 12. Reaction mechanism of Ce–Fe/WMH catalyst[19].

Figure 13. Typical SO_2-tolerant catalysts with different supports at low temperatures for SCR reaction[18][20][19][21][22][23][24].

3.3. Composite Oxide Catalysts

In recent years, extensive work has been done in the area of composite oxide catalyst. Compared with the supported catalysts, these catalysts all use metal oxides and have no clear support or active components. Many achievements have been made in the research of the catalytic performance and sulfur tolerance of catalyst.

3.4. Other Strategies to Improve the SO_2 Resistance

Among all the measures to enhance the sulfur resistance of the catalyst, some researchers have tried to find the influence of preparation methods，acidification，preparation and reaction conditions, further promoting the acidity and catalytic efficiency of catalyst.

4. Conclusions and Perspectives

Facing progressively strict legislation and policies to control NO emission, the research and design of low-temperature catalysts for NH_3-SCR have received a great deal of attention. Although the poisoning mechanism of catalyst at low temperatures has been studied thoroughly, how to maintain the high catalytic efficiency of catalyst at low temperatures and promote the SO_2-resistance-poisoning ability of catalyst to achieve practical application is still an urgent problem.

In the presence of O_2, SO_3 is easily formed on the catalyst due to the oxidation reaction of SO_2, and further combined with NH_3 to produce NH_4HSO_4 and/or $(NH_4)_2SO_4$, which can deposit on the surface of catalyst and inhibit the reaction gas to be adsorbed on the catalyst to participate in the SCR reaction. Besides, sulfate of active components can be formed and cause irreversible deactivation of catalyst. Therefore, it is effective to adopt several measurements to improve the SO_2 tolerance. Firstly, it is to reduce the adsorption of SO_2 on the catalyst. The highly acidic catalysts are effective to prevent the SO_2 adsorbing. Secondly, preventing the oxidation of SO_2 to SO_3 plays a significant role in high SO_2 tolerance by reducing the redox ability of catalyst, which can cut off the oxidation of SO_2 to some extent. Furthermore, the synergistic effect between catalyst components can also improve the sulfur resistance of catalyst, such as the construction of sacrificial sites, which is responsible for the reduction of active components sulfation. Along with these existing excellent sulfur resistant catalysts, it is expected that future studies will focus on optimizing the supports and preparation methods and concentrating on the application of new structures and technology, which are effective strategies to improve the low-temperature SO_2 tolerance of SCR catalysts.

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