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Review

Review on the latest developments in modified vanadium-titanium-based SCR catalysts

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ARTICLE INFO

Article history:

Received 5 March 2018

Accepted 3 April 2018

Published 5 August 2018

Keywords:

Vanadium-titanium-based catalyst

Selective catalytic reduction

Low-temperature denitration

Hg⁰ oxidation

Slip ammonia

SO₂ oxidation

ABSTRACT

Vanadium-titanium-based catalysts are the most widely used industrial materials for NO_x removal from coal-fired power plants. Owing to their relatively poor low-temperature deNO_x activity, low thermal stability, insufficient Hg⁰ oxidation activity, SO₂ oxidation, ammonia slip, and other disadvantages, modifications to traditional vanadium-titanium-based selective catalytic reduction (SCR) catalysts have been attempted by many researchers to promote their relevant performance. This article reviewed the research progress of modified vanadium-titanium-based SCR catalysts from seven aspects, namely, (1) improving low-temperature deNO_x efficiency, (2) enhancing thermal stability, (3) improving Hg⁰ oxidation efficiency, (4) oxidizing slip ammonia, (5) reducing SO₂ oxidation, (6) increasing alkali resistance, and (7) others. Their catalytic performance and the influence mechanisms have been discussed in detail. These catalysts were also divided into different categories according to their modified components such as noble metals (e.g., silver, ruthenium), transition metals (e.g., manganese, iron, copper, zirconium, etc.), rare earth metals (e.g., cerium, praseodymium), and other metal chlorides (e.g., calcium chloride, copper chloride) and non-metals (fluorine, sulfur, silicon, nitrogen, etc.). The advantages and disadvantages of these catalysts were summarized. Based on previous studies and the author's point of view, doping the appropriate modified components is beneficial to further improve the overall performance of vanadium-titanium-based SCR catalysts. This has enormous development potential and is a promising way to realize the control of multiple pollutants on the basis of the existing flue gas treatment system.

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1. Introduction

Nitrogen oxide (NO_x), one of the main precursor substances of photochemical smog, the greenhouse effect, acid rain, ozone depletion, and PM_{2.5}, is an atmospheric pollutant in coal-fired flue gas that causes great harm to the ecosystem and human life [1]. According to a recent survey, NO_x emissions in China increase annually. Thus, in 2010, the emission load was about twice that recorded in 2000 and is expected to reach 19.7 Mt by 2020 [2]. Additionally, coal-fired power plants are considered

to be the largest source of NO_x emissions, discharging ~46% of the total NO_x emissions [1]. Therefore, reduction of the NO_x generated by coal-fired power plants has become imperative in the environmental field.

The current NO_x control technologies can be classified into three categories: combustion, pre-combustion, and post-combustion NO_x control [3]. Pre-combustion control refers to the selection of low-nitrogen fuel to inhibit the formation of NO_x from the source. Owing to fuel limitations, this method is rarely used in industry. Combustion control, also

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This work was supported by the Science and Technology Plan Project of Hebei Province of China (16273703D) and the Fundamental Research Funds for the Central Universities (2015ZD24, 2017XS123).

DOI: 10.1016/S1872-2067(18)63090-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 39, No. 8, August 2018

known as low-nitrogen oxide combustion technology, is mainly employed to reduce NO_x emissions by changing the combustion conditions and improving the production technique. This method requires relatively low cost. However, its NO_x removal rate can only reach 15%–30%, making it difficult to meet the current requirements for environmental protection [4]. Post combustion control is the use of flue gas denitrification technology. It refers to the installation of denitrification devices in the flue tail by which the NO_x in the flue gas is converted into harmless nitrogen and other substances through physical and chemical reactions. Owing to its good NO_x removal performance and simple operation, this technique has been extensively utilized in coal-fired power plants.

Flue gas deNO_x technology can be divided into selective catalytic reduction (SCR), non-SCR (NSCR), selective non-catalytic reduction (SNCR), SNCR/SCR mixed technology, oxidation, solid adsorption, absorption, catalytic decomposition, electron beam irradiation, etc. [5,6]. Among them, SCR has become the most widely used NO_x emission control method for flue gas treatment in coal-fired power plants, globally. This can be attributed to its high NO_x conversion efficiency and relatively mature process [7]. Its reaction principle is to reduce NO_x (including NO and minor NO₂) to N₂ selectively by ammonia, urea, H₂, HC, or other reductants present on a particular catalyst [1,7–9]. This method has the advantages of no by-product formation, simple equipment structure, high deNO_x efficiency, reliable operation, convenient maintenance, and low one-time investment. Ammonia is the most commonly used reductant in the SCR unit of a coal-fired power plant. The main NH₃-SCR reactions are as follows [10]:

2. Research progress in SCR catalysts

2.1. Overview of SCR catalysts

Table 1

Summary of the major SCR catalysts.

Catalyst type	Active component	Carrier	Advantages	Disadvantages	Ref.
Commercial vanadium-titanium-based catalyst	V ₂ O ₅	TiO ₂	High low-temperature SCR activity; high SO ₂ resistance	SO ₂ oxidation	e.g. [11–14]
Noble metals	Ag, Sn, etc.	TiO ₂ , Al ₂ O ₃ , etc.	High low-temperature SCR activity; high SO ₂ and H ₂ O resistance	Narrow temperature window; NH ₃ oxidation; N ₂ O generation; high cost	e.g. [15–17]
Metal oxides	V ₂ O ₅ , CeO ₂ , MnO _x , CuO, FeO _x , CoO _x , CrO _x and some metal composite oxides	TiO ₂ , Al ₂ O ₃ , etc.	High SCR activity at 300–400 °C; good thermal stability; high poisoning resistance	Poor low-temperature activity	e.g. [18–32]
Zeolite	Ce, Mn, Cu, Fe, Co, Cr, etc.	Zeolite	Broad temperature window	Poor hydrothermal stability	e.g. [33–39]
Carbon-based catalyst	V ₂ O ₅ , CeO ₂ , MnO _x , etc.	Active carbon (AC), active carbon fiber (ACF), carbon nanotubes (CNTs)	Easy to regenerate; large specific surface area; high chemical stability; high low-temperature activity	Frequent regeneration; high energy consumption; poor SO ₂ resistance	e.g. [40–43]

As the core of the SCR technology, catalysts are used to reduce the activation energy and reaction temperature of NO_x decomposition, increase the N₂ selectivity in NO_x reduction products, avoid the occurrence of side reactions, and thereby improve the reaction efficiency. The selection of catalysts is important. Specifically, the qualified SCR catalysts should possess the following characteristics:

- (1) High deNO_x activity;
- (2) Strong anti-poisoning ability;
- (3) High mechanical strength;
- (4) Suitable operating temperature range.

Many catalysts have been proven to be active for SCR reactions. The main active components are noble and transition metal oxides, while TiO₂, Al₂O₃, SiO₂, zeolite, and carbon are often used as carriers. These catalysts possess different deNO_x properties and advantages and disadvantages, which are summarized in Table 1.

2.2. Commercial vanadium-titanium-based catalysts

Among the numerous denitrification catalysts, V₂O₅-WO₃ (MoO₃)/TiO₂ catalysts have been the most widely used SCR catalysts in coal-fired power plants for many years [11–13]. Their NO_x conversion rates are >90%, while N₂ selectivity among the production processes is high when the temperature is >300 °C. TiO₂ is employed as the carrier for these catalysts. It provides a large specific surface area and porosity, which are beneficial to the catalytic reaction and adsorption of the reactants. As the main active substance in the catalysts, V₂O₅ exhibits strong catalytic activity and stability. It has a remarkable catalytic effect on NO reduction and performs even better when supported on TiO₂. However, the vanadium content in the catalyst is usually low (0.8%–1.2%) because SO₂ can be oxidized to undesirable SO₃ by V₂O₅ [44]. Thus, WO₃ or MoO₃ is used as adjuvant. By interacting with anatase TiO₂, WO₃ shows high catalytic activity [45], increases the Lewis sites on the catalysts [46], inhibits TiO₂ sintering [47], improves SO₂ resistance [48], and extends the reaction temperature window [49].

The specific NO_x removal mechanism over vanadi-

um-titanium-based SCR catalysts has been studied in recent years [50–55]. It is generally accepted that adsorption of the reducing agent (NH_3) on the catalyst surface is strong, while NO adsorption is negligible. Thus, the deNO_x process is considered as the reaction of gaseous NO and adsorbed NH_3 , which follows the Eley-Rideal mechanism. According to previous studies, both Brönsted and Lewis acid sites have been found on the surface of vanadium-titanium-based catalysts [56]. Most researchers consider that Brönsted acid sites play an important role in the deNO_x reaction. They believe that the NH_3 adsorbed on the Brönsted acid sites would form NH_4^+ ions that are then oxidized into $-\text{NH}_3^+$ by $\text{V}^{5+}=\text{O}$, while $\text{H}-\text{O}-\text{V}^{4+}$ is generated. Subsequently, $-\text{NH}_3^+$ reacts with gaseous NO to produce $-\text{NH}_3^+\text{NO}$ and decomposes to N_2 and H_2O . Moreover, $\text{H}-\text{O}-\text{V}^{4+}$ is reoxidized by O_2 in the flue gas and thus, returns to its initial state (Fig. 1) [57]. However, a few people insist that NH_3 is first adsorbed on the Lewis acid sites. Thus, NH_2 is formed after activation and dehydrogenation of NH_3 and reacts with gaseous NO to generate nitrosamines (NH_2NO) as the intermediate [51]. Considering these two points of view, the SCR reaction would occur following the oxidative dehydrogenation of NH_3 , regardless of the adsorption sites of ammonia [58].

The vanadium-titanium-based SCR catalyst has been proven to oxidize elemental mercury (Hg^0) into oxidized mercury (Hg^{2+}) in flue gas [59–62]. However, its Hg^0 oxidation efficiency is unsatisfactory under most conditions. Only in the presence of sufficient HCl and O_2 can the oxidation rate reach 80%–90% [63]. The reaction is as follows:

Two possible mechanisms have been proposed for this reaction, namely, the Eley-Rideal and Langmuir-Hinshelwood mechanisms. The former considers that gaseous Hg^0 reacts with HCl , which adsorbs on the vanadium-titanium-based catalyst surface to form HgCl_2 [64–68]. On the other hand, the latter considers that the reaction takes place between the adsorbed Hg^0 and HCl [69,70]. The vanadium oxides in the catalyst also play a major role in the reaction process [71], while tungsten and molybdenum can enhance the mercury oxidation performance [71,72]. Commercial SCR catalysts can oxidize Hg^0 in the flue gas as HCl is added [66,73–75] and the generated Hg^{2+} would subsequently be removed by the desulfurization system. To date, this is the most economical and feasible method available to control the mercury discharged from

coal-fired power plants. However, inadequate HCl in the flue gas would significantly inhibit Hg^0 oxidation [69]. Therefore, to achieve the synergistic removal of mercury when using low chlorine coal as a fuel, the stability and mercury oxidation effect of the SCR catalyst should be further improved.

2.3. Influencing factors of vanadium-titanium-based catalysts

The operating conditions of the SCR system in coal-fired power plants are very complex. Many factors may affect the deNO_x efficiency of the SCR catalysts, mainly in the following areas.

2.3.1. Flue gas velocity

An increase in flue gas velocity would accelerate the abrasion of the catalyst, as well as decrease the contact time of the catalyst and flue gas. This limits diffusion, adsorption, and the full reaction of the reactants, thereby reducing the NO_x removal rate. On the other hand, excessive contact time can lead to the oxidation of ammonia, which would also reduce the NO_x removal rate. The actual flue gas velocity of the SCR system in a coal-fired power plant is usually set to 3000–5000 h^{-1} .

2.3.2. NH_3/NO_x ratio and degree of gas mixing

Reactions (1)–(4) suggest that the NO_x removal efficiency improves as the NH_3/NO_x ratio increases. However, the addition of an excessive amount of NH_3 does not change the NO_x removal rate significantly. Instead, more NH_3 is directly discharged into the atmosphere, causing secondary pollution. Thus, the NH_3/NO_x ratio in the SCR system is usually maintained in the range of 0.8–1.2. Furthermore, the flue gas must be thoroughly mixed with the reductant before entering the SCR system to ensure that NO_x is adequately reduced by NH_3 . Limited reduction would also be detrimental to NO_x removal from the coal-fired power plant.

2.3.3. Reaction temperature

Based on previous studies, the operating temperature window of industrial vanadium-titanium-based catalysts is relatively narrow (300–400 $^\circ\text{C}$) [29,39]. In fact, increasing the temperature to its optimum value requires high energy consumption that cannot be reached in some power plants; thus, the actual deNO_x efficiency is rather low. When the operating temperature is $<320^\circ\text{C}$, the activity and selectivity of the catalysts decrease and SO_2 poisoning becomes more significant. In addition, high temperatures ($>400^\circ\text{C}$) can lead to TiO_2 sintering [76] and cause some side reactions, such as the production of NO and N_2O from NH_3 oxidation.

2.3.4. Degradation of the catalytic performance

Denitration efficiency decreases gradually with the aging of the catalysts. Thus, high-temperature sintering, catalyst pore plugging by particles, and the existence of SO_2 , water vapor, alkali metals, alkaline earth metals, lead, and arsenic [29,77–79] cause SCR catalyst deactivation during the SCR process. SO_2 inhibition of the catalytic activity is the most prevalent. In the NH_3 -SCR process, the following SO_2 poisoning

Fig. 1. Brönsted acid mechanism of the SCR reaction [57].

mechanism is supposed: SO_2 is oxidized on the catalyst surface. The generated SO_3 reacts with the reductant to produce NH_4HSO_4 and $(\text{NH}_4)_2\text{SO}_4$. These two substances deposit in the catalysts pores, covering some active sites and leading to a sharp decline in the specific surface area of the catalysts [80]. Under normal SCR operating conditions, the SO_2 conversion rate is in the range 1%–2% [81]. Studies have shown that the V=O bond in the vanadium-titanium-based catalyst plays a key role in SO_2 oxidation [82]. Therefore, the V_2O_5 content in the catalyst is usually set to be quite small to suppress SO_3 generation. Water appears in the form of water vapor in the flue gas. The water vapor condensed on the catalyst surface not only exacerbates poisoning by the soluble salts of alkali metals, such as K and Na, but also vaporizes and swells as the temperature increases. This impairs the fine structure and leads to cracking of the catalyst. Water vapor has been reported to compete with NO and NH_3 for physical adsorption on the catalyst surface, thereby decreasing the deNO_x activity [48]. The alkali metals in fly ash (K, Na) also degrade the catalytic performance since they become deposited in the active centers of the catalyst. Thus, long-term accumulation can block the pores on the catalyst and lead to catalyst poisoning [79].

2.3.5. Ammonia slip

Ammonia slip, the residual ammonia present in the downstream flue gas after the SCR system, is an important factor that influences the normal operation of the flue gas treatment system. A high gas velocity, high NH_3/NO_x ratio, uneven NH_3 and flue gas mixing, as well as a decrease in SCR catalytic activity all lead to the addition of slip ammonia [83]. This increase would severely affect the stability of the exhaust system. This occurs because slip ammonia further promotes the formation of the sulfate, leading to catalyst poisoning, a reduction in the heat transfer efficiency of the air preheater, corrosion, and blocking of the catalyst pores [84]. Moreover, studies have shown that NH_3 competes for the active sites with Hg^0 . Hence, the Hg^0 oxidation performance decreases with an increase in ammonia concentration [68]. Therefore, considering both the Hg^0 conversion efficiency and the potential impact of ammonia emission, ammonia slippage from the SCR system should be minimized and is generally controlled to $\sim 3 \times 10^{-6}$. During actual operation, a reduction in the NH_3/NO_x ratio has been considered as the main reducing method of ammonia slippage from coal-fired power plants. Nevertheless, as previously discussed, this method is not conducive to the SCR reaction.

3. Recent advancements in modified vanadium-titanium-based SCR catalysts

In view of the abovementioned influence factors, the vanadium-titanium-based catalysts in the NH_3 -SCR system have been modified in many studies to adapt to the various coal-fired power plant operating conditions to remove NO stably and efficiently. The main research directions are as follows: (1) broadening the reaction temperature of the catalysts, especially expansion to the low-temperature region, (2) improving the thermal stability, (3) enhancing the co-oxidation efficiency

of elemental mercury, (4) controlling the slip ammonia, (5) reducing the rate of SO_2 oxidation, (6) increasing the alkali resistance, and (7) others. In this paper, the research status of modified SCR catalysts in these aspects is analyzed and summarized.

3.1. Improving low-temperature deNO_x efficiency

When the boiler starts and stops or is operated under low load, the flue gas temperature may be lower than the optimum operating temperature of a conventional SCR catalyst. Improving the low-temperature deNO_x efficiency of the SCR catalyst is beneficial to adapt to the actual operating conditions and cut down the energy consumption and deNO_x cost. Furthermore, a high temperature would promote SO_2 oxidation, which is not expected to happen in an SCR system. Accordingly, many researchers have recently attempted to develop low-temperature ($<250\text{ }^\circ\text{C}$) SCR catalysts [84–87]. As they are placed before the desulfurization unit, these catalysts must withstand the high concentrations of SO_2 present in the flue gas. This SO_2 would lead to the destruction of the active components in the catalyst, while the surface-active sites would be covered by the generated metal and ammonium sulfates, which will completely inactivate the catalyst. Thus, poor sulfur resistance is considered to be the biggest bottleneck of most novel low-temperature SCR catalysts. Conversely, vanadium and other substances present in traditional SCR catalysts usually show excellent activity in high concentrations of SO_2 . Modification based on these components may be more feasible to develop ideal low-temperature SCR catalysts with good SO_2 resistance.

Deng et al. [45] explored the influence of WO_3 content on the low-temperature deNO_x performance of SCR catalysts. According to their study, the V-W-Ti catalyst with increased WO_3 content exhibited higher NH_3 -SCR activity at low temperatures compared to the vanadium-titanium catalysts. Particularly, the catalytic efficiency was $>80\%$ at $180\text{ }^\circ\text{C}$ when 7% tungsten was loaded. The highly dispersed V_2O_5 and WO_3 on the catalyst surface and the exposed acidic sites may be responsible for this increase.

Tables 2 and 3 show some modified vanadium-titanium-based SCR catalysts with deNO_x activity at low temperatures, including both metal and non-metal doping catalysts. The preparation method, modification effect, and anti-poisoning performance are summarized.

3.1.1. Metal-modified catalysts

Owing to the strong redox ability and oxygen storage capacity of CeO_2 , ceria-based catalysts have been attracting increasing attention worldwide [88–90]. Ce can significantly increase both the low-temperature deNO_x efficiency and reaction rate of vanadium-titanium-based SCR catalysts when doped into the carrier [91] or loaded as an additive [87,92]. Current studies generally believe that Ce and V may work synergistically. Ce^{3+} species would cause charge imbalance, vacant sites, and unsaturated chemical bonds, which increase the amount of chemisorbed oxygen and NO oxidation. Rich surface acidity, strong redox properties, and active intermediate species are the main

Table 2Metal-modified vanadium-titanium-based SCR catalysts for improving low-temperature deNO_x activity.

Modified component	Catalyst	Preparation method	<i>T</i> (°C)	DeNO _x efficiency (%)	N ₂ selectivity (%)	Active temperature window (°C)	Anti-poisoning performance	Ref.
Ce	1 wt% V ₂ O ₅ -10 wt% WO ₃ /CeO ₂ -TiO ₂ (molar ratio of Ce/Ti = 1:10)	Incipient wetness impregnation	325	100	—	250–475	Good SO ₂ resistance	[91]
Ce	0.1 wt% V ₂ O ₅ -6 wt% WO ₃ -10 wt% Ce/TiO ₂	Wet impregnation	200	90	>95	200–475	Good SO ₂ and H ₂ O resistances over 200 °C	[87]
Promoters (W/Ce)	Promoter/V/TiO ₂ ; V/promoter/TiO ₂ ; promoter-V/TiO ₂	Step-by-step impregnation and co-impregnation	300	>90	>79	225–375	—	[92]
Zr,Ce	CeO ₂ -3 wt% V ₂ O ₅ /TiO ₂ -ZrO ₂ (molar ratio of Zr/Ti and Ce/Ti-Zr = 1:1, 0.2, respectively)	Co-precipitation and wet impregnation	200 /210–50	90/100	—	150–475	—	[95]
Zr,Ce	1 wt% V ₂ O ₅ -CeO ₂ /TiO ₂ -ZrO ₂ (molar ratio of Zr/Ti = 1:1, Ce/Ti = 0.2)	Co-precipitation and step-by-step impregnation	250	92	—	225–375	Poor H ₂ O resistance but good SO ₂ resistance. Inhibition of SO ₂ and H ₂ O is reversible	[94]
Zr,Ce	3.0 wt% Zr-CeVO ₄ /TiO ₂ -NS	Impregnation	220–450	>80	>90	220–450	Good SO ₂ and H ₂ O resistances	[98]
Ce, CNT	V ₂ O ₅ -CeO _x /TiO ₂ -CNTs (molar ratio of Ce/V=9)	Sol-gel	200 /250	92/98	—	175–300	SO ₂ poisoning effect relied heavily on the temperature and gas velocity	[96]
Sb	2 wt% Sb/2 wt% V ₂ O ₅ /TiO ₂	Impregnation	300	100	—	225–400	Good SO ₂ resistance in the presence of H ₂ O	[106]
Sb, Ce	2 wt% Sb-2 wt% V ₂ O ₅ -10 wt% Ce/TiO ₂	Deposition-precipitation and impregnation	200	84%	>95	220–450	Enhanced the SO ₂ resistance	[93]
Sb, Ce	Sulfated 2 wt% Sb/2 wt% V/10 wt% Ce/TiO ₂ (SO ₂ processing at 300/400/500 °C)	Incipient wetness co-impregnation and deposition-precipitation	220	>90	>99	200–300	—	[97]
Pr	3 wt% V ₂ O ₅ -6 wt% MoO ₃ /4 wt % Pr ₆ O ₁₁ -TiO ₂	Sol-gel and impregnation	220	98	>95	220–400	Strong SO ₂ and H ₂ O resistances	[99]
Fe	1 wt% V ₂ O ₅ -10 wt% WO ₃ /3 wt% Fe ₂ O ₃ /TiO ₂ nanoparticles	Impregnation	250	81.3	—	250–500	Good SO ₂ resistance. Inhibition of SO ₂ was reversible	[100]
Fe	VFe/TiO ₂ nanoparticles (molar ratio of Fe/Ti ratio = 0.03, V/Ti = 0.17) (using 20 wt% sepiolite as binder)	Sol-gel	<200	<60	—	—	—	[103]
Cu	10 wt% CuO-1 wt% V ₂ O ₅ /TiO ₂	Wet impregnation	270 /300	70 /100	—	230–320	Good resistances to H ₂ O and SO ₂ at activated temperature	[101]
Cu	Cu-1 wt% V ₂ O ₅ /WO ₃ -TiO ₂ (molar ratio of Cu/V = 1:1)	Incipient wetness impregnation	250	84	~ 95	250–400	—	[102]

The deNO_x efficiency was >80% in the active temperature window.

—No data available

reasons for the high deNO_x activity of Ce-doped SCR catalysts [87,91–97]. Furthermore, Zhang et al. [94,95] and Li et al. [96] respectively chose TiO₂-ZrO₂ and TiO₂-carbon nanotubes (CNT) to replace raw TiO₂ as the carrier for Ce-doping catalysts. In these cases, higher low-temperature deNO_x activity was exhibited. However, the V₂O₅-CeO₂/TiO₂-ZrO₂ catalysts possessed

poor stability and H₂O resistance despite the good resistance to SO₂ poisoning. Additionally, the SO₂ resistance of V₂O₅-CeO_x/TiO₂-CNTs varied greatly at different temperatures; thus, it was excellent at 250 °C but poor at 200 °C. In contrast, the Zr-CeVO₄/TiO₂ catalyst prepared from TiO₂ nanosheets (TiO₂-NS) as the support showed the desired stability and

Table 3
Non-metallic modified vanadium-titanium-based SCR catalysts to improve low-temperature deNO_x activity.

Modified component	Catalyst	Preparation method	T (°C)	DeNO _x efficiency (%)	Active temperature window (°C)	Anti-poisoning performance	Ref.
F	F-1 wt% V ₂ O ₅ /TiO ₂ (molar ratio of F/Ti = 1.35 × 10 ⁻²)	Sol-gel and impregnation	240	73	—	—	[107]
			210	81.8	—	Inhibitions of H ₂ O and SO ₂ were both reversible	[110]
			240	98	200–250	Significantly increased the resistances to SO ₂ and H ₂ O	[108]
N	1 wt% V ₂ O ₅ /N-TiO ₂ (molar ratio of N/Ti = 1.0 × 10 ⁻²)	Sol-gel and impregnation	240/270	79.4/92	240–270	Excellent SO ₂ and H ₂ O resistances	[112]
S	S-1 wt% V ₂ O ₅ /TiO ₂ (molar ratio of S/Ti = 3 × 10 ⁻²)	Sol-gel and impregnation	240	87	210–240	—	[113]
BFS	2 wt% V ₂ O ₅ -5 wt% WO ₃ /TiO ₂ -SiO ₂ (pH = 1)	Successive impregnation	200–400	80	—	Excellent SO ₂ and H ₂ O resistances	[116]
HPA	15 wt% HPA-5 wt% V ₂ O ₅ /TiO ₂	Wet impregnation	300	100	—	Excellent resistance to alkali	[117]
					250–300		

H₂O/SO₂ durability in low-temperature SCR reactions [98]. This may occur because the formation of NH₄NO₃ and (NH₄)₂SO₄/NH₄HSO₄ was significantly inhibited and abundant active oxygen species and Brönsted acid sites were not covered in the presence of H₂O and SO₂. Similarly, Pr, another rare earth metal, was also proven to be a good modifier [99]. When the doping content of Pr₆O₁₁ was 4 wt%, 98% of the NO_x was converted into N₂ at 220 °C by V₂O₅-MoO₃/Pr₆O₁₁-TiO₂. Strong SO₂ and H₂O resistances were also exhibited.

Doping the common transition metals Fe [100] and Cu [101,102], which would increase the amount of adsorbed oxygen and acid activity centers on the catalyst surface, often shows good low-temperature SCR efficiency and anti-poisoning performance. The transition metals and vanadium would form a redox cycle, thus improving the redox behavior of the catalyst. For example, the denitrification activity of the V₂O₅-WO₃/Fe₂O₃/TiO₂ nanoparticle catalyst was enhanced in the range 200–400 °C because of the promotional effect of V⁴⁺+Fe³⁺ ↔ V⁵⁺+Fe²⁺ (Fig. 2) [100]. Moreover, the presence of Cu²⁺+V⁴⁺ ↔ Cu⁺+V⁵⁺ (Fig. 3) promoted the Cu-doped V₂O₅/WO₃-TiO₂ catalyst to reach a deNO_x efficiency of 84% and a N₂ selectivity of ~95% at 250 °C [102]. However, the V-Fe/TiO₂ nanoparticle catalysts did not show good SCR activity at low temperatures in the presence of 20 vol% H₂O. Their denitrification efficiencies were <60% at 200 °C [103]. In addition,

although loading on TiO₂ can improve the SCR activity at low temperatures (150–250 °C) [104,105], when added into V₂O₅/TiO₂ as promoter, MnO_x had a negative effect on the SCR performance and slightly reduced N₂O generation [92].

Sb is another promising modifier for commercial SCR catalysts. Compared to other modified SCR catalysts, the Sb-promoted SCR catalyst performed better during NO_x conversion at 150–400 °C, and was still effective at 230 °C after 90 h of SO₂ deactivation (Fig. 4) [106]. Since more ammonium bisulfates were formed on 10 wt% W-V₂O₅/TiO₂ than on 2 wt% Sb-V₂O₅/TiO₂ [106], antimony may be a good substitute for tungsten to act as the auxiliary of the catalysts in low-temperature or low-sulfur content environments. In addition, Sb-Ce co-doping [93,97] of the SCR catalysts also achieved a desirable NO_x reduction efficiency at low temperatures. Processing strong surface acidity and redox performance, 2 wt% Sb-2 wt% V₂O₅-10 wt% Ce/TiO₂ revealed the highest NO_x conversion rate of 84% and excellent N₂ selectivity (>95%) at 200 °C [93]. Moreover, after SO₂ processing at high temperatures, excellent deNO_x activity was still revealed [97]. This was attributed to the substantial Ce³⁺ ions and acid sites existing on its surface after the sulfidation treatment.

Fig. 2. Redox cycle of low-temperature deNO_x on V₂O₅-WO₃/Fe₂O₃/TiO₂ nanoparticles [100].

Fig. 3. Redox cycle of low-temperature deNO_x on Cu-doped V₂O₅/WO₃-TiO₂ [102].

Fig. 4. SO_2 deactivation study at 240 °C over 1% $\text{Sb}/\text{V}_2\text{O}_5/\text{TiO}_2$ (a), $\text{V}_2\text{O}_5/\text{TiO}_2$ (b), 1% $\text{Se}/\text{V}_2\text{O}_5/\text{TiO}_2$ (c), 1% $\text{S}/\text{V}_2\text{O}_5/\text{TiO}_2$ (d) and 1% $\text{Cu}/\text{V}_2\text{O}_5/\text{TiO}_2$ (e). Reaction conditions: $800 \times 10^{-6} \text{ NO}_x$, $800 \times 10^{-6} \text{ NH}_3$, 3 vol% O_2 , 6 vol% H_2O , $500 \times 10^{-6} \text{ SO}_2$, $\text{SV} = 60000 \text{ h}^{-1}$ [106].

The impregnation sequence of the promoters and V also influences the SCR activity and N_2O selectivity [92]. According to research on Ce-, W-, Zr-, and Mn-SCR, the catalyst first added vanadium showed higher low-temperature deNO_x activity. This superiority can be attributed to the formation of more V_2O_5 aggregates on the sample, which provides valuable information for the development of new SCR catalysts with excellent SCR performance.

3.1.2. Non-metallic modified catalysts

Common non-metals such as F [107–111], N [112], and S [113] can also improve the low temperature denitrification performance of vanadium-titanium-based catalysts (Table 3). They are usually doped into the TiO_2 supporter by a sol-gel method to change the catalyst structure. Anatase TiO_2 is more favorable to the SCR reaction [114]. Fortunately, these doped non-metals can inhibit the phase transition of TiO_2 from anatase to rutile according to a series of characterization methods such as XPS, TPD, and EPR [107–113]. Moreover, the surface acidity, oxygen vacancies, and active sites can also be increased. The electron donors NO and NH_3 reduce vanadium, and superoxide ions (O_2^-) are then formed at the V sites. These superoxide ions promote the SCR reactions so that the SCR activity of the catalysts is directly proportional to the concentration of these superoxide ions. However, the coexistence of H_2O and SO_2 would synergistically inhibit the formation of V^{4+} and superoxide ions, thus restricting the SCR reaction [109].

These experimental results were also confirmed by theoretical calculations. Zhang et al. [115] investigated the cluster molecules of F-doped $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts based on first-principle molecular dynamics and density functional theory. They found that atomic F replaced the bridge oxygen in TiO_2 and formed an oxygen vacancy with high activity. Tungsten could interact with the oxygen vacancy, which can be promoted by vanadium, thus making the formation of superoxide ions advantageous.

Tran et al. [116] prepared $\text{TiO}_2\text{-SiO}_2$ supports using Ti-bearing blast furnace slags (BFS). On loading with V_2O_5 and

WO_3 , their low-temperature deNO_x performance was significantly better than that of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$. The presence of SiO_2 and some impurities such as CaO, MgO, Al_2O_3 , Fe_2O_3 , and SO_4^{2-} increased the surface area and acidity and promoted adsorption of the reactant.

Heteropoly acids (HPA), including $\text{H}_3\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, and $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ [117], were also used as a modifier to enhance the low-temperature deNO_x performance of commercial SCR catalysts. All the 15-wt% HPA- $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts achieved $\sim 100\%$ deNO_x efficiency at 300 °C when the V_2O_5 content was 3–6 wt%, which was better than that achieved by 10 wt% $\text{WO}_3\text{-V}_2\text{O}_5/\text{TiO}_2$. The addition of HPA could add acid sites and V^{4+} ions on the catalysts and promote the resistance to alkali poisoning. Further, neither N_2O generation nor non-selective NH_3 oxidation was increased.

3.2. Enhancing thermal stability

Following long-time running at high temperatures, conventional SCR catalysts would be sintered and TiO_2 would convert from the anatase to the rutile phase. Therefore, the surface area and the catalytic activity of the catalysts can be greatly reduced [118]. To mitigate this problem, researchers have committed to improving the thermal stability of SCR catalysts.

Adding silicon to the carrier may be an available measure. The unfavorable phase transformation of TiO_2 and the decrease in catalytic surface area can both be inhibited by Si doping. After hydrothermal treatment at 750 °C in 10 vol% $\text{H}_2\text{O}/\text{air}$ for 24 h, the stable structure of a $\text{TiO}_2\text{-WO}_3\text{-SiO}_2$ supporter caused the vanadium oxide to form the most active polymer, other than V_2O_5 crystals, (Fig. 5) and maintain a good dispersion [119]. However, Casanova et al. [120] hold that Si doping alone could not efficiently promote the stability of vanadium-containing catalysts. They added rare earth and transition metals to the $\text{V}_2\text{O}_5/\text{TiO}_2\text{-WO}_3\text{-SiO}_2$ catalyst and studied the resulting SCR performance [120–124]. Among these doping metals, Fe, Ce, La, Nd, and Pr were relatively sensitive to heat treatment, while Tb, Er, Dy, Sm, and Gd showed outstanding anti-deactivation properties and high deNO_x activity after thermal aging at 750 °C in air [120,122,123]. The formed rare earth vanadates inhibited the rutilization of anatase TiO_2 . These components only partially decomposed at high temperatures and thus, improved the thermal resistance of the catalysts [123]. Similarly, the $\text{Fe}_x\text{Er}_{1-x}\text{VO}_4/\text{TiO}_2\text{-WO}_3\text{-SiO}_2$ catalyst possessed better thermal stability than the $\text{FeVO}_4/\text{TiO}_2\text{-WO}_3\text{-SiO}_2$

Fig. 5. Changes in $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ and $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2\text{-SiO}_2$ catalysts after hydrothermal treatment [119].

Fig. 6. TEM images (A, B) recorded over sample $\text{Fe}_{0.5}\text{Er}_{0.5}\text{VO}_4/\text{TiO}_2\text{-WO}_3\text{-SiO}_2$ catalyst aged at $750\text{ }^\circ\text{C}$ [124].

catalyst due to the presence of erbium-iron vanadate after thermal aging at $750\text{ }^\circ\text{C}$ (Fig. 6) [124].

Similarly, zirconium was used as a modifier to increase the thermal stability of the vanadium-containing catalysts by changing the vanadium speciation [125]. After aging treatment at $750\text{ }^\circ\text{C}$ for 12 h, the 10 wt% Zr-1 wt% $\text{V}_2\text{O}_5/\text{TiO}_2\text{-WO}_3$ catalyst showed high SCR efficiency at $150\text{--}400\text{ }^\circ\text{C}$. However, the deNO_x activity on the fresh catalysts was reduced by zirconium doping at temperatures $<400\text{ }^\circ\text{C}$, which can be attributed to the decreased $\text{V}^{5+}=\text{O}$ and Brønsted active sites.

The presence of tungsten and barium would also influence the thermal stability of the SCR catalysts [126]. After thermal aging at $600\text{ }^\circ\text{C}$ for 6 h, the deNO_x efficiency of 6 wt% W-2 wt% $\text{V}_2\text{O}_5/\text{sulfated TiO}_2$ did not change significantly since TiO_2 conversion was low. However, the 2 wt% Ba-2 wt% $\text{V}_2\text{O}_5/\text{sulfated TiO}_2$ was dramatically deactivated due to the generation of V-O-Ba , an inactive vanadium species for the SCR reaction.

Yu et al. [127] found that the deposited potassium could form V-O-K species, inhibited the aggregation of vanadium oxides, and thus, improved the thermal stability of the catalysts (Fig. 7). Compared to unmodified vanadium-titanium-based catalysts, this species could increase the deNO_x efficiency threefold after treatment at $800\text{ }^\circ\text{C}$ for 4–5 h.

These studies may help us find more detail on the sintering and rutilization processes of TiO_2 , and are conducive to improving the stability and denitrification activity of SCR catalysts to increase their service life.

3.3. Improving the Hg^0 oxidation efficiency

Mercury is a volatile and poisonous trace element that ex-

Fig. 7. Rutilization process of the SCR catalyst and formation of the K/SCR catalyst [127].

hibits migration, persistence, high biological enrichment, as well as nerve toxicity. It can easily cause environmental pollution and serious health hazards to human beings and thus, has been recognized as one of the persistent environmental pollutants to be preferentially controlled globally [128,129]. In 2013, the EPA updated the Mercury and Air Toxics Standard (MATS) requirements, in which the total mercury emissions from new units using low-rank raw coal as a fuel should be controlled to levels $<0.003\text{ lb/GWh}$ [130].

Currently, coal combustion accounts for $\sim 45\%$ of the anthropogenic mercury sources [131]. According to the literature, the mercury in coal-fired flue gas usually exists in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate mercury (Hg^p) [132], of which Hg^0 is the most difficult to handle because of its high volatility and low water solubility. Among the current Hg^0 removal technologies from coal-fired flue gas, the use of catalysts to convert Hg^0 to Hg^{2+} , which can be removed by existing desulphurization equipment, is economical and practical. This technique has good future application prospects. In this method, the ratio of Hg^{2+} in the flue gas determines the mercury removal efficiency. Therefore, it is of great significance to improve the catalytic oxidation performance of Hg^0 .

Kamata et al. [67] investigated the Hg^0 oxidation performance of metallic oxide-modified TiO_2 catalysts. According to their study, the mercury oxidation efficiency is of the order of $\text{MoO}_3 > \text{V}_2\text{O}_5 > \text{CrO}_3 > \text{Mn}_2\text{O}_3 > \text{Fe}_2\text{O}_3 > \text{CuO} > \text{NiO}$ in the absence of NH_3 . This indicates that V_2O_5 , as the main active component in commercial SCR catalysts, is one of the most effective metal oxides for Hg^0 catalytic oxidation. In fact, many mercury oxidation catalysts have been developed [133], such as Au/TiO_2 [134], CuO/TiO_2 [135], $\text{CeO}_2/\text{TiO}_2$ [136], $\text{MnO}_x\text{-CeO}_2/\text{TiO}_2$ [137,138], $\text{CuO-CeO}_2/\text{TiO}_2$ [139,140], $\text{V}_2\text{O}_5/\text{ZrO}_2\text{-CeO}_2$ [141], $\text{MnO}_x\text{-CeO}_2\text{-ZrO}_2$ [142], Co-Ce-ZrO_2 [143], $\text{Mn}/\gamma\text{-Al}_2\text{O}_3$ [144], $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ [145], $\text{Nb-Co-Ce}/\text{Al}_2\text{O}_3$ [146], Fe-Ti-Mn spinel [147], and Co-MF [148]. Although all these catalysts demonstrated a high mercury oxidation efficiency, their components are quite different from the traditional vanadium-titanium-based catalysts and thus, their application to deNO_x flue gas is uncertain. Moreover, the addition of these mercury oxidation catalysts may require transformation of the existing flue gas treatment equipment, which will result in a significant increase in cost. Therefore, adding other substances without altering the existing components of the SCR catalysts, to enhance the Hg^0 oxidation performance while maintaining high deNO_x efficiency, has aroused great concern.

According to previous studies, modification by transition metals (Fe [149], Cu [150], Ag [151], Ru [152,153], Ce [154–156], etc.), metal chlorides (CaCl_2 [157], CuCl_2 [158], etc.), and non-metallic species (Si [159], etc.) can improve the elemental mercury oxidation properties of $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts, which are summarized in Table 4. The reaction conditions are also listed here since they may dramatically affect the mercury oxidation efficiency.

Huang et al. [149] investigated the influence of transition metal oxide doping on the mercury oxidation of traditional SCR catalysts. Fig. 8 reveals that in the presence of $8 \times 10^{-6}\text{ HCl}$, ZnO ,

Table 4

Modified vanadium-titanium-based SCR catalysts for synergistic mercury oxidation.

Modified components	Catalyst	Preparation method	Hg ⁰ oxidation efficiency (%)	Reaction conditions	DeNO _x activity	Anti-poisoning performance	Ref.
Fe	1 wt% Fe ₂ O ₃ /SCR	Impregnation	>90	120 μg/m ³ Hg ⁰ , 8 × 10 ⁻⁶ HCl, 5% O ₂ , N ₂ as balance gas, GHSV = 7.2 × 10 ⁵ h ⁻¹ , 350 °C	—	SO ₂ slightly inhibited Hg ⁰ oxidation	[149]
Cu	3 wt% CuO-0.8 wt% V ₂ O ₅ -WO ₃ /TiO ₂	Improved impregnation	85.43	7 μg/m ³ Hg ⁰ , 5% O ₂ , 12% CO ₂ , 600 × 10 ⁻⁶ SO ₂ , 300 × 10 ⁻⁶ NO, 8% H ₂ O, N ₂ as balance gas, GHSV = 1.2 × 10 ⁵ h ⁻¹ , 350 °C	—	SO ₂ and H ₂ O slightly inhibited Hg ⁰ oxidation	[150]
Ag	Ag-V ₂ O ₅ -TiO ₂ -polyvinyl pyrrolidone (PVP) (molar ratio of Ag/Ti = 1, V/Ti = 1)	Impregnation	>90	Hg ⁰ , 5 × 10 ⁻⁶ HCl, 4% O ₂ , N ₂ as the balance, SV = 4.26 × 10 ⁵ h ⁻¹ , 350 °C	—	Exhibited some SO ₂ resistance	[151]
Ru	Ru/SCR (molar ratio of Ru/Ti = 0.5)	Multi-impregnation	>90	50 × 10 ⁻⁶ Hg ⁰ , 500 × 10 ⁻⁶ SO ₂ , 300 × 10 ⁻⁶ NO, 4% H ₂ O, 5 × 10 ⁻⁶ HCl, and air as the balance, SV = 7.9 × 10 ⁵ h ⁻¹ , 350 °C	No obvious negative effects	Excellent SO ₂ , H ₂ O, and NH ₃ resistances; no significant negative effects on SO ₂ transformation	[152]
Mo, Ru	Mo-Ru/SCR (molar ratio of Ru/Ti = 0.2%, Mo/Ti = 1%)	Wet impregnation	86	200 μg/m ³ Hg ⁰ , 4% O ₂ , 500 × 10 ⁻⁶ SO ₂ , 50 × 10 ⁻⁶ NH ₃ , 100 × 10 ⁻⁶ NO, 4% H ₂ O, 5 × 10 ⁻⁶ HCl, and N ₂ as the balance, SV = 5.9 × 10 ⁵ h ⁻¹ , 350 °C	Maintained high deNO _x efficiency and N ₂ selectivity	SO ₂ and NH ₃ resistances were increased	[153]
Si	SiO ₂ -6 wt% TiO ₂ -5 wt% V ₂ O ₅	Sol-gel	99	15–16.5 ppb Hg ⁰ , 4% O ₂ , 12% CO ₂ , 8% H ₂ O, 10 × 10 ⁻⁶ HCl, 400 × 10 ⁻⁶ SO ₂ , 300 × 10 ⁻⁶ NO, 10 × 10 ⁻⁶ NO ₂ , N ₂ as balance gas, total flow rate = 1.5 LPM	—	H ₂ O inhibited the Hg ⁰ oxidation while SO ₂ had no significant effect	[159]
CaCl ₂	1.0 wt% CaCl ₂ -SCR	Physical drying mixed	78.8	41 μg/Nm ³ Hg ⁰ , 6% O ₂ , 12% CO ₂ , 5% H ₂ O, 1000 × 10 ⁻⁶ SO ₂ , 300 × 10 ⁻⁶ NO, N ₂ as balance gas, SV = 10000 h ⁻¹ , 350 °C	No significant effects	Good H ₂ O resistance, SO ₂ slightly promoted Hg ⁰ oxidation, no significant effect on SO ₂ conversion	[157]
CuCl ₂	3 wt% CuCl ₂ -SCR	Improved impregnation	88.4	7 μg/m ³ Hg ⁰ , 20 × 10 ⁻⁶ HCl, 5% O ₂ , 12% CO ₂ , 500 × 10 ⁻⁶ SO ₂ , 300 × 10 ⁻⁶ NO, 8% H ₂ O, N ₂ as balance gas, GHSV = 3 × 10 ⁵ h ⁻¹ , 350 °C	Reached 92.1% at 350 °C	250–430 °C SO ₂ and H ₂ O slightly inhibited Hg ⁰ oxidation	[158]
Ce	0.8 wt% V ₂ O ₅ -8 wt% WO ₃ /TiO ₂ -CeO ₂ (molar ratio of Ce/Ti = 0.08)	Sol-gel and ultrasound-assisted impregnation	88	70 μg/m ³ Hg ⁰ , 700 × 10 ⁻⁶ NO, 700 × 10 ⁻⁶ NH ₃ , 5 vol% O ₂ , 400 × 10 ⁻⁶ SO ₂ , GHSV = 50000 h ⁻¹ , 250 °C	Reached 89% at 250 °C	Good resistances to SO ₂ and H ₂ O	[154]
Ce	0.8 wt% V ₂ O ₅ -8 wt% WO ₃ /TiO ₂ -CeO ₂ (quality ratio of CeO ₂ /TiO ₂ = 0.25)	Sol-gel and impregnation	88.93	70 μg/m ³ Hg ⁰ , 500 × 10 ⁻⁶ SO ₂ , 1000 × 10 ⁻⁶ NO, 12% CO ₂ , 5% O ₂ , N ₂ as balance gas, GHSV = 1.0 × 10 ⁵ h ⁻¹ , 250 °C	—	Good H ₂ O resistance, SO ₂ slightly promoted Hg ⁰ oxidation	[155]
Ce	1 wt% V ₂ O ₅ -10 wt% CeO ₂ /TiO ₂	Ultra-sound-assisted impregnation	81.55	60 μg/m ³ Hg ⁰ , 5 vol% O ₂ , 500 × 10 ⁻⁶ NO, 500 × 10 ⁻⁶ NH ₃ , N ₂ as balance gas, GHSV = 65000 h ⁻¹ , 250 °C	Reached 91.25% at 300 °C	SO ₂ and H ₂ O irreversibly inhibited SCR reaction and Hg ⁰ oxidation	[156]
Cu, Ce	7 wt% Ce-1 wt% Cu/1.5% V ₂ O ₅ -5% MoO ₃ /TiO ₂	Ultrasonic-assisted impregnation	79.17	30 μg/m ³ Hg ⁰ , 5% O ₂ , 500 × 10 ⁻⁶ NO, 500 × 10 ⁻⁶ NH ₃ , N ₂ as balance gas, GHSV = 45000 h ⁻¹ , 250 °C	>97% at 200–400 °C	SO ₂ and H ₂ O inhibited Hg ⁰ oxidation	[160]

— No data available.

Y₂O₃, NiO, and ZrO₂ tend to inhibit this process, while the reverse holds for Co₃O₄, Fe₂O₃, and MnO₂. Their promotional effects can be ordered as Fe₂O₃ > MnO₂ > Co₃O₄. Overall, 1% wt Fe₂O₃/SCR exhibited the best Hg⁰ oxidation efficiency (>90%) at 350 °C. Even in the presence of 400 × 10⁻⁶ SO₂, its mercury

oxidation effect was only slightly reduced to 80%. Hg⁰ may be oxidized to Hg⁰ by Fe₂O₃ on the Fe₂O₃/SCR catalyst surface [149]. When HCl was added to the flue gas, the intermediate (Hg-OH-Fe-Cl) was generated. Chemisorbed oxygen and Fe³⁺ would then oxidize HCl to active chlorine by the Mars-Maessen

Fig. 11. Hg^0 oxidation mechanism on the active surface of the chlorine species [163].

V_2O_5 (b). These two types of HgCl are both oxidized to HgCl_2 by active surface chlorine or chlorine atoms and then removed from the surface. Therefore, an increase in active chlorine species could significantly enhance Hg^0 oxidation. For the CuCl_2 -SCR catalysts, both active Cl species and Cu^{2+} ions present on its surface played roles in Hg^0 oxidation. Fig. 12 illustrates that the Cl species released by CuCl_2 react with the adsorbed Hg^0 to form HgCl_2 , while CuCl_2 is reduced to CuCl . The formed CuCl would react with O_2 and generate the intermediate copper oxychloride (Cu_2OCl_2). This could be re-chlorinated to CuCl_2 by the adsorbed HCl on the catalyst surface when HCl is added to the flue gas [158]. Therefore, doping of CuCl_2 significantly improved the Hg^0 oxidation efficiency.

Almost all the studies on CeO_2 -modified SCR catalysts showed that >80% Hg^0 efficiency could be achieved in the absence of HCl [154–156]. CeO_2 and V_2O_5 would work synergistically in these catalysts. The formed redox cycle of $\text{Ce}^{4+} + \text{V}^{4+} \leftrightarrow \text{Ce}^{3+} + \text{V}^{5+}$ not only greatly improved the NO conversion rate but also promoted Hg^0 oxidation. This Hg^0 oxidation process follows the Mars-Maessen mechanism, where the adsorbed Hg^0 combines with the chemisorbed or lattice oxygen, produced by O–O bond breakage on the V_2O_5 surface, and forms the weakly bonded Hg-M-O_{x-1} ($\text{M} = \text{Ce}$ or V). HgO is generated thereafter (in Fig. 13). The presence of gaseous O_2 would promote the regeneration of the lattice and chemically adsorbed oxygen; thus, a reaction cycle is formed. Additionally, $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2\text{-CeO}_2$ showed good resistance to SO_2 and H_2O [154,155]. On the other hand, the presence of SO_2 and H_2O would reversibly inhibit NO transformation and Hg^0 oxidation over the $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2$ catalyst and thus, limits its application [156].

The co-modification of Ce and Cu was also found to be effective in improving the Hg^0 oxidation in the absence of HCl [160].

Fig. 12. Schematic diagram of Hg^0 oxidation over a CuCl_2 -SCR catalyst [158].

Fig. 13. Hg^0 oxidation mechanism of the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2\text{-CeO}_2$ catalyst [155].

These two dopants form the redox cycle $\text{Cu}^{+} + \text{Ce}^{4+} \leftrightarrow \text{Cu}^{2+} + \text{Ce}^{3+}$ in Ce-Cu/SCR catalysts, which promotes the formation of more chemisorbed oxygen and thus, exhibits good redox properties and Hg^0 oxidation performance.

Notably, over all these catalysts, ammonia exhibits the most significant inhibitory effect on mercury oxidation, which is similar to the phenomenon observed for traditional SCR catalysts. To some extent, the NO reacted with most of the NH_3 , thereby reducing this inhibitory effect. However, the slip ammonia that is not consumed in the denitration reaction should be removed to ensure good Hg^0 oxidation performance.

3.4. Oxidizing slip ammonia simultaneously

It is generally recognized that automotive ammonia can be effectively converted to harmless N_2 by dual layer (noble metal-SCR) catalysts [164,165]. However, to date, no suitable solution to mitigate slip ammonia from the SCR system of coal-fired power plants has been found. Unfortunately, reducing the NH_3/NO ratio, as the main existing control method, would significantly reduce the deNO_x efficiency. Therefore, some researchers have focused on the preparation of new types of catalysts to inhibit slip ammonia while maintaining satisfactory deNO_x performance.

Owing to the inherent characteristics of coal-fired flue gas, the catalysts suitable for slip ammonia treatment in power plants require an excellent ammonia conversion efficiency and nitrogen selectivity at high SO_2 concentrations and $\sim 350^\circ\text{C}$. In general, the temperature of the catalytic decomposition of ammonia is $>500^\circ\text{C}$ [166], while the selective catalytic oxidation (SCO) of ammonia requires relatively low temperatures, thus may be an alternative process.

Chen et al. [152] found that a Ru -modified $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst would perform well on slip ammonia oxidation. When installed behind the commercial SCR catalyst, it could effectively oxidize the slip ammonia in the flue gas as keeping a relatively high NO conversion efficiency. Additionally, its N_2 selectivity can reach $\sim 90\%$. The addition of Mo could further promote the ammonia oxidation performance of Ru-SCR catalysts [153]. At 350°C , the Mo-Ru/SCR catalyst can remove >95% slip ammonia, of which 97% is converted to harmless N_2 . Its ammonia oxidation efficiency can still reach >70% in the presence of SO_2 . Simultaneously, >99% Hg^0 could be oxidized when the HCl concentration in the flue gas was only 5×10^{-6} . Thus, Hg^0 , NH_3 , and NO_x can be efficiently removed simultaneously when a

Mo-Ru/SCR catalyst is used as a SCR-plus catalyst (Fig. 14).

The unsaturated Ru (cus-Ru) and reactive oxygen species on the Ru/SCR catalyst surface play important roles in ammonia oxidation. The NH_3 adsorbed on the surface would form the intermediate product with high activity, which is much more easily oxidized (Eqs. (7)–(12) [153]). The addition of Mo further increases the amount of cus-Ru, and thus, promotes the oxidation of slip ammonia.

However, addition of the noble metal ruthenium greatly increases the cost of the catalyst, which is not conducive to commercial application. To date, no other studies of vanadium-titanium-based catalysts for controlling slip ammonia have been reported. Undoubtedly, there are wide areas and great application values to seek more economical and efficient SCO catalysts for slip ammonia from coal-fired power plants.

3.5. Reducing SO_2 oxidation

In addition to burning low-sulfur coal, mixing coal, and spraying calcium- or magnesium-based absorbents, scholars have tried to control SO_3 generation from coal-fired power plants through the modification of commercial SCR catalysts. Changing the physical properties of the catalyst and doping other compounds into the traditional vanadium-titanium-based catalyst can both reduce the SO_2 oxidation efficiency.

DeNO_x reaction and SO_2 oxidation occur at different parts of the vanadium-based catalysts. According to chemical kinetics studies, the SCR reaction, controlled by external diffusion, mainly occurs in the 0.1-mm surface of the catalyst. On the other hand, the SO_2 oxidation process occurs in the whole catalyst and thus, the SO_2 conversion rate is proportional to the wall thickness of the SCR catalyst [167]. Therefore, decreasing the wall thickness or using flat catalysts can reduce the formation of SO_3 [168]. Others hold that corrugated SCR catalysts may have a lower oxidative effect on SO_2 than other shapes of catalysts [169].

Fig. 14. Mo-Ru/SCR used as an SCR-Plus catalyst and its properties [153].

With the growth of the catalyst service life, the SO_2 oxidation rate of SCR catalysts would increase [170]. In addition to $\text{K}_2\text{O}/\text{TiO}_2$, all the TiO_2 -loaded metal oxides can oxidize SO_2 into SO_3 . Their SO_2 oxidation performance is as follows: $\text{V}_2\text{O}_5/\text{TiO}_2 > \text{Fe}_2\text{O}_3/\text{TiO}_2 > \text{Re}_2\text{O}_7/\text{TiO}_2 > \text{CrO}_3/\text{TiO}_2 > \text{Nb}_2\text{O}_5/\text{TiO}_2 > \text{MoO}_3/\text{TiO}_2 > \text{WO}_3/\text{TiO}_2$ [171]. Since $\text{V}_2\text{O}_5/\text{TiO}_2$ displays a strong SO_2 oxidation ability [114], reducing the vanadium content in the SCR catalyst can inhibit SO_3 generation; however, the deNO_x efficiency will also significantly decrease [171].

As early as 1981, Morikawa et al. [172] have studied the SO_2 oxidation of vanadium-titanium-based catalysts doped with metal oxides. Their oxidation activities are of the order of: $\text{WO}_3\text{-V}_2\text{O}_5\text{-TiO}_2 > \text{MoO}_3\text{-V}_2\text{O}_5\text{-TiO}_2 > \text{V}_2\text{O}_5\text{-TiO}_2 > \text{Ta}_2\text{O}_5\text{-V}_2\text{O}_5\text{-TiO}_2 > \text{Y}_2\text{O}_3\text{-V}_2\text{O}_5\text{-TiO}_2 > \text{GeO}_2\text{-V}_2\text{O}_5\text{-TiO}_2 > \text{ZnO-V}_2\text{O}_5\text{-TiO}_2$. Thus, WO_3 or MoO_3 doping can enhance the SO_2 oxidation of vanadium-titanium-based catalysts, while GeO_2 and ZnO would inhibit it. Some studies have suggested that tungsten can promote SO_2 oxidation [173,174]. However, others argue that doping with WO_3 or MoO_3 would increase the surface acidity, which can effectively reduce the SO_2 conversion rate [175]. When the loading mass fraction of MoO_3 is $>9\%$, the SO_2 conversion rate could be $<1\%$ [176]. Moreover, the decomposition of NH_4HSO_4 can be markedly enhanced by WO_3 doping, which promotes the reaction of NH_4HSO_4 and NO and inhibits N_2O production during the reaction [177].

Shi et al. [178,179] doped the transition metal Cu into a traditional SCR catalyst. A 0.6% addition reduced the SO_2 conversion rate from 0.73% to 0.68%, while maintaining a denitrification efficiency of 94.47%. They found that the amount of V^{4+} ions in the doped catalyst increased, while those of the V^{5+} ions and lattice oxygen decreased. This may abate the transfer of lattice oxygen, thereby inhibiting SO_2 oxidation. Theoretical calculations have shown that the oxygen charge in the V–O–M oxygen bridge changed from negative to positive in Me-doped catalysts. This indicated that the basicity of oxygen decreased and thus, SO_2 oxidation was inhibited.

Li et al. [180] found that doping BaO, MgO, SrO, and their mixtures would reduce the SO_2/SO_3 conversion rate of the SCR catalysts in high-sulfur flue gas, wherein the SO_2 oxidation rate of BaO addition is the lowest. Adding SiO_2 into the three single-doped catalysts can significantly improve the denitrification efficiency, which is originally slightly reduced. Their SO_2 oxidation rate was only $\sim 0.5\%$, while the denitrification efficiency was $>80\%$ at 300–440 °C. Some studies found that vanadium tended to be present in a lower oxidation state when BaO [181] or SiO_2 [173,174,182] was added. The redox capacity and SO_2 adsorption sites were also reduced and thus, SO_2 oxidation was inhibited. For example, the $\text{V}_2\text{O}_5\text{-BaO}/\text{TiO}_2$ catalyst, which contains 2% BaO, showed less than half the SO_2 oxidation efficiency of an unmodified or tungsten-added catalyst. Further, when the Ti/Si molar ratio in the $\text{V}_2\text{O}_5/\text{TiO}_2\text{-SiO}_2$ catalyst was 8/2, a high deNO_x efficiency was maintained, while the SO_2 conversion was only about a third of that of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst [174].

Rare earth, niobium, and silicon-aluminum composite oxides have also been used simultaneously as additives of vanadium, titanium, and tungsten to prepare a new catalyst for low SO_3 generation [183]. This prepared catalyst showed the same

deNO_x activity as the conventional SCR catalyst, while the SO₂ oxidation rate was reduced by 20%–40%. However, its inhibitory mechanism has not been revealed.

In general, doping of the oxidizing substances can improve the Hg⁰ and slip NH₃ oxidation efficiency of the SCR catalyst. However, SO₂ oxidation may also be promoted. This will lead to catalyst poisoning, thereby causing a reduction in the Hg⁰ and NO_x removal efficiencies. However, the additives that inhibit SO₂ oxidation tend to reduce the oxidation properties of the catalysts. Moreover, NH₃ oxidation is an adverse reaction of the SCR process, which may reduce the denitrification efficiency. Therefore, both the oxidation capacity and the selectivity of the catalysts should be taken into account when choosing the appropriate modified compounds. As a result, it is rather complicated to inhibit SO₂ oxidation while efficiently reducing NO_x, oxidizing mercury, and slip ammonia at the same time. A comprehensive selection of catalyst formulations and preparation methods should therefore be made.

3.6. Increasing alkali resistance

Studies have shown that alkali metals in the flue gas would deposit on the surface of the catalysts used in coal-fired power plants [184]. This can lead to catalyst deactivation when these substances are in excess [185,186]. These alkali metals would significantly decrease both the surface acidity and reducibility of the vanadium-titanium-based catalysts, change the V=O groups, and thus, inhibit the SCR reaction [185,187,188].

Fortunately, the modification of ceria would improve the alkali poisoning resistance of the V₂O₅-WO₃/TiO₂ catalyst. Fig. 15 reveals that the deNO_x activity of V₂O₅-CeO₂-WO₃/TiO₂ was much higher, even after doping with K and Na [185]. This phenomenon may be due to the good oxygen storage capacity of ceria and the high reducibility produced by the redox properties of Ce⁴⁺ to Ce³⁺. Additionally, the adsorption amount of alkali metals on the active V species was reduced since the K or Na atoms would easily bond to the CeO₂ (110) surface [187]. The co-doping of Sb and Nb can also enhance the K₂O poisoning resistance of the V₂O₅/TiO₂ catalyst. The K₂O-doped 1 wt%

V₂O₅-Sb-Nb/TiO₂ (atomic ratio of Sb/V = 0.5, Nb/V = 1) catalyst even demonstrated higher deNO_x performance than fresh vanadium-titanium catalysts [189]. However, the relevant mechanism was not explained in this study. Moreover, the addition of Nb possibly facilitated the dissociation of water, which generated surface hydroxyl species and increased the surface acidity. Therefore, the V₂O₅-Sb-Nb/TiO₂ catalyst showed higher water resistance than the vanadium-titanium catalysts.

In fact, compared to the study of the SO₂ and H₂O resistances of the catalysts, the influence of alkali metal poisoning has rarely been investigated. This could be a promising research direction for the industrial application of SCR catalysts.

3.7. Others

In addition to the above five types of catalysts, some other modified catalysts have also been studied. For example, modification by Mn [190], Si [191], nanotubes [192], and cordierite supports [14] would further increase the denitrification activity; low-cost Fe [193,194] and Cu [195] enhance N₂ selectivity; addition of BaSO₄ [196] improves the SO₂ resistance; and cordierite-loaded SCR catalysts [14] possess excellent mechanical strength and wash coating stability. These catalysts are summarized in Table 5.

4. Conclusions

Although for several years, new types of SCR catalysts have aroused great interest, vanadium-titanium-based catalysts remain unchallenged owing to their excellent performance and experience in application. However, their low-temperature deNO_x efficiency, thermal stability, and synergistic mercury oxidation performance, still leaves much to be desired and the problems of SO₂ oxidation and ammonia slip need to be urgently addressed.

By doping different materials such as noble metals (e.g. Ag, Ru), transition metals (e.g. Mn, Fe, Cu, Zr, etc.), rare earth metals (e.g. Ce, Pr), and other metal chlorides (e.g. CaCl₂, CuCl₂) and non-metals (F, S, Si, N, etc.), these modified vanadium-titanium catalysts have been proven to exhibit a corresponding promoted performance. Their reported advantages and disadvantages are summarized in Table 6.

In fact, owing to equipment and experimental condition limitations, the N₂O selectivity of many of these catalysts was not considered in previous studies, and the impact of flue gas composition such as SO₂ and H₂O on the catalyst properties is still unclear. Further studies on their shortcomings and practicality are also needed.

5. Perspectives

In summary, more studies are needed to further improve the comprehensive performance of modified vanadium-titanium-based SCR catalysts to adapt to various operating conditions in coal-fired power plants. Future research may involve the following aspects:

(1) Great effort should be made to explore vanadi-

Fig. 15. Activity of 1% alkali-doped V_{0.4}-Ce₅W₅/Ti and V_{0.4}-W₁₀/Ti catalysts [185].

Table 5

Other modified SCR catalysts and their properties.

Modified components	Catalyst	Preparation method	Temperature (°C)	DeNO _x efficiency	N ₂ selectivity (%)	Active temperature window (°C)	Anti-poisoning performance	Ref.
Mn	1 wt% V ₂ O ₅ -2 wt% MnO ₂ /TiO ₂	Impregnation	300–400	>90	~100	275–425	Inhibitions of SO ₂ and H ₂ O were reversible.	[190]
Si	Si-1 wt% V ₂ O ₅ /TiO ₂ (mole ratio of Si/Ti = 0.2)	Sol-gel and impregnation	300	>94	—	300–400	Showed better H ₂ O and SO ₂ resistances than V ₂ O ₅ /TiO ₂	[191]
Nanotube	3 wt% V ₂ O ₅ -10 wt% WO ₃ /TiO ₂ -nanotube	Sol-gel	380	>93	—	300–400	Good SO ₂ resistance, H ₂ O slightly inhibited the deNO _x efficiency.	[192]
Cordierite	0.9 wt% V ₂ O ₅ -7.2 wt% MoO ₃ /TiO ₂ /Monolithic cordierite	Sol-gel and impregnation	400	98	~95	300–500	SO ₂ and H ₂ O resistances were >90% at 350–450 °C	[14]
Fe	8 wt% Fe-ZSM-5 zeolite-1.68 wt% V ₂ O ₅ -7.6 wt% WO ₃ /TiO ₂	Solid-state sublimation technique	300–500	>78	>97	300–450	—	[193]
Fe	2 wt% V ₂ O ₅ /Fe ₂ O ₃ -TiO ₂ (Fe ²⁺ :Fe ³⁺ :Ti ⁴⁺ =3:2:1)	Co-precipitation and impregnation	300–450	>90	>95	300–450	Good H ₂ O and SO ₂ resistances	[194]
Cu	4 wt% Cu-6 wt% V/TiO ₂	Co-impregnation	225–375	>85	>95	225–375	Showed good stability and SO ₂ /H ₂ O resistance	[195]
BaSO ₄	Sulfurated 1 wt% V ₂ O ₅ /BaSO ₄ -TiO ₂ (weight ratio of BaSO ₄ :TiO ₂ = 2.5:97.5)	Incipient wetness impregnation	300/400	85/96	100/98	350–450	Excellent SO ₂ resistance	[196]

Table 6

Summary of the main modified vanadium-titanium-based SCR catalysts.

Catalyst system	Doping elements	Advantages	Disadvantages	Ref.
Noble metal-modified SCR catalysts	Ag, Ru	High Hg ⁰ oxidation activity; high NH ₃ oxidation activity	High cost	e.g. [151–153]
	Cu, Fe, Mn	High low-temperature NH ₃ -SCR activity; high Hg ⁰ oxidation activity	—	e.g. [100–103,149,150,160,178,179,190,193–195]
Transition metal-modified SCR catalysts	Zr	High low-temperature NH ₃ -SCR activity; high thermal stability	—	e.g. [94,95,98,125]
	Nb	high H ₂ O resistance; Good alkali poisoning resistance	—	e.g. [189]
Rare earth-modified SCR catalysts	Ce, Pr, Er	High low-temperature NH ₃ -SCR activity; high thermal stability; high Hg ⁰ oxidation activity; good alkali poisoning resistance	—	e.g. [87,91–99,120–122,124,154–156,160,185]
Metal chloride-modified SCR catalysts	CaCl ₂ , CuCl ₂	High Hg ⁰ oxidation activity	—	e.g. [157,158]
Alkali-modified SCR catalysts	K	High thermal stability	Cause deactivation of the catalyst	e.g. [127,185–189]
Alkaline earth metal-modified SCR catalysts	Ba	Low SO ₂ oxidation	Low NO _x removal activity; low thermal stability	e.g. [126,180,181,196]
	Sr, Mg	Low SO ₂ oxidation	Low NO _x removal activity	e.g. [180]
Pnictogen-modified SCR catalyst	Sb	High SO ₂ resistance; Good alkali poisoning resistance	—	e.g. [93,97,106,189]
Carbon element-modified SCR catalyst	Ge	Low SO ₂ oxidation	—	e.g. [172]
Non-metallic modified SCR catalysts	F, N, S	High low-temperature NH ₃ -SCR activity; high low-temperature NH ₃ -SCR activity; high thermal stability; high Hg ⁰ oxidation activity; low SO ₂ oxidation	—	e.g. [107–113,115]
	Si	High low-temperature NH ₃ -SCR activity; high low-temperature NH ₃ -SCR activity; high thermal stability; high Hg ⁰ oxidation activity; low SO ₂ oxidation	—	e.g. [119,120, 159, 173, 174, 182, 191]

um-titanium-based catalysts with high deNO_x performance, high N₂ selectivity, good SO₂ and H₂O resistance, and a wide operating temperature window. Considering both catalytic activity and cost, transition metal oxides, rare earth metal ox-

ides, and non-metallic elements are still the main modifiers. Moreover, modification of the carrier is also a possible research direction.

(2) As the key to the synergistic control of mercury pollution

Graphical Abstract

Chin. J. Catal., 2018, 39: 1347–1365 doi: 10.1016/S1872-2067(18)63090-6

Review on the latest developments in modified vanadium-titanium-based SCR catalysts

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Commercial vanadium-titanium-based SCR catalysts were doped with some modified components to obtain higher thermal stability, low-temperature NH_3 -SCR and Hg^0 oxidation activity, and reduce slip ammonia and SO_3 generation.

by SCR catalysts, Hg^0 oxidation performance and its enhancing method should be thoroughly investigated. Moreover, slip ammonia in the tail of the SCR system significantly inhibits Hg^0 oxidation. The reaction of slip ammonia and the generated SO_3 would affect the stable operation of the catalyst and the downstream flue gas equipment and should therefore be inhibited. Much effort should be made to realize the cooperative control of multiple pollutants in the SCR system.

(3) Mechanisms affecting the catalytic properties of the modified constituents should be revealed. Many experimental results have shown that doping suitable metallic oxides and non-metallic elements can significantly enhance the NH_3 -SCR performance of vanadium-titanium-based SCR catalysts. This is attributed to many aspects, including a larger surface area, increased acidic sites, and added surface oxygen. However, their detailed mechanisms are still unclear. The mechanism of mercury oxidation and poisoning of vanadium-titanium-based SCR catalysts should also be studied intensively. Moreover, blind experimental screens would waste resources and research efforts, which could be avoided by theoretical calculation of possible modified components.

(4) Larger pilot tests are also needed to develop modified SCR catalysts suitable for commercial application. To date, most of the catalysts and the flue gas produced at the laboratory level are somewhat different from the actual situation, and thus, there is insufficient data to exhibit the actual effect of the catalysts in practical applications. Studies that more closely simulate the actual industrial conditions are needed to further investigate the value of using these catalysts.

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改性钒钛基 SCR 催化剂的研究进展

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摘要: 钒钛基选择性催化还原催化剂是目前燃煤电厂应用最为广泛的脱硝催化剂。由于传统钒钛基催化剂存在低温脱硝效率低、热稳定性差、单质汞氧化效率低、二氧化硫氧化、氨逃逸、碱金属中毒等问题, 人们开始尝试通过对传统 SCR 催化剂进行改性, 以期改善其综合性能。本文从(1) 拓宽催化剂的反应温度窗口, 尤其是向低温区扩展, (2) 提高催化剂的热稳定性, (3) 协同氧化单质汞, (4) 控制氨逃逸, (5) 降低 SO_2 至 SO_3 的转化率和 (6) 提高催化剂抗碱金属中毒性能等方面综述了改性钒钛基 SCR 催化剂的研究进展, 总结了其催化性能和相关影响机理。

研究表明, 某些金属及非金属的改性可以增加钒钛基 SCR 催化剂的表面酸度、活性位点及氧化还原性能, 非金属的掺杂还可以抑制 TiO_2 载体由锐钛矿向金红石型转化、增加表面氧空位, 从而改善了钒钛基催化剂的低温脱硝性能; 硅、钨、钼和稀土金属等的添加也可抑制 TiO_2 的金红石化过程, 锆、钾则改变了钒氧化物的存在形态, 抑制其高温聚合, 提高了钒钛基催化剂的热稳定性; 贵金属、过渡金属、金属氯化物及非金属的改性改变了钒钛基催化剂的汞氧化机制, 均可有效促进低氯甚至无氯条件下钒钛基催化剂对单质汞的氧化; 贵金属钌及助剂钼添加的钒钛基催化剂可在维持较高脱硝效率的同时, 实现单质汞及逃逸氨的高效去除, 在 SCR 尾部将逃逸氨选择性氧化生成无害的氮气和水; 被铜、氧化钡、氧化硅等物质改性后, 更多的钒以低价态存在, 使催化剂的氧化还原性能降低, 并抑制了二氧化硫的吸附, 从而减少了三氧化硫的生成; 由于具有高储氧能力和氧化还原特性, 还可降低碱金属的吸附量, 铈的掺杂可提高钒钛基催化剂的抗碱金属中毒性能。

此外, 本文还汇总了包括贵金属 (如银、钨)、过渡金属 (如锰、铁、铜、钴等)、稀土金属 (铈、镨) 等金属、金属氯化物 (如氯化铜、氯化钙) 及非金属 (氟、硫、硅等) 改性钒钛基 SCR 催化剂的优缺点. 基于前人研究及作者观点, 改性组分的掺杂有利于进一步提高钒钛基催化剂的综合性能, 具有巨大的发展潜力, 也是在现有基础上实现多污染物控制的方法之一.

关键词: 钒钛基催化剂; 选择性催化还原; 低温脱硝; 汞氧化; 逃逸氨; 二氧化硫氧化

收稿日期: 2018-03-05. 接受日期: 2018-04-03. 出版日期: 2018-08-05.

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基金来源: 河北省科学技术计划项目 (16273703D); 中央高校基本科研业务费专项资金 (2015ZD24, 2017XS123).

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