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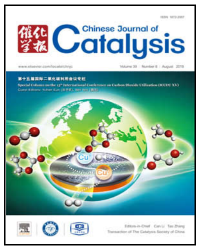

Review

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

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A B S T R A C T

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 Hg^0 oxidation activity, SO_2 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 Hg^0 oxidation efficiency, (4) oxidizing slip ammonia, (5) reducing SO_2 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.

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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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 NO_2) to N_2 selectively by ammonia, urea, H_2, 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 NH_3-SCR reactions are as follows [10] :

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \quad (2)$$

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \quad (3)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \quad (4)$$

2. Research progress in SCR catalysts

2.1. Overview of SCR catalysts

As the core of the SCR technology, catalysts are used to reduce the activation energy and reaction temperature of NO_x decomposition, increase the N_2 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 TiO_2, Al_2O_3, SiO_2, 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, V_2O_5-WO_3 (MoO_3)/TiO_2 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 N_2 selectivity among the production processes is high when the temperature is >300 °C. TiO_2 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, V_2O_5 exhibits strong catalytic activity and stability. It has a remarkable catalytic effect on NO reduction and performs even better when supported on TiO_2. However, the vanadium content in the catalyst is usually low (0.8%–1.2%) because SO_2 can be oxidized to undesirable SO_3 by V_2O_5 [44]. Thus, WO_3 or MoO_3 is used as adjuvant. By interacting with anatase TiO_2, WO_3 shows high catalytic activity [45], increases the Lewis sites on the catalysts [46], inhibits TiO_2 sintering [47], improves SO_2 resistance [48], and extends the reaction temperature window [49].

The specific NO_x removal mechanism over vanadi-

Table 1
Summary of the major SCR catalysts.

Catalyst type	Active component	Carrier	Advantages	Disadvantages	Ref.
Commercial vanadium-titanium-based catalyst	V_2O_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_2O_3, etc.	High low-temperature SCR activity; high SO_2 and H_2O resistance	Narrow temperature window; NH_3 oxidation; N_2O generation; high cost	e.g. [15–17]
Metal oxides	V_2O_5, CeO_2, MNO_x, CuO, FeO_x, CoO_x, CrO_x and some metal composite oxides	TiO_2, Al_2O_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_2O_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]