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Review (Special Issue on Rare Earth Catalysis)

The use of ceria for the selective catalytic reduction of NO_x with NH₃

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ABSTRACT

The selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is one of the widely used NO_x control strategies for stationary sources (particularly for power plants) and mobile sources (particularly for diesel vehicles). The application is aimed at meeting the increasingly stringent standards for NO_x emissions. Recently, ceria has attracted much attention for its applications in NH₃-SCR catalysts owing to its unique redox, oxygen storage, and acid-base properties. In this article, we comprehensively review recent studies on ceria for NH₃-SCR catalysts when used as support, promoter, or the main active component. In addition, the general development of ceria for NH₃-SCR catalysts is discussed.

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1. Introduction

NO_x, which mainly refers to NO and NO₂, is considered a major air pollutant owing to adverse effects on human health and other impacts on the environment. It can lead to acid rain and photochemical smog and also contributes significantly to the formation of haze. In humans, it can cause direct damage to the respiratory system. According to a recent estimate, NO_x emissions in China increased rapidly from 11.0 Mt in 1995 to 26.1 Mt in 2010. Power plants, industrial activities and transportation were major NO_x sources. Based on current legislation and current implementation status, NO_x emissions are estimated to increase by 36% by 2030 from the 2010 level. Failure to implement the operation of flue gas denitrification for power plants would be expected to increase NO_x emissions dramatically in the next 5–10 years. Failure to control heavy diesel vehicle emissions is expected to be associated with more adverse effects in the long term [1].

The reduction of NO_x emissions has become one of the greatest challenges in environmental protection, especially for China. The selective catalytic reduction of NO_x with NH₃ (NH₃-SCR) is a widely used NO_x control strategy for stationary sources (particularly for power plants) and mobile sources (particularly for diesel vehicles). It has a major role in helping to meet the increasingly stringent standards for NO_x emissions [2]. There are some differences between the applications of NH₃-SCR to stationary sources and to mobile sources. For safety reasons, urea (in aqueous solution) is a preferred reductant rather than NH₃ for mobile sources. In addition, the different emission conditions of stationary sources and mobile sources require the NH₃-SCR catalysts to work under different operational conditions, and different specific catalytic properties are needed. For example, the catalyst for stationary sources is required to resist sulfur poisoning and minimize the oxidation of SO₂ to SO₃ owing to the relatively high SO₂ concentrations in flue gas. The catalyst for mobile sources needs to be active in a

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wide temperature range under very high space velocities owing to the variation of engine operating conditions and the limited space on board for the required reactor system.

Vanadium-based NH_3 -SCR catalysts, $\text{V}_2\text{O}_5\text{-WO}_3$ (or MoO_3)/ TiO_2 , were developed for NO_x abatement from stationary sources and also found use in the diesel vehicle market, owing to their effectiveness for NH_3 -SCR reaction and resistance to SO_2 poisoning. However, the toxicity of active vanadium species, together with the low stability and large N_2O formation at high temperatures, has limited their use as catalysts in diesel vehicles. Although the use of vanadium-based NH_3 -SCR catalysts is still permitted in China and some other developing countries at present, these catalysts will be removed from the market for mobile applications in the next few years when stricter environmental protection demands are introduced [3]. This has led to great efforts being made to develop substitute, environmentally benign NH_3 -SCR catalysts.

Many types of catalysts, including oxides and zeolites, based on transition metals and/or rare earth metals have been studied for the NH_3 -SCR reaction [4]. Several transition metals such as Fe, Mn, and Cu have been used in NH_3 -SCR catalysts, while the investigation of rare earth metals for NH_3 -SCR has mainly focused on Ce. Ce has been widely used as a crucial component in three-way catalysts (TWCs) for (gasoline) automotive emission control. Owing to its unique redox, oxygen storage, and acid-base properties, ceria has attracted much attention for its applications in NH_3 -SCR catalysts as support, promoter, or main active component [4,5]. In this review, we will focus on the recent studies of ceria for NH_3 -SCR catalysts. In addition, the future developments in using ceria in NH_3 -SCR applications will be discussed.

2. Ceria as a catalyst support

Pure ceria is not suitable for use as a support for NH_3 -SCR catalysts owing to its high reduction temperature and loss of surface area by sintering. When zirconium oxide was added into ceria, the oxygen storage capacity and the thermal stability of the oxide were significantly increased [6]. This led to $\text{CeO}_2\text{-ZrO}_2$ being investigated as an NH_3 -SCR catalyst support in some detail by several researchers.

Six transition metal oxides (WO_3 , MoO_3 , Mn_2O_3 , CrO_3 , Fe_2O_3 , and Co_2O_3) were deposited on $\text{CeO}_2\text{-ZrO}_2$ to investigate their catalytic activities and thermal stabilities (Fig. 1). Among these catalysts, $\text{WO}_3/\text{CeO}_2\text{-ZrO}_2$ showed the highest NO_x conversion levels and exhibited good high temperature stability [6]. Another study on the same catalyst system showed that the addition of WO_3 led to a significant increase in NH_3 storage capacity (acidity) not initially present in the Ce-Zr mixed oxide support, and this was reflected in a strong enhancement of catalytic activity in the NH_3 -SCR reaction [7].

Nickel and sulfate were impregnated on $\text{CeO}_2\text{-ZrO}_2$ to enhance the activity and N_2 selectivity for the NH_3 -SCR reaction by Si *et al.* [8]. Ni addition improved the Lewis acidity of $\text{CeO}_2\text{-ZrO}_2$ and thereby enhanced the low-temperature activity. In contrast, Brønsted acid sites, introduced by sulfate modification, were less oxidative than the Lewis acid sites. These sites

Fig. 1. NO conversion as a function of temperature over various $\text{MO}_x/\text{CeO}_2\text{-ZrO}_2$ mixed oxide catalysts [6]. Reaction conditions: 1 mL catalyst, total flow rate = 1500 mL/min, 550 ppm NO , 550 ppm NH_3 , 6 vol% O_2 , 10 vol% CO_2 , 10 vol% H_2O , N_2 balance and GHSV = 90 000 h^{-1} . Reproduced with permission from the RSC.

facilitated NH_3 adsorption instead of NH_3 oxidation and thereby enhanced high-temperature activity and selectivity. Phosphates were also impregnated on $\text{CeO}_2\text{-ZrO}_2$ to improve its NH_3 -SCR catalytic performance [9]. In addition, $\text{CeO}_2\text{-ZrO}_2$ was used as a support for Mn-based catalysts for the low temperature NH_3 -SCR reaction and contributed significantly to catalytic performance [10,11].

3. Ceria as an NH_3 -SCR catalyst promoter

Cerium has been widely used as an additive to enhance the catalytic performance of various catalysts. For NH_3 -SCR catalysts, Ce has also been shown to be an effective catalyst promoter. Addition of Ce could exert a promotional effect on traditional V-based catalysts. Chen *et al.* [12] found that Ce addition to $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ could enhance the adsorption and then accelerate the SCR reaction owing to a synergistic interaction between Ce, V, and W species (Fig. 2A). The added Ce species existed mainly in the form of Ce^{3+} oxide in the catalyst, which was beneficial for the oxidation of NO to NO_2 . Moreover, the Ce additive on $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ could provide stronger and more active Brønsted acid sites, which were beneficial for the SCR reaction. Ceria-modified $\text{V}_2\text{O}_5\text{-ZrO}_2/\text{WO}_3\text{-TiO}_2$ catalyst was also evaluated for the NH_3 -SCR of NO_x in diesel engines [13]. Compared with the $\text{V}_2\text{O}_5/\text{WO}_3\text{-TiO}_2$ catalysts having only Zr addition, the co-addition of Ce greatly enhanced the low-temperature activity of the catalyst, but the material obviously deactivated with age. Characterization measurements suggest that enrichment of Ce^{3+} and enhanced redox properties take place. In addition, the more active adsorbed nitrates on CeO_2 -modified catalysts aided the NH_3 -SCR reaction. Catalyst deactivation was mainly owed to sintering and segregation of CeO_2 on the catalyst's surface, consistent with a poor hydrothermal stability of the Ce component. However, the additional NO_2 will compensate for the activity loss owing to hydrothermal aging and significantly improve the low temperature SCR activity. This suggests a high sensitivity of the Ce component towards NO_2

Fig. 2. Enhancements of catalytic performance owing to addition of Ce to (A) V₂O₅-WO₃/TiO₂ [12], (B) Fe-ZSM-5 [17], and (C) Mn/TiO₂ [19] catalysts. Reaction conditions: (A) 500 mg sample, 500 ppm NO, 500 ppm NH₃, 3% O₂, N₂ as balance gas, GHSV = 28 000 h⁻¹; (B) 20 mg sample (0.025 mL), 2000 ppm NO, 2000 ppm NH₃, 3% O₂, balance He, total flow rate 138.3 mL/min, GHSV = 332 000 h⁻¹; (C) 2 mL sample, 1000 ppm NO, 1000 ppm NH₃, 3% O₂, 3% water, balance N₂, GHSV = 40 000 h⁻¹. Reproduced with permission from the ACS, the RSC, and Elsevier, respectively.

[13]. In another study, it was found that the addition of ceria to an Sb-V₂O₅/TiO₂ catalyst could enhance the total acidity and redox properties of the catalyst, leading to higher NO_x conversions in a wide temperature window [14].

Fe-exchanged ZSM-5 has received much attention for applications on diesel vehicles as an NH₃-SCR catalyst [15]. During the development of Fe-ZSM-5 for NH₃-SCR by Long and Yang [16], Ce was found to be an effective promoter for the catalyst. The addition of a small amount of Ce to Fe-ZSM-5 could not only increase the activity but also play a stabilization role, enhancing the catalyst's SO₂/H₂O resistance and hydrothermal stability. The poor low-temperature activity is a major problem for Fe-ZSM-5 catalysts. Carja *et al.* [17] significantly improved the low-temperature catalytic performance of the Fe-ZSM-5 catalyst by the addition of Ce. Further, they demonstrated that the joint action of Ce and Fe within the zeolite framework gave rise to a high activity catalyst (Fig. 2B). In addition, the incorporation of CeO₂ into an Fe³⁺-exchanged TiO₂-pillared clay (Fe-TiO₂-PILC) was also found to lead to an improvement in catalytic activity. This was attributed to an increase in the activity of NO oxidation to NO₂ by O₂ (NO₂ being an important intermediate for the SCR reaction on this catalyst [18]).

Manganese oxides are the most active components for NH₃-SCR at low temperatures. Therefore, Mn-based oxide catalysts have been studied extensively for NO_x abatement for both stationary and mobile sources. However, the low N₂ selectivity and pronounced SO₂/H₂O negative impact on performance are big challenges for the application of Mn-based catalysts [20]. Ce has been proved to be an effective promoter for Mn oxide to improve its catalytic performance [21–24]. A Mn-Ce mixed oxide catalyst developed by Qi and Yang [21] showed excellent low-temperature NH₃-SCR activity together with high N₂ selectivity and good SO₂/H₂O resistance. The catalytic performance of MnO_x-CeO₂ could be further improved by the addition of other metal elements such as Fe, Pr, and Nb [22,23]. In addition, it was found that Ce addition could improve the catalytic activity of Mn/TiO₂ owing to the increase in chemisorbed oxygen, improved acidity, and an enhancement of

redox properties (Fig. 2C) [19]. Moreover, the resistance of the Mn/TiO₂ catalyst to SO₂ could be greatly enhanced by Ce addition. The improved behavior was associated with the prevention of formation of metal sulfates and the inhibiting effects of (NH₄)₂SO₄ and NH₄HSO₄ deposition [25].

4. Ceria as the main active component for NH₃-SCR catalysts

Labile oxygen vacancies and bulk oxygen species with relatively high mobility are easily formed on cerium oxide during the redox shift between Ce³⁺ and Ce⁴⁺ under oxidizing and reducing conditions, respectively. Therefore, Ce-based oxide could be used effectively as a main active component for NH₃-SCR catalysts.

Pure CeO₂ oxides usually possess poor NH₃-SCR activity (Fig. 3A) [26,28]. However, CeO₂-zeolites, obtained by the combination of CeO₂ with zeolites (BEA, ZSM-5, MOR, and FER) using simple physical mixing methods, could achieve excellent NO_x conversions at very high space velocities, owing to the synergetic effect between the acidic sites of zeolite and the oxidation component present (Fig. 3B) [27]. The catalytic performance of CeO₂ could also be greatly improved by surface sulfation. This process could result in an enrichment of Ce³⁺ (leading to an increase in active oxygen content) and could also lead to strong acid sites (favoring NH₃ chemisorption and activation) on the CeO₂ surface (Fig. 3A) [25]. Yang *et al.* [29] proposed a novel effect of sulfation on the SCR reaction over CeO₂. In this system the adsorption of NH₃ on CeO₂ was promoted, enhancing the Eley-Rideal mechanism. The sites for -NH₂ adsorption and the oxidizing agents for -NH₂ oxidation on CeO₂ were separated after the sulfation, resulting in an inhibition of the catalytic oxidation of -NH₂ to NO. As a result, the SCR activity of CeO₂ obviously increased after sulfation.

Ce-based composite oxide catalysts are more attractive than single oxide catalysts because other metal elements can promote the catalytic properties of CeO₂. In our previous study, Xu *et al.* [30] developed a promising CeO₂/TiO₂ catalyst, prepared

Fig. 3. Improved catalytic performance of CeO₂ by surface sulfation (A) [26] and combination with zeolites (B) [27]. Reaction conditions: (A) [NH₃] = [NO] = 1000 ppm, [O₂] = 3 vol%, N₂ balance, GHSV = 60 000 h⁻¹; (B) 1000 ppm NO, 1000 ppm NH₃, 10 vol% O₂, 9 vol% H₂O, balance N₂, GHSV = 500 000 h⁻¹. Reproduced with permission from Elsevier and the RSC, respectively.

by an impregnation method, and this showed high SCR activity and N₂ selectivity at 275–400 °C. A comparative study involving three preparation methods for CeO₂/TiO₂ catalysts was reported by Gao *et al.* [31], and the results indicated that the catalyst prepared by a single step sol-gel method had the highest SCR activity and SO₂ resistance. High surface area and good redox properties are important for catalytic activity, while the strong interaction between Ce and Ti and a high concentration of amorphous, or highly dispersed nanocrystalline, ceria could explain the excellent performance of the catalyst. Using various methods, Li *et al.* [32] confirmed that the active site of a CeO₂/TiO₂ catalyst was the Ce-O-Ti short-range ordered species with the interaction between Ce and Ti being at the atomic level. To improve the resistance to alkali metal poisoning, a titanate nanotube in which CeO₂ was confined was designed and synthesized by Chen *et al.* [33]. To enhance the catalytic activity and the SO₂ resistance of CeO₂/TiO₂, Liu *et al.* [34] supported CeO₂ on TiO₂-SiO₂, while Chen *et al.* [35,36] co-impregnated CeO₂ and WO₃ onto TiO₂. Furthermore, Peng *et al.* [37] improved the low-temperature activity of CeO₂-WO₃/TiO₂ by SiO₂ addition. Other transition metals such as Mo [38], Fe [39], Zr [40], and Nb [41] were also investigated as modifying agents.

Recently, many studies have focused on the Ce-based mixed oxide catalysts for the NH₃-SCR reaction. Chen *et al.* [42] prepared a CeO₂-WO₃ catalyst using a coprecipitation method. The catalyst exhibited high activity, high N₂ selectivity, and good SO₂ durability in a broad temperature range of 175–500 °C at a space velocity of 47 000 h⁻¹. Ge and Mn were used by Chang *et al.* [43] for further improving the CeO₂-WO₃ catalyst. Liu *et al.* [44] compared CeO₂-WO₃ catalysts prepared by various methods and concluded that the high NH₃-SCR activity could be attributed to large surface area, high surface concentrations of Ce and Ce³⁺, enhanced NO oxidation ability, and high concentration of surface acid sites. Based on an *in situ* IR and Raman spectroscopic study, Peng *et al.* [45] suggested an NH₃-SCR reaction mechanism of CeO₂-WO₃ consisting of two independ-

ent cycles. These were denoted as a redox cycle, owing to the excellent oxygen storage capability and reducibility of cubic fluorite-structured CeO₂ (for NH₃ activation), and an acid site cycle. The latter resulted from Brønsted acid sites formed on the W-O-W species of Ce₂(WO₄)₃ (for NH₃ adsorption).

In addition, Liu *et al.* [46] developed a superior Cu-Ce-Ti oxide catalyst with dual redox cycles (Cu²⁺ + Ce³⁺ ↔ Cu⁺ + Ce⁴⁺, Cu²⁺ + Ti³⁺ ↔ Cu⁺ + Ti⁴⁺) and demonstrated that the dual redox cycles play key roles in the catalytic behavior. Peng *et al.* [47] prepared a MoO₃-CeO₂ catalyst and extensively investigated its structure-activity relationship for the NH₃-SCR reaction. Cai *et al.* [48] synthesized three-dimensional ordered macroporous (3DOM) Ce_{0.75}Zr_{0.2}Mo_{0.05}O_{2-δ} (M = Fe, Cu, Mn, Co) using a colloidal crystal template method for NH₃-SCR. A novel niobia-ceria-based catalyst was reported by Casapu *et al.* [49] to be useful for NO_x abatement as well as the catalytic regeneration of diesel particulate filters (DPF) in diesel engines. The catalyst is successful because of its multi-functionality in NH₃-SCR, the hydrolysis of urea to NH₃, and the oxidation of soot. The relationship between structure and performance of the niobia-ceria catalyst for NH₃-SCR was examined by Qu *et al.* [50]. Because there have been many reports on Ce-based oxides for both NH₃-SCR and soot oxidation, the further development of multi-functional Ce-based oxide catalysts merits more attention.

5. High-efficiency Ce-based NH₃-SCR catalysts

There are limitations to the catalyst volume that can be placed on diesel vehicles, which requires that the catalyst possesses superior NH₃-SCR performance under high space velocity conditions. However, the above mentioned Ce-based oxide catalysts have been tested at relatively low GHSVs (< 150 000 h⁻¹). Because the reduction of NH₃-SCR catalyst volume is one of the main challenges for diesel vehicle applications, it is very important to develop highly efficient NH₃-SCR catalysts capable of operating successfully at high space velocities [2].

In our previous study, a Ce-Ti oxide catalyst was prepared by a facile homogeneous precipitation method [51]. Compared with the Ce-Ti oxide catalysts previously reported, this catalyst showed a remarkably improved low-temperature SCR activity and, in turn, a significantly wider reaction temperature window. Further optimization of the preparation method resulted in significantly enhanced high-temperature activity and an even further broadened temperature window [52]. In addition, the SCR activity at high space velocity conditions was also clearly improved.

A superior Ce-W-Ti oxide catalyst was prepared by doping W into the Ce-Ti oxide catalyst [53]. The Ce-W-Ti oxide catalyst showed both enhanced low-temperature activity and high-temperature activity simultaneously, combined with enhanced N₂ selectivity, compared with the undoped Ce-Ti oxide catalyst. The effects of W species in the Ce-W-Ti oxide catalyst were investigated, and the results showed that the introduction of W species increased the concentration of surface oxygen vacancies and enhanced the redox properties of the catalyst. The latter attribute can benefit the low-temperature activity by facilitating the “fast SCR” reaction. The introduction of W species could also simultaneously increase the amount of surface Brönsted and Lewis acid sites, which, in turn, enhances both the high-temperature activity and the N₂ selectivity by inhibiting the unselective oxidation of NH₃ at high temperatures.

Investigations on the Ce-W-Ti oxide catalyst showed that the role of Ti species, such as acidity promotion, could be fulfilled by W species. Therefore, a novel Ce-W oxide catalyst with a Ce/W molar ratio of 1:1 was developed for the NH₃-SCR reaction [54]. The Ce-W oxide catalyst showed much higher SCR activity than the previous Ce-Ti and Ce-W-Ti oxide catalysts (Fig. 4). Further, the catalyst exhibited a near 100% NO_x conversion over a wide temperature range from 250 to 425 °C under an extremely high GHSV of 500 000 h⁻¹. The Ce-W oxide catalyst also exhibited excellent N₂ selectivity, good stability, and high resistance to poisoning. Under the same test conditions, the Ce-W oxide catalyst showed much better SCR performance than V₂O₅-WO₃/TiO₂ and Fe-ZSM-5 catalysts, which

Fig. 4. NO_x conversion as a function of temperature over Ce-Ti, Ce-W-Ti, and Ce-W oxide catalysts. Reaction conditions: 0.06 mL catalyst, total flow rate = 500 mL/min, 500 ppm NO, 500 ppm NH₃, 5 vol% O₂, N₂ balance, GHSV = 500 000 h⁻¹.

have been industrially and commercially used for NO_x abatement from diesel engine exhausts.

6. Perspectives

Cerium is relatively cheap and accounts for a large part of the rare earth element market. With the increase in the industrial application of heavy rare earth elements, coproduced light rare earth elements, such as Ce, appears to be surplus to current demands, especially in China [55]. Therefore, the development of new applications for Ce is urgently needed. The pursuit of NH₃-SCR applications of Ce, especially in the development of Ce-based NH₃-SCR catalysts, is a very promising undertaking.

Despite much progress, there remain some problems and challenges for the use of Ce-based NH₃-SCR catalysts. For stationary applications, Ce has been shown to be an effective promoter for V₂O₅-WO₃/TiO₂ catalysts [12]. However, the catalysts with Ce as a main active component are inferior to V-based catalysts regarding SO₂ resistance [56]. For mobile applications, Ce is a good promoter for Fe-ZSM-5 and enhances its catalytic activity, hydrothermal stability, and SO₂/H₂O resistance [16,17]. In contrast, the thermal stabilities of the oxide catalysts with CeO₂-ZrO₂ as the support or Ce as the main active component are generally lower than those of zeolite catalysts. This is especially true of the recently developed Cu-based small-pore zeolite catalysts [13,48]. In addition, although the combination of CeO₂ and WO₃ has been shown to be very effective for the NH₃-SCR reaction and can form the basis for high efficiency catalysts, the high cost of WO₃ implies that there is a need for reducing or eliminating WO₃ in such systems.

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Graphical Abstract

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This review presents the progress in research on the use of ceria for the selective catalytic reduction of NO_x with NH₃.

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氧化铈在氨选择性催化还原氮氧化物中的应用

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摘要: NH₃选择性催化还原NO_x (NH₃-SCR)是一种广泛应用于以燃煤电厂为代表的固定源和以柴油发动机为代表的移动源NO_x排放控制的技术。近年来, 氧化铈由于具有优异的氧化-还原、储氧和表面酸性等特性而在NH₃-SCR催化剂研究中受到广泛关注。本文系统综述了氧化铈用作NH₃-SCR催化剂载体、助剂和主催化组分的相关研究, 并对该领域未来可能的研究方向进行展望。

关键词: 氧化铈; 柴油车尾气; 氮氧化物控制; 选择性催化还原

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1. 前言

氮氧化物(NO_x , 主要指 NO 和 NO_2)是主要的大气污染物, 可以引发酸雨、光化学烟雾和灰霾等污染问题, 并且对人体健康尤其呼吸系统产生直接危害. 研究表明, 我国 NO_x 排放量从1995年的11.0 Mt迅速增至2010年的26.1 Mt, 热电厂、工业和交通是主要 NO_x 排放源. 按照现有立法和执行情况预测, 2030年我国 NO_x 排放量将会在2010年的基础上继续增长36%. 如果我国不能有效进行电厂脱硝, 未来5至10年的 NO_x 排放量将会迅速增加, 而如果不能有效控制重型柴油车的 NO_x 排放将会在未来很长时间内造成严重后果^[1].

控制 NO_x 排放已经成为环境保护领域的一个重要挑战, 尤其是在我国. NH_3 选择性催化还原 NO_x ($\text{NH}_3\text{-SCR}$)是一种广泛应用于以燃煤电厂为代表的固定源烟气脱硝和以柴油车为代表的移动源 NO_x 排放控制的技术^[2]. 该技术在固定源和移动源 NO_x 控制的应用中有所不同. 因为安全原因, 在移动源上使用时通常以尿素(水溶液)替代 NH_3 用作还原剂. 另外, 由于固定源和移动源废气排放特征不同, $\text{NH}_3\text{-SCR}$ 催化剂的工作条件不同, 因此对催化剂的性能要求也不同. 例如, 由于固定源烟气含 SO_2 浓度较高, 要求 $\text{NH}_3\text{-SCR}$ 催化剂具有很强的抗硫中毒能力和弱的氧化 SO_2 为 SO_3 的能力; 而移动源由于其不断变化的发动机工况以及有限的安装空间则要求催化剂必须在高空速环境下、宽温度窗口内具有优异的催化活性.

以 $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ 为代表的钒基 $\text{NH}_3\text{-SCR}$ 催化剂, 由于具有很好的催化活性和抗硫中毒能力已在固定源烟气脱硝领域应用多年, 并被引入柴油车尾气净化市场. 然而, 由于主要活性组分钒具有生物毒性, 高温稳定性较差且副产物 N_2O 生成量较大, 钒基催化剂在柴油车上的应用受到了限制. 尽管中国和一些其他发展中国家目前仍然允许钒基催化剂在移动源上使用, 但随着环境保护要求的不断提高, 全面淘汰钒基催化剂也只是时间问题^[3]. 因此, 诸多研究致力于开发环境友好的替代型非钒基 $\text{NH}_3\text{-SCR}$ 催化剂.

目前已有多种基于过渡金属和稀土元素的氧化物和分子筛催化剂被用于 $\text{NH}_3\text{-SCR}$ 研究^[4]. 用于 $\text{NH}_3\text{-SCR}$ 催化剂的过渡金属元素主要有Fe, Mn和Cu等, 而稀土元素则主要为Ce. Ce在汽油车尾气控制中已被广泛用作三效催化剂(TWCs)的重要组分. 氧化铈由于具有优异的氧化-还原、储氧和表面酸性等特性而在 $\text{NH}_3\text{-SCR}$ 催化剂的研究中被用作载体、助剂和主催化组分^[4,5]. 本文对氧化铈在 $\text{NH}_3\text{-SCR}$ 催化剂中的最新研究报道进行了系统综述, 并对该领域未来可能的发展方向进行了讨论.

2. 氧化铈用作 $\text{NH}_3\text{-SCR}$ 催化剂载体

单纯的氧化铈由于还原温度较高且易于高温烧结而不适合用作 $\text{NH}_3\text{-SCR}$ 催化剂的载体, 而添加氧化锆后, 其储氧能力和热稳定性显著改善^[6]. 因此, $\text{CeO}_2\text{-ZrO}_2$ 经常被用作 $\text{NH}_3\text{-SCR}$ 催化剂载体.

Li等^[6]以 $\text{CeO}_2\text{-ZrO}_2$ 为载体, 分别负载 WO_3 , MoO_3 , Mn_2O_3 , CrO_3 , Fe_2O_3 和 Co_2O_3 制备了 $\text{NH}_3\text{-SCR}$ 催化剂, 并对催化剂活性和热稳定性进行了测试(图1). 其中 $\text{WO}_3/\text{CeO}_2\text{-ZrO}_2$ 表现出最优的催化活性以及很好的热稳定性^[6]. 研究表明^[7], WO_3 的引入可以改善催化剂的酸性, 因而在很大程度上提高其 NH_3 吸附能力, 进而大幅度提高催化剂的 $\text{NH}_3\text{-SCR}$ 活性.

Si等^[8]采用Ni浸渍和硫酸化的方式改善 $\text{CeO}_2\text{-ZrO}_2$ 的 $\text{NH}_3\text{-SCR}$ 催化活性和 N_2 选择性. 研究表明, Ni的引入可以改善 $\text{CeO}_2\text{-ZrO}_2$ 的Lewis酸性进而提高其低温活性, 而硫酸化可以引入氧化性较弱的Brønsted酸性位, 促进 NH_3 的吸附并降低 NH_3 的氧化, 从而改善其高温活性和选择性. 此外, 磷酸盐浸渍也被用于改善 $\text{CeO}_2\text{-ZrO}_2$ 的催化性能^[9]. $\text{CeO}_2\text{-ZrO}_2$ 还被用作锰基低温SCR催化剂的载体并被证实对催化剂性能有重要贡献^[10,11].

3. 氧化铈用作 $\text{NH}_3\text{-SCR}$ 催化剂助剂

Ce被广泛用作各种催化剂的助剂以提高催化性能. 对于 $\text{NH}_3\text{-SCR}$ 催化剂, Ce也是一种非常有效的助剂. Ce的添加可以促进传统钒基催化剂的催化性能. Chen等^[12]发现, Ce加入 $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ 后, 可以增强对 NO_x 的

吸附,进而通过Ce与V和W物种的协同作用促进NH₃-SCR反应(图2A)。加入的Ce物种主要以Ce³⁺形式存在于催化剂中,有利于氧化NO为NO₂;同时还可以提供更多的活性Brønsted酸性位,有利于NH₃-SCR反应的发生。此外,Ce还被用来修饰V₂O₅-ZrO₂/WO₃-TiO₂催化剂,以期用于柴油发动机尾气的NO_x催化去除^[13]。与只有Zr掺杂的V₂O₅/WO₃-TiO₂相比,同时掺杂Ce以后,低温活性可以得到明显改善,但稳定性有所降低。表征结果表明,Ce加入后,大量存在的Ce³⁺可以改善催化剂的氧化-还原性质,而且可以通过促进催化剂对活性硝酸盐物种的吸附来提高催化活性。催化剂老化失活的主要原因与烧结作用和CeO₂在催化剂表面的相分离有关,表明Ce组分的水热稳定性较差。但是,向反应气氛中加入NO₂以后,可以补偿由于水热失活造成的活性损失,并明显提高其低温SCR活性,表明Ce组分在SCR反应中有很强的NO₂反应敏感性^[13]。研究还发现^[14],Ce的加入可以同时改善Sb-V₂O₅/TiO₂催化剂的表面酸性和氧化-还原性质,进而在很宽的温度窗口内实现NO_x的高效转化。

Fe离子交换的ZSM-5催化剂在柴油车NO_x控制领域受到了广泛关注^[15]。在早期研究中,Long和Yang^[16]就发现Ce是一种很好的Fe-ZSM-5催化剂助剂,少量Ce的加入不但使催化活性有所增加,而且可以增强抗水抗硫性能和水热稳定性。Fe-ZSM-5催化剂的一个致命弱点是低温活性较差。Carja等^[17]通过采用新颖的制备方法将Ce添加到Fe-ZSM-5催化剂中,显著提高了其低温活性,这与分子筛骨架内Ce和Fe的协同作用有关(图2B)。另外,CeO₂的添加对促进Fe³⁺离子交换的TiO₂柱撑粘土(Fe-TiO₂-PILC)的NH₃-SCR活性也非常有效,这主要与促进NO向NO₂的氧化过程有关^[18]。

锰氧化物是最好的低温NH₃-SCR催化组分。因此,锰基氧化物催化剂在固定源和移动源NO_x控制领域都受到了广泛关注,但必须解决其N₂选择性低和抗水抗硫性差的问题^[20]。研究表明,Ce是改善锰基氧化物NH₃-SCR催化性能的良好助剂^[21–24]。Qi和Yang^[21]开发了一种锰铈复合氧化物催化剂,表现出了优异的低温NH₃-SCR活性、N₂选择性和抗水抗硫性能。通过添加其他金属组分如Fe,Pr和Nb等,该MnO_x-CeO₂催化剂的催化性能进一步改善^[22,23]。除此之外,Ce的添加可以通过增加化学吸附氧和酸性位以及改善氧化-还原能力来提高Mn/TiO₂催化剂的催化活性(图2C)^[19];还可以通过阻止金属硫酸盐的生成以及抑制(NH₄)₂SO₄和NH₄HSO₄的沉积来提高Mn/TiO₂催化剂的抗硫性能^[25]。

4. 氧化铈用作NH₃-SCR催化剂主催化组分

在氧化和还原条件下,Ce³⁺和Ce⁴⁺之间的氧化-还原转换可以在氧化铈上分别形成不稳定的氧空位和流动性好的晶格氧物种。因此,铈基氧化物可以被用作NH₃-SCR催化剂的主催化组分。

单纯CeO₂的NH₃-SCR活性通常较差(图3A)^[26,28]。但是,通过简单的物理混合方法将CeO₂和分子筛(BEA,ZSM-5,MOR和FER)结合后,制备的CeO₂分子筛催化剂可以在高空速条件下表现出优异的NO_x去除效率。这主要与分子筛酸性位与CeO₂氧化组分的协同作用有关(图3B)^[27]。另外,表面硫酸化也可以通过增加表面Ce³⁺含量(有利于增加活性氧组分)和强酸性位(有利于增加NH₃的化学吸附和活化)显著改善CeO₂的NH₃-SCR催化性能(图3A)^[26]。Yang等^[29]提出了一种硫酸化对CeO₂表面NH₃-SCR反应的影响机制:表面硫酸化后CeO₂对NH₃的吸附明显改善,进而促进了Eley-Rideal反应机制,并且硫酸化后CeO₂表面-NH₂的吸附位和氧化位分离,进而可以有效抑制-NH₂向NO的催化氧化。

铈基多组分氧化物由于添加的金属组分可以改善CeO₂的催化性能而比单纯基于CeO₂的催化剂受到更多的关注。Xu等^[30]采用浸渍法开发了一种CeO₂/TiO₂催化剂,可以在275–400 °C温度范围内具有较高的SCR活性和N₂选择性。随后,Gao等^[31]对比了三种方法制备的CeO₂/TiO₂催化剂,发现一步溶胶-凝胶法制备的催化剂具有最佳的催化活性和抗SO₂中毒能力,同时指出,较高的比表面积和良好的氧化-还原能力对催化活性非常重要,而Ce和Ti之间紧密的相互作用以及大量无定形或高度分散的纳米氧化铈颗粒应该是一步溶胶-凝胶法制备的催化剂具有优异催化性能的原因。Li等^[32]结合多种手段证实CeO₂/TiO₂催化剂中的活性位是在原子尺度上存在Ce和Ti相互作用的短程有序的Ce-O-Ti物种。Chen等^[33]将CeO₂负载到钛纳米管内,提高了CeO₂/TiO₂的抗碱金属中毒能力。为了提高催化剂的催化活性和抗SO₂中毒能力,Liu等^[34]改变载体采用TiO₂-SiO₂负载CeO₂,而Chen等^[35,36]则添加助剂将CeO₂和WO₃共同浸渍到TiO₂表面,Peng等^[37]进一步采用SiO₂添加改进了CeO₂-WO₃/TiO₂的低温活性。除了W以外,Mo^[38],Fe^[39],Zr^[40]和Nb^[41]等过渡金属也被用于改进CeO₂/TiO₂的催化性能。

近年来,铈基复合氧化物在NH₃-SCR领域的应用广受关注。Chen等^[42]采用共沉淀法制备了CeO₂-WO₃催化剂。该催化剂于47 000 h⁻¹空速条件下,在175–500 °C的

宽温度范围内表现出了优异的催化活性、 N_2 选择性和抗 SO_2 中毒能力。Chang等^[43]采用Ge和Mn进一步改进了 CeO_2 - WO_3 催化剂。Liu等^[44]对比了不同方法制备的 CeO_2 - WO_3 催化剂,发现高 NH_3 -SCR活性与大的比表面积、高的Ce和 Ce^{3+} 表面含量、强的NO氧化能力以及大量的表面酸性位有关。基于原位红外和Raman光谱研究,Peng等^[45]提出, CeO_2 - WO_3 的 NH_3 -SCR反应机理包括两种独立的循环,即基于 CeO_2 优异的储氧能力和还原能力而存在的氧化-还原循环(NH_3 活化),和基于 $Ce_2(WO_4)_3$ 中W-O-W物种表面Brönsted酸性位的酸性位循环(NH_3 吸附)。

此外,Liu等^[46]制备了一种具有双重氧化-还原循环($Cu^{2+} + Ce^{3+} \leftrightarrow Cu^+ + Ce^{4+}$, $Cu^{2+} + Ti^{3+} \leftrightarrow Cu^+ + Ti^{4+}$)的Cu-Ce-Ti复合氧化物催化剂,并指出这种双重氧化-还原循环对催化性能起关键作用。Peng等^[47]制备了 MoO_3 - CeO_2 催化剂并深入研究了该催化剂在 NH_3 -SCR反应中的构效关系。Cai等^[48]使用胶晶模板法制备了具有三维有序大孔(3DOM)结构的 $Ce_{0.75}Zr_{0.2}M_{0.05}O_{2-\delta}$ ($M = Fe, Cu, Mn, Co$),并将其用于 NH_3 -SCR反应。Casapu等^[49]开发了一种铈钨复合氧化物,该催化剂具有 NH_3 -SCR、尿素水解制 NH_3 和炭烟氧化等多重功能,既可以用于 NO_x 催化去除,又可以用于柴油机颗粒过滤器(DPF)再生。Qu等^[50]随后研究了铈钨复合氧化物在 NH_3 -SCR反应中的构效关系。由于目前在 NH_3 -SCR领域和炭烟氧化领域均已有多项针对Ce基氧化物催化剂的研究,Ce基氧化物多功能催化剂的开发应该引起相关研究者的关注。

5. 高效铈基氧化物 NH_3 -SCR催化剂

由于柴油车上的催化剂安装空间非常有限,这就要求催化剂能够在高空速条件下具有优异的 NH_3 -SCR催化性能。然而,前述的铈基氧化物催化剂大多采用粉体催化剂进行活性评价,评价空速一般低于 $150\,000\ h^{-1}$ 。当前, NH_3 -SCR技术在柴油车上应用需要解决的一个重要问题是减小催化剂体积。因此,开发可适用于高空速环境的高效铈基氧化物催化剂具有重要的意义^[2]。

本课题组通过简单易行的均匀沉淀法制备出了铈钨氧化物催化剂,显著改善了催化剂的低温活性,从而拓宽了操作温度窗口^[51]。通过优化均匀沉淀法,又成功改善了铈钨催化剂的高温活性,进一步拓宽了其操作温度窗口,并明显改善了其耐高空速性能^[52]。

通过对铈钨氧化物催化剂掺杂过渡金属钨制备出了铈钨钨氧化物催化剂,该催化剂同时提高了铈钨催化剂的低温和高温活性以及 N_2 生成选择性^[53]。采用多种手段系统分析了钨物种在促进催化剂 NH_3 -SCR活性中的作用。结果表明,钨物种的引入尽管使催化剂的比表面积有所降低,但可以增加表面氧空穴数量,提高催化剂的氧化还原能力,进而增强催化剂低温时氧化NO为 NO_2 的能力,通过“快速SCR”作用促进催化剂的低温活性;另外,钨物种的引入可以同时增加催化剂表面的Brönsted酸性位和Lewis酸性位,进而抑制 NH_3 的非选择性氧化,提高催化剂的高温活性和 N_2 生成选择性。

对铈钨钨氧化物催化剂的研究表明,钨物种在催化剂中可以起到与钨物种相同的提供酸性位等作用,因此采用铈和钨完全替代催化剂中的钨,首次开发出了铈钨钨氧化物催化剂^[54]。该催化剂表现出比铈钨氧化物和铈钨钨氧化物催化剂更为优异的 NH_3 -SCR催化性能(图4),即使在 $500\,000\ h^{-1}$ 的高空速条件下,仍可在 250 – $425\ ^\circ C$ 的范围内实现100%的 NO_x 转化率,同时具有优异的 N_2 生成选择性、高温热稳定性和抗中毒能力。在相同的评价条件下,该催化剂的催化性能明显优于已经工业化应用的 V_2O_5 - WO_3/TiO_2 和Fe-ZSM-5催化剂。

6. 展望

Ce在稀土市场中占有很大比重且相对廉价。随着中、重稀土用量的不断增加,Ce等高丰度轻稀土元素大量积压,尤其在中国,Ce的应用领域亟需得到进一步拓展^[55]。因此,开发Ce在 NH_3 -SCR的应用途径,尤其是开发Ce基氧化物催化剂,具有非常好的发展前景。然而,该研究领域仍然存在很多问题和挑战。对于固定源脱硝,Ce对 V_2O_5 - WO_3/TiO_2 催化剂可以起到很好的助催化作用^[12]。但是以Ce作为主催化成分制备的催化剂在抗硫性方面仍然无法与钨基催化剂相比^[56]。对于移动源 NO_x 控制,Ce是Fe-ZSM-5很好的催化助剂,可以起到提高催化活性、改善水热稳定性和增强抗 SO_2/H_2O 中毒能力的作用^[16,17]。但是,以 CeO_2 - ZrO_2 作为载体和以Ce作为主催化组分的氧化物催化剂在热稳定性方面都无法与分子筛催化剂(尤其是最近开发的铜基小孔分子筛催化剂)相比^[13,48]。此外,尽管目前已经发现 CeO_2 和 WO_3 的结合可以起到很好的 NH_3 -SCR催化作用,而且可以被开发成高效催化剂,但由于使用 WO_3 的成本较高,需要对其进行减量或替代。