Review (Special Issue on Rare Earth Catalysis)

The use of ceria for the selective catalytic reduction of NO$_x$ with NH$_3$

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ABSTRACT

The selective catalytic reduction of NO$_x$ with NH$_3$ (NH$_3$-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 NH$_3$-SCR catalysts owing to its unique redox, oxygen storage, and acid-base properties. In this article, we comprehensively review recent studies on ceria for NH$_3$-SCR catalysts when used as support, promoter, or the main active component. In addition, the general development of ceria for NH$_3$-SCR catalysts is discussed.

1. Introduction

NO$_x$, which mainly refers to NO and NO$_2$, 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 NH$_3$ (NH$_3$-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 NH$_3$-SCR to stationary sources and to mobile sources. For safety reasons, urea (in aqueous solution) is a preferred reductant rather than NH$_3$ for mobile sources. In addition, the different emission conditions of stationary sources and mobile sources require the NH$_3$-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 SO$_2$ to SO$_3$ owing to the relatively high SO$_2$ concentrations in flue gas. The catalyst for mobile sources needs to be active in a

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, V_2O_5-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 CeO_2-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 CeO_2-ZrO_2 to investigate their catalytic activities and thermal stabilities (Fig. 1). Among these catalysts, WO_3/CeO_2-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 CeO_2-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 CeO_2-ZrO_2 and thereby enhanced the low-temperature activity. In contrast, Brönsted acid sites, introduced by sulfate modification, were less oxidative than the Lewis acid sites. These sites
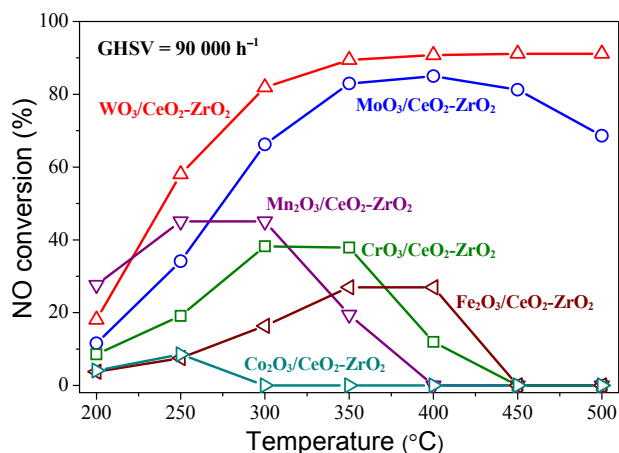

Fig. 1. NO conversion as a function of temperature over various MO_x/CeO_2-ZrO_2 mixed oxide catalysts [6]. Reaction conditions: 1 mL catalyst, total flow rate = 1500 mL/min, 550 ppm NO, 550 ppm NH_3, 6 vol% O_2, 10 vol% CO_2, 10 vol% H_2O, N_2 balance and GHSV = 90 000 h^{-1}. Reproduced with permission 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 CeO_2-ZrO_2 to improve its NH_3-SCR catalytic performance [9]. In addition, CeO_2-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 V_2O_5-WO_3/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 V_2O_5-WO_3/TiO_2 could provide stronger and more active Brönsted acid sites, which were beneficial for the SCR reaction. Ceria-modified V_2O_5-ZrO_2/WO_3-TiO_2 catalyst was also evaluated for the NH_3-SCR of NO_x in diesel engines [13]. Compared with the V_2O_5/WO_3-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
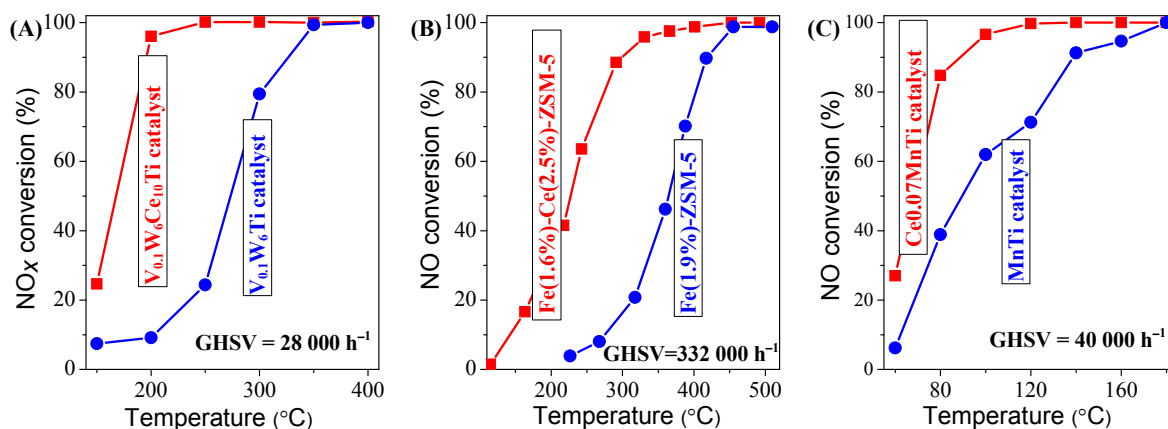
Fig. 2. Enhancements of catalytic performance owing to addition of Ce to (A) V_2O_5-WO_3/TiO_2 [12], (B) Fe-ZSM-5 [17], and (C) Mn/TiO_2 [19] catalysts. Reaction conditions: (A) 500 mg sample, 500 ppm NO, 500 ppm NH_3, 3% O_2, N_2 as balance gas, GHSV = 28 000 h^{-1}; (B) 20 mg sample (0.025 mL), 2000 ppm NO, 2000 ppm NH_3, 3% O_2, balance He, total flow rate 138.3 mL/min, GHSV = 332 000 h^{-1}; (C) 2 mL sample, 1000 ppm NO, 1000 ppm NH_3, 3% O_2, 3% water, balance N_2, 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-V_2O_5/TiO_2 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 NH_3-SCR catalyst [15]. During the development of Fe-ZSM-5 for NH_3-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 SO_2/H_2O 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 CeO_2 into an Fe^{3+}-exchanged TiO_2-pillared clay (Fe-TiO_2-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 NO_2 by O_2 (NO_2 being an important intermediate for the SCR reaction on this catalyst [18]).

Manganese oxides are the most active components for NH_3-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 N_2 selectivity and pronounced SO_2/H_2O 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 NH_3-SCR activity together with high N_2 selectivity and good SO_2/H_2O resistance. The catalytic performance of MnO_x-CeO_2 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/TiO_2 owing to the increase in chemisorbed oxygen, improved acidity, and an enhancement of

redox properties (Fig. 2C) [19]. Moreover, the resistance of the Mn/TiO_2 catalyst to SO_2 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 $(NH_4)_2SO_4$ and NH_4HSO_4 deposition [25].

4. Ceria as the main active component for NH_3-SCR catalysts

Labile oxygen vacancies and bulk oxygen species with relatively high mobility are easily formed on cerium oxide during the redox shift between Ce^{3+} and Ce^{4+} under oxidizing and reducing conditions, respectively. Therefore, Ce-based oxide could be used effectively as a main active component for NH_3-SCR catalysts.

Pure CeO_2 oxides usually possess poor NH_3-SCR activity (Fig. 3A) [26,28]. However, CeO_2-zeolites, obtained by the combination of CeO_2 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 CeO_2 could also be greatly improved by surface sulfation. This process could result in an enrichment of Ce^{3+} (leading to an increase in active oxygen content) and could also lead to strong acid sites (favoring NH_3 chemisorption and activation) on the CeO_2 surface (Fig. 3A) [25]. Yang *et al.* [29] proposed a novel effect of sulfation on the SCR reaction over CeO_2. In this system the adsorption of NH_3 on CeO_2 was promoted, enhancing the Eley-Rideal mechanism. The sites for –NH_2 adsorption and the oxidizing agents for –NH_2 oxidization on CeO_2 were separated after the sulfation, resulting in an inhibition of the catalytic oxidation of –NH_2 to NO. As a result, the SCR activity of CeO_2 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 CeO_2. In our previous study, Xu *et al.* [30] developed a promising CeO_2/TiO_2 catalyst, prepared
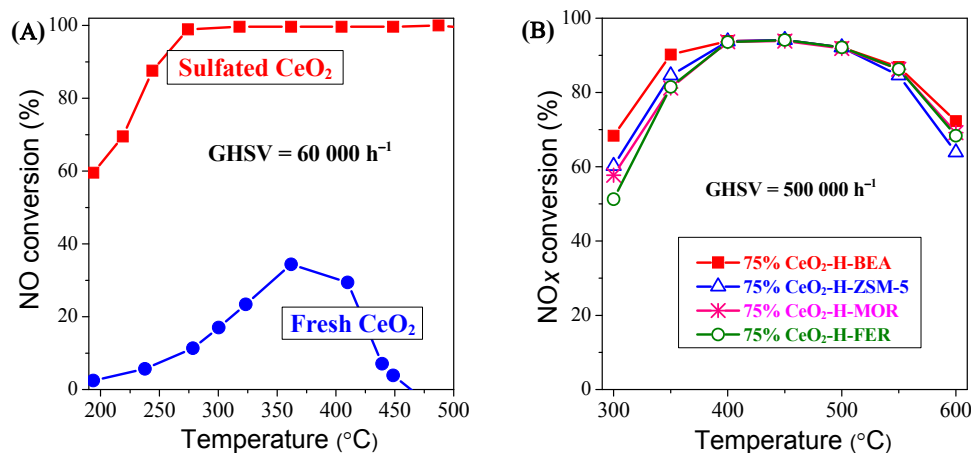
Fig. 3. Improved catalytic performance of CeO_2 by surface sulfation (A) [26] and combination with zeolites (B) [27]. Reaction conditions: (A) $[NH_3]$ = $[NO]$ = 1000 ppm, $[O_2]$ = 3 vol%, N_2 balance, GHSV = 60 000 h^{-1}; (B) 1000 ppm NO, 1000 ppm NH_3, 10 vol% O_2, 9 vol% H_2O, balance N_2, GHSV = 500 000 h^{-1}. Reproduced with permission from Elsevier and the RSC, respectively.

by an impregnation method, and this showed high SCR activity and N_2 selectivity at 275–400 °C. A comparative study involving three preparation methods for CeO_2/TiO_2 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 SO_2 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 CeO_2/TiO_2 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 CeO_2 was confined was designed and synthesized by Chen *et al* [33]. To enhance the catalytic activity and the SO_2 resistance of CeO_2/TiO_2, Liu *et al.* [34] supported CeO_2 on TiO_2-SiO_2, while Chen *et al.* [35,36] co-impregnated CeO_2 and WO_3 onto TiO_2. Furthermore, Peng *et al.* [37] improved the low-temperature activity of CeO_2-WO_3/TiO_2 by SiO_2 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 NH_3-SCR reaction. Chen *et al.* [42] prepared a CeO_2-WO_3 catalyst using a coprecipitation method. The catalyst exhibited high activity, high N_2 selectivity, and good SO_2 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 CeO_2-WO_3 catalyst. Liu *et al.* [44] compared CeO_2-WO_3 catalysts prepared by various methods and concluded that the high NH_3-SCR activity could be attributed to large surface area, high surface concentrations of Ce and Ce^{3+}, enhanced NO oxidization ability, and high concentration of surface acid sites. Based on an *in situ* IR and Raman spectroscopic study, Peng *et al.* [45] suggested an NH_3-SCR reaction mechanism of CeO_2-WO_3 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 CeO_2 (for NH_3 activation), and an acid site cycle. The latter resulted from Brönsted acid sites formed on the W-O-W species of $Ce_2(WO_4)_3$ (for NH_3 adsorption).

In addition, Liu *et al.* [46] developed a superior Cu-Ce-Ti oxide catalyst with dual redox cycles (Cu^{2+} + Ce^{3+} ↔ Cu^+ + Ce^{4+}, Cu^{2+} + Ti^{3+} ↔ Cu^+ + Ti^{4+}) and demonstrated that the dual redox cycles play key roles in the catalytic behavior. Peng *et al.* [47] prepared a MoO_3-CeO_2 catalyst and extensively investigated its structure-activity relationship for the NH_3-SCR reaction. Cai *et al.* [48] synthesized three-dimensional ordered macroporous (3DOM) $Ce_{0.75}Zr_{0.2}M_{0.05}O_{2-\delta}$ (M = Fe, Cu, Mn, Co) using a colloidal crystal template method for NH_3-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 NH_3-SCR, the hydrolysis of urea to NH_3, and the oxidation of soot. The relationship between structure and performance of the niobia-ceria catalyst for NH_3-SCR was examined by Qu *et al.* [50]. Because there have been many reports on Ce-based oxides for both NH_3-SCR and soot oxidation, the further development of multi-functional Ce-based oxide catalysts merits more attention.

5. High-efficiency Ce-based NH_3-SCR catalysts

There are limitations to the catalyst volume that can be placed on diesel vehicles, which requires that the catalyst possesses superior NH_3-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 NH_3-SCR catalyst volume is one of the main challenges for diesel vehicle applications, it is very important to develop highly efficient NH_3-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 N_2 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 N_2 selectivity by inhibiting the unselective oxidation of NH_3 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 NH_3-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 N_2 selectivity, good stability, and high resistance to poisoning. Under the same test conditions, the Ce-W oxide catalyst showed much better SCR performance than V_2O_5-WO_3/TiO_2 and Fe-ZSM-5 catalysts, which

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 NH_3-SCR applications of Ce, especially in the development of Ce-based NH_3-SCR catalysts, is a very promising undertaking.

Despite much progress, there remain some problems and challenges for the use of Ce-based NH_3-SCR catalysts. For stationary applications, Ce has been shown to be an effective promoter for V_2O_5-WO_3/TiO_2 catalysts [12]. However, the catalysts with Ce as a main active component are inferior to V-based catalysts regarding SO_2 resistance [56]. For mobile applications, Ce is a good promoter for Fe-ZSM-5 and enhances its catalytic activity, hydrothermal stability, and SO_2/H_2O resistance [16,17]. In contrast, the thermal stabilities of the oxide catalysts with CeO_2-ZrO_2 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 CeO_2 and WO_3 has been shown to be very effective for the NH_3-SCR reaction and can form the basis for high efficiency catalysts, the high cost of WO_3 implies that there is a need for reducing or eliminating WO_3 in such systems.
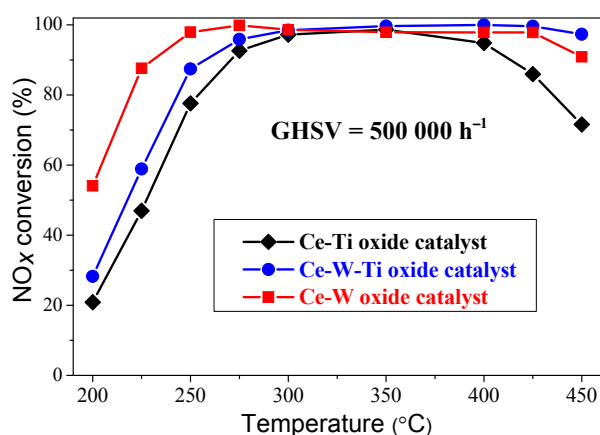

Fig. 4. NO_x conversion as a function of temperature over Ce-Ti, Ce-W-Ti, and Ce-W oxide catalysts. Reaction conditions: 0.06 mL catalyst, total flow rate = 500 mL/min, 500 ppm NO, 500 ppm NH_3, 5 vol% O_2, N_2 balance, GHSV = 500 000 h^{-1}.

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Graphical Abstract

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The use of ceria for the selective catalytic reduction of NO$_x$ with NH$_3$

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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 NH$_3$.
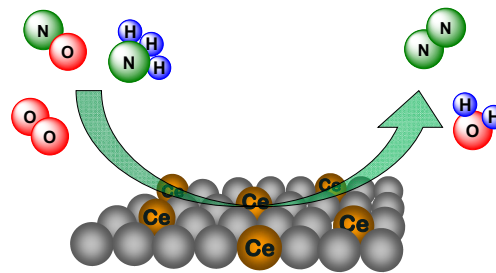
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