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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

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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, 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

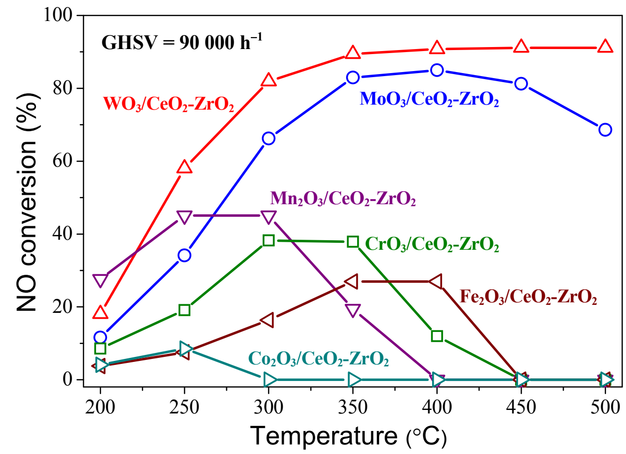

Fig. 1. NO conversion as a function of temperature over various MO_x/CeO_2-ZrO_2 mixed oxide catalysts [6]. Reaction conditions: 1 mL catalyst, total flow rate = 1500 mL/min, 550 ppm NO, 550 ppm NH_3, 6 vol% O_2, 10 vol% CO_2, 10 vol% H_2O, N_2 balance and GHSV = 90 000 h^{-1}. Reproduced with permission 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