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A mechanistic study on soot oxidation over CeO_2–Ag catalyst with ‘rice-ball’ morphology

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ABSTRACT

A CeO_2–Ag catalyst with a ‘rice-ball’ morphology, consisting of Ag particles in the center surrounded by fine CeO_2 particles, exhibits exceptional catalytic performance for soot oxidation by O_2 below 300 °C. The reaction mechanism over this catalyst was studied by O_2 temperature-programmed desorption (O_2-TPD), $^{18}O/^{16}O$ isotopic exchange (IE) reaction, and electron spin resonance (ESR) techniques. It is speculated that adsorbed oxygen species on the Ag surface migrate to the CeO_2 surface via the Ag/CeO_2 interface to form O_n^{x-} species (at least partly O_2^-) and further migrate onto the soot particles. Due to morphological compatibility of the moderately large Ag particles (ca. 30–40 nm) and the extremely large interfacial area with the CeO_2 particles, the formation and migration rates of the oxygen species on the CeO_2–Ag catalyst are efficiently promoted, resulting in its distinguished catalytic performance and relative insensitivity to the contact mode of the soot–catalyst mixture.

1. Introduction

In recent years, diesel-powered vehicles have increased their market share in the world, due to lower fuel consumption, higher durability and reliability in comparison with gasoline-powered vehicles. Diesel engines are expected to play a positive role in the prevention of global warming by increased fuel efficiency and thus lower CO_2 emission than gasoline engines. However, there is a strong demand for the abatement of nitrogen oxide (NO_x; $NO + NO_2$) and particulate matter (PM; mainly ‘soot’) from diesel engines, which can give rise to serious environmental and health problems. The severity of new emission regulations requires solutions based on suitable after-treatment technologies, as well as technical improvements to the engines. The most effective and widely applied after-treatment technology for PM control is based on the diesel particulate filter (DPF). Soot trapped in a DPF must be periodically removed by combustion, due to unacceptable back pressure levels in the gas exhaust line. The direct oxidation of soot over the un-catalyzed DPF requires high temperatures around 600 °C and is generally carried out by injecting diesel fuel into the exhaust. This strategy incurs additional fuel consumption, requires a complex means of control, and can create significant thermal stress for the DPF and the other after-treatment devices (i.e., the de-NO_x catalysts).

A catalyzed diesel particulate filter (C-DPF) is regarded as the most promising solution to reduce PM emissions from diesel engines, where the soot is trapped and oxidized with a catalyst at lower temperature. However, large soot particles are immobile and barely penetrate into the catalyst micropores or mesopores, and thus, catalytic soot oxidation is quite slow [1,2]. The major problem with the C-DPF is the poor contact between the external catalyst surface and the soot particles. To overcome this problem, many catalysts and technologies based on different principles have been proposed. Using gas-phase NO_2 in the application of so-called continuously regeneration trap (CRT) technology causes a decrease in the soot oxidation temperature [3]. NO_2 is generated from the oxidation of NO over a platinum catalyst and functions as a mobile species for soot oxidation by creating catalyst–soot contact; however, a new trend in diesel engines to decrease NO_x emission could impose significant restrictions on the application of CRT technology. Organometallic fuel additives, also known as fuel-borne catalysts (FBCs), lead to the formation of catalyst-doped soot during combustion in the engine, which lowers the soot oxidation temperature in the DPF [4,5]; however, the continuous consumption of FBCs and the accumulation of metal oxide as an ash inside the DPF restrict their application strongly. A large number of molten salt catalysts, which can wet the soot surface as a mobile catalyst and therefore decrease the soot oxidation temperature, have been studied in recent years; the formulations are based on the addition of potassium or cesium to transition metal (such as Cu, V, Mo, Co, or Fe) oxides [6–10], combinations of Co, K/MgO or Ba, K/CeO_2 [11–13], and perovskites such as $LaCrO_3$ and $La_{0.9}K_{0.1}Cr_{0.9}O_3$ [14].

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However, these catalysts have drawbacks in some practical applications that are related to either thermal degradation or selective leaching in condensed water during the soot oxidation process [15].

Recently, many researchers have reported that CeO_2-based oxides have good activity for soot oxidation at lower temperature [16–23]. Aneggi et al. studied the effect of Ag addition on the soot oxidation activity of various metal oxides [24]; the addition of Ag to ZrO_2 and Al_2O_3 resulted in very active catalysts, while addition to CeO_2 had little benefit. On the other hand, Machida et al. and Shimizu et al. reported that Ag loading onto CeO_2 enhanced the catalytic activity for soot oxidation [25,26]. However, the design concept of these catalysts, i.e., morphology control based on the functions of Ag and CeO_2, has not been devoted to the problem of catalyst–soot particle contact. In addition, silver-supporting catalysts may suffer from performance degradation due to Ag sintering under oxidative conditions at temperatures around 400 °C [27].

Considering this background, we have developed an innovative CeO_2–Ag catalyst, which exhibits exceptional performance for soot oxidation with gaseous oxygen at temperatures below 300 °C [28]. This catalyst has a unique agglomeration morphology, as shown in Fig. 1, in which the scanning electron microscopy (SEM) image (a) shows that this catalyst consists of numerous spherical 'balls' with diameters of about 100 nm and the transmission electron microscopy (TEM) image of the cut plane of a single ball (b) shows that the center Ag metal is surrounded by fine CeO_2 particles. The morphology of this catalyst is schematically illustrated in Fig. 2, in which the unique agglomeration nanostructure is similar to a Japanese 'rice-ball', consisting of a center composed of Ag particles (rice-ball filling) surrounded by fine CeO_2 particles (grains of rice). This morphology was designed to increase the Ag/CeO_2 interface area per unit surface area of Ag particles and to inhibit Ag sintering, because thermally stable CeO_2 particles act as barriers to sintering. A CeO_2–Ag catalyst with such morphology was synthesized by a novel nanofabrication method based on precipitation between aqueous solutions of nitrates and ammonia [28].

In this study, temperature-programmed oxidation (TPO) over the soot/catalyst mixture under tight and loose contact modes was used to evaluate the catalytic performance. To reveal the different aspects involved in catalytic soot oxidation, oxygen temperature-programmed desorption (O_2-TPD), $^{18}O/^{16}O$ isotopic exchange (IE) reaction, and electron spin resonance (ESR) techniques were employed to characterize the active property of oxygen species, oxygen mobility or migration rates and identification of oxygen species, respectively. Through discussing these characterization results and correlating with their catalytic performances, we tried to elucidate the mechanism involved in catalytic soot oxidation, especially over the CeO_2–Ag catalyst with unique "rice-ball" morphology, which exhibits an overwhelmingly high catalytic performance among the prepared catalysts.

2. Experimental

2.1. Catalyst preparation

A CeO_2–Ag catalyst was synthesized by a coprecipitation-based method. One hundred and fifty milliliters aqueous solution of $AgNO_3$ (Toyo Chemical Industrial, 29.63 g) and $Ce(NO_3)_3{\cdot}6H_2O$ (Wako Pure Chemical Industries, 50.49 g) was added to a diluted ammonia solution (35.6 g of 25% ammonia solution, diluted by 100 mL of water) instantly (in less than a second) with a rotary stirrer (350 rpm) at room temperature. The mixture was stirred for 1 min, and the coprecipitate was heated uniformly by steam in an autoclave at 120 °C for 10 min. The gained coprecipitate was separated by centrifugation and calcined at 500 °C for 5 h in air. The Ag content of the obtained CeO_2–Ag catalyst was 39 wt.%. A more detailed description of the catalyst preparation is given elsewhere [28].

Ag(x)/CeO_2, Ag(x)+CeO_2, Ag(x)/Al_2O_3, and CeO_2 catalysts, where 'x' denotes the Ag content in wt.%, were used as reference catalysts. The CeO_2 catalyst was obtained by calcination of a commercial CeO_2 powder (Rhodia, BET surface area 150 m^2/g) at 600 °C for 50 h, with a BET surface area of 78 m^2/g. The Ag(x)/CeO_2 catalysts were prepared by impregnation of the CeO_2 catalyst with aqueous $AgNO_3$ solution and calcination at 500 °C for 5 h in air. The Ag(x)+CeO_2 catalysts were prepared by physical mixing of the CeO_2 catalyst and a commercial Ag powder (Nisshin Engineering, BET surface area 9 m^2/g) with a magnetically driven mortar for 20 min followed by calcination at 300 °C for 5 h in air. The Ag(x)/Al_2O_3 catalysts were prepared by impregnation of a commercial Al_2O_3 powder (Showa Denko, UA-5205 with BET surface area 25 m^2/g) with aqueous $AgNO_3$ solution followed by calcination at 500 °C for 5 h in air.

2.2. Catalytic performance evaluation

The catalytic performance for soot oxidation was evaluated by temperature-programmed oxidation (TPO) of soot–catalyst mixtures so as to compare the CeO_2–Ag catalyst with other reference catalysts. Two kinds of carbon black powder (Degussa AG, Printex-V with BET surface area 85 m^2/g, and Degussa AG, Printex-U with BET surface area 92 m^2/g) were used as the model soot in this

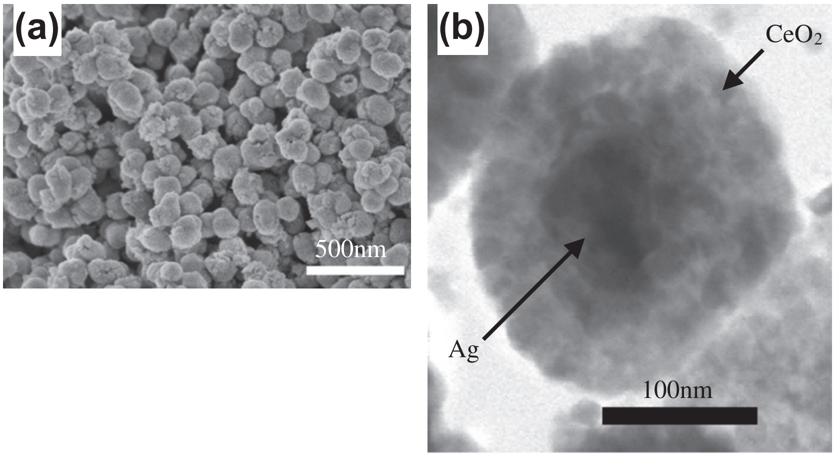

Fig. 1. (a) SEM image of CeO_2–Ag catalyst particles and (b) TEM image of the cut plane of a single spherical agglomerate of CeO_2–Ag catalyst [28].