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The remote oxidation of soot separated by ash deposits via silver–ceria composite catalysts

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ABSTRACT

One of the main issues of catalyzed diesel particulate filter is ash deposition onto catalyst coated on the filter. The effects of ash deposition on the catalysis of soot oxidation with gaseous oxygen were determined using multi-layered samples composed of a catalyst, an ash material and soot particles deposited on a thin cordierite plate in sequence. Catalysts composed of silver and ceria were used to enhance the oxidation of soot particles separated from the catalyst by ash deposits of either alumina or calcium sulfate. The effectiveness of remote soot oxidation was found to extend across an ash thickness of more than 50 μm for both ash materials, although a catalyst composed only of ceria did not show any catalytic performance for remote soot oxidation. Using an $^{18}O/^{16}O$ isotopic exchange reaction and electron spin resonance techniques, a possible mechanism for this phenomenon was proposed, whereby a superoxide ion (O_2^-) species generated on the catalyst surface first migrates to the ash surface and then to the soot particles, which it subsequently oxidizes.

1. Introduction

Emission control technologies for nitrogen oxides (NO_x) and particulate matter (PM; mainly 'soot') is strongly required for clean diesel-powered vehicles. Recently development in diesel particulate filter (DPF) technology is the washcoating of the base filter element with mixture of catalytic agents or so called catalyzed diesel particulate filter (C-DPF), which is regarded as the most promising solution, especially for removal of PM in exhausts [1].

Many types of catalysts and technologies for the C-DPF based on different principles have been reported so far. They can be classified broadly into two categories depending on whether utilizing NO_x in exhausts or not for soot oxidation. In the category utilizing NO_x, which possesses higher oxidation ability than gaseous O_2, continuously regenerating trap (CRT) system, where NO is oxidized to NO_2 on a platinum catalyst and this NO_2 oxidizes soot trapped in the DPF at temperatures from 200 to 450 °C, has been developed by Johnson Matthey [2]. Teraoka et al. reported that perovskite-type and spinel-type oxides showed higher catalytic activity for simultaneous NO_x–soot removal than simple metal oxides [3,4]. Diesel particulate–NO_x reduction (DPNR) system, which is capable of simultaneous abatement of PM and NO_x in diesel exhausts by using surface nitrate species generated from gaseous NO, has been developed by Toyota [5,6]. Recently, Makkee et al. and Bueno-López et al. have reported that rare-earth modified CeO_2 and ceria–zirconia catalysts present greater activity than pure CeO_2 for soot oxidation by NO_x/O_2 [7,8]. However, the above category utilizing NO_x depends on the amount of NO_x in the exhausts. A new trend in diesel engines to decrease NO_x emission could restrict their application [6]. The category utilizing only O_2, not using NO_x, for soot oxidation would be preferred for the next generation of catalysts and technologies. In this category, many researchers have reported molten salt catalysts, which can wet the soot and therefore decrease the soot oxidation temperature [9–11]. Moreover, CeO_2-based catalysts have been reported to have good activity for soot oxidation with O_2 [12–14]. Recently, Machida et al. and Shimizu et al. have reported that Ag loading onto CeO_2 enhances the activity for soot oxidation with O_2 [15,16]. Aneggi et al. have reported that the addition of Ag to ZrO_2 and Al_2O_3 results in very active catalysts for soot oxidation by O_2 [17].

As an alternative to catalysts washcoated on DPFs, 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 [18]. As a matter of fact, the PSA Peugeot fuel additive system for passenger cars has been commercialized in the market since 2000, and there seems no operating problem.

One of the main issues of the C-DPF is ash deposition onto catalysts coated on the filter. PM is composed of mainly soot, soluble organic fraction (SOF), sulfates, and slightly inorganic

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metal materials (ash). Ash generally is generated from lubricant oil additives, engine cleaning detergents, trace metals in diesel fuels, engine wear metals and corrosion products [1]. Although soot and SOF are oxidized over the catalysts, ash could remain as fine particles during regeneration process. After repetitive regenerations, the ash would deposit as a layer on the filter walls, and subsequent soot would be trapped on the ash layer. As a result, the ash layer form a barrier separating the soot from the catalyst coated on the DPF walls. In soot oxidation by O_2 over catalyst, contact between the catalyst and the soot is necessary, since the reaction processes take place at the three-phase boundary between the two solids and the gaseous O_2. Therefore, even just a thin ash layer may interrupt the contact between the catalyst and the soot, and the catalytic performance of C-DPF for soot oxidation could decrease drastically.

Catalytic soot oxidation with gaseous O_2 is basically a solid-catalyzed gas–solid reaction. This heterogeneous catalysis is very challenging since it has an inherent drawback: loss of contact between the solid catalyst and the solid reactant as unreactive inorganic materials (ash) are deposited onto the catalyst surface. Therefore, it is very meaningful to verify scientifically if remote catalytic soot oxidation can actually occur when a physical barrier of ash deposit exists between the catalyst and the solid soot, because the oxygen species need to diffuse and transfer throughout the above disjunctive space and still remain active onto the soot particles. Meanwhile, this information is also very valuable for the development of PM removal technology, which closely relates to tolerance for ash deposition and longevity of the whole system. Unfortunately, how the ash deposit exactly affects the activity of catalytic soot oxidation and the related information are not available in the publications so far.

An innovative CeO_2–Ag catalyst exhibited exceptional performance of soot oxidation by gaseous O_2 in our previous research [19]. This catalyst has a unique agglomeration morphology with diameter of about 100 nm, consisting of metallic Ag particles in the center surrounded by fine CeO_2 particles, called 'rice-ball morphology'. We concluded that the compatibility of the moderately large Ag particles (ca. 30–40 nm) and the extremely large interface between the Ag and CeO_2 particles due to this morphology causes its excellent catalytic performance for soot oxidation [20]. As a consecutive study leading to actual application, we managed to prepare multi-layered samples composed of a catalyst, an ash material of varied thickness and soot, all deposited in sequence on a thin cordierite plate, and then verify if the gaseous oxygen can actually oxidize the solid soot and how exactly the activity varies on the ash-deposited CeO_2–Ag catalyst on a quantitative base. The involved reaction mechanism was further elucidated by use of an isotopic ^{18}O tracer technique to characterize the migration of oxygen species, and electron spin resonance (ESR) to specify the oxygen species. Hopefully, we can obtain some valuable information and hints for the development of a soot oxidation catalyst for C-DPF with a high tolerance for ash deposition.

2. Experimental

2.1. Catalyst preparation

The CeO_2–Ag catalyst was prepared using a coprecipitation-based method. A 150 mL portion of an 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 rapidly added (in less than one second) to a dilute ammonia solution (35.6 g of a 25% ammonia solution diluted with 100 mL of water) using a rotary stirrer operating at 350 rpm, at room temperature. The mixture was stirred for 1 min and the coprecipitate was then uniformly heated by steam in an autoclave at 120 °C for 10 min and subsequently 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.%. The CeO_2 catalyst was obtained by the calcination of a commercial CeO_2 powder (Rhodia, BET surface area 150 m^2/g) at 600 °C for 50 h, generating a final BET surface area of 78 m^2/g. A Ag/CeO_2 catalyst in which the silver content was 10 wt.% was prepared by impregnation of the CeO_2 catalyst with an aqueous $AgNO_3$ solution followed by calcination at 500 °C for 5 h in air. This catalyst was found to exhibit higher catalytic performance for soot oxidation than the Ag/CeO_2 catalyst with 39 wt.% silver content [20]. A more detailed description of the catalyst preparation processes is given elsewhere [19].

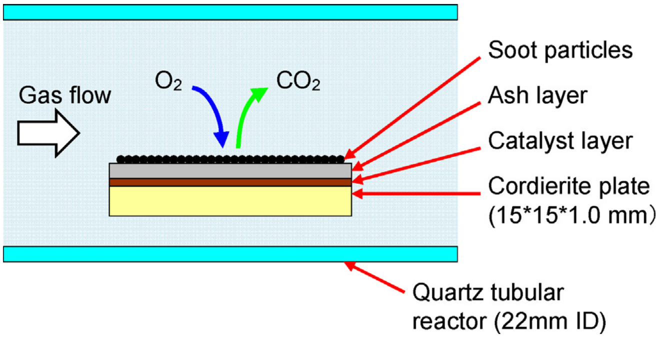

Fig. 1. Schematic of a test specimen consisting of a catalyst layer, an ash layer and a soot particle layer, all deposited on a square cordierite plate. The sample is installed in a quartz tubular reactor on a quartz bead bed.

An ^{18}O-exchanged CeO_2–Ag catalyst was prepared by introducing 5650 Pa of pure $^{18}O_2$ (99.2% ^{18}O, ICON) to the CeO_2–Ag catalyst at 500 °C for 1 h followed by evacuating the sample at the same temperature in a recirculated reactor (ca. 100 cm^3) used in a previous study [21]. This sequence was repeated eight times. The ^{18}O-exchange ratio in the catalyst was calculated by analyzing $^{18}O^{16}O$ and $^{16}O_2$ molecules released from the catalyst into the gas phase using a quadrupole mass spectrometer (Q-MS) coupled to the recirculated reactor and was found to be more than 96%.

2.2. Multi-layered sample preparation

Multi-layered samples consisting of a catalyst, an ash material of varied thickness and soot deposited on a cordierite plate were employed to examine remote catalytic soot oxidation (Fig. 1). It is well known that ash spans a wide range in composition, depending on factors such as engine type, driving conditions, fuel additives, lubricant oil, and metallurgy of the exhaust lines. It generally consists of one or more the following components; sulfates, phosphates or other oxides of calcium, zinc and magnesium, as well as oxides of metals such as iron, copper, chromium, nickel and aluminum [1]. To avoid the contact between the catalyst and the soot, alumina and calcium sulfate are chosen as ash materials, because they are inert materials and should have no catalytic performance for soot oxidation.

A commercial Al_2O_3 powder (α-Al_2O_3, Wako Pure Chemical Industries, BET surface area 7.8 m^2/g) was used as the ash material without treatment. A $CaSO_4$ powder with a BET surface area of 3.2 m^2/g obtained by the calcination of a commercial $CaSO_4 \cdot 0.5H_2O$ powder (Wako Pure Chemical Industries, 3.6 m^2/g) at 700 °C for 5 h was also used as an ash material. A carbon black powder (Degussa, Printex V, 85 m^2/g) was employed as model soot. Separate ethanol dispersions of the catalyst powder, the ash material and the soot were obtained by adding 0.2 g of the desired material to 50 mL of ethanol and agitating in an ultrasonic bath. As the initial step in forming a test specimen, several drops of the ethanol dispersion of the catalyst were placed onto a square cordierite plate (1 mm thick and 15 mm in length) which was then dried at 110 °C for 1 h to