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Effect of an additive in a CeO_2-based oxide on catalytic soot combustion

Hiroki Muroyama, Hiroki Asajima, Shigeki Hano, Toshiaki Matsui, Koichi Eguchi*

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Nishikyo-ku, Kyoto 615-8510, Japan

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ABSTRACT

Since the emission of diesel soot damages both the environment and human health, a method for the catalytic combustion of soot at low temperatures is needed. In this study, CeO_2-based oxides were investigated with respect to their catalytic activities in soot combustion to clarify the roles of ceria and an additive. The oxidation behavior of a carbon black layer over CeO_2 and Al_2O_3 substrates in air was examined by *in situ* microscopy. While the carbon layer over Al_2O_3 gradually became thinner with an increase in temperature, it disappeared from the circumference over the CeO_2 substrate. The produced gas species was also analyzed during carbon oxidation over CeO_2-based catalysts containing a transition metal or rare earth oxide. Complete oxidation to CO_2 was facilitated by the addition of transition metal elements to the catalysts, which could be explained by the activities of the catalysts for CO oxidation. Moreover, the effect of the support material on the carbon oxidation activity was studied for supported CuO catalysts. The reducing property of CuO over the support was related to its catalytic activity.

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1. Introduction

Diesel engines are attractive for energy conversion due to their superior fuel efficiency, low emission of CO_2, and high durability. They are widely used in trucks, buses, ships, trains, etc. Diesel-powered automobiles are also widespread in Europe. However, nitrogen oxides (NO_x) and particulate matter (PM) in diesel exhaust gas can cause both environmental and health problems. Thus, the exhaust emission regulations for these pollutants have been made stricter. For the purification of emission gas, nitrogen oxides are removed with NO_x storage–reduction systems and selective catalyst reduction processes, while the elimination of PM is achieved by the use of diesel particulate filters (DPFs).

Diesel particulate matter mainly consists of soot (carbon), organic compounds from fuel and lubricating oil (soluble organic fraction: SOF), and sulfate. In a DPF system, the particulate matter is trapped by a filter. When a filter clogged with soot need to be regenerated, high-temperature treatment is required for the gasification of soot. Although the addition of fuel to exhaust gas makes it possible to raise the temperature in the system, the use of excess fuel reduces the advantages of a diesel engine. Instead of increasing the temperature, catalysts on a DPF facilitate the removal of PM via the oxidation reaction at lower temperatures [1]. Carbon combustion over catalysts has been investigated, and the following reaction scheme has been proposed [2–5]:

$$O_2(g) \rightarrow 2O_{ad} \tag{1}$$

$$C_f + O_{ad} \rightarrow C^*[O] \tag{2}$$

$$C^*[O] \rightarrow CO(g) \tag{3}$$

$$C^*[O] + O_{ad} \rightarrow CO_2 \tag{4}$$

$$C^*[O] + 1/2O_2 \rightarrow CO_2 \tag{5}$$

where O_{ad} is an adsorbed oxygen atom, C_f is a free carbon site, and $C^*[O]$ is an active intermediate (surface oxygen complex: SOC). First, a gaseous oxygen molecule is dissociatively adsorbed on the catalyst to form an oxygen species (reaction (1)). The spillover of adsorbed oxygen to a free carbon site then gives rise to the formation of an oxygen-containing active intermediate (reaction (2)). This intermediate desorbs as carbon monoxide (reaction (3)) and/or reacts with oxygen species to produce carbon dioxide (reactions (4, 5)). The apparent activation energy for carbon oxidation is scarcely dependent on the catalyst materials, and the contact condition between carbon and the catalyst [6,7]. Thus, it has been concluded that the rate-determining step is the formation of intermediate by the attack of a carbon site by active oxygen species [2,7]. Furthermore, these reports suggested that these catalysts help to increase the reaction rate, especially the rates of active oxygen absorption

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* Corresponding author. Tel.: +81 75 383 2519; fax: +81 75 383 2520.
E-mail address: eguchi@scl.kyoto-u.ac.jp (K. Eguchi).

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and the transfer of oxygen species from the catalyst to the carbon surface [7].

Considerable effort has been devoted to the development of CeO_2-based catalysts and elucidation of the reaction mechanism for carbon oxidation [7–22]. CeO_2-based oxides have a high potential to promote carbon oxidation due to their prominent capacity to store and release oxygen. Bueno-López suggested an oxidation scheme with the use of a CeO_2-based catalyst [10]. Oxygen species in the catalyst transfer to free carbon sites to form a surface intermediate, and the Ce^{4+} ions are simultaneously reduced to Ce^{3+} ions. The resulting intermediates are then gasified as CO or CO_2, and the Ce^{3+} ions are rapidly oxidized by oxygen in the gas phase. Our research group has also investigated CeO_2-based oxides as potential carbon combustion catalyst [19]. The addition of a transition metal element to CeO_2 was effective for lowering the carbon oxidation temperature and the reducing property of the components in the catalyst was related to their catalytic activity. Thus, it was tentatively concluded that the amount of oxygen species available for the oxidation reaction was an important factor for a superior catalyst. This was reasonable, considering that a CeO_2-based catalyst provides active oxygen species to carbon sites [10,11]. However, in the previous study, the roles of ceria and any additive upon carbon oxidation were not sufficiently clarified. In this study, therefore, the carbon combustion behavior over CeO_2 was observed under an optical microscope to understand the function of the oxygen species in the catalyst. We also examined the catalytic activity and the composition of the produced gas for carbon oxidation over CeO_2-based oxides to clarify the effect of an additive on the reaction process.

2. Experimental

2.1. Catalyst preparation

Catalysts of CeO_2 and MO_x–CeO_2 (M=Fe, Mn, Cu, La, Nd) were synthesized in accordance with a previous report [19]. The metal nitrates $Ce(NO_3)_3{\cdot}6H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, $Mn(NO_3)_3{\cdot}6H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$, $La(NO_3)_3{\cdot}6H_2O$, and $Nd(NO_3)_3{\cdot}6H_2O$ (Wako Pure Chemical Industries) were used as starting materials. Nitrates with an atomic ratio of $M/Ce = 1/4$ were dissolved in distilled water. Aqueous ammonia (Wako Pure Chemical Industries) was added dropwise to the solution until the pH reached 10. After the mixture was stirred for 1 h, filtered, and washed with distilled water, the resulting precipitate was dried at 120 °C for 6 h and calcined at 650 °C for 5 h in air. CeO_2-based samples with an additive component are hereafter abbreviated as M–Ce oxide. The composition of samples other than the Cu–Ce oxide was regarded as 20 mol% MO_x–80 mol% CeO_2 (M=Fe, Mn, La, Nd), since the metal species could readily precipitate. In contrast, the stable formation of a copper ammonia complex occurred in the solution, and copper species could not completely precipitate. Thus, the molar ratio of CuO in the Cu–Ce oxide was confirmed to be only 11 mol% by UV–vis spectrophotometry [19].

Cerium oxide was also prepared by the citric acid complex method. After an aqueous solution of cerium nitrate at 60 °C for 1 h was stirred, citric acid (Wako Pure Chemical Industries) was added to the solution in a 1.1:1 molar ratio to Ce cation. The solution was stirred at 60 °C for 2 h and evaporated to dryness at 90 °C. The obtained precipitate was then heated at 300 °C for 1 h and calcined at 650 °C for 5 h. This fabricated CeO_2 is hereafter represented as CeO_2 (ca).

CuO catalysts supported on metal oxide were fabricated by the impregnation method. Metal oxides of as-prepared CeO_2 (ca), γ-Al_2O_3 (JRC-ALO-8, The Catalysis Society of Japan), TiO_2 (JRC-TIO-4, The Catalysis Society of Japan), and ZrO_2 (Aldrich) were selected as support materials. The metal oxide was impregnated with $Cu(NO_3)_2{\cdot}3H_2O$ to give a CuO loading of 5.4 wt%, which is equal to that in 11 mol% CuO–89 mol% CeO_2 (Cu–Ce oxide). The mixture was kept on a steam bath at 80 °C until the solvent was evaporated. The resulting powder was calcined at 650 °C for 5 h in air. These samples are denoted as CuO/MO_x.

2.2. Characterization

X-ray diffraction (XRD, Rigaku, Ultima IV X-ray diffractometer) measurement was conducted to examine the crystalline structure and the lattice constant of CeO_2-based samples. The specific surface area was studied by the BET method with N_2 adsorption (BEL Japan, Belsorp-miniII). Prior to the measurement, the sample was heated at 300 °C for 30 min under a vacuum. The reduction behavior of a sample was evaluated by temperature-programed reduction (TPR, Quantachrome Instruments, CHEMBET 3000). A gaseous mixture of 5% H_2/Ar was supplied at a flow rate of 30 ml min^{-1} to the sample (50 mg) placed in a quartz tube reactor. The temperature was raised at a heating rate of 10 °C min^{-1} and the rate of H_2 consumption was measured by a thermal conductivity detector (TCD).

2.3. Carbon black oxidation

The combustion of soot over oxides was studied by *in situ* observation. A carbon black (Cabot Inc., V-XC72R, surface area: 224.0 $m^2\ g^{-1}$) was applied as a model diesel soot. The as-received γ-Al_2O_3 and obtained CeO_2 (ca) were selected as oxide materials. A small amount of carbon black was pressed to form a thin film on the pelletized oxide substrate. The fabricated sample was set on a heating stage and heated at a rate of 10 °C min^{-1}. Air was supplied to the sample at a flow rate of 50 ml min^{-1}. The oxidation behavior of carbon black was observed by an optical microscope (KEYENCE, VHX-600).

The oxidation behavior of carbon black over various oxides under a tight contact condition was examined in terms of the combustion rate and the composition of the produced gas species. A mixture of the catalyst and carbon black at a weight ratio of 4:1 was ground for 10 min, pelletized, and pulverized into particles measuring 0.60–1.7 mm. The combustion rate of carbon black was evaluated by thermogravimetric (TG) analysis (Shimadzu, TGA-51). Prior to the measurement, nitrogen was supplied at a flow rate of 100 ml min^{-1} while the sample was heated at 300 °C for 1 h to remove any absorbed water. The sample was then cooled to 200 °C with a supply of air (100 ml min^{-1}). TG measurements were conducted at 200–800 °C at a heating rate of 5 °C min^{-1} in air. The oxidation rate of carbon black as a function of temperature was obtained by differentiating the TG profile. For the analysis of the composition of gas produced from carbon black oxidation, a sample (28.5 mg) was set in a fixed bed flow reactor. A gas mixture of 20% O_2–80% He was supplied to the reactor at a flow rate of 20 ml min^{-1}. The temperature was then increased from room temperature to 1000 °C at a rate of 5 °C min^{-1}. The CO and CO_2 concentrations in the outlet gas were analyzed by a Fourier transform infrared spectrometer (DX-4000L, Temet Instruments).

2.4. CO oxidation

The catalytic activities of CeO_2-based oxides for CO oxidation were studied using a fixed bed flow reactor. A reaction gas of 5% CO–15% O_2–80% N_2 was supplied at a flow rate of 80 ml min^{-1} (space velocity: 48,000 l $kg^{-1}\ h^{-1}$). The temperature was increased at a rate of 1 °C min^{-1}. The composition of the produced gas was measured by a non-dispersive infrared (NDIR) gas analyzer (CGT-7000, Shimadzu).

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