



Plasma-assisted oxidation of carbon particle by lattice oxygen on/in oxide catalyst

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ABSTRACT

Oxidation of carbon particles by lattice oxygen on/in catalysts was investigated with and without electrical discharge at 673 K in a fluidized bed reactor. Application of dielectric barrier discharge promoted the evolution of lattice oxygen in the oxide catalyst, and oxidation of carbon by the evolved lattice oxygen was accelerated by application of the discharge. The total amount of consumed lattice oxygen in/on the catalyst was not changed by the application of the discharge due to the low diffusion rate of bulk oxygen at low temperature. Metal-loaded catalysts such as Ni/CeO₂ evolved larger amounts of lattice oxygen because of interaction between the supported Ni particle and ceria support.

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1. Introduction

Solid carbon particles such as char, soot, and coke derived from combustion and gasification of diesel fuel, heavy oil, coal and biomass have low reactivity compared to that of gaseous/liquid products. Especially, solid carbon exhausted from a diesel engine, called particulate matter (PM), brings on air pollution and is known as a hazardous material to the human body [1–4]. In addition, char and coke produced by gasification or combustion of coal [5–9] or biomass [10–16] are known to have low reactivity. Oxidative removal of these solid carbon species by gas-phase oxygen in air requires high temperatures because of its high activation energy. Recently, many investigations have been made into catalytic oxidation of these carbon species at lower temperature with solid oxides such as CeO₂. These processes include redox processes; that is to say, solid carbon species are oxidized by active lattice oxygen in oxides such as CeO₂, and consumed lattice oxygen is regenerated by gaseous oxygen in air. Some modified CeO₂ oxides with rare-earth metal catalyzes low-temperature oxidation of solid carbon because of its effect of promoting evolution of lattice oxygen [17–20]. In addition, metal oxides having a low melting point such as alkaline metals and alkaline earth metals show high reactivity because these metal oxides easily melt on carbon at the reaction temperature. The melt phase brings increased contact interfaces between catalyst and carbon particles. For the oxidation of solid carbon with oxide catalysts, the contact state between catalyst and carbon is very important. Especially for oxidation of PM or soot, some reports have

described that the contact state of catalyst and carbon, whether soft-contact or tight-contact determined the oxidation rate of carbon species [21,22]. In this work, we examined the oxidation of solid carbon particle by solid oxides in a fluidized bed reactor to maintain stable contact between the catalyst and carbon particles.

Furthermore, these solid oxide catalysts evolve lattice oxygen to oxidize carbon particles, but the evolution rate of oxygen is the rate-determining step, especially at lower temperatures such as 673 K. Some researchers investigated the application of plasma to accelerate the oxidation of carbon species [23–27]. We also previously studied oxidation of methane over solid oxide catalysts with electric discharge. The electric discharge promoted the release of lattice oxygen in/on catalysts to increase the oxidation activity [28].

Therefore, we conducted all experiments of oxidation of carbon with oxide catalysts in a fluidized bed to determine the “real” reaction rate with an application of electrical discharge (dielectric barrier discharge). In this study, we investigated the oxidation rate of carbon by oxide catalyst. The regeneration of lattice oxygen in the oxide was not evaluated.

2. Experimental

2.1. Catalysts

Regarding the catalysts, we prepared various Ce-containing oxides—CeO₂, CePrO_x, BaCeMnO_x, Pt/BaCeMnO_x. In addition, for CeO₂ oxide, we prepared two samples: CeO₂-1 (JRC-CEO-1; supplied by the Catalysis Society of Japan) and CeO₂-2 (Kanto Chemical Co. Inc.). To investigate the effect of supported metal, we also prepared some metal-supported ceria catalysts: X/CeO₂-1

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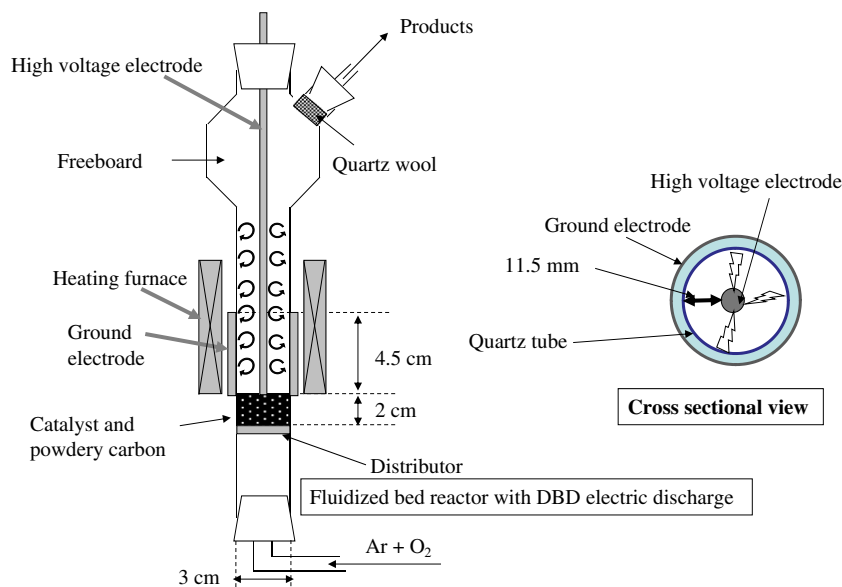


Fig. 1. Schematic diagram of the reaction apparatus.

($X = \text{Ni, Fe, Pt, or Pd}$) and $\text{Ni/CeO}_2\text{-2}$. These metal-loaded catalysts were prepared using an impregnation method with a solution of nitrate of metal precursor; 1 wt.% Pd/CeO_2 was obtained by impregnating acetate aqueous solution. In addition to these Ce-containing oxides, we prepared other perovskite catalysts: LaBaMnO_x , SrLaMnO_x , LaFeO_3 (these perovskites were prepared using a polymerized complex method [29]). TiO_2 (Kanto Chemical Co. Inc.) and ZrO_2 (JRC-ZRO-5) which were reported as an effective solid oxide for oxidation [21], La_2O_3 (Kanto Chemical Co. Inc.), and Sm_2O_3 (Kanto Chemical Co. Inc.) were also used as catalysts. All catalysts were calcined once and used without pre-reduction before the reaction.

2.2. Experimental condition

For evaluation of the catalytic oxidation activity of the catalyst at low temperature, we used a fluidized-bed flow reactor with dielectric barrier discharge (DBD). Fig. 1 portrays a schematic diagram of the reaction apparatus. Fine particle carbon (industrially available activated carbon) was used as a model reactant of solid carbon. The reaction temperature was 673 K; the reaction pressure was atmospheric pressure. For applying DBD in the reaction zone, we used a high-voltage power supply with voltage of 2.5 kV. The current and voltage waveforms were observed using a digital phosphor oscilloscope (TDS 3052B; Tektronix Inc.). Well-mixed 4 g of catalyst and 2 g of carbon were filled in the reactor. The oxygen concentration in the feed gas was 0%, 1%, or 5% with Ar carrier gas. The total amount of feed gas was 1200 ml min^{-1} . Under these conditions, the carbon conversion was maintained as a very low value for the evaluation of the kinetics of oxidation. Therefore, the total carbon conversion after the reaction was less than 1%. For rapid increase of the reaction temperature, a pre-conditioned heater at 673 K was attached to the reactor, and the reaction was started. Products of CO, CO_2 , and non-reacted O_2 were analyzed using two gas chromatographs (GC-FID column, gaschropack-54 with methanizer; GC-TCD column, Molecular Sieve 5A).

2.3. Characterization

The BET specific surface area of oxide was measured using N_2 physisorption (AUTOSORB-1; Quantachrome Instruments) and

the crystalline structure of oxide was analyzed using XRD (RINT 2100; Rigaku Corp.) before and after the reaction. The reduction ratio of oxide was measured using temperature-programmed reduction (TPR) with a thermogravimetry (Thermo plus Evo; Rigaku Corp.) in 10% of hydrogen atmosphere (50 ml min^{-1} flow rate). TPR was conducted at the temperature range from ambient to 1123 K, and the heating rate was 10 K min^{-1} .

3. Results and discussion

3.1. Activities of various catalysts

First, we evaluated the activities of our prepared catalysts for the oxidation of carbon particles. We observed the formation of CO_2 through oxidation of carbon particles, and no other product such as CO or hydrocarbons was detected. Oxidation of carbon by evolved lattice oxygen was terminated within 30 min of the reaction for all catalysts. Table 1 presents results for activity tests over various catalysts with 1% oxygen. In this table, the “peak time” represented the time at which the highest oxidation rate was observed. The “peak reaction rate” was the reaction rate at the “peak time”. The amount of lattice oxygen consumption in/on the oxide catalyst was evaluated from the CO_2 formation.

Without catalysts, CO_2 was not produced with and without discharge or under any oxygen concentration. Reportedly, the catalytic activity of CeO_2 for oxidation depended on the properties of ceria such as the BET specific surface area [30]. Therefore, we prepared two ceria catalysts having different BET specific surface areas. In fact, $\text{CeO}_2\text{-2}$, which had a very small BET specific surface area ($3.6 \text{ m}^2/\text{g}$), showed little activity (not shown). Among the many oxides, Ce-containing oxide showed higher activity for the oxidation of carbon particles, and $\text{Ni/CeO}_2\text{-1}$ showed especially high activity among the catalysts. Fig. 2 presents results for integrated lattice oxygen consumption for various catalysts. Based on these results, $\text{Ni/CeO}_2\text{-1}$ catalyst showed the highest activity for oxidizing carbon among $\text{CeO}_2\text{-1}$ and various metal-supported $\text{CeO}_2\text{-1}$ catalysts.

3.2. Evolution of lattice oxygen with and without dielectric barrier discharge

Regarding the above screening for better oxidation catalysts, results showed that $\text{Ni/CeO}_2\text{-1}$ had the highest activity among

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