

Investigation of Soot Oxidation Carried out on Membrane Filters Composed of SiC Nanoparticles

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ABSTRACT

The diesel particulate membrane filter (DPMF) is a good solution to the problem of high pressure drop that exists across diesel particulate filters (DPFs) as a result of the soot trapping process. Moreover, DPMFs that have a membrane layer composed of SiC nanoparticles can reduce the oxidation temperature of soot and the apparent activation energy. The SiC nanoparticles have an oxide layer on their surface, with a thickness less than 10 nm. From the visualization of soot oxidation on the surface of SiC nanoparticles by an environmental transmission electron microscope (ETEM), soot oxidation is seen to occur at the interface between the soot and oxide layers. The soot oxidation temperature dependency of the contact area between soot and SiC nanoparticles was evaluated using a temperature programmed reactor (TPR). The contact area between soot and SiC nanoparticles was varied by changing the ratio of SiC nanoparticles and carbon black (CB), which was used as an alternative to soot. If the contact area between CB and SiC nanoparticles was large enough, CB oxidation temperatures were almost the same whether Pt was embedded in the oxide layer or not. Furthermore, the CB oxidation temperature was found to depend on the oxygen concentration in the gas phase. Pt helped increase the amount of adsorbed oxygen on the surface of SiC nanoparticles.

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INTRODUCTION

Diesel engines have high thermal efficiency. They can effectively reduce CO₂ in the air and help to improve fuel economy. However, the exhaust gases from diesel engines contain nitrogen oxide (NO_x) and particulate matter (PM), which is a problem. [1, 2] PM accumulates on the wall of the DPF, thus enhancing the pressure drop. Therefore, it is necessary to remove the PM from DPFs. This process is called the "regeneration process", in which, PM is oxidized at a high temperature. The fuel employed to increase the temperature of a DPF cannot be utilized to operate the engine in which it is used. Therefore, a high efficiency regeneration process is desirable. [3] We have previously suggested that a DPMF effectively reduces the pressure drop caused by the soot trapping process. [4, 5] Moreover, we found that a membrane layer composed of SiC nanoparticles can reduce the oxidation temperature of soot and the apparent activation energy. [6, 7, 8] Generally, the temperature of soot oxidation by oxygen in the gas phase is over 550-600°C and the apparent activation energy is 120-150 kJ/mol. In the case of soot oxidation by

a DPMF, soot began to oxidize at a temperature below 400°C and the apparent activation energy was 85±10 kJ/mol. In this study, we tried to clarify the reaction process of soot oxidation on a DPMF.

EXPERIMENTAL PROCEDURES AND EQUIPMENT

Diesel Particulate Membrane Filter (DPMF) [6, 7, 8]

Information regarding the samples is presented in Table 1. Each DPMF was prepared by coating the membrane onto the wall surface of a conventional SiC-DPF, as shown in Fig. 1(a) and (b). To obtain permeability of the membrane, SiC nanoparticles having two average diameters were mixed and coated. The thickness of the membrane layer was about 20 μm, as shown in Fig. 1(b). Porosity and mean pore size of membrane layer (w/o and with Pt) are 60% and 1 μm. The membrane was composed of SiC and SiC nanoparticles, as shown in Fig. 2. The surface of the SiC

nanoparticles was covered with an oxide layer of SiC (silicon-oxy-carbide: $\text{Si}_x\text{O}_y\text{C}_z$), which had a thickness of about 5 nm. Figures 3(a) and (b) show the TEM (JEM-2010F, JEOL Ltd.) images of the SiC nanoparticles without and with Pt, respectively. In Fig. 3(b), single nanosized Pt particles seem to be embedded in the oxide layer of SiC. In our previous studies [6, 7, 8], using a scanning transmission electron microscope (STEM), we observed that single nanosized Pt particles were completely embedded in the oxide layer on the surface of SiC nanoparticles.

Table1. Specification of Samples

Sample	Amount of Pt per DPF Volume	Diameter of SiC particles
DPMF(w/o Pt)	none	35 nm and 800 nm
DPMF(with Pt)	4.8 g/L	35 nm and 800 nm

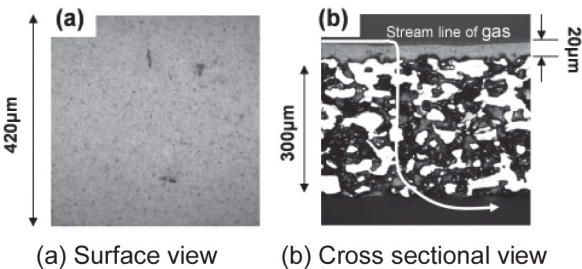


Figure 1. Optical surface and cross-sectional views of a DPMF

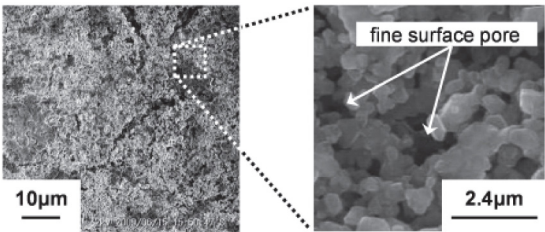


Figure 2. SEM images of a DPMF surface

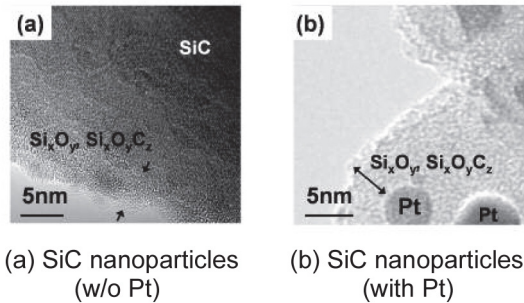


Figure 3. TEM images of SiC nanoparticle

Soot Oxidation Experiment by DPMF [6, 7, 8]

Experimental Set Up

Figures 4 and 5 show the schematic diagrams of the experimental setup used for the soot oxidation experiment on the DPMF, which entails trapping and oxidizing the predominant ultrafine soot particles. The soot produced by a diesel fuel (conventional diesel fuel, JIS K2204 No. 2) lamp, similar to an oil lamp, was used in the

trapping process in order to simulate the soot emitted from modern diesel engines. Part of the soot inside the diffusion flame was introduced into the DPMF through a glass suction pipe. Figure 6 shows the DPMF (without and with Pt) for soot oxidation experiment. All soot oxidation experiments of the regeneration processes were performed using the set-up shown in Fig. 4 and 5. The amount of soot trapped on the DPMF was controlled by visualizing the trapping process. The superficial velocity of the inlet gas traveling through the DPF wall was fixed at approximately 12 cm/s. In general, soot in the exhaust gas of diesel engines contains a soluble organic fraction (SOF), as well as solid carbon spheres. The SOF is oxidized at a lower temperature than the solid carbon spheres (under 400°C). During the regeneration process of a DPF, the SOF is oxidized earlier than the solid carbon.

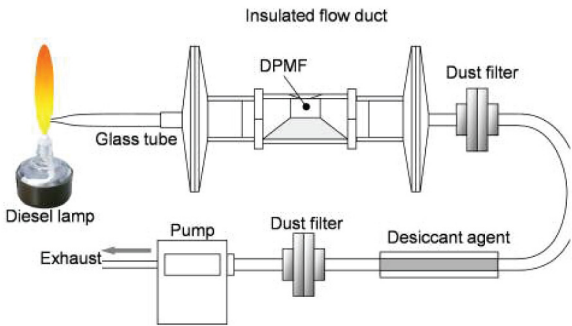


Figure 4. Schematic diagram of the experimental setup for the soot oxidation experiment on the DPMF (soot trapping process)

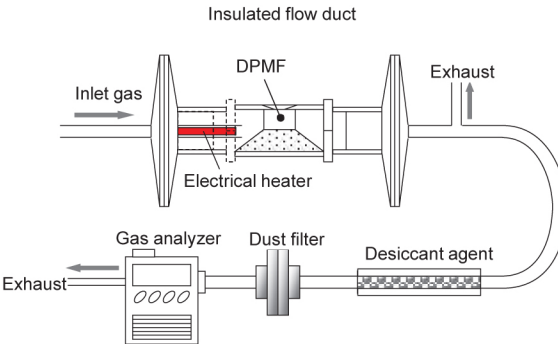


Figure 5. Schematic diagram of the experimental setup for the soot oxidation experiment on the DPMF (regeneration process)

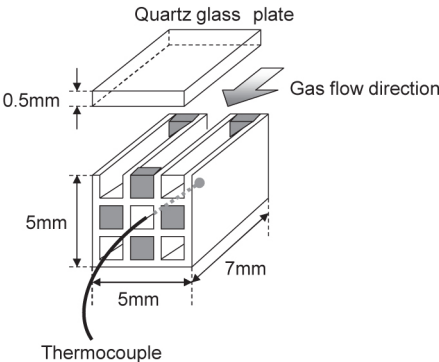


Figure 6. DPMF (without and with Pt) sample for soot oxidation experiment

Soot Oxidation Experiment with Rising Temperature

In order to regenerate a DPF completely, all of the carbon spheres must be oxidized. This investigation was therefore focused on the oxidation of solid carbon spheres. For this reason, a pre-treatment operation was performed prior to the soot oxidation experiment in order to remove the SOF from the soot trapped on the DPMF. The DPMF was heated from room temperature (RT) to 650°C and maintained at that temperature (isothermal) for 10 min. Next, the DPMF was cooled to 60°C. Throughout this pre-treatment, nitrogen gas was introduced in order to prevent oxidation of the soot. After the pre-treatment operation, the DPMF was heated from 60°C to 700°C, using a working gas that was heated by an electric heater. Before heating the DPMF, the working gas was quickly changed from nitrogen to a mixture of oxygen (7%) and nitrogen (balance). The temperature was raised by 20°C at intervals of 1 min. During the regeneration process, the concentrations of carbon monoxide and carbon dioxide that were emitted by the oxidation reaction of the trapped particulates were measured using a real-time infrared gas analyzer. The temperature profile and gas conditions of the temperature programmed oxidation (TPO) (rising temperature) experiment are shown in Fig. 7.

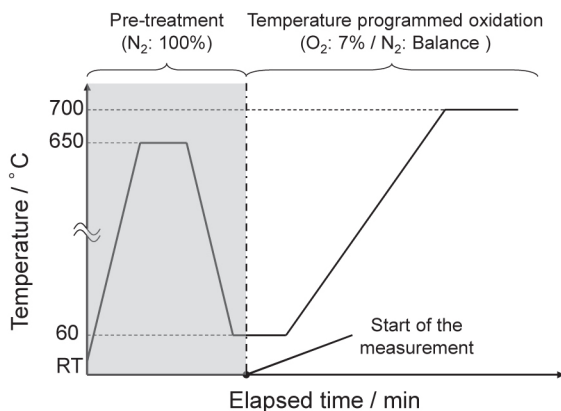


Figure 7. Temperature profile and gas conditions of the soot oxidation experiment on the DPMF with rising temperature

Soot Oxidation Experiment at Constant Temperature

To analyze the kinetics of soot oxidation in detail, the soot oxidation rate at each constant temperature was evaluated by measuring the concentrations of carbon monoxide and carbon dioxide produced by the soot oxidation. Figure 8 shows the temperature profile and gas conditions of the TPO (at each constant temperature) experiment. The criteria used were similar to those mentioned above in the TPO (rising temperature) experiment. After the pre-treatment operation, the temperature was raised to each of the target temperatures in an atmosphere of nitrogen gas. Once the temperature was stabilized, the working gas was quickly changed from nitrogen to a mixture of oxygen (7%) and nitrogen (balance). The gas was analyzed in a manner similar to that used in the TPO (rising temperature) experiment.

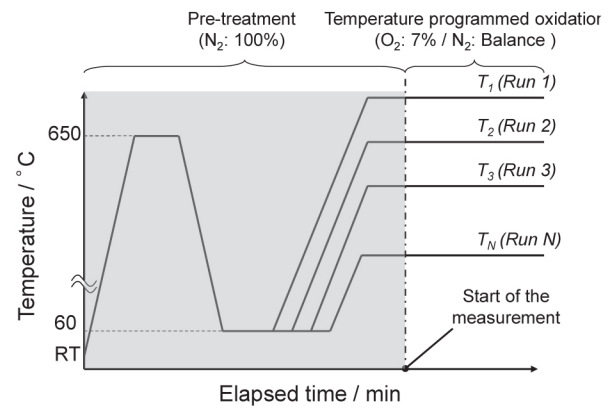


Figure 8. Temperature profile and gas conditions of the soot oxidation experiment on the DPMF at each constant temperature

Observation of Soot Oxidation on the Membrane Layer [6, 7, 8]

Environmental Transmission Electron Microscope (ETEM)

A schematic diagram of the ETM (in-situ TEM, Hitachi High-technologies Corp.) sample holder is shown in Fig. 9. The set-up consisted of a heater and a gas injector. The sample consisted of a mixture of a small amount of SiC nanoparticles and soot in an aqueous solution of ethanol. The heater was coated with the solution. The ETM study was performed under vacuum, with a resulting pressure of 1.0×10^{-5} Pa in the vacuum chamber. During this process, water vaporized as a result of the low pressure. Subsequently, the heater temperature was raised to 450°C. After the temperature was raised, air was introduced into the sample holder until a partial pressure of approximately 2.0×10^{-2} Pa was attained. The oxidation process of the soot was observed using a transmission electron microscope at 450°C.

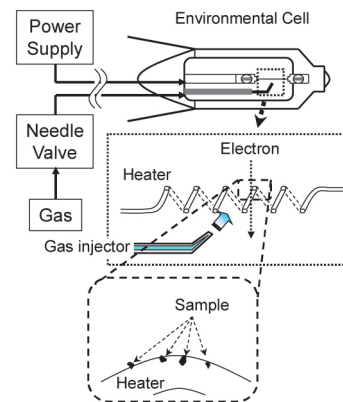


Figure 9. Schematic diagram of the ETM sample holder

Soot Oxidation Experiment in the Mixture of CB and SiC Nanoparticles

Temperature programmed oxidation experiment (TPO)

Figure 10 shows the schematic diagram of a cross sectional view of the DPF wall, the membrane layer, and the soot cake layer. Contact between the soot and membrane layers occurs only at the interface. In other words, the majority of soot in the soot cake layer does not come