

Visualization of Oxidation of Soot Nanoparticles Trapped on a Diesel Particulate Membrane Filter

2011-01-0602

Published
04/12/2011

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doi:10.4271/2011-01-0602

ABSTRACT

Through microscopic visualization experiments, a process generally known as depth filtration was shown to be caused by surface pores. Moreover, the existence of a soot cake layer was an important advantage for filtration performance because it could trap most of the particulates. We proposed an ideal diesel particulate filter (DPF), in which a silicon carbide (SiC) nanoparticle membrane (made from a mixture of 80 nm and 500 nm powders) instead of a soot cake was sintered on the DPF wall surface; this improved the filtration performance at the beginning of the trapping process and reduced energy consumption during the regeneration process. The proposed filter was called a diesel particulate membrane filter (DPMF).

A diesel fuel lamp was used in the trapping process to verify the trapping and oxidation mechanisms of ultrafine particulate matter. Thus, the filtration performance of the membrane filters was shown to be better than that of conventional DPFs. Furthermore, we found that surface pore filtration was initiated by Brownian motion in the pore and by electrostatic force between the particulates and the SiC-particles.

In the regeneration process, the activation energy for soot oxidation on the DPMF was lower than that on the conventional non-catalyzed DPF because the soot might react effectively with oxygen adsorbed on the thin oxide layer that completely covered the SiC-nanoparticles and since the soot came into close contact with the oxide layer owing to the large specific surface area of the DPMF. This suggests that the SiC nanoparticle membrane filter had some catalytic activity similar to that of the conventional catalyzed DPF.

INTRODUCTION

Among the various types of internal combustion engines, diesel engines have the highest thermal efficiency. However, diesel particulate matter (PM) must be removed from the exhaust emitted by diesel engines because of its harmful effects on the environment and human health. PM consists of a solid fraction and a soluble organic fraction (SOF). Primary particles composed of carbon and metallic ash are coated with SOF and sulfate. The mean diameter of the primary and agglomerated particles is usually in the range of 20-60 nm and 60-200 nm, respectively. The composition of particles emitted by a diesel engine may vary widely according to the operating conditions and fuel composition [1,2,3,4,5].

The nanostructures of primary soot particles have been characterized using transmission electron microscopy (TEM) to understand them in detail. A primary soot particle has two distinct parts: an inner core and an outer shell. The inner core has a diameter of 10 nm, and it is located in the central region of the primary particle [6, 7].

The electric charge on carbon particles sampled from combustion flames and diesel engines has been reported. Carbon particles in later stages of growth are assumed to be charged by thermionic emission and electron capture. The number of charges per particle varies; the average is two. The potential energy increases with increasing charge when the radius of the soot particle is fixed, and it decreases with increasing radius for a constant charge [8, 9].

Diesel particulate filters (DPFs) play an important role in particulate trapping and oxidation (regeneration of DPFs). A DPF is generally made of ceramic materials such as cordierite or silicon carbide (SiC), consisting of many rectangular channels with alternate channels blocked using cement at each end. The exhaust gas is forced to flow through a channel

wall having numerous micron-scale pores that trap the PM. Furthermore, the collected PM must be oxidized to regenerate the DPF and reduce back pressure on the diesel engine. A number of studies have been carried out to simulate particulate trapping and chemical reactions inside DPFs, thereby providing valuable information for design purposes [10,11,12].

The real-time filtration efficiency of DPFs during the trapping process has been measured using a scanning mobility particle sizer and a motor exhaust gas analyzer for particle number analysis and mass analysis, respectively. Results showed that the soot penetration depth into the wall was affected to a greater degree by particulate characteristics than by filtration velocity [13,14,15].

Catalytic fuel additives and catalyzed DPFs have been proven to reduce the overall activation energy required for particulate oxidation, resulting in lower temperature oxidation compared to non-catalyzed DPFs [16, 17]. The oxidation reaction of soot has been investigated using thermogravimetric analysis and temperature program oxidation to evaluate catalytic activities [18,19,20]. However, the main disadvantage of catalyzed DPFs for practical use is the small contact area between the soot and the active sites of catalyst particles. Thus, the geometry of a DPF wall and the catalyst nanostructures play an important role in the efficient regeneration of the filter [21].

Although particulate trapping and oxidation processes involve complex behaviors, very little information is available to aid the understanding of such phenomena. However, macro-scale and microscopic visualization of particulate trapping behavior and active regeneration inside a DPF have been successfully achieved; this has improved our understanding of such phenomena, and it can potentially facilitate the future design of ideal DPF configurations [22,23,24].

According to visualization results, a major disadvantage of conventional DPFs is the filtration performance at the beginning of the trapping process. During this phase, some diesel particulates pass through the DPF wall from the upstream to the downstream side. The amount of trapped particulates gradually increases with time along the shape of the surface pores after the mean pore-scale channels that are connected with the surface pores are blocked by particulates trapped during the initial stage. As a result, the filtration performance improves with time, and most particulates are trapped by the soot cake layer after it develops. The surface pores are filled with particulates, and only a few particulates that may have passed through at the beginning of the trapping process are trapped in the deeper pores. However, the filtration performance deteriorates again after the DPF is regenerated. Consequently, a process generally known as depth filtration is strongly related to the surface pores. The

existence of the soot cake layer is an important advantage for filtration performance because it can trap most particulates.

In the present study, we propose an ideal DPF, in which a nanosized silicon carbide (SiC) particle membrane is pasted and sintered on the DPF wall surface instead of the soot cake in order to improve the filtration performance (including ultrafine soot particles) at the beginning of the trapping process and to reduce energy consumption during the regeneration process. The proposed filter is called a diesel particulate membrane filter (DPMF).

EXPERIMENTAL SETUP AND EVALUATION OF REACTION ACTIVITY

Figure 1 shows a schematic of an experimental setup for microscopic visualization of trapping and oxidation of the predominantly ultrafine soot particulates. The soot produced by a diesel fuel (conventional diesel fuel, JIS K2204 No. 2) lamp such as an alcohol lamp was used in the trapping process to simulate soot emitted from recent diesel engines. Part of the soot inside the diffusion flame was introduced into a diesel particulate filter (DPF) through a bypass line. The superficial velocity of the inlet gas traveling through the DPF wall was fixed at approximately 12 cm/s. In the visualization experiment of oxidation, the DPF was heated from 200 °C to 600 °C, as in the case of an actual vehicle, using a high-temperature working gas that was a mixture of nitrogen (93%) and oxygen (7%). To analyze the characteristics of the soot oxidation reaction, the DPF was regenerated at constant temperatures, i.e., 530, 550, 568, 591, 607, 638, 656, or 673 °C. In this case, after the DPF was preheated with N₂ to the fixed temperature, the working gas was changed quickly from N₂ to the mixture with 7% oxygen. During regeneration, the concentrations of CO and CO₂ emitted during the oxidation reaction of the trapped particulates were measured using a real-time infrared gas analyzer.

Figures 2(a) and (b) show the conventional DPF and a proposed DPMF, respectively. Three kinds of DPFs were tested. The conventional DPF is made of SiC micron particles, and it has a wall thickness of 300 μm and porosity of 42%. On the other hand, the DPMF has a membrane composed of SiC nanoparticles with mixed sizes of 80 and 500 nm, sintered on the conventional DPF at 1700 °C. The membrane has a wall thickness of 20 μm and porosity of 60%. For the conventional catalyzed DPF (CDPF), a Pt/Pd-catalyst was coated on the conventional DPF.

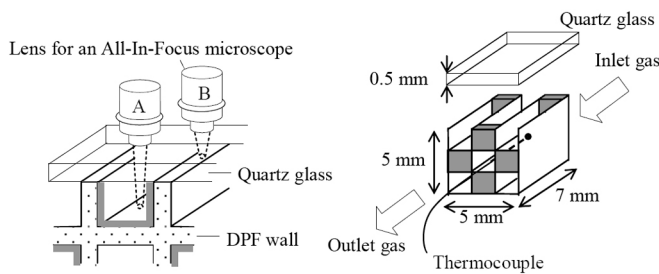


Figure 1. Experimental setup for microscopic visualization of trapping and regeneration processes.

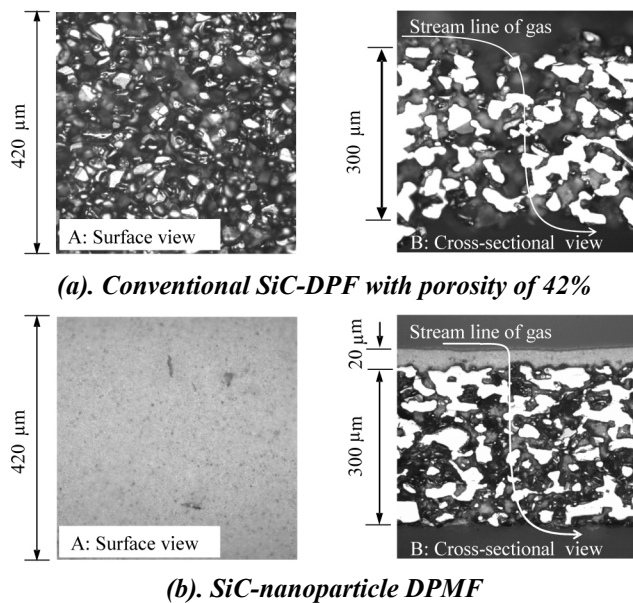
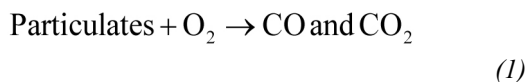


Figure 2. Optical surface (A: left-hand side) and cross-sectional (B: right-hand side) views of (a) the conventional DPF 42% and (b) the DPMF.

In order to evaluate the reaction activity of the nanoparticle membrane, the apparent activation energy for the oxidation of particulates in regeneration was compared with those of the conventional DPF and CDPF. Here, the particulates trapped on the filters were assumed to be reacted with oxygen, resulting in the production of CO and CO₂ as follows:



The particulates' reaction rate converted from the production rates of CO and CO₂ can be expressed as:

$$-\frac{d[Y]}{dt} = k[Y]^n[\text{O}_2]^m \quad (2)$$

Here, $[Y]$ is the summation of the number of remaining moles of carbon at each time step during regeneration. The

reaction coefficient k can be described by the Arrhenius-type reaction rate expression. As a result, the apparent activation energy was obtained from the Arrhenius plot consisting of the reciprocal absolute temperature of the filters and the particulates' reaction rate converted from the production rates of CO and CO₂ from the following equation:

$$\ln \left[\frac{-1}{[Y]^n} \frac{d[Y]}{dt} \right] = -\frac{E}{RT} + (\ln A + m \ln [\text{O}_2]) \quad (3)$$

Here, E is the apparent activation energy, A is the frequency factor, R is the gas constant, T is the absolute temperature of the DPF, and the last term on the right-hand side is assumed to be constant. In the present study, the reaction order n was assumed to be 2/3, based on the shrinking core model [18, 20, 25,26,27,28].

RESULTS AND DISCUSSION

MICRO AND NANOSTRUCTURES OF SOOT PARTICLES

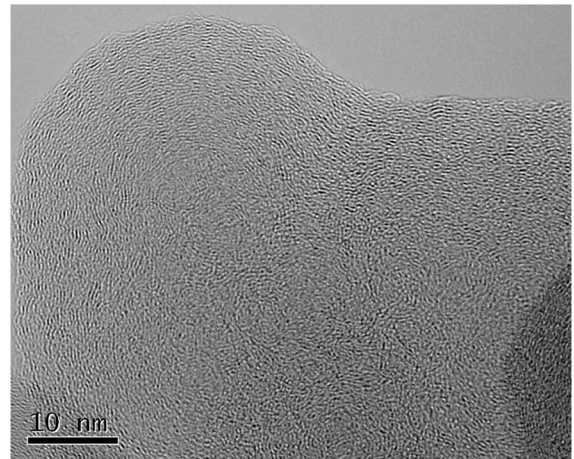
Figures 3 (a), (b), and (c) show the SEM image of soot, the TEM image of agglomerated soot, and the TEM image of the primary particle emitted from a diesel engine (Robin SDG2200, manufactured by Subaru Co. Ltd.), respectively. As shown in Fig. 3(a), the soot has a round shape and a large scale size around several hundred nanometers. It consists of many primary particles, with an average size from 20-60 nm, as shown in Fig. 3 (b). The primary particles may be agglomerated into round soot through capillary force by liquid-phased soluble organic fractions (SOF) and volatile organic fractions (VOF) that are not seen in the SEM and TEM images. Furthermore, we find that the nanostructure of the primary particle is quite similar to that reported by Vander Wal et al. (2007) [7], as shown in Fig.3(c).

Figures 4 (a), (b), and (c) show the SEM image of soot, the TEM image of agglomerated soot, and the TEM image of the primary particle sampled from a location 5 mm from the bottom of the fuel lamp flame, respectively. As shown in Fig. 4 (a), the soot has a chain-like structure. The agglomerated soot with a size around 100~300 nm can be seen in Figs. 4 (a) and (b). The scale and structure of the soot emitted from the fuel lamp are different from those emitted from the engine. However, the primary particles of the soot emitted from both sources are much the same as shown in Figs. 4(c) and 3(c).

The normalized particulate matter size distribution of approximately 250 particles picked up from the SEM images is shown in Fig. 5. A large amount of 20-300 nm size particles were observed for both the diesel engine and the diesel fuel lamp emissions. Both size distributions, including

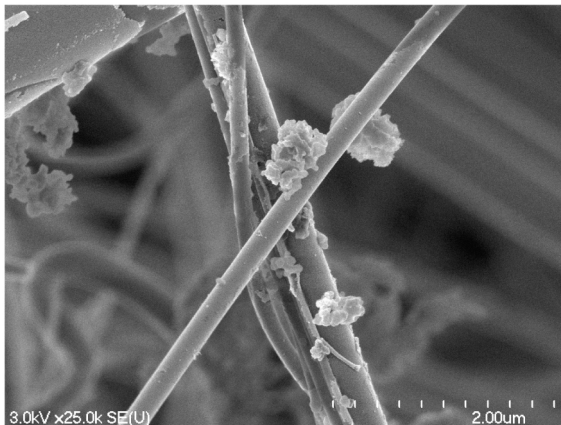
the particle diameter at the peak number, are similar. However, for the diesel engine emission, a few 600-1000 nm particles were also observed. Even though they were fewer in number, the large volume of such large particles strongly affected particulate trapping behavior. As a result, the fuel lamp was used in order to gain a better understanding of the trapping and oxidation of ultrafine particulates.

In addition, the composition of particulates emitted from the diesel engine and the diesel fuel lamp was characterized using a carbon-hydrogen-nitrogen (CHN) analyzer (oxidized gas analysis) and compared with that of carbon black. Much larger amounts of hydrogen atoms were detected from particulates emitted by the diesel engine, as compared with those emitted by the fuel lamp and carbon black. As a result, we verified that a hydrocarbon such as SOF or an unburned hydrocarbon was adsorbed on the particulates emitted by the diesel engine.

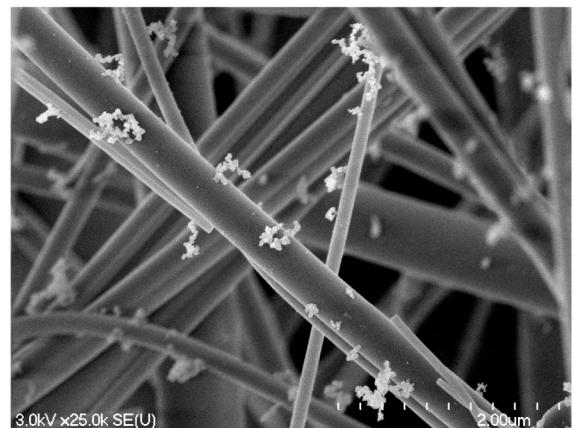


(c)

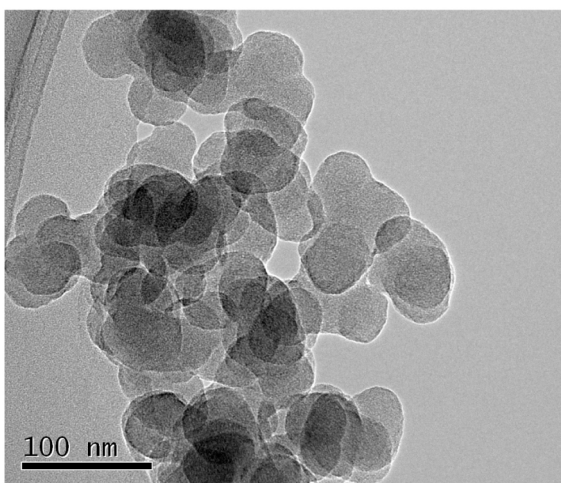
Figure 3. (a) SEM image and (b), (c) TEM images of the soot particles emitted by the diesel engine.



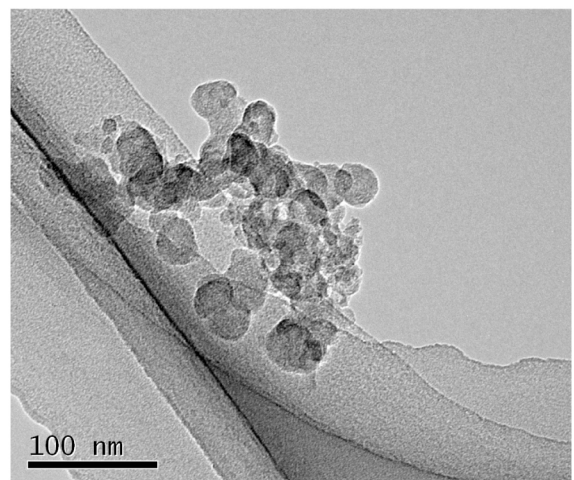
(a)



(a)



(b)



(b)