Soot Trapping by High-permeability Porous Membrane Filter Made of Aggregates of Alumina Nanoparticles

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ABSTRACT: A new diesel particulate filter (DPF) with a highly porous membrane made of alumina submicron particles, which are aggregates of alumina nanoparticles, was proposed to eliminate the radical increase in pressure drop caused by the soot accumulation in surface pores at the beginning of soot trapping and to improve the initial filtration efficiency of the DPF. The alumina membrane was manufactured by introducing particles-suspended nitrogen gas into the conventional DPF. The particle size of alumina and the particle-carrying gas velocity, which are significant parameters to determine the permeability of the layer, were optimized to make a low pressure drop membrane.

Key Words: heat engine, post treatment system, particulate filter, soot accumulation, membrane filter [A1]

1. Introduction

Diesel engines are effective for reducing the usage of fossil fuels because their thermal efficiency is higher than that of gasoline engines. Additionally, because of their large torque, diesel engines are widely used in commercial vehicles, particularly heavy-duty trucks. However, diesel engines have harmful emissions of particulate matter (PM) and nitrogen oxides (NOx). To reduce these emissions, a multi-stage aftertreatment system consisting of diesel particulate filters (DPFs) and selective catalysis reduction, combined with a diesel oxidation catalyst (DOC), is used, for example, in heavy-duty trucks. For the aftertreatment of PM using the DPF, an active regeneration process is used for the complete removal of the PM trapped on the DPF. In this case, the primary component of the PM is soot which is oxidized by a high-temperature exhaust gas produced by the combustion of unburnt fuel introduced into the DOC through the post-injection of fuel in engine systems. Then, the temperature of the DPF increases above 600 °C for complete oxidation of soot during the regeneration process. Therefore, the DPF requires considerable thermal durability because of the high operating temperatures. For this reason, silicon carbide (SiC) or cordierite (Mg2Al2Si5O18) are used as the primary material for the elements of the DPF. During the PM-trapping process, the pressure drop between the inlet and outlet of the DPF increases. This increase in pressure drop causes a decline in the thermal efficiency of the engines. Therefore, a new DPF that can trap soot while maintaining a low pressure drop is required.

Recently, the mechanism of the increase in the pressure drop with respect to soot loading was revealed 1) (Figure 1). At the beginning of soot deposition, the soot is trapped on the surface of grains, which are the elements of the DPF. Because of this deposition, a bridging structure is formed by soot at a depth of 10–20 microns from the top inlet surface of the DPF wall. After this bridging structure is completely formed, the soot is deposited on it. Additionally, once the bridging structure is formed, the filtration efficiency becomes ~100% because the soot cannot pass through the bridging structure. In this phase, the soot is deposited in surface pores of the DPF that are open to the inlet channel below the surface. The soot deposition causes a large increase in the pressure drop with respect to the soot loading because the flow velocity increases along the depth of the surface pores of the DPF wall.

After the deposition in the surface pores is complete, the soot is deposited on the top surface of the wall, forming a soot cake layer. During this phase, the pressure drop increases linearly. Consequently, if the bridging structure is formed at the entrance of the surface pore of the DPF wall, the pressure drop is reduced drastically during the soot-trapping process.

As a method for avoiding the soot deposition in the surface pores, the fabrication of a membrane layer on the surface of the DPF was proposed 2-4). A schematic of the DPF with a membrane layer is shown in Figure 2. The membrane avoids the soot accumulation inside surface pore which causes a drastic increase in pressure drop. On the other hand the pressure drop through the membrane should be minimized because the initial pressure drop of DPF is represented by the summation of the pressure drop through DPF substrate and that through the membrane layer. Thus in this study more highly porous membrane consisting of submicron aggregates is proposed. For testing, the membrane was fabricated by introducing alumina-particles-suspended nitrogen gas into the conventional DPF. The particle size and the particle-carrying gas velocity, which are significant parameters to determine the permeability of the layer and the PM accumulation depth, were optimized to make a low pressure drop membrane. The aggregates were fabricated by drying a droplet of an alumina nanoparticle dispersion liquid. Here, the permeability of membrane and the penetration depth of submicron particles are the key factors.
Fig. 1 Schematic of increase in pressure drop in DPF with respect to soot loading

An advantage of this fabrication method is the ability to achieve a uniform thickness of the membrane layer along the longitudinal direction of the DPF. One benefit of the membrane layer is the improvement in the efficiency of the soot trapping at the beginning of the trapping process.

Fig. 2 Schematic of structure of membrane layer fabricated on conventional DPF wall

2. Experimental method

2.1. Experimental setup

Figure 3 shows the arrangement for the fabrication process of the alumina aggregates as well as the experimental setup for the fabrication of the membrane layer on the DPF. This setup mainly consists of an ultrasonic atomizer, a ceramic tube for evaporation, and a DPF holder. For the experiment, the alumina nanoparticle dispersion liquid was diluted by distilled water. The specifications of the undiluted dispersion liquid are presented in Table 1, and the DPF specifications are presented in Table 2.

First, the dispersion liquid was atomized into several microns droplets by ultrasonic atomization at a frequency of ~0.9 MHz. The droplets were carried by pure nitrogen gas with a flow rate fixed at 200 cc/min. To control the flow-rate conditions, the droplet-suspended nitrogen gas was diluted with another pure nitrogen gas flow. As shown in Figure 4, only the water component in the droplet was evaporated—in a ceramic tube with a ribbon-type electric heater—allowing the formation of aggregates of the alumina nanoparticles. Finally, the alumina aggregates were introduced to the DPF holder and trapped on the DPF wall as shown in Figure 2. The pressure drop between the DPF inlet and the outlet was measured using a digital differential manometer.

Table 1 Specifications of the nanoparticle dispersion liquid

| Dispersoid   | Alumina          |
|--------------|------------------|
| Medium       | H₂O              |
| Manufacturer | Wako Pure Chemical Industries, Ltd. |
| Mean diameter| 44 nm            |
| Concentration| 23 wt%           |

Table 2 Specifications of the conventional DPF

| Mean pore diameter | 6.5 microns |
|--------------------|-------------|
| Porosity           | 42 %        |
| Wall thickness     | 400 microns |
| Cell size          | 1.41 x 1.41 mm² |

2.2. Visualization method of DPF cross-section

A schematic of a DPF sample for visualization is shown in Figure 5. The sample was comprised of a 5 x 5 matrix where individual cells were alternately plugged. To visualize the cross-section of the vertical wall of the DPF, the horizontal outer wall was removed from the sample(1). The top surfaces of the vertical...
walls were well-polished uniformly using abrasive papers with
grit sizes ranging from P400 to P4000. Then, a quartz glass plate
was put on the polished surfaces to cover the open channels
instead of the removed wall during the deposition of the alumina
aggregates. After the deposition, cross-sectional images were
obtained by scanning electron microscopy (SEM) from the
direction of the arrow shown in Figure 5.

Fig. 5 DPF sample for visualization by SEM

2.3. SEM observation of different diameter aggregates

Figure 6 shows SEM images of alumina aggregates obtained
using different concentrations of the dispersion liquid. The images
were taken by a field-emission scanning electron microscope. The
aggregates were made using 1.15, 0.115, and 0.023 wt%
dispersion liquids. In every test condition, most of the aggregates
had a sphere-like shape.

The size distribution of the diameter of the aggregates was
determined using the SEM images, as shown in Figure 7. The
average diameters for the test conditions were 673, 355, and 290
nm. The results indicate that for a lower concentration of the
dispersion liquid, the alumina aggregates have a smaller diameter.
For the SEM images used to measure the size distribution, the
aggregates were introduced to the glass-fiber filter for
only 30-s, to observe only single dispersed aggregates deposited
on the filter one-by-one and there were no dendrite-structured
agglomerated aggregates.

2.4. Measurement of alumina loading amount

Alumina particles were deposited on a glass-fiber filter to
estimate the mass of alumina aggregates that was deposited on the
DPF per unit time. Table 3 shows the weight gain of the glass-
fiber filter after deposition. For a concentration of 0.023 wt%, the
weight gain was too minute to measure with an electronic balance.
Therefore, for subsequent deposition experiments, dispersion
concentrations of 1.15 and 0.115 wt% were primarily used. The
amount of the alumina aggregate loading was based on the mass
emission rate experimentally obtained.

Fig. 6 SEM images of alumina aggregates
made of alumina nanoparticle dispersion liquids of
1.15 wt% (top), 0.115 wt% (middle), and 0.023 wt% (bottom)

Fig. 7 Particle-size distribution of alumina aggregates determined
using SEM images
Table 3 Weight gain of the glass-fiber filter after alumina deposition

| Nanoparticle concentration in dispersion liquid (wt%) | 1.15 | 0.115 | 0.023 |
|-----------------------------------------------------|------|-------|-------|
| Weight gain (g)                                     | 0.0014 | 0.0007 | -     |
| Deposition time (min)                               | 10   | 50    | -     |
| Emission rate (g/s)                                 | 2.3 x 10^{-5} | 2.3 x 10^{-7} | -     |

3. Experimental results

3.1. Effect of particle diameter on pressure drop

The effect of the particle diameter on the pressure drop across the membrane layer was investigated using aggregates whose mean diameters were 673 or 355 nm. Figure 8 shows the increase in the pressure drop during the membrane-fabrication process. These results suggest that a membrane filter made of larger aggregates has a lower pressure drop under the same velocity of flowing gas. To investigate the relationship between the particle size and the pressure drop, a comparison of the permeability of the cake layer made of the aggregates was performed using the following two kinds of models.

3.1.1. Permeability of aggregate cake layer obtained using Darcy’s law

According to Darcy’s law, the permeability of a cake layer made of aggregates is given by the following equation:

\[ \Delta P = \frac{\eta v L}{k} \]  

(1)

Here, \( v \) is the superficial velocity, \( L \) is the thickness of the cake layer, \( \eta \) is the viscosity, and \( k \) is the permeability. For this experiment, \( v \) was obtained using the filtration area of the DPF sample and the flow rate in the experiment, and \( L \) was obtained using the SEM images taken before and after growth of the cake layer made of alumina aggregates, as shown in Figure 9. The pressure drop \( \Delta P \) was obtained using the slope of the increase in the pressure drop with respect to the aggregate loading during the cake-layer growth, as shown in Figure 8.

The obtained \( \Delta P, L, \eta \) and the \( k \) calculated using Darcy’s law are shown in Table 4. The membrane made of 673-nm aggregates had a larger permeability than that made of 355-nm aggregates, as shown in Table 4.

Table 4 Permeabilities of cake layers made of aggregates with mean diameters of 673 and 355 nm

| Concentration | 1.15 wt% | 0.115 wt% |
|---------------|----------|-----------|
| Mean diameter of alumina aggregates (nm) | 673 | 355 |
| \( \Delta P \) (Pa) | 19.4 | 23.0 |
| \( L \) (microns) | 10.8 | 8.6 |
| \( \mu \) (Pa·s) | 2.03 x 10^{-5} | - |
| \( k_{\text{Darcy}} \) (m²) | 7.8 x 10^{-14} | 5.2 x 10^{-14} |

3.1.2. Permeability of aggregate cake layer obtained using cell model

The permeability of a cake layer made of aggregates can be expressed by Eq. (2), as reported by Kuwabara et.al (5-7), using the mean particle diameter \( d \) and packing fraction \( \varepsilon \).

\[ k_{\text{Kuwabara}} = \frac{d^2}{18 \varepsilon} \left( 1 - \frac{9}{5} \varepsilon^3 + \varepsilon - \frac{1}{5} \varepsilon^2 \right) \]  

(2)

To determine the packing fraction \( \varepsilon \) experimentally, the weight gain of the membrane layer \( \Delta m \), the membrane growth layer \( L \), the filtration area \( A \), and the apparent density of alumina aggregates \( \rho'_{\text{Al}_2\text{O}_3} \) were used, as described in Eq. (3). The apparent density of aggregates was estimated according to the bulk density of Al₂O₃ and the expected packing fraction \( \varepsilon_1 \) of the alumina nanoparticles that composed the alumina aggregates. Here, the bulk density of the alumina was obtained from a databook as 3.95 g/cm³, and the packing fraction \( \varepsilon_1 \) of the alumina nanoparticles in the aggregates was calculated as 74%, assuming a hexagonal close-packed structure of nanoparticles in the aggregates. Consequently, the apparent density \( \rho'_{\text{Al}_2\text{O}_3} \) was 2.92 g/cm³. The packing fraction \( \varepsilon \) of the membrane was calculated by substituting these values into Eq. (3). Porosity values \( \phi \) of 90.9% and 94.3% were obtained for membranes made of aggregates with diameters of 673 and 355 nm, respectively. The calculated results are presented in Table 5.

\[ \varepsilon = \frac{\Delta m}{\rho_{\text{Al}_2\text{O}_3} \times A \times L} = \frac{\Delta m}{\varepsilon_1 \times \rho_{\text{Al}_2\text{O}_3} \times A \times L} \times (1 - \phi) \]  

(3)
As shown in Table 5, the permeability in the case of the 673-nm diameter aggregate was higher than that for the 355-nm aggregate. Here, the permeability obtained using Darcy’s law is almost the same as that obtained using the Kuwabara model. The difference was slightly larger in the case of 355 nm than in the case of 673 nm.

The porosity in the dendrite-structured membrane increased as the nanoparticle size decreased, owing to the relative increase in the contact force and van der Waals force compared with the gravity force, as shown by R. Y. Yang et al. Similarly, as shown in Table 5, the porosity of the membrane increased as the alumina aggregate size decreased. However, the permeability decreased with increasing porosity because the number of nanoparticles increased with decreasing particle size. That is, the summation of Stokes’s drag force acting on a fine particle increased; as a result, large aggregates were preferable for fabricating a highly permeable membrane.

Table 5 Comparison of permeability obtained using Darcy’s law and Kuwabara model

| Mean diameter of alumina aggregates (nm) | 673 | 355 |
| Packing fraction $\varepsilon$ (%) | 9.1 | 5.7 |
| Porosity $\phi$ (= 100 $- \varepsilon$) (%) | 90.9 | 94.3 |
| $k_{\text{Kuwabara}}$ ($m^2$) | $7.7 \times 10^{-14}$ | $4.4 \times 10^{-14}$ |
| $k_{\text{Darcy}}$ ($m^2$) | $7.8 \times 10^{-14}$ | $5.2 \times 10^{-14}$ |

3.2. Effect of superficial velocity on pressure drop

The effect of the superficial velocity on the pressure drop of a membrane layer during the membrane-fabrication process was investigated. Table 6 shows the experimental conditions. In the experiment, the flow rate of the carrier gas that traveled through the atomizer was fixed at 200 cc/min, and the carrier gas was diluted downstream of the atomizer with pure nitrogen of 0, 400, and 800 cc/min. Therefore, the alumina nanoparticle loading amount per unit time did not change in any of the conditions. In every condition, the mean diameter of the alumina aggregates was 673 nm.

Table 6 Experimental conditions under different superficial velocities

| Flow rate (cc/min) | 200 | 600 | 1000 |
| Filtration area ($mm^2$) | $4.85 \times 10^2$ |
| Superficial velocity (mm/s) | 6.9 | 20.7 | 34.5 |
| Mean diameter of aggregates (nm) | 673 |

Figure 10 shows the increase in the pressure drop for each superficial velocity. In the case of 34.5 mm/s, similarly to the case of the soot-trapping process in the previous work, we observe three phases of the increase in the pressure drop: caused by the bridging-structure formation, the deposition of nanoparticles in surface pores, and the growth of the cake layer. With decreasing velocity, the increase in the pressure drop due to the deposition in surface pores became smaller. To evaluate the increase in the pressure drop under the same flow velocity, the ratio of the pressure drop to the superficial velocity, $\Delta P/\nu$, was investigated, as shown in Figure 11. In the case of no loading, $\Delta P/\nu$ was initially almost the same and then increased with respect to the alumina nanoparticles aggregate loading. The pressure drop of the membrane made of alumina nanoparticles aggregates increased with the superficial velocity in the manufacturing process. To investigate the difference, SEM images of the cross-section after the deposition of nanoparticles aggregates are shown in Figure 12. The left and right images correspond to superficial velocities of 6.9 and 57 mm/s, respectively. The broken line in Figure 12 represents the location of the top surface of the DPF wall. The upper part of the broken line is regarded as the cake layer, and the lower part is thought to reflect the aggregates being deposited in the surface pores. The penetration depth of the alumina aggregates into the surface pore was not clearly observed in the case of 6.9 mm/s, and it was ~50 microns for 57 mm/s. As previously discussed, the particles deposited in surface pores caused a large increase in the pressure drop. Therefore, a large increase in the pressure drop for a higher superficial velocity is caused by an increase in the penetration depth into the surface pore. On the other hand, even in the case of 6.9 mm/s, there was an increase in the pressure drop caused by penetration, as shown in Figure 11, although this is not clearly observed in the SEM image shown in Figure 12 (left). In addition, as shown in Figure 12, the porosity of the cake layer in the case of 6.9 mm/s appears sparse compared with that for 57 mm/s. Thus, the pressure-increase rate due to the cake-layer deposition in the case of 6.9 mm/s was smaller than that for 34.5 mm/s, as shown in Figure 11.

The filtration efficiency of a particle filter decreases as the filtration velocity increases, according to Rafal Przekop et al. These results indicate that for a high filtration velocity, particles can penetrate deeply into the filter. Our experiment indicated that to fabricate a low-pressure-drop membrane layer, it is preferable that the particles composing the membrane layer should be deposited outside of the surface pores of the DPF wall by using a low superficial velocity.
3.3. Soot-trapping experiment

Figure 13 shows the pressure drop during soot trapping by the DPF with and without a membrane made of alumina aggregates having a mean diameter of 673 nm under the condition of a superficial velocity of 57 mm/s. The pressure drop increase for the membrane fabrication was also shown before the elapsed time of zero, the soot was introduced with the same superficial velocity as alumina aggregates deposition to compare the difference in pressure drop increase for the surface pore filtration due to the large permeability of membrane. Here, soot particles produced by a generator (DNP-2000) were used instead of practical soot.

The DPF with the membrane had a higher pressure drop than the conventional DPF at the elapsed time of zero, that is, without soot loading. With respect to the elapsed time (with increasing soot loading), the pressure drop for the conventional DPF increased drastically because of the surface-pore filtration, as previously mentioned. On the other hand, the pressure drop for the DPF with the membrane increased almost linearly from the beginning of soot loading. Consequently, there was no drastic increase in the pressure drop. The increase rate with respect to the elapsed time was almost the same as that for the soot cake-layer filtration for the conventional DPF. The initial pressure drop, which is the pressure drop of the DPF with no particle deposition, were not completely same for the two results of DPF samples with and without membrane. This repeatability error was caused by the hand-made process of the sample which may affect to the superficial area of the sample.

Figure 14 shows an SEM image of the cross-sectional view of a DPF-wall sample with a membrane made of alumina nanoparticle aggregates after soot trapping. It is clearly observed that only the soot cake layer (top dark gray layer) was developed on the membrane (middle light gray layer). On the other hand, although the surface-pore filtration was not clearly observed, the penetration depth of soot into the membrane was negligible because there was no drastic increase in the pressure drop at the beginning of the soot trapping, as shown in Figure 13. This method of membrane would be applied for the catalyst coating by doping nano catalytic particles on aggregates, which may result in more effective contact between catalyst and soot. For the practical use, the thermal resistance of the membrane should be examined. It is our future plan to manufacture the catalyst doped submicron membrane and examine its oxidation characteristics. Furthermore, the effect of membrane layer on the ash accumulation should also be studied.
Soot trapping by a membrane filter made of aggregates of alumina nanoparticles was investigated. A highly porous membrane layer with a porosity higher than 90% was successfully developed on the surface of a conventional DPF wall under the condition of a low superficial velocity of 6.9 mm/s, using alumina aggregate-suspended nitrogen gas. The pressure drop for a membrane wherein the mean diameter of a single aggregate was 673 nm was smaller than that for the case of 355 nm. Using the membrane filter, soot was deposited only on the membrane, as a cake layer. Consequently, although the initial pressure drop was large because of membrane, the pressure drop through the DPF with membrane fell below that of the conventional DPF along with the soot trapping. It is because there was no surface-pore filtration that contributed to a drastic pressure drop at the beginning of the soot trapping.

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