Development of Membrane filter Made of Alumina and Silver-Palladium Particles for High-Filtration Efficiency, Low-Pressure Drop and Low-Soot Oxidation Temperature

Teerapat Suteerapongpun 1) Yuji Kitagawa 1) Mek Srilomsak1) Katsunori Hanamura 1)

1) Tokyo Institute of Technology
2-12-1 Ookayama, Meguro City, Tokyo 152-8550, Japan (E-mail: suteerapongpun.t.aa@titech.ac.jp)

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ABSTRACT: A membrane filter was coated on conventional filter made of SiC. The first and second layers consisted of alumina-particles with diameter of 0.5 and 1.5 micrometer, respectively; because small particles have higher filtration efficiency to prevent soot penetration into the membrane layer while large particles with a higher permeability can achieve lower pressure drop. Nanoscale silver-palladium particles were dispersedly deposited on the surface of the alumina particles layer as a top layer. The novel membrane filter demonstrated lower pressure drop while keeping high trapping efficiency during the soot trapping and presented lower soot oxidation temperature compared to the conventional filter.

KEY WORDS: Heat engine, Particulate filter, Membrane filter, Pressure drop, Soot oxidation catalyst [A1]

1. INTRODUCTION

Internal combustion engines will continue to be used for an environmental-friendly power source in a category of transportation. Based on well-to-wheel perspective, the internal combustion engines combined with hybrid system can provide the lowest carbon dioxide emission and even greater than the pure electric vehicles [1]. However, the exhaust gas from the internal combustion engines, especially diesel engines, contains high amount of particulate matter (PM), which has soot as the main components. As a result, those pollutants which are harmful for human health and environment should be removed by after-treatment systems in order to develop more advanced internal combustion engines. To trap the soot and prevent soot emission in atmosphere, particulate filters were introduced and installed in exhaust pipeline for soot trapping. However, the major issue of the particulate filters is the pressure drop caused by soot deposition during soot trapping and it adversely affects the engine performance which leads to higher fuel consumption.

Currently, there are two main types of particulate filter including gasoline particulate filters (GPFs) and diesel particulate filters (DPFs). In this research we have conducted the experiment using DPF samples, made of silicon carbide (SiC), because it has many advantages over GPF, made of cordierite, such as less fragile and compatibility with scanning electron microscope because of higher electrical conductivity properties.

The recent study [2] has revealed the pressure drop increasing phenomenon due to the soot accumulation on the particulate filter. It was clarified that the pressure drop between the inlet and the outlet of DPF drastically increases during soot-bridge formation and surface pore filtration inside pores of DPF wall at the beginning of soot trapping process as shown in figure 1. In addition, it was revealed that filtration efficiency becomes ~100% after bridging phase because soot particles cannot penetrate though the bridging structure, and then the soot cake layer provides perfect filtration efficiency with a low-linear increasing rate of pressure drop. As a result, the membrane filter, made of ~1.5 micrometer-alumina particles (Al2O3), was developed and coated on the conventional DPF [3] as shown in figure 2. The membrane can prevent the soot accumulating inside the surface pore which lead to reduction of a drastic increase in pressure drop cause by soot deposition at the beginning of trapping process. The membrane filter can also provide almost 100% filtration efficiency from the beginning of trapping process because there is a pre-bridging and pore filtration by alumina particles instead of soot.

The manufacturing of membrane filter on conventional DPF has been researched by many researchers [3] [4] [5] [6] although there is a tradeoff by the thick membrane layer that causes a high pressure drop. As a result, the multi-layer membrane filter composed of various sizes of alumina particles was develop in order to reduce the pressure drop as lowest as possible while keeping high filtration efficiency from the beginning of trapping process. Thus, large particles (~1.5µm), which have a higher permeability, were coated as a first layer to fulfill the bridging and surface pore filtration phases of trapping process and then small particles (~0.5µm), which have higher filtration efficiency, were supported on a base layer to prevent soot penetration into the membrane layer.
Moreover, conventional particulate filters essentially require an additional energy to clean up the filter when it is clogged with soot; this process is called active regeneration. Although the active regeneration process cleanly burns off the excess soot deposited in the filter, it consumes additional energy that affects a higher fuel consumption of vehicle. To decrease the regeneration energy, the nanoscale-catalyst particles, made of silver-palladium (AgPd), were coated as a top-layer membrane filter which is expected to reduce the soot-oxidation temperature [7] as shown in figure 2.

In this study, the membrane filter fabrication process for both base layer, made of alumina particles, and catalyst layer, made of AgPd particles, was demonstrated. The structures of the membrane, including top surface view and cross-sectional view, were observed by using field emission scanning electron microscope (FESEM). Moreover, the experiment on pressure drop of soot trapping for both conventional DPF and diesel particulate membrane filter (DPMF) were compared and discussed. Finally, the temperature programmed oxidation (TPO) was conducted in order to present the soot oxidation temperature influenced by catalytic effects. The ultimate goal of this research is not only to lower the pressure drop during soot trapping but also to minimize the soot-oxidation temperature, which lead to minimize fuel consumption of vehicles.

![Fig. 1](image1) The increase in pressure drop in conventional DPF with respect to soot loading

![Fig. 2](image2) The schematic of membrane layer coated on conventional DPF wall (cross-sectional view)

2. EXPERIMENTAL PROCEDURE AND METHODOLOGY

2.1. Membrane Fabrication

The experimental setup for fabricating membrane filter made of aggregated microscale-alumina particles on the surface of the conventional DPF is shown in Figure 3. The experimental conditions were controlled as follows; total N₂ flow rate = 0.2 L/min, total filtration area of a DPF sample = 485 mm², and superficial velocity through DPF wall = 6.9 mm/s. This setup consists of an ultrasonic atomizer, a ceramic tube with ribbon heater, a DPF holder, and a glass fiber filter. First, nanoscale-alumina particle, which has the primary particle size around 40nm, was diluted by distilled water. Then, the dispersion water was atomized into droplets with several micron diameter via ultrasonic atomization at frequency of ~0.9 MHz. The droplets were carried by pure nitrogen gas with a flow rate of 0.1 L/min. Next, the droplets suspended in nitrogen gas were diluted with another pure nitrogen gas line to control the desired flowrate. After that, droplets suspended in nitrogen gas will pass through the ceramic tube swabbed ribbon heater at 573K to evaporate the aqueous phase of droplets. In this system, the sizes of aggregated particle were controlled by changing the concentration of the alumina suspension. Finally, aggregates of microscale-alumina particle were introduced into the DPF holder and trapped on the conventional DPF wall forming a membrane layer. During the introduction of aggregates into the DPF, the pressure drop between inlet and outlet of DPF was monitored through a digital differential manometer. To reinforce the structure of membrane, the membrane was sintered at 1570K with the heating speed at 300K/hour. This sintering condition can form a stronger porous structure of the membrane from any mechanical damages.

![Fig. 3](image3) The experimental setup for fabricating membrane filter

2.2. Catalyst synthesis and support on membrane filter

Silver-palladium (AgPd) catalyst was prepared by liquid phase chemical reduction method [8]. Polyvinylpyrrolidone (PVP) was added in disodium tetrachloropalladate (Na₂PdCl₄) and silver...
nitrate (AgNO₃) solution to prevent the aggregation. After the solution was dispersed for 30 minutes by ultrasonic dispersion, Sodium hydroxide (NaOH) was dripped to adjust the pH of solution to 11; to obtain small particles of PdO and Ag₂O. Finally, sodium borohydride (NaBH₄), which is a reduction agent, was added to reduce Na₃PdCl₄ and AgNO₃ to obtain the silver palladium (AgPd) nanoparticles, in which mole ratio of Ag to Pd was 2:1. To fabricate the catalyst layer, we use the same method as described in figure 3 by applying the catalyst suspension, AgPd particles were atomized, heated, and trapped on the membrane. After that, the sample was heated up to 500°C to obtain AgPd alloy catalyst and remove the contamination.

2.3 Soot deposition

The soot generator (DNP-2000), used to produce soot at the average diameter of 70 nm with a superficial gas velocity of 50 mm/s, was set at the inlet of DPF as shown in figure 4. Soot was introduced and trapped in a DPF composed of membrane filter. During soot trapping, pressure drop was measured astride the inlet and outlet of DPF by the differential manometer. Finally, glass fiber filter was installed at the outlet of DPF to prevent soot emission into atmosphere.

![Fig. 4 The experimental setup for soot deposition](image)

2.4 Soot oxidation experiment

Oxidation of soot trapped on the membrane filter with dispersed AgPd catalyst particles was investigated through a temperature programed oxidation (TPO). Temperature of a sample with soot was increased constantly with a 20°C/min ramping rate under a fixed 10%O₂, and 90% N₂ concentration condition. During the soot regeneration process, the concentration of CO₂ and CO, emitted from oxidation of soot trapped in a sample, were measured and recorded real-time using an infrared analyzer (model CGT-7100 manufactured by Shimadzu). The temperature profile and peak of gas concentration are shown in Figure 5.

![Fig. 5 Temperature programed oxidation (TPO) of soot oxidation](image)

2.5 miniature-size DPF sample preparation

The commercial DPF was cut into a miniature sized sample of 10*10*10 mm³ which composed of 7*7 channel matrix [9]. Each channel was plugged by ceramic paste at the one end as shown in figure 6 (1), to make its structure like a full-sized DPF. After that, it was put into a DPF holder made of 304 grade stainless steel and was sealed by ceramic paste around the sample to prevent leakage as shown in figure 6 (2). Then, the top surface was removed by polishing machine using abrasive paper with grit sizes ranging from 200-4000 until the mirror-like surface was observed in microscope as shown in figure 6 (3). Finally, the top channels were covered with a quartz glass plate compressed with the outer case by bolts and nuts as shown in figure 6 (4). Both top surface and cross-sectional view of a sample were visualized by field emission scanning electron microscope (FESEM).

![Fig. 6 Miniature-size DPF sample preparation](image)

3. RESULTS AND DISCUSSION

3.1. Size of alumina particles under different suspension concentration

Alumina nanoparticle liquid, which has the primary particle size around 40nm, was diluted by distill water into four different concentrations including: 1.2wt%, 2.3wt%, 4.6wt% and 23wt%. Alumina particles produced by equipment, shown in figure 3, were trapped on a glass fiber filter for 15 minutes. Most of aggregates were shaped spherically for all four cases. Figure 7 demonstrates the water droplet drying mechanism. After passed through a heater, water will be evaporated, only alumina remained and it aggregated with other particles, which yield the secondary alumina particle aggregation. The higher the suspension concentration, the larger the particle size because they have a higher number of alumina primary particle in the certain size of water droplet, produced by the atomizer. Figure 8 (A), (B), (C) and (D) represent the SEM images of aggregated alumina particles from suspensions with a concentration of 1.2wt%, 2.3wt%, 4.6wt% and 23wt%, respectively. The average diameter of aggregated-alumina particle (dₐₐᵥ) was estimated from 50 aggregated particles per each case, which are: 0.5µm, 0.8µm, 0.9µm, and 1.5µm, respectively.
### 3.3. Pressure drop during membrane fabrication

According to a previous study, the results showed that smaller-particle size and higher-superficial flow velocity gave a higher pressure drop due to the deep penetration into surface pore of DPF [3]. Therefore, large-alumina particles \( \sim 1.5\mu m \) were selected as a base layer of the membrane as well as using a low superficial flow velocity in order to minimize an initial pressure drop. During membrane fabrication, pressure drop increased with respect to particle loading. The shape of pressure drop tends to be an s-shape like the case that we found in soot trapping on DPF as shown in figure 10 (top); that means, alumina particle has full filled the bridging and surface pore filtration phase already. After completion of surface pore filtration phase, we stopped introducing large alumina particles, meanwhile, small-alumina particles \( \sim 0.5\mu m \) were continuously trapped on the top of a first layer. The reason we pick small particles on top is that it has a higher filtration efficiency that can prevent soot penetrate through base layer. Finally, two-layers membrane, consisted of large particles at based and small particles on top, was successfully fabricated on conventional DPF as shown in figure 11.

### 3.2. Membrane sintering

Figure 9(a), (b), (c) and (d) show SEM image after 4-hour sintering at 1370K, 1470K, 1570K and 1670K, respectively. The structure of the membrane remained the same except in the case of 1670K; the porous structure was destroyed because the particles melted and aggregated. Thus, the suggested condition is 1570K.

To confirm stability of membrane, soot trapping test with a high superficial velocity was made. Using the membrane sintered at 1570K, there is no damage by a high superficial velocity soot trapping, and no crack in this membrane after ultrasonic vibration and cross section polishing.

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**Fig. 7** Schematic of aggregation of alumina particle in case of high-concentration (top) and low-concentration liquid (bottom)

**Fig. 8** FESEM images of aggregated alumina particles

(A) \( d_{ave} = 0.5\mu m \)  
(B) \( d_{ave} = 0.8\mu m \)  
(C) \( d_{ave} = 0.9\mu m \)  
(D) \( d_{ave} = 1.5\mu m \)

**Fig. 9** SEM image of membrane sintering under (a)1370K, (b)1470K, (c)1570K and (d)1670K

**Fig. 10** Pressure drop during membrane fabrication (Top). Cross sectional FESEM image of DPMF in case of 1.5µm diameter alumina particle (Bottom)
Fig. 11 SEM image of two layers membrane made of alumina particle, yellow line shows the interface between two layers

To explain these phenomena, Darcy’s law was applied as formulated in following equation:

\[ k_{\text{Darcy}} = \frac{v\mu}{L}\Delta P \]  

(1)

Here: \( k_{\text{Darcy}} \) is permeability, \( v \) is discharge velocity, \( \mu \) is viscosity, \( L \) is thickness measured by the cross-sectional FESEM image of membrane, and \( \Delta P \) is pressure drop. The permeability calculated under each condition are shown in table 1. The permeability of membrane became higher for the larger size of particle. In addition, the permeability of membrane was almost the same as soot cake layer [10], it means this membrane has a high permeability and a low pressure drop.

To verify the high permeability, the porosity of membrane was obtained as following equation:

\[ \phi = 1 - \frac{\Delta m}{\rho_{\text{Al}_2\text{O}_3} \times V} \]  

(2)

Where: \( \Delta m \) is the total weight of material used for membrane fabrication, \( \rho_{\text{Al}_2\text{O}_3} \) is the apparent density of aggregates assuming that the primary nanoparticles were composed of alumina and formed aggregates; where \( V \) is the volume of cake obtained geometrically through visualization of the membrane layer thickness. As shown in Table 1, the membrane with a large aggregate lead to a filtration with low pressure drop.

### Table 1  Relationship aggregate average diameter, permeability and porosity for each membrane

| Case | Aggregate average diameter | Permeability | Porosity |
|------|---------------------------|--------------|----------|
| A    | 0.5µm                     | 1.2 x 10^{-14} m² | 79%      |
| D    | 1.5µm                     | 4.1 x 10^{-14} m² | 90%      |

3.4. Pressure drop during Soot Trapping

Figure 12 shows a cross-sectional FE-SEM image of soot trapping on a DPF coated with alumina layer. From the image, soot cannot pass through the membrane into the DPF wall, but it can formulate soot cake layer only on the membrane structure surface. As a result, a low initial pressure drop and a low increasing rate of pressure drop can be achieved by two-layered membrane filters.

Figure 13 shows the pressure drop during soot trapping process. In case of membrane with a 0.5µm particle diameter, the pressure drop increases linearly with respect to soot loading time. As a result, only soot cake layer filtration occurs. On the other hand, in the case of 1.5µm particles showing the s-curve feature, the pressure drop increases similarly to conventional DPF without membrane from the beginning to 100 second, although the increase rate is not so high compared with that of without membrane. It may be shown that there are small and shallow surface pores even in the case of membrane with a 1.5µm particle diameter. In contrast, soot was trapped only on surface of membrane made of 0.5µm aggregates particles.

As shown in Fig. 13, the initial pressure drop in case of membrane with a 1.5 µm aggregate average diameter is much smaller than that of membrane with a 0.5 µm diameter. On the other hand, in case of membrane with 0.5µm diameter, there is no drastic increase in pressure drop around the beginning of soot
trapping. As a result, two layered membrane, which consists of membranes with a 1.5 µm diameter as a first layer, and a 0.5 µm diameter as the second layer, has combined the advantages of both type of membrane, and shows the lowest pressure drop for soot trapping among others. Using the multilayer membrane, the small and shallow surface pores at the beginning of soot trapping almost disappeared. Consequently, the pressure drop in case of multilayer membrane increases almost linearly from the beginning of soot trapping as well as the initial pressure drop at the beginning of soot loading does not increase so much compared to the case of membrane with a 1.5 µm diameter particle alone.

3.5. Catalyst layer

The morphology of AgPd primary particle, synthesized by chemical reducing method, was analyzed via transmission electron microscope (TEM). The lattice fringe spacing fcc(111) of AgPd particle, averaged from 50 fringes, was measured around 2.29 angstrom (Å), which is between the lattice fringe spacing of Ag (2.4 Å) and Pd (2.2 Å). This indicated AgPd is formed as an alloy structure [11] [12]. The average diameter-size of primary particle was in the range of 5-10 nm as shown in figure 14. AgPd catalyst was supported on only surface of membrane by trapping catalyst using the same equipment as alumina, shown in figure 3. By doing this, most of all catalyst could contact soot and exert the catalysis effectively. To observe the aggregated catalyst particle trapped on alumina membrane filter, back scattered electron (BSE) mode in FESEM was used. In BSE mode, the elements which have large atomic number tend to be brighter; in our sample, AgPd appears as a brighter particle compared to alumina particle as shown in figure 15. The size of aggregated catalyst particle is around 50-100 nm measured by FESEM. The size of final catalyst particle trapped on membrane (figure 15) became larger than primary particle (figure 14) because during the catalyst fabrication process, the catalyst primary particle agglomerates within the water droplet as same as in the case of alumina membrane fabrication process as shown in figure 7.

3.5. Temperature programmed oxidation (TPO) results

Temperature programmed oxidation of two types of DPF, including conventional type and AgPd catalyst on alumina membrane coated type, were compared in order to distinguish the effects of catalyst on soot oxidation. By observing through a microscope, all of soot trapped on the conventional DPF (figure 16) was considered to be present as a thick cake layer, while the soot trapped on the AgPd-catalyzed DMPF (figure 17) was considered as a thin-disperse soot cake because we obtain the high-catalyst/soot ratio in order to observe the catalyst performance. During soot regeneration, the off-gas concentration reflects the total amount of soot which oxidized into CO, and CO2. Figure 16 presents the TPO of conventional type DPF. In the absence of catalyst CO was dominant over CO2, which is a normal phenomenon of soot regeneration. On the other hand, in the presence of catalyst CO2 was dominant over CO as shown is figure 17. That means, AgPd catalyst has ability to converse CO into CO2 which is called solid-gas reaction between catalyst and CO gas. The CO gas was adsorbed on the surface of AgPd, then the CO oxidation was promoted crucially by oxygen activation all over close-packed fcc(111) surfaces of AgPd on membrane [13].

In addition, the peak of soot oxidation on catalyzed membrane appeared around 500°C, while the peak of soot oxidation on conventional DPF was found around 615°C. That means the AgPd catalyst plays important role in decreasing the soot-oxidation temperature by reduction of activation energy for soot oxidation. The mechanism of soot-oxidation reaction influenced by catalytic effects was explained by diffusing of reactive oxygen species from the surface of catalyst to surface of soot. More oxygen vacancies facilitate adsorbing more reactive
oxygen species from gaseous oxygen, which then diffuse through the crystalline structure to the contact point between soot and catalyst and oxidize soot. As a result, the contact surface between catalyst was found to be the major impact of this solid-solid-gas reaction, the high ratio of contact, the better soot oxidation reaction. Moreover, since the catalyst layer is very thin like dispersed nanoparticles cover the alumina membrane, the residence time for CO to CO\textsubscript{2} conversion might be insufficient. Thus, a direct reaction from carbon (soot) to CO\textsubscript{2} by reactive oxygen species is dominant over the solid-gas reaction between catalyst and CO gas. As a result, we could see the emission of CO\textsubscript{2} start from 250°C by a high activity of reactive oxygen species as shown in figure 17.

Filter can eliminate the surface pore filtration by soot and obtain a low pressure drop with high filtration efficiency from the beginning of soot trapping compared with a conventional DPF.

Silver-palladium catalyst, sized around 50-100nm, was coated on the top surface of alumina membrane filter with a similar method as alumina membrane fabrication. It can provide a low soot oxidation temperature which has a peak around 500°C, 115°C lower than a peak of conventional DPF. Moreover, it can converse CO into CO\textsubscript{2}, which is better in terms of an environmentally friendly technique.

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