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A study of Multi-Functional Membrane Filters made of Fine Catalyst Particles

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ABSTRACT

A multi-functional membrane filter was developed through deposition of agglomerated Three-Way Catalyst particles with a size of 1 ~ 2 microns on the conventional bare particulate filter. The filtration efficiency reaches almost 100 % from the beginning of soot trapping with a low pressure drop and both reductions of NO and CO emission were achieved.

INTRODUCTION

Recently, development of electric vehicles (EVs) is accelerated drastically accompanied with research and development of electric batteries from a point of view of achievement of carbon neutrality. According to a scenario of CO_2 net-zero emission by 2050 [1], the direct consumption of fossil fuels should be reduced up to 1 or 2 % among the total energy consumption: others are renewable energies, produced hydrogen and ammonia (sometimes accompanied with carbon capture storage) and nuclear energy. However, it takes long time to develop a sustainable society using carbon free power trains. During a modal shift process, there are some choices to decrease the emission of pollutants including CO_2. The one of important issues is an increase in thermal efficiency of all energy conversion systems including internal combustion power trains. The other is a choice of carbon free fuels such as hydrogen, ammonia and synthesized fuels. It is still very challenging to develop those from a balance between the output power and the emission control and from how to produce from the primary energy source. The higher the thermal efficiency is, the lower the exhaust gas temperature: as a result, it is not easy to complete the zero-emission of pollutants using the conventional after-treatment systems under a low temperature condition. On the other hand, depending on the kind of carbon-free fuels, the amount of chemical species compound emitted from power trains will be changed: as a result, we have to prepare many kinds of catalyst converters to achieve zero emission of pollutants. Moreover, even if we can use a perfect carbon-free fuel, particulate matters including soot and ash will be emitted because of oxidation of lubricant oils and wear at any contact sliding portions in the internal combustion power trains especially for vehicles. Consequently, a new concept of after-treatment system should be needed to develop zero-emission technologies accompanied with development of high thermal efficiency power trains.

The authors proposed a membrane filter made of spherical particles with a mean diameter of 1 ~ 2 microns [2] and a porosity of around 60 % [3] for a new filter with a high filtration efficiency and a low pressure drop for diesel particulate filters (DPFs) and gasoline particulate filters (GPFs). The spherical particles membrane filter has a potential and a flexibility to customize the design of any catalysts depending on the kinds of pollutant species and make a superimposed multi-layer. In addition, since the mean pore size is approximately several microns, the filtration efficiency for particulate matters will be expected to achieve almost 100 % from the beginning of trapping with a low pressure drop increase. Because the concept comes from a time-lapse visualization of soot trapping using scanning electron microscopy [4, 5]. In the current study, using the conventional three-way catalyst nanometer-sized particles, a multi-functional membrane filter with a high filtration efficiency, a low pressure drop and a high catalytic activity is developed and evaluated experimentally.

EXPERIMENTAL SETUP AND METHOD

Figure 1(a) and 1(b) show miniature-sized particulate filter samples composed of 7 x 7 channels with a dimension of 10 mm^3. Those were cut off from the conventional full-size particulate filter substrates made of cordierite and silicon carbide. A high temperature-resistance ceramic paste was used to plug at both

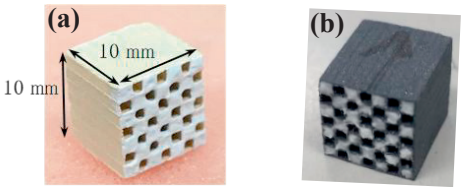

Fig.1 Miniature sized filters made of cordierite (a) and SiC (b)

ends of the channels alternately to make a wall-flow, in which a working gas passes through the channel wall. Those samples were set up inside a stainless-steel holder as shown in Fig.2. The top horizontal wall was removed and then the cross-section of the vertical wall was polished to achieve up to a mirror-like grain surface by using various abrasive discs (P600 to P4000). The top surface was covered by a quartz glass plate to close the open channels and to seal the working gas flow through the clearance between the glass plate and the mirror-like grain surface of the substrate. Since the glass can be removed and set up easily, deposition under atmospheric condition and visualization by SEM under vacuum condition have been easily made alternatively for a time-lapse SEM visualization [4, 5].

(a) Cordierite (b) SiC

Fig.2 Filter holders with an open channel for time-lapse SEM visualization

Figure 3 shows a schematic diagram of fabricating a Three-Way Catalyst (TWC) particles membrane filter on the conventional filter substrates. A slurry of primary nanometer-sized TWC particulates (approximately 200 nm in average diameter as shown in the SEM image in Fig.3) with distilled water is prepared: the weight percentage of TWC particulates is 20 wt%. The chemical composition of the primary TWC particulates is the same as that of commercialized monolith converter as shown in Table 1. The TWC particulates slurry was placed in an acrylic tube and atomized into small droplets (approximately 5-10 microns) using an ultrasonic atomizer (60 Hz frequency). The carrier gas (Nitrogen) was introduced into the acrylic tube to push out the atomized water droplets under a flow rate of 50 mL/min. Then, gas suspended water droplets including TWC particulates flow out from the tube. After that, a dilution gas was mixed to obtain the desired superficial velocity and a lower humidity than a dew point even at the room temperature. The nitrogen gas-diluted dispersant water droplets were introduced into an evaporator which is kept at constant temperature of 280°C by using a ribbon heater. Since only water was vaporized, the primary TWC particulates was agglomerated as show in the SEM image in Fig.3. The agglomerated nitrogen dispersant TWC particles with a size of 1 or 2 microns were deposited as a membrane layer on the conventional bare particulate filter substrate. The thickness of the TWC-particles membrane is approximately 50 μm. The size of the agglomerated TWC particle can be controlled by weight percentage of the primary TWC particulate in the slurry. During fabricating the membrane, the pressure drop increase according to the deposited weight was measured using a high-precision digital manometer by tap-fixing at the upstream and the downstream sides of the sample, P_1 and P_2, respectively, as shown in Fig.3.

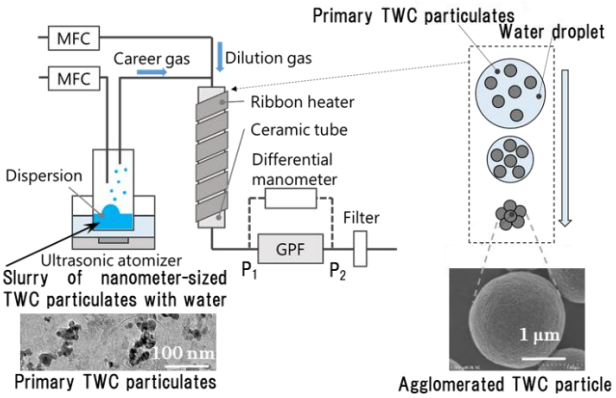

Fig.3 Schematic diagram for fabricating agglomerated TWC particle

Table 1 Chemical composition of catalyst slurry

Chemical compounds		%
Palladium oxide	PdO	1.45
Rhodium oxide	Rh_2O_3	0.26
Cerium oxide	CeO_2	18.3
Zirconium dioxide	ZrO_2	26.1
Aluminum oxide	Al_2O_3	47.7
Lanthanum oxide	La_2O_3	3.28
Neodymium oxide	Nd_2O_3	2.90

Figure 4 shows a schematic diagram setup for soot trapping. The soot is generated by electric discharge in a gap between carbon electrodes (DNP-2000, Palace). Nitrogen gas is used as a carrier gas for introducing soot into membrane filters set up in the GPF holder. In order to investigate an effect of TWC on soot oxidation, after small amount soot deposition, concentration of CO_2 is measured through a temperature program oxidation method using an oxygen concentration of 20 % from a point of view of a fuel-cut operation.

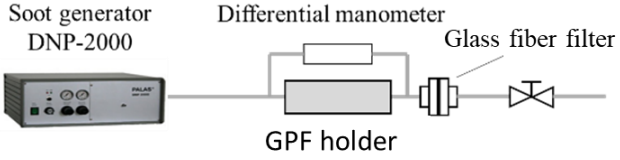

Fig.4 Schematic diagram of setup for soot trapping

In addition, simultaneous reduction of emission of CO and NO by TWC particles membrane filter is evaluated using a mixture of components as shown in Table 2.

The ratio of components without oxygen concentration is similar to the practical one [6] though the concentration is 12 times lower due to the limitation of gas supply system. The emission concentrations of CO and NO after passing through the TWC particles membrane are detected by an infrared gas analyzer (CGT-7100, Shimadzu) and a chemical luminescence nitrogen oxide analyzer (NOA-7000, Shimadzu), respectively.

Table 2 Gas species condition (1.9 L/min.)

Species	Concentration (ppm)
CO	200
NO	58
C_3H_6	25
O_2	125
N_2	Balance

MANUFACTURING MEMBRANE FILTERS

Figure 5 shows a pressure drop increase during manufacturing of the TWC particles membrane on the cordierite GPF substrate. The superficial velocity is 5.4 mm/s and the concentration of TWC particulates in slurry is 20 wt%. Figure 6 shows time-lapse SEM images of cross-sectional views during deposition of TWC particles. From the beginning of deposition of TWC particles, the pressure drop increases drastically up to the inflection point from 8 Pa to around 20 Pa with respect to time as shown in Fig.5 to make a bridge at the first narrow area in the surface pore as shown in Fig.6. After that, the TWC particles accumulate in the surface pore as shown in Fig.6: as a result, the pressure drop increases more from 20 Pa to around 40 Pa. After the surface pore is filled up, the TWC particles are deposited on the surface of the substrate wall as a cake layer. Then the pressure drop increases linearly. Those deposition phenomena are very similar to those of soot trapping obtained by the same time-lapse SEM visualization method [4, 5].

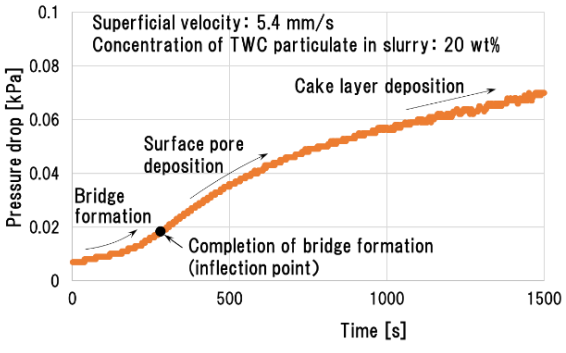

Fig.5 Pressure drop increase during deposition of TWC particulates on the conventional cordierite GPF substrate

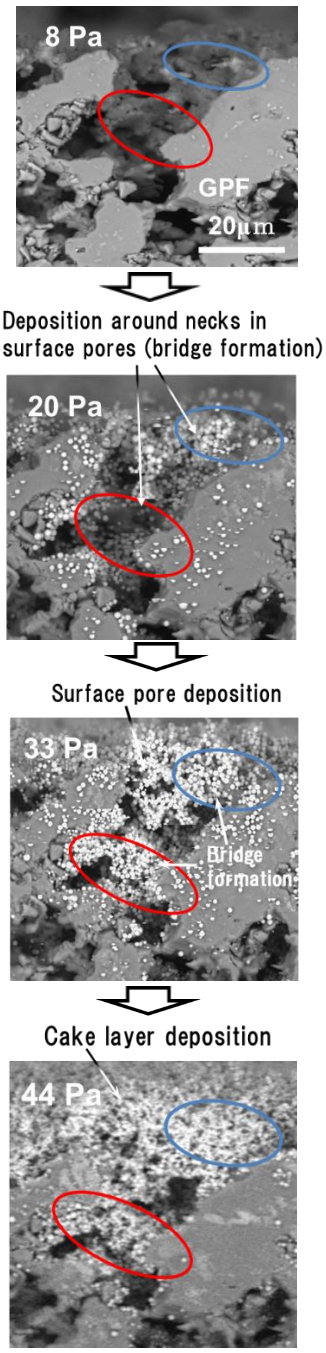

Fig.6 Time-lapse SEM images of cross-sectional views during deposition of TWC particles around surface pores of cordierite GPF substrate

Figures 7(a) and 7(b) show TWC particles membrane filters made on the cordierite substrate and on the SiC substrate, respectively. The thickness of membrane layer is around 50 μm. For a low pressure drop filter, the permeability which depends on the porosity and the mean diameter of TWC particles [7] is a significant parameter. The porosity measured by the previous work [3] was around 64 %, while the mean diameter is around 1.2 μm.

Although the permeability becomes higher with increasing diameter, it is not easy to introduce such a large TWC particle by the working gas suspension method presented here. As a result, the permeability

obtained in the previous work was around $1.2x10^{-14}$ m^2 [3]. In addition, it is very important to avoid deposition at deep area. As shown in Figs.7(a) and 7(b), most of all TWC particles are deposited around shallow area in the surface pores, using a low superficial velocity.

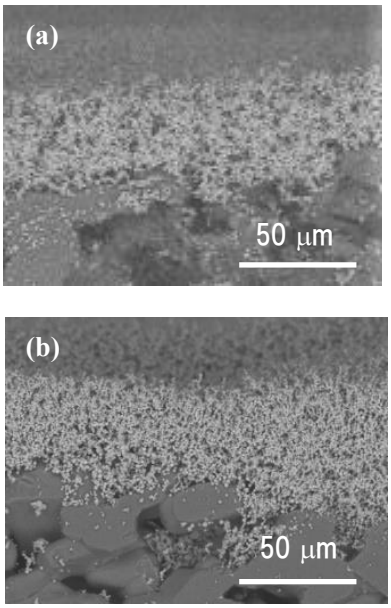

Fig.7 SEM images of cross-sectional view of TWC particles membrane on cordierite (a) and SiC (b) GPF substrates

SOOT TRAPPING BY TWC MEMBRANE FILTERS

Figure 8 shows a comparison between pressure drop increases during soot trapping process by the membrane filter and by the conventional bare filter. The superficial velocity is 25 mm/s which is similar to the conventional gasoline particulate filter. In the case of conventional bare filter as depicted by a grey line, the pressure drop increases drastically from the beginning with an S-shape since a bridge by soot is formed and then much amount of soot is stacked in the surface pores as visualized in the previous work [4, 5]. On the other hand, in the case of membrane filter as depicted by a blue line, although the initial pressure drop is much higher than that of the conventional one, the pressure drop increases almost linearly which means that the soot accumulation in the surface pores can be prevented and then only soot cake layer filtration takes place. As a result, the pressure drop for the TWC membrane filter becomes lower than that for the conventional bare filer during soot is stacking in the surface pore of the conventional bare filter (later than 240 seconds).

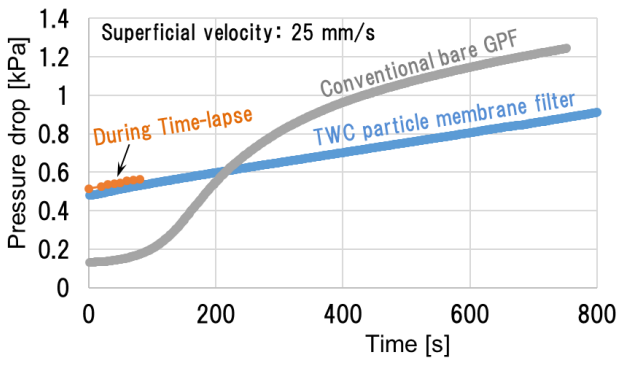

Fig.8 Pressure drop increase during soot deposition on TWC particles membrane filter on the cordierite GPF substrate and the conventional bare cordierite GPF

Figure 9 shows time-lapse scanning electron microscopic visualization images (top views) at the elapsed time of 20, 30 and 50 seconds, respectively. Since the surface pore size is much the same as that of TWC particle: that is 1 or 2 μm, the bridge formation is completed up to 20 sec. later. Moreover, the surface pore depth is very shallow: that might be 2 or 4 μm. As a result, as shown by orange symbols in Fig.8, the pressure drop increases almost linearly from the beginning of soot trapping and become much the same pressure drop as that of the continuous measurement as shown by the blue line in Fig.8. It is noted there is no soot trapped by a glass fiber filter set up at the exit of the TWC particles membrane filter. It is clearly shown that the filtration efficiency is almost 100 % from the beginning of soot trapping.

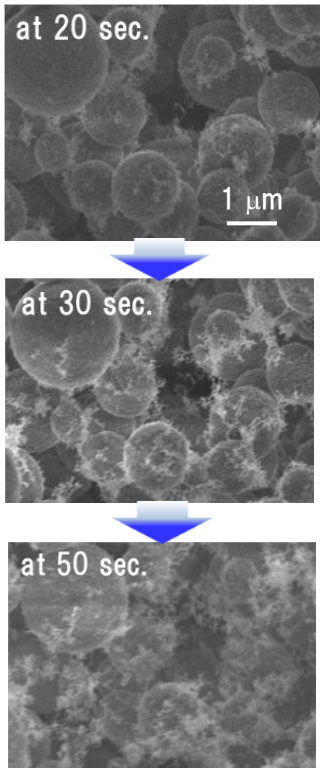

Fig.9 Time-lapse SEM images of surface views during soot deposition on the surface of TWC particles membrane filter

SOOT OXIDATION AND SIMULTANEOUS REDUCTION OF CO AND NO BY TWC PARTICLES MEMBRANE FILTER

Figure 10 shows an emission concentration of CO_2 by temperature program oxidation of soot trapped on the TWC particles membrane filter using a working gas with an oxygen concentration of 20 % (N_2 balance). The ramping rate for temperature rise is 10 Degrees/min. Before the experiment, CO_2 adsorbed on the TWC particle surface was removed by N_2 gas supply at 600 Degrees Celsius. Then, the soot of 45 mg/L is loaded to investigate an enhancement of oxidation of soot contacted with the TWC particles. Although some emission of CO_2 could be detected around 500 Degree Celsius, soot oxidation takes place mainly in a range of temperature from 600 to 700 Degrees Celsius. In the TWC particles, catalyst metals such as Pd and Rh supported by an oxygen storage material such as ceria are included. However, since there is only small contact area between soot particles and TWC particles as shown in the time-lapse SEM visualization in Fig.9, it is not easy to reduce the oxidation temperature even in the case of small soot loading under the condition of a loose contact or a tiny contact as usually experienced in the practical soot trapping.

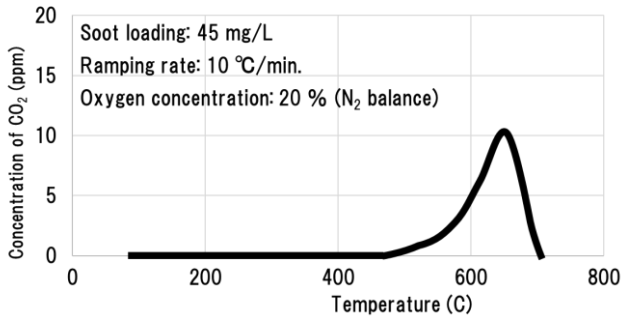

Fig.10 Temperature program oxidation of soot trapped on the TWC particles membrane filter

Figure 11 shows emission concentrations of CO and NO through isothermal conversion reaction by the TWC membrane filter under the condition of the temperature of 475 Degrees Celsius and the mixture components of CO (200 ppm), NO (58 ppm), C_3H_6 (25 ppm), O_2 (125 ppm) and N_2 (balance) as shown in Table 2. The Space Velocity (SV) is 114,000 /h. In this case, the superficial velocity of 25 mm/s is similar to that of the conventional gasoline particulate filter. The conversion of CO and NO achieved 94% and 93%, respectively. In this case, oxygen concentration is fixed to obtain the maximum conversion of CO and NO, simultaneously. In usual cases, since oxygen concentration is close to that of CO, the conversion of CO is almost 100 % at the same temperature of 475 Degrees Celsius, while the conversion of NO will be reduced up to 80 or 85 % [8, 9]. Moreover, in the case of modulation between lean and rich fuel/air ratios, depending on the frequency and the diffusion rate of oxygen in the oxygen storage materials, both conversion will be increased [8]. In the current case of TWC particles membrane filter with a thickness of 50 μm, despite the residence time of reactants passing through the membrane is only 5 milliseconds, the simultaneous reduction of CO and NO emission is achieved up to a competitive to those by the conventional one. Although emission concentration of C_3H_6 is not measured, it might be converted with much the same conversion or more.

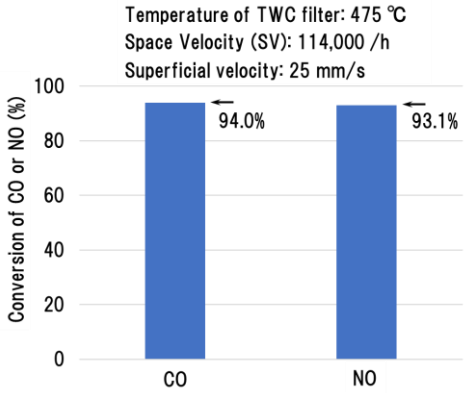

Fig.11 Conversion of CO and NO by TWC particles membrane filter

CONCLUSION

A Three-Way Catalyst (TWC) particles membrane filter was developed for a high soot filtration efficiency with a low pressure drop and simultaneous reduction of CO and NO emission. A highly-porous TWC particles membrane filter was consisting of agglomerated TWC particles with a size of 1 ~ 2 microns. The filtration efficiency reaches almost 100 % from the beginning of soot trapping. The pressure drop increase becomes lower than that of the conventional gasoline particulate filter. Moreover, simultaneous reduction of CO and NO emission can be achieved. However, since the soot oxidation is not enhanced by loose contact between soot and TWC particles, another functional particles membrane layer for soot oxidation should be superimposed on the top of the TWC particles membrane layer. As a result, the particles membrane filter has a potential to customize the functions and superimpose together for zero-emission technologies.

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