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**Investigation of Percolation Structure Durability and Oxygen-
atom Diffusion-controlled Reaction in Three-way Catalyst
Membrane Filters**

by

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*A dissertation submitted for the degree of Doctor of Philosophy in
Mechanical Engineering*

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Abstract

A Three-way Catalyst (TWC) particles membrane filter was fabricated to enhance initial soot filtration efficiency and reduce gaseous pollutant emissions in a single unit. Electron microscopy image analysis was utilized to measure the porosity of the cross-sectional area of the membrane, while its durability was investigated at various sintering temperatures. Furthermore, isothermal oxidation of CO through the TWC membrane filter was conducted under low-temperature conditions. In the experiment, a significant decrease in CO₂ emission with respect to time was observed. A numerical simulation model on diffusion-controlled oxygen transport through ceria-zirconia (CZ) particulates was developed for the CO oxidation. The simulation results indicated that the transport distance of oxygen atoms was constrained due to the agglomeration structure of TWC particles.

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Chapter 1

Introduction

1.1 Research background

To achieve the goal of net-zero emission by 2050 set by the International Energy Agency (IEA) as described in **Fig. 1**, the urgent need for a global transition to clean energy sources in order to mitigate the effects of climate change were mainly highlighted [1]. According to the EAA report in 2018 [2], the transport sector has been facing with the task of reducing emissions while accommodating the growing demand for transportation, with road transport currently being the second largest source of CO₂ emissions as shown in **Fig. 2**. Owing to transition of sustainability for the fuels used in automotive vehicles, utilization of synthetic fuel, also known as E-fuels, instead of fossil fuels will play a major role, which can enable a nearly-carbon-neutral operation of internal combustion engines [3-5].

Presently, the Mahle and Porsche companies are actively exploring the feasibility of applying synthetic fuel in engine test benches and conducting road tests using vehicles [6]. The main advantages of synthetic fuels (also well-known as E-fuels) is that the production process utilizes renewable electricity, atmospheric CO₂ extracted from the air, and hydrogen derived from water as described in **Fig. 3** [7]. This innovative approach can substantially reduce greenhouse gas (GHG) emissions, contributing to the mitigation of environmental impact. Besides, E-fuels can be used as standalone fuels or mixing with conventional fuels at any ratio for a better performance. Preliminary findings from engine test bench experiments have revealed significant potential in reducing particulate and gaseous pollutants emissions using the synthetic fuel [8, 9].

Although the innovative alternative fuels are promising for the future emission target, lubrication system in an engine is also one of the important systems to take into account in order to satisfy with the goal. The lubrication system is essential for minimizing friction, dissipating heat, removing contaminants, preventing corrosion, and increasing the longevity of the engine. On the other hand, the hydrocarbon composition of the lubrication system in an engine might still have a minor impact on the emission of solid soot particles and gaseous pollutants in the exhaust gases [10, 11].

Thus, in order to achieve the ambitious goal of achieving net-zero emissions by 2050, it remains crucial to implement efficient and effective exhaust gas aftertreatment systems in future automotive vehicles. These systems play a vital role in reducing harmful pollutants emitted from vehicle exhausts, ensuring compliance with increasingly stringent emission regulations and addressing environmental concerns.

1.2 Exhaust gas aftertreatment system

The emission of exhaust gases from automobile engines has emerged as a significant contributor to air pollution, leading to a global concern for its adverse effects on public health. Consequently, there has been an increasingly tightening of emission standards in recent years [12]. These regulations aim to reduce the release of carbon monoxide (CO), hydrocarbons (HCs), nitrogen oxides (NO_x), and particulate matter (PM) originating from gasoline and diesel engines in vehicles. In this regard, effective after-treatment systems are essential for the purpose of purification of the exhaust gases from gasoline and diesel engines, respectively.

1.2.1 Gasoline particulate filter

A gasoline particulate filter (GPF) is designed to capture and reduce the emission of particulate matter (PM) from gasoline-fueled engines. It is similar in function to a diesel

particulate filter (DPF), which is commonly used in diesel engines. The GPF is typically made of porous ceramic material with a honeycomb-like structure. As exhaust gases flow through the filter, the fine particles suspended in the exhaust stream, including soot and other solid pollutants, become trapped within the filter's porous walls as described in **Fig. 4**. To maintain the efficiency and prevent the filter from becoming clogged, a process known as regeneration takes place. During regeneration, the accumulated soot and particulate matter are oxidized at high temperatures, either through passive or active regeneration process. Passive regeneration occurs naturally when the exhaust gas temperature is high enough to oxidize the captured particles. Active regeneration, on the other hand, involves introducing additional heat to facilitate the oxidation of the trapped particulates [13, 14].

1.2.2 Three-way catalytic converter

A three-way catalytic converter (TWC) plays a crucial role in reducing harmful gaseous pollutants emitted from the engine, specifically carbon monoxide (CO), nitrogen oxides (NO_x), and hydrocarbons (HCs). The TWC contains a ceramic or metallic substrate coated with various catalysts, such as platinum, palladium, and rhodium [15].

Cerium oxides (Ceria) are well-established oxygen storage materials that have been widely used in various catalytic applications. Ceria is a cubic fluorite structure in which the Cerium (Ce) cations occupy the corners of a cube, and the Oxygen (O) anions are located at the center of each face of the cube as shown in **Fig 5**. Besides, the chemical formula for Ceria (CeO₂) stands for two oxygen atoms for every Ce atom in the lattice. It is particularly important as a catalyst component in monolithic three-way catalytic converters (TWCs) installed in the exhaust gas aftertreatment system for gasoline engines [16, 17]. The main role of ceria in a three-way catalyst is as an oxygen storage material. Ceria has the ability to store and release

oxygen through redox (reduction-oxidation) reactions as shown in the conceptual schematic image of **Fig. 6**.

Through oxidation and reduction reactions, the TWC can effectively reduce all three pollutants (NO_x , CO, and HCs) simultaneously. The maximum yields of conversion can be achieved under the condition of the air-fuel ratio near the stoichiometric point (i.e., $A/F = 14.6$) for gasoline engines as described in **Fig. 7**. Even if there were fluctuation of concentration, especially oxygen concentration, in the positive (fuel-lean) or negative (fuel-rich) direction around the stoichiometric point, the excess oxygen can be stored by cerium oxides under the condition of fuel-lean while additional oxygen atoms can be supplied from cerium oxides under the condition of fuel-rich. Therefore, the range of air-fuel ratio for simultaneous reduction becomes wider slightly around the stoichiometric point as well-known as a window [18, 19].

To enhance the high-redox catalytic performance of Ceria in TWCs, Ceria-Zirconia (CZ) catalysts are commonly utilized to increase the oxygen storage capacity. Since the exhaust gas temperature in gasoline-fueled engines typically reaches around 900 °C, CZ is composited with Alumina (Al_2O_3) to prevent the sintering effect or thermal degradation [20].

1.2.3 Recent advances in catalytic converter

Several literatures have extensively investigated the purification performance of combination of Three-Way Catalytic Converters (TWCs) and Gasoline Particulate Filters (GPFs) using wash-coating technology, commonly known as catalyzed gasoline particulate filters (cGPF) as shown in **Fig. 8**. The most common arrangements of integrated layout for TWC and GPF were shown in the **Fig. 9**. Through the application of catalyst materials deposited on the cGPF's filter substrate, an integrated catalytic filter can offer a distinct advantage of not only trapping soot, but also facilitating the purification of gaseous pollutants in a single unit. [21, 22].

1.2.4 Membrane particulate filters

According to the previous works from our laboratory, various catalyst components were fabricated as a membrane on a conventional particulate filter substrate which can result significant effect on soot filtration and oxidation phenomena. In contrast to wash-coated catalyzed particulate filters, the catalyst particles were percolated as a membrane at the shallow area of the GPF substrate as shown in the schematic image of **Fig. 10**, which results in a significantly increased in initial soot filtration efficiency and the ability to produce membrane filters with low pressure-drop.

In an internal combustion engine, back pressure caused by particulate filters is the accumulation of soot along the pores of the substrate and the formation of soot cake layer. By using time-lapse visualization method, pressure-drop characteristics (S-shape) in the conventional DPF can be clearly identified into three major stages as bridging, surface pore filtration and cake layer formation. In the DPF, the drastic increase in pressure drop is the result of soot accumulation in the surface pores [23, 24]. Manufacturing membrane particulate filter on the conventional DPF is one of the solutions to lessen the substantial pressure drop increase caused by the surface pore filtration stage. In fact, when a membrane covers the entrance of the surface pore, soot is deposited only in the small pores of the membrane. As a result, high gradient of pressure drop increase caused by the surface pore filtration stage was significantly reduced as compared in **Fig. 11**. By fabricating a catalyst membrane on the conventional DPF, not only total increase in pressure drop was lower but also initial soot filtration efficiency became higher [25]. A diesel particulate membrane filter made of zeolite mixing with K, Na and Cs catalyst advanced soot oxidation kinetics compared to the conventional DPF. Because of the catalytic performance of mixed zeolite catalyst membrane, the activation energy needed to oxidize the soot cake layer during regeneration was reduced to about 20% [26]. Recently, a catalyst membrane made of nano- catalyst particles such as Pt-Pd and Ag-Pd fabricated on an

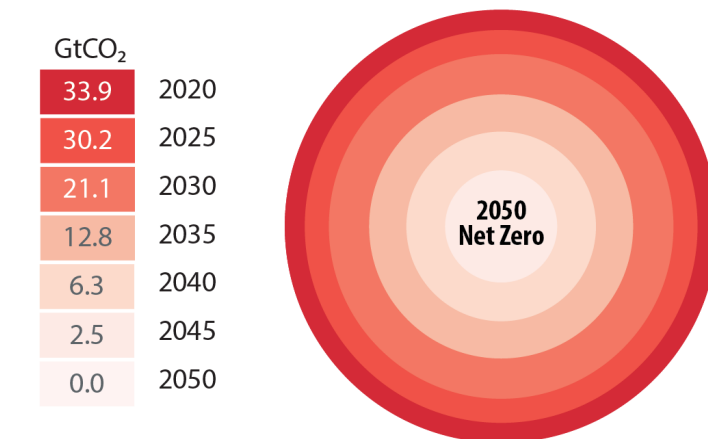
alumina supporter showed lower soot oxidation temperature and CO emission can be reduced [27, 28].

1.3 Objectives and contents of dissertation

In order to achieve a higher initial soot filtration efficiency, and to reduce the exhaust gaseous pollutants such as CO, NO_x and HCs emitted from gasoline-fueled engines, a three-way catalyst (TWC) particles membrane filter was fabricated. The contents of the dissertation for each chapter are summarized as followed. In chapter 1, current global challenges of the emissions of automotive vehicles and the importance of exhaust gas aftertreatment systems, research background, the fundamentals of aftertreatment system which are currently in use, the advanced technologies and the summary of previous works from our laboratory were discussed. In chapter 2, the fabrication process of TWC-particles membrane filter and the porosity of cross-sectional area of the membrane were measured. A parametric study was conducted in the fabrication process and porosity measurement by using different particle sizes and superficial velocities conditions. In chapter 3, CO purification performance of TWC-particles membrane was discussed through both isothermal and temperature-programmed oxidation experimental results. The durability and performance of the TWC-membrane were investigated under different sintering temperature conditions. In chapter 4, the elemental composition distribution of the TWC-particles were analyzed at first. In order to estimate the oxygen transport distance from the TWC-particles which are percolated as a membrane, a numerical simulation model was proposed for the isothermal CO oxidation experimental result. In chapter 5, to increase the specific surface of the TWC-particles, a porous TWC-particles membrane was fabricated. The pressure-drop increase in fabricating the membrane and porosity of the porous particles membrane were analyzed. Besides, the enhanced CO purification performance of porous

particles were compared to that of solid TWC-particles membrane. In chapter 6, conclusion and key findings of this study were summarized.

Figures



Source: International Energy Agency (IEA). 2021. "Net zero by 2050." Paris.
Note: GtCO₂ = gigatons of carbon dioxide.

Fig. 1 Net-zero emission target by 2050 [1]

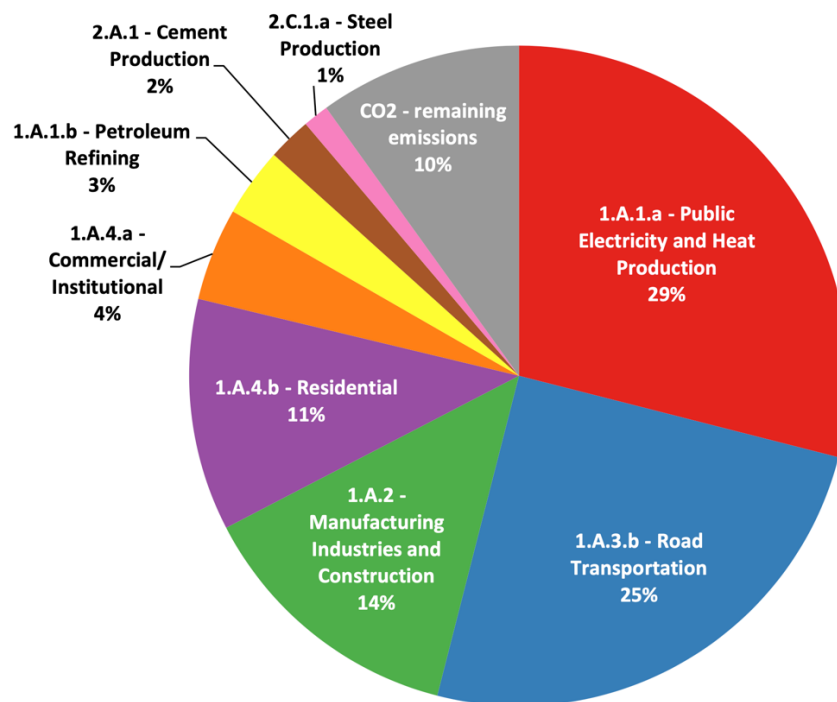


Fig. 2 Key source of CO₂ emission in 2016 for EU-28 and Iceland [2]

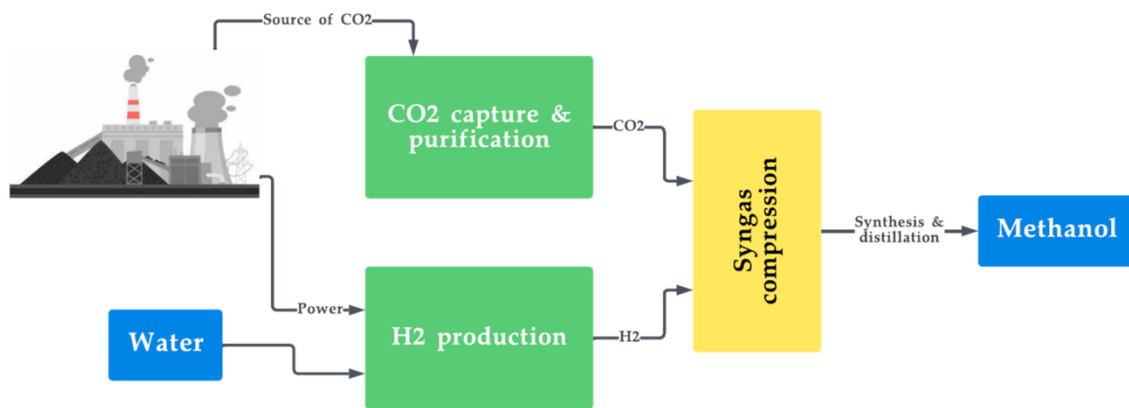


Fig. 3 Production of synthetic fuel from CO₂ capture and H₂ production [7]

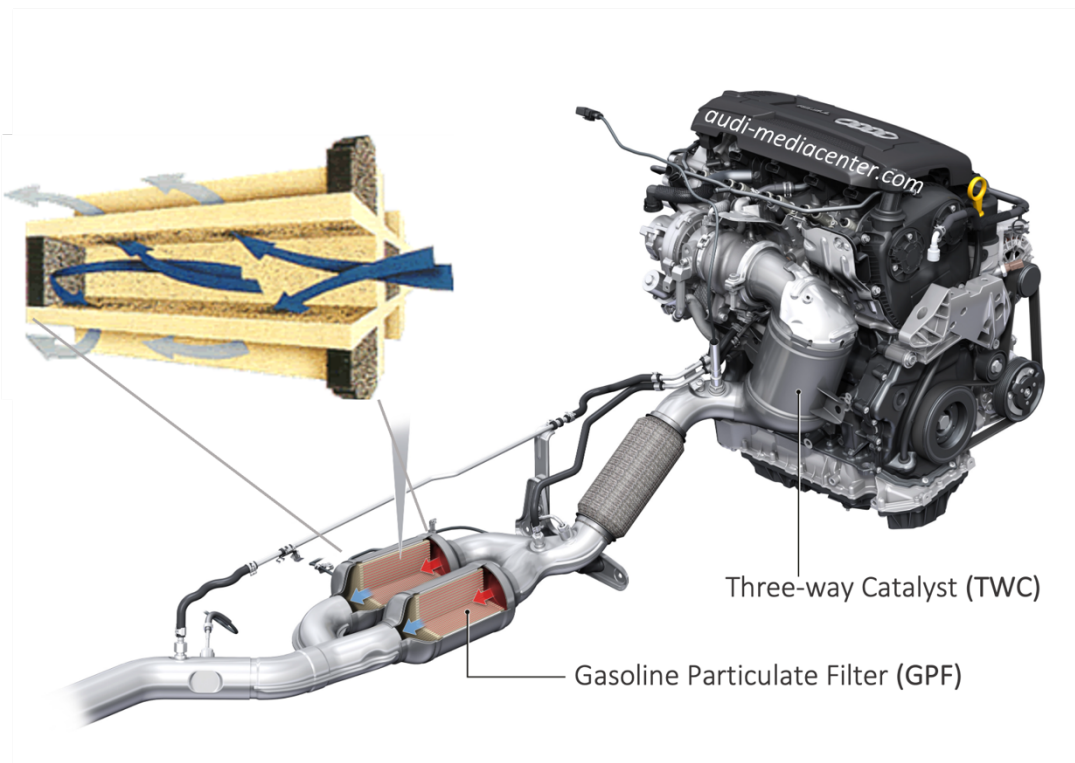


Fig. 4 Exhaust gas aftertreatment system in a gasoline fueled engine [15]

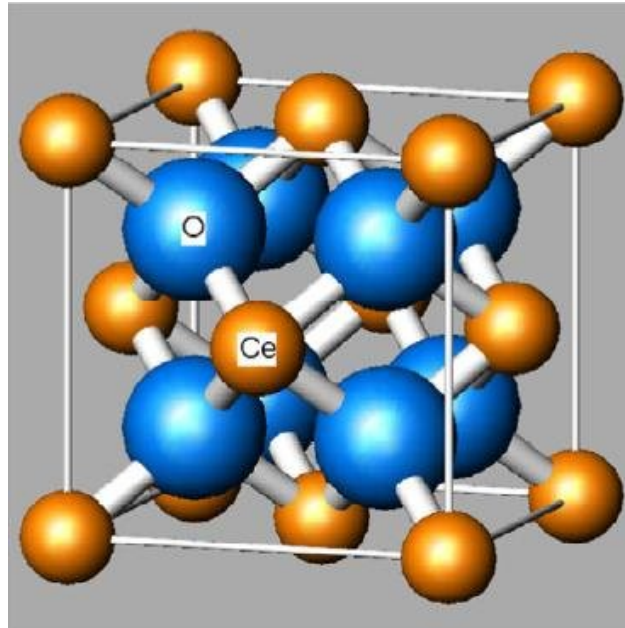


Fig. 5 Cubic crystallite structure of Ceria (Cerium oxide) material

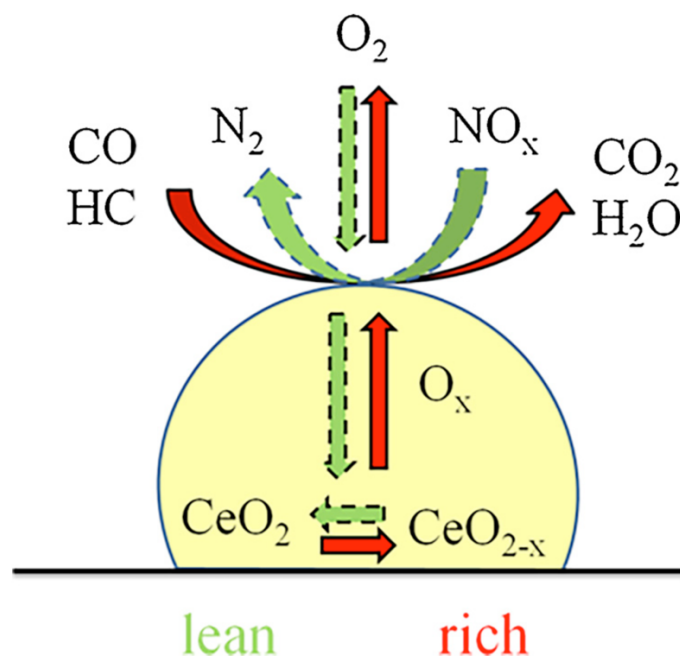


Fig. 6 The function of oxygen storage capacity under a redox condition in the automotive exhaust application [19]

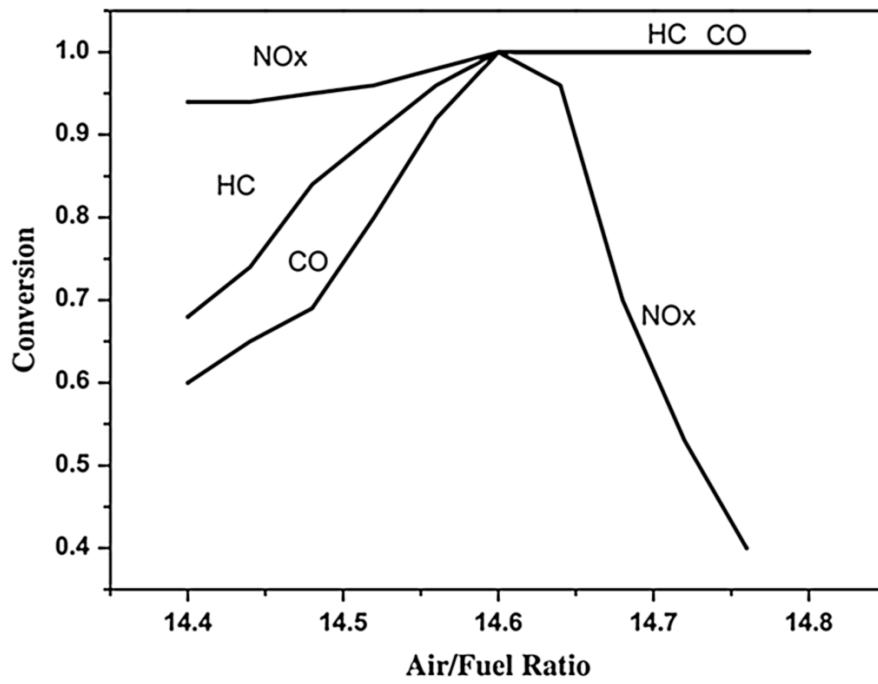


Fig. 7 The performance of TWC as a function of A/F ratio [19]

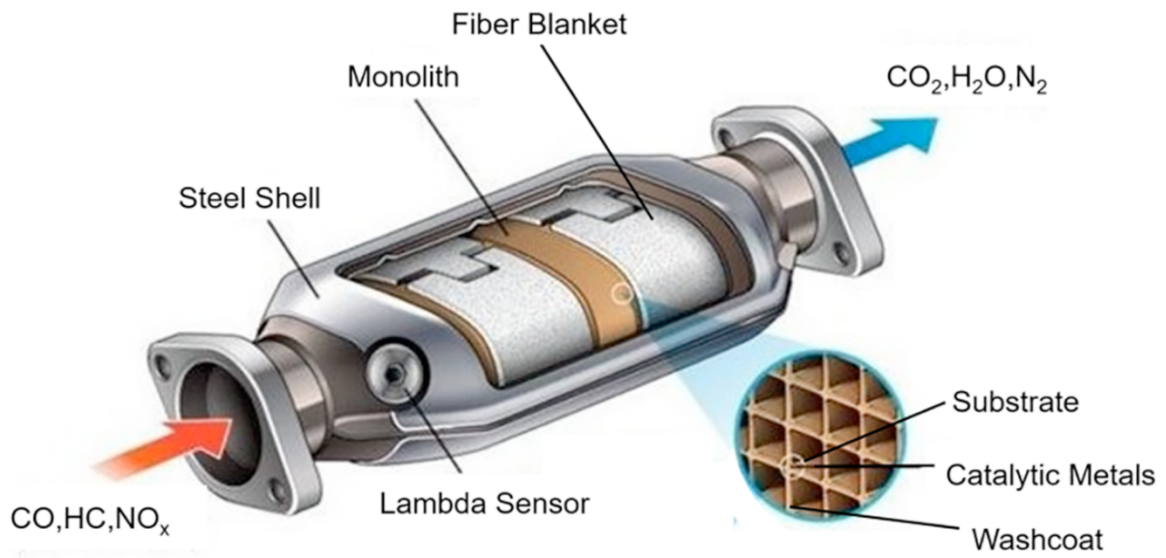


Fig. 8 Catalyzed gasoline particulate filter (cGPF) [21]

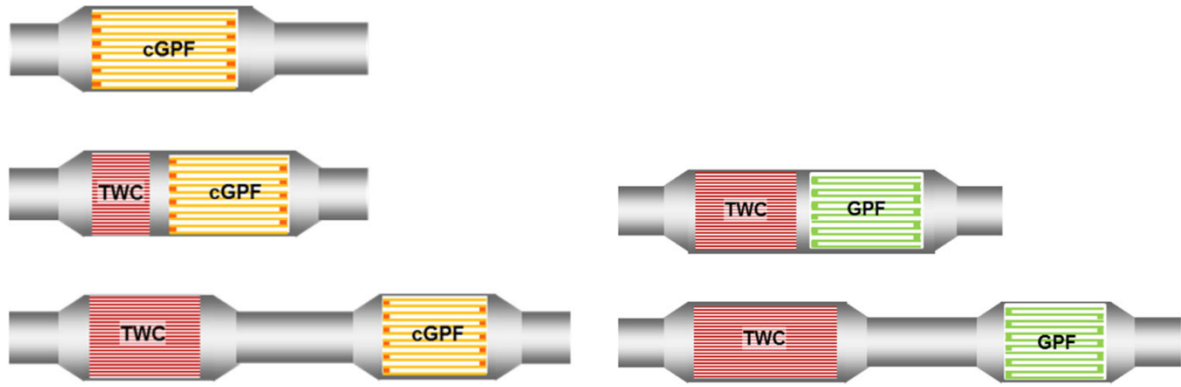


Fig. 9 The common arrangements of integrated layouts for combination of TWC and GPF

[22]

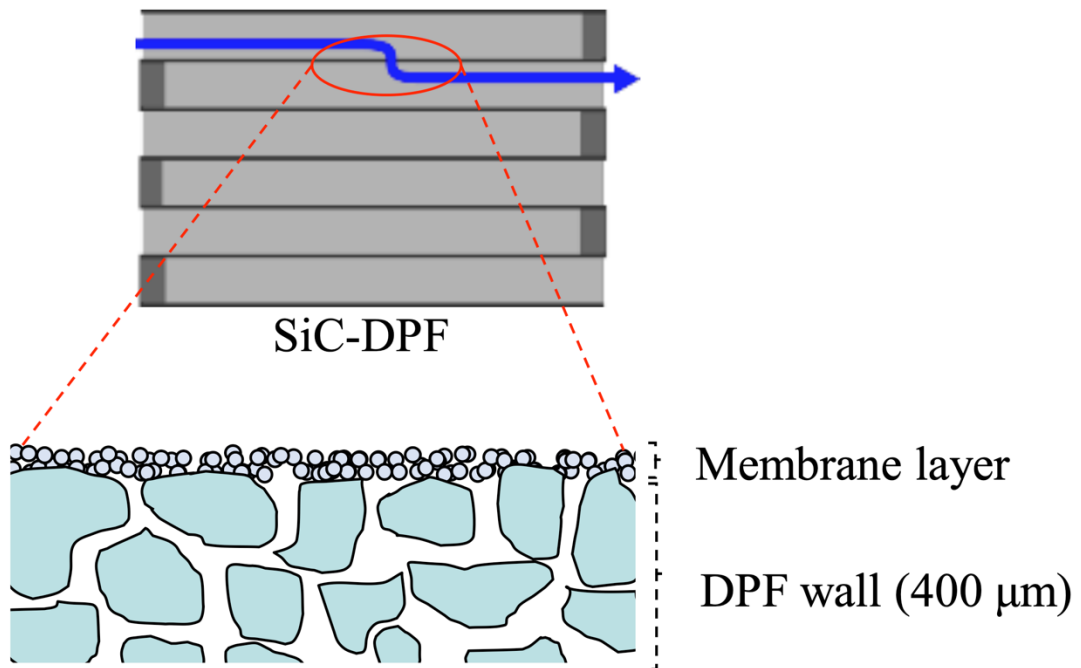


Fig. 10 A schematic image of membrane particulate filter [25]

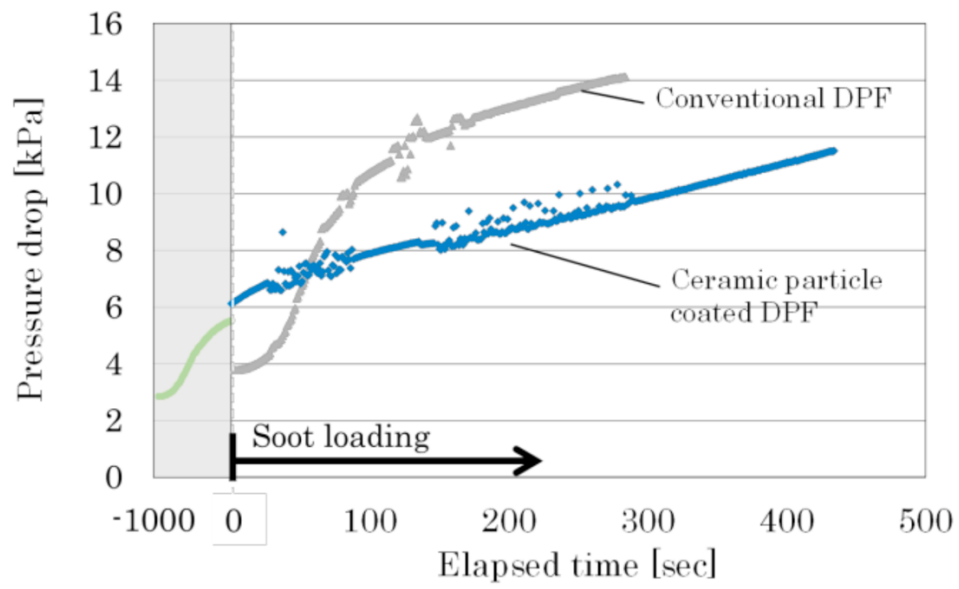


Fig. 11 Comparison of pressure-drop increase in conventional and membrane particulate filter during soot deposition [25]

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Chapter 2

Porosity Measurement in TWC Membrane Filter

2.1 Background

In this chapter, fabrication process of Three-way Catalyst (TWC) particles membrane filter and measurement of its porosity will be discussed. During fabricating, a parametric study was conducted by introducing three different agglomerated TWC-particle sizes under three superficial velocity conditions.

In the past, several membrane filters were fabricated using various catalyst components with the aim of improving soot oxidation kinetics, mitigating exhaust gas pollutants, and other related objectives in our laboratory [12 – 14]. The main advantage of a membrane filter is that the catalyst particles were percolated as a membrane at the shallow area of the conventional filter substrate, which results in significantly increased in initial soot filtration efficiency, but to produce a membrane particulate filter with low pressure-drop [15]. Here, a TWC-particles membrane was manufactured on a bare particulate filter substrate in order to enhance initial soot filtration efficiency and reduce the exhaust gas pollutants such as carbon monoxide (CO), nitrogen oxides (NO_x) and unburnt hydrocarbons (HCs) simultaneously in an integrated unit. A porosity measurement method which was measured on the cross-sectional area of the membrane through electron microscopy image analysis was introduced.

2.2 Methodology

2.2.1 Experimental procedure of preparing a miniature-sized sample

As shown in **Fig. 2.1**, a miniature particulate filter sample composed of 7x7 channels with a precise dimension of 10 mm³ was extracted from a conventional full-size silicon carbide (Si-C) particulate filter substrate. In order to create a wall-flow configuration, a high temperature resistance ceramic paste was used to plug at the end of the channels alternately as illustrated in **Fig. 2.2**, in which working gas pass through the channel walls. After plugging the alternate channels, the total filtration area of the inlet channels was calculated as about 829.8 mm². Then, the plugged sample was placed inside a stainless-steel holder. The top surface of the sample was polished to achieve up to a mirror-like top surface by using various abrasive discs (P600 to P4000). The top surface was covered by a quartz glass plate and clamped with bolts and nuts as described in **Fig. 2.3**. As a result, there was no gas leakage from the cross-sectional top surface when the working gas was introduced from the upstream side channels of the sample.

2.2.2 Fabrication process of a TWC-membrane

A slurry comprising 20 wt.% of aggregated nanometer-sized TWC-particulates, with an average diameter of approximately 200 nm as illustrated in the TEM image in the **Fig. 2.4**, was prepared using distilled water. The chemical composition of the primary TWC-particulates is the same as that of the commercialized monolith converter, as shown in **Table 1**. **Fig. 2.5** displays a schematic diagram of the fabrication process of a Three-Way Catalyst (TWC) particles membrane filter on a miniature-sized filter substrate [16]. The TWC particulates slurry was introduced into an acrylic tube and generated into small droplets with a size range of 5-10 microns using an ultrasonic atomizer (60 Hz frequency). Nitrogen gas was introduced into the acrylic tube to transport the atomized water droplets including TWC-particulates from the tube

under a flow rate of 50 mL/min. The gas-suspended droplets including TWC-particulates were then mixed with a dilution gas to achieve a superficial velocity of 5 mm/s and a lower humidity than a dew point even at 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 shown in the SEM image in **Fig. 2.5**. The agglomerated nitrogen dispersant TWC-particles, ranging in size from 1 to 2 microns, were deposited as a membrane layer onto the miniature-sized filter substrate. The thickness of the TWC-membrane on the filter substrate was about 40 microns. Then, according to our previous study, the fabricated membrane filter was sintered at 900 °C for a duration of 4 hours in order to maintain the percolation structure of the TWC-membrane with the least peeling rate [17]. Regarding to the process of atomization, the concentration of TWC-particulates in the slurry varies the sizes of agglomerated particle. Therefore, the sizes of agglomerated TWC-particles were controlled by diluting the original 20 wt.% TWC particulates slurry using distilled water.

2.2.3 Investigation of pressure-drop increase in fabrication

During fabricating the membrane, the pressure drop increase according to the deposited weight was intermittently measured. The pressure drop 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. 2.5**, while a digital micro-weighing scale was used to measure the deposited weight. In this case, the weight of the intermittently-fabricated sample with the holder and the quartz glass plate was measured at each interval of deposition after the bolts and nuts clamping setup was removed.

Here, to investigate the pressure-drop increase with respect to deposited weight of the TWC-particles, membrane fabrication process was conducted in a humidity-controlled gloves

box to remove an erratic moisture concentration in the sample [18]. Relative humidity in the gloves box was constantly maintained at 30% with only $\pm 2\%$ discrepancy during the whole membrane fabrication process.

In the manufacturing process, a low superficial velocity is preferable to deposit the agglomerated TWC-particles just around the entrance of the surface pores of the substrate according to the experience of the previous works using time-lapse visualization [13 - 15]. However, since a superficial velocity such as a few milli-meters per second is close to a falling velocity caused by a gravitational force, it is not controllable to manufacture a uniform particle layer. In the current study, the superficial velocity of 5 mm/s was fixed as the minimum one to confirm the convective flowing deposition.

2.2.4 Porosity measurement in TWC membrane

The experimental procedure of porosity measurement in TWC-membrane is shown in **Fig. 2.6**. To measure the porosity of the cross-sectional TWC-particles membrane layer, epoxy resin containing 2:1 ratio of resin and hardener was infiltrated through the membrane. The resin gradually flows inward through the membrane to avoid the membrane deformation caused by infiltration. After the resin was steadily poured from the bottom part of the sample and thoroughly embed, the sample was placed under a vacuum pressure (-50 kPa) for 15 minutes to penetrate the resin evenly until the deeper area of the pores. The ramping rate of vacuum pressure may affect the deterioration of the porous structure of the membrane. Therefore, some trials have been conducted under different pressure ramping conditions such as (i) rapidly increase the vacuum pressure from atmospheric pressure to -50 kPa, varying pressure ramping rates as well as (ii) -2 kPa/min and (iii) -10 kPa/min. It was found that there were no differences in porous structure of the TWC-membrane although various ramping rates were introduced. In fact, the sintered TWC-particles can resist to infiltrate the epoxy resin under the vacuum

pressure. The resin infiltrated sample was cured in the atmosphere for 24 hours. Finally, the sample was polished under water polishing to visualize the cross-sectional view of TWC-membrane layer. Due to less electron conductivity property of epoxy resin under scanning electron microscopy observation, cross-sectional top surface was transparent through deeper area. Therefore, Gold (Au) sputtering process was essential to utilize to observe the cross-sectional surface. The top surface of the sample was coated with a 50 nm Au-layer which can provide higher electron conductivity at the cross-sectional top surface.

2.3 Results and discussion

2.3.1 Particle size distribution of agglomerated TWC particles

Fig. 2.7(a) describes the morphology of agglomerated TWC-particles obtained by different concentration of TWC-particulates in the slurry. **Fig. 2.7(b)** shows measurement result of particle size distribution of agglomerated TWC-particles. By introducing different TWC-particulate concentration such as 0.5, 5 and 20 wt.% in the water-slurry as mentioned above, different sizes of agglomerate particles can be manufactured. As a result, a wider range of particle size distribution (ranging between 0.9 to 1.5 μm) were produced in 20 wt.% condition while a small range of particles (0.4 to 0.7 μm) were produced in 0.5 wt.% condition. Arithmetic mean diameters of the particles (measured as 200 particles in total) in each 20, 5 and 0.5 wt.% concentration was measured as 0.50, 0.93 and 1.2 μm respectively.

2.3.2 Pressure-drop increase in fabricating TWC-particles membrane

Fig. 2.8 shows the effect of TWC-particle sizes of 0.5, 0.93 and 1.2 μm on the pressure-drop increase and its increase rate under the condition of superficial velocity of 5 mm/s. The pressure drop is drastically increased with respect to the accumulated weight up to an inflection point whereas the bridge formation by the TWC-particles is completed [13, 14]. During the

bridge formation process from the beginning of deposition, the pressure drop increase rates for all TWC-particle sizes are much the same due to the same mechanism of the bridge growth [14]. Then, the larger TWC-particle size the faster the surface pores are closed by the bridge made of TWC-particles. As a result, a slightly smaller amount of TWC-particles is used to reach the inflection point in the case of larger TWC-particles. Moreover, during both surface pore and cake layer accumulation, the pressure drop for the larger TWC-particle size is lower than that of smaller particle sizes. Because at the same accumulated weight of TWC-particles, the particle number might become smaller, and the pore size might become larger in the case of larger particle size. Here, when the Stokes' force around a single TWC-particle is assumed, the total pressure drop depends on the product of the particle number and the Stokes' force, while many straight capillary pores are assumed in the TWC-particles membrane structure, the total pressure is proportional to the inverse of the square of pore diameter.

Fig. 2.9 shows the effect of the superficial velocities of 5, 25 and 50 mm/s on the pressure drop increase under the condition of the TWC-particle size of 1.2 μm . The initial pressure drop increases almost in proportion to the superficial velocity. However, during both bridge formation and surface pore accumulation processes, the pressure drop increase rate is not proportional to the superficial velocity since some TWC-particles reach the deep area of substrate pores and complete the bridge formation at the deeper location in the case of the higher superficial velocity [15]. As a result, although much the same amounts of TWC-particles are used (except for the case of the superficial velocity of 25 mm/s) to reach the inflection points as mentioned above, the pressure drop increase becomes higher than the proportional increase. On the other hand, during the cake layer accumulation, the pressure drop increase rate increases almost in proportion to the superficial velocity.

In the case of the superficial velocity of 25 mm/s, the initial pressure drop without deposition of TWC particles reaches the almost proportional value with increase in superficial

velocity from 5 to 25 mm/s. However, during bridge formation and surface pore deposition, the pressure drop does not increase as expected, that is, the pressure drop increase rate (right hand side vertical axis) goes down around the accumulated weight of 1.4 mg and then keeps at constant unlike the cases of 5 and 50 mm/s. This is because there is some flowing-gas leakage which is caused by the disassembly of fixing setup during each interval of deposited weight measurement. It is confirmed that in the case of almost-perfect assembly, there is a high reproducibility as shown in Fig.7, in which the first measured pressure drop increase (1) are much the same as the second one (2) with respect to the accumulated TWC-particles weight.

2.3.3 Morphology of cross-section of TWC-particles

Fig. 2.10(a) ~ 2.10(f) display SEM micrographs of the cross-sectional views of TWC-particles membranes fabricated on a conventional filter substrate for all experimental conditions. Although the bridge location cannot be determined clearly, the TWC-particles are deposited only around the entrance of the surface pore of the substrate filter in the case of particle size of 0.5 μm under the condition of superficial velocity of 5 mm/s as shown in **Fig. 2.10(a)**. With increasing particle-size to 0.93 and 1.2 μm , the TWC-particles reach slightly the deeper area of the surface pores and make the bridge at the deeper location as shown in **Fig. 2.10(b) and 2.10(c)** due to the greater inertial force of the larger particles, but the bridge formation was not very deep. On the other hand, the number of TWC-particles for closing the surface pores decreases with increasing particle-size if the average surface pore diameters are the same in **Fig. 2.10(a), 2.10(b) and 2.10(c)**.

Using the same TWC-particle size of 1.2 μm , with increasing superficial velocity from 5 mm/s to 25 mm/s and 50 mm/s, the penetration depth of TWC-particles becomes deeper as shown in **Fig. 2.10(d), 2.10 (e) and 2.10 (f)**. Because a trapping possibility by Van der Waals force will be reduced due to a high momentum of TWC-particles as the velocity becomes higher.

The accumulation of TWC-particles from the deep location to the entrance of surface pores causes a high pressure drop increase during the surface pore accumulation process as mentioned in **Fig. 2.9**.

2.3.4 Porosity measurement in the TWC-particles membrane

To measure the porosity of the TWC-membrane, the resin infiltrated cross-sectional area was observed through SEM and FE-SEM as described in **Fig. 2.11(a) and 2.11(b)**, respectively, at the same location. Here, the back-scattered electron (BSE) image is used in the case of the SEM. Although the borderlines between the cross-sectional TWC-particles and the resin are not clear enough for image processing analysis, the SEM images are useful to specify the location even if a whole particle is completely immersed as shown in **Fig. 2.11(a)**. On the other hand, using the secondary electron in the FE-SEM, the borderlines of cross-sectional TWC-particles separated from the resin surface can be observed clearly as shown in **Fig. 2.11(b)**, where the image of immersed particles are completely disappeared.

Fig. 2.12 show highly-magnified FE-SEM images of the cross-sectional areas depicted by the dotted, the dashed and the solid lines in the same image as **Fig. 2.11(b)**. It is clarified that the primary TWC particulates are homogeneously agglomerated in the whole area of the single TWC-particle from the surface to the center because the morphology is similar to that of the spherical surface as shown in **Fig. 2.5**. The borderlines of the cross-sectional area of TWC-particles can be observed clearly and are almost absolute circular shapes as depicted in the figure. However, some cross-sectional areas are not absolutely circular because of partial separation of a thin resin film covering the spherical surface of the TWC-particle as illustrated in **Fig. 2.13**. Moreover, a thin resin-covered portion can be observed as the cross-sectional area due to electron penetration. Therefore, to measure the true cross-sectional TWC-particle area, an inscribed circle area should be used as the cross-sectional area of a single TWC-particle. In

addition, during water polishing, it was inevitable that some particles can be released and remained as lacks on the resin surface. Therefore, the inscribed circle lack areas should be counted as cross-sectional TWC-particle areas in the porosity measurement. The conceptual schematic image of depicting inscribed-circles on the electron micrographs were illustrated in **Fig. 2.14**.

Fig. 2.15 and 2.16 show processes of image analysis using an “Image-J” image processing program to obtain the porosity. **Fig. 2.15(a), 2.15(b) and 2.15(c)** are for the TWC-particle sizes of 1.2, 0.93 and 0.5 μm , respectively, under the condition of the superficial velocity of 0.5 mm/s. **Fig. 2.16(a), 2.16(b) and 2.16(c)** are for the superficial velocities of 0.5, 25 and 50 mm/s, respectively, under the condition of the particle size of 1.2 μm .

The total cross-sectional area of the TWC-particles is expressed as a summation of total depicted inscribed circle areas as shown in each right-hand side image in **Fig. 2.15 and 2.16**. The porosity, ϕ is defined as the ratio of the total cross-sectional area of the TWC-particles and total measured square-area as described as shown in Eq. 2-1.

$$\phi = \left(1 - \frac{\text{Total area of TWC particles}}{\text{Measured area}} \right) \quad (2-1)$$

The measurement process was repeated up to three times for each sample to express the uncertainty of manually depicting the cross-sectional area. The average porosities for three particle sizes and three superficial velocities conditions are summarized in **Table 2**. The average porosity of TWC-particles membrane fabricated with the mean diameter of 1.2 μm under the superficial velocity of 5 mm/s was measured as approximately 64.4 %. With decreasing particle-size to 0.93 and 0.5 μm , the porosity increases slightly. In the current range of TWC-particle size, since impaction and interception phenomena are dominant as the particle deposition mechanism, much the same porosities are obtained. Only small increase in porosity

with decreasing size might come from a decrease in inertial force of the TWC-particle. Moreover, the porosity distribution along the thickness direction of the membrane were expressed in **Fig. 2.17**. As a result, the percolation structure is consistent since the discrepancy of porosity in the thickness directions was measured as only 2.3%. In the previous work [15], the porosity of 94.3 % was obtained in the case of alumina-particle with the mean diameter of 0.355 μm due to slight contribution of random walk (also known as Brownian motion). On the other hand, the porosity decreases slightly with increasing superficial velocity from 5 mm/s to 25 and 50 mm/s under the condition of TWC-particle size of 1.2 μm . Since with increasing superficial velocity, the momentum of TWC-particle increases, the TWC-particles might be deposited slight-densely.

2.3.5 The effect of higher superficial velocity on the agglomeration process

Fig. 2.18 display the SEM images of cross-sectional TWC-particles membrane fabricated under different superficial velocity conditions such as 5, 20, 25 mm/s respectively. As shown in **Fig. 2.18(b) and 2.18(c)**, a few doughnut-like particles were observed in the case of fabricating the membranes under the superficial velocities of 20 and 25 mm/s. In fact, a high working gas velocity might disarrange the water droplet particles during agglomeration process before passing through the evaporator. As a result, the resin area can be observed at the center of the doughnut-like particles as depicted in the electron micrographs in the **Fig. 2.19**. Therefore, lower superficial velocity as low as 5 mm/s would be preferable to introduce in the TWC-particles membrane manufacturing process to achieve a low pressure drop membrane filter composed of homogeneously agglomerated TWC-particles.

2.3.6 Permeability of a TWC-particles membrane

The permeability of the TWC-particles membrane filter was estimated using a Kuwabara's model [19] using the parameters such as porosity, ϕ , and the diameter of the TWC-particle, d , as described as described in Eq. 2-2.

$$k = \frac{d^2}{18(1-\phi)} \left(1 - \frac{9}{5} (1-\phi)^{\frac{1}{3}} + (1-\phi) - \frac{1}{5} (1-\phi)^2 \right) \quad (2-2)$$

The estimated permeability of the TWC-particles membrane filter for all experimental conditions are described in **Table 2**. In this model, the permeability depends directly on the square of particle diameter. As a result, the permeability is dominantly increased with TWC-particle size as 0.27×10^{-14} (0.5 μm), 0.86×10^{-14} (0.93 μm) and 1.23×10^{-14} m^2 (1.2 μm) since there is only small difference of porosity.

This high permeability will affect the pressure drop increase during bridge formation and surface pore deposition. As shown in **Fig. 2.20**, the bridge formation starts from deposition of TWC-particles on the surface of the Si-C substrate around the first narrow area from the entrance of the surface pore. At this term, most of flowing-gas as depicted by red arrows passes through the center hole since the pressure drop for flowing through the hole is smaller than that of flowing through the TWC-particles membrane. Therefore, the flying TWC-particles are trapped at the tip of the bridge made of TWC-particles. Then, the TWC-particles bridge makes a growth towards the center of the substrate pore. During the bridge formation, the center hole becomes smaller and smaller. Here, when the permeability of the TWC-particles membrane is low, there is no flowing through the membrane until the hole is closed, i.e., completion of bridge formation, which contributes to a high pressure drop increase around the inflection point. On the other hand, in the case of the high permeability, it is expected that there is some gas flowing through the membrane as depicted by blue arrows from quite a while before the hole

is closed. As a result, the pressure drop at the inflection point for the 1.2 μm size as shown in Fig.5 is low compared with those for 0.5 and 0.93 μm sizes, moreover, the inflection point might not be necessarily coincident with the completion of bridge formation.

On the other hand, under the condition of the same TWC-particle diameter of 1.2 μm , a 2.7% difference of porosity between 64.4 and 61.75 % leads to almost 25 % difference of permeability as 1.23×10^{-14} and $0.98 \times 10^{-14} \text{ m}^2$. As mentioned above, in our previous work^[15], a high-permeability porous membrane was manufactured on the conventional filter substrate using fine alumina particles. The permeability was estimated as $7.7 \times 10^{-14} \text{ m}^2$ with a porosity of 94.3%. Since the density of TWC-particles is higher than that of alumina-particles, it is not easy to increase the porosity even under the condition of smaller TWC-particle. Consequently, a high permeability TWC-particles membrane filter can be manufactured by a range of particle size around 1~2 μm which should be completely suspended in flowing gas.

2.3.7 Effect of tortuosity on permeability of the membrane

Tortuosity is an important factor for permeability of a porous medium since it directly affects the efficiency of fluid flow through porous media by altering the length, geometry, and distribution of flow pathways. Therefore, in this study, the tortuosity of the TWC-particles membrane was estimated by a GeoDict software as described in **Fig. 2.21**. In the software, the tortuosity was measured as a ratio of actual path length (i.e., the arithmetic mean path lengths of the fluid flow) by straight line distance. As a result, the tortuosity (τ) was estimated as 1.02. In fact, since the TWC-particles membrane was composed of spherical agglomerated particles with a high porosity (i.e., approximately 64.4%), the tortuosity factor is small in this study.

$$k_{Kozeny-Carman} = \frac{d^2}{72\tau^2} \frac{\phi^3}{(1-\phi)^2} \quad 2-3$$

The permeability (k) of a TWC-particles membrane including the effect of tortuosity was estimated by using a Kozeny-Carman model as described in Eq. 2-3. As a result, the

estimated permeability of the TWC-particles membrane was 1.52×10^{-14} which was comparable to the Kuwabara model. As previously mentioned, since the percolation structure is less tortuous due to the presence of spherical TWC-particles with a high porosity, the tortuosity effect was not influenced in permeability in this study.

2.4 Summary

In the TWC-particles membrane manufacturing process, a similar analogical percolation structure is obtained under the conditions of the particle sizes of 0.5, 0.93 and 1.2 μm and the superficial velocities of 5, 25 and 50 mm/s. The porosity of the TWC-particles membrane filter was estimated by using infiltration of the epoxy resin into the micrometer-sized pores and then by making the comparison between the cross-sectional areas of TWC-particles and the resin. The porosity of the TWC-particle membrane layer is around 64 % (61.8 ~ 67 %). The permeability of the TWC-particles membrane layer with the particle size of 1.2 μm becomes highest, and the value is estimated as $1.23 \times 10^{-14} \text{ m}^2$. The permeability depends strongly on the TWC-particle size since the porosity is not increase drastically with decreasing particle size in this study. Moreover, a TWC-particles membrane which is composed of 1.2 μm would be an optimal particle size in fabrication due to the properties of higher permeability, porosity and 100% soot filtration efficiency.

Table

Table 2.1 Chemical composition of three-way catalyst slurry

Chemical compounds		Composition (%)
Palladium oxide	PdO	1.45
Rhodium oxide	Rh ₂ O ₃	0.26
Cerium dioxide	CeO ₂	18.3
Zirconium dioxide	ZrO ₂	26.10
Aluminum oxide	Al ₂ O ₃	47.70
Lanthanum oxide	La ₂ O ₃	3.28
Neodymium oxide	Nd ₂ O ₃	2.90

Table 2.2 Measured porosity and permeability of three-way catalyst particles membrane

Mean diameter of TWC-particle (um)		Porosity (%)	Permeability (m ²)
Superficial velocity = 5 mm/s	0.5	67.04 (±1.17)	0.27 x10 ⁻¹⁴
	0.93	66.83 (±1.64)	0.86 x10 ⁻¹⁴
	1.2	64.40 (±1.44)	1.23 x10 ⁻¹⁴
Superficial velocity (mm/s)		Porosity (%)	Permeability (m ²)
Mean diameter of TWC-particle = 1.2 um	5	64.40 (±1.44)	1.23 x10 ⁻¹⁴
	25	63.85 (±3.32)	1.18 x10 ⁻¹⁴
	50	61.75 (±1.15)	0.98 x10 ⁻¹⁴

Figures

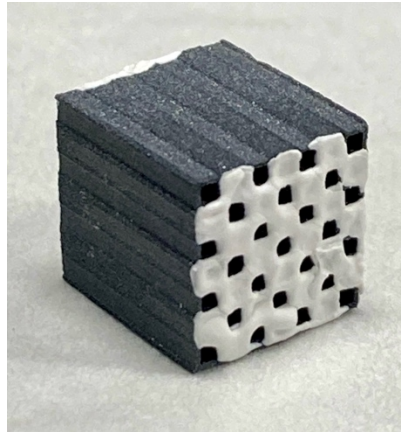


Fig. 2.1 Miniature-sized particulate filter made of Si-C

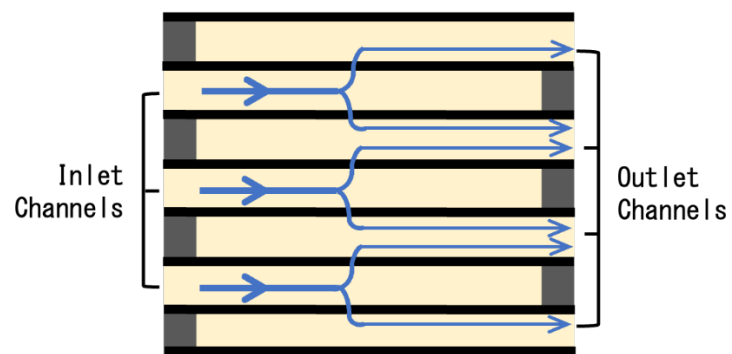


Fig. 2.2 Schematic image of wall-flow filter



Fig. 2.3 A miniature sample clamped with bolts and nuts setup

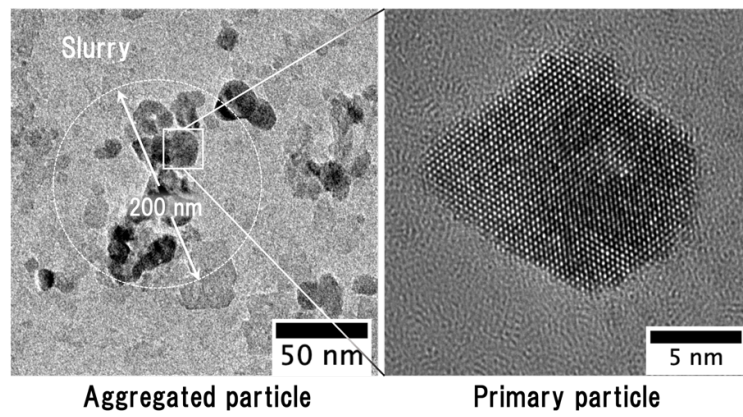


Fig. 2.4 TEM images of aggregated TWC-particulates (left) and primary particulate (right) in the catalyst slurry

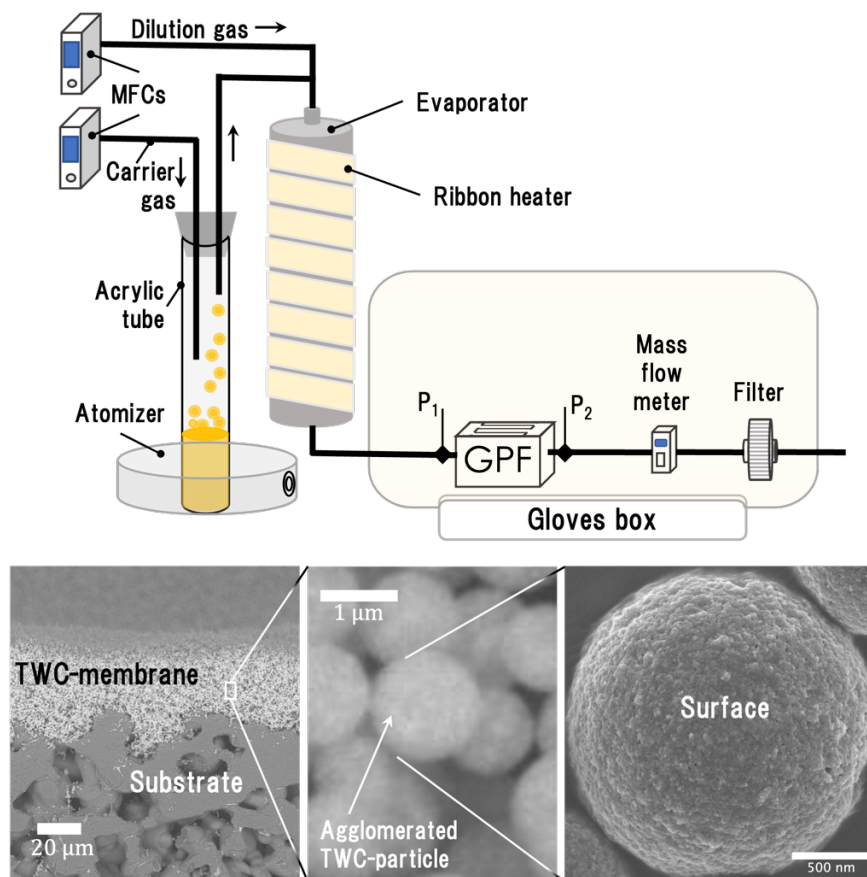


Fig. 2.5 Experimental setup of manufacturing TWC-particles membrane on the conventional filter substrate

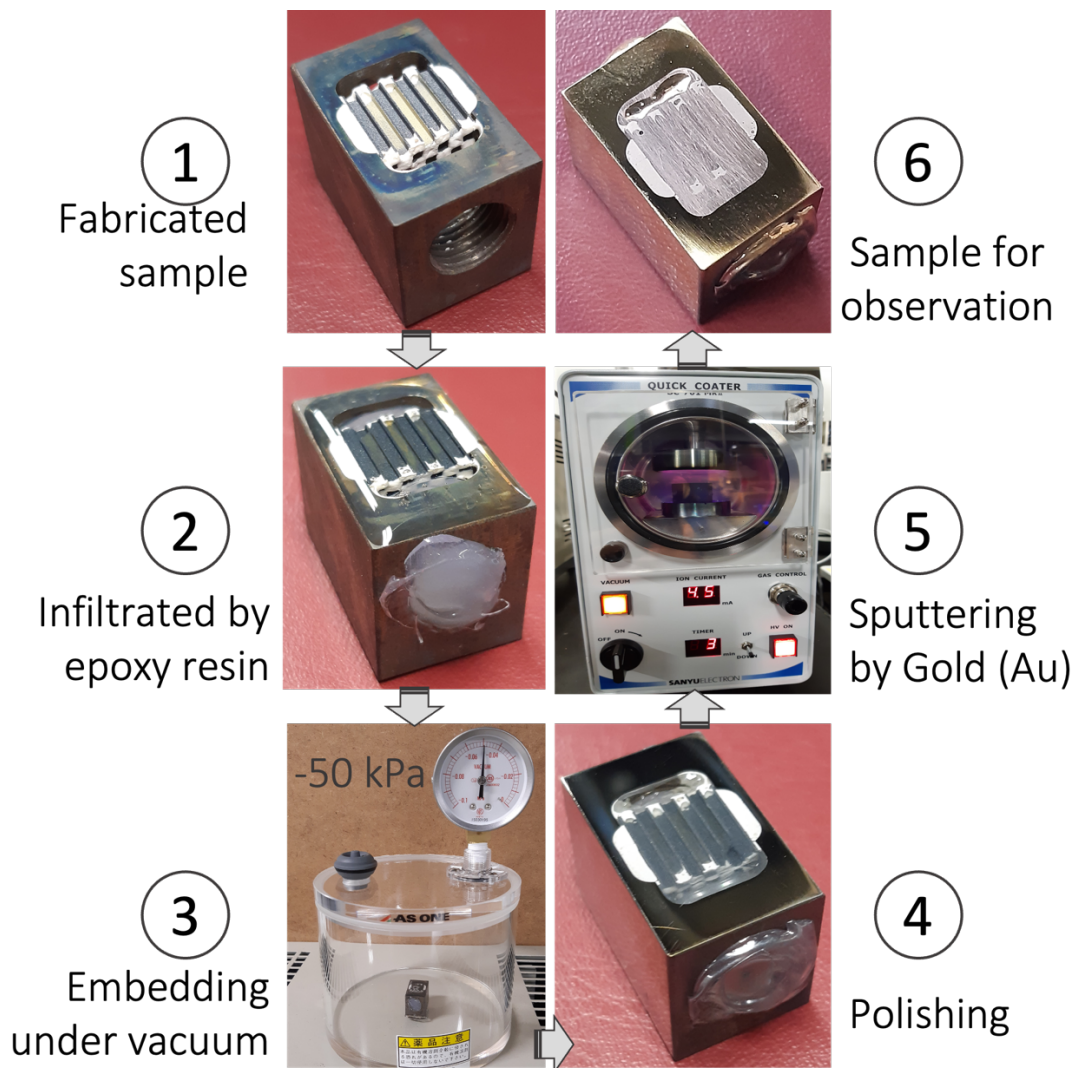
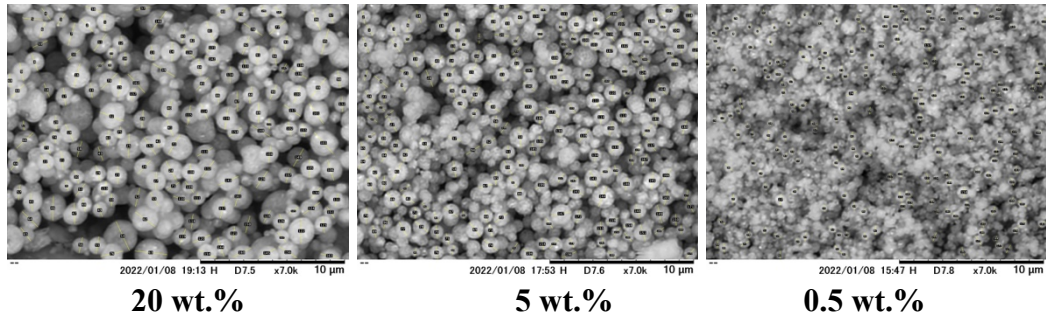
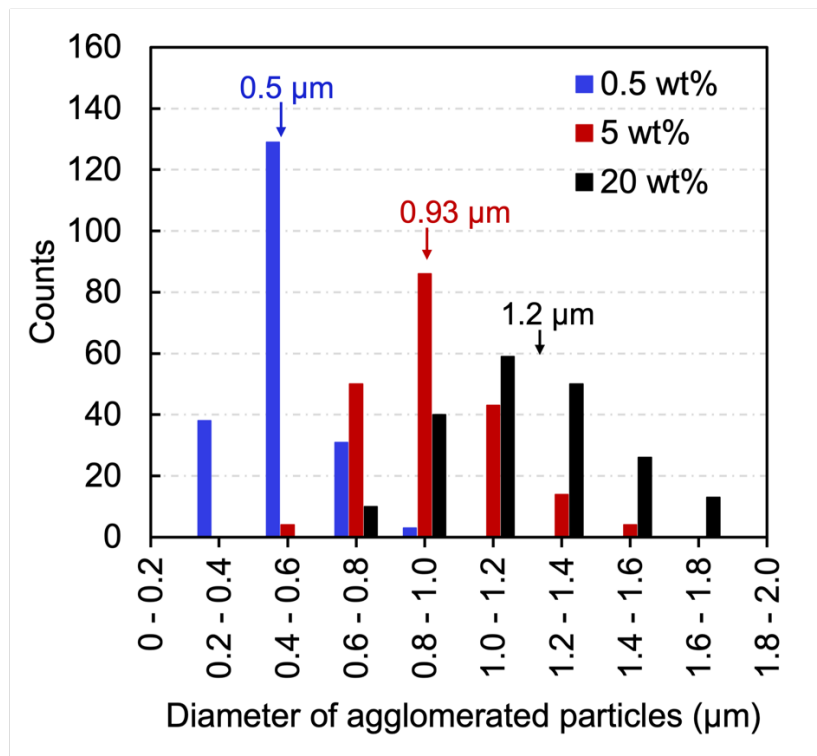


Fig. 2.6 Experimental procedure of infiltration resin for porosity measurement of TWC-particles membrane



(a) Morphology of agglomerate TWC-particles using different TWC-particulates concentrations



(b) Agglomerate particle size distribution under different TWC-particulates concentration

Fig. 2.7 (a) Morphology and (b) Particle size distribution of agglomerated TWC-particles under different particulate concentrations such as 20, 5 and 0.5 wt.% in the slurry

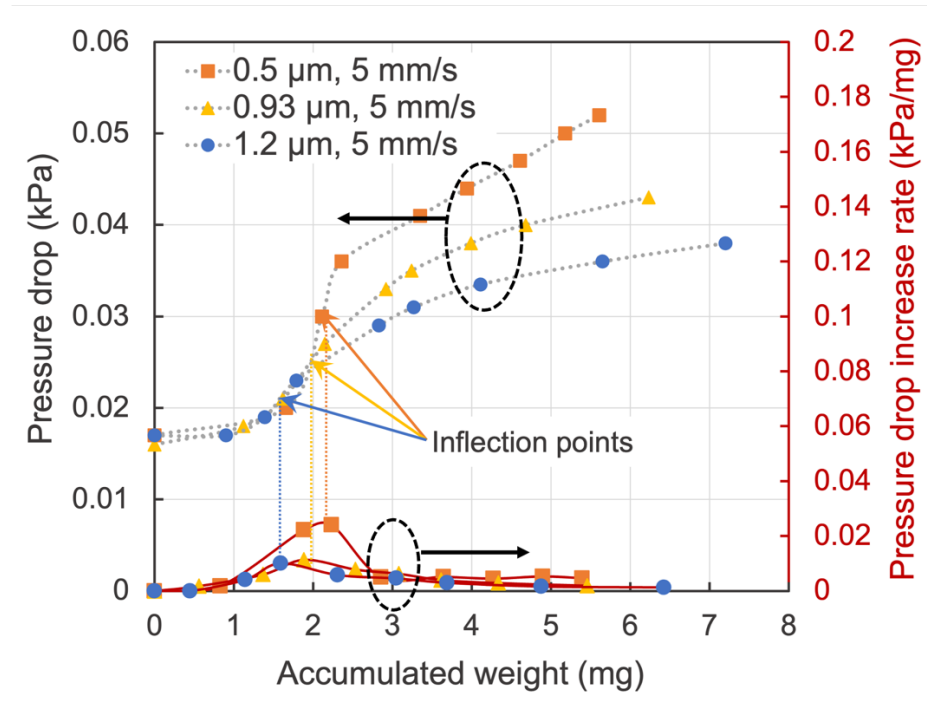


Fig. 2.8 Pressure drop increase in fabricating TWC-membrane by introducing different particle sizes (0.5, 0.93 and 1.2 μm) under the same superficial velocity of 5 mm/s

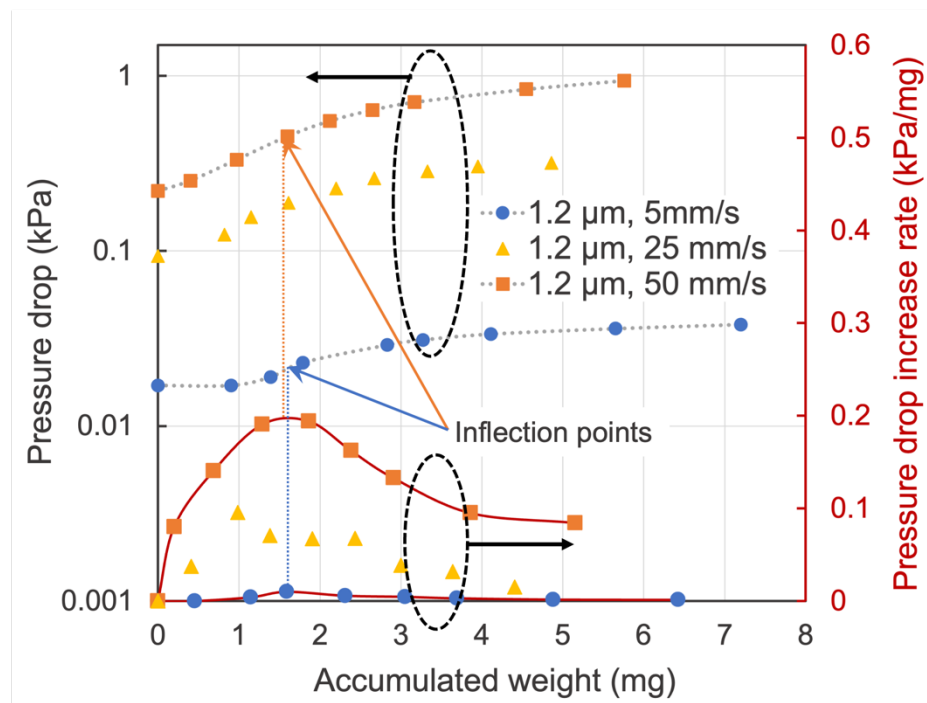


Fig. 2.9 Pressure drop increase in fabricating TWC-membrane by introducing same particle size of 1.2 μm under different superficial velocity conditions

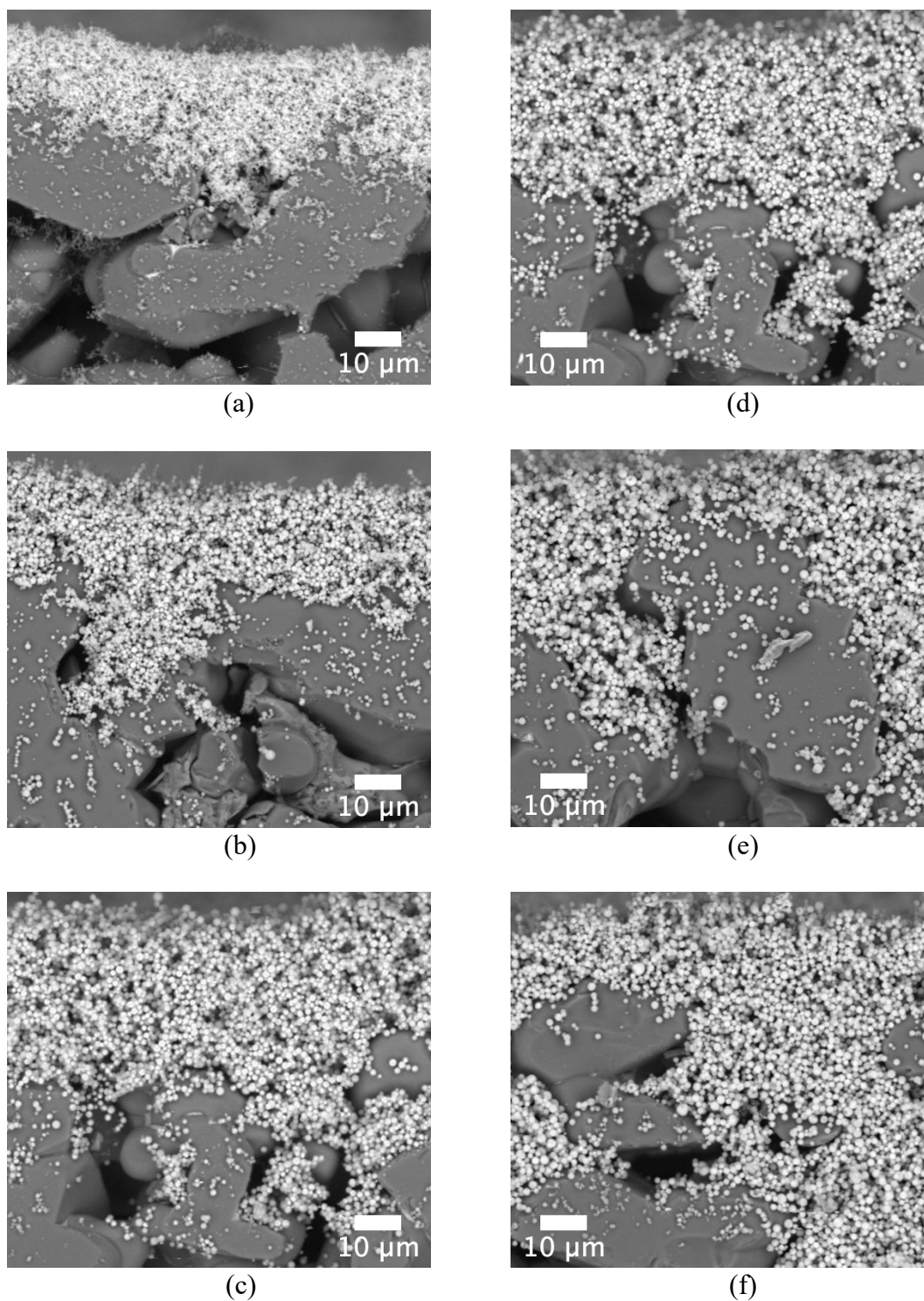
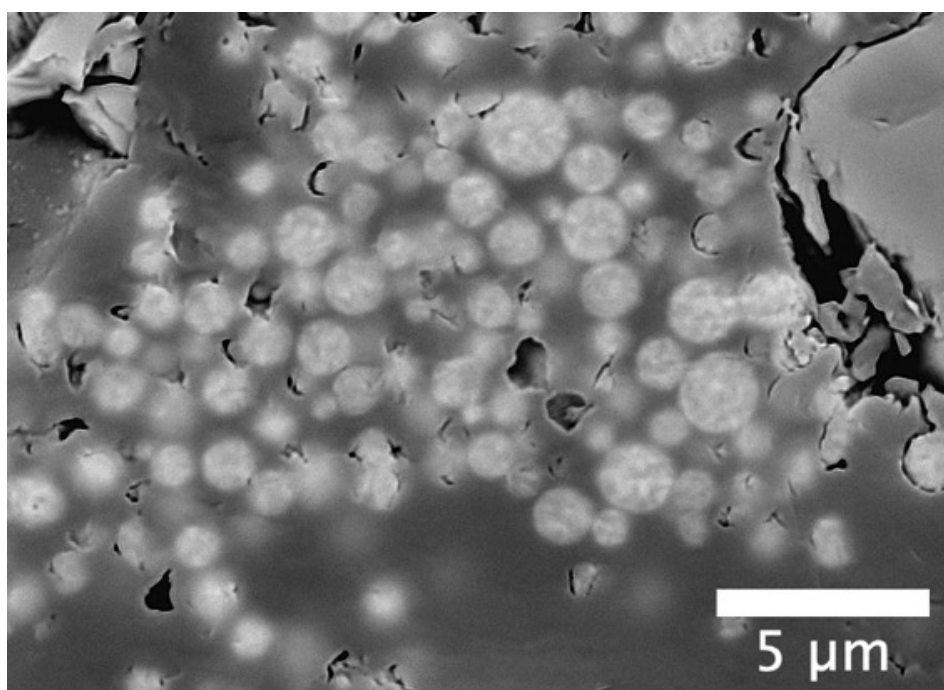
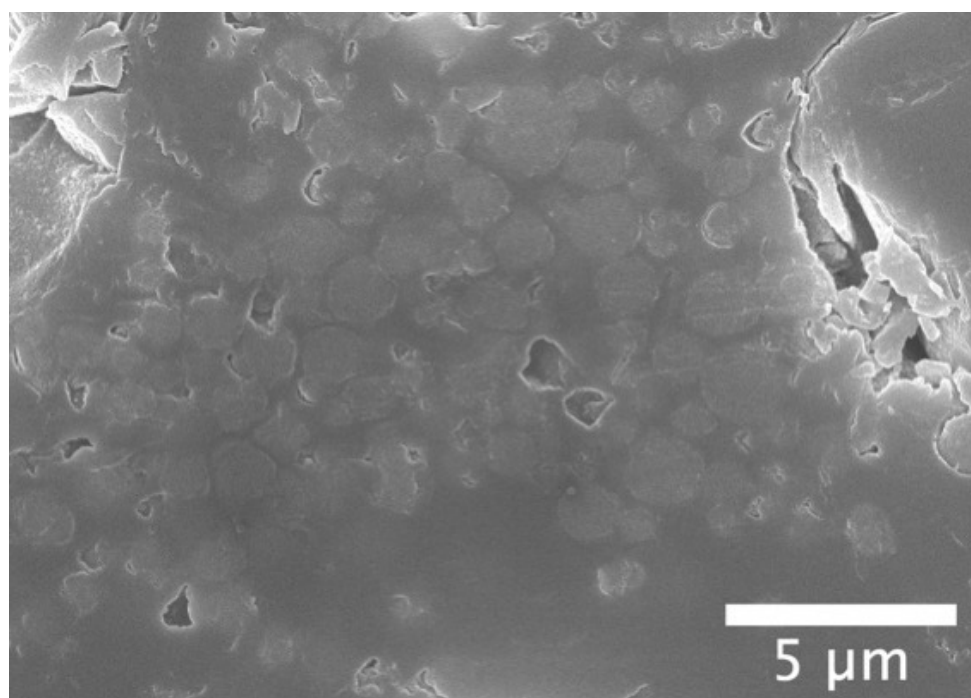


Fig. 2.10 SEM micrographs of cross-sectional view of TWC-particles membrane fabricating by using different particle sizes (a) 0.50 μm (b) 0.93 μm and (c) 1.2 μm under a same superficial velocity of 5 mm/s, and same particle size of 1.2 μm under different superficial velocities (d) 5 mm/s (e) 25 mm/s and (f) 50 mm/s



(a)



(b)

Fig. 2.11 Cross-sectional view of resin-infiltrated TWC-membrane through (a) SEM (b) FE-SEM

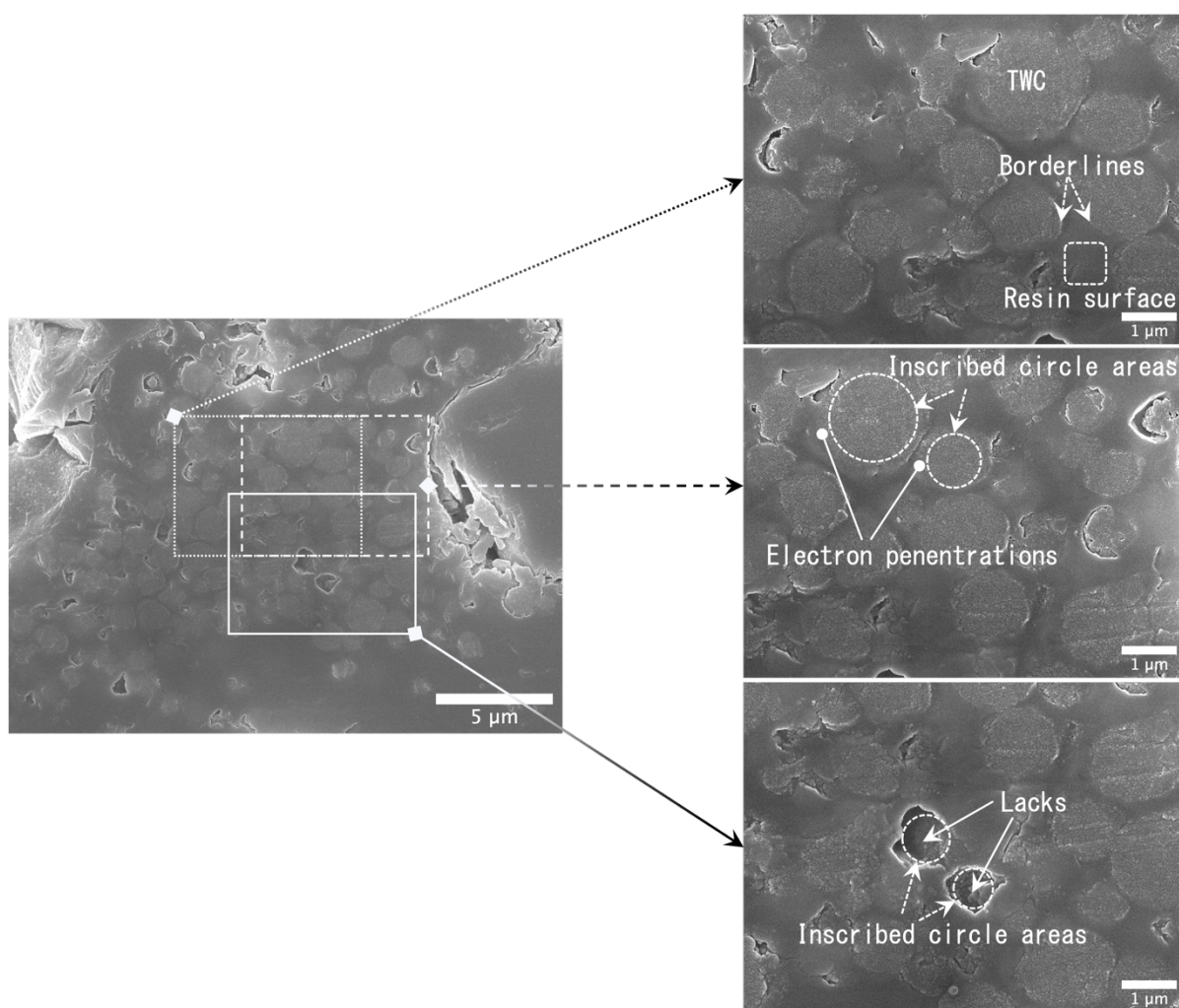


Fig. 2.12 Highly-magnified FE-SEM images of cross-sectional view of dresin infiltrated TWC-particles membrane

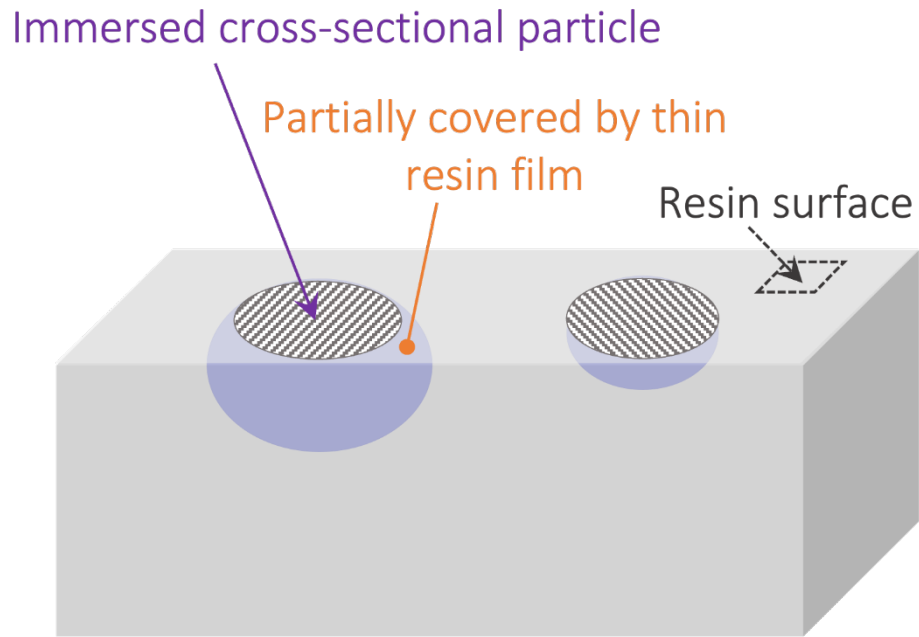


Fig. 2.13 Conceptual schematic image of immersed cross-sectional particle caused by electron penetration

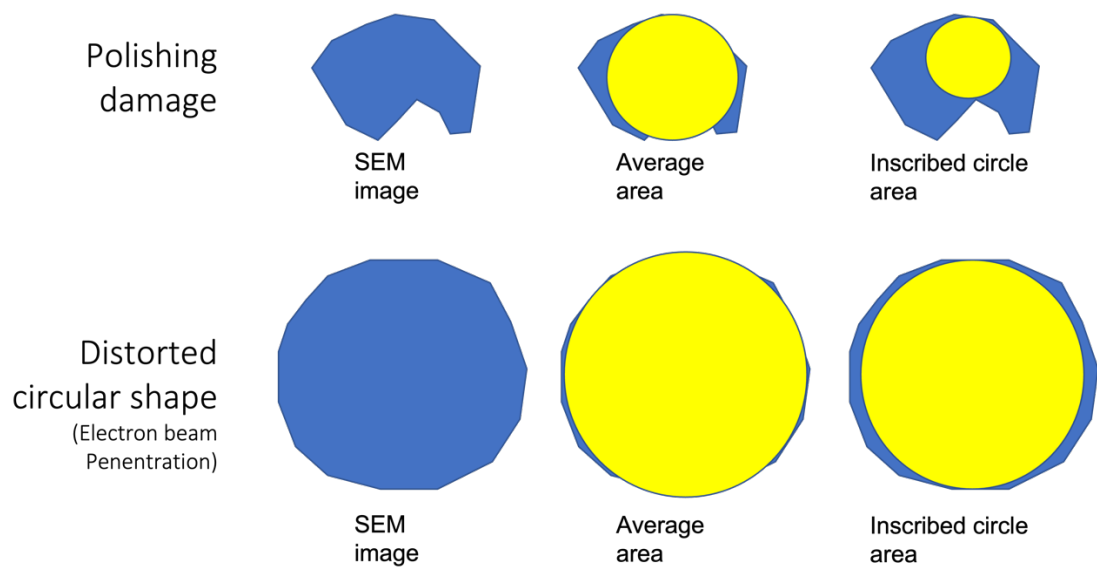
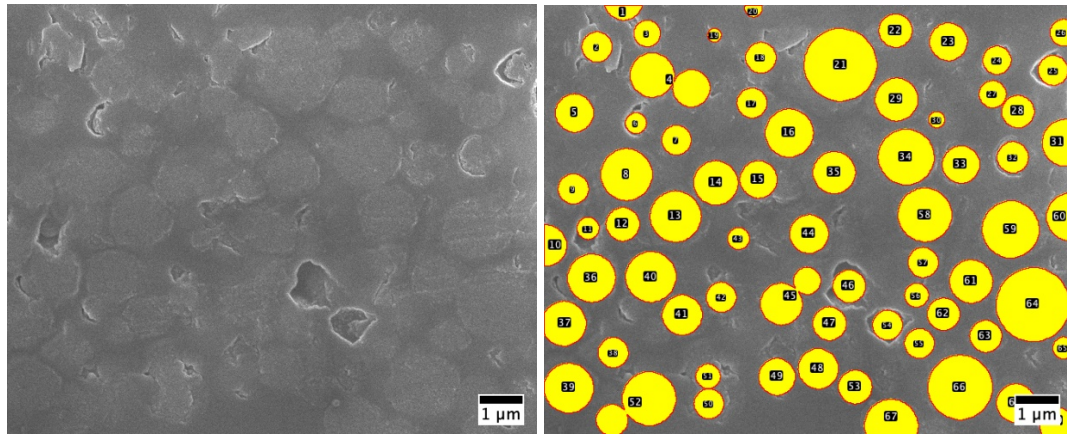
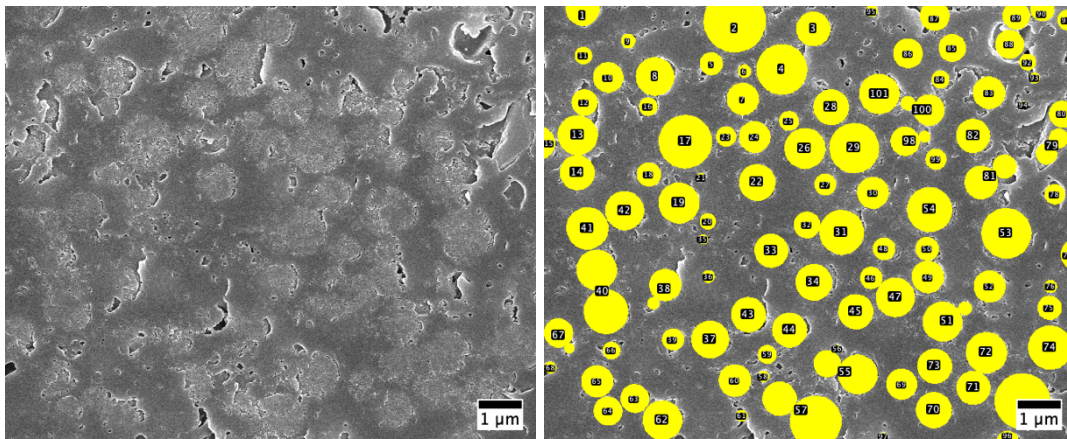


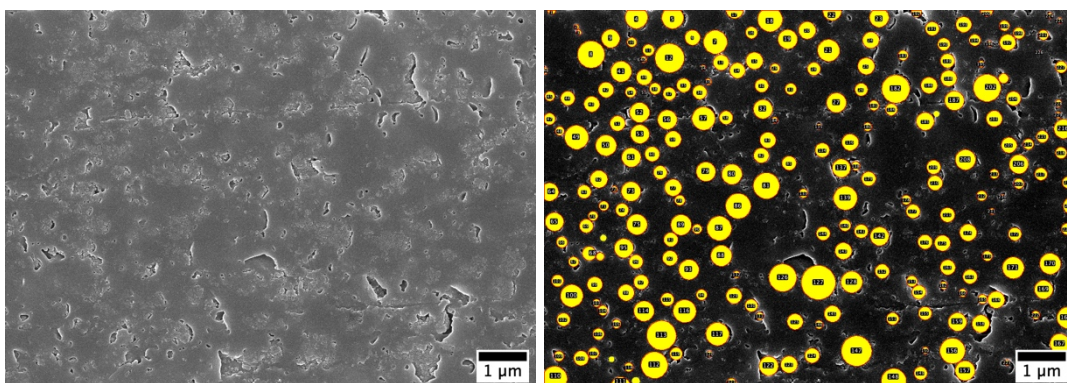
Fig. 2.14 Conceptual schematic image of depicting inscribed-circles on the electron micrographs



(a)

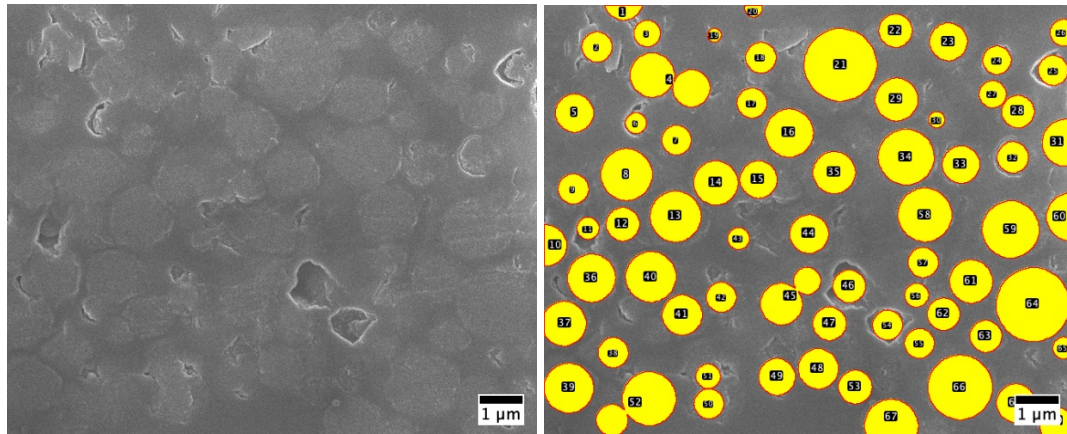


(b)

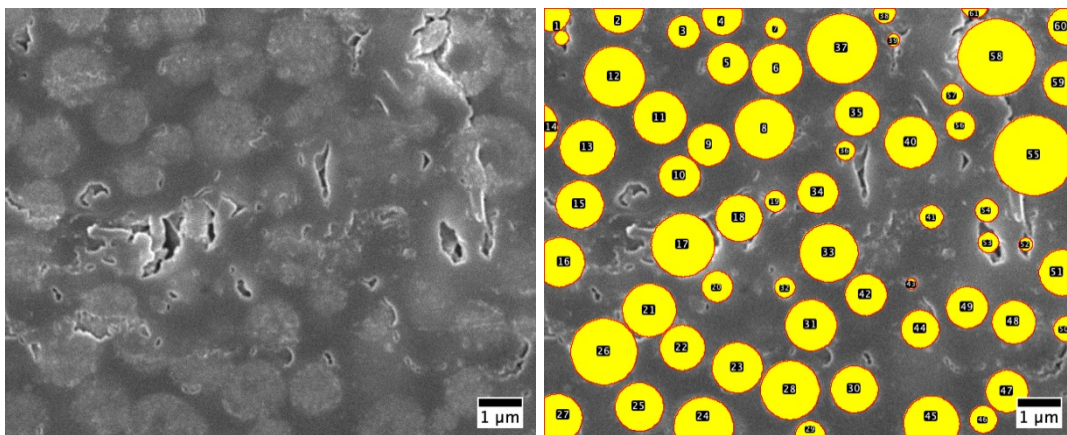


(c)

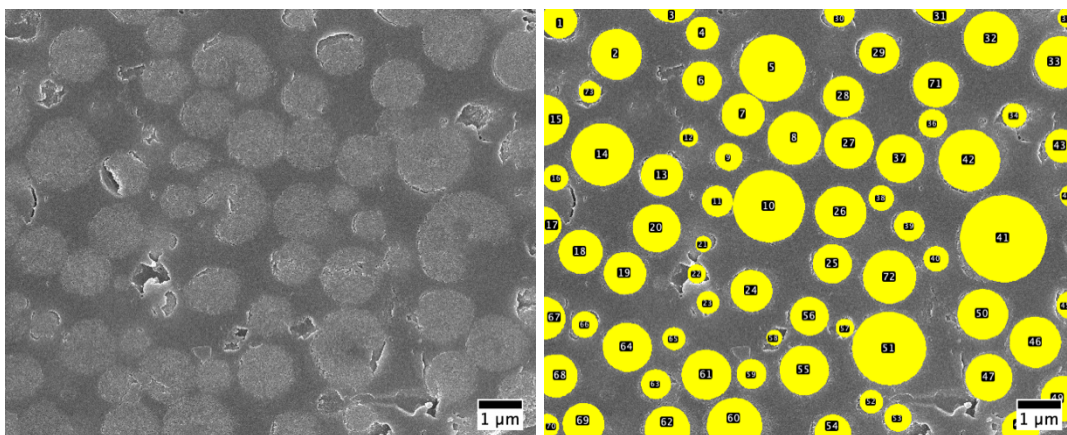
Fig. 2.15 Image processing analysis of porosity measurement comparing different TWC-particle sizes (a) 1.2 μm (b) 0.93 μm (c) 0.50 μm under the superficial velocity of 5 mm/s



(a)



(b)



(c)

Fig. 2.16 Image processing analysis of porosity measurement comparing under the TWC-particle size of 1.2 μm under superficial velocities of (a) 5 mm/s (b) 25 mm/s (c) 50 mm/s

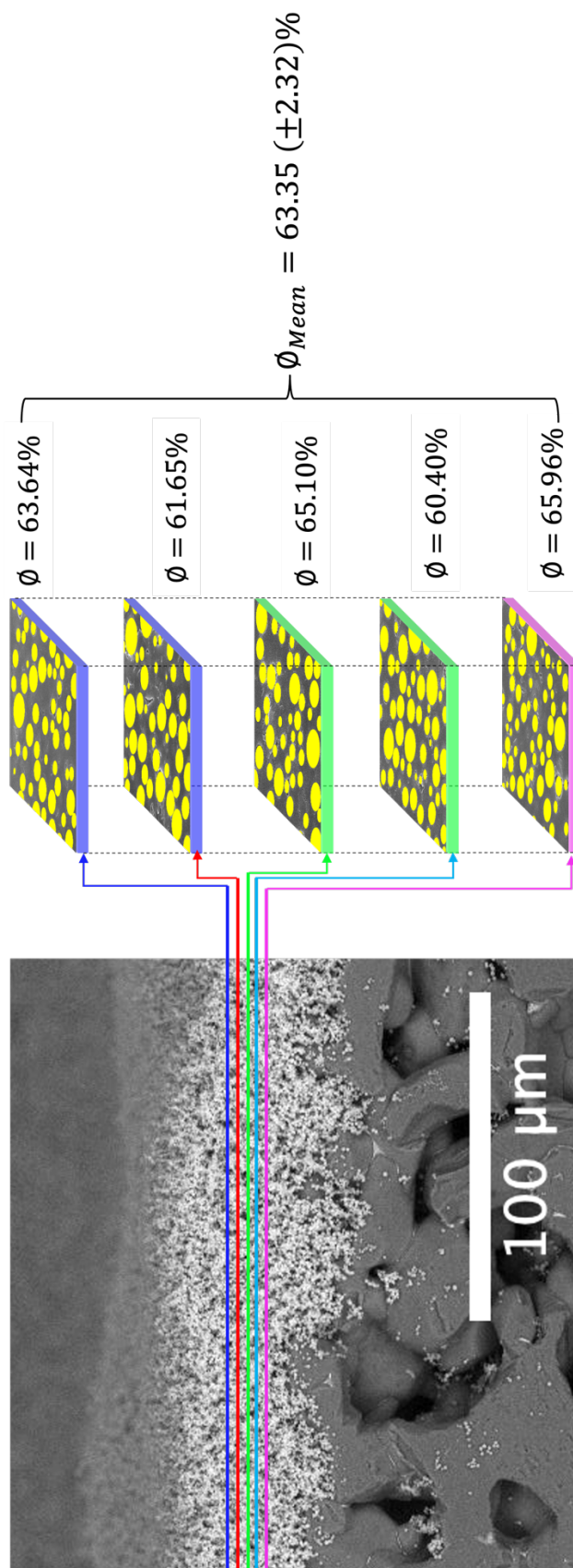
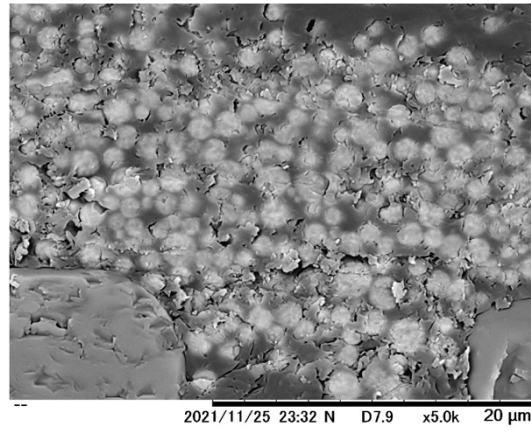
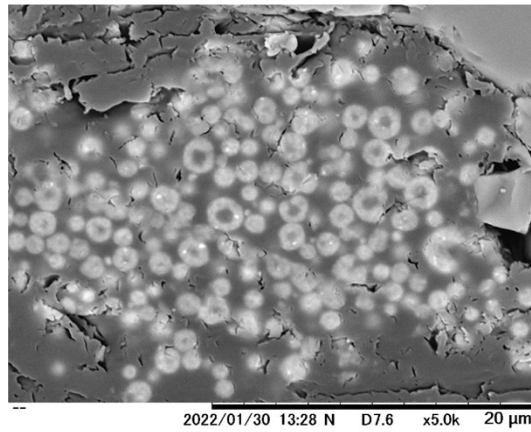


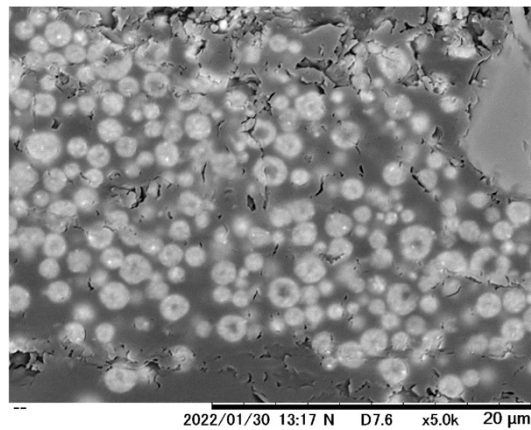
Fig. 2.17 Porosity distribution along the membrane thickness direction



(a) 5 mm/s



(b) 20 mm/s



(c) 25 mm/s

Fig. 2.18 Morphology of cross-sectional TWC-particles under superficial velocities of (a) 5 mm/s (b) 25 mm/s (c) 50 mm/s

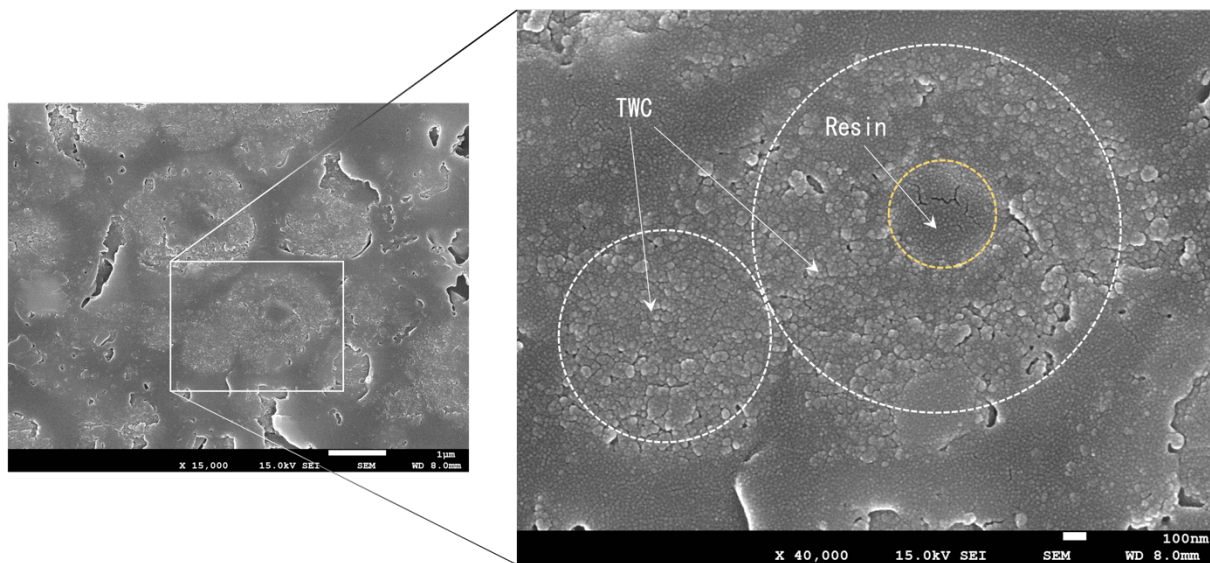


Fig. 2.19 High magnification FESEM micrographs of doughnut-like cross-sectional TWC-particle which was fabricated under a superficial velocity of 25 mm/s

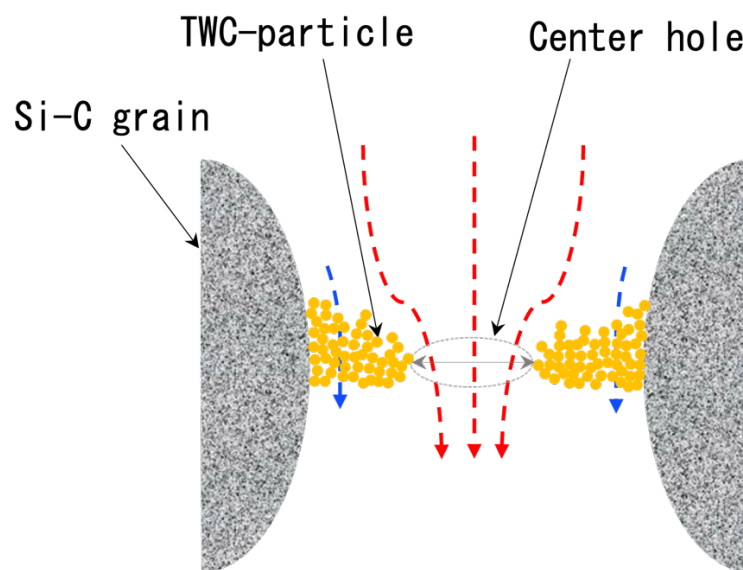


Fig. 2.20 Schematic image of TWC-particles deposition

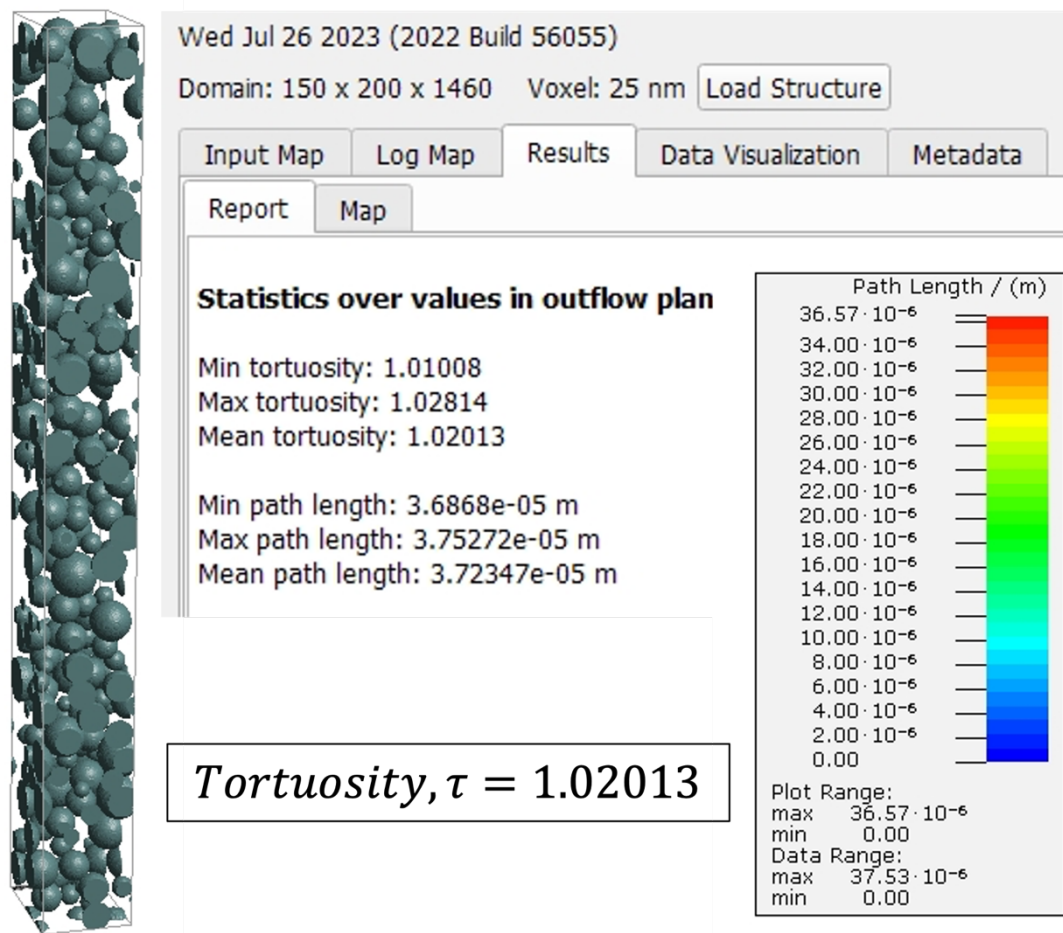


Fig. 2.21 Estimation of tortuosity in a TWC-particles membrane

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Chapter 3

Durability and Purification Performance Measurements

3.1 Background

In the previous chapter, a fabrication process of TWC-particles membrane using gas-dispersant micro-sized agglomerated TWC-particles was presented. A parametric study was conducted in the fabrication process and porosity measurement by introducing three different particle sizes under three different superficial velocity conditions. The porosity of the cross-sectional area of the membrane was measured and the permeability of the membrane was estimated according to different particle sizes and superficial velocities. The porosity of the membrane was measured as approximately 64.4 % with a slight difference about 3 % depending upon varying mean particle sizes and superficial velocities. Moreover, the cross-section view of agglomerate particles were revealed as homogeneously agglomerated particles.

In this chapter, the CO purification performance of the TWC-particles membrane was conducted through both isothermal and temperature programmed oxidation (TPO) by introducing CO as a reducing agent. The durability of the membrane was investigated by comparing different sintering temperatures such as 700 °C, 900 °C and 1100 °C through soot oxidation on the membrane. There is a trade-off relation between the durability and redox performance of three-way catalyst particles membrane. In fact, although the percolation structure of the membrane will become stronger by increasing the sintering temperature, the redox performance will be decreased due to the effect of thermal degradation. Therefore, a preferable sintering temperature which can provide enough durability of the membrane without compromising the redox performance is essential to be determined.

3.2 Methodology

3.2.1 Experimental procedures for CO oxidation through TWC membrane

The schematic diagram of the experimental setup was described in **Fig. 3.1**. The temperature which was detected by a thermocouple inserted in an outflow channel of the substrate filter which was fixed by an electric heater with a PID feedback system. The concentrations of CO and CO₂ were measured by an infrared gas analyzer after passing through the membrane with respect to time. Before the experiment, all pre-adsorbed gas molecules on the catalyst surface were removed by degases process. In the degases process, the sample temperature was increased steadily from room temperature up to 800 °C under 10 °C/min by introducing only N₂ gas. The desorption of gas molecules from the surface of the catalyst can be classified into physisorption (occurred by the weak adsorption of gas molecules from the atmosphere at low temperature) and chemisorption (chemically adsorbed on the surface by the emitted gas molecules from the prior experiment which was conducted at higher temperature) [1]. The desorbed gas concentration of CO and CO₂ during degases process was described in **Fig. 3.2**. The concentration of desorbed gas molecules can be varied time to time since it is mainly dependent upon the type of prior experiment and the exposed condition of the sample with the atmosphere before the experiment. After the degases process, the sample was cooled down to room temperature to initiate the experiment.

In the isothermal CO oxidation experiment, only CO (44 ppm) balanced with N₂ (without introducing any oxygen supply) was introduced under a condition of a superficial velocity of 20 mm/s through the membrane. The sample temperature was maintained constant for about 7 minutes for each temperature condition. The supplied CO concentration was calibrated after each measurement under each temperature condition through a by-pass line.

As for the temperature-programmed oxidation, CO (44 ppm) balanced with N₂ gas was introduced through the membrane under a superficial velocity of 20 mm/s. The degases process

was also conducted before the experiment to remove the pre-adsorbed gas species. The introduced amount of CO was calibrated before and after the experiment using a by-pass line. The sample temperature was increased from 25 °C to 700 °C with different ramping rates such as 5, 10 and 20 °C/min by using a PID feedback control system.

3.2.2 Investigation of durability of TWC-particles membrane

In order to investigate the durability of the TWC-particles membrane from the perspective of soot oxidation occurred on the membrane, three fabricated samples which were sintered at different sintering temperatures such as 700 °C, 900 °C and 1100 °C using 5 °C/min (within 4 hours) were used.

The schematic diagram of soot deposition on the sintered TWC-membrane is described in **Fig. 3.3**. The flame soot which has similar characteristics of soot particles emitted from diesel engines was collected from a diesel fuel lamp. The size distribution of collected soot particles depending upon the location of the flame height was discussed in detail in the previous study [2]. A suction pump was installed to collect the soot particles from the flame and deposited on the membrane under a superficial velocity of 20 mm/s. The increase in pressure-drop ΔP during soot deposition on the membrane was measured by tapping the digital manometer depicted in the **Fig. 3.3**. A fiber paper filter was used after the outlet of the sample to ensure the escaped soot particles. As a result, the soot cake layer as thick as 40 microns can be obtained within 5 minutes of deposition.

The trapping mechanism of soot particles on the membrane filter was investigated by using time-lapse visualization technique in our previous study [3]. As shown in **Fig. 3.4**, since the soot particles were deposited on the particles membrane, the substantial increase in pressure-drop can be reduced. The electron micrographs of deposited soot cake layer on the TWC-particle membrane filter is described in **Fig. 3.5**.

3.3 Results and Discussion

3.3.1 Isothermal CO oxidation through TWC-particles membrane

Fig. 3.6 shows the experimental result of isothermal CO oxidation under 225 °C condition. As shown in the figure, the temperature of the sample was maintained constant for 30 minutes at 225 °C (as indicated in the right vertical y-axis). The concentration of evolved CO and CO₂ were plotted in the left vertical y-axis. At the beginning of the experiment, CO was completely oxidized into CO₂, since there is no CO emission. However, a drastically decrease in CO₂ emission can be observed with respect to time even under a constant temperature condition. When the elapsed time for 30 minutes had passed, the supplied CO was stopped, then both CO and CO₂ concentration were reduced to 0 ppm. The amount of supplied CO concentration was calibrated through by-pass line and the introduced amount of CO was shown as 44 ppm. This is a one-cycle of isothermal CO oxidation through TWC-particles membrane for one temperature condition.

Fig. 3.7 shows the experimental result of isothermal CO oxidation within in the range of 75 °C to 700 °C. The CO₂ emission was increased by increasing the temperature while CO emission was decreased proportionally. There was no conversion of CO at low temperature conditions within in the range of 50 °C - 100 °C. The attenuation (similar to spike characteristics) of CO₂ emission can be observed within in the temperature range of 175 °C to 300 °C which is slightly below the light-off temperature region that will discuss in detail later. Starting from 300 °C condition, there was no decreased in CO₂ emission with respect to time. However, a trend of slightly increased in CO emission can be observed within in the temperature range of 400 °C to 700 °C conditions. As shown in **Fig. 3.8**, it was confirmed that CO conversion performance was gradually decreased at high temperature range (i.e., 400 °C to 700 °C). In fact, only CO was introduced as a reducing agent without any oxygen gas supplied in the working gas, and therefore, the oxidation reaction was occurred only by reacting

with diffused oxygen atoms from the bulk of three-way catalyst particles. Furthermore, as a similar case in the conventional catalytic converters as described in **Fig. 3.9**, either oxygen storage or release capacity can be decreased at high temperature conditions ($\geq 450\text{ }^{\circ}\text{C}$) due to the reduced oxygen released capacity of the three-way catalyst materials [4].

3.3.2 Investigation of light-off temperature

The light-off temperature of a three-way catalyst (TWC) refers to the temperature at which the catalyst becomes active and efficient in reducing gas emissions in a vehicle's exhaust system. The light-off temperature varies depending on the specific composition and design of the catalyst, as well as the exhaust system of the vehicle. However, in general, the light-off temperature of a three-way catalyst, the temperature at 50% conversion also known as T_{50} , typically ranges from around 250 to 400 degrees Celsius [5]. It's important to note that modern vehicles often employ additional technologies, such as preheating the catalytic converter and advanced engine management systems, to help achieve faster light-off temperatures for the TWC especially for cold-start condition [6, 7]. These technologies assist in reaching the optimal operating temperature more quickly, allowing the catalyst to function efficiently and effectively in reducing emissions.

To investigate the light-off temperature, the temperature-programmed oxidation of CO under different ramping rates such as 5, 10, 20 $^{\circ}\text{C}/\text{min}$ conditions was conducted as shown in **Fig. 3.12**. The light-off temperatures were determined as 50% conversion of supplied CO concentration (i.e., 44 ppm). As a result, the light-off temperature of CO conversion using TWC-particles membrane for 5, 10, 20 $^{\circ}\text{C}/\text{min}$ conditions were found out as 158 $^{\circ}\text{C}$, 177 $^{\circ}\text{C}$ and 224 $^{\circ}\text{C}$ respectively. According to the result, the light-off temperature was shifted to the right (i.e., higher temperatures) by increasing the ramping rates. In fact, catalyst can achieve preheating effect in slow ramping rate condition (similar to preheating the catalyst in the

practical advanced emission control system in the automobiles as mentioned above) which leads to lower light-off temperature. By comparing the results of ramping rates between 5 °C/min and 10 °C/min, there was not much difference with regard to light-off temperature for T_{50} . However, a slow ramping rate such as 2 °C/min or 5 °C/min can take longer operating time to investigate the light-off temperature of the catalyst in the experiment. Therefore, 10 °C/min is preferable to choose for efficiently measure the light-off temperature in temperature-programmed oxidation experiments. **Fig. 3.13** describes the light-off curve for CO and NO conversion under 10 °C/min ramping rate using TWC-particles membrane. As a result, the light-off temperature T_{50} for CO and NO conversion were determined as 178 °C and 212 °C respectively, which is notably lower than that of a conventional catalytic converter.

The mechanism of conversion of gaseous pollutants in a conventional three-way catalytic converter is governed by convection as discussed in **Fig. 3.14**. Hence, the width of metal channel is about 1.2 mm, the effective convection distance between the gas flow and the catalyst on the metal substrate is as far as 0.6 mm. On the other hand, as shown in **Fig. 3.15**, since the pore diameter of TWC-particles membrane filter is about 1.5 μm, a higher conversion efficiency can be achieved. In fact, CO gas molecules can collide more frequently when passing through the pores of the membrane compared to the much larger metal channels in a conventional catalytic converter. Therefore, the light-off temperature in a TWC-particles membrane was lower than that of the conventional catalytic converter although the composition of the catalyst are identical.

3.3.3 Temperature-programmed oxidation of soot

Fig. 3.16 displays the evolved gas concentration of CO and CO₂ during temperature-programmed soot oxidation by using a temperature ramping rate of 10 °C/min. The sample in this experiment was sintered at 800 °C. In the figure, the horizontal x-axis shows the elapsed

time in minutes, while vertical left y-axis is the concentration percent of evolved gas (i.e., CO and CO₂) and the vertical right y-axis represents the temperature in degrees C. According to the experimental result, the emission of CO by soot oxidation was almost closed to zero for the whole duration of TPO soot oxidation, due to a complete purification performance by TWC-particles membrane. On the other hand, in our previous study from our laboratory, the evolved gas concentration of CO during TPO soot oxidation was significantly higher than that of CO₂ by using conventional particulate filter made up of Si-C [8]. In the temperature range of 300 °C to 400 °C, a pre-oxidation was occurred and there was a small amount emission of CO₂ at low temperature region. The peak (maximum amount of soot oxidation) was occurred at around 700 °C. Although TWC-particles is mainly composed of metal-oxide materials such as Ceria, Alumina and so on, the soot oxidation temperature was not advanced by this composition.

3.3.4 Influence of sintering temperature on purification performance

Fig. 3.17 compares the experimental result of CO oxidation using temperature-programmed oxidation technique under 10 °C/min for the samples sintered at 800 °C and 900 °C. As shown in the figure, the CO conversion performance of the 900 °C at low temperature conditions within in the range of 100 °C to 200 °C was slightly decreased due to the effect of sintering the TWC-membrane at higher temperature condition, although there was no significant decrease in the conversion performance at higher temperature ranges (> 200 °C). The light-off temperature T_{50} of the 900 °C sintered sample was 192 °C while that of 800 °C sintered sample was about 180 °C.

Fig. 3.18 and **Fig. 3.19** compares the isothermal CO oxidation result (within in the temperature range of 75 °C to 250 °C) of the samples which were sintered at 800 °C and 900 °C. As shown in Fig. 3.17, the CO₂ emission of 900 °C sintered sample was slightly lower conversion performance especially in low temperature conditions (< 150 °C). However, the

conversion performance of CO at higher temperature conditions (≥ 200 °C) was much the same as that of the sample sintered at 800 °C. The slight reductions in CO conversion performance between the TWC-membranes which were sintered at 800 °C and 900 °C were consistent according to the TPO and isothermal CO oxidation experimental results.

Fig. 3.20 shows the evolved gas concentration during soot oxidation under temperature-programmed oxidation for the sample sintered at 900 °C. Compared to the sample sintered at 800 °C as previously discussed in Fig. 3.14, the CO purification performance was maintained since there is not much difference between those results.

However, as shown in **Fig. 3.21**, when the membrane was sintered at 1100 °C, the CO emission was significantly higher, due to thermal degradation caused by higher sintering temperature, while there is almost zero emission of CO in the samples sintered at 800 °C and 900 °C samples through the experiments (as compared in Fig. 3.14 and Fig. 3.18 respectively).

Fig. 3.22 shows the morphology of percolation structure of TWC-particles membrane which were sintered at different sintering temperatures such as 800 °C, 900 °C and 1100 °C. According to the result, the percolation structure of the samples sintered at 800 °C and 900 °C, as compared in **Fig. 3.22 (a)** and **Fig. 3.22 (b)** were not much difference while that of 1100 °C sintered sample was started transition to a molten state.

Fig. 3.23 describes the SEM micrographs of overview of the 800 °C sintered membrane after the soot oxidation experiments were done for two times. The percolation structure was destroyed by the soot oxidation which was occurred on the TWC membrane. Not only peeling from the cross-sectional wall, but grooves were also occurred on the surface due to the soot oxidation. On the other hand, as shown in **Fig. 3.24**, there were no grooves or cracks on the surface of the substrate after soot oxidation experiments, although there were some peelings from the cross-sectional wall. It is an inevitable cause in the case of multiple experiments for one sample, because the glass plates covered on the sample has to be detached several times

during observation and sample preparations. However, there is almost no grooves, cracks or peeling were observed in the sample which was sintered at 1100 °C as displayed in the **Fig. 3.25**. In fact, higher sintering temperature can provide a stronger membrane percolation structure which can resist the cause of damages by soot oxidation.

3.4 Summary

In this article, in order to investigate the CO purification performance of TWC-particles membrane, isothermal CO oxidation, temperature-programmed oxidation of CO, and soot oxidation were conducted. In the isothermal CO oxidation, the CO₂ emission were escalated by increasing the temperature, and the attenuations were observed at the temperatures slightly below the light-off temperature of the catalyst. According to temperature-programmed oxidation of CO experimental results, the light-off temperatures (T_{50}) of CO and NO, using three-way catalyst particles membrane filter were determined as 178 °C and 212 °C respectively. Moreover, there was almost no emission of CO in the temperature programmed soot oxidation.

The durability of the percolation structure of the membrane were investigated by comparing the samples which were sintered at different temperatures such as 800 °C, 900 °C and 1100 °C. The membrane structure which was sintered at 800 °C cannot resist for soot oxidation since there were peelings from the cross-sectional walls and grooves on the surface of the substrate. Although almost no damage were occurred on the membrane which was sintered at 1100 °C, the CO purification performance was degraded due to high sintering temperature. As for the case of the membrane sintered at 900 °C, the CO purification performance is still similar to that of the membrane sintered at 800 °C. Besides, only a few peelings on the cross-sectional wall caused by the glass-plate detachment were found after soot oxidation. Therefore, sintering temperature at 900 °C would be preferable to choose in order to achieve for both purification performance and durability of the TWC-particles membrane. Moreover, according to our recent report for the durability of the membrane from the viewpoint of shear stress by the working gas on the particles, the sintering temperature at 900 °C was also suggested in order to maintain the percolation structure of the TWC membrane with the least peeling rate [17].

Figures

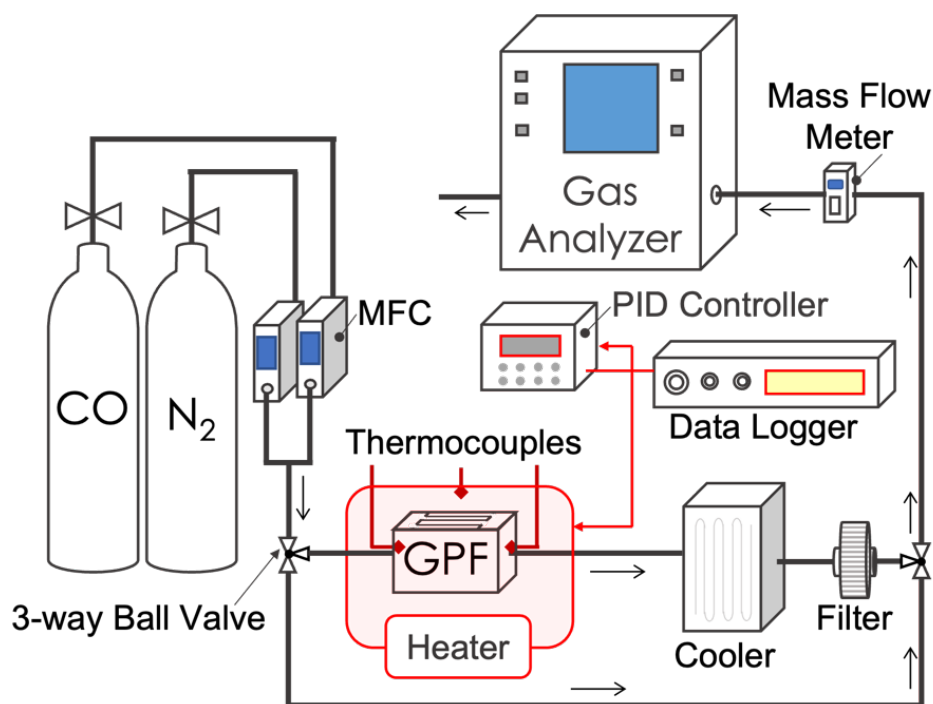


Fig. 3.1 Schematic diagram of experimental setup for CO oxidation reaction

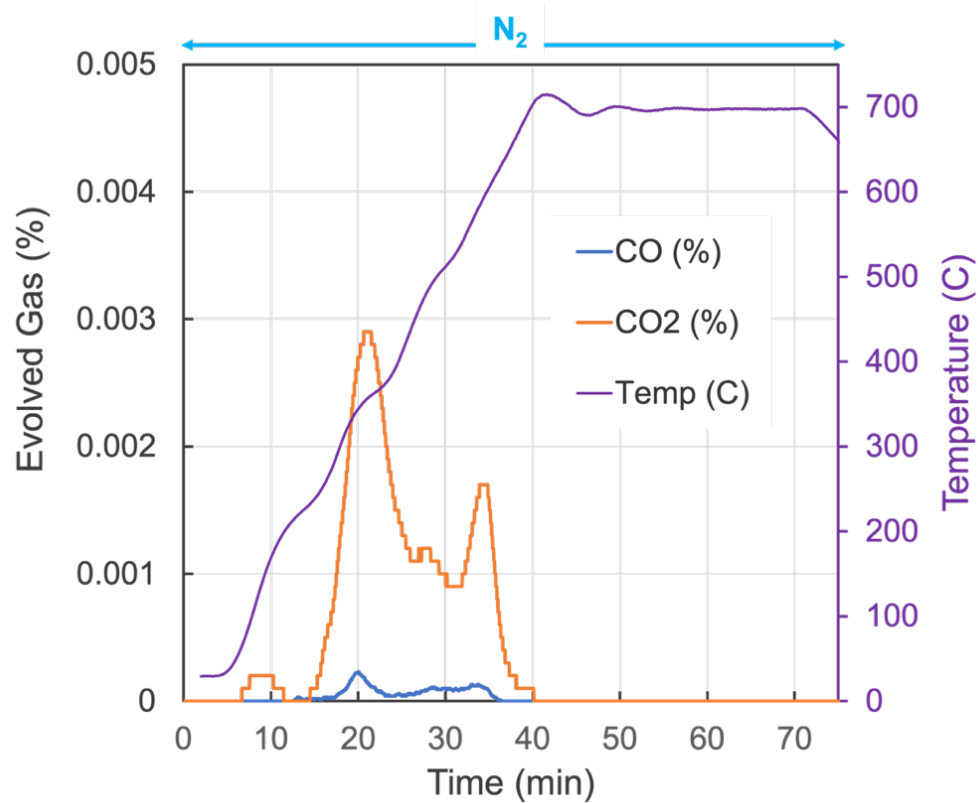


Fig. 3.2 Evolved gas concentration during degas process

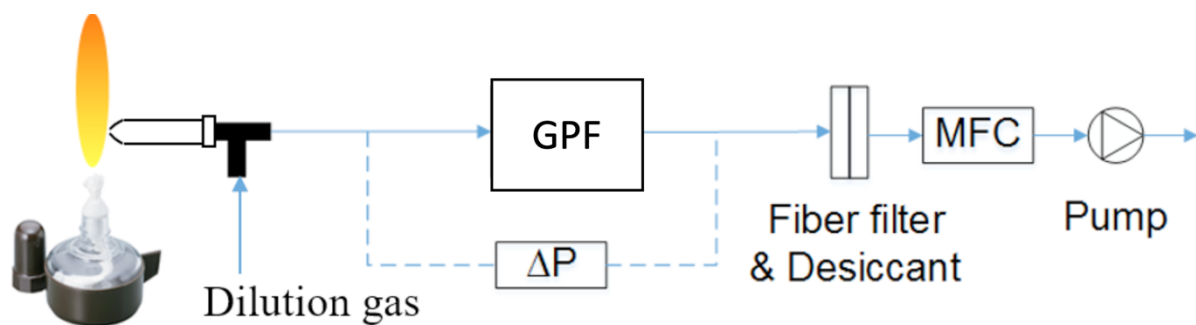


Fig. 3.3 Schematic diagram of soot deposition on the sample [8]

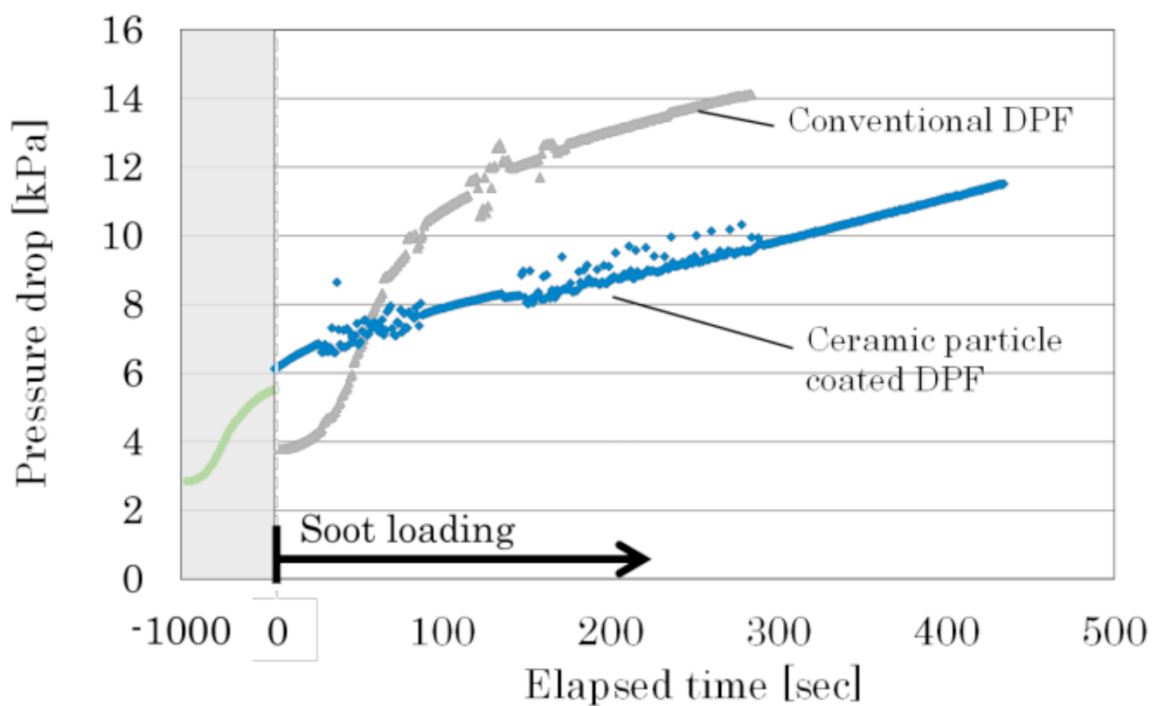


Fig. 3.4 Pressure drop increase in soot deposition on the bare substrate and membrane particulate filter [2]

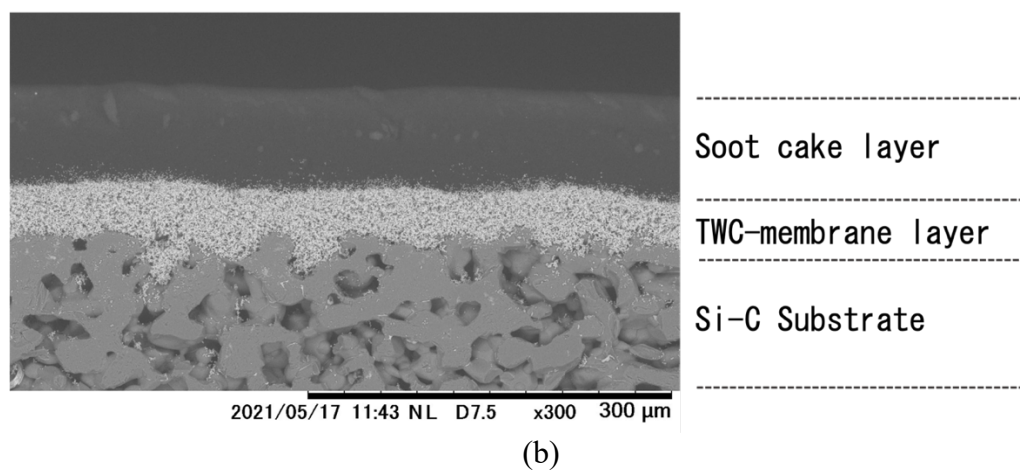
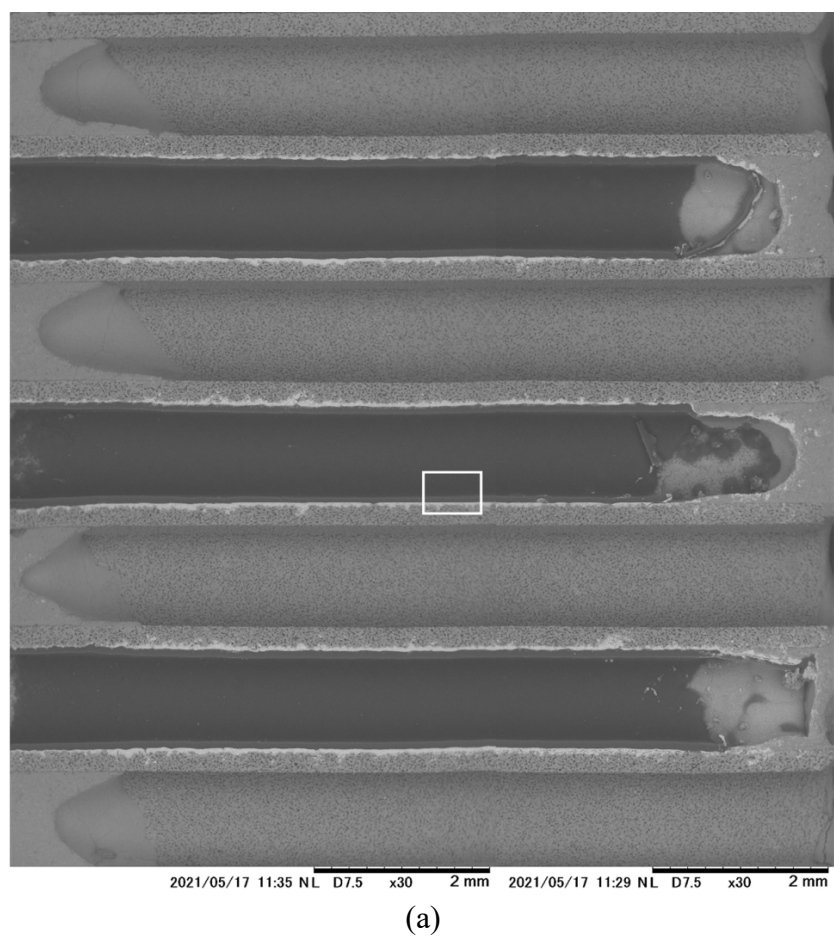


Fig. 3.5 SEM images of soot deposition of three-way catalyst particles membrane (a) overview (b) specific magnified region

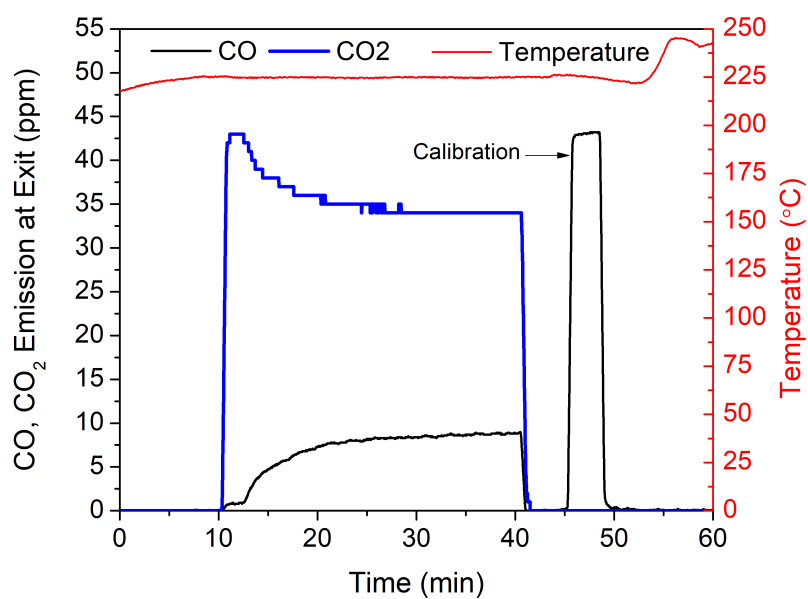


Fig. 3.6 Isothermal CO oxidation through TWC-particles membrane at 175 °C

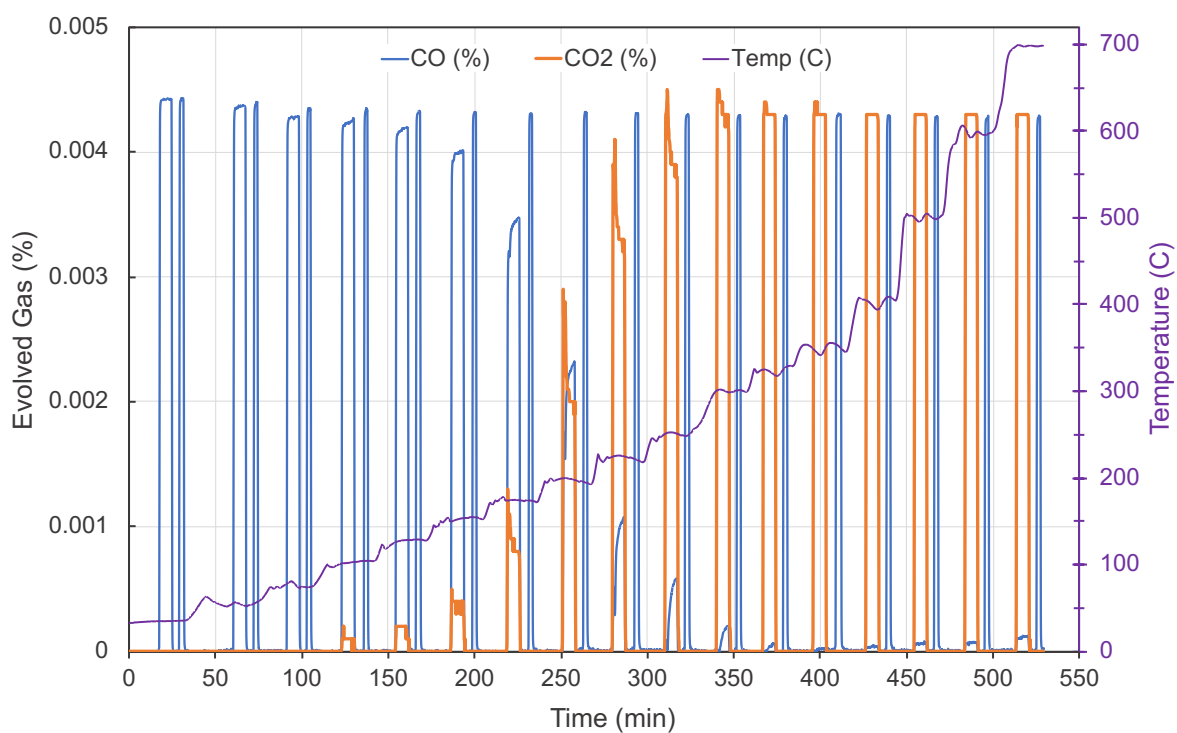


Fig. 3.7 Isothermal CO oxidation through TWC-particles membrane at 75 °C to 700 °C

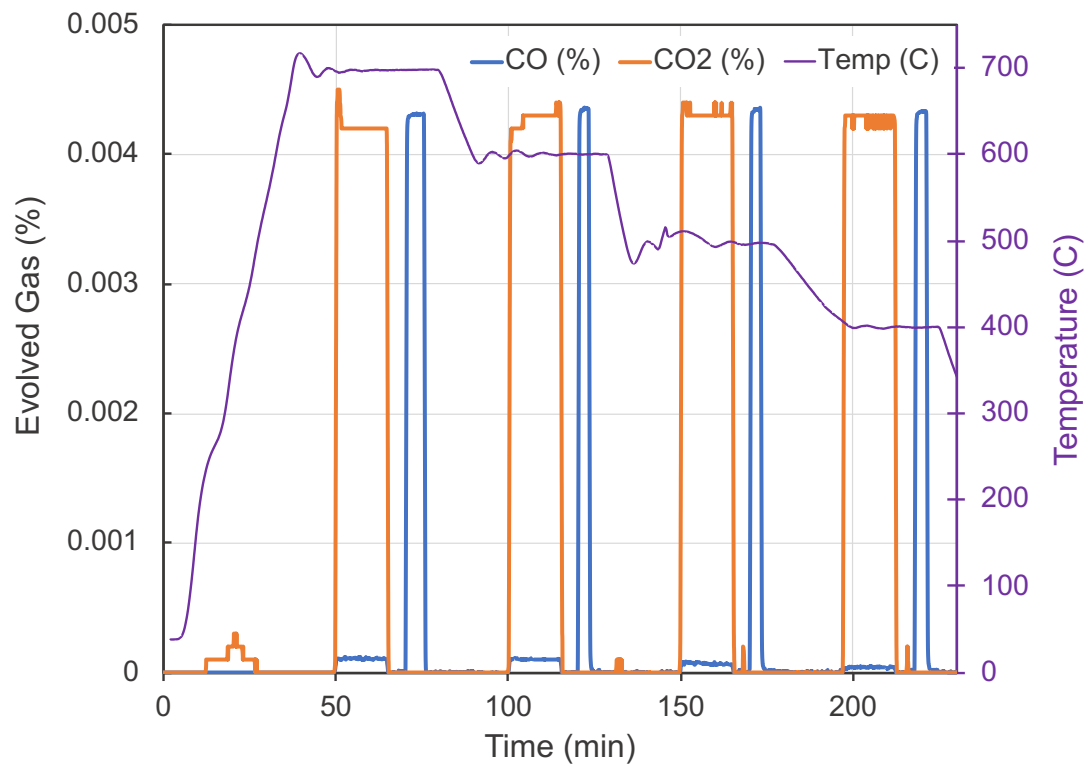


Fig. 3.8 Isothermal CO oxidation through TWC-membrane at 400 °C to 700 °C

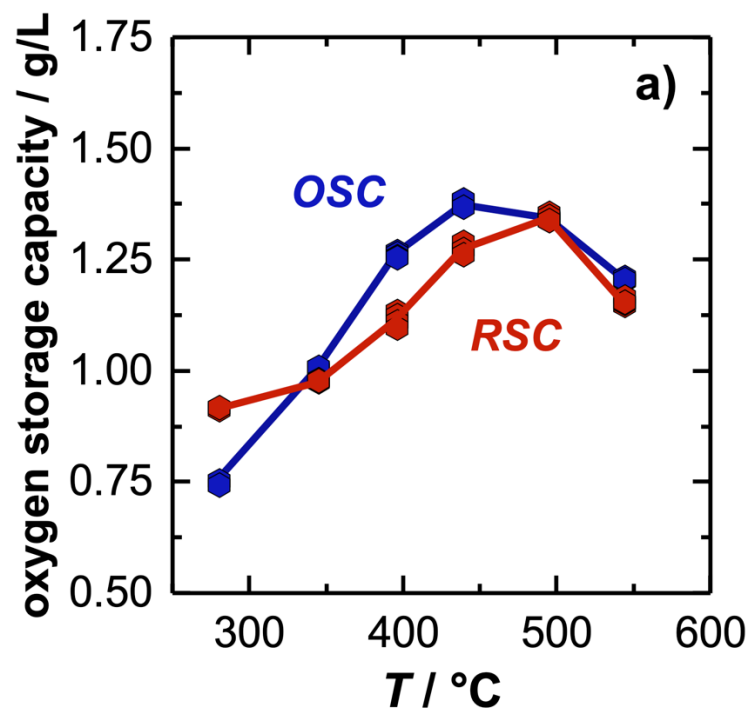


Fig. 3.9 Effect of catalyst temperature on oxygen storage and release capacity [4]

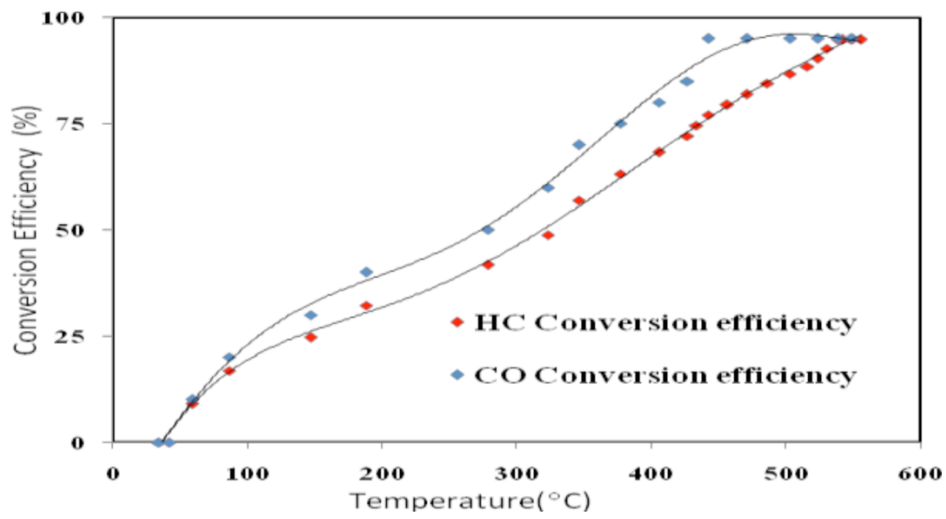


Fig. 3.10 Light-off Temperature of carbon monoxide and unburnt hydrocarbons in a commercial three-way catalytic converter [5]

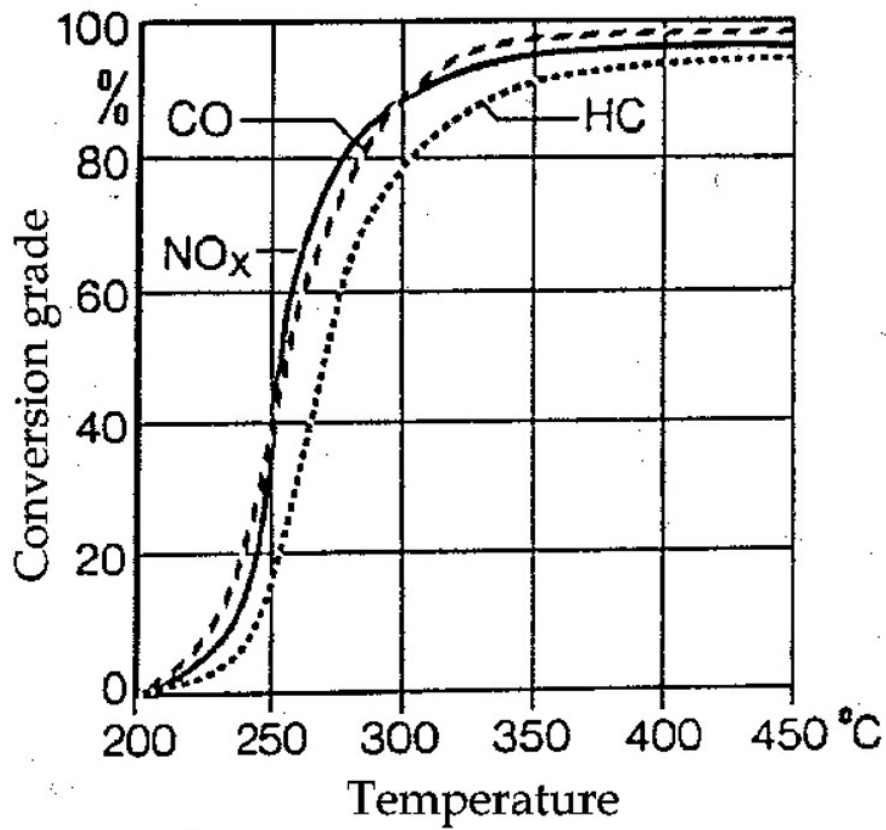


Fig. 3.11 Light-off temperature of a conventional catalytic converter [6]

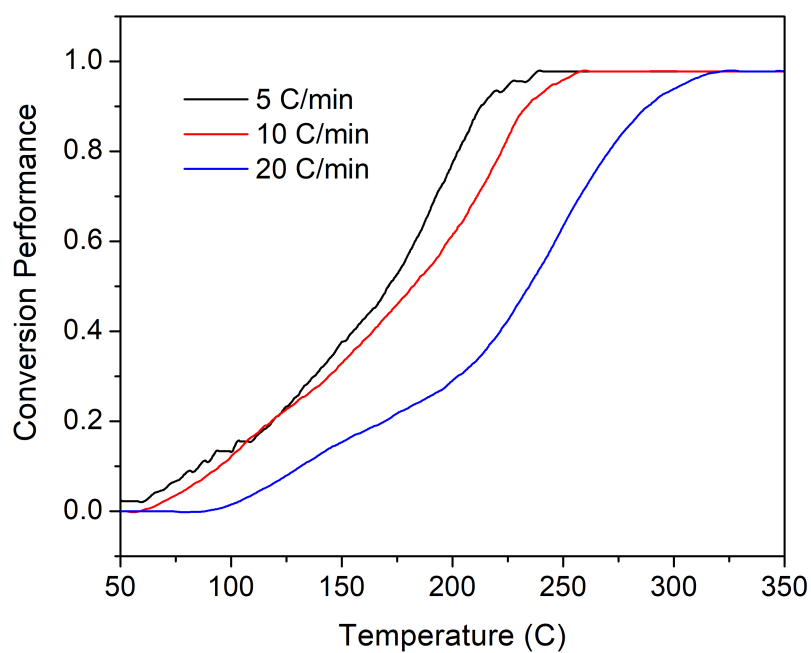


Fig. 3.12 Light-off temperature for CO conversion of TWC-particles membrane under different ramping rates such as 5, 10 and 20 $^{\circ}\text{C}/\text{min}$

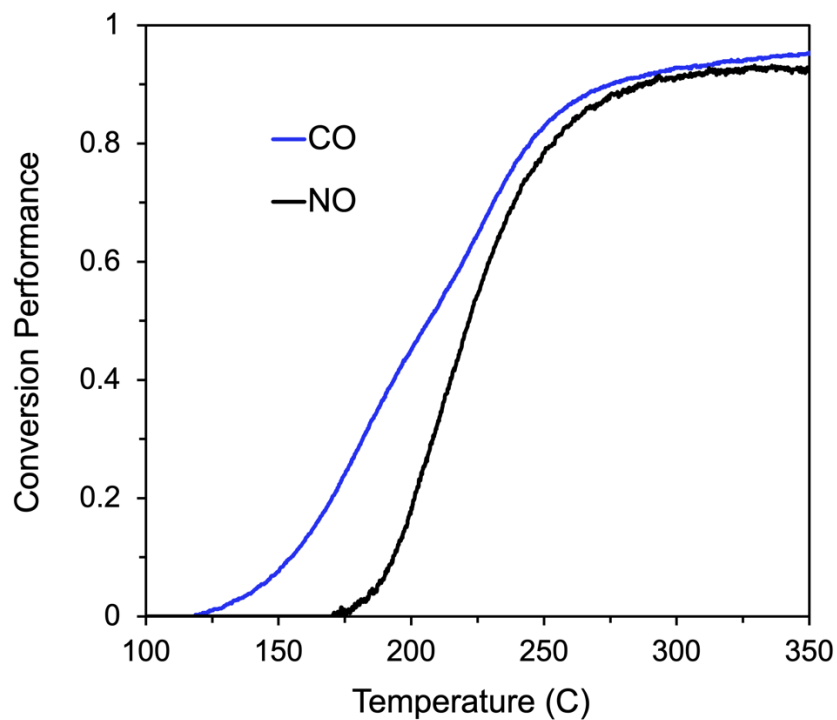


Fig. 3.13 Light-off temperature for CO and NO conversion of TWC-particles membrane under 10 $^{\circ}\text{C}/\text{min}$ ramping rate

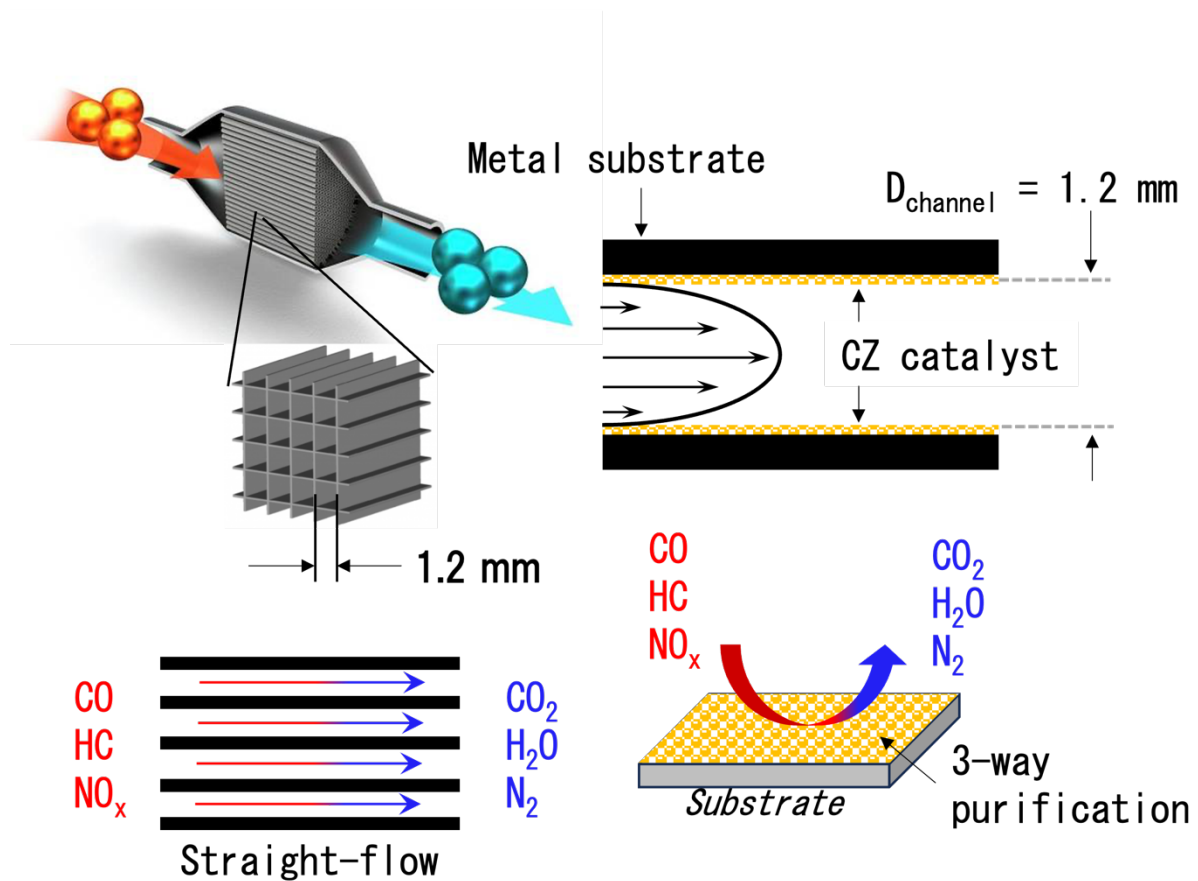


Fig. 3.14 Mechanism of purification of exhaust gas pollutants in a conventional catalytic converter

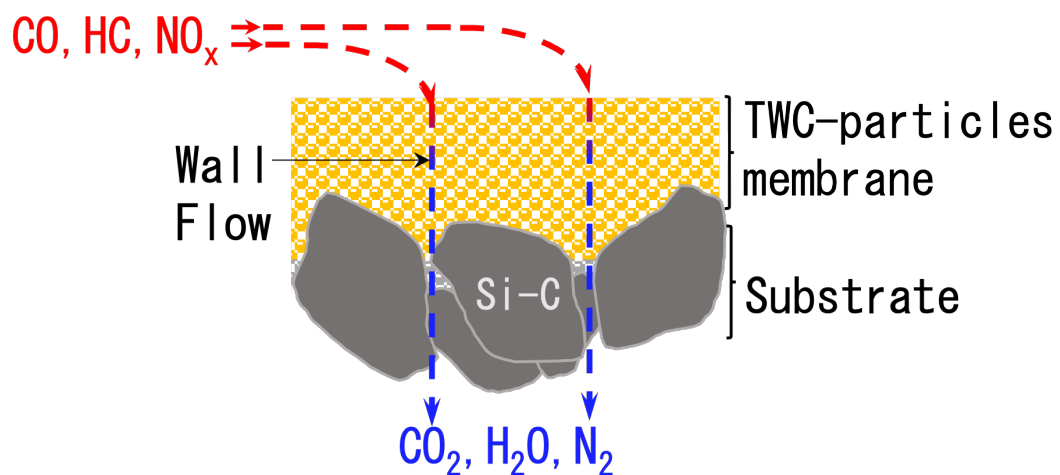


Fig. 3.15 Mechanism of purification of exhaust gas pollutants in a three-way catalyst particles membrane

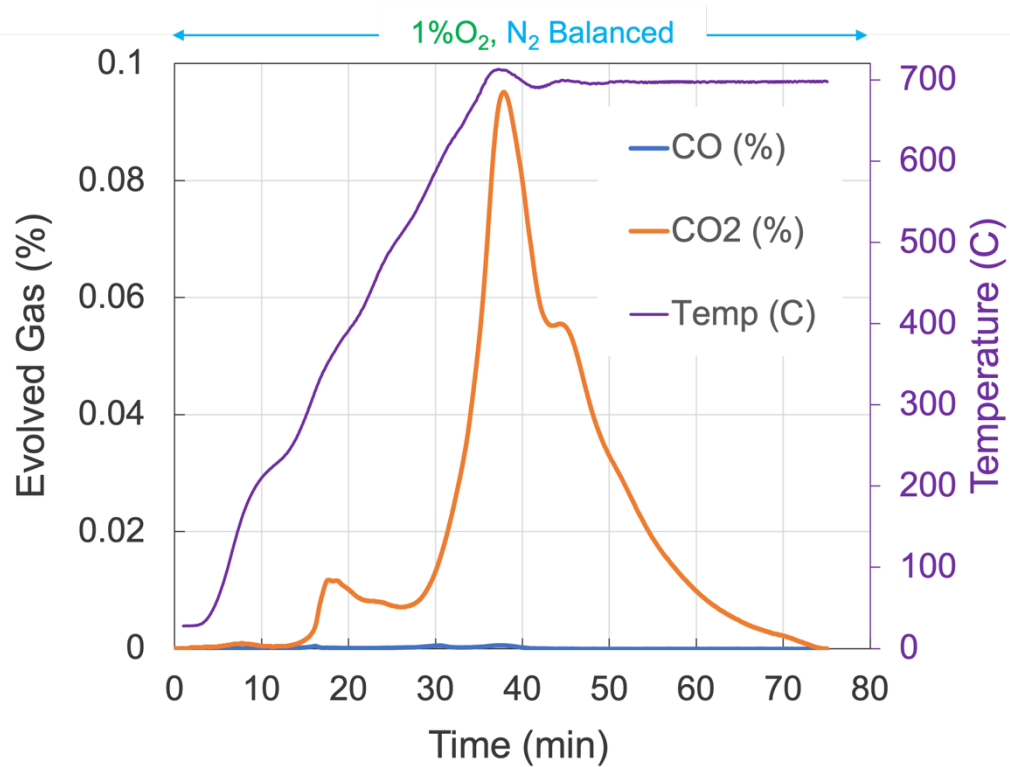


Fig. 3.16 Evolved gas concentration during soot oxidation (sintered at 800 °C)

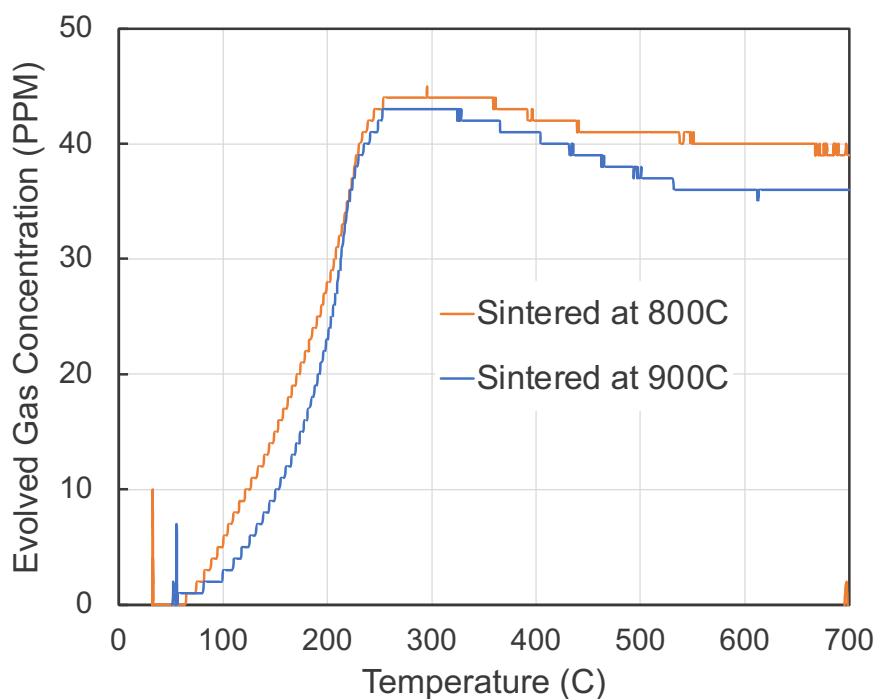


Fig. 3.17 Light-off temperature for CO conversion of TWC-particles membrane sintered at 800 and 900 °C

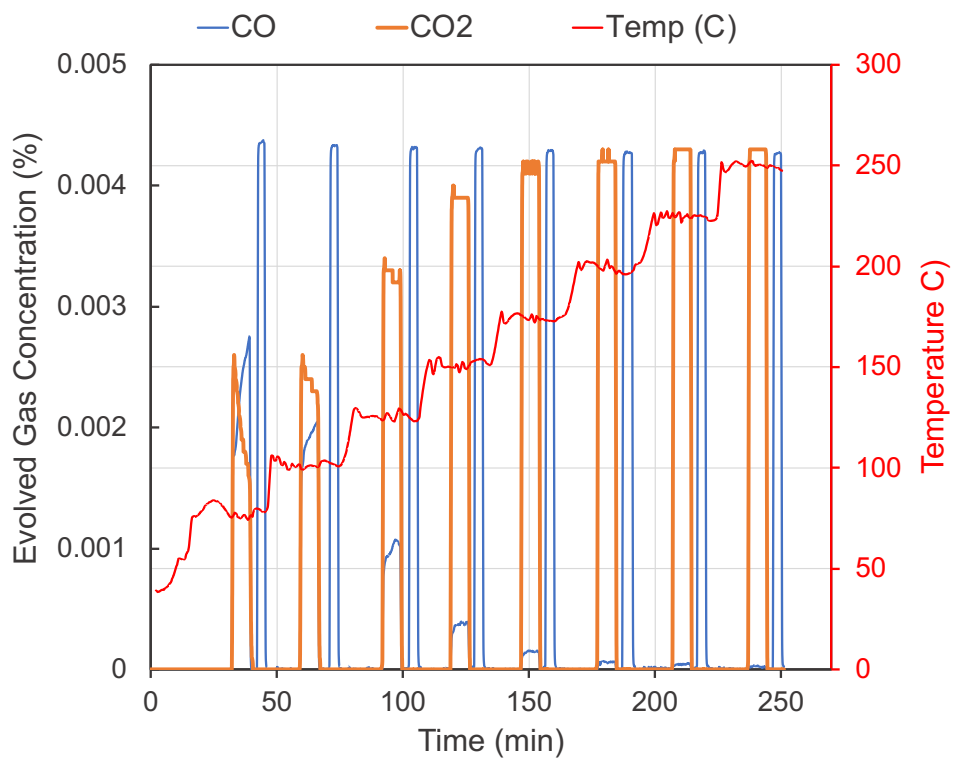


Fig. 3.18 Isothermal CO oxidation through TWC-particles membrane sintered at 800 °C

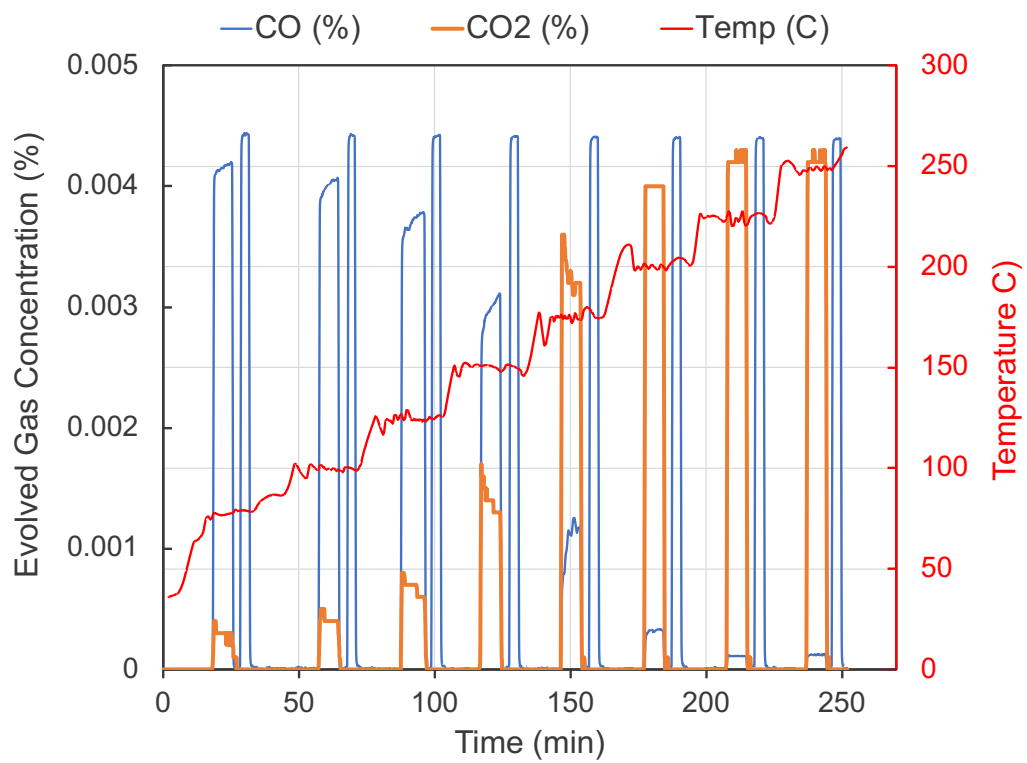


Fig. 3.19 Isothermal CO oxidation through TWC-particles membrane sintered at 900 °C

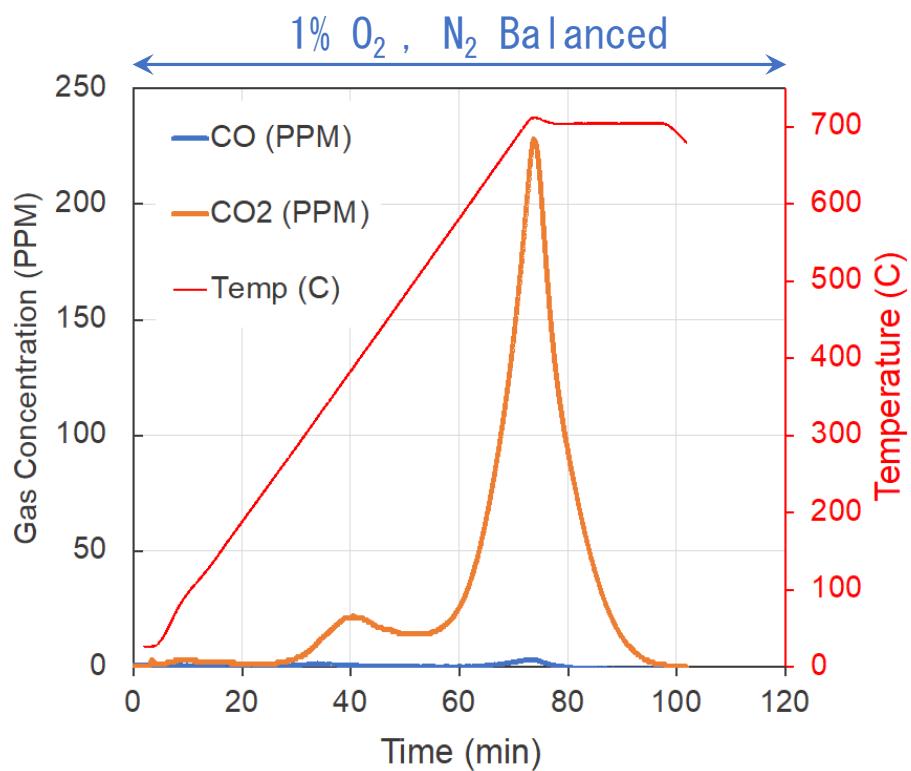


Fig. 3.20 Evolved gas concentration during soot oxidation (sintered at 900 °C)

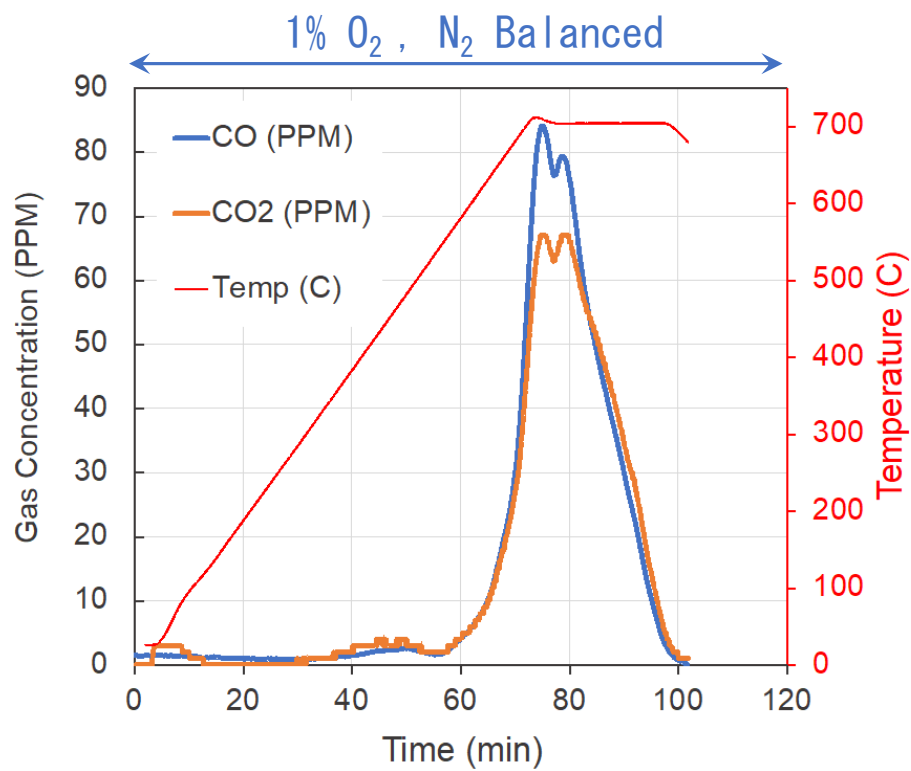
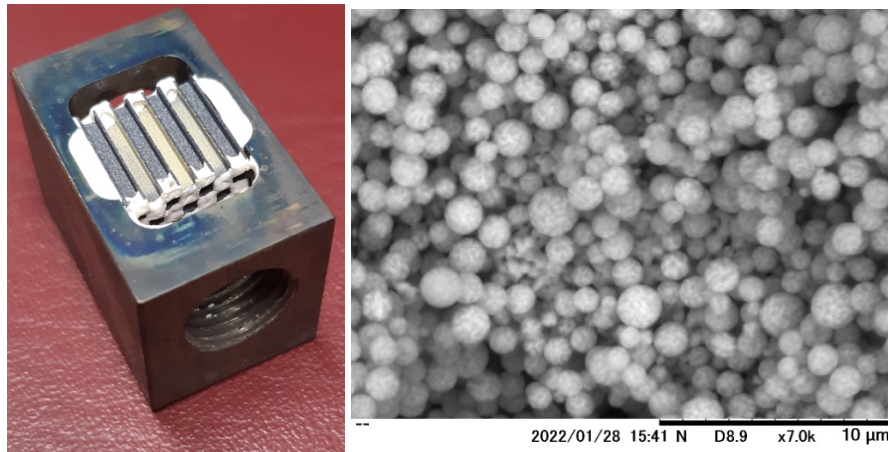
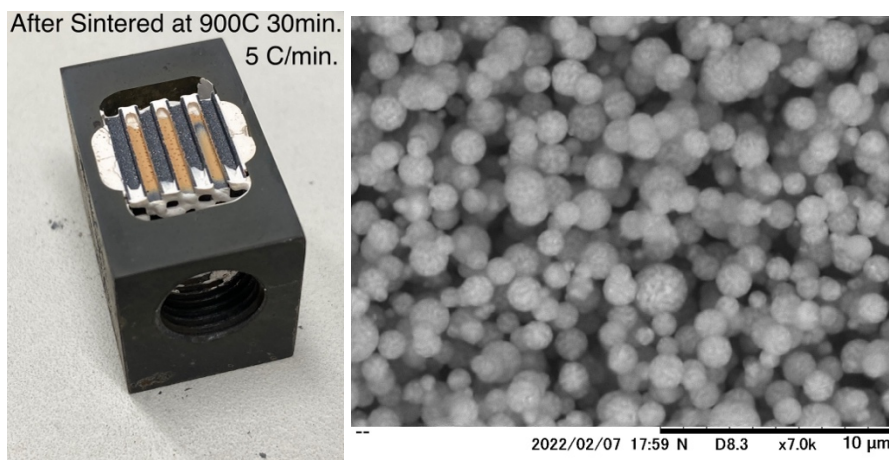


Fig. 3.21 Evolved gas concentration during soot oxidation (sintered at 1100 °C)



(a)



(b)



(c)

Fig. 3.22 Morphology of TWC particles sintered at 800 °C (a), 900 °C (b) and 1100 °C (c)

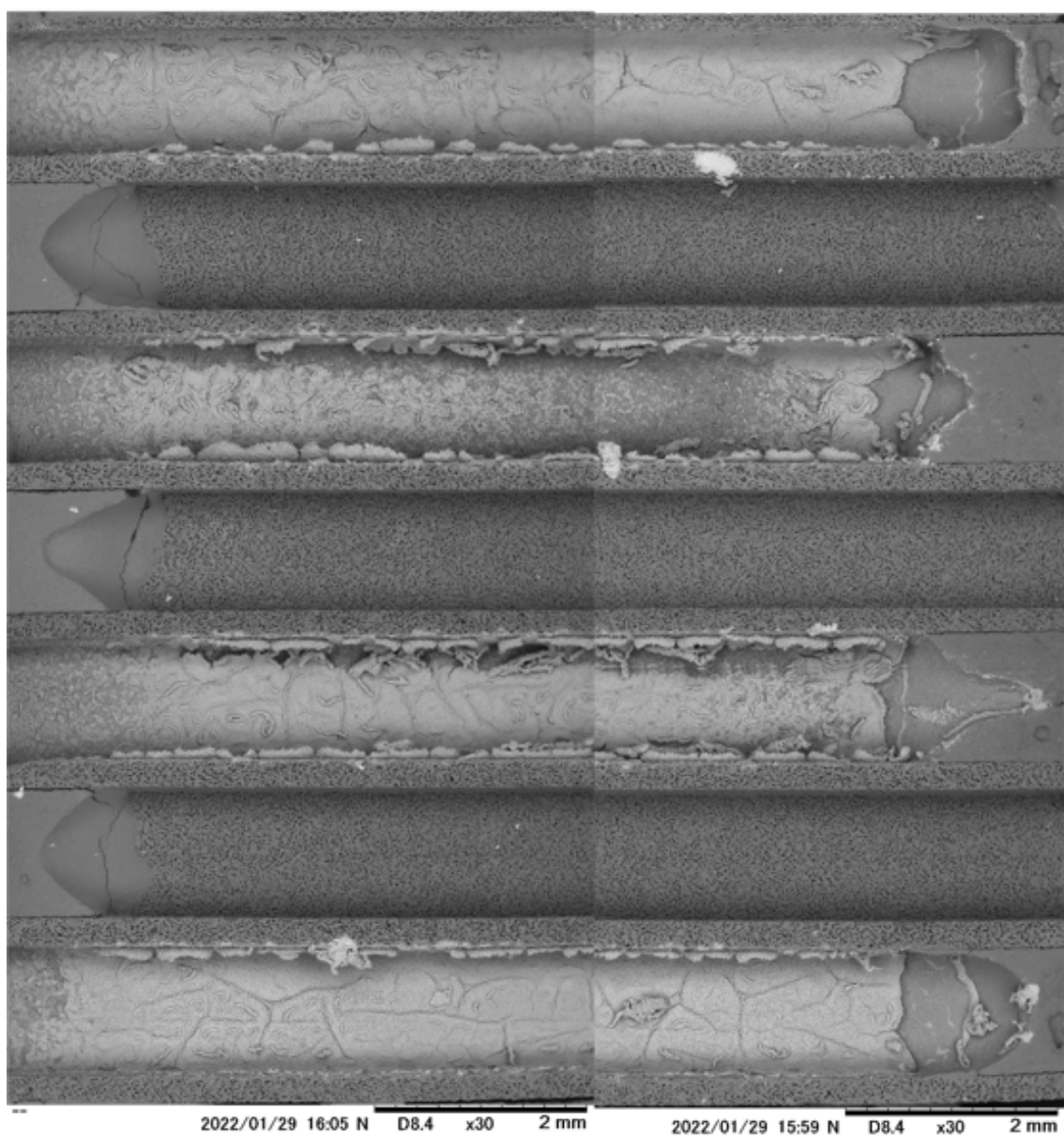


Fig. 3.23 Overview of morphology of TWC membrane after soot oxidation comparing the samples sintered at 800 °C

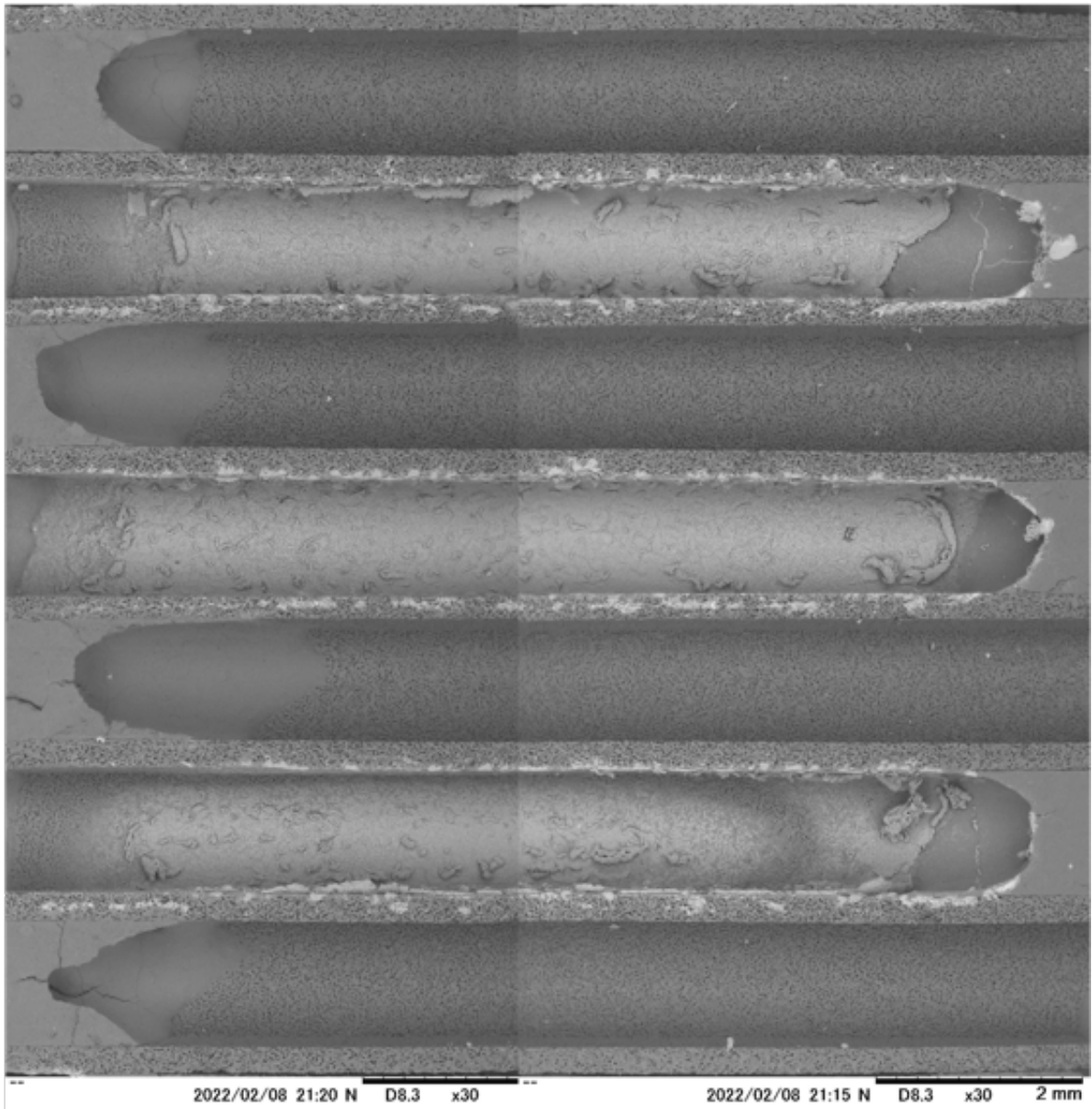


Fig. 3.24 Overview of morphology of TWC membrane after soot oxidation comparing the samples sintered at 900 °C

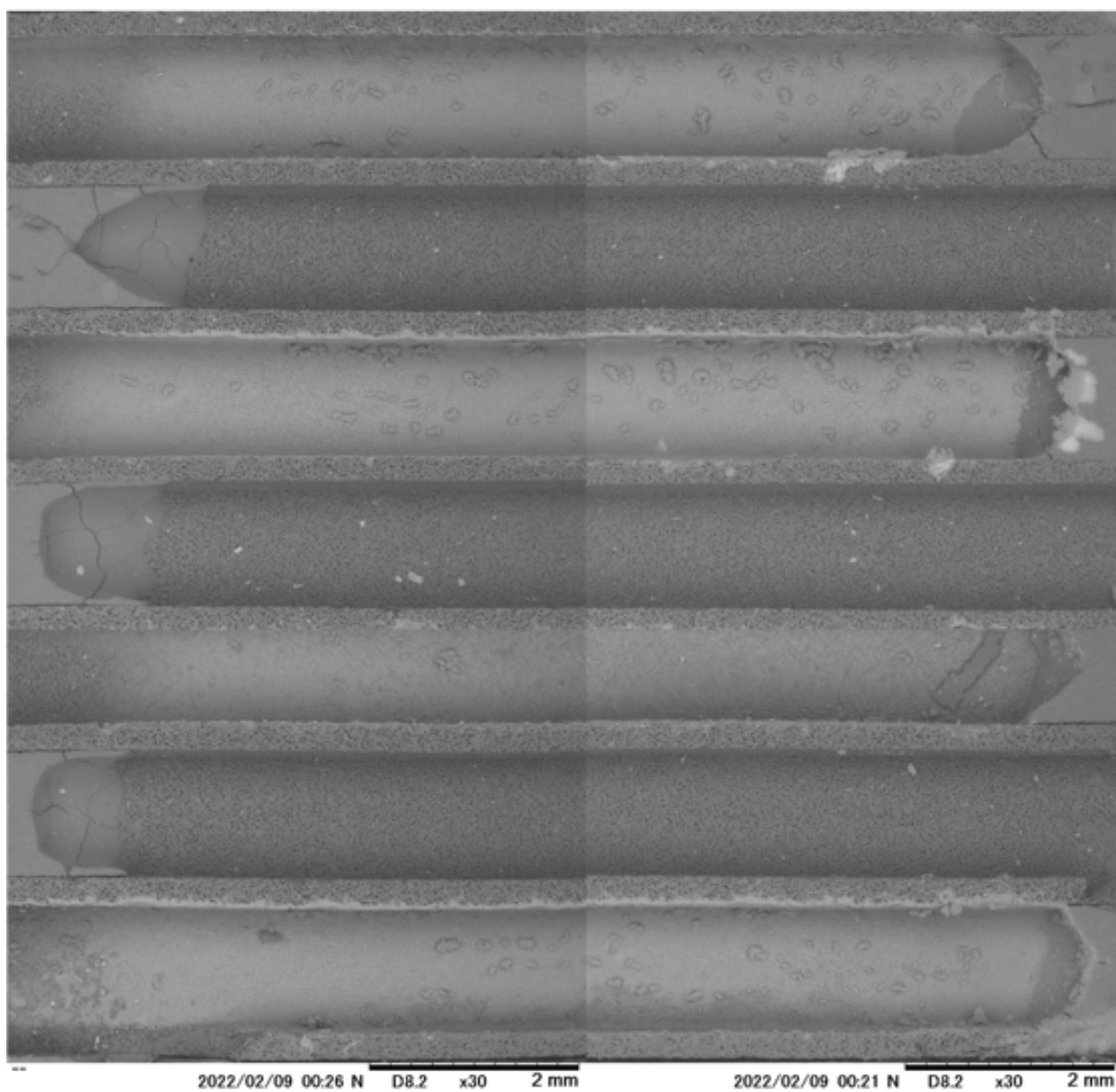


Fig. 3.25 Overview of morphology of TWC membrane after soot oxidation comparing the samples sintered at 1100 °C

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Chapter 4

Modeling of CO Oxidation by TWC-particles Membrane

4.1 Background

In the previous chapter, as discussed in the article 3.3.1, even under isothermal conditions, the transient states of attenuation of decreased in CO₂ emission with respect to time was observed, in the isothermal CO oxidation experimental result within in the temperature range of 175 °C to 300 °C. This temperature range is slightly below the light-off temperature of the catalyst which is currently in use in this study. Besides, it was found that there was no decrease in CO₂ emission rate when the catalyst temperature was beyond 300 °C.

Therefore, in this chapter, isothermal CO oxidation through TWC-particles membrane, which was emphasized on the temperature range of 175 °C to 300 °C was conducted. In the experiment, only CO was used as a reducing agent to investigate the diffusion of oxygen atoms from CZ catalyst particulates interacting with CO gas species. The elapsed time for holding the isothermal condition was increased up to 30 minutes in order to investigate the attenuation characteristics of CO₂ emission with respect to time. After introduction of CO, emission of CO₂ decreases drastically with respect to time under a low temperature condition, as previously observed. To analyze the observed phenomena, a one-dimensional diffusion numerical simulation model was introduced to predict the experimental results. Through the fitting of experimental and simulation results over a time period of 400 seconds, the oxygen transport process via temperature dependent diffusion within the TWC-particles membrane will be discussed.

4.2 Methodology

4.2.1 Physicochemical characteristics of agglomerated TWC-particles

As discussed in the article 2.3.4, the cross-sectional view of micro-sized agglomerated TWC-particles were homogeneously agglomerated with TWC-particulates. Due to low space resolution in FESEM-EDS, it was uncertain to detect the elemental composition distribution of the agglomerated particles as described in the Appendix B. However, using a back-scattered electron mode in FESEM as described in **Fig. 4.1**, non-homogeneous composition distribution can be observed. In the figure, high bright color areas were regarded as Ceria-Zirconia (CZ) particulates since CZ has the highest atomic number compared to the other components containing in the slurry. The dark gray areas, on the other hand, were identified as Aluminum oxide particulates. In the previous report, SEM (back-scattered electron mode) was also utilized to analyze the area ratio of $\text{CeO}_2\text{-ZrO}_2$ grains which were dispersed in Alumina [1].

4.2.2 Area ratio analysis of alumina and ceria-zirconia particulates

The ratio between alumina and ceria-zirconia areas were analyzed by depicting the area of CZ on the micrographs of the **Fig. 4.1(b)** using an Image-J program. The measurement process was conducted up to (3) times for multiple samples, which were measured in different locations. The results presented in **Fig. 4.2** revealed that the average CZ-particulate area occupied as approximately 50 % of the whole cross-sectional area of a single agglomerated TWC particle as summarized in **Table 4.1**. In the case of internal combustion under stoichiometric condition, since there is almost no oxygen in the exhaust gas, oxygen atom diffusion from the CZ material plays an important role for the oxidation of unburnt components, including CO.

4.2.3 Experimental procedures of CO oxidation through TWC membrane

Fig. 4.3 shows a schematic diagram of an isothermal CO oxidation experiment setup. In order to investigate the transport of oxygen atom in the TWC particles, a working gas consisting of CO (44 ppm) with N₂ balanced was introduced (without any oxygen supply in the working gas) through the TWC particles membrane under the conditions of a superficial velocity of 20 mm/s and temperatures of 175, 200 and 225 °C. The temperature which was detected by a thermocouple inserted in an outflow channel in the substrate filter was fixed by an electric heater with a PID feedback system. The concentrations of CO and CO₂ were measured by an infrared gas analyzer after passing through the membrane with respect to time. The supplied CO concentration was calibrated after each measurement under each temperature condition through a by-pass line. Before the experiment, all pre-adsorbed gas molecules on the catalyst surface were removed by introducing N₂ gas through the membrane.

4.2.4 Numerical methods

A finite difference approximation method was used to perform a numerical simulation for the diffusion-controlled oxygen atoms diffused from the bulk of TWC-particulates. A one-dimensional diffusion equation for oxygen atom in the x direction was used as expressed in Eq. 4-1. The discretized arithmetic form of the governing equation was using an explicit method is shown in the Eq. 4-2.

$$\frac{\partial c_o}{\partial t} = D \frac{\partial^2 c_o}{\partial x^2} \quad (4-1)$$

$$\frac{c_{o,i}^{j+1} - c_{o,i}^j}{\Delta t} = D \frac{c_{o,i+1}^j - 2c_{o,i}^j + c_{o,i-1}^j}{\Delta x^2} \quad (4-2)$$

where C_o represents the concentration of oxygen, D is diffusion coefficient, Δx is discrete spatial coordination and Δt is time steps respectively. The arrangement of discretized finite difference scheme is shown in **Fig. 4.4**. A stable scheme was prepared under a condition of $\frac{D\Delta t}{\Delta x^2} \leq 0.5$. A spatial resolution of 240 nodal points was chosen in order to achieve the error percent as low as 0.003 in the finite difference scheme as shown in the **Fig. 4.5**.

4.2.5 Boundary conditions

The boundary conditions for $x = 0$ and $x = L$ are expressed in Eq. 4-5 and Eq. 4-6. That is, there is no diffusion at $x = 0$, while the mole flux of oxygen atom obtained by the concentration gradient at $x = L$ in the CZ material is equal to the consumption rate of CO by oxidation at the TWC particle surface, as follows.

$$\frac{\partial C_o}{\partial x} = 0 \quad \text{at } x = 0 \quad (4-5)$$

$$-D \frac{\partial C_o}{\partial x} = A d_{Lattice} C_{O,x=L} C_{CO} \exp\left(\frac{-E_c}{RT}\right) \quad \text{at } x = L \quad (4-6)$$

To achieve a stable scheme with less error percent due to resolution, a second-order accurate three-point forward difference method was applied to discretize the boundary condition at the surface (i.e., $x = L$) through Taylor's series expansion as described below.

$$f(x + 2dx) = f(x) + f'(x) 2dx + \frac{f''(x)}{2!} dx^2 + \dots \quad (4-7)$$

$$4f(x + 2dx) = 4f(x) + 4f'(x) 2dx + \frac{4f''(x)}{2!} dx^2 + \dots \quad (4-8)$$

By subtracting Eq. (3-8) from Eq. (3-7) and the equation becomes,

$$f'(x) = \frac{-3f(x) - f(x+2dx) + 4f(x+dx)}{2dx} \quad (4-9)$$

Let $f(x) = C(x)$, and the equation becomes,

$$\frac{\partial C}{\partial x} = \frac{-3C_N + 4C_{N-1} - C_{N-2}}{2dx} \quad (4-10)$$

$$\therefore -D \frac{\partial C}{\partial x} = -D \frac{3C_N - 4C_{N-1} + C_{N-2}}{2dx} \quad (4-11)$$

Therefore, the discretized arithmetic form of the boundary condition at $x = L$ can be written as follows.

$$-D \frac{3C_N - 4C_{N-1} + C_{N-2}}{2dx} = A d_{Lattice} C_N C_{CO} \exp\left(\frac{-E_c}{RT}\right) \quad (4-12)$$

4.2.6 Numerical simulation

Fig. 4.6 shows a conceptual schematic diagram of streamlines in the membrane filter. Here, the working gas (CO = 44 ppm) is fed into the membrane layer through an inlet channel in a wall-flow pattern with a uniform distribution of flow. Assuming a one-dimensional, incompressible, and uniform flow with a characteristic velocity (superficial velocity) in the membrane layer, only a decrease in CO concentration through oxidation should be considered along the flow direction (in the z direction). In addition, it was hypothesized that CO is reacted with oxygen atoms diffused from the inside of the CZ material, and the reaction is occurred at the TWC particle surface as follows.



The rate of the reaction can be expressed as an Arrhenius-type equation which is proportional to the CO concentration, the number of oxygen atoms present at the TWC particle surface, and the number density of TWC particles. Thus, the governing equation can be written as described in **Eq. 4-14**.

$$\frac{\partial C_{CO}}{\partial t} + u \frac{\partial C_{CO}}{\partial z} = 0.5 n 4\pi a^2 d_{Lattice} C_{O,x=L} A C_{CO} \exp\left(\frac{-E_c}{RT}\right) \quad (4-14)$$

Here, the concentration of CO (C_{co}), superficial velocity (u), time (t), space axis in the flow direction (z), number of TWC particles in a unit volume (n), radius of the TWC particle (a), lattice constant of CZ material ($d_{Lattice}$), oxygen atom concentration in the CZ material ($C_{o,x=L}$), activation energy for oxidation at the surface of TWC particle (E_c), gas constant (R), and absolute temperature (T) are all parameters in the governing equation (Eq. 4-14), which describes the reaction rate as an Arrhenius-type expression that is proportional to the CO concentration, the number of oxygen atoms at the TWC particle surface, and the number density of TWC particles. The product of $4\pi a^2$ and $d_{lattice}$ represents a thin shell volume at the TWC particle surface. The lattice constant of CZ material $d_{lattice}$ was obtained as 0.5 nm by the previous work [2]. The factor of 0.5 on the right-hand side represents the CZ surface area ratio of 50% among the spherical surface area of the TWC particle, which will be discussed later. In order to obtain the oxygen atom concentration at the TWC particle surface, a transport of oxygen atom by diffusion in the CZ material should be calculated simultaneously.

In **Fig. 4.7**, a schematic illustration of diffusion-controlled CO oxidation is presented. Only the CZ particulates (depicted by yellow color) located around the surface of an agglomerate particle contribute to CO oxidation. Since the CZ particulate is isolated, it is assumed here that the oxygen atom will be transported one-dimensionally from inside to the surface in the same CZ particulate colored by yellow in the x direction. The mole number of

oxygen atom obtained by the concentration gradient at the surface should be equal to the amount of consumed CO moles by oxidation. Moreover, it is assumed that the isolated CZ surface area has 50 % of the whole surface area of the spherical TWC particle because the ratio of cross-sectional area of the primary CZ particulates is 50 % to the whole one as previously mentioned in **Fig. 4.2**. Therefore, one-dimensional diffusion equation for oxygen atom in the x direction is expressed in Eq. 4-15.

$$\frac{\partial C_o}{\partial t} = D \frac{\partial^2 C_o}{\partial x^2} \quad (4-15)$$

Here, C_o represents oxygen atom concentration, t is time, x is the axis from the inside to the surface of the CZ area and D is the diffusion coefficient of oxygen atom in the CZ material. The diffusion coefficient is described by Arrhenius type expression as follows.

$$D = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (4-16)$$

Here, D_0 is the pre-exponential diffusivity and E_a is the activation energy for diffusion. The boundary conditions for $x = 0$ and $x = L$ are expressed in Eq. 4-17 and Eq. 4-18. That is, there is no diffusion at $x = 0$, while the mole flux of oxygen atom obtained by the concentration gradient at $x = L$ in the CZ material is equal to the consumption rate of CO by oxidation at the TWC particle surface, as follows.

$$\frac{\partial C_o}{\partial x} = 0 \quad \text{at } x = 0 \quad (4-17)$$

$$-D \frac{\partial C_o}{\partial x} = A d_{Lattice} C_{O,x=L} C_{CO} \exp\left(\frac{-E_c}{RT}\right) \quad \text{at } x = L \quad (4-18)$$

In order to perform a numerical simulation, the diffusion coefficient for oxygen atom transport in the CZ material is unknown. Therefore, the inverse problem approach is used to estimate the diffusion coefficient D in Eq. 4-18, by fitting the time history of the oxygen atom flux at the TWC particle surface with respect to time under all isothermal temperature conditions. The activation energy E_a and pre-exponential diffusivity D_o in Eq. 4-16 are estimated simultaneously from an Arrhenius plot. Additionally, for CO oxidation at the TWC particle surface, the pre-exponential factor A needs to be estimated by fitting the time history of the oxygen atom flux, while the activation energy E_c was obtained as 9 kJ/mol by the previous literatures [3, 4]. The mean radius of the TWC particle a and the mean size of the primary CZ particulate L are assumed to be 0.6 mm and 200 nm, respectively, based on SEM and TEM images obtained in the experiment.

4.3 Results and Discussion

4.3.1 Isothermal CO oxidation by TWC-membrane filter

Fig. 4.8 presents the experimental result of isothermal CO oxidation by TWC particle membrane under different temperature conditions such as 175, 200, and 225 °C. The temperature of the miniature-sized filter with the membrane is indicated in red color on the right-hand side vertical y-axis and it is increased by an electric heater using nitrogen atmosphere. At the start of the experiment, CO (44 ppm) was introduced when the temperature was fixed at 175 °C. In the figure, the black and blue lines illustrate the emission of CO and CO₂, respectively. At the elapsed time of 30 minutes, CO and CO₂ emissions were approximately 7 ppm and 37 ppm, respectively. Therefore, a significant amount of CO was oxidized by the TWC particles membrane even in the absence of oxygen gas supply. However, CO₂ emission was decreased over time while CO emission was increased inversely. The isothermal CO oxidation experiment was stopped after 21 minutes, and before proceeding with

the next higher temperature experiment, the supplied CO concentration was confirmed as 44 ppm. This cycle represents an isothermal CO oxidation experiment for one temperature condition. With increasing temperature from 175 to 225 °C, the initial CO emission approaches to zero, and the decrease in CO₂ emission is not significant. Furthermore, it was observed that CO₂ emission does not decrease over time when the temperature exceeds 300 °C.

4.3.2 Oxygen atoms flux fittings

Fig. 4.9 shows fitting results between experimental and numerical oxygen atom fluxes at the TWC particle surface. Here, the oxygen atom flux in experiment is estimated from the required number of oxygen atom to produce total mole number of CO₂ calculated from emission concentration with respect to time. In numerical simulation, the flux is obtained from the gradient of oxygen atom concentration at the surface of CZ material. The fitting parameter A which is the pre-exponential factor for oxidation contributes to an increase or a decrease in flux in the entire region of the elapsed time while D is the diffusion coefficient of oxygen atom contributes to a decreasing rate of flux with respect to time. The numerical results are agreed well with the experimental ones using the combination of the fitting parameters as shown in **Table 4.2**. There are some discrepancies between those around the beginning of oxidation, especially at the higher temperature condition. Because the introduced concentration of CO is a stepwise initial condition in the numerical simulation while a gradually-increased initial condition from 0 to 44 ppm in the experiment. Therefore, to remove the uncertainties at the initial times, the calculated oxygen atom flux from the experiment were fitted starting from 10 seconds of elapsed time history (i.e., 400 seconds) as shown in **Fig. 4.9**. Using the obtained diffusion coefficient D from the fitting, the activation energy E_a and pre-exponential factor D_o are estimated as 96.4 kJ/mol and $3.904 \times 10^{-8} \text{ m}^2/\text{s}$ from the Arrhenius plot as shown in **Fig. 4.10**.

4.3.3 Concentration distribution of CO along the membrane

Fig. 4.11 shows variation of CO concentration distributions along the flow direction with respect to time from the beginning to the elapsed time of 400 seconds under the conditions of temperatures of 175, 200 and 225 °C using the fitting parameters obtained above. Here, the working gas flows from the right to the left with the superficial velocity of 20 mm/s, and the concentration of CO at the right-hand side is fixed at 2.2×10^{-9} mol/m³ (44 ppm). Through CO oxidation in the membrane even in the case of temperature of 175 °C (**Fig. 4.11(a)**), the concentration of CO introduced is decreased along the thickness, while there is no emission of CO up to the elapsed time of 100 seconds though it doesn't agree with the experimental results. However, with respect to time, the CO concentration in entire region of the membrane is increased due to a decrease in oxidation rate even under isothermal oxidation condition. Then, at 400 seconds later, much amount of CO is emitted in the case of 175 °C (**Fig. 4.11(a)**). With increasing temperature from 175 to 225 °C, since the more CO is oxidized, the emission at 400 seconds later becomes smaller.

4.3.4 Concentration profiles of ceria-zirconia particulates

Fig. 4.12(a), 4.12(b) and 4.12(c) show variations of oxygen atom concentration distributions in the CZ material in the TWC particle located at the top surface of the membrane with respect to time under the condition of temperatures of 175, 200 and 225 °C, respectively. On the other hand, **Fig. 4.13(a), 4.13(b) and 4.13(c)** and **Fig. 4.14(a), 4.14(b) and 4.14(c)** show those at the middle and bottom surface of the membrane. Here, since at the right-hand side end of each graph the oxygen atom is reacted with CO, the oxygen atom concentration is decreased with respect to time. According to CO oxidation rate at the right-hand side end, the oxygen atom is supplied by diffusion from the inside of the CZ particulate. As a result, the oxygen concentration is decreased in the x direction at each time step. Moreover, according to

consumption of oxygen atom, the concentration in the CZ particulate is decreased with respect to time. With increasing temperature from 175 °C (**Fig. 3.10(a)**) to 225 °C (**Fig. 3.10(c)**), since the diffusion coefficient of oxygen atom is increased by the Arrhenius type expression, the concentration gradient at the surface (at the right-hand side end) becomes smaller while the transport range becomes wider. Moreover, the concentration gradient at the bottom surface of the membrane is smaller than that of the top surface because the CO concentration decreases along the flow direction. From the simulation results, the transport distance of oxygen atom is mainly within a range of 100 nm from the surface of the TWC particle for those temperature ranges.

Summary

From experiment and numerical simulation for transient and isothermal CO oxidation without any oxygen gas supply, the reaction rate is controlled by diffusion of oxygen atom through ceria-zirconia (CZ) particulates located at the surface of the spherical TWC particles which are the elements of the TWC membrane filter. The oxygen atoms are supplied by the concentration gradient within a range of the depth of about 100 nm from the CZ particulate surface under the condition of temperature range from 175 to 225 °C. Using the Arrhenius-type diffusion coefficient, the transient phenomena of isothermal CO oxidation with respect to time can be described well, and the oxygen atom fluxes required for CO oxidation with respect to time agrees well with those estimated from experimental results. Although the TWC particle size of around 1.2 μm is chosen from a point of view of development of a low pressure drop filter, CZ particulates completely emerged in the TWC particle should be activated in future.

Tables

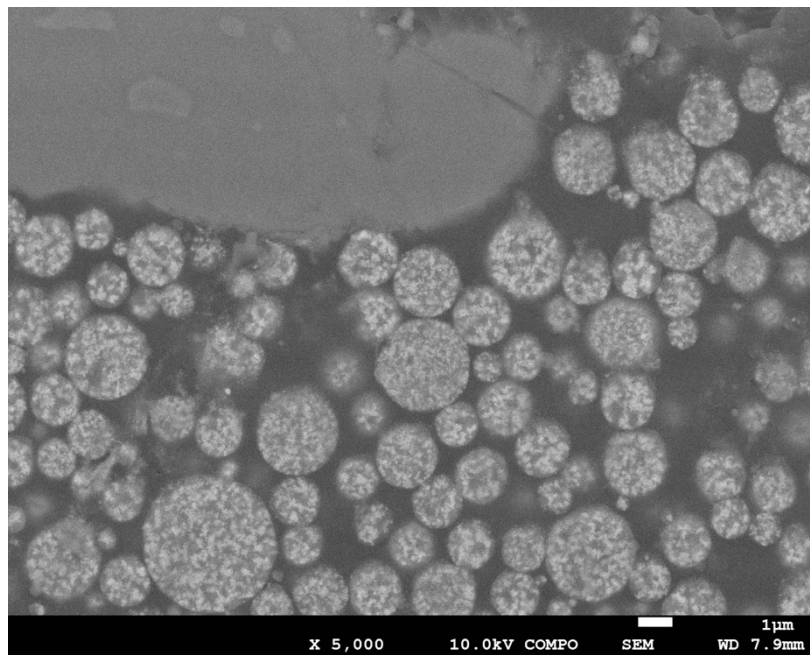
Table 4.1 Area ratio analysis between CZ and Alumina particulates in cross-sectional TWC-agglomerate particles

Sample	CZ Area (%)	Alumina Area (%)
1	50.935	49.065
2	53.465	46.535
3	48.537	51.463

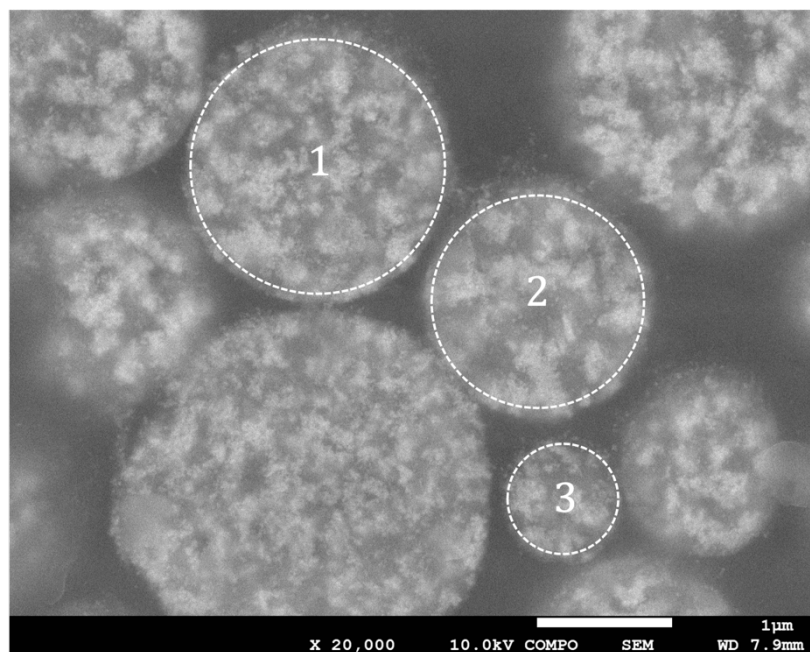
Table 4.2 Summary of fitted diffusion parameters

Temperature (°C)	Diffusion coefficient, D (m ² sec ⁻¹)	Collision Frequency, A (m ³ mol ⁻¹ sec ⁻¹)
175	2.3×10^{-19}	1.55×10^9
200	8.4×10^{-19}	
225	3.1×10^{-18}	

Figures

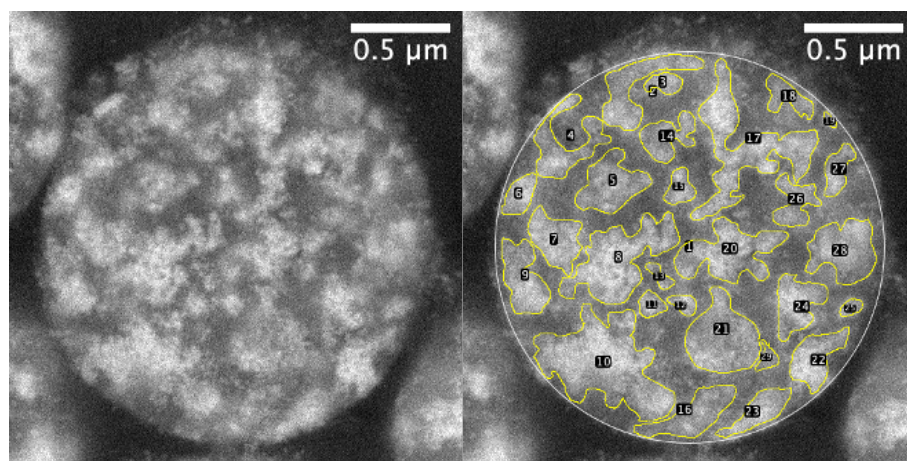


(a)

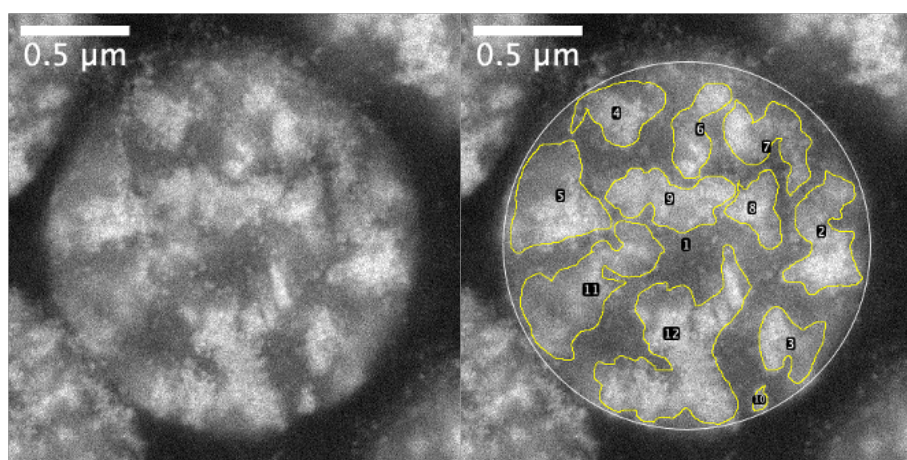


(b)

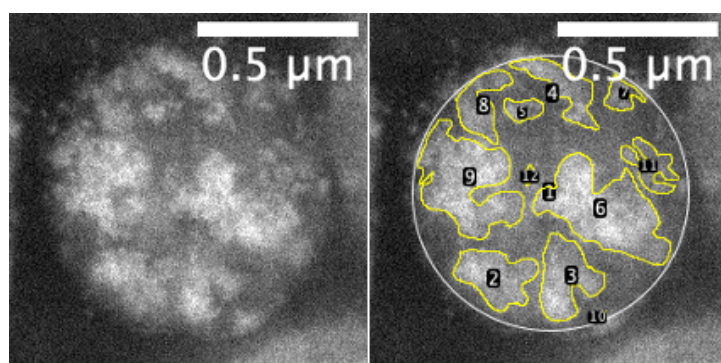
Fig. 4.1 FESEM micrographs under back-scattered electron mode of cross-sectional agglomerated TWC-particles (a) overview (b) analyzed magnified region



(a)



(b)



(c)

Fig. 4.2 Elemental analysis of cross-sectional agglomerated particles under back-scattered electron mode (a) Location 1 (b) Location 2 and (c) Location 3

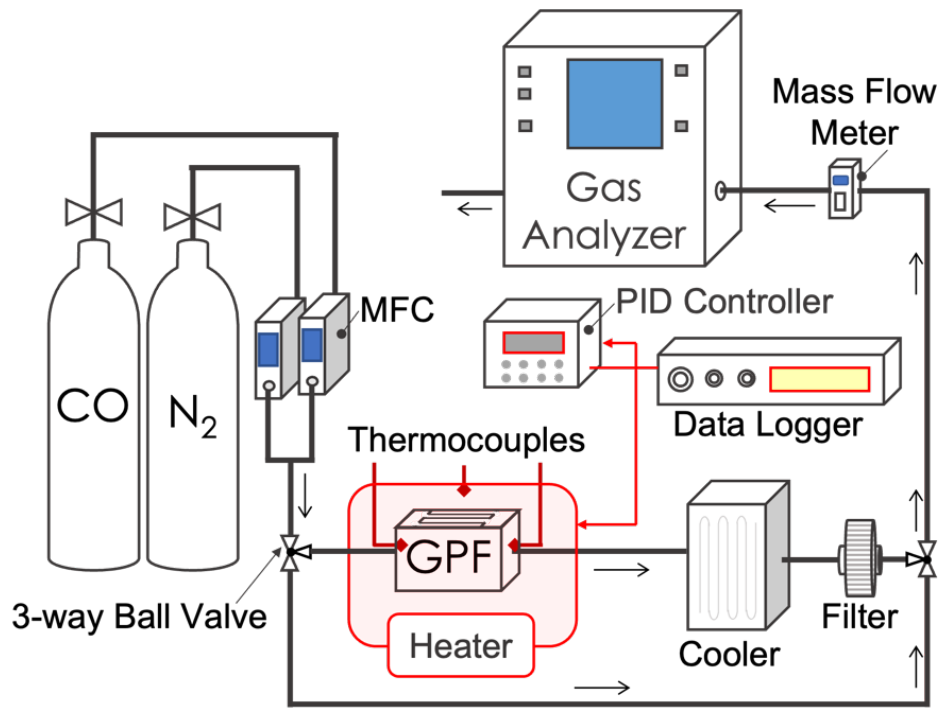


Fig. 4.3 Schematic image of CO oxidation through TWC-particles membrane

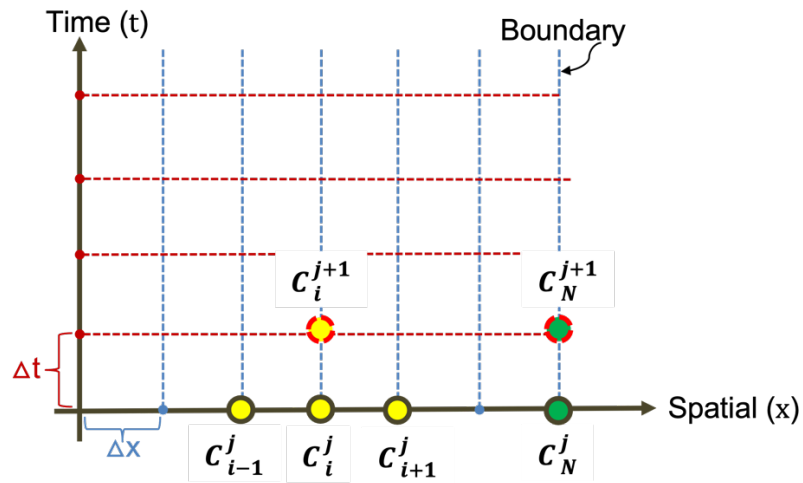


Fig. 4.4 Discretized finite difference scheme

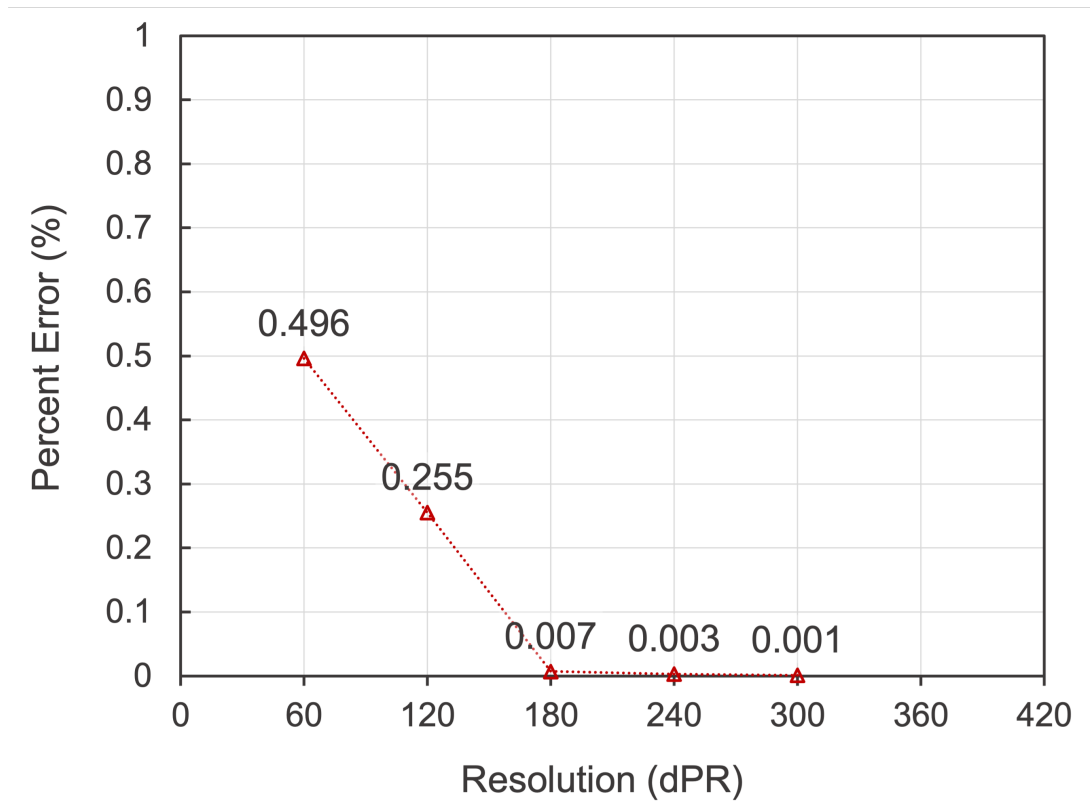


Fig. 4.5 Percent error of finite different scheme with respect to spatial resolutions

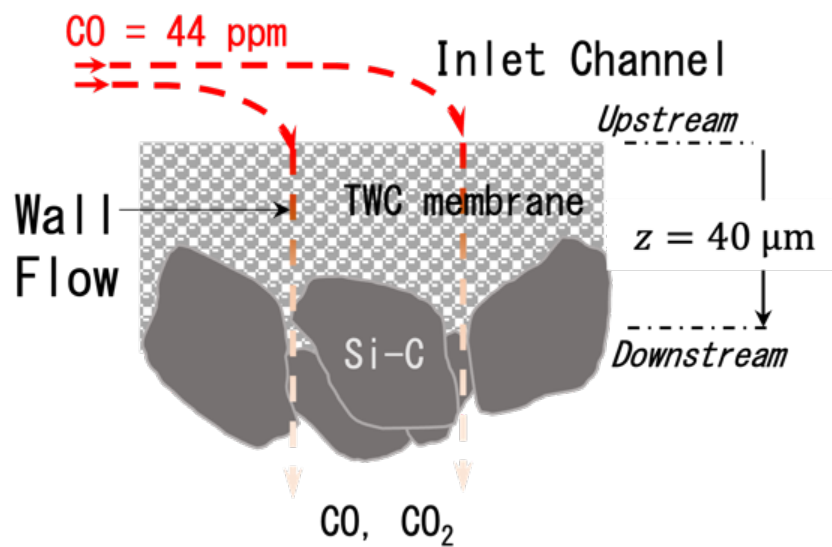


Fig. 4.6 Schematic image of CO concentration distribution in a TWC-particles membrane

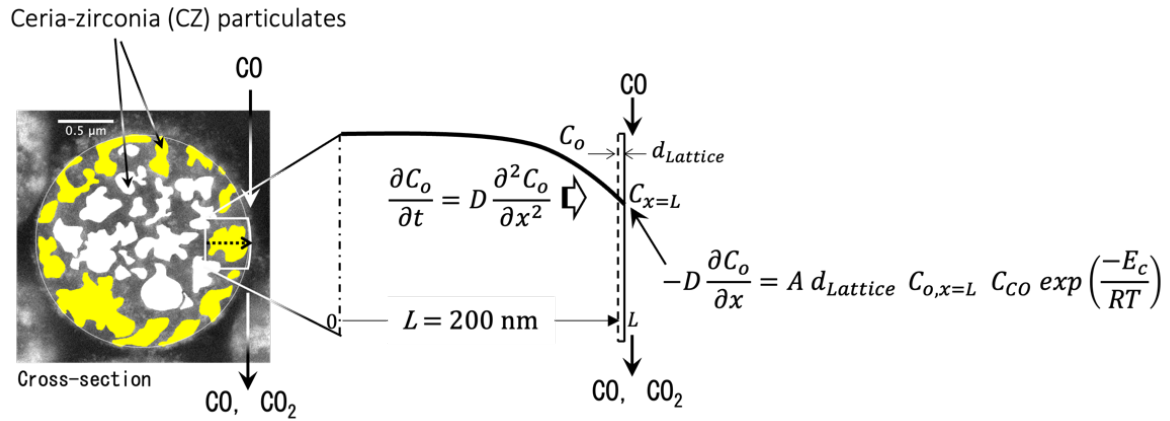


Fig. 4.7 Schematic image of diffusion-controlled CO oxidation by three-way catalyst particles membrane model

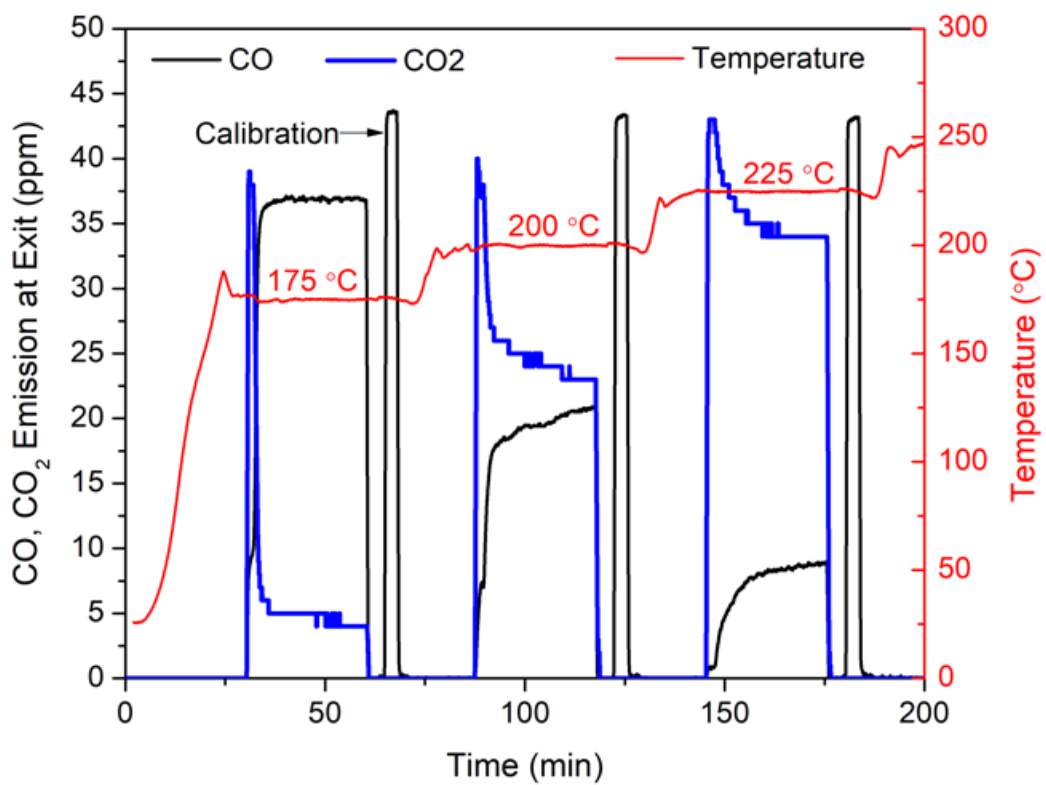


Fig. 4.8 Isothermal CO oxidation by TWC membrane at 175, 200 and 225 °C

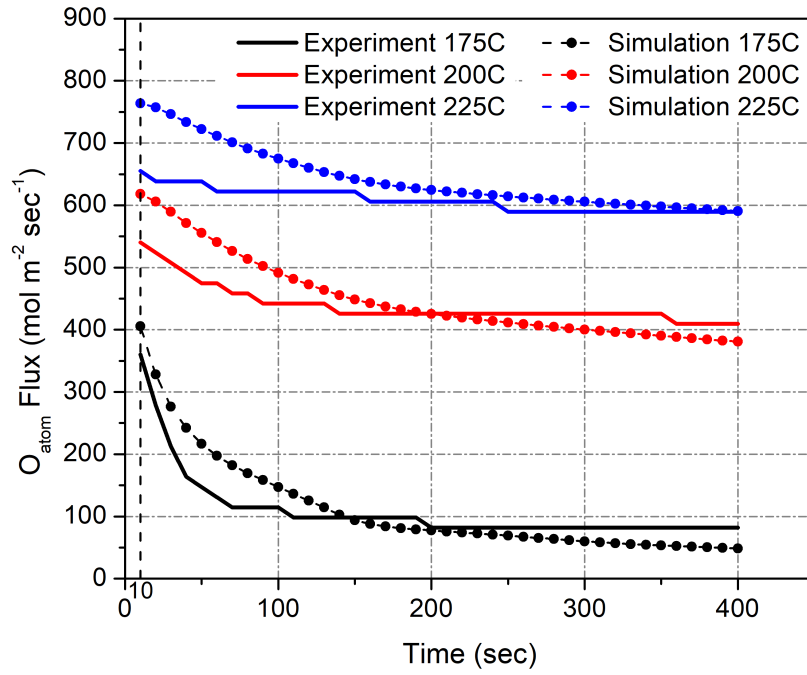


Fig. 4.9 Fittings of oxygen atoms flux

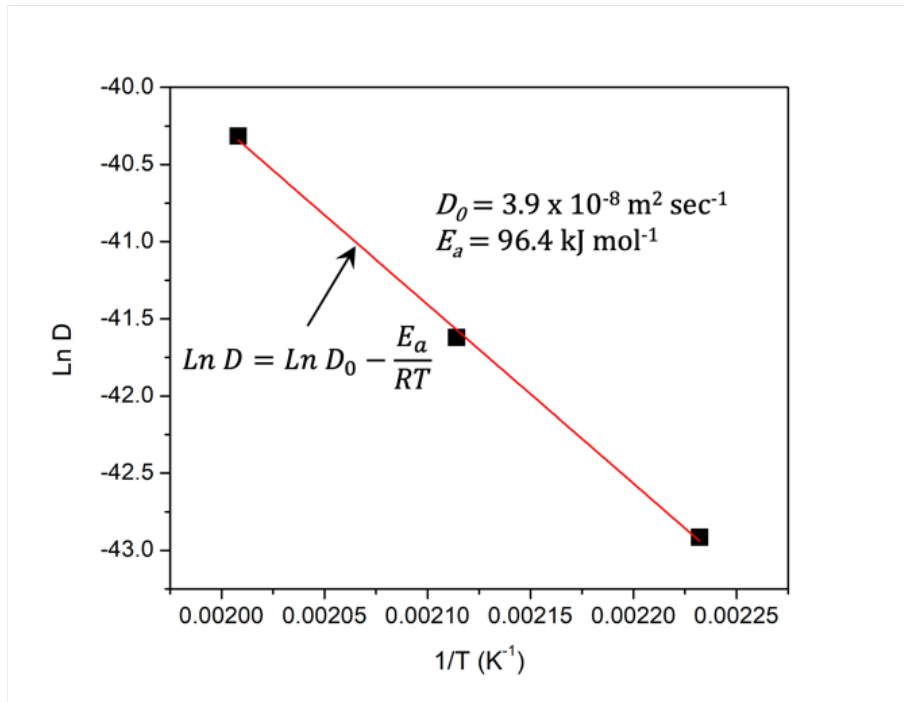
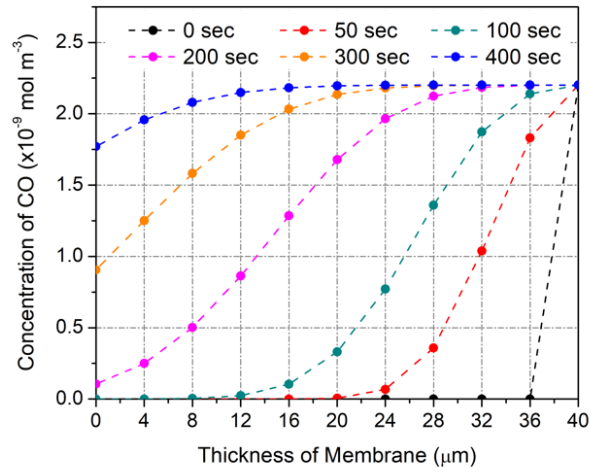
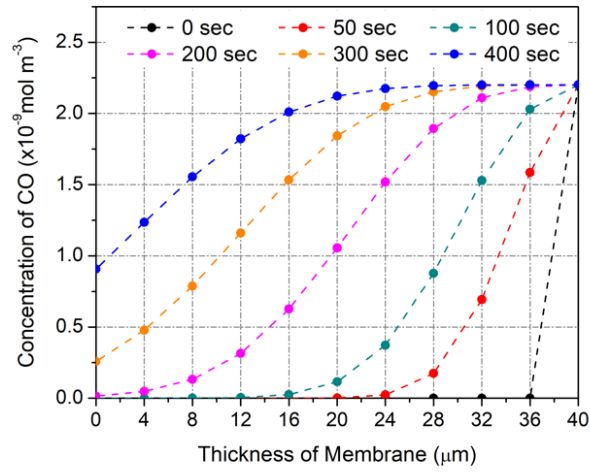


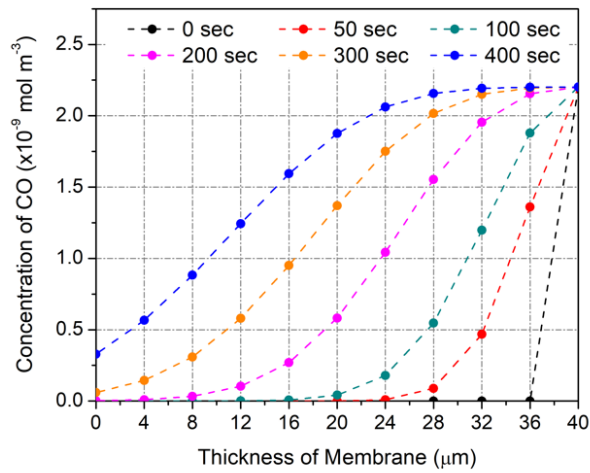
Fig. 4.10 Arrhenius plot for activation energy and pre-exponential factor of oxygen atom diffusion



(a) 175 °C



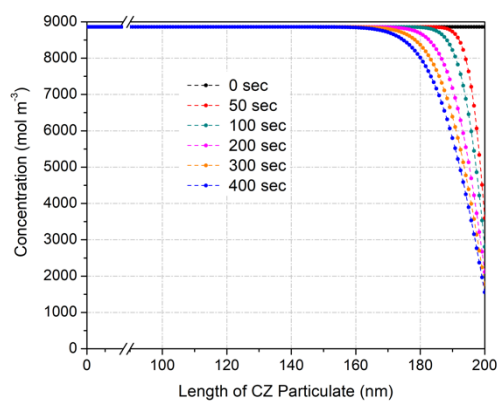
(b) 200 °C



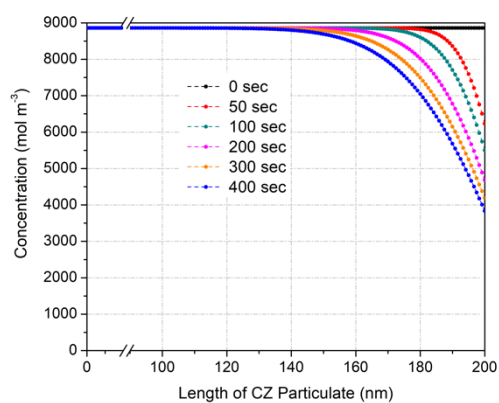
(c) 225 °C

Fig. 4.11 Concentration distribution of CO along the membrane thickness direction at 175 °C

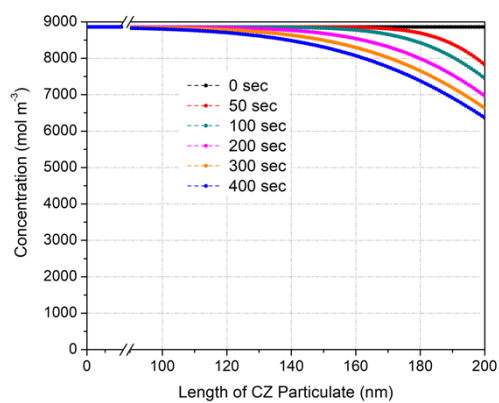
(a), 200 °C (b) and 225 °C (c)



(a) 175 °C

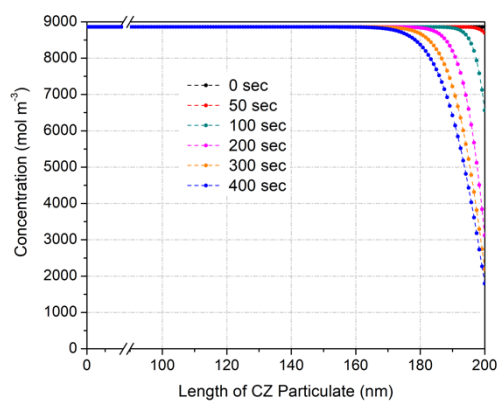


(b) 200 °C

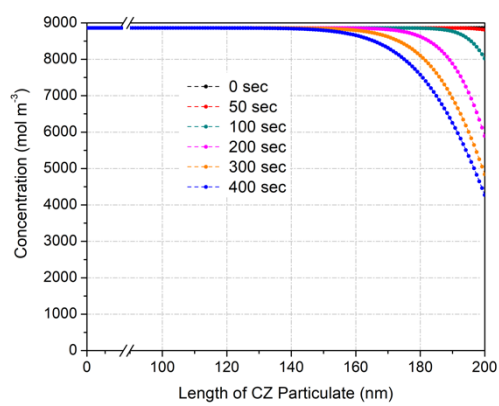


(c) 225 °C

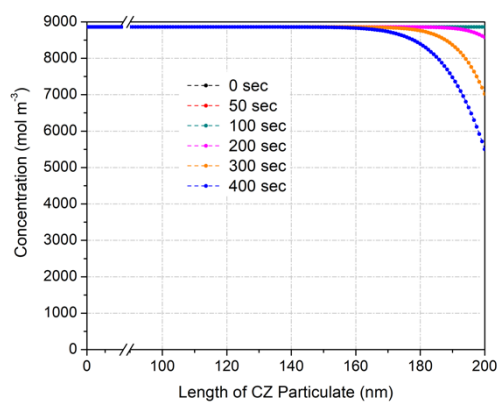
Fig. 4.12 Concentration profiles of CZ-particulates located at the upstream at 175 °C (a), 200 °C (b) and 225 °C (c)



(a) 175 °C

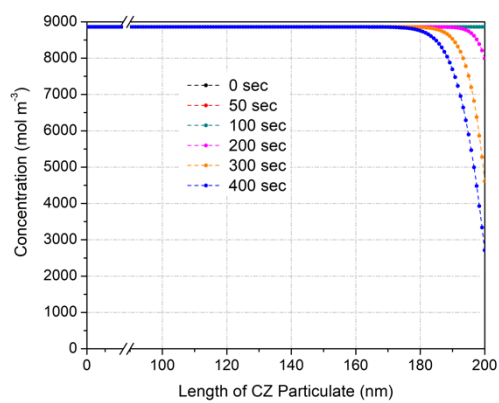


(b) 200 °C

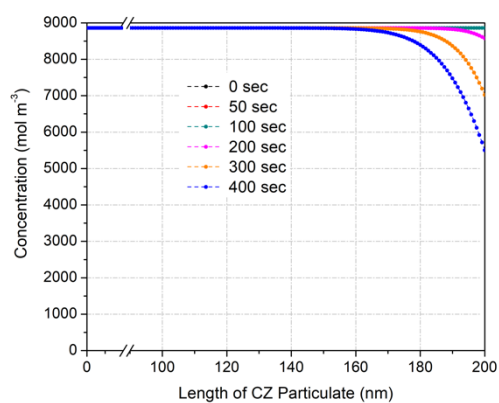


(c) 225 °C

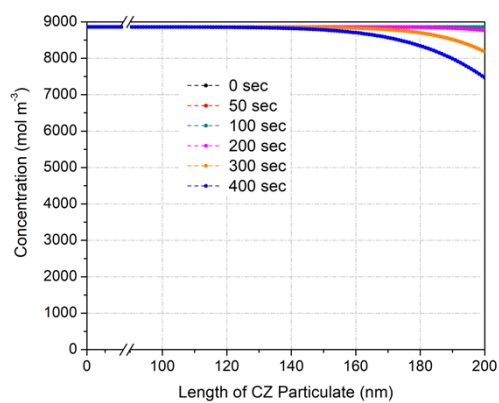
Fig. 4.13 Concentration profiles of CZ-particulates located at the middle at 175 °C (a), 200 °C (b) and 225 °C (c)



(a) 175 °C



(b) 200 °C



(c) 225 °C

Fig. 4.14 Concentration profiles of CZ-particulates located at the downstream at 175 °C (a), 200 °C (b) and 225 °C (c)

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Chapter 5

Porous TWC-particles Membrane Filter

5.1 Background

In the previous chapter, modeling of oxygen atoms diffusion in TWC-particles membrane for the experimental result of isothermal CO oxidation was discussed. The model was based on single CZ-particulates and the concentration distribution of CO gas molecules along the membrane thickness were also considered. Using the Arrhenius- type diffusion coefficient, the transient phenomena of isothermal CO oxidation with respect to time can be described well, and the oxygen atom fluxes required for CO oxidation with respect to time agrees well with the experimental results. Numerical simulation result revealed that only a limited oxygen atoms transport range of about 200 nm from the spherical surface were mainly contributed to the reaction due to the structure of agglomerated TWC-particles.

Here, in this article, to increase the purification performance of TWC-particles, the structure of agglomerated TWC-particles were modified as porous TWC-particles during the fabrication process. Due to the presence of pores in the agglomerated particles, the specific surface area to interact with gaseous molecules of the working gas will be increased, yielding a better purification performance. In this study, not only the fabrication process of porous TWC-particles membrane, but measurement of its porosity, CO purification performance using both isothermal and temperature-programmed oxidation will be discussed.

5.2 Methodology

5.2.1 Fabrication process of porous TWC-particles membrane

In order to fabricate porous agglomerated particles, the same TWC-slurry used in the article 2.2.2 was mixed with Poly (Methyl methacrylate) PMMA as a ratio of 1:5. FESEM micrographs of PMMA particles used in this study were described in the Appendix C. As shown in **Fig. 5.1**, the same fabrication setup was used, but an additional furnace was installed to decompose the PMMA before depositing the particles on the substrate as a membrane structure. The FESEM image of the agglomerated TWC-particles mixed with PMMA were shown in the figure before it was entered through the furnace. After passing through the furnace which is preheated at 800 °C, all of the PMMA were decomposed, and the porous TWC-particles were deposited as a membrane on the substrate.

5.3 Results and Discussion

5.3.1 Morphology of porous TWC-particles

Fig. 5.2 describes the particle size distribution of porous agglomerated TWC-particles. The range of size distribution were mostly in the range of 0.6 to 1.2 microns, and it was similar to the solid agglomerated TWC-particles in the case of 20 wt. % catalyst which was measured in the article 2.3.1. The arithmetic mean diameter of porous particles was also measured as about 1.2 microns.

Fig. 5.3(a) shows SEM images of morphology of fabricated porous TWC-particles membrane which was sintered at 900 °C for 4 hours. As described in the **Fig. 5.3(b)**, the percolation structure was apparently more compact than the solid particles membrane, and the porosity measurement of the cross-sectional area of the membrane will be discussed later. **Fig. 5.3(c)** shows high-resolution FESEM micrograph of surface view of an agglomerated porous

TWC-particle. By using the mixing ratio of 1:5 between TWC and PMMA, the pores were homogeneously distributed on the surface of an agglomerated particle.

5.2.2 Pressure-drop increase in fabricating the membrane

Fig. 5.4(a) and **Fig. 5.4(b)** compare the pressure-drop increase in fabricating TWC-particles membrane on the substrate using solid and porous particles under superficial velocities of 5 and 10 mm/s. In the fabrication process, the working gas flow rate, temperature and the thickness of the membranes were much the same for both solid and porous particle conditions. As a result, the pressure-drop increase in fabricating porous TWC-particles was significantly higher than that of the solid particles for both superficial velocity conditions.

Fig. 5.5 and **Fig. 5.6** display the morphology of fabricated TWC-particles membrane using solid and porous TWC-particles under 5 mm/s and 10 mm/s conditions. As compared in the **Fig. 5.5(b)** and **Fig. 5.6(b)**, the surface view of porous TWC-particles were apparently more compact than that of solid TWC-particles even under the same experimental setup condition. Due to the presence of pores on the spherical surface of porous particles, the Van Der Waals force between each particle in the membrane will be smaller than that of the solid particles. Therefore, the deposited porous particles can be moved due to the working gas during the fabrication process, which might lead to a packed percolation structure in the membrane. A brief explanation of higher pressure-drop increase in fabricating porous TWC-particles membrane will be continued in the article 5.2.3.

5.2.3 Investigation of porosity and permeability of the membrane

Fig. 5.7 display the FESEM micrographs of resin infiltrated cross-sectional view of porous TWC-particles membrane. The experimental procedure was exactly the same as in the solid particle case (as discussed in article 2.2.4). According to the result, the morphology of

TWC-particulates, pillars and the pores can be clearly observed. Moreover, it was revealed that the pores were uniformly distributed not only on the surface but also up to the inside of the porous TWC-particles.

Fig. 5.9 shows the porosity measurement result of a cross-section of porous TWC-particles membrane. Due to the damages caused by polishing, there were more fragments on the resin surface than the solid one, and it was difficult to depict the inscribed circles as porous circles. Besides, according to the simulation result obtained by our laboratory, the tendency of gas flow through until the deep inside of the porous particle is also very low. Therefore, in this regard, the comparison of the porosity value between solid and porous particles was only emphasized on their percolation structure of the membrane. According to the result, the porosity of porous TWC-particles membrane was measured as approximately 56.8 % which is less than the solid particles membrane (i.e., 64.4%), as mentioned in the article 2.3.4.

The permeability of the porous particles membrane calculated by Kuwabara's model as the same procedure in the article 2.3.6 for each experimental conditions were summarized in **Table 5.1**. In the case of superficial velocity under 5 mm/s, 13.3% difference of permeability between porous and solid particles membrane leads to 18% difference of final pressure-drop increase during fabricating. Besides, in the case of superficial velocity under 10 mm/s, 30% difference of permeability between porous and solid particles membrane leads to 40% difference of final pressure-drop increase. Therefore, it was concluded that the lower porosity of the porous particles membrane might be the main cause of higher pressure-drop increase during the fabrication process.

5.2.4 CO purification performance

Fig. 5.10(a) and **Fig. 5.10(b)** compare the experimental result of isothermal CO oxidation through TWC-particles membrane composed of solid particles and porous particles. Compared to CO purification performance of solid TWC-particles membrane as shown in Fig. 5.9(a), the gas conversion performance of porous particles were similar as described in Fig. 5.9(b). It is important to note that the composition of three-way catalyst particulates in the porous particles were 5 times less than that of solid particles. In other words, the CO purification performance of porous TWC-particles membrane were 5 times higher than that of the solid particles membrane due to the larger specific area which can promote the chemical reaction.

Fig. 5.11 shows the experimental result of temperature-programmed oxidation of CO comparing solid and porous TWC-particles membrane. The temperature ramping rate for both conditions were as the same as previous experiments (i.e., 10 °C/min). According to the result, the light-off temperature T_{50} of solid particles and porous particles for were 177 °C and 142 °C respectively. The specific surface area of three-way catalyst particles were estimated by GeoDict software as described in **Fig. 5.12**. The total surface area for a chemical reaction was expanded by reducing the pore size in an agglomerated particle. According to the result, the specific surface areas of solid and porous particle (with 350 nm PMMA particles) were estimated as $1.71 \times 10^6 \text{ m}^2/\text{m}^3$ and $3.88 \times 10^6 \text{ m}^2/\text{m}^3$ respectively. Therefore, by increasing the surface area about two times between solid and porous particles, the conversion efficiency was increased which leads to lower light-off temperature in a porous particles membrane.

Summary

In this chapter, in order to enhance the purification performance of TWC-particles membrane filter, porous TWC-particles membrane was successfully manufactured by mixing Poly (Methyl methacrylate) PMMA with the original three-way catalyst slurry. After decomposing the PMMA in the manufacturing process, porous agglomerated particles were deposited on the substrate as a membrane layer. According to the high-resolution FESEM micrographs of surface and cross-sectional views, the pores (sizing around 350 nm) were uniformly distributed not only on the surface but also inside of the agglomerated particle. Since the smaller porosity of the membrane layer composed of porous particles, the pressure-drop increase during the fabrication process was significantly higher than that of the solid particles membrane. Due to larger effective specific surface area of porous TWC-particles membrane, although the composition of the catalyst composition is 5 times smaller in the porous particles, the CO purification performance under isothermal condition still maintained the same as of solid particle membrane. Furthermore, the light-off temperature T_{50} of the porous TWC-particles were about 18.86% lower compared to that of solid TWC-particles membrane.

Tables

Table 5.1 Permeability of porous TWC-particles membrane

Superficial Velocity	Particles	Permeability (m ²)
5 mm/s	Solid	4.5 x10 ⁻¹⁴
	Porous	3.9 x10 ⁻¹⁴
10 mm/s	Solid	3.5 x10 ⁻¹⁴
	Porous	2.4 x10 ⁻¹⁴

Figures

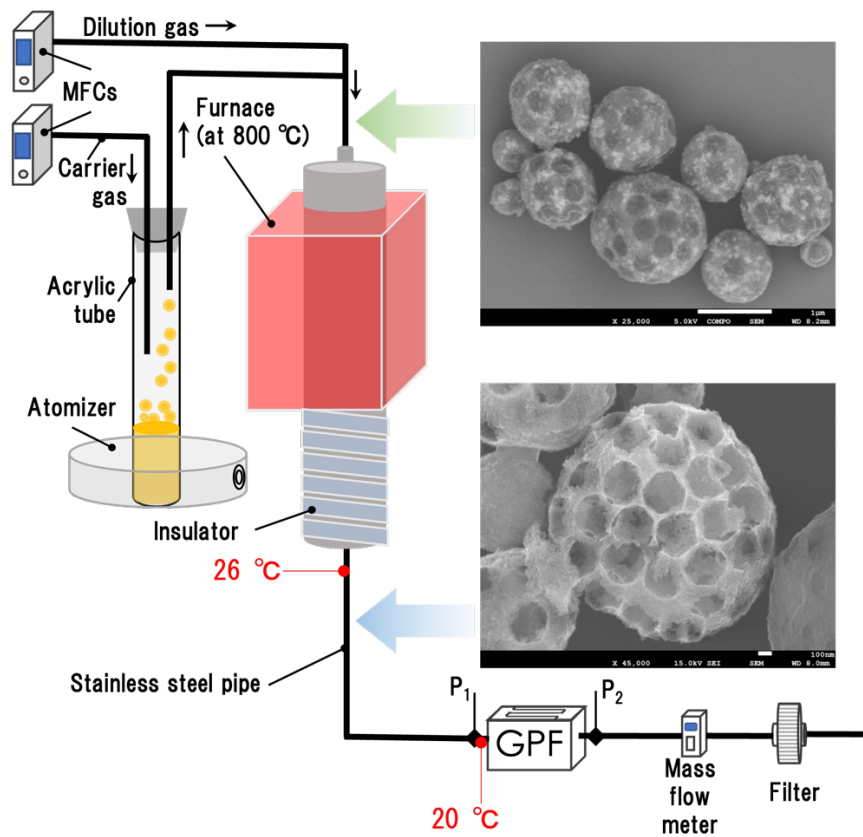


Fig. 5.1 Schematic diagram of fabricating porous TWC-particles membrane filter

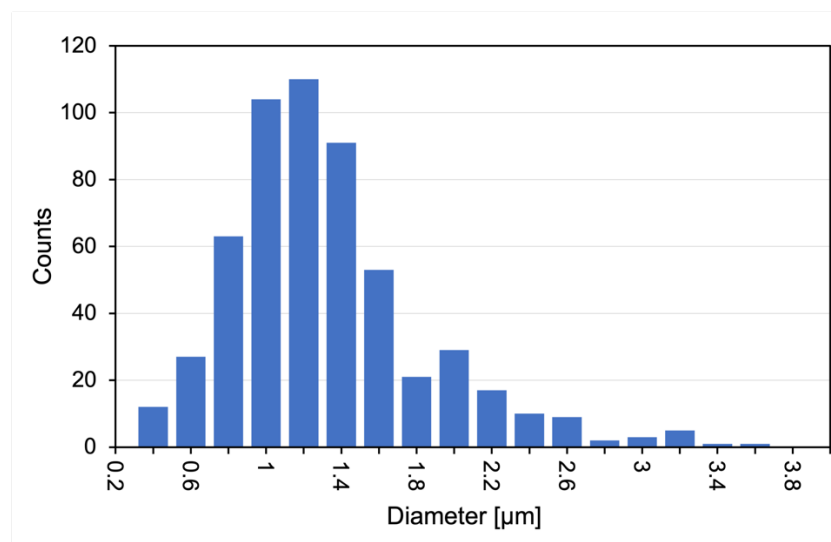
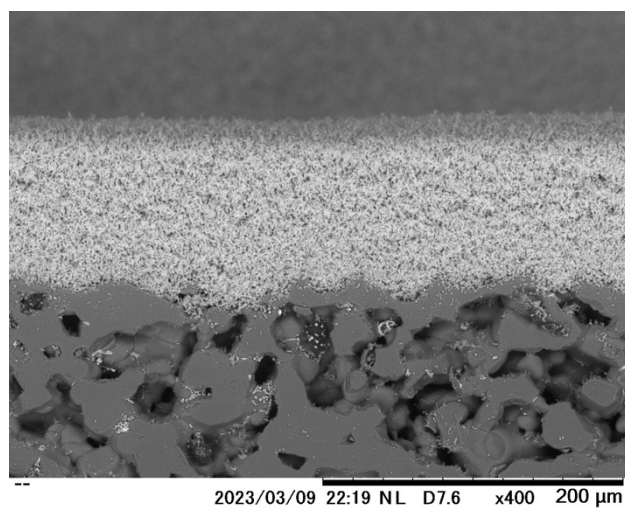
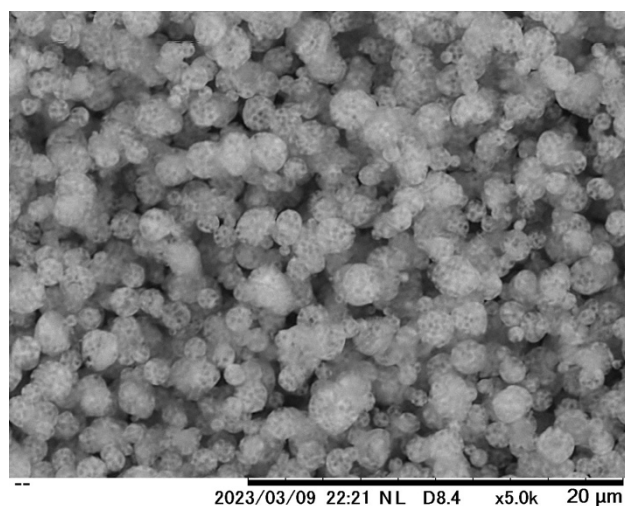


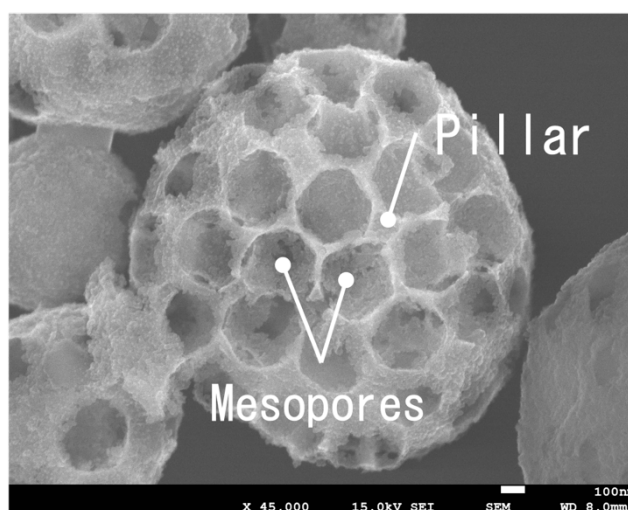
Fig. 5.2 Particle size distribution of porous TWC-particles



(a)

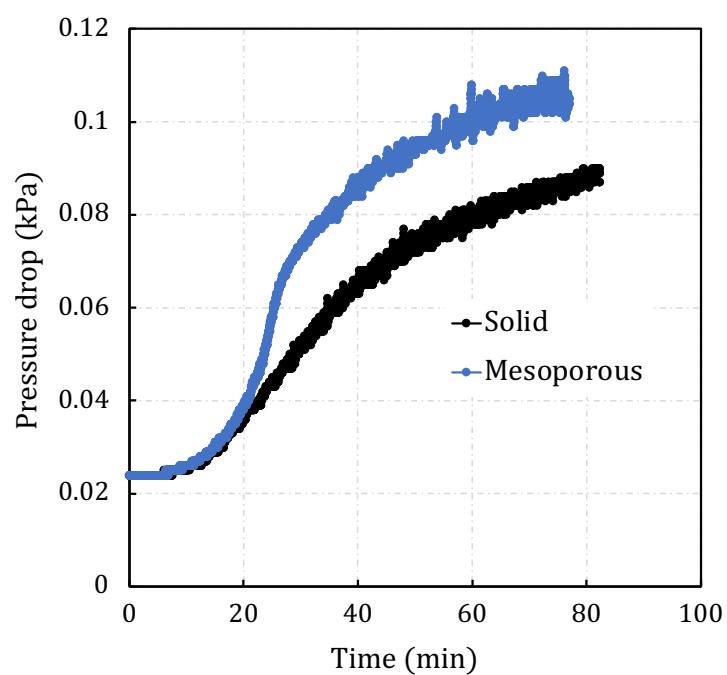


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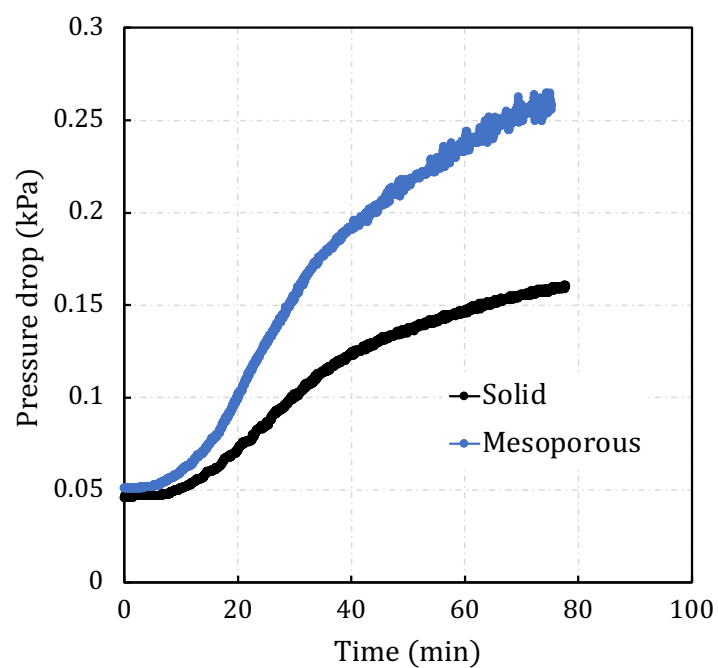


(c)

Fig. 5.3 Morphology of porous TWC-particles membrane (a) cross-sectional view and (b) surface view and (c) surface view of an agglomerated particle

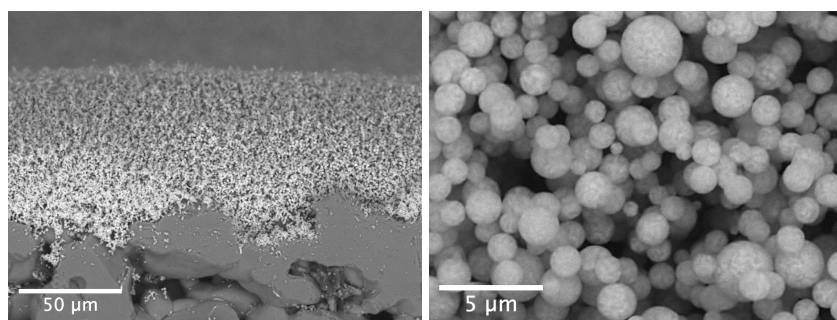


(a) 5 mm/s

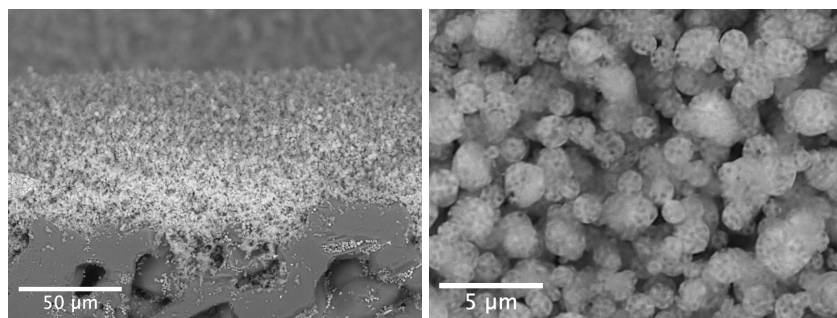


(b) 10 mm/s

Fig. 5.4 Pressure-drop increase in fabrication solid and porous TWC-particles membrane under a superficial velocity of (a) 5 mm/s and (b) 10 mm/s

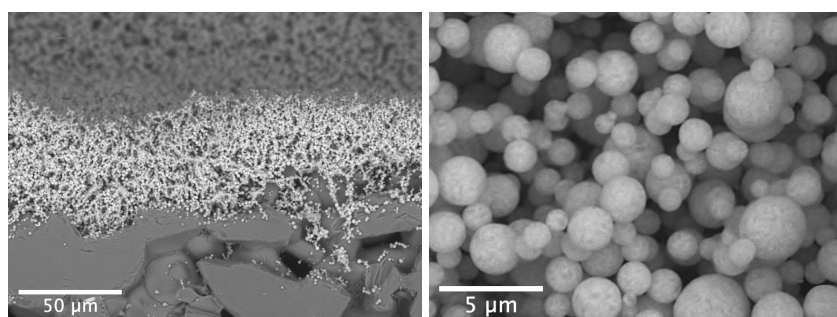


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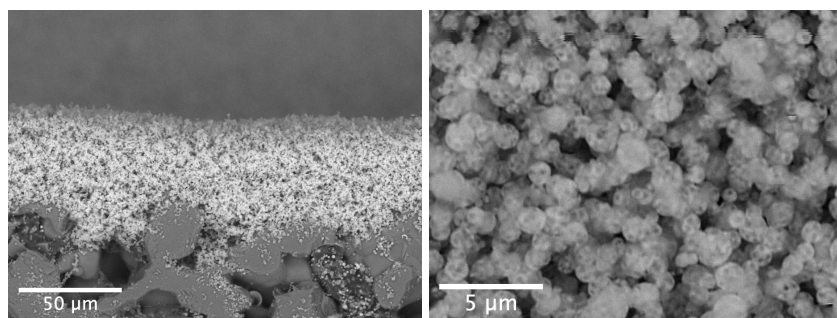


(b)

Fig. 5.5 Morphology of fabricated TWC-particles membrane composed of (a) solid TWC-particles and (b) porous TWC-particles under a superficial velocity of 5 mm/s

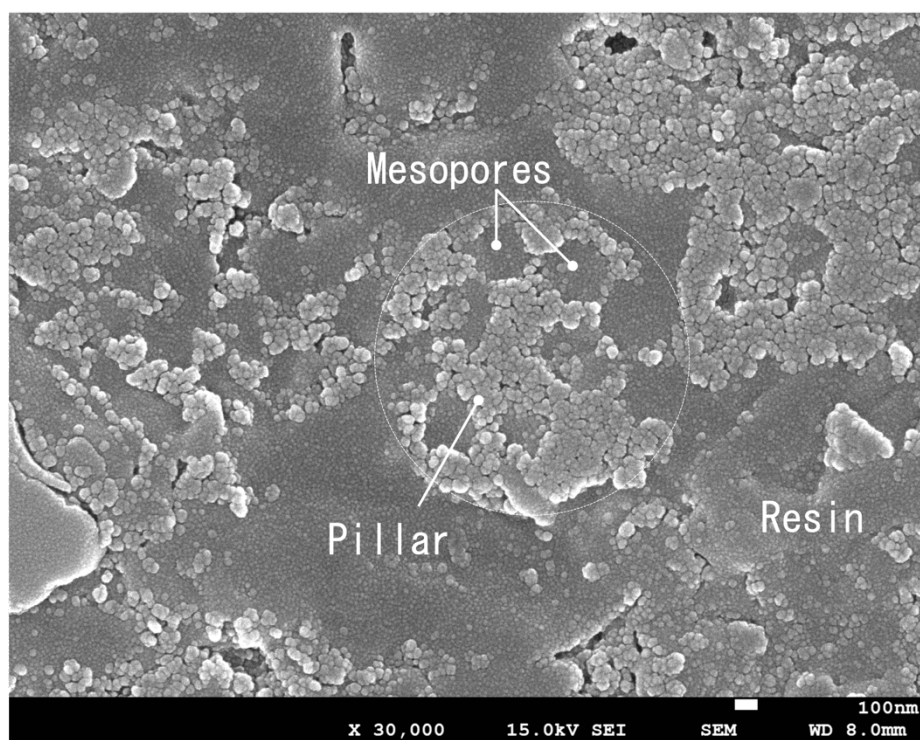


(a)

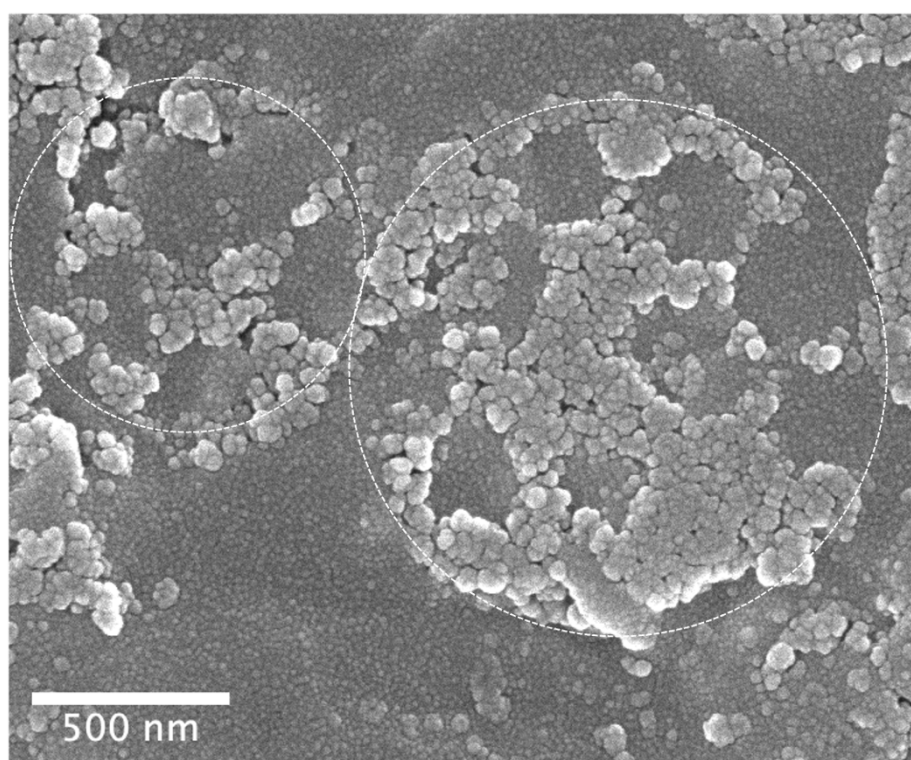


(b)

Fig. 5.6 Morphology of fabricated TWC-particles membrane composed of (a) solid TWC-particles and (b) porous TWC-particles under a superficial velocity of 10 mm/s



(a)



(b)

Fig. 5.7 Cross-sectional view of resin infiltrated porous TWC-particles membrane (a) overview and (b) magnified image

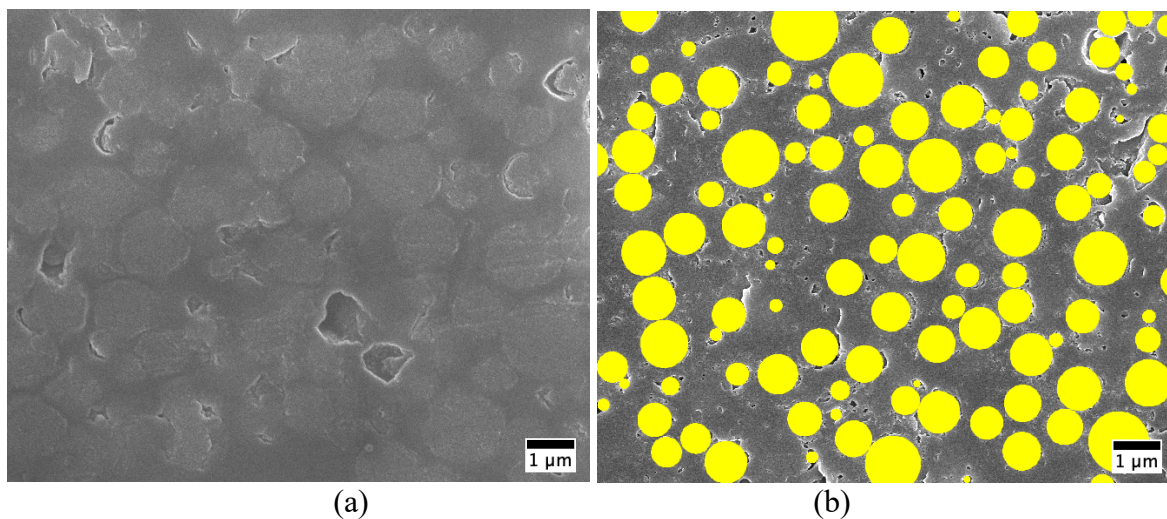


Fig. 5.8 FESEM electron micrographs of cross-sectional view of resin infiltrated solid TWC-particles (a) and analyzed image of image processing technique for porosity measurement (b)

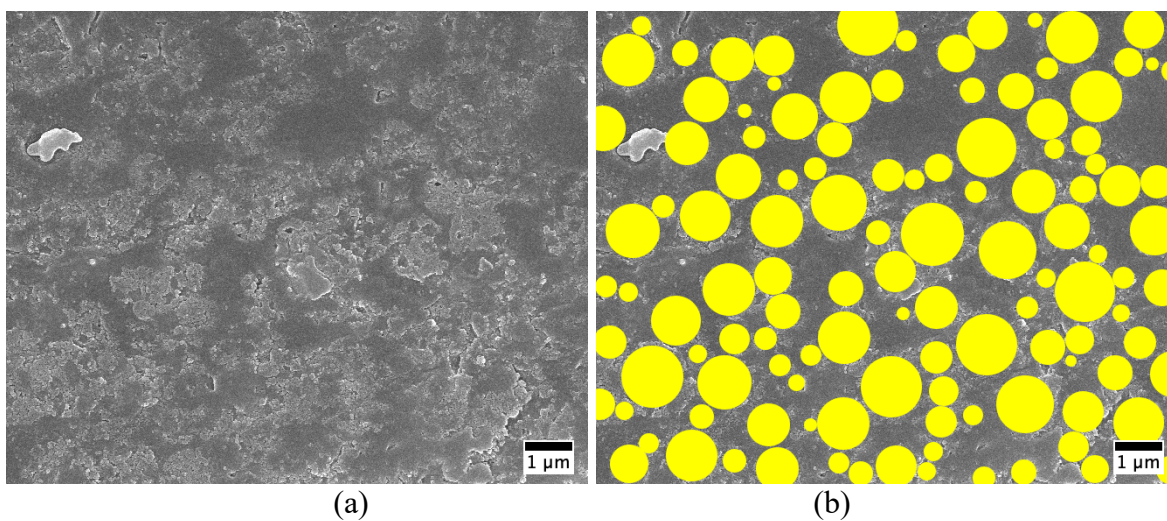
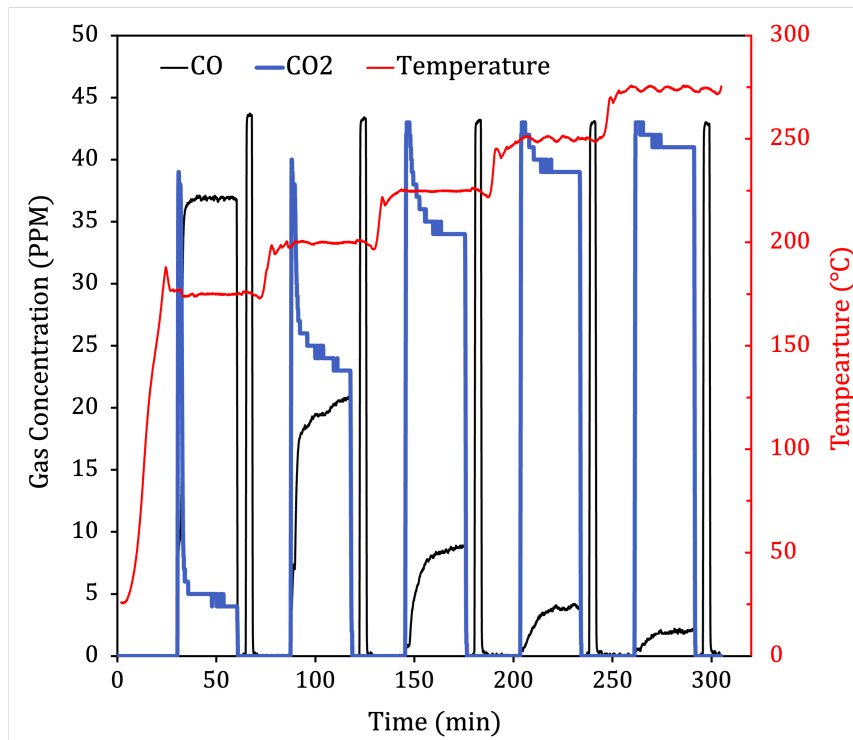
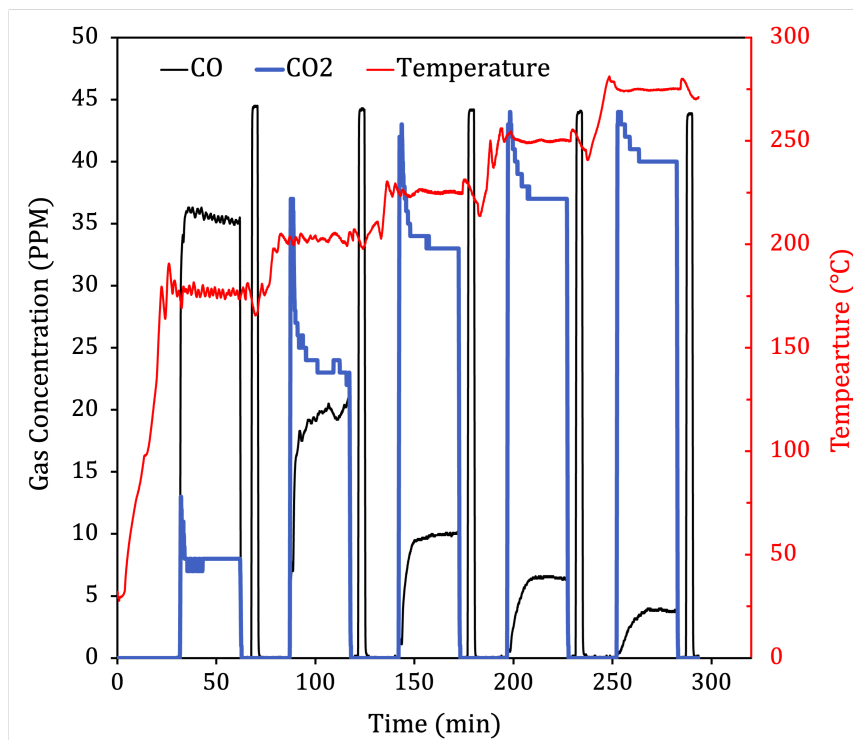


Fig. 5.9 FESEM electron micrographs of cross-sectional view of resin infiltrated porous TWC-particles (a) and analyzed image of image processing technique for porosity measurement (b)



(a) Solid TWC-particles Membrane



(b) Porous TWC-particles Membrane

Fig. 5.10 Isothermal CO oxidation through TWC-particles membrane composed of solid particles (a) and porous particles (b)

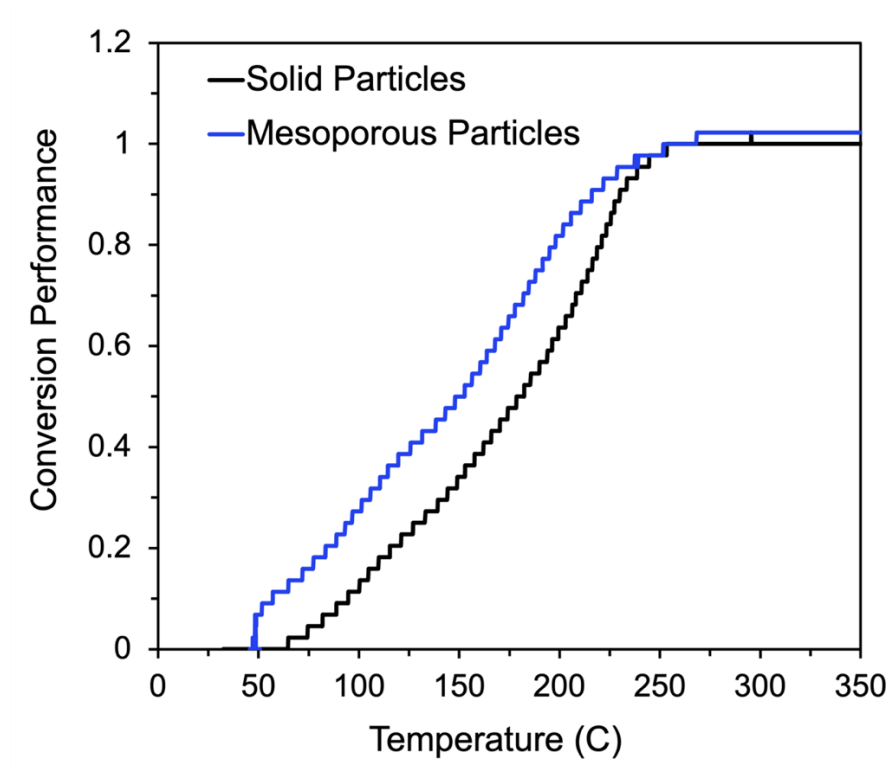


Fig. 5.11 Light-off temperature for CO conversion by TWC-membrane composed of solid particles (a) and meso-porous particles (b)

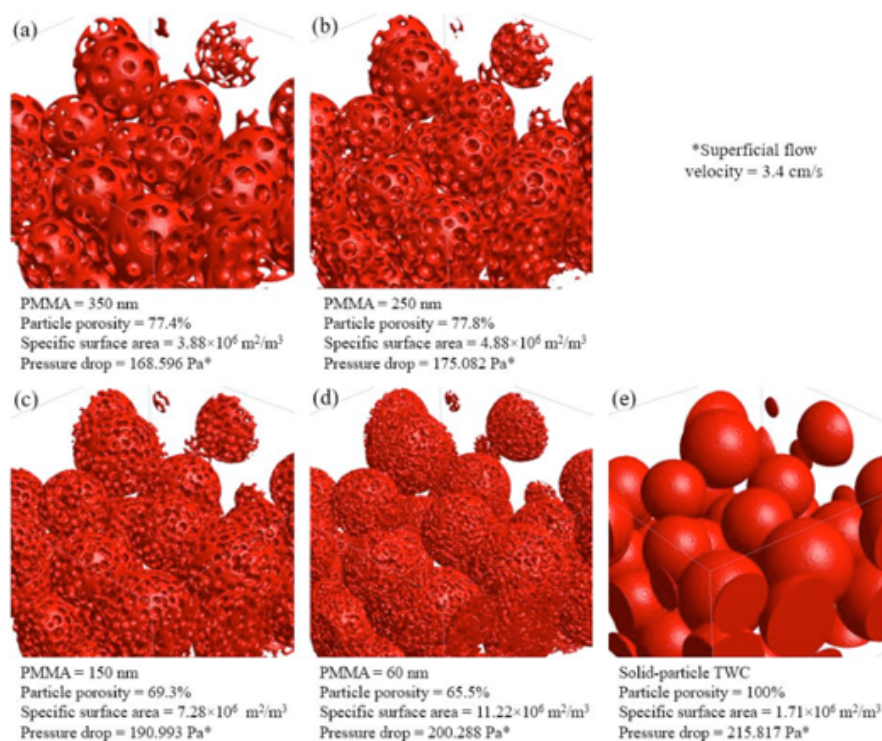


Fig. 5.12 Specific surface area of three-way catalyst particles

Chapter 6

Conclusion

6.1 Key findings and research outcomes

In this dissertation, a three-way catalyst membrane particulate filters for the purpose of achieving higher soot filtration efficiency with low pressure-drop, and reducing exhaust gaseous pollutants such as carbon monoxide, nitrogen oxides and hydrocarbon simultaneously. The key findings and research outcomes from each chapter by this study are summarized as followed.

In the chapter 2, a new porosity measurement method, which was measured the cross-section of the membrane filter, percolated with micro-sized agglomerated three-way catalyst particles using electron microscopy image analysis technique was introduced. Through the measurement process, a cross-sectional view of an agglomerated TWC-particle was revealed as a homogeneously agglomerated spherical particle. As result, the porosity of the TWC-particles membrane fabricated with 1.2 micron mean diameter of particles under 5 mm/s superficial velocity was measured as approximately 64.4%.

In the chapter 3, a preferable sintering temperature which can provide enough durability of the membrane and maintaining the CO purification performance was found as 900 °C. Through isothermal CO oxidation experimental results, temperature dependence phenomena for a transient state of oxygen transport from the bulk of ceria-zirconia (CZ) particulates was observed. The light-off temperature T_{50} of three-way catalyst membrane filter for CO oxidation was enhanced about 29.2 % compared to conventional catalytic converters.

In the chapter 4, a numerical model on diffusion-controlled oxygen transport through ceria-zirconia particulates included in the TWC particles membrane filter was developed for

the CO oxidation using an Arrhenius-type diffusion coefficient. The transient phenomena of isothermal CO oxidation with respect to time can be described well, and the oxygen atom fluxes required for CO oxidation with respect to time agrees well with the experimental results. Simulation results revealed that although the TWC particle sizes of around 1.2 μm is chosen from a point of view of development of a low pressure drop filter, the oxygen atom transport range was restricted within around 100 nm from the surface of spherical TWC particles under the condition of the operation temperature due to the agglomeration structure of solid TWC-particles.

In the chapter 5, as for the purpose of increasing specific surface area of the agglomerated particles which can lead to a better performance, porous TWC-particles were successfully fabricated. According to the geometry of a porous particle, the reactant gas interact with diffused oxygen atoms from the bulk of the CZ particulates more effectively. In the isothermal oxidation experiment, the CO purification performance of porous TWC-particles membrane filter were 5 times higher than that of solid particles membrane. Furthermore, the light-off temperature of the porous particles membrane filter was enhanced about 19.8 % compared to that of solid particles membrane filter.

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Koko Phyozin

Tokyo Institute of Technology

July 25th, 2023

Appendix A

Validation of depicting inscribed circles in porosity measurement

A.1 Introduction

As discussed in the article 2.3.4, inscribed circles area were depicted for some of the non-circular shape cross-sectional TWC-particles which are caused by electron penetration through thin resin film at the borderline areas.

A.2 Validation results

As shown in the **Fig. A-1**, the red circle symbols represent the inscribed circles which were depicted for the non-circular shape particles (caused by electron penetration) and lacks (caused by particle release from the resin surface due to polishing), while the blue circles represent the circumscribed circles which were depicted for the circular shape particles.

According to the result, the total depicted number of inscribed circles and circumscribed circles were 28 and 24 particles respectively. Hence, considering that the electron-penetrated particles and lacks as inscribed circles areas within a measurement zone, it was a justifiable approach to treat them as inscribed circles when estimating porosity. Therefore, it was concluded that the measurement of porosity in this study can be considered as a volumetric porosity due to the similar ratio of inscribed circle and circumscribed circle areas, although it was a two-dimensional measurement through image processing technique.

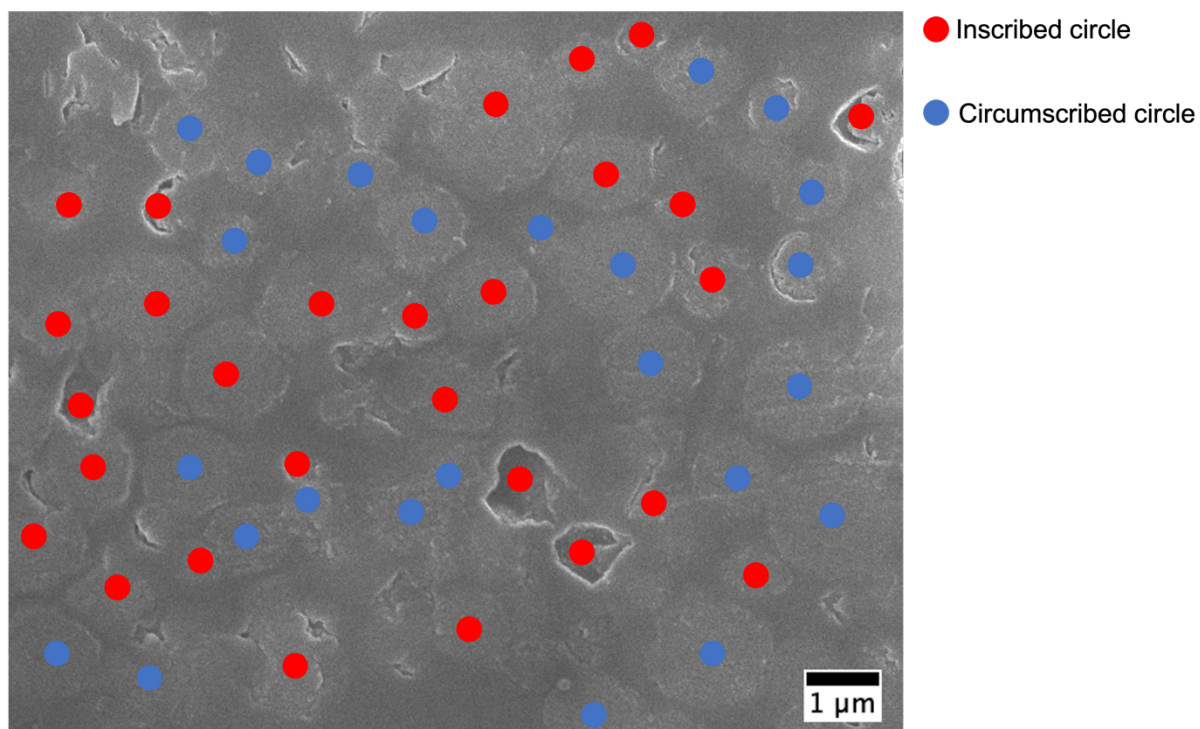
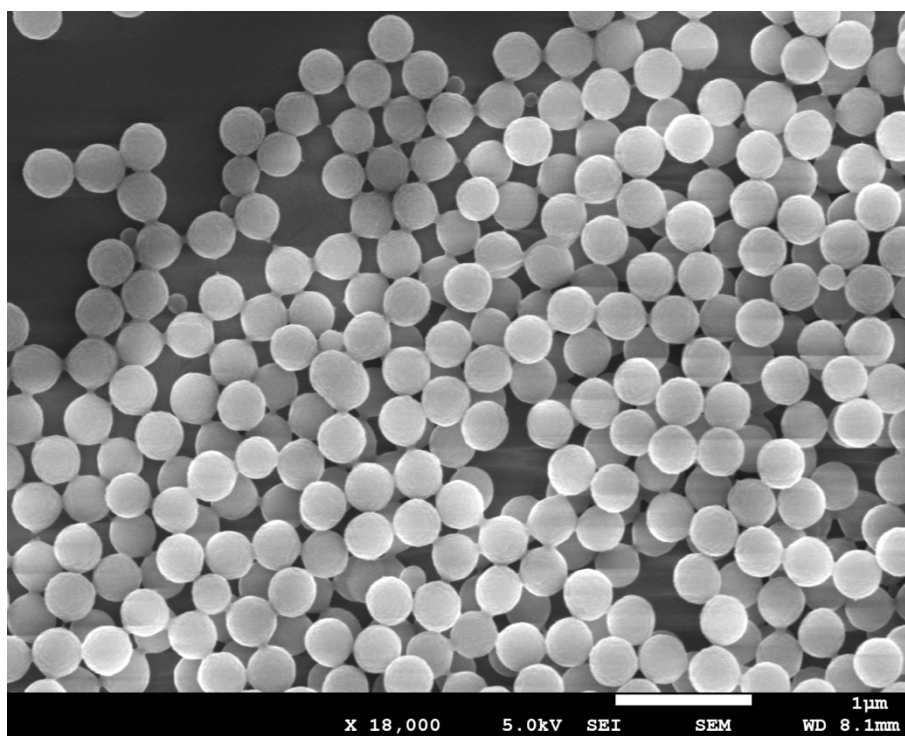
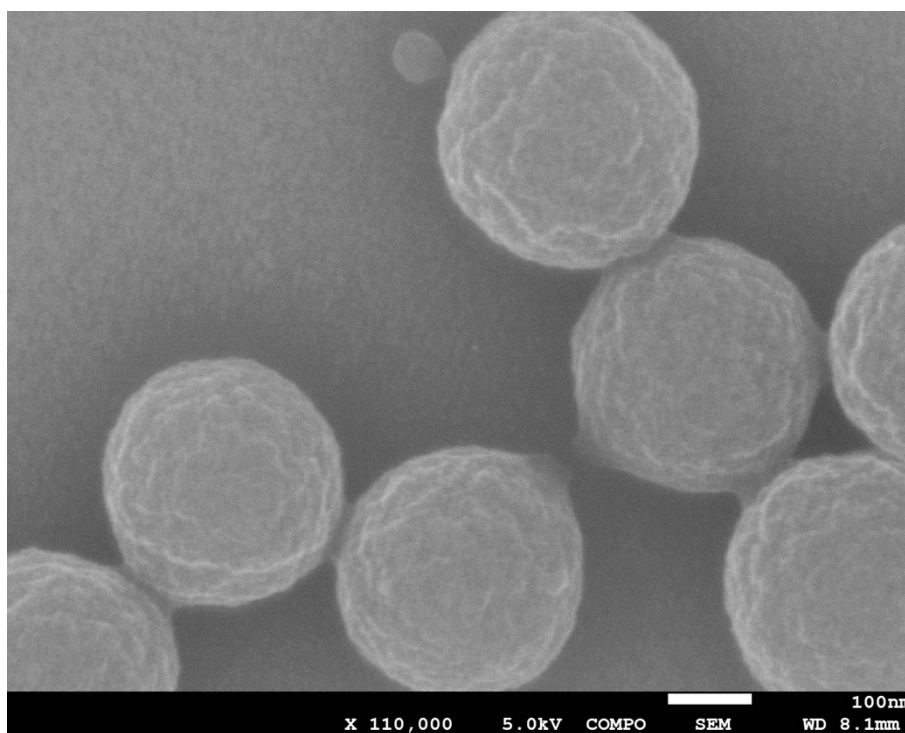


Fig. A-1 Validation of total number of inscribed circles and circumscribed circles on the cross-sectional view of resin-infiltrated TWC-particles membrane for the porosity measurement

Appendix B



(a)



(b)

Fig. B-1 Morphology of Poly (Methyl Methacrylate) PMMA

Publications

- Koko, P., Suteerapongpun, T., Hanamura, K., 2022, Measurement of porosity in three-way catalyst particles membrane filter using electron microscopy image analysis, International Journal of Automotive Engineering, Vol.14 (1) [Published]
- Koko, P., Hanamura, K., 2023, Modeling of CO oxidation by diffusion of oxygen atom in ceria-zirconia particulates in three-way catalyst particle membrane filter, Global Journal of Researches in Engineering, Vol.23 (2) [Published]

Related articles

- Arai, S., Shimpei, F., Koko, P., Suteerapongpun, T., Hanamura, K., 2023, Durability of three-way-catalyst-particles membrane filter for fluid-dynamic shear stress, Transaction of Society of Automotive Engineers of Japan, Vol. 54 (3)