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Eugene GATETE

eugene.g.ce41@m.isct.ac.jp

Institute of Science Tokyo

Yuji TOKUMASU

Institute of Science Tokyo

Tsuyoshi NAGASAWA

Institute of Science Tokyo

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CO Oxidation and Oxygen Transport Characteristics of Three-Way Catalyst Microparticles Membrane for Gasoline Particulate Filter

Eugene GATETE^{1*}, Yuji TOKUMASU², Tsuyoshi NAGASAWA^{3*}

^{1*,2&3} Department of Mechanical Engineering, School of Engineering, Institute of Science Tokyo, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8550, Japan

*Corresponding author(s) E-mail(s): eugene.g.ce41@m.isct.ac.jp (EG), nagasawa.t.1752@m.isct.ac.jp (TN)

Contributing authors: tokumasu.y.3209@m.isct.ac.jp, nagasawa.t.1752@m.isct.ac.jp

Abstract

Gasoline particulate filters with integrated three-way catalyst membranes provide simultaneous filtering and conversion, however requiring structure optimization for performance. This study investigates the influence of membrane fabrication parameters on the structure of TWC microparticles and correlation between CO oxidation performance and oxygen mass transport in TWC microparticles using isotope labeling. TWC microparticles were ultrasonically atomized into 1-2 μm spherical microparticles, and CO oxidation was evaluated at various metal loadings and firing temperatures. The T_{100} for CO oxidation using TWC microparticles fired at 800 °C and 900 °C increased by 20 °C and 25 °C, respectively, compared to the unfired particles, showing active-site sintering. While doubling and quadrupling precious-metal loading decreased T_{100} by 5 °C and 20 °C compared to the standard loading, respectively. TWC/GPF integration decreased T_{50} by 49 °C relative to standard TWC microparticles for the 900 °C-fired case, contrarily, the T_{100} increased by 56 °C due to short contact time between the gas and the catalyst for the TWC/GPF membrane than for the TWC microparticles. Measurements of the oxygen isotope distribution in TWC microparticles show that ^{18}O is uniformly distributed in the cross-section at locations where the $\text{CeO}_2\text{-ZrO}_2$ (CZ) is present, and that the ^{18}O concentration increases with an increase in the precious metal content. Furthermore, the surface exhibits a higher ^{18}O concentration compared to the cross-section of the microparticles, indicating that while both the surface and internal precious metals in TWC microparticles contribute to the purification reaction, the surface plays a more effective role.

Keyword: After-treatment systems, CO conversion, GPF, SIMS, Oxygen isotope labeling, TWC microparticles.

1. Introduction

The global transportation sector is rapidly changing due to stricter pollution standards and international climate obligations. Road cars emit over 25% of anthropogenic CO_2 emissions, making them a significant contributor to greenhouse gas accumulation Khalifa *et al.*, (2022), Krause *et al.*, (2020). Although electrification is fast increasing, internal combustion engine (ICE) cars will continue to be a significant part of the worldwide fleet over the multi-decade transition to carbon neutrality Jakob *et al.*, (2021), Hannappel, (2017). As a result, enhancing exhaust aftertreatment systems is critical for lowering pollutant emissions from gasoline engines throughout this transition phase. Catalytic converters (CCs) are vital exhaust after-treatment systems designed to reduce pollutant emissions such as CO, HC, PM, and NO_x , helping vehicles meet stringent environmental

standards. The three-way catalytic converter (TWC) represents the most successful and widely deployed exhaust aftertreatment technology for stoichiometrically-operated gasoline engines Qian *et al.*, (2019), Twigg, (2011). In addition, a gasoline particulate filter (GPF) is used to capture solid particulate matter from gasoline direct injection (GDI) engines. In the conventional after-treatment systems, both components (CCs, GPF) are installed separately. However, there is a growing demand for more compact after-treatment systems. Therefore, the catalyzed GPFs, which integrate the functionalities of both three way catalyst (TWC) and GPF into a single component is more emphasized to achieve low pressure loss, high particulate collection efficiency, and excellent catalytic activity Guoquan *et al.*, (2021), Karin and Hanamura, (2010). This structure achieves high gas purification performance, high PM capture efficiency, and low-pressure drop, demonstrating high potential as a next-generation aftertreatment technology. Furthermore, the high specific surface area of the nanoscale primary TWC particulates within each agglomerated sphere provides excellent catalytic activity per unit catalyst mass Phyozin *et al.*, (2023). The particle membrane filter concept was initially developed for diesel particulate applications by Karin and Hanamura, (2010), who demonstrated that a membrane composed of alumina nanoparticulate aggregates achieves essentially complete PM filtration efficiency from the very first particle, compared to the progressive efficiency build-up of conventional depth-filtration DPF operation. This was followed by systematic studies on membrane formation from various catalyst components. Suteerapongpun *et al.*, (2020) developed alumina-silver-palladium particle membranes achieving simultaneously high filtration efficiency, low pressure-drop, and reduced soot oxidation temperature, demonstrating the multi-functional potential of the approach. Nakajima *et al.*, (2017) characterized the permeability and soot trapping behavior of high-porosity alumina nanoparticle membranes. Hanamura and Kawabe, (2022) demonstrated that NO_x diffusion into PM deposits on catalyzed membrane filters significantly enhances soot oxidation kinetics a synergy. Phyozin *et al.*, (2023) conducted a detailed parametric study of TWC particle membrane filter fabrication, establishing relationships between slurry concentration, atomization conditions, superficial velocity, and the resulting membrane porosity, particle size distribution, and percolation structure. Koko and Hanamura, (2023) studied the mechanical durability of TWC particle membrane filters under fluid-dynamic shear stress, a critical practical consideration for real-world deployment. However, there are still several challenges, including increasing the mechanical strength of the membrane and improving catalytic performance at low temperatures.

The major difference between the GPF membrane filter addressed in this study and other catalyzed GPFs is that, in order to achieve both high purification performance and low pressure drop, TWC particles with a primary particle size of several tens of nanometers are layered onto the GPF as microparticles consisting of spherical aggregates with a particle size of 1–2 μm as highlighted in the work of Phyozin *et al.*, (2023). This is expected to result in a significant reduction in pressure drop compared to simply depositing fine particles of tens of nanometers in size. For the practical application of membrane filters, it is necessary to simultaneously achieve high purification performance, high durability, and low-pressure drop; to this end, optimization of

membrane fabrication parameters and membrane structure is required. In particular, if the membrane is made thin to achieve low pressure drop, sufficient purification activity may not be obtained, so it is extremely important to expand the effective reaction area of the membrane. Therefore, identifying which parts of the TWC microparticles are effectively utilized in the reaction provides a significant clue for structural optimization.

This study investigates the influence of membrane fabrication parameters on the CO oxidation performance of TWC microparticles and TWC membranes on GPF. In addition, oxygen isotope labeling visualization is introduced to investigate oxygen transport characteristics within TWC microparticles. Based on these results, the aim is to obtain guidelines for the structural optimization of TWC microparticle membrane filters.

2. Experimental Facility

2.1. TWC Microparticle Collection during Membrane Fabrication

The experimental setup for fabricating membrane filter made of aggregated microscale-TWC particles on the surface of the substrate is shown in Figure 1. Figure 1(a) displays a schematic diagram of the modified membrane fabrication process of a three-way catalyst (TWC) microparticle collections. The experimental procedure used the same process as of the membrane fabrication discussed in detail in the previous literature (Phyozin et al., 2023), however, in this study the membrane fabrication apparatus was modified by replacing the GPF holder with the fiber filter as shown in the Figure 1. The slurry used in its fabrication was comprised of 20 wt.% of primary nanometer-sized TWC particulates prepared using distilled water. The TWC particulate slurry was introduced into an acrylic tube to generate small droplets with a size range of 5-10 μm using an ultrasonic atomizer (60 Hz frequency). Nitrogen gas was also introduced into the acrylic tube at a flow rate of 50 mL/min to transport the atomized water droplets, including TWC particulates from the tube. The gas suspended droplets containing TWC particulates were then mixed with a dilution gas 255 mL/min to achieve a superficial velocity of 5 mm/s calculated using the Equation (1)

$$v = \frac{Q}{A} \quad (1)$$

Where, A is the total filtration area in mm^2 , v is the Superficial velocity in mm/sec, Q is the total flow rate of dilution gas and carrier gas in mL/min. Nitrogen gas-diluted dispersed water droplets were introduced into an evaporator, which was kept at temperatures of 700 °C using a ribbon heater. To collect the TWC microparticles for SEM and SIMS analysis, as well as the CO oxidation test, the membrane fabrication apparatus was modified by substituting the GPF holder with a fiber filter, as illustrated in the Figure 1(a). For SEM analysis, the collected microparticles were mixed with ethanol, put onto a substrate, dried, and fired at temperatures of 900°C for 4 hours to maintain the filtration structure of the TWC particle with a minimal peeling rate. Figure 1(c) shows a SEM image of a sample with TWC microparticles dispersed on an alumina substrate for

SIMS observation. For the CO oxidation of TWC microparticle test, the obtained microparticles were employed either as it is for non-fired or after firing tests.

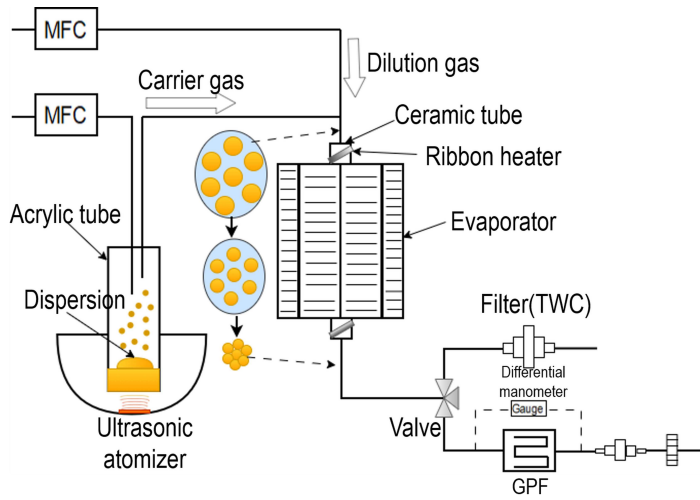
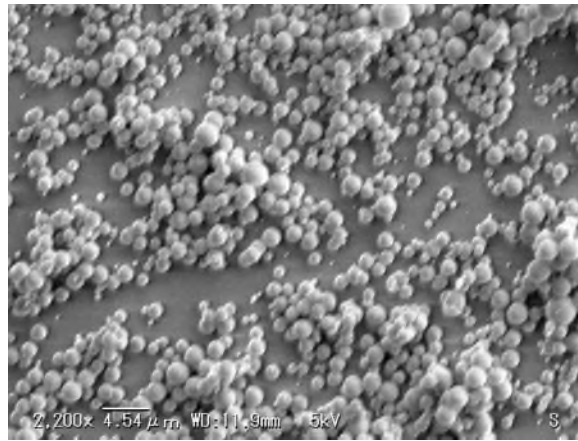


Table 1: Experimental conditions

Full flow rate	305mL/min
Carrier gas	50mL/min
Dilution gas	255mL/min
Evaporator temperature	700°C
Collection time	30 min each loading stage
Superficial velocity (mm/Sec)	5.0 mm/sec
Type of TWC slurry	20wt%

(a)

(b)



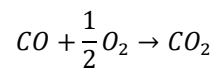
(c)

Fig. 1: Experimental apparatus (a) TWC particle collection, and (b) Experimental condition, (c) SEM visualization TWC standard respectively

2.2. Catalytic Performance Test

2.2.1. CO Oxidation Using Three-Way Catalytic (TWC) Microparticle

The Figure 2 illustrates the catalytic reaction apparatus. The reaction equation of the experiment is the oxidation of CO:



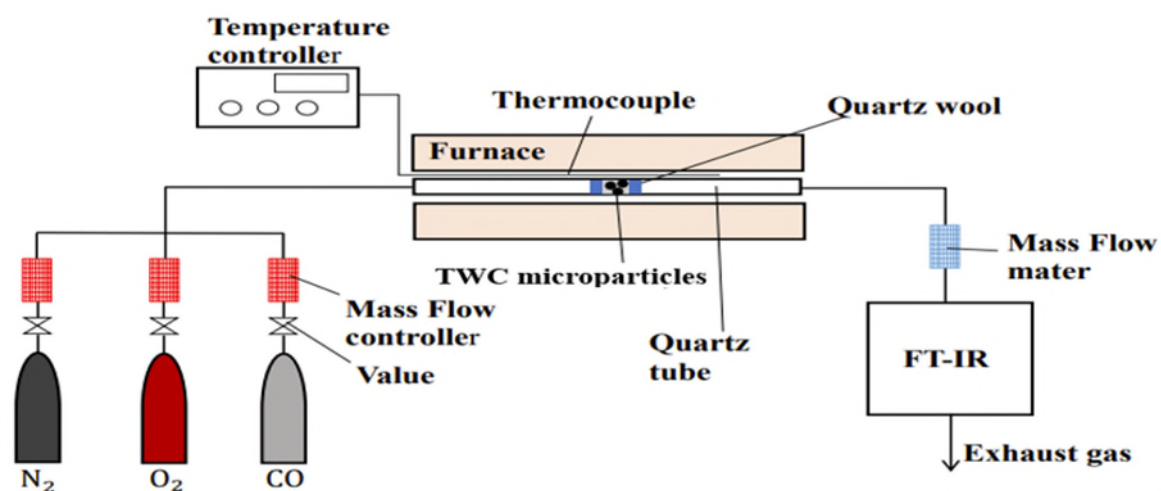
The CO oxidation activity and stability tests were conducted to investigate the catalytic performance of the TWC microparticles under different conditions. The catalytic performance of the TWC microparticles collected from the membrane fabrication apparatus was evaluated using the set up in Figure 2(a), The catalytic performance was prepared by mixing 25 mg of the TWC

microparticles with 260 mg of a mixture of quartz sand and SiC 250 mg and 10 mg respectively and placed in a quartz tube of the inner diameter of 4 mm. A mixture of the catalyst and diluent were packed approximately 12.5 mm in middle of quartz tube at and fixed by quartz wood to both ends. The leakage was checked by introducing 100 mL/min N₂ and confirmed at approximately 95 mL/min reaches at the exhaust gas flowmeter. The TWC microparticles inside the quartz tube were first pretreated and activated by passing 50 mL/min of N₂ gas at 400 °C for one hour, followed by 50 mL/min of H₂ gas at 400 °C for 30 minutes. During the CO reaction experiment, a mixture of N₂, O₂, and CO controlled by a mass flow controller was fed into the quartz tube, and the CO concentration in the outlet of the catalytic reactor was measured by FT-IR (IR Tracer-100, Shimadzu) with gas cell with optical path length of 10 cm (PIKE Technologies). The catalytic activity of the TWC microparticles was evaluated in 50mL/min gaseous mixture of 2.5 vol.% CO, 2.5 Vol.% O₂, and balance gas 95 vol.% N₂.. The catalytic reaction temperature was controlled using an electric furnace equipped with a temperature controller from 70 °C to 260 °C. When each temperature stabilized, the measurement of CO concentration was started. The gaseous mixture was flowed for a half to 1 hour, and the CO conversion was calculated after confirming that the CO concentration at the outlet of the reactor had reached a sufficiently steady state. The CO conversion test was performed by investigating the effects of standard TWC precious-metal amounts, and firing temperatures. The resulting structure–transport relationships are correlated with exhaust gas purification performance, providing design guidelines for advanced GPF/TWC membrane systems as shown in Figure 2 (b) with optimized oxygen storage, catalytic activity, and pressure-loss characteristics.

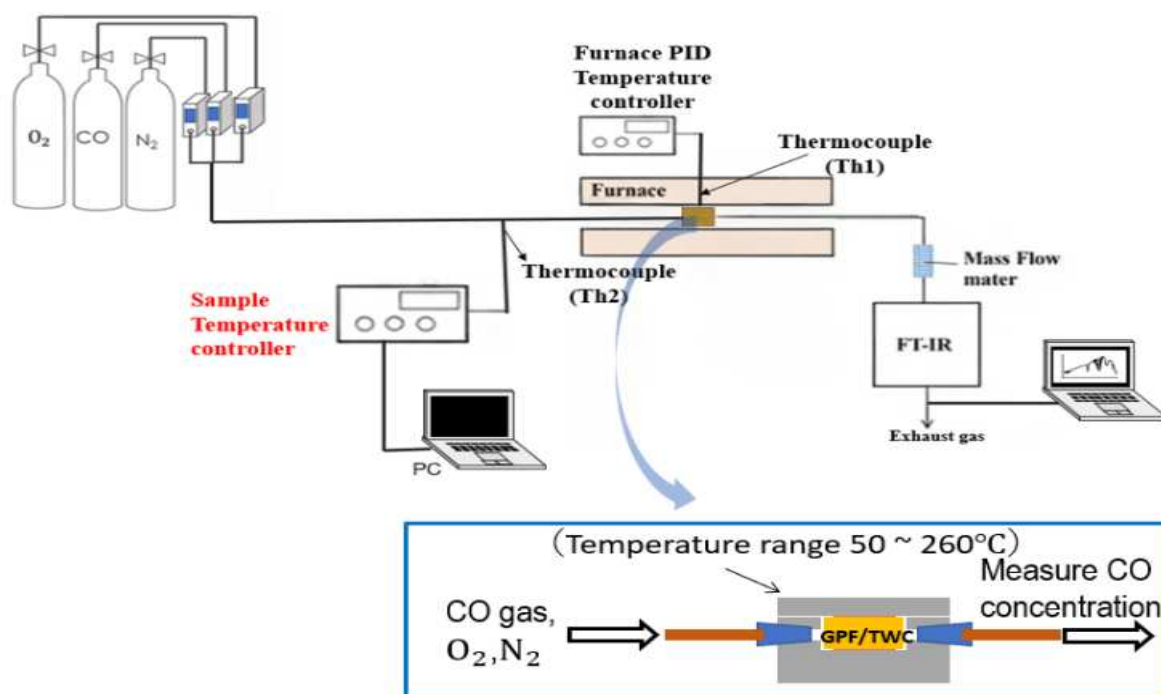
2.2.2. CO Oxidation Using TWC/GPF

The Figure 2(b) shows the setup of the catalyst reaction apparatus used to evaluate the CO oxidation activity and characteristic stability of TWC/GPF. During membrane fabrication, a digital manometer was used to measure the pressure loss, mass was measured on GPF both before and after coating each TWC loading, and the weight quantity of TWC microparticles was converted into the flowrate Q₂ (mL/min) using the correlation of the weight and flowrate of similar standard TWC microparticles packed into the quartz glass tube. The TWC microparticles inside the GPF were also pretreated and activated by placing the TWC/GPF sample inside a ceramic tube flow path installed in an electric furnace and pre-treated by passing 50mL/min of N₂ gas at 400 °C for one hour, followed by 50 mL/min of H₂ gas at 400 °C for half an hour. Similarly to TWC microparticle, the CO conversion test was performed following the experimental procedures used during TWC microparticles characteristics flowing into the packed quartz glass tube, the leakage was also first checked by introducing 100mL/min N₂. The reactor temperature was controlled using an electric furnace, a mixture of N₂, O₂, and CO controlled by a mass flow controller was fed into the TWC/GPF sample installed inside the furnace, and the CO concentration in the outlet of the catalytic reactor was measured by FT-IR (IR Tracer-100, Shimadzu) with gas cell with optical path length of 10 cm (PIKE Technologies). The catalytic activity of the TWC/GPF was evaluated in the flowrate Q₂ (mL/min) gaseous mixture of 2.5 vol.% CO, 2.5 Vol.% O₂,

and balance gas 95 vol.% N₂. The catalytic reaction temperature was controlled using an electric furnace equipped with a temperature controller from 50 °C to 260 °C as shown in Figure 2(b). The CO concentration measurement started when each temperature had nearly stabilized after 30 to 60 minutes of flowing gas, and after confirming that the CO concentration in FT-IR LabVIEW spectrum had reached a sufficiently steady state, the CO conversion was computed. For TWC/GPF, since the sample temperature did not achieve precise stability throughout the tests, the mean sample temperature values at each furnace temperature were used in CO conversion study.



(a)



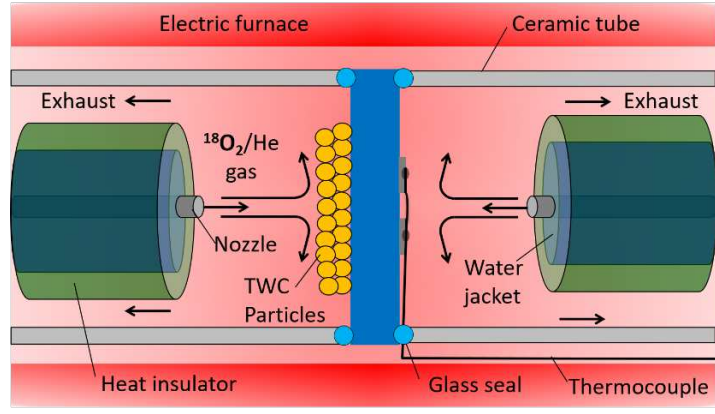
(b)

Fig. 2. Catalytic Reaction Apparatus (a) CO Reaction Experiment of TWC microparticles Performance Activity (b) CO Reaction Experiment of Integrated TWC/GPF Performance Activity

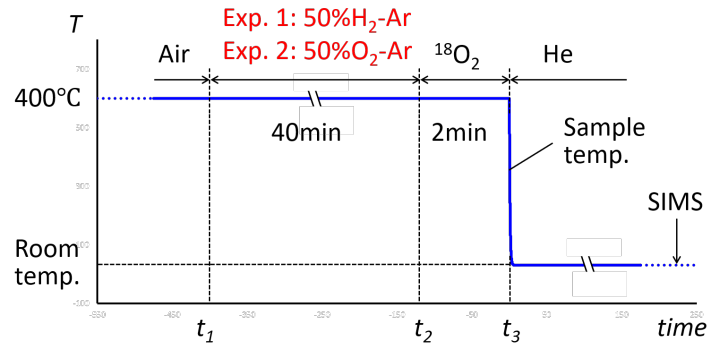
2.3. Oxygen Isotope labeling and Quenching Experimental Procedure

Oxygen isotope experiments shown in Figure.3 were conducted using an isotope-quench technique to preserve transient oxygen distributions within the catalyst. This experiment used an isotope quenching reactor capable of instantly freezing the distribution of chemical species at high temperatures. The main components of the apparatus are a ceramic tube and a He-gas injection nozzle equipped with a water-cooling jacket inside. The TWC particle agglomerated on substrate is placed between two ceramic

tubes, and atmosphere control inside the electric furnace is enabled by sealing with glass rings. The water-cooling jacket is surrounded by thermal insulation, contains coolant circulation channels and He-gas supply channels inside, and is designed so that He gas at approximately room temperature can be injected directly onto the specimen even inside the high-temperature electric furnace as shown in Figure 3. Oxygen mass transport in three-way catalyst (TWC) systems was investigated using an integrated methodology combining particle membrane fabrication, isotope labeling, rapid reaction quenching, and high-resolution microstructural characterization following the same procedure in the work of Nagasawa *et al.*, (2023). Mounted samples were first subjected to a leak check using Ar or N₂ at a flow rate of 30 cm³ min⁻¹ on both sides of the sample for approximately 7 min, with N₂ supplied to the stone side. The samples are heated to 800 °C, sealed with glass, and there were then oxidized in O₂ at 30 cm³ min⁻¹ for 5 min. Subsequently, the temperature was decreased to either 400 °C to evaluate the effect of annealing temperature on oxygen transport behavior. Residual oxygen was removed by purging with Ar or N₂ at 30 cm³ min⁻¹ for 3 min. Following the purge step, the samples were exposed to a reducing atmosphere consisting of Ar and H₂ (15 cm³ min⁻¹ each) for 40 min to establish a reduced catalyst state. Oxygen isotope labeling was then performed by introducing ¹⁸O₂ at a flow rate of 30 cm³ min⁻¹ for 2 min at the target temperature (400 °C). Immediately after isotope exposure, the reaction was quenched by rapidly cooling the samples using a helium gas jet precooled with water, thereby fixing the diffused isotope distribution within the microparticles as shown in Figure 7(b). This approach minimized post-reaction diffusion and enabled direct interrogation of oxygen storage and exchange processes.



(a)



(b)

Fig. 3: Quench Experimental Setup and Oxygen isotope Labelling Procedures

2.4. Sample Preparation and SIMS Analysis

Figure 4 illustrates SIMS sample preparation of a three-way catalyst (TWC) particle agglomeration. After isotope quenching, the samples were embedded in epoxy and polished into cross sections using a cross-section polisher as shown in Figure 4(a) and (b). Secondary ion mass spectrometry (SIMS) was used to investigate oxygen isotope distributions. SIMS measurements were conducted with a primary Cs^+ ion beam. Secondary ions corresponding to ^{16}O , ^{18}O , $^{12}\text{C}_2$, $^{27}\text{Al}^{16}\text{O}$, $^{90}\text{Zr}^{16}\text{O}$, $^{104}\text{Pd}^{16}\text{O}$, $^{140}\text{Ce}^{16}\text{O}$ signal were collected to construct high-resolution cross-sectional isotope maps. Line profiles were taken from the isotope maps, and the C^{18}O_2 ratio shown in the Equation (2) was determined to quantify oxygen isotope incorporation. Oxygen transport parameters were evaluated by fitting extracted line profiles to diffusion-based models. Comparative analyses were performed to assess the effects of precious-metal loading (standard, 2x and 4x metal amounts), annealing temperature (400 °C), and firing temperature (900 °C) on oxygen isotope distribution.

$$C^{18}O_2 = \frac{{}^{18}O_Signal}{({}^{18}O_Signal + {}^{16}O_Signal)} \quad (2)$$

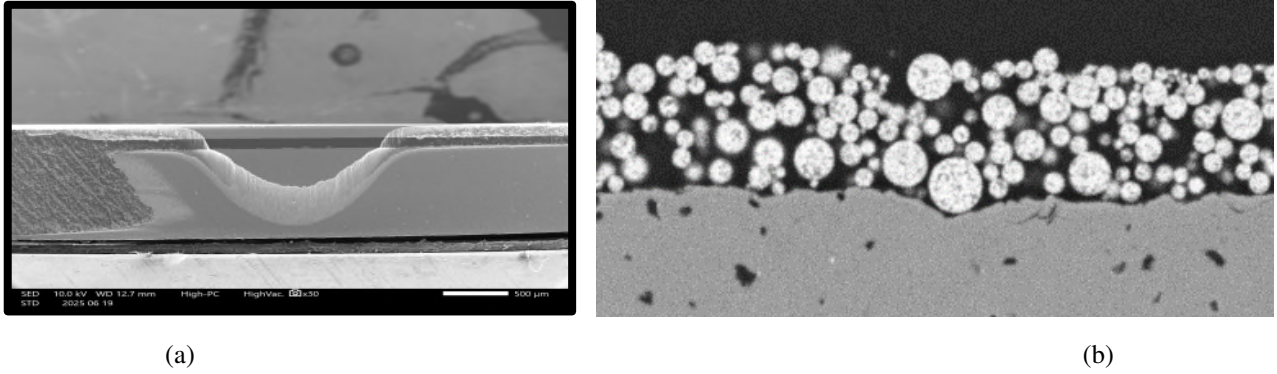


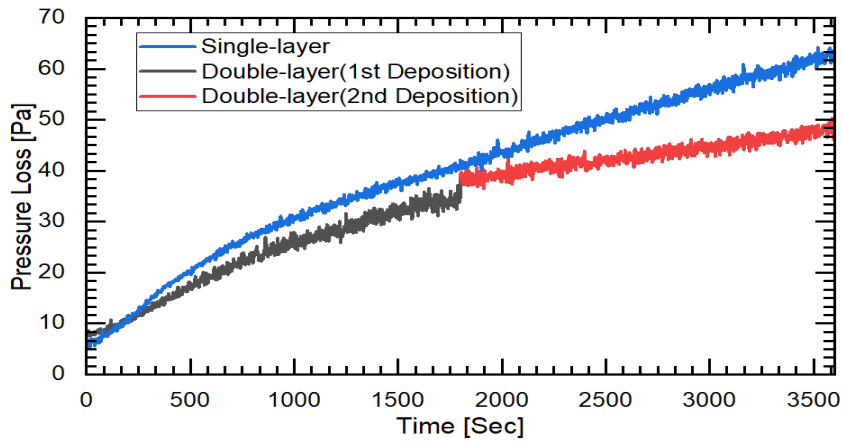
Fig. 4: TWC SIMS sample preparation (a) Osmium coating and Surface Epoxy punishment, and (b) TWC particle agglomeration Cross Sectional Visualization

3. Results and Discussion

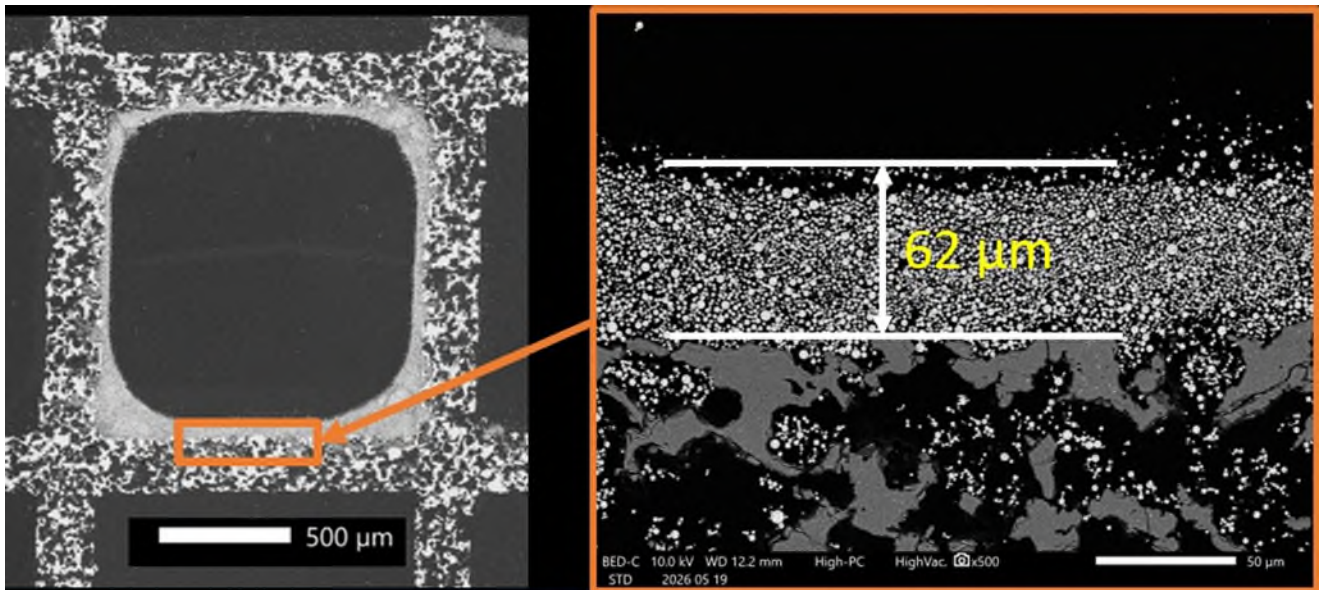
3.1. Membrane Fabrication Experiments

In this section, the results of pressure loss during membrane fabrication are presented to discuss the relationship of single-layer and double-layer depositions (two-stage sintering). Figure 5(a) shows the pressure loss changes for two different samples during two-layer deposition, single layer non fired deposition and double layers deposition fired at 900 °C, respectively. In both cases, a rapid pressure increase occurred during the initial approximately 12 minutes, followed by gradual deposition and layer formation between 13 and 30 minutes. Thereafter, the pressure increased almost linearly, remaining consistently higher for the single-layer sample likely due to residual moisture within the microparticles. For the double layer depositions, the slight deviation in the slope of the pressure loss before and after the first firing stage, and the gap in the absolute value of the pressure

loss before and after the two-stage firing, were obtained through many improvements in the experimental setup. Since, no cracks were observed in the double-layer sample, this confirmed improved structural integrity. This process also promoted particle bonding through Van der Waals interactions, enabling uniform catalyst coating and achieving a balance between filtration efficiency, low pressure, and catalytic activity. Figure 5(b) shows an SEM image of a GPF with a TWC membrane deposited on it, which was impregnated with epoxy and then smoothed before imaging. This reveals that the TWC layer is approximately 62 μm thick.



(a)



(b)

Fig. 5: (a) Time-dependent pressure loss during membrane fabrication and (b) Image of cross-section of a GPF channel with TWC particle agglomerated layer

3.2. Effect of Precious Metal Amount and Firing Temperature on the CO Conversion Performance of TWC Particle

The catalytic performance of the TWC microparticles collected from the membrane fabrication apparatus was evaluated.

Figure 6 (a), and (b) show the results of CO oxidation tests using three types of TWC microparticles with various precious metal loadings (standard, 2x and 4x the standard amount unfired) and with different firing conditions (fired at 800 °C, and 900 °C). As shown in Figure (a), (b), and (c), the particle size of TWC microparticles is mostly 1 to 2 µm. The light-off temperature T_{20} and T_{50} and the temperature for complete CO conversion T_{100} were evaluated. For all samples and conditions, CO conversion was calculated after waiting for the CO concentration at the reactor outlet to reach a steady state. For the precious metal loading series without firing case, the precious metal loading series using TWC Standard 1x, 2x, and 4x metal content reveals a clear effect on the CO oxidation performance in the TWC particle membrane. In the TWCs containing a standard metal amount, the CO conversion reached 20% at approximately 165 °C (T_{20}), 50% at 173 °C (T_{50}), and 100% at 175 °C (T_{100}). Increasing the metal loading to TWC standard 2 and 4times metal amount reduced T_{20} to 151 °C and 112 °C, T_{50} to 158 °C and 145 °C and T_{100} to 170 °C and 155 °C, respectively as shown in Table 1, demonstrating enhanced CO oxidation performance with higher metal content. The precious metal loading series fired at 800 and 900 °C were evaluated and compared, the temperature at which CO conversion reaches 20% (T_{20}) is approximately 151°C, CO conversion reaches 50% (T_{50}) is 176 °C and the CO conversion reaches 100% (T_{100}) is 195°C for TWC standard metal fired at 800°C. In contrast, T_{20} , T_{50} and T_{100} of the TWC standard metals fired at 900°C is 159°C, 183°C and 200°C, respectively. T_{20} , T_{50} and T_{100} of the TWC/GPF standard 4 times metals is 150°C, 165°C and 185°C, respectively. As shown in the results of CO conversion performance of TWC Micro-particle: effect of sintering temperature and precious metal amount, firing process improves light-off performance (T_{20} and T_{50} decreases) while T_{100} shifts toward the high temperature range. Therefore, it is thought that sintering of the microparticles progressed during firing, preventing reaction gas from reaching the interior of the particles and increasing T_{100} . This could be attributed to the CO adsorption volume per catalyst weight (cm³/g) growth as increasing the firing temperature, preventing reaction gas from reaching the interior of the particles and increasing T_{100} as revealed in the correlation between the microparticle metal dispersion and CO oxidation performance influenced by the firing temperature and precious metal amount as shown in Table 3. This observation corresponds with the findings made by Minegishi *et al.*, (2024) who experimentally evaluated Pt/CeO₂ Catalyst Synthesis via Flame-Assisted Spray Pyrolysis and confirmed that sintering increased the particle size of the precious metal, which had contributed to the promotion of CO oxidation at low temperatures and also by Phyozin *et al.*, (2023) who explained the effect of sintering temperature on TWC membrane filter performance in their study.

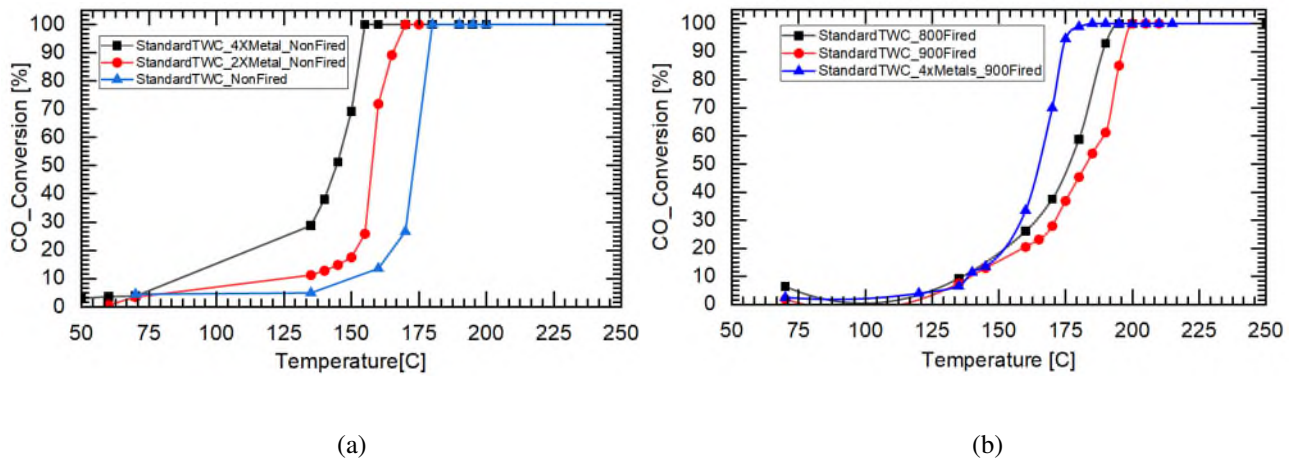


Fig. 6: Effect of TWC particle Precious Metal Amount on CO-Conversion Performance Analysis (a) Unfired, and (b) Sintering Temperature

Table 2: Light-Off Temperature in CO-Conversion Performance comparison

Metal Type & Firing Temperature	TWC Standard amount of metal	TWC_2Xmetal	TWC_4Xmetal	TWC_800 Firing(4hrs)	TWC_900 Firing(4hrs)	TWC_4x_900 Firing(4hrs)
T100	175	170	155	195	200	185
T50	173	158	145	176	183	165
T20	165	151	112	151	159	150

Table 3: Effect of Firing Temperature and Precious Metals on TWC Microparticle Metal Dispersion and CO Oxidation Performance.

Firing temperature & Precious metals	Standard TWC_Non-Fired	Standard TWC_800Fired	Standard TWC_900Fired	Standard TWC_2xMetal_900Fired	Standard TWC_4xMetal_900Fired
CO adsorption amount	0.88 cm ³ /g	0.55 cm ³ /g	0.21 cm ³ /g	0.63 cm ³ /g	0.78 cm ³ /g

3.3. Oxygen Isotope Labelling using a Model System of TWC Microparticles

The oxygen transport behavior within TWC microparticles was investigated using ¹⁸O isotope labeling combined with SIMS analysis. Microparticles collected from membrane fabrication test were immobilized on alumina substrates and sintered at 900 °C to ensure structural stability prior to isotope experiments. Secondary ion mass spectrometry (SIMS) mapping using primary Cs⁺ irradiation enabled high-spatial-resolution visualization of oxygen isotope distributions within TWC microparticles. Cross-sectional maps and signals of ¹⁶O, ¹⁸O, ¹²C₂, ²⁷Al¹⁶O, ⁹⁰Zr¹⁶O, ¹⁰⁴Pd¹⁶O, ¹⁴⁰Ce¹⁶O provided direct insight into oxygen transport

and storage behavior at the microscale for the TWC microparticle standard precious-metal-loading samples with double-metal-loading (2x-metal) shown in Figure 7. Figure 7 presents representative cross-sectional isotope maps and corresponding secondary ions. In contrast to the inward-decreasing ^{18}O concentration profile expected for diffusion-limited uptake, cross-section of the 2 times-metal samples exhibited a nearly uniform ^{18}O distribution across the microparticle cross sections. This behavior was consistently observed in CZ-rich domains, indicating that gas-phase diffusion through the particle network is sufficiently rapid under the applied conditions. Instead, the absence of a concentration gradient suggests that bulk oxygen incorporation and exchange within the CZ phase govern the overall isotope uptake. The influence of catalyst composition was evaluated by comparing standard TWC precious-metal-loading, two times metal loading (2x-metal) and four-time metal amount, with particular attention to ceria– zirconia (CZ)-rich regions that dominate oxygen storage functionality.

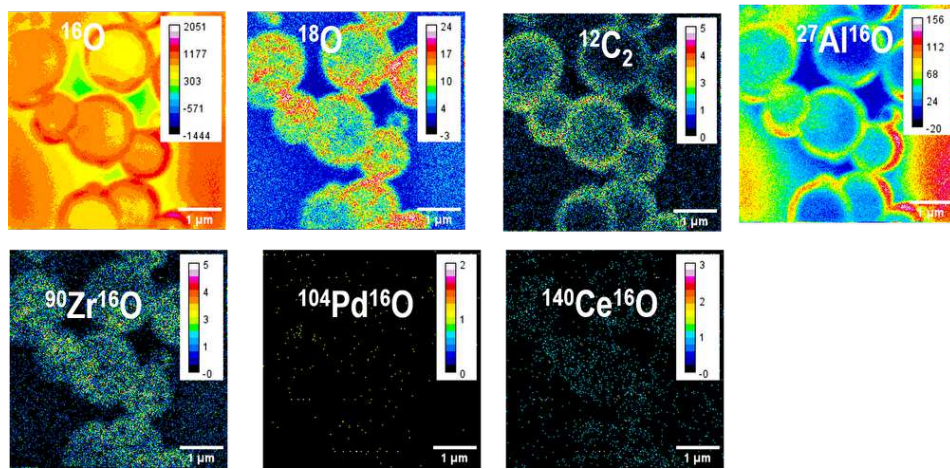


Fig. 7: Cross Sectional SIMS Visualization of Oxygen Isotope Distribution in Standard TWC 2x -Metal Amount

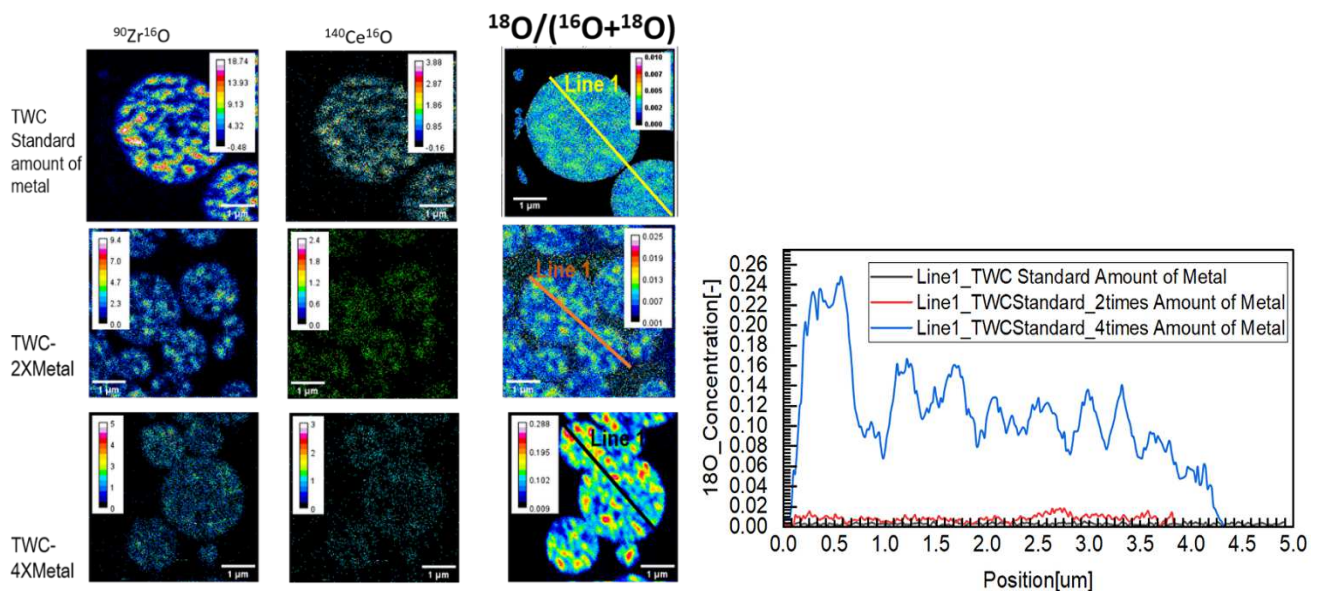


Fig. 8: Effect of Precious Amount Metal on Oxygen Isotope Distribution Inside TWC Microparticle (Cross-Section)

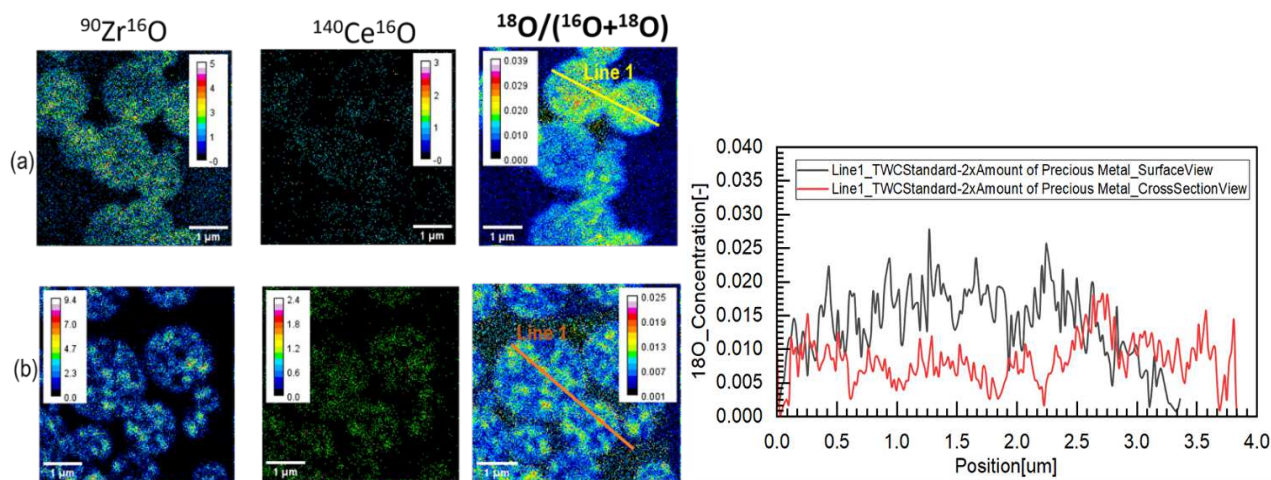


Fig. 9: Qualitative analysis of Oxygen Isotope Distribution Inside TWC Microparticle (a) Surface and (b) Cross-Section
TWC-2XMetal, Resolution: 20nm/px

The Oxygen isotope concentration line profile mapping analysis of the $^{18}\text{O}_2$ ratio supports this interpretation. The mean ^{18}O fraction increased from approximately 0.003 in the standard TWC-metal sample, 0.008 in the 2x metal sample to approximately 0.116 in the 4x metal sample, exceeding the natural abundance of ^{18}O (0.002) in both cases as shown in Figure 9. The substantially higher enrichment observed for the 4x metal catalyst indicates that increased precious-metal loading enhances oxygen exchange throughout the microparticle interior. This finding implies that precious metals distributed within the bulk remain catalytically accessible and actively promote oxygen activation and transfer to the CZ lattice, rather than being confined to surface-dominated reactions. This has good agreement with the results of TWC- CO oxidation performance analysis as well as the metal dispersion as shown in Table 3. Furthermore, at the surface and cross section of TWC microparticles-2x metal amount, $^{18}\text{O}_2$ concentration increases uniformly in areas where CZ is present in both cases. The ^{18}O concentration is approximately 0.015 and 0.008 on the surface and inside the particle respectively, a slight increase compared to natural ratio (0.002). Additionally, the surface exhibits a higher ^{18}O concentration compared to the cross-section of the microparticles as shown in Figure 9. Therefore, while both the surface and internal precious metals in TWC microparticles contribute to the purification reaction, it is believed that the surface plays a more effective role. Overall, these results collectively indicate that, under the present experimental conditions, oxygen storage and lattice exchange kinetics within the CZ phase constitute the rate-limiting step, rather than external or internal gas-phase diffusion. The uniform isotope distribution further suggests that microstructural connectivity within the microparticles effectively facilitates oxygen penetration, while compositional factors primarily control the extent of oxygen incorporation.

3.4. TWC particle and TWC/GPF Membrane Filter Light-off Temperatures on CO-Conversion Performance Analysis

Figure 10 (a), and (b) compare the results of CO oxidation tests using TWC microparticle and GPF/TWC fired at 900 °C. The light-off temperature T_{20} and T_{50} and the temperature for complete CO conversion T_{100} were compared. It was initially observed that, for the TWC/GPF fired at 900 °C, the temperature at which CO conversion reaches 20% (T_{20}) is approximately 131°C, CO conversion reaches 50% (T_{50}) is 143 °C and the CO conversion reaches 100% at 256 °C (T_{100}). Comparing both Standard TWC microparticle and TWC/GPF fired at 900 °C, it can be seen that the light-off temperature (T_{50}) of the TWC/GPF has increased the catalyst activity performance by 56 °C over the TWC microparticle and decreased by 49 °C the full CO conversion (T_{100}) over standard TWC microparticles, highlighting a performance trade-off when combining TWC membranes with GPF structures. As shown in Figure 10 and Table 4, compared to TWC particles, the TWC/GPF system exhibits improved light-off performance but worse T_{100} performance. These discrepancies could be attributed to the TWC microparticles diluted with inert particles, the membrane contains TWC at a high spatial density. Consequently, the exothermic reaction of CO oxidation may have proceeded rapidly within the membrane, causing a local temperature rise, which may have led to the improvement in light-off. On the other hand, since the contact time between the gas and the catalyst is much shorter for the TWC/GPF membrane than for the TWC microparticles by approximately of 104 msec and 2.4 sec respectively, it is thought that sufficient contact time could not be secured in the case of the membrane, leading to a decline in performance, particularly in the high CO conversion range.

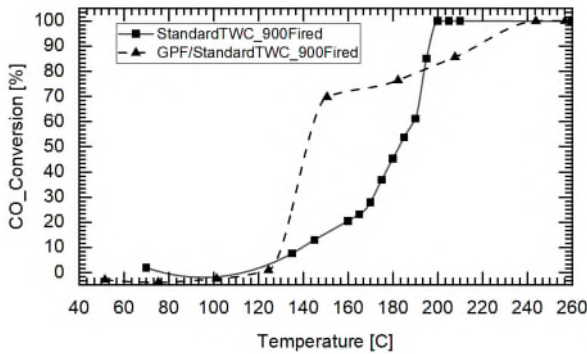


Fig. 10: (a) Light-Off Temperature in CO-Conversion Performance Comparison between TWC Microparticle and TWC/GPF both Sintered at 900 °C

Table 4: CO-Conversion Performance Comparison between TWC Microparticle and TWC/GPF both Sintered at 900°C

Firing Temperature (T)	Standard TWC _900Fired	Standard TWC/GPF _4xmetal_ 900 fired
T100	200	256
T50	183	134
T100	159	131

4. Conclusion

This work demonstrated how membrane fabrication parameters govern the structure and catalytic behavior of TWC microparticles. The influence of membrane fabrication parameters on the structure of TWC microparticles and their exhaust gas purification performance was investigated. The CO conversion test was performed to investigate the effect of firing temperatures (800 °C and 900 °C) and precious metal amount in standard TWC 20wt% slurry. The isotope labeling was also conducted to investigate oxygen isotope active site inside the TWC microparticles at different precious metals loading. The two-stage TWC membrane fabrication firing showed a consistent pressure loss increase across both loading stages. CO-conversion testing revealed that higher firing temperatures reduce CO oxidation activity, while increased precious-metal loading significantly enhances performance. Increasing the firing temperature improved light-off behavior (lower T_{20} and T_{50}) but shifted T_{100} to higher values due to decreased amount of CO adsorption as increasing the firing temperature. This suggests that as the firing temperature increases, agglomeration of the precious metals proceeds, leading to a decrease in active sites. Consequently, it is believed that a shortage of active sites, particularly in the region where CO conversion is high, led to an increase in T_{100} . Increasing precious-metal loading from the standard TWC to 2- and 4-times precious metal improved CO adsorption capacity and reduced T_{100} by 5 °C and 20 °C, respectively. Additionally, integrating the TWC/GPF system exhibits improved light-off performance of CO oxidation but worsen T_{100} performance with approximately 56 °C increase compared with standard TWC microparticles, highlighting a performance trade-off when combining TWC membranes with GPF structures. Oxygen isotope profiling shows that ^{18}O is consistently integrated throughout the cross-section of TWC microparticles where CZ is present, with overall ^{18}O uptake rising with precious metal loading. The microparticle surface has greater ^{18}O concentrations than the interior, indicating active oxygen exchange at the outer regions. The purifying reaction involves both surface and interior precious metal sites. However, the surface sites play a more dominant and effective role in facilitating oxygen activation and transport. Furthermore, isotope-labeling results confirmed that higher metal loading promotes oxygen exchange throughout the entire microparticle, indicating that bulk-dispersed metals remain catalytically accessible and actively contribute to oxygen activation and transfer into the CZ lattice.

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