Electronic Supplementary Information

Enhancing CO oxidation performance by controlling the interconnected pore structure in porous three-way catalyst particles

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1. TWC NPs

TWC NPs are commercial catalytic materials designed to simultaneously reduce harmful emissions such as carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x) from vehicle exhaust systems. This catalyst consists of precious metals (e.g., palladium and rhodium) supported on a metal oxide substrate (i.e., CeZrO₄ and Al₂O₃) as thermal stabilities and oxygen storage capacities. Morphology analysis using SEM shows that TWC NPs are generally spherical or irregularly shaped (**Figure S1**). With an average size of 8.4 nm for their primary nanoparticles, the TWC NPs exhibit excellent dispersibility, ensuring uniform distribution during precursor preparation.



Figure S1. SEM image of TWC NPs.

2. Stability of porous TWC particles during the synthesis process

The synthesis and template removal processes of porous TWC particles involve high temperatures, which can influence their structural integrity, such as pore collapse, framework degradation, or sintering of nanoparticles and their components. Thus, the stability of the porous structure of TWC particles after the spray and template removal processes will be discussed in this section. **Figures S2** compares the morphology of TWC NPs (**Figures S2a and d**), aggregate TWC particles (**Figures S2b and e**), and porous TWC particles from TP2 sample (**Figures S2c and f**). Aggregate TWC particles were prepared through the spray process of the precursor from a TWC concentration of 1 wt% without the addition of PMMA. These particles were heated under the same heating conditions as the template removal process to provide a reliable comparison with porous TWC particles. The morphology comparison of these samples reveals that the primary TWC NPs (**Figure S2d**) are still visible within the aggregate (**Figure S2e**) and porous TWC particles (**Figure S2f**). This result indicates that no sintering occurs in the aggregate and porous TWC particles after the synthesis process. In addition, the porous TWC particles also exhibit good structural integrity, as evidenced by the absence of pore collapse and framework degradation after the synthesis process.



Figure S2. SEM images of (a and d) TWC NPs, (b and e) aggregate TWC particles, and (c and f) porous TWC particles at (a-c) low and (d-f) high magnification.

TEM-EDS elemental mapping analysis was also conducted to investigate the distribution of TWC components after the template removal process (**Figure S3**). The result reveals a stable distribution of elements from the TWC components across the porous particles. This result indicates that the removal of the PMMA template does not disrupt the catalytic components. Moreover, the mapping also shows no significant agglomeration of elements, further demonstrating the stability of the porous TWC particles. In addition, the stable distribution of TWC components after high-temperature exposure also demonstrates their excellent thermal stability and structural integrity.



Figure S3. (a and g) TEM images and EDS elemental mapping of (b and h) Pd, (c and i) Rh, (d and j) Ce, (e and k) Zr, and (f and l) Al in the porous TWC particles from TP2 samples (a-f) before and (g-l) after template removal process.

High magnification of TEM-EDS elemental mapping serves to also analyze the factors that maintain the structural stability of porous TWC particles after high temperature exposure during the synthesis process (**Figure S4**). As shown in **Figures S4b and c**, the TWC materials used in this study consist of active elements such as palladium (Pd) and rhodium (Rh). Moreover, the TWC also includes cerium (Ce), zirconium (Zr), and aluminum (Al), originating from the support materials CeZrO₄ and Al₂O₃ (**Figures S4d-f**). **Figures S4h–I** demonstrate that the active TWC components of Pd and Rh in aggregate TWC particles synthesized without PMMA remain remain unchanged within the particles after the synthesis process. In the porous TWC particles, a similar result was observed, with the stable distribution of TWC components within the frameworks of particles. In both the aggregate sample (produced without a PMMA template) and the porous TWC particles, no aggregation of the active components, Pd and Rh, is observed. This finding suggests that the stable distribution of the active components is attributed to the inherent properties of the TWC support materials, CeZrO₄ and Al₂O₃.



Figure S4. (a, g, and m) TEM images and EDS elemental mapping of (a-f) TWC NPs, (g-l) aggregate, and (m-r) porous TWC particles from TP2 sample for (b, h, and n) Pd, (c, i, and o) Rh, (d, j, and p) Ce, (e, k, and q) Zr, and (f, l, and r) Al.

3. Surface pore and particle-size distribution

The particle-size distributions were determined by measuring the geometric diameters (D_g) of approximately 300 porous three-way catalyst (TWC) particles. The results demonstrated that the particle size increased from 0.66 to 1.29 µm with an increase in the PMMA concentration from 0.1 to 2 wt%, respectively (**Figure S5**).



Figure S5. Particle-size distribution of porous TWC particles at PMMA concentrations of (a) 0.1, (b) 0.5, (c) 1, and (d) 2 wt%.

Surface pore-size distributions were determined by measuring the D_g of 150 pores on each sample of porous TWC particles. The results indicated that all the samples had a similar mean geometric surface pore of 0.30 µm (**Figures S6a–d**). This consistency was due to the spherical shape (**Figure S6e**) and uniform size of the PMMA particles (diameter = 0.36 µm) (**Figure S6f**).



Figure S6. (a–d) Pore-size distribution of porous TWC particles at PMMA concentrations of(a) 0.1, (b) 0.5, (c) 1, and (d) 2 wt%. (e) scanning electron microscopy (SEM) image and (f) particle-size distribution of PMMA particles.

4. Surface pore density

The number of surface pores per particle surface area for each particle (n_{SPAi}) was calculated using the following equation.

$$n_{SPAi} = \frac{n_{SPi}}{0.5A_{ci}} = \frac{n_{SPi}}{0.5\pi (D_{pi})^2},$$
(1)

where n_{SPi} is the number of pores on the surface of a particle. A_{ci} and D_{pi} represent the surface area and diameter of a particle where several surface pores are present. Here, $0.5A_{ci}$ was used because only half of the particle surface area was observed in the SEM images. The average of the n_{SPAi} measurements is defined as the surface pore density (number of surface pores per area). **Table S1** presents the number of surface pores per particle surface area.

PMMA concentration [wt%]	Surface pore density [pore/µm ²]
0.1	0.67
0.5	2.38
1	2.95
2	3.31

Table S1. Surface pore density of porous TWC particles at various PMMA concentrations.

The pores in the particles were generated from the decomposition of PMMA particles. Thus, the overall number of pores equaled the number of PMMA particles in one droplet $(n_{PMMA/droplet})$, which can be calculated using the equation below.

$$n_{PMMA/droplet} = \frac{M_{PMMA} \times \rho_d \times \frac{1}{6} \pi \times (D_d)^3}{\rho_{PMMA} \times \frac{1}{6} \pi \times (D_{PMMA})^3},\tag{2}$$

where M_{PMMA} is the PMMA concentration. ρ_d and ρ_{PMMA} are the densities of the droplet (1.00 g/cm³) and PMMA particle (1.18 g/cm³), respectively. D_d and D_{PMMA} represent the diameters

of the droplet (5 μ m) and PMMA particle (0.36 μ m). Furthermore, assuming that all the pores were present and distributed on the particle surfaces, the theoretical surface pore density was determined using the following equation.

Theoretical surface pore density
$$= \frac{n_{PMMA/droplet}}{\pi (D_{pc})^2}$$
. (3)

Regarding the particle diameter from the calculation process (D_{pc}) , this value can be obtained using **Equation 4** by assuming the mass conservation law that one droplet transforms into one particle.

$$D_{pc} = D_d \left(\frac{1}{1-\varepsilon} \sum \frac{M_i}{\rho_i}\right)^{1/3},\tag{4}$$

where ε is the porosity of the particles. M_i and ρ_i represent the concentration and the density of the raw components in the precursor solution, respectively. For TWC, the concentration and density were 1 wt% and 4.83 g/cm³, respectively. *i* is the type of raw components added to the precursor. The raw components included TWC and PMMA. Thus, after drying, the particles obtained prior to the template removal process were composite particles comprising TWC NPs and PMMA particles. Assuming that the TWC NPs were smaller than the PMMA particles, they can fill up all the spaces between the PMMA particles in the composite particles. As a result, the empty space within the compacted composite particles is minimal. Since porosity is defined as the ratio of empty space to total volume, this minimal empty space leads to a porosity value close to zero. Thus, $\varepsilon = 0$ was used in the calculations. Based on **Equations 2–4**, the calculation results for the overall number of pores per particle surface area are presented in **Table S2**.

M _{PMMA}	$n_{PMMA/droplet}$	D_{pc}	Theoretical surface pore density
[wt%]	[particle]	[µm]	[pore/µm ²]
0.1	2	0.71	1.24
0.5	11	0.92	4.10
1	22	1.10	5.82
2	45	1.33	8.03

 Table S2. Theoretical surface pore density of porous TWC particles at various PMMA concentrations.

5. Framework thickness and macroporosity

For the experimental value, the framework thickness was determined by measuring the width of 15 frameworks in focused ion beam (FIB) cross-sectional SEM images and averaging the results. In addition, the framework thickness can be predicted through mathematical calculations. All the equations used below to calculate the framework thickness were based on a study.¹ Here, the average surface pore size ($D_{macropore}$) was 0.30 µm. Thus, the number of TWC NPs completely covering one macropore ($n_{TWC-macropore}$) was calculated as follows:

$$n_{TWC-macropore} = \frac{\pi (D_{macropore} + D_{TWC})^2}{\sqrt{(2D_{TWC})^2 - (D_{TWC})^2}} \times 2,$$
(5)

where D_{TWC} represents the diameter of TWC NPs (8 nm). Furthermore, the number of TWC layers between the macropores ($n_{TWC \ layer}$) was calculated as

$$n_{TWC\ layer} = \frac{n_{TWC/PMMA}}{n_{TWC-macropore}} \times 2.$$
(6)

The number ratio of TWC NPs and PMMA particles in one droplet $(n_{TWC/PMMA})$ was calculated as follows.

$$n_{TWC/PMMA} = \frac{\frac{M_{TWC}}{\rho_{TWC} \times (D_{TWC})^3}}{\frac{M_{PMMA}}{\rho_{PMMA} \times (D_{PMMA})^3}},$$
(7)

where M_{TWC} and ρ_{TWC} are the concentration and density (4.83 g/cm³) of the TWC particles, respectively. The framework thickness ($L_{framework}$) was calculated as follows.

$$L_{framework} = n_{TWC \ layer} \times D_{TWC}.$$
(8)

Figure S7a shows the results from the measurement and calculation of the framework thickness.

Regarding the macroporosity of TWC particles, the binarization method using Otsu's global threshold from the ImageJ software was employed to determine the macroporosity based on the FIB cross-sectional image. To predict the macroporosity mathematically, the following equation from a previous study was used.

$$Macroporosity = \left(1 - \frac{D_{aggc^3}}{D_{pc^3}}\right) \times 100\%,\tag{9}$$

where D_{aggc} and D_{pc} are the diameters of aggregate and porous TWC particles from the calculation, determined using **Equation 4**. Figure S7b shows the measurement and calculation results of macroporosity.



Figure S7. FIB cross-sectional SEM image of porous TWC particles for the measurements of (a) framework thickness, indicated by yellow line and (b) macroporosity of porous TWC particles before (top image) and after (bottom image) application of the Otsu thresholding

method.

6. Critical conditions of interconnected pore structure formation

The porous particle surface area was calculated using the data of D_{pc} that were previously obtained. To determine the area of one PMMA particle including its framework thickness $(A_{c-FWPMMA})$, a schematic illustration was made based on the pore arrangement of real particles (**Figure S8**). Assuming that all the pores were evenly distributed in the maximum hexagonal arrangement on the surface of the TWC particles with the same pore size owing to the homogeneous size of the PMMA particles (D_{PMMA}) and framework thickness ($L_{framework}$), the area of one PMMA particle including its framework thickness ($A_{c-FWPMMA}$) is

$$A_{c-FWPMMA} = a \times b. \tag{10}$$

$$a = (L_{framework} + D_{PMMA}).$$
⁽¹¹⁾

$$b = \sqrt{(D_{PMMA} + L_{framework})^2 - \left(\frac{D_{PMMA} + L_{framework}}{2}\right)^2}.$$
 (12)

In addition, the maximum number of PMMA on the surface of a porous particle $n_{max-sPMMA}$ can be determined as follows.

$$n_{max-sPMMA} = \frac{A_{spc}}{A_{c-FWPMMA}}.$$
(13)

Table S3 presents the calculation results of $A_{c-FWPMMA}$ and $n_{max-sPMMA}$.



Porous TWC particles

Figure S8. Schematic illustration of the calculation of the area of one PMMA particle including its framework thickness.

PMMA concentration	$n_{PMMA/droplet}$	$A_{c-FWPMMA}$	n _{max-sPMMA}
[wt%]	[particle]	[µm ²]	[particle]
0.1	2	56.01	4
0.5	11	51.22	12
1	22	50.01	23
2	45	52.40	41
3	67	44.87	55

 Table S3. Area of one PMMA particle including its framework thickness.

7. Critical conditions of broken structure formation

Figure S9 shows that the number of TWC NPs must be sufficient to cover the entire PMMA particles. When there was one layer of TWC NPs, the remaining uncovered space caused the frameworks to easily be broken. Thus, frameworks built from at least two layers of TWC NPs were necessary. Thus, based on Equation 5, the number of TWC NPs needed to cover one PMMA in two layers $(2n_{TWC-macropore})$ was

$$2n_{TWC-macropore} = 2\left(\frac{\pi (D_{macropore} + D_{TWC})^2}{\sqrt{(2D_{TWC})^2 - (D_{TWC})^2}} \times 2\right).$$
(14)

Thus, the minimum required TWC NPs to cover all the PMMA particles in two layers $(2n_{TWCmin})$ was calculated as follows.

$$2n_{TWCmin} = n_{TWC/PMMA} \times 2n_{TWC-macropore}.$$
(15)

Table S4 presents the calculation results for $2n_{TWCmin}$. In addition, the provided TWC NPs in one droplet ($n_{TWC/droplet}$) were 505467 particles, calculated as follows.

$$n_{TWC/droplet} = \frac{M_{TWC} \times \rho_d \times \frac{1}{6} \pi \times (D_d)^3}{\rho_{TWC} \times \frac{1}{6} \pi \times (D_{TWC})^3}.$$
(16)



Figure S9. Schematic illustration of the calculation of the covered area of TWC NPs for a good framework (I) arrangement of TWC nanoparticles (NPs) on PMMA particles to form macropores, (II) presence of uncovered spaces when there is only a single layer of TWC NPs, and (III) complete coverage with no uncovered spaces in a double layer of TWC NPs.

 Table S4. Area of one PMMA particle including its framework thickness and the minimum number of TWC required to form a good framework.

PMMA concentration [wt%]	2n _{TWCmin} [particle]
0.1	21527
0.5	118397
1	236793
2	484350
3	721143



8. Mechanism of interconnected pore structure formation in porous TWC particles

Figure S10. Schematic illustration of the formation of porous TWC particles at different

PMMA concentrations.

9. Physical properties of porous TWC particles

As the TWC concentration was maintained at 1 wt%, further analysis of the physical properties was conducted only on the porous TWC particles with PMMA concentrations of 0.5, 1, and 2 wt%, which were selected as representative of the porous TWC particles. These analyses aim to investigate the effect of introducing macropores on the physical properties of TWC particles, which may influence the catalytic performance of porous TWC particles. Xray diffraction (XRD) revealed that the TWC NPs comprised CeZrO₄ and Al₂O₃ (Figure S11a). The same prominent diffraction patterns observed at 2θ from 20° to 80° confirmed that the samples had the same crystal structure, which remained unchanged during synthesis. This result revealed the good thermal stability of TWC particles. Furthermore, porous TWC particles from various PMMA concentrations exhibited the same type-II isotherm curves, indicating the presence of macropores and mesopores² (Figure S11b). Furthermore, the samples exhibited similar pore-size distribution curves, mainly dominated by mesopores owing to the presence of TWC NPs (Figure S11c). The lower pore volume distribution for macropores corresponded to the limitations of the Barrett-Joyner-Halenda method in measuring pores larger than 200 nm. The measurement of the specific surface area (SSA) indicated that the three samples had similar SSA values, differing by less than 10% (Table S5). Similar physical properties, such as the crystal structure, N₂ adsorption-desorption isotherms, pore-size distributions, and SSA, of the porous TWC particles suggested that the catalytic performance of the prepared samples was primarily dependent on their morphological structure. Therefore, the enhancement in catalytic performance of porous TWC particles with increasing PMMA concentrations arises from the effective diffusion of gaseous reactants, which is facilitated by the interconnected pore structure, thin framework thickness, and high microporosity.



Figure S11. (a) XRD patterns, (b) N₂ adsorption–desorption isotherms, and (c) pore-size distributions of porous TWC particles at different PMMA concentrations.

Table S5. SSA of	porous TWC	particles at	different l	PMMA	concentrations.

PMMA concentration [wt%]	$SSA[m^2/g]$
0.5	90.5
1	95.3
2	97.9

10. Stability of porous TWC particles during the catalytic performance investigation

The stability of porous TWC particles was evaluated using TP2 samples through a 6 h measurement at 130°C under the same mixture and gas flow rates used in the catalytic performance evaluation. The selected conditions simulate prolonged exposure to elevated temperatures and gas flow rate in determining the long-term stability of the particles under catalytic operating environments. SEM imaging was employed to analyze the morphology of the particles before (**Figures S12a and c**) and after (**Figures S12b and d**) the test. The results of this investigation showed that the porous structure of TP2 samples remained unchanged after the 6 h stability test without any signs of framework collapse, pore coalescence, or structural degradation. This result demonstrates the excellent porous structure stability of the nanostructured TWC particles under the tested conditions. Furthermore, the catalytic performance investigation in our previous study demonstrated that porous TWC particles with a stable structure led to sustained high performance over a 7-hour period.³



Figure S12. SEM images of porous TWC particles from TP2 samples at (a and b) low and (c and d) high magnification (a and c) before and (b and d) after 6 h catalytic performance

evaluation.

Reference

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