Electronic Supplementary Material (ESI) for RSC Advances.

Supplemental Information

Site-targeted Decoration of Palladium Nanocrystals for catalytic CH_4 removal in Lean-burn Exhaust

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Contents

S1. Preliminary study of Pd crystal size with thermal treatment

S1.1 Backgrounds of the preliminary study

The as-synthesized (AS) -Pd/Al_2O_3 used in this study had a relatively small Pd crystal size. When considering site-targeted decoration of Ni on the edge of Pd nanocrystals for CH_4 removal, we decided to use Pd crystals intentionally grown rather than as-prepared and applied a prior thermal treatment in the expectation that it would be easier to distinguish the difference in Ni decoration positions and Ni decoration/non-decoration in various analysis and evaluations.

S1.2 Experimental

AS-Pd/ Al_2O_3 was calcined at 550C for 1hour as described in manuscript. Specifically, an aliquot of 3 g AS-Pd/Al_2O_3 powder was heat-treated in an electric furnace at 750 °C, 850 °C, and 950 °C for 10h.

XRD analysis was carried out with D8 ADVANCE made by BRUKER and the diffraction peak of Pd at 2θ = around 54.9 ° was used to calculate Pd crystal size by Scherrer equation.

CO adsorption measurement was conducted in a CO pulse chemisorption method with Catalyst Analyzer BELCAT II made by Microtrac BEL Corp. The Pd crystal size was calculated from the amount of CO chemisorption by the calculation equation reported in the literature[S1-S2].

An aliquot of about 0.35 g of Pd/Al_2O_3 was placed in the sample holder. It was heated from room temperature to 400 °C under 100% He gas stream at 150 mL/min. After 15 min at 400 °C, the gas stream was changed to 100% H_2 at 150 mL/min, then pre-treated for 10min. Then 100% H_2 was changed to 100% Helium at 400 °C, kept 10min, then cool to 50 °C. After the pretreatment, 0.935 cm^3 / pulse, as STD, of CO was fed 12 times and CO in the outlet gas was detected by TCD. The amount of chemisorption was calculated by subtracting the small area of the 1st to 9th pulses from the area of the inlet pulse. The Pd crystal size was calculated from the amount of CO chemisorption by the calculation equation reported in the literature [S1-S2].

S1: C. N. Costa, S. Y. Christou, G. Georgiou, A. M. Efstathiou, J. Catal., 219 (2003) 259.

S2: J.J.F. Scholten, A.P. Pijpers, A.M.L. Hustings, Catal. Rev.-Sci. Eng., 27 (1) (1985), p. 151.

The prepared materials were characterized with a scanning transmission electron microscope (STEM, JEOL HD2000). The sample powder was dispersed over a copper (Cu) grid mesh for STEM observations. Elemental analysis was carried out at several points in a sample by an energy-dispersive X-ray spectroscope (EDS) equipped with STEM to confirm that the white spot in the image was Pd (not shown the EDS spectra). STEM image analysis was carried out by WinROOf produced by MITANI CORPORATIN and the perimeter of the

white spot was measured, and the circle equivalent diameter was calculated for that perimeter.

S1-3 Results

S1-3-1. XRD pattern and calculated PdO crystal size

Figure S1 showed XRD pattern of AS-, 750 °C, 850 °C, and 950 °C_Pd/Al_2O_3. Diffraction peaks derived from PdO and Al_2O_3 were observed. Triangle marks showed the significant peak of PdO crystal. When the pre-treatment temperature was 750°C, the diffraction peak intensity was almost the same as that of AS, but as the pre-treatment temperature increased beyond 750°C to 850°C and 950°C, the diffraction peak intensity from PdO increased. The diffraction peak at 2θ around 54.9 °was selected for the calculation of PdO crystal size because it has relative higher intensity and less degree of overlap with peaks derived from Al_2O_3. Calculated PdO crystal size was summarized in Table S1.

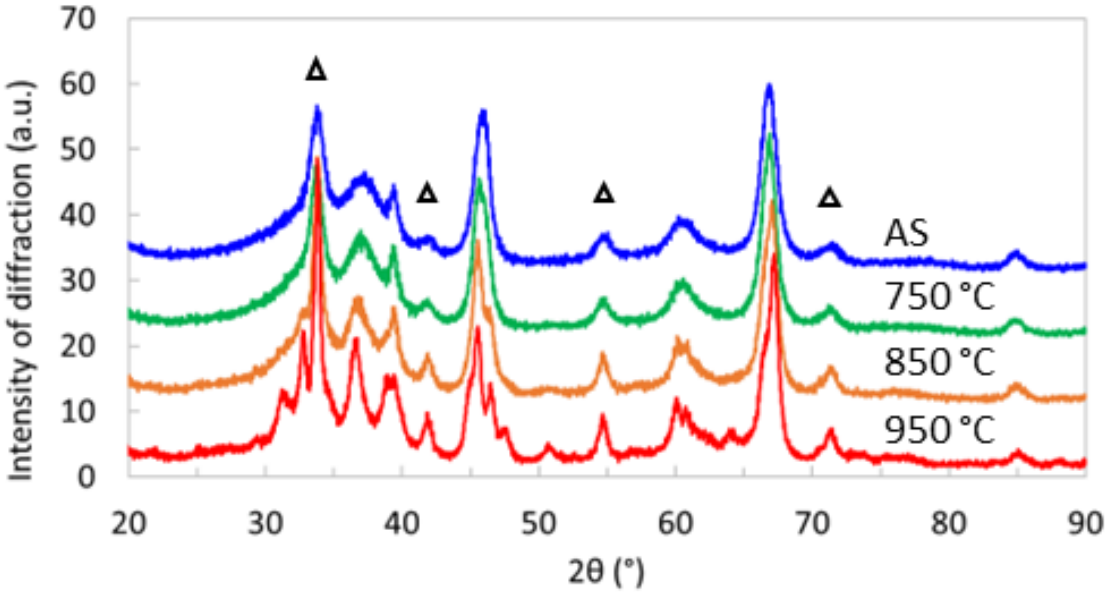

Figure S1. XRD pattern of AS-Pd/Al_2O_3 and pre-treated at 750℃ 850℃ and 950℃ for 10 hours.

Table S1. PdO crystal size calculated from XRD peak.

Sample	2θ (°)	Calculated PdO crystal size (nm)
AS	55.0	6.8
750℃×10h	55.0	6.5
850℃×10h	54.8	10.7
950℃×10h	54.8	14.3

S1-3-2. CO pulse experimental results and calculated Pd crytal size

CO adsorption amount in CO pulse experiment and calculated Pd crystal diameter were summarized in Table S2. Pd content in the sample was necessary to calculate from CO adsorption amount to Pd crystal diameter and 2.87 wt% of Pd which was ICP analysis result

Table S2. Pd crystal size calculated with CO pulse experiment.

Sample	CO adsorption amount (cm3/g)	Calculated Pd crystal diameter (nm)
AS	0.77	8.6
750°C×10h	0.68	9.8
850°C×10h	0.45	15
950°C×10h	0.25	27

on AS-Pd/Al2O3 was used.

S1-3-3. STEM observation and image analysis results

We carried out STEM observation on AS-, 750 °C, 850 °C, and 950 °C_Pd/Al_2O_3 samples to get Pd size distribution through image analysis with WinROOF. Figure S2 showed an example

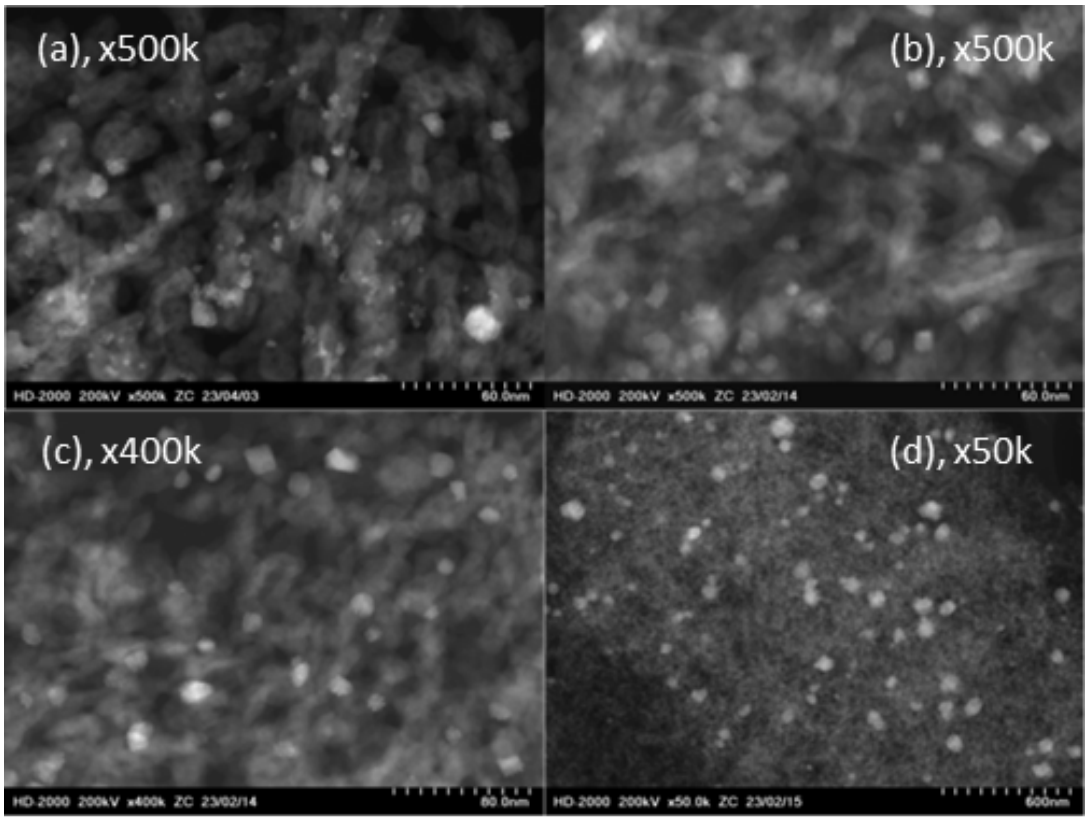

Figure S2. Examples of STEM image on Pd/Al_2O_3 samples. AS (a), 750°C x 10h aged (b), 850°C x 10h aged (c) and 950°C x 10h aged (d).

of STEM image of samples for the image analysis.

Table S3 summarized Pd particle size based on image analysis of STEM observation images (φ_STEM), and Table S4 & Figure S3 showed the particle size distribution.

Table S3. Calculated diameters based on STEM image analysis with WinROOF.

Sample	AS	750C 10h Aged	850C 10h Aged	950C 10h Aged
Average diameter (nm)	6.0	7.5	10.3	50.9
Maximum diameter (nm)	17.1	16.6	135	119
Minimum diameter (nm)	2.4	2.5	3.0	20.6

Table S4. Particle size distribution of Pd based on STEM image analysis by WinROOF.

		Frequency (%)			
Sample		AS	750C 10h Aged	850C 10h Aged	950C 10h Aged
Number of particle for analysis		1335	869	1610	1653
Range (nm)	0-1	0.0%	0.0%	0.0%	0.0%
	1-2	0.0%	0.0%	0.0%	0.0%
	2-3	2.2%	1.0%	0.0%	0.0%
	3-4	16.4%	6.1%	2.4%	0.0%
	4-5	21.7%	10.9%	3.3%	0.0%
	5-6	17.8%	13.7%	4.8%	0.0%
	6-7	15.4%	17.0%	7.2%	0.0%
	7-8	9.4%	12.5%	11.3%	0.0%
	8-9	5.8%	10.0%	12.9%	0.0%
	9-10	4.4%	10.0%	14.8%	0.0%
	10-11	3.7%	6.9%	11.1%	0.0%
	11-12	2.2%	5.4%	10.9%	0.0%
	12-13	0.4%	4.0%	6.7%	0.0%
	13-14	0.4%	1.4%	5.9%	0.0%
	14-15	0.1%	0.6%	3.1%	0.0%
	15-16	0.0%	0.2%	2.4%	0.0%
	16-17	0.0%	0.1%	0.9%	0.0%
	17-18	0.1%	0.0%	0.4%	0.0%
	18-19	0.0%	0.0%	0.1%	0.0%
	19-20	0.0%	0.0%	0.0%	0.0%
	20-21	0.0%	0.0%	0.0%	0.2%
	21-22	0.0%	0.0%	0.0%	0.0%
	22-23	0.0%	0.0%	0.0%	0.1%
	23-24	0.0%	0.0%	0.0%	0.2%
	24-25	0.0%	0.0%	0.0%	0.2%
	25-26	0.0%	0.0%	0.0%	0.5%
	26-27	0.0%	0.0%	0.0%	0.8%
	27-28	0.0%	0.0%	0.0%	0.8%
	28-29	0.0%	0.0%	0.0%	1.1%
	29-30	0.0%	0.0%	0.0%	1.6%
	30-31	0.0%	0.0%	0.0%	2.1%
	31-32	0.0%	0.0%	0.0%	1.6%
	32-33	0.0%	0.0%	0.0%	1.3%
	33-34	0.0%	0.0%	0.0%	1.5%
	34-35	0.0%	0.0%	0.0%	1.4%
	35-36	0.0%	0.0%	0.0%	1.9%
	36-37	0.0%	0.0%	0.0%	2.2%
	37-38	0.0%	0.0%	0.0%	2.4%
	38-39	0.0%	0.0%	0.0%	3.1%
	39-40	0.0%	0.0%	0.0%	2.0%
	40-41	0.0%	0.0%	0.0%	2.8%
	41-42	0.0%	0.0%	0.0%	2.7%
	42-43	0.0%	0.0%	0.0%	2.7%
	43-44	0.0%	0.0%	0.0%	2.3%
	44-45	0.0%	0.0%	0.0%	2.7%
	45-46	0.0%	0.0%	0.1%	3.4%
	46-47	0.0%	0.0%	0.0%	2.7%
	47-48	0.0%	0.0%	0.0%	2.7%
	48-49	0.0%	0.0%	0.0%	2.6%
	49-50	0.0%	0.0%	0.0%	2.2%
	>50	0.0%	0.0%	1.0%	48.3%

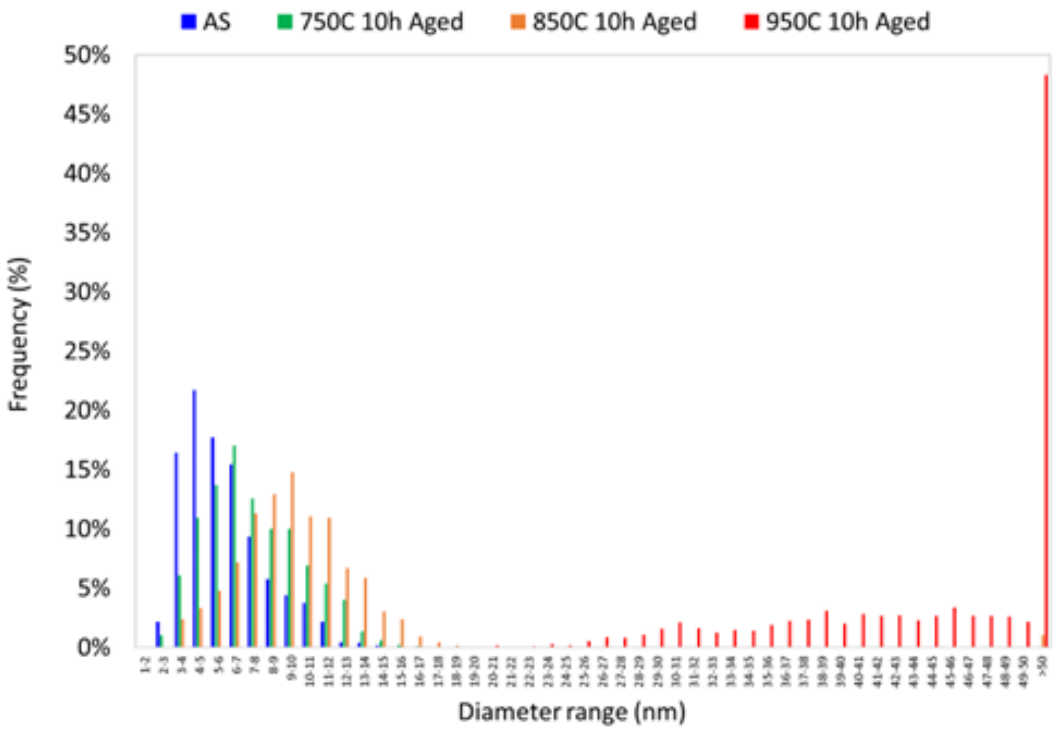

Figure S3. Particle size distribution of Pd based on STEM image analysis by WinROOF.

S 1-3-4. Summary of PdO crystal size & Pd particle size by thermal treatment

Table S5 summarized PdO crystal size calculated by XRD (φ_XRD), Pd crystal size calculated by CO pulse experimental results (φ_CO), and average Pd particle size based on image analysis of STEM observation images (φ_STEM).

Table S5. Summary of the dispersed Pd size.

Pretreament conditions	PdO crytal size (nm)	Pd crystal size (nm)	Pd particle size (nm)
	XRD	CO pulse	STEM_average
(AS)	6.8	9	6
750 °C 10 h	6.5	10	8
850 °C 10 h	10.7	15	10
950 °C 10 h	14.3	27	51

φ_XRD of AS-Pd/Al_2O_3 was 6.8nm and it was almost the same for that of 750 °C_Pd/Al_2O_3 (6.5nm). The growth of φ_XRD was confirmed at 10.7nm in the 850 °C_Pd/Al_2O_3 sample and 14.3nm in the 950 °C_Pd/Al_2O_3 sample. A similar trend was observed in the results of φ_CO and φ_STEM. Raising the pre-treatment temperature up to 950 °C above 850 °C could result in excessive sintering of Pd crystals.

S 1-3-5. Catalytic performance test for CH_4 removal

We carried out the catalytic performance test for CH_4 removal on AS-, 750 °C, 850 °C, and 950 °C_Pd/Al_2O_3 samples to decide pre-treatment temperature not to degrade excessively. Figure S4 showed CH_4 removal focusing at around 270 °C to 390 °C (left) and Pre-treatment temperature effect on CH_4-T20 (right). Pre-treatment at 850 °C showed moderate

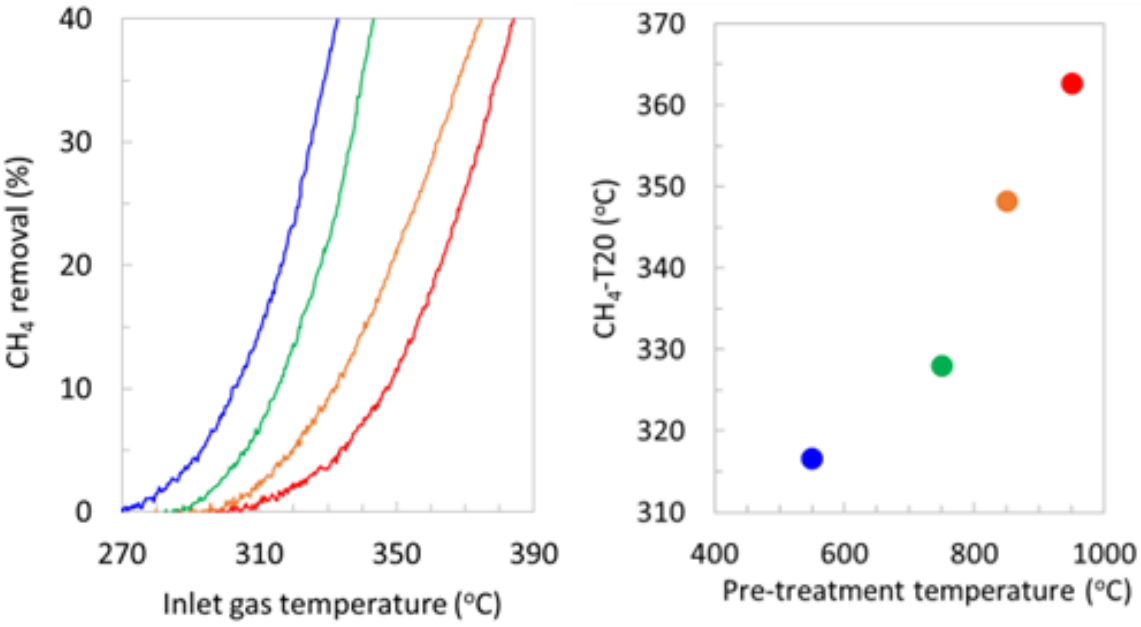

Figure S4. Catalytic performance test results for CH_4 removal (left) and pre-treatment temperature effect on CH_4-T20 (right). Blue: AS-Pd/Al_2O_3, Green: 750 °C x 10h aged, Orange: 850 °C x 10h aged, Red: 950 °C x 10h aged.

degradation effect on CH_4-T20 compared that at 750 °C and 950 °C

S 1-3.6. Conclusion of the preliminary study

Considering the degree of intentional growth of Pd crystals using sintering by pretreatment and its effect on activity, we decided to proceed with this study by applying pre-treatment at 850 °C for 10 h. From the viewpoint of intentional growth of Pd crystals, a temperature beyond 750 °C was appropriate. On the other hand, the effect of pre-treatment temperature on the catalytic performance for CH_4 removal was smaller at lower temperatures in the range investigated, and there was a concern that excessive deactivation may occur at 950 °C. These were reasons to decide 850 °C.

S2. Experimental details of Ni decoration methods

S2-1. Detail experimental information about the CVD method

The chemical vapor deposition (CVD) method was applied using the pyrolysis of $Ni(CO)_4$ to load Ni at the edge of Pd crystals. Figure S5 showed the detailed experimental information about Ni-CVD. It consisted of H_2 reduction of Ni for 20 minutes, H_2 reduction of Pd for 20

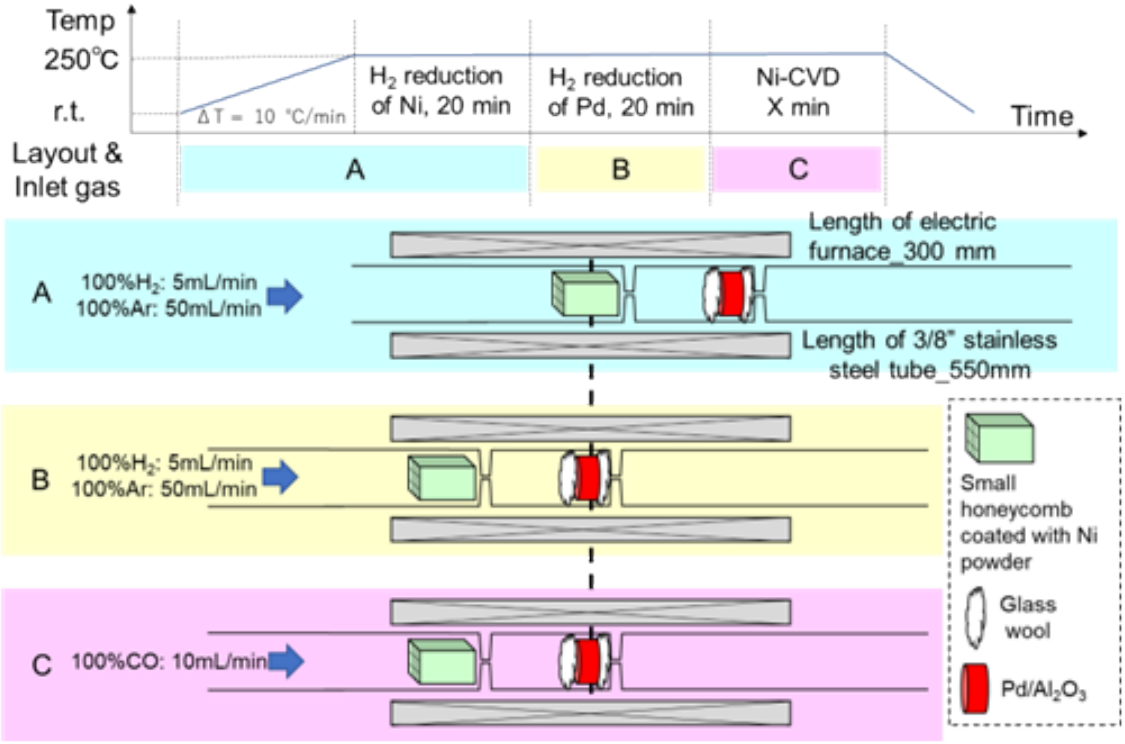

Figure S5. Detail experimental information about Ni-CVD. Temperature program and setting position of 3/8" Stainless steel tube and samples filled in it in relation to electric furnace

minutes and Ni-CVD for the necessary duration.

First, Nickel powder was coated on the small honeycomb substrate. The cordierite honeycomb (NGK, C558, 300 cell 12 mil) was cut into 3 x 3 gas channels with 50 mm length. A 40 wt% Ni dispersed slurry was prepared by mixing 100 g of Nickel powder (<50μm, 99.7% trace metals basis, Sigma-Aldrich) and 150 g of pure water. The small cordierite honeycomb was immersed in the well-stirred Ni-dispersed slurry for 10 seconds, then removed and centrifuged at 1000 rpm for 1 minute. The resulting honeycomb was dried at 180 °C for 1.5 hours. As a result, a honeycomb loaded with 0.03 g of Ni powder per unit was obtained.

A 3/8” stainless steel tube with a total length of 550 mm was used as the sample holder. A recess was made at 315 mm from the inlet side for the stopper and filled with 0.1 g of glass wool, an aliquot of 0.3 g of Pd/Al_2O_3 powder, and 0.1 g of glass wool in that order. The honeycomb coated with Ni powder was then installed, after making another recess for a

stopper at a position 215 mm from the inlet side. The sample-filled holder was placed in a 300 mm long electric furnace (ARF-30KC, Asahi Rika Seisakusyo Corporation), where the hydrogen reduction of Ni, the hydrogen reduction of Pd/Al_2O_3, the generation of $Ni(CO)_4$ and its pyrolysis of it on the Pd/Al_2O_3 powder were sequentially performed.

In hydrogen treatments, the sample-filled holder was first set up so that the Ni-coated honeycomb was positioned in the center of the electric furnace, and the temperature was increased from room temperature to 250 °C at 10 °C /min under a mixed gas flow of 5 mL/min H_2 gas and 50 mL/min Ar gas, and treated at 250 °C for 20 min. Then, the sample holder was moved to position the Pd/Al_2O_3 installation part at the center of the electric furnace for H_2 treatment of the Pd/Al_2O_3 part and treated at 250°C for 20 minutes in the same manner.

After the completion of the preliminary hydrogen treatments, the feed gas was changed to CO at 10 mL/min while the temperature of the Pd/Al_2O_3 powder part was maintained at 250°C. It was reported that Nickel reacts with carbon monoxide to form nickel carbonyl gas, $Ni(CO)_4$, at around 50-80 °C.[18-19] Temperature is an important experimental parameter in Ni-CVD and details temperature distribution at the outer surface of the 3/8" stainless steel tube was shown in Figure S6. The temperature of the Ni powder-coated honeycomb part was around 55-170 °C based on it. The pyrolysis treatment of $Ni(CO)_4$ was conducted for 1h,

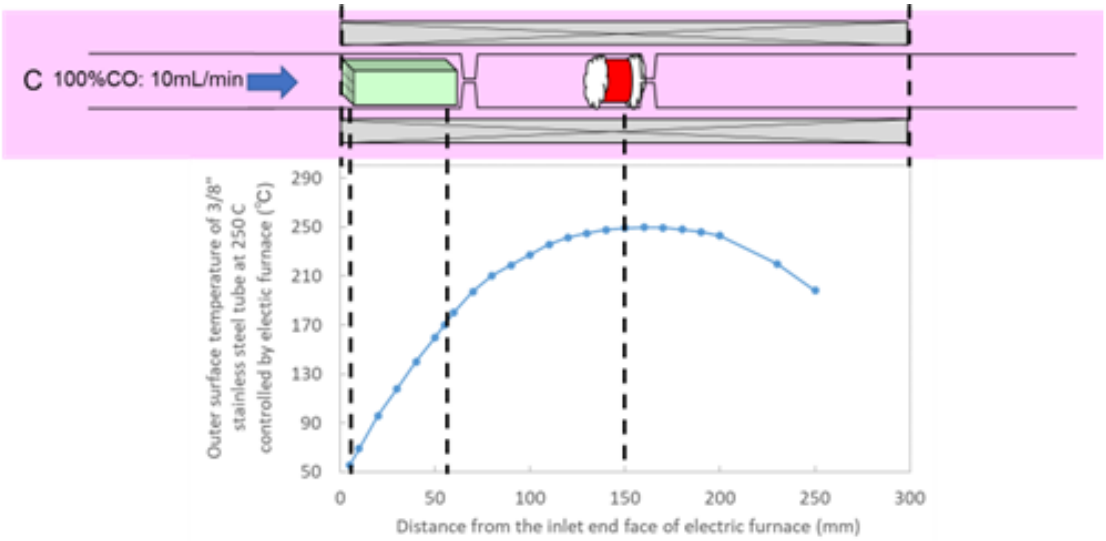

Figure S6. Measurement result of the outer surface temperature of 3/8" stainless steel tube during Ni-CVD at 250 ℃ which was controlled by electric furnace.

6h, 20h, and 100h, respectively.

After the $Ni(CO)_4$ pyrolysis, the feed gas was changed to Ar gas at 50 mL/min, the temperature was lowered to room temperature, and the sample holder was removed from the treatment line. The stainless-steel tube was then cut and Ni decorated Pd/Al_2O_3

(Ni@Pd/ Al_2O_3) powder was recovered and used for subsequent the catalytic performance test for CH_4 removal and various characterizations. The resulting sample was labeled *X*_Ni@Pd/Al_2O_3 (*X* = 1, 6, 20, and 100) based on the duration of thermal decomposition hereafter.

The experimental procedure of Ni-CVD was performed for AS-Pd/Al_2O_3 as same as for Pd/Al_2O_3 described above. The resulting sample was labeled X_Ni@AS-Pd/Al_2O_3, X means the Ni-CVD duration time, hereafter.

S2-2. Detail experimental information about Wet impregnation (WI) method

10 wt% aqueous solution of Nickel (II) Acetate (NiAc) Tetrahydrate ($Ni(CH_3COO)_2 \cdot 4H_2O$: NiAc, KANTO CHEMICAL Co. Inc.) solution was prepared with De-Ionized Water (DIW). The NiAc aqueous solution was mixed with an aliquot of 0.3 g of Pd/Al_2O_3 powder to the desired amount of Ni. The mixture was dried overnight at 80 °C and calcined in an electric furnace at 550 °C for 1 hour.

S3. Experimental details of characterizations

Pd and Ni content in each sample were quantified by inductively coupled plasma atomic emission spectrometry (ICP-AES) with ICPS-8100 made by SHIMADZU CORPORATION. At first, sulfuric acid and Nitric acid was mixed in a conical beaker, and $Ni@Pd/Al_2O_3$ powder was added into the mixed acid solution and heated up to 300 °C for the thermal decomposition. After the pyrolysis, the liquid solution was used for Ni quantification. For Pd quantification, the solid obtained by cooling after the pyrolysis was dissolved in hydrochloric acid, a co-precipitant tellurium (Te) was added, and Pd was precipitated with a reducing agent such as tin chloride ($SnCl_2$), thereby Pd was separated and recovered. The separated and recovered Pd was dissolved in hydrochloric acid and used for quantitative determination by ICP.

S4. The other Supplemental figures

Table S6 summarized Pd nanocrystal size of Pd/Al_2O_3 and *X*_Ni@Pd/Al_2O_3 (*X* = 1, 6, 20, and 100). XRD diffraction patters were shown in Figure 1*b* of the manuscript.

Table S6. Pd nanocrystal size before and after Ni-CVD treatment

Pretreament conditions	Duration of Ni-CVD	Observed diffraction peak of Pd	2θ, selected for the crystal size calculation	Pd crystal size (nm)
850 °C 10 h	none	PdO	54.8	11
850 °C 10 h	1 h	Pd metal	82	14
850 °C 10 h	6 h	Pd metal	82	13
850 °C 10 h	20 h	Pd metal	82	11
850 °C 10 h	100 h	Pd metal	82	12

Figure S7 showed STEM image (a), and EDS mapping of Pd (b) and Ni (c) in WI at 17400 wtppm Ni sample. Figure S5d showed Pd and Ni overlay mapping and Ni was located on

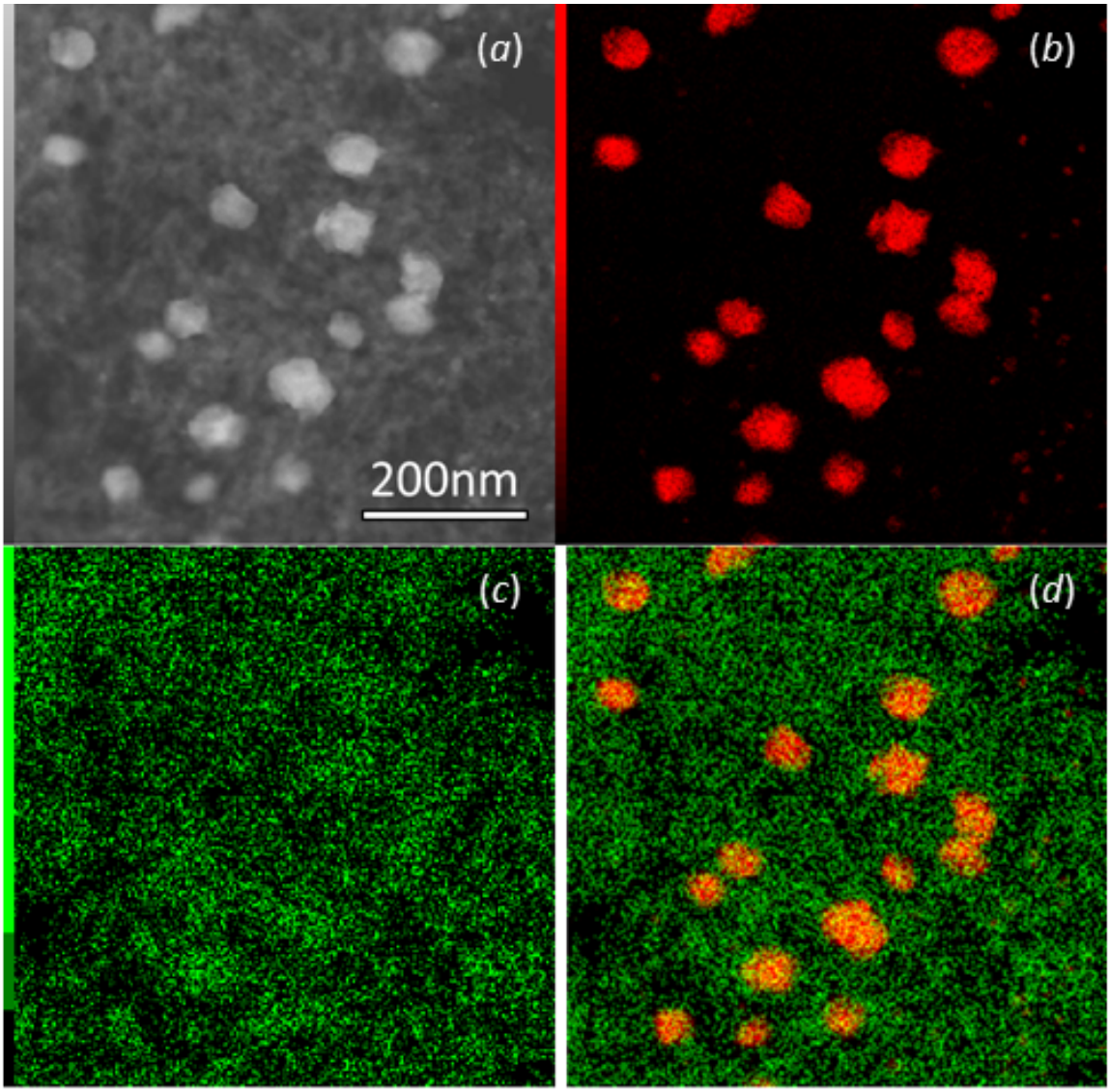

Figure S7. STEM-EDS results of WI at 17400 wt ppm Ni sample. STEM image (*a*), EDS mapping of Pd (*b*), EDS mapping of Ni (*c*) and Pd and Ni overlay mapping (*d*).

both Pd crystal and the other place which was Al_2O_3 support material.

Figure S8 showed STEM image (a), and EDS mapping of Pd (b) and Ni (c) in WI at 1300 wtppm Ni sample. Figure S6d showed Pd and Ni overlay mapping and Ni was located on both Pd crystal and the other place which was Al_2O_3 support material as same as WI-H

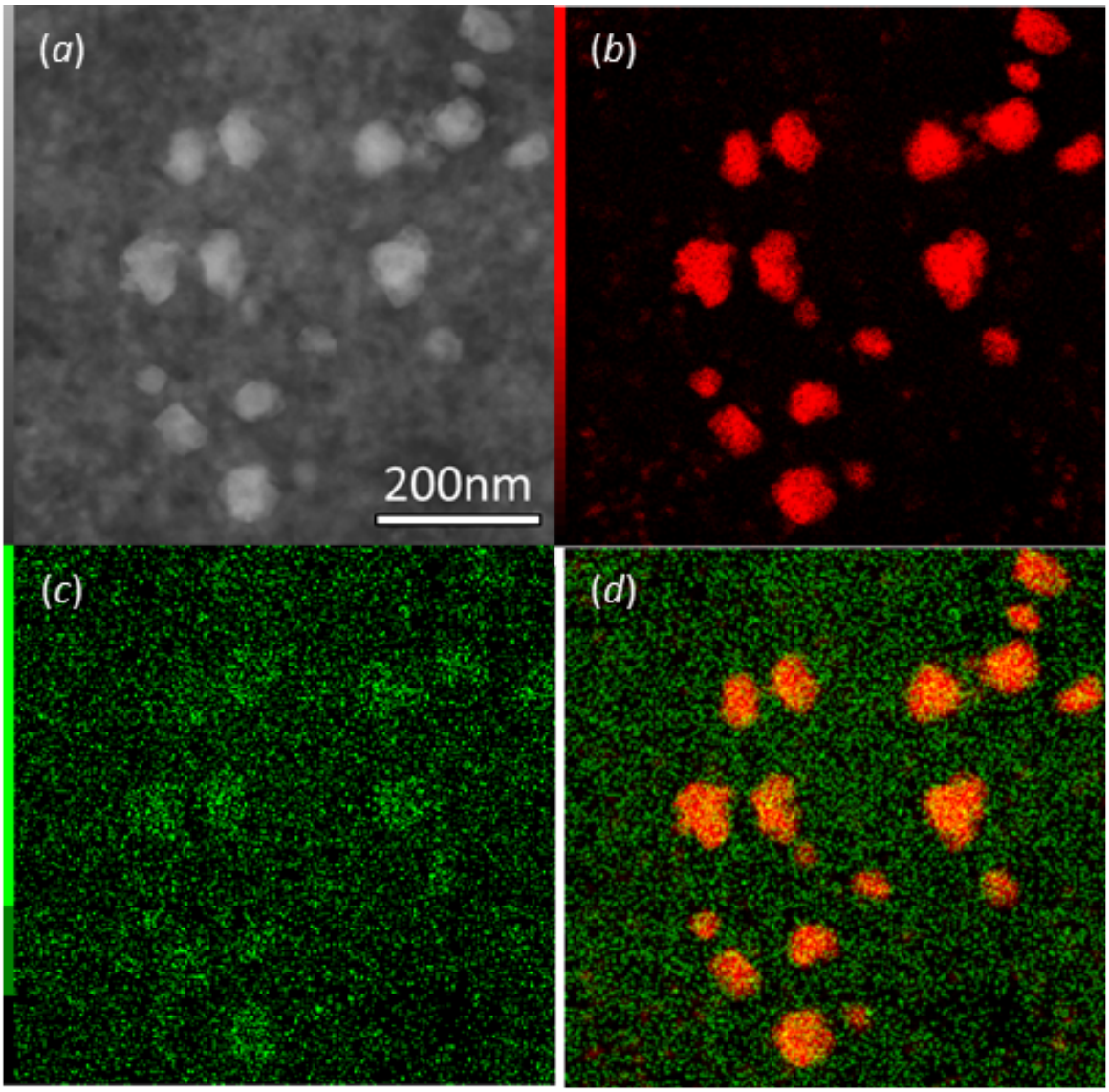

Figure S8. STEM-EDS results of WI at 1300 wt ppm Ni sample. STEM image (*a*), EDS mapping of Pd (*b*), EDS mapping of Ni (*c*) and Pd and Ni overlay mapping (*d*).

sample shown in Figure S5.

Figure S9 showed STEM image (a), and EDS mapping of Al (b), Ni(c) and Pd (d) in 20_Ni@Pd/Al_2O_3 sample. The existence of Pd was confirmed on Al_2O_3 support material. However, the intensity of Ni was too low to be detectable because Ni content was 110 ppm

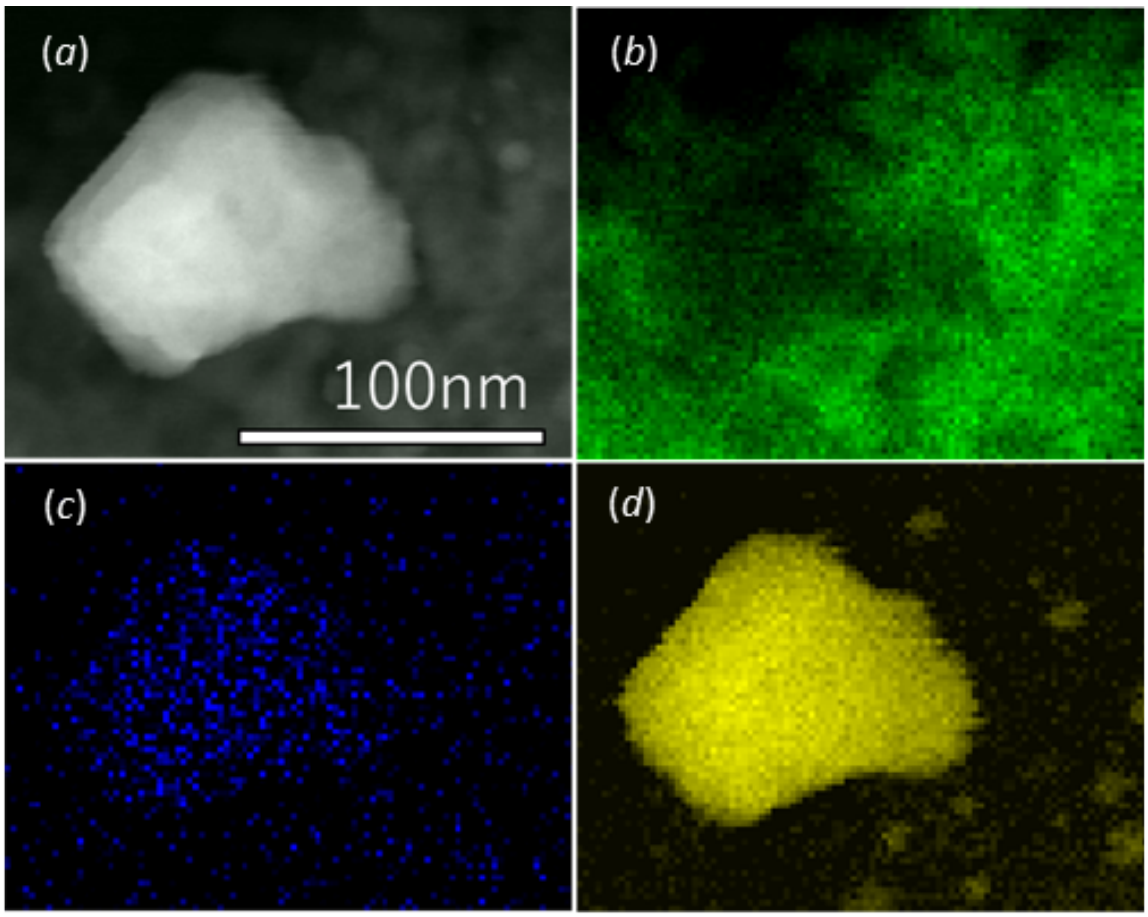

Figure S9. STEM-EDS results of 20_Ni@Pd/Al_2O_3 sample. STEM image (*a*), EDS mapping of Al (*b*), EDS mapping of Ni (*c*) and EDS mapping of Pd (*d*).

reported in Figure 2a.

Figure S10 showed STEM image (a), and EDS mapping of Al (b), Ni (c) and Pd (d) in 6_Ni@Pd/Al_2O_3 sample. Pd and Ni distribution was like 20_Ni@Pd/Al_2O_3 sample shown in Figure S7. The existence of Pd was confirmed on Al_2O_3 support material. However, the intensity of Ni was too low to be detectable because Ni content was 150 ppm reported in Figure 2a.

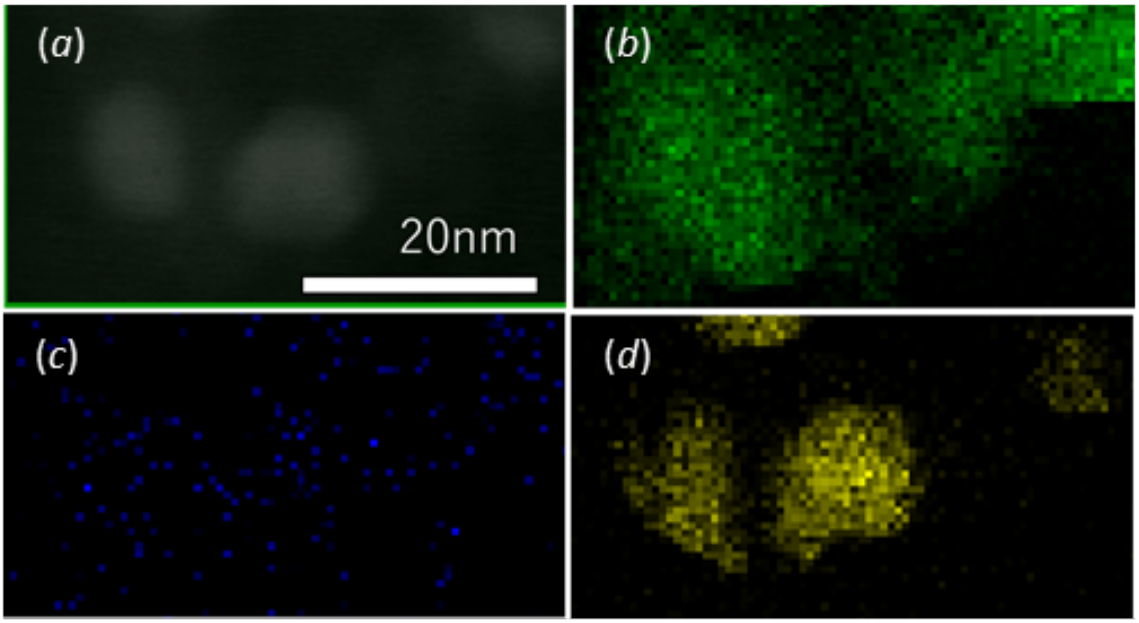

Figure S10. STEM-EDS results of 6_Ni@Pd/Al_2O_3 sample. STEM image (*a*), EDS mapping of Al (*b*), EDS mapping of Ni (*c*) and EDS mapping of Pd (*d*).

Figure S11 showed STEM-EDS results of 100_Ni@AS-Pd/Al_2O_3 sample at low magnification. STEM image (*a*), EDS mapping of Oxygen (*b*), Aluminum (*c*), Pd (*d*) and Nickel (*e*). Nickel was detected only from on and around Pd particles, not detected from on Al_2O_3.

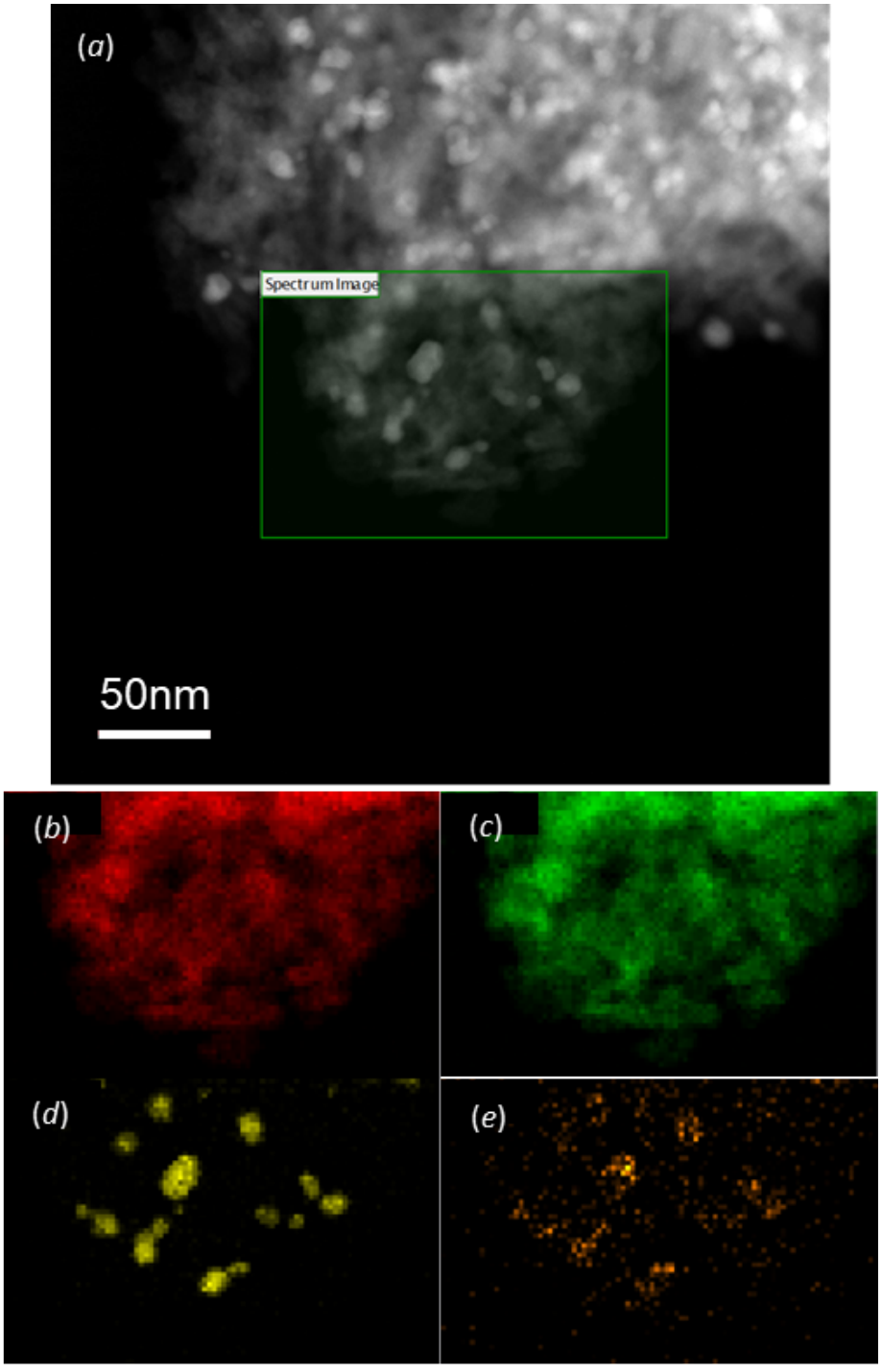

Figure S11. STEM image at low magnification of Ni-decorated Pd nanocrystals in 100_Ni@AS-Pd/Al_2O_3 (*a*) and EDS mapping images of Oxygen (b), Aluminum (c), Pd (*d*), and Ni (*e*).

Figure S12 showed STEM-EDS results of 100_Ni@AS-Pd/Al_2O_3 sample at high magnification. STEM image (*a*), a morphological model of Pd nanocrystal (*b*), and EDS mapping images of the same Pd nanocrystals for the elemental distribution of Ni (c) and Pd (*d*). Nickel was decorated near the edges of the polyhedral palladium nanocrystals, which resembled

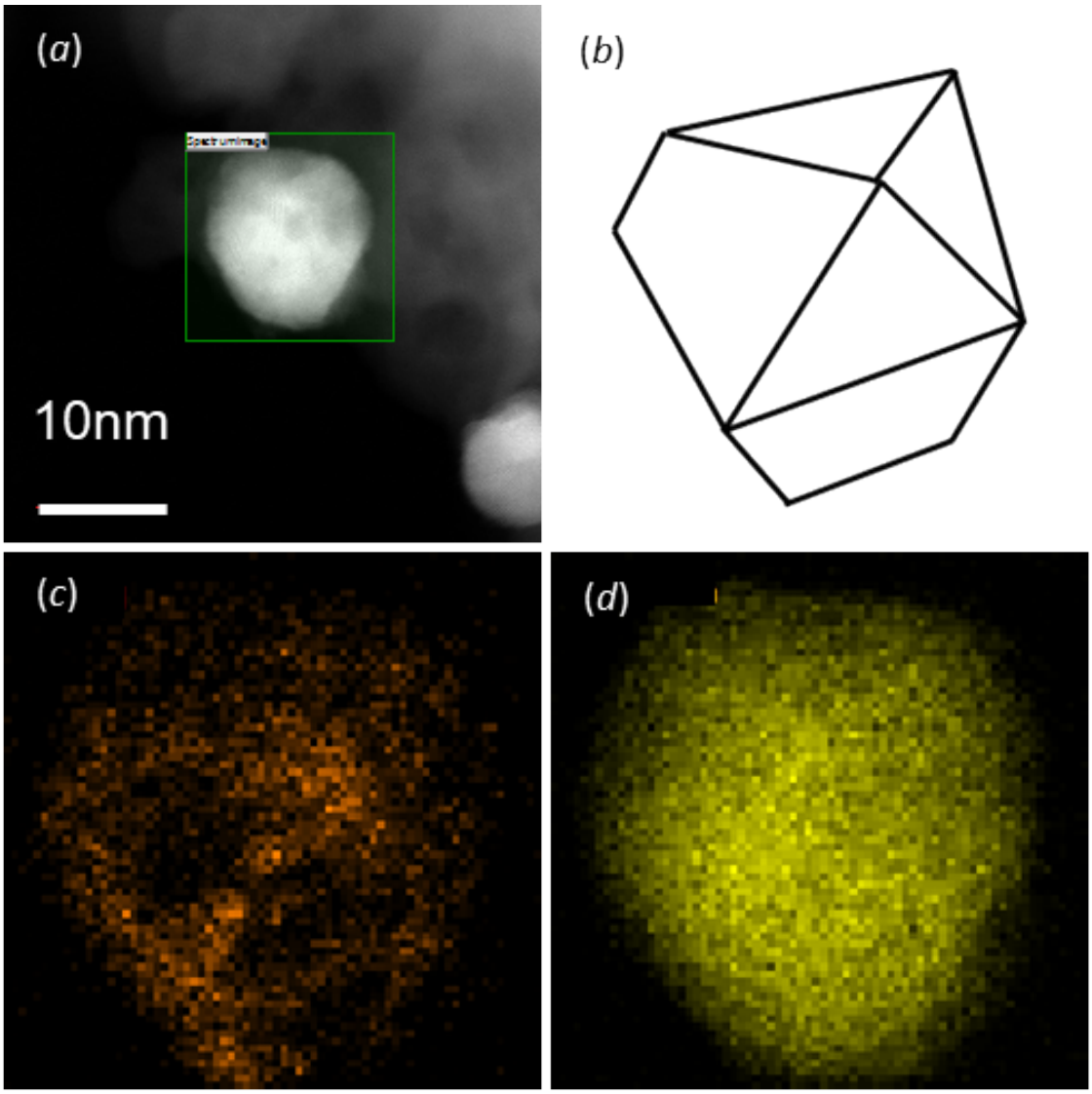

Figure S12. STEM image at high magnification of Ni-decorated Pd nanocrystals in 100_Ni@AS-Pd/Al_2O_3 (*a*) and its morphological model (*b*). EDS mapping images of the same Pd nanocrystal as (*a*) for the elemental distributions of Ni (*c*) and Pd (*d*).

octahedrons.

Table S7 summarized Pd and Ni content, CH_4-T20 of AS-Pd/Al_2O_3 samples with Ni decoration by both WI and Ni-CVD. There were 2 lots of "AS-Pd/Al_2O_3" in this study. The target Pd loading amount was 3wt% for both lots. Lot A resulted in 2.87 wt% of Pd and Lot B in 2.69wt% quantified by ICP. CH4 removal efficiency depends on Pd content. Lot A and B had an 8.4 ℃ difference in CH_4-T20. For the consideration of the effect of site-targeted decoration on AS-Pd/Al_2O_3, we calculated the temperature decrease of CH_4-T20 from AS-Pd/Al_2O_3 without Ni decoration in each lot and compared the effect between different decoration method, CVD and WI. The reduction of CH_4-T20 by Ni decoration was similar for Ni-CVD and WI, but the amount of Ni required was about 1/10 of that for CVD compared to WI.

Table S7. Comparison of Pd & Ni content and CH_4-T20 of AS-Pd/Al_2O_3 with Ni decoration by both WI and Ni-CVD

Sample	Content		CH_4-T20	Temperature decrese of CH_4-T20 from AS-Pd/Al_2O_3 without Ni decoration
	Pd	Ni		
	wt%	wtppm	℃	℃
AS-Pd/Al_2O_3_Lot A	2.87	—	316.2	0.0
0.32% Ni decorated by WI on AS-Pd/Al_2O_3_Lot A	—	3150	314.4	-1.7
1.23% Ni decorated by WI on AS-Pd/Al_2O_3_Lot A	—	12290	314.6	-1.6
5.07% Ni decorated by WI on AS-Pd/Al_2O_3_Lot A	—	50690	316.7	0.5
AS-Pd/Al_2O_3_Lot B	2.69	—	324.6	0.0
1_Ni@AS-Pd/Al_2O_3_Lot B	—	40	322.4	-2.2
100_Ni@AS-Pd/Al_2O_3_Lot B	—	290	322.8	-1.9

Figure S13 showed Ni content dependence of the temperature decrease of CH_4-T20 from AS-Pd/Al_2O_3 without Ni decoration. The reduction of CH_4-T20 by Ni decoration was similar for Ni-CVD and WI, but the amount of Ni required was about 1/10 of that for CVD compared

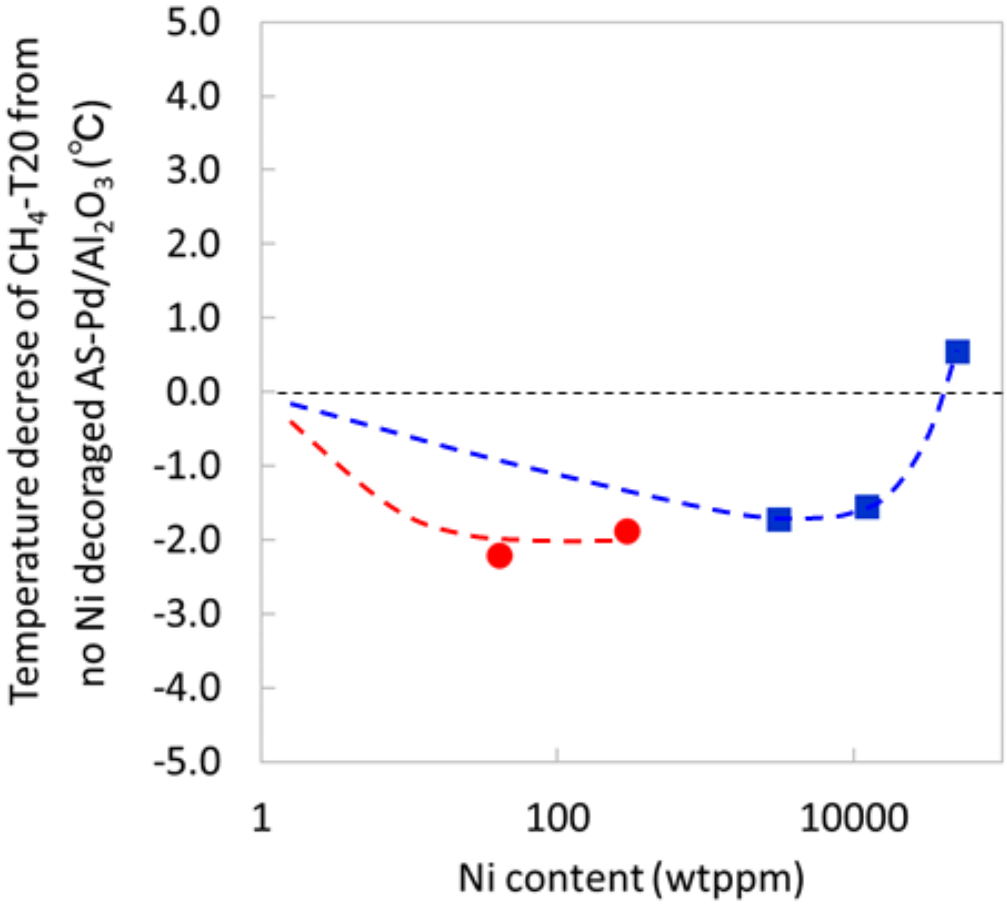

Figure S13. Temperature decrease of CH_4-T20 from AS-Pd/Al_2O_3 without Ni decoration. Black dash line correspond the CH_4-T20 of AS-Pd/Al_2O_3 without Ni decoration, Red plot and dash line correspond to Ni@AS-Pd/Al_2O_3, blue plot and dash line correspond to AS-Pd/Al_2O_3 with Ni decoration by Wet impregnation.

to WI.