

Supplementary Information

Carbon doping of Ceria-supported Palladium for low-temperature oxidation of methane

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Table S1. CO adsorption result of AS-Pd/CeO₂.

CO adsorption amount [cm ³ /g]	Pd particle size [nm]
5.29	1.3

CO adsorption measurement was conducted in a CO pulse chemisorption method with Catalyst Analyzer BELCAT II made by Microtrac BEL Corp.

An aliquot of 0.3347 g of AS-Pd/CeO₂ 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 % H₂ at 150 mL/min, then pre-treated for 10 min. Then 100 % H₂ was changed to 100 % He at 400 °C, kept 10 min, then cooled to 50 °C.

After the pretreatment, 0.935 cm³/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 particle size was calculated from the amount of CO chemisorption by the calculation equation reported in the literature [1-2].

- 1) C. N. Costa, S. Y. Christou, G. Georgiou, A. M. Efstathiou, *J. Catal.*, 219 (2003) 259.
- 2) J.J.F. Scholten, A.P. Pijpers, A.M.L. Hustings, *Catal. Rev.-Sci. Eng.*, 27 (1) (1985), p. 151.

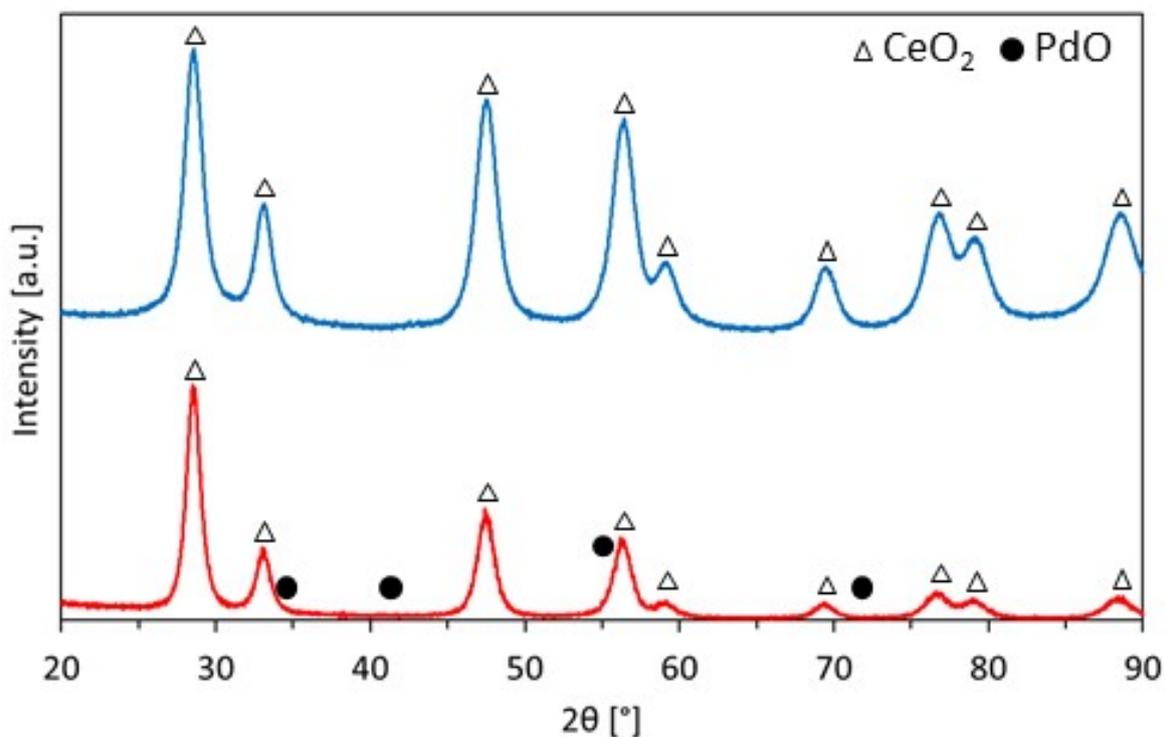


Figure S1. XRD pattern of CeO_2 and AS-Pd/ CeO_2 .

CeO_2 and AS-Pd/ CeO_2 were characterized by XRD with D8 ADVANCE made by BRUKER and diffraction patterns were shown in Figure S1.

Diffraction peaks originating from Cerium (IV) Oxide were confirmed in both CeO_2 and AS-Pd/ CeO_2 but there was no peak relating to Pd, for example, PdO in AS-Pd/ CeO_2 . We speculated the reason Pd was highly dispersed on CeO_2 and could not be likely to form Pd and/or PdO crystal but amorphous. This speculation is consistent with the characterization results of CO chemisorption shown in Table S1 and STEM-EDS shown in Figure S2.

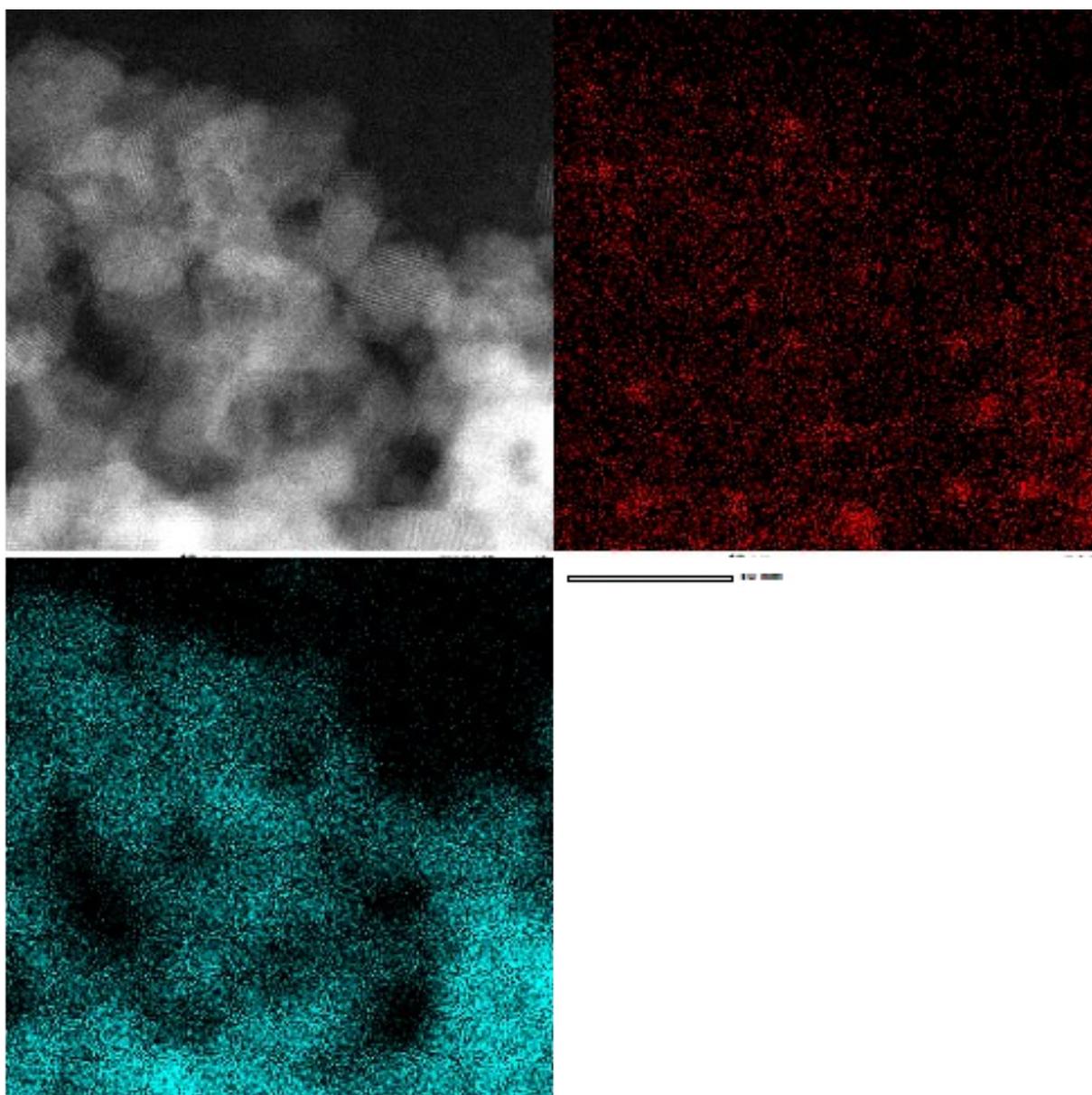


Figure S2. STEM image of AS-Pd/CeO₂.
(a) STEM image, (b) EDS mapping of Palladium, (c) EDS mapping of Cerium.

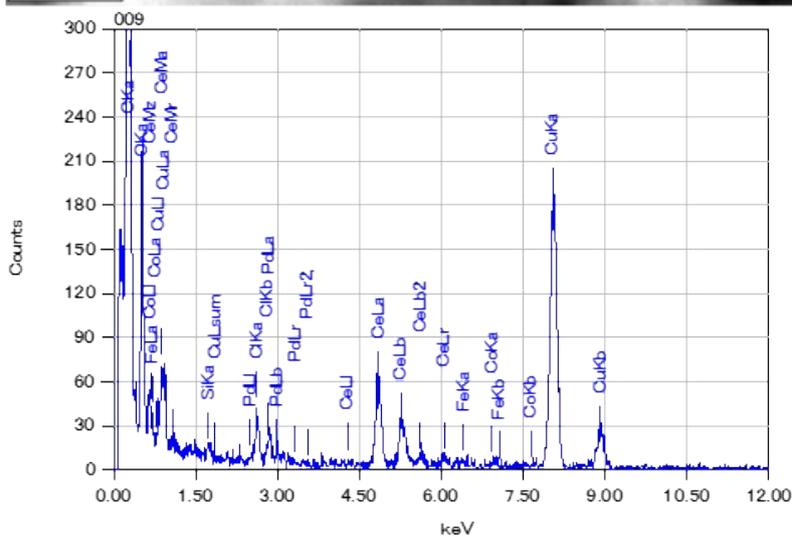
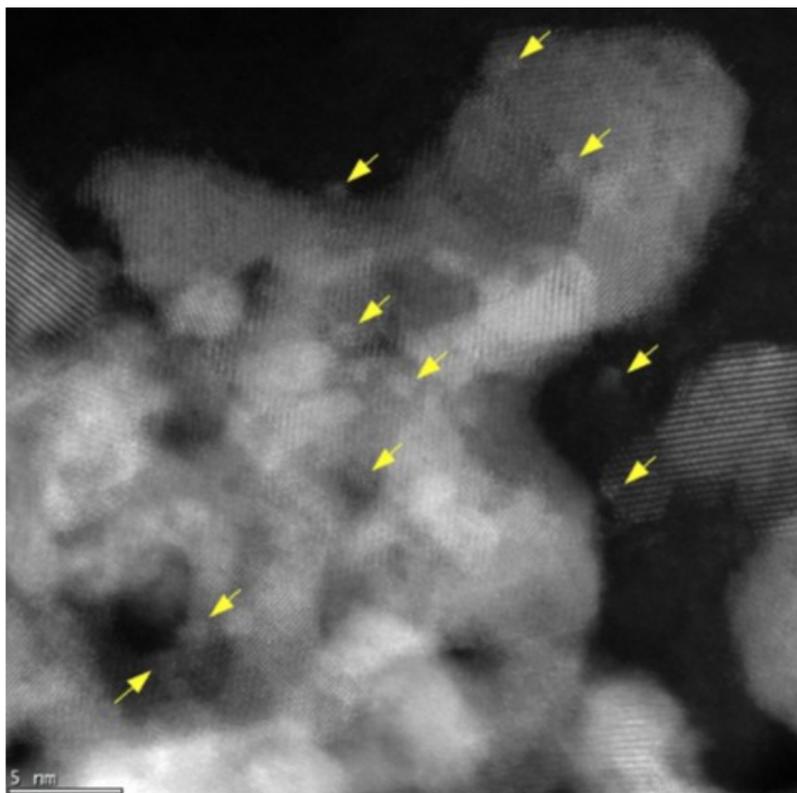


Figure S3. STEM image and EDS of AS-Pd/CeO₂. (a) STEM image, (b) EDS spectrum of #1 shown in (a), observed by JEM-ARM200F, accelerated electron volt 200 kV

Points indicated with yellow arrows are Pd particles confirmed by EDS. Pd was highly dispersed on CeO₂ and particle size was less than 1 nm. The size was consistent with the Pd particle size calculated by CO adsorption measurement.

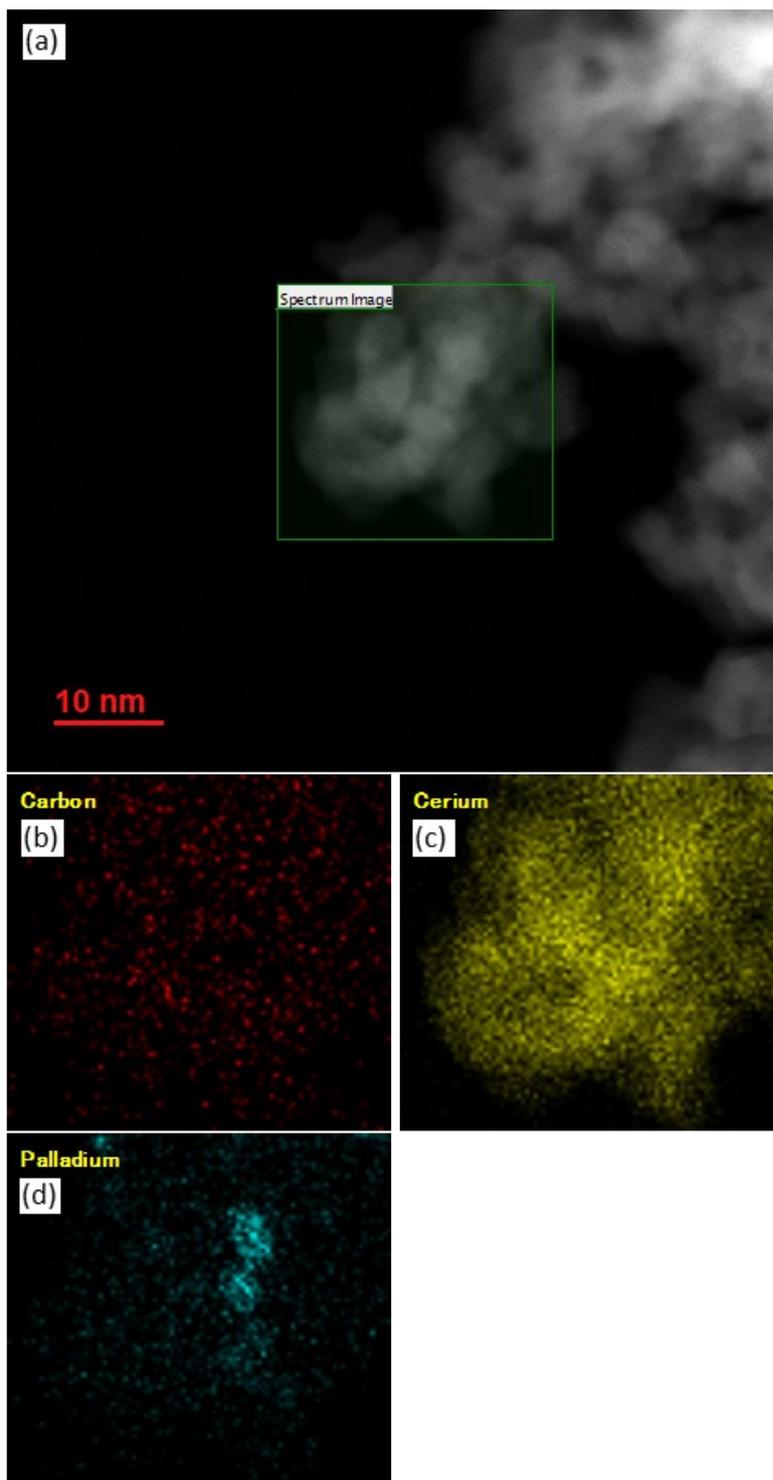


Figure S4. STEM-EDS of ST-Pd/CeO₂.
(a) STEM image, EDS mapping of (b) Carbon, (c) Cerium, and
(d) Palladium.

No Carbon above background levels was detected.

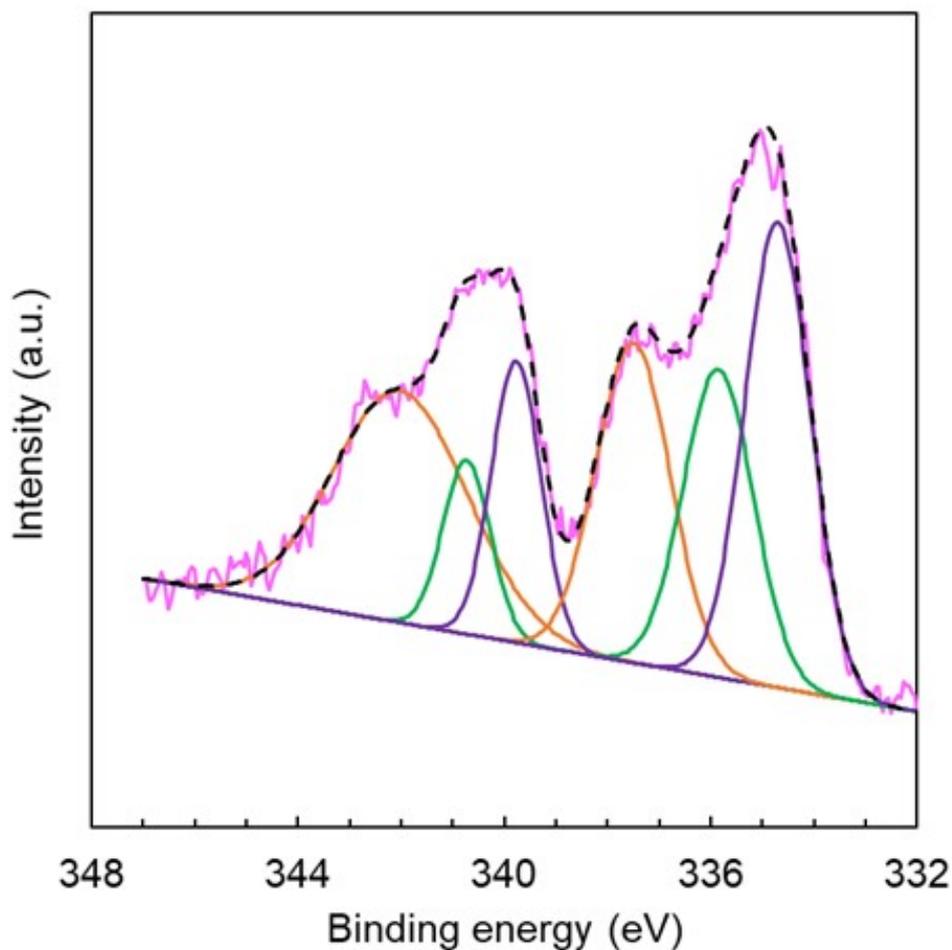


Figure S5. Pd 3d XPS spectra of ST-Pd/CeO₂.

The pink curve is XPS measurement results. Each of the Pd 3d_{5/2} and Pd 3d_{3/2} emission peaks were deconvoluted into multiple peaks. The deconvoluted Pd 3d_{5/2} peaks for ST-Pd/CeO₂ at 337.5 eV, 335.9 eV, and 334.7 eV were assigned to PdO_y, Palladium carbides (PdC_x), and Pd metal, respectively, similar to LT-Pd/CeO₂ as shown in Fig. 2. Violet: the deconvoluted peak of Pd metal, Green: the deconvoluted peak of PdC_x, Orange: the deconvoluted PdO_y. The broken curve is the sum of deconvoluted peaks of Pd metal, PdC_x, and PdO_y.

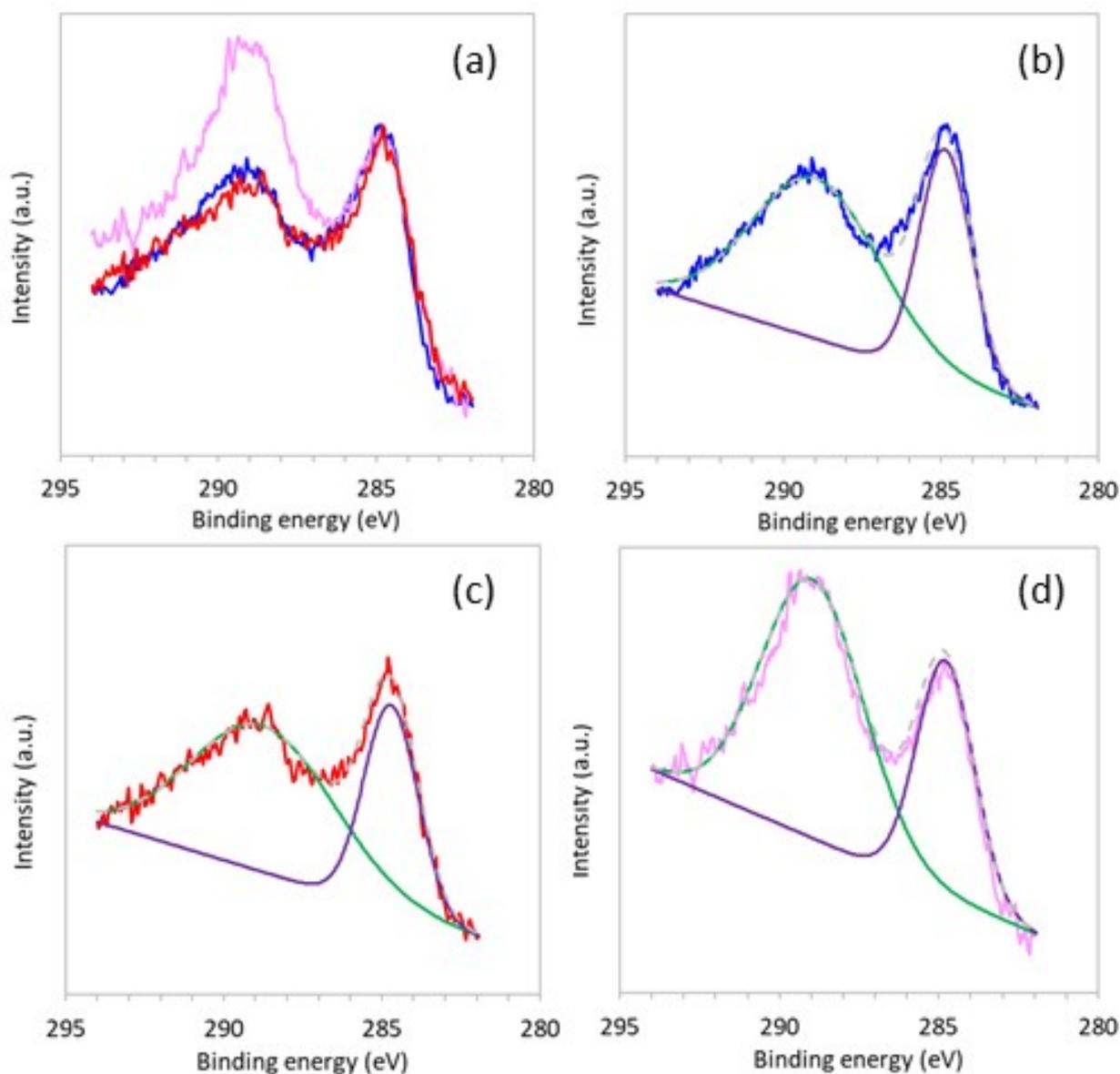


Figure S6. Carbon 1s XPS spectra of AS-, LT- and ST-Pd/ CeO₂ (a), Curve-fitted spectra of AS-Pd/CeO₂ (b), LT-Pd/CeO₂ (c), and ST-Pd/CeO₂ (d).

Blue: AS-Pd/CeO₂, Red: LT-Pd/CeO₂, Pink: ST-Pd/CeO₂. Green and Violet lines were deconvoluted spectra and the gray dash line was the sum of deconvoluted lines.

Table S2. Deconvoluted peak area analysis for Carbon 1s.

Sample	Assigned as O-C=O		Assigned as C=C, C-C		Area ratio "O-C=O" / "C=C, C-C"
	Binding energy (eV)	Area	Binding energy (eV)	Area	
AS-Pd/CeO ₂	289.0	58.5	284.9	35.0	1.67
LT-Pd/CeO ₂	288.8	58.6	284.7	31.4	1.87
ST-Pd/CeO ₂	289.0	75.0	284.8	38.2	1.96

High-resolution XPS C 1s spectra are shown in Figure S5-(a). Each spectrum had two peaks, one was at around 289 eV and the other was at around 285 eV. Concerning the previous literature relating to Graphene oxides (GO) and Carboxylated-Graphene studied by Alex *et al.* [*ACS Nano* 2017, 11, 1789-1797], the former peak was assigned as carboxylic carbons (labeled O-C=O), and the latter peak was assigned as *sp*² carbon C=C and/or *sp* carbon C-C (labeled C=C, C-C). Deconvoluted peaks in each spectrum were shown in SI figure 5-(b) AS-Pd/CeO₂, (c) LT-Pd/CeO₂, and (d) ST-Pd/CeO₂, respectively. Deconvoluted peak areas were summarized in SI Table 2. The peak area ratio of "O-C=O"/"C=C, C-C" increased from 1.67 in AS-Pd/CeO₂ to 1.87 in LT-Pd/CeO₂ and 1.96 in ST-Pd/CeO₂. When the increase of O-C=O was considered in combination with the increase of PdC_x, Pd nanoparticles would interact with Carbon in O-C=O. From these considerations, we interpreted that oxo-carbon species might also present on and/or next to Pd nanoparticles and it might be increased by the Carbon doping.

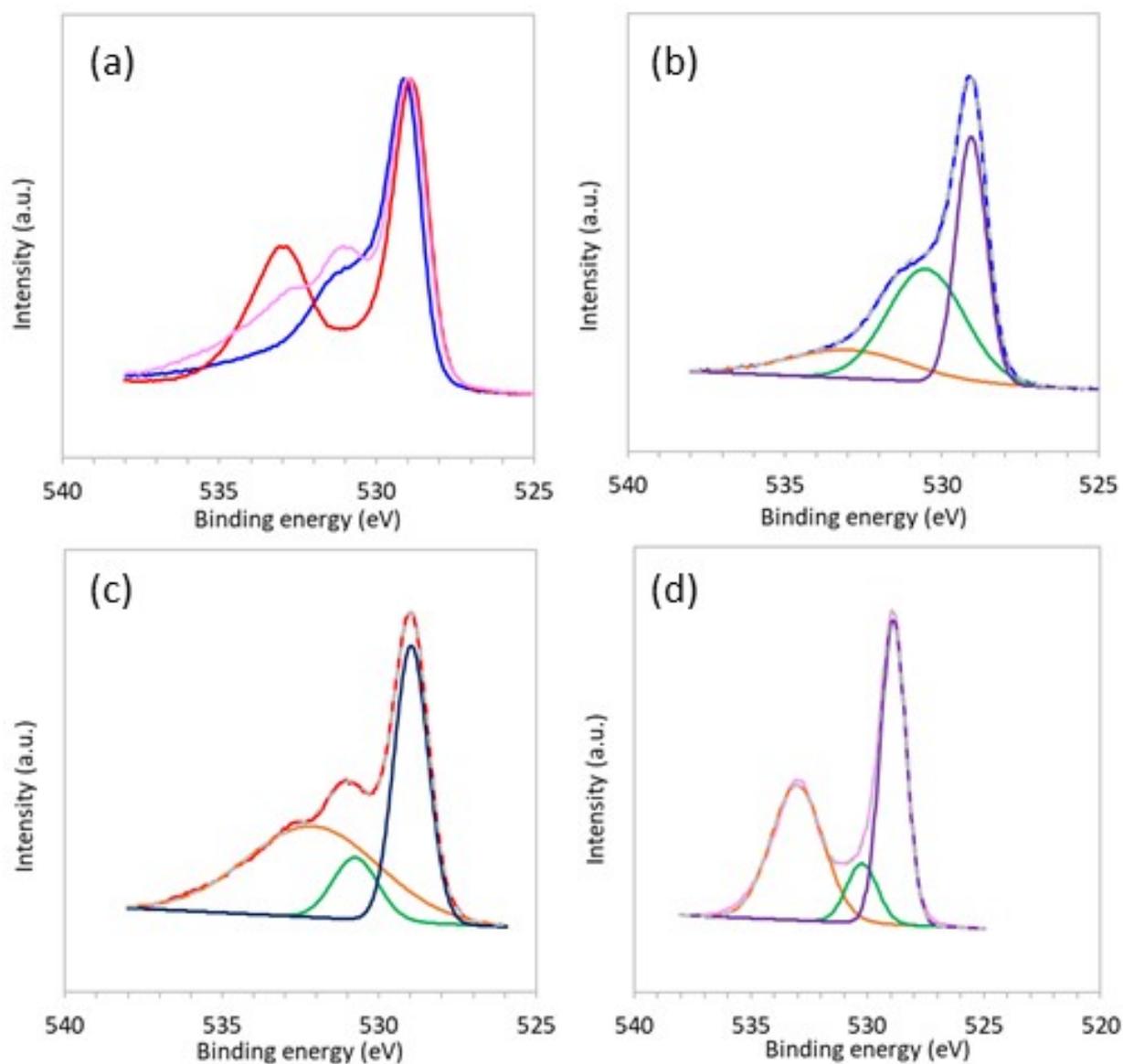


Figure S7. Oxygen 1s XPS spectra of AS-, LT- and ST-Pd/CeO₂ (a), Curve-fitted spectra of AS-Pd/CeO₂ (b), LT-Pd/CeO₂ (c), and ST-Pd/CeO₂ (d).

Blue: AS-Pd/CeO₂, Red: LT-Pd/CeO₂, Pink: ST-Pd/CeO₂. Orange, green and Violet lines were deconvoluted spectra and the gray dash line was the sum of deconvoluted lines.

Table S3. Deconvoluted peak area analysis for Oxygen 1s.

Sample	Assigned as -COOH		Assigned as PdO		Assigned as CeO ₂		Area ratio "-COOH" / "CeO ₂ "	Area ratio "PdO" / "CeO ₂ "
	Binding energy (eV)	Area	Binding energy (eV)	Area	Binding energy (eV)	Area		
AS-Pd/CeO ₂	533.0	8.7	530.5	22.0	529.1	19.3	0.45	1.13
LT-Pd/CeO ₂	532.1	30.4	530.8	7.1	529.0	23.9	1.27	0.30
ST-Pd/CeO ₂	533.0	23.7	530.2	6.2	528.9	26.4	0.90	0.24

High-resolution XPS O 1s spectra were shown in Figure S6-(a), and each spectrum had three peaks at around 532.8 eV, 530.5 eV, and 529 eV.

The peak at around 532.8 eV was assigned as Oxygen in the carboxyl group interacted with Palladium referred to the previous literature studied by Aas N., Bowker M. et. Al. [*J. Chem. Soc. Faraday Trans.* 89, 1249 (1993)]. The peak at around 530.5 eV was assigned as Oxygen in PdO referring to the previous literature studied by Militello M.C. et. Al. [*Surf. Sci. Spectra* 3, 395 (1994)]. The peak at around 529 eV was assigned as Oxygen in CeO₂ referring to the previous literature studied by Paparazzo E. et al. [*Surf. Sci.* 234, L253 (1990)].

Deconvoluted peaks in each spectrum were shown in SI figure 6-(b) AS-Pd/CeO₂, (c) LT-Pd/CeO₂, and (d) ST-Pd/CeO₂, respectively. Deconvoluted peak areas were summarized in Table S3. The peak area ratio of "PdO" / "CeO₂" decreased from 1.13 in AS-Pd/CeO₂ to 0.30 in LT-Pd/CeO₂ and 0.24 in ST-Pd/CeO₂. It was reasonable because of atmosphere treatment under CH₄-rich gas conditions. The peak area ratio of "-COOH" / "CeO₂" increased from 0.45 in AS-Pd/CeO₂ to 1.27 in LT-Pd/CeO₂ and 0.90 in ST-Pd/CeO₂. The increase of "-COOH" was consistent with the increase of "O-C=O" in Carbon 1s.

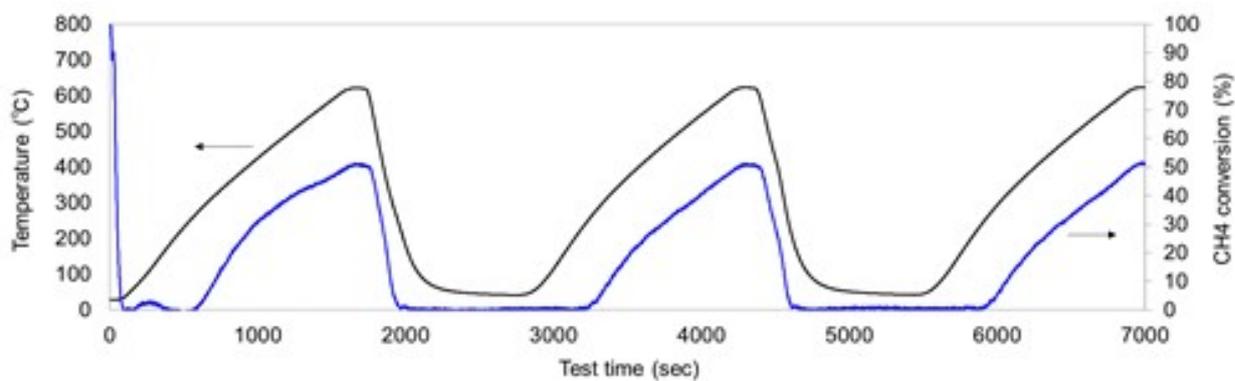


Figure S8. Example of the consecutive CH₄ L/O test under the simulated lean-burn exhaust, in the case of AS-Pd/CeO₂.

AS-Pd/CeO₂ and LT-Pd/CeO₂ were evaluated under lean inlet gas conditions in the consecutive CH₄ L/O test. Test results of 1st and 2nd L/O were shown in Fig. 4c.

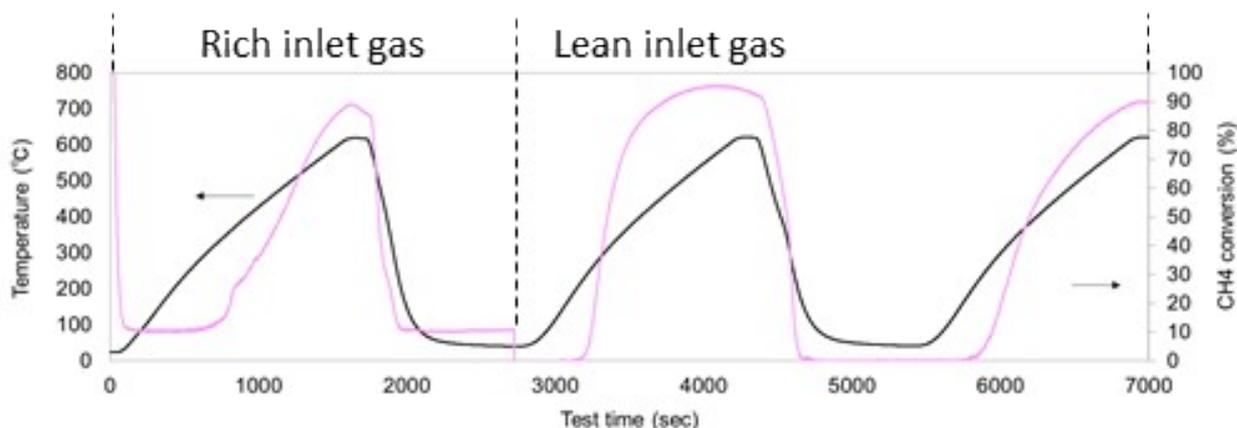


Figure S9. Consecutive CH₄ L/O test of ST-Pd/CeO₂ which consist of 1st L/O under rich gas condition and 2nd & 3rd L/O under lean gas condition.

In the case of ST-Pd/CeO₂, an aliquot of 50 mg of AS-Pd/CeO₂ was exposed in a stream of a mixture gas consisting of 0.5 % and 0.2 % of CH₄ and O₂ during 1st-L/O. And 2nd and 3rd L/O test was conducted after the inlet gas was changed to lean inlet gas composition.

Test results of 1st and 2nd L/O under lean gas, *i.e.* a mixture gas containing 0.1 % and 8 % of CH₄ and O₂, shown in Fig. 4c was corresponding to the 2nd and 3rd L/O test results in this Figure S9, respectively.

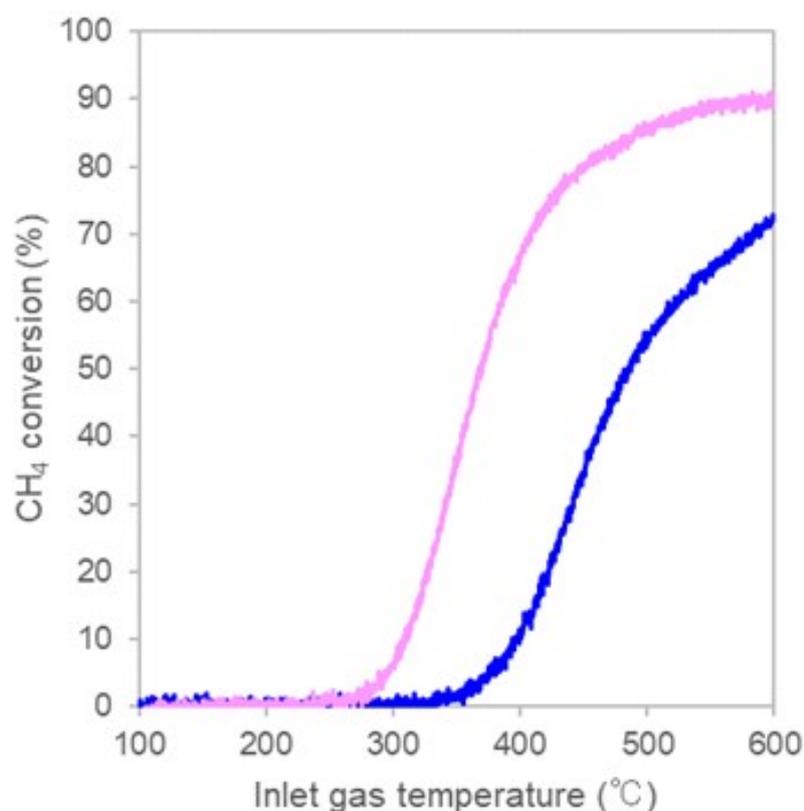


Figure S10. CH₄ L/O test under inlet gas including 2% H₂O.
 . Blue: AS-Pd/CeO₂, Pink: ST-Pd/CeO₂.

Co-existing H₂O in the inlet gas disturbed catalytic oxidation of CH₄ compared to the dry condition which was adopted in the evaluation tests shown in Fig. 4, Figure S7 and Figure S8. But the atmosphere treatment under CH₄-rich gas condition was effective to lower CH₄ L/O temperature even in the wet condition as shown in this Figure S10.

The catalyst performance test including H₂O in the inlet mixed gas was conducted with a mass flow-controllable system (BELCAT-A, MicrotracBEL Corp.). An aliquot of 50 mg of catalyst powder was placed in a glass sample tube, sandwiched between glass wool. The mixed gas was fed containing 0.1 %, 2 % and 8 % of CH₄, H₂O and O₂, respectively. He gas was bubbled into the thermostatic water bath at 50 °C, and 2% of H₂O was achieved by the control of the mass flow of the He. The total gas stream was balanced with pure He with another gas line to adjust the flow to 300 mL/min. The sample temperature was raised from room temperature up to 600 °C at a ramping rate of 20 °C/min and lowered down to 40 °C. The outlet gas from the sample tube during the test was introduced to the FTIR (DATABIRD FAST-1200NE, IWATA DENGYO CO., LTD) to quantify the gas composition.

Table S4. CH₄-T50 results without and with pretreatment from published literatures

Source	Sample conditions		CH ₄ -T50 °C	Evaluation conditions					
	Catalyst	Pre-treatment		O ₂ (%)	H ₂ O(%)	WHSV	GHSV	Sample weight	Flow rate
				%	%	L/(hr*g)	h-1	mg/test	mL/min
Our result	3%Pd/CeO ₂	-	615						
		Short-term atmosphere treatment from 40 to 600C & from 600C to 40C	308		0				
		Long-term atmosphere treatment at 230C for 100hr	310	8		360	-	50	300
		-	481			2			
		Short-term atmosphere treatment from 40 to 600C	367						
ACS Catal. 2021, 11, 4870-4879	2%Pd/Al ₂ O ₃	-	342		0				
		-	428/430	4		120	-	-	-
		Short Rich Pulse (SRP) from 300C to 600C	373			10			
Ind. Eng. Chem. Res. 2019, 58, 12561-12570	2%Pd/Al ₂ O ₃	-	309						
		Pre-reduction with H ₂ at 400C for 30min	289		0				
		Pre-reduction with CH ₄ at 400C for 30min	289						
		-	421						
	Pre-reduction with H ₂ at 400C for 30min	399		12					
	Pre-reduction with CH ₄ at 400C for 30min	399	10		-	80k	300	-	
	-	353							
2%Pd/CeO ₂	Pre-reduction with H ₂ at 400C for 30min	303			0				
	-	409							
	Pre-reduction with H ₂ at 400C for 30min	381			12				
Energy Technology, 2014, 2, 243-249	1.2%Pd/Al ₂ O ₃	-	270						
	1.2%Pd/Al ₂ O ₃	Pre-reduction with H ₂ at 300C for 2 hrs	280	20	0	-	33k	250	-

CH₄-T50 of Pd catalyst reported in previous literature which was pretreated by various conditions, as far as we have been able to know, was summarized in Table S4. There was the result of Pd/CeO₂, although Pd content, pretreatment conditions, and evaluation conditions were different from our study. CH₄-T50 in the published paper was 303 °C (dry) / 381 °C (wet w 12 % H₂O). Our results showed 310 °C (dry) / 367 °C (wet w 2% H₂O) as CH₄-T50 and were not significantly different from results in the previous study.

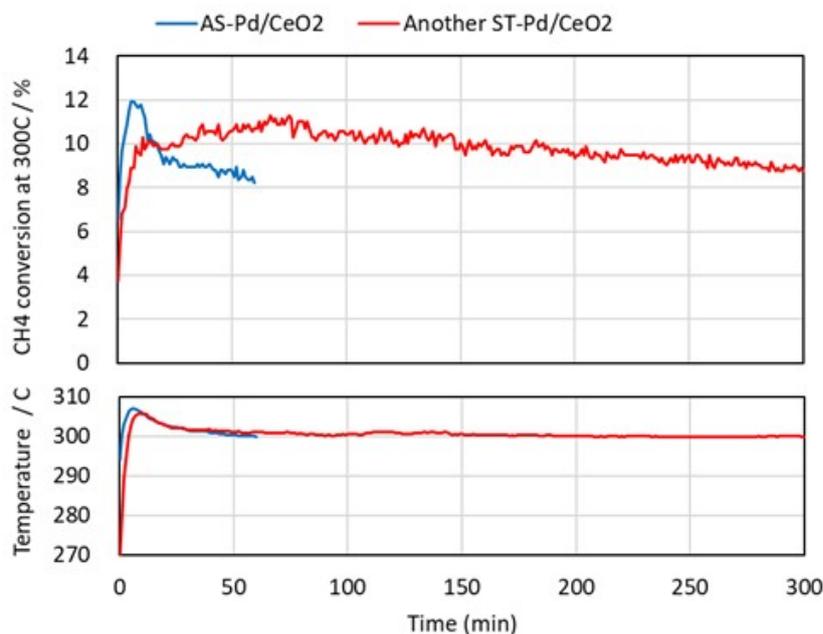


Figure S11. CH₄ combustion test under steady state condition at 300C. Blue: AS-Pd/CeO₂, Red: Another ST-Pd/CeO₂.

CH₄ combustion test under steady-state conditions was carried out to demonstrate the catalyst life and/or catalyst durability of atmosphere-treated Pd/CeO₂.

The hand-made experimental set-up was used for another atmosphere treatment and it was also used for the catalytic activity test with combination use of FTIR for the quantification of the outlet gas. FTIR was IR Prestige-21 made by SHIMAZU.

The conditions of this other atmosphere treatment were almost the same as the treatment of LT-Pd/CeO₂, but different in the sample amount, and the duration time of the treatment. An aliquot of 50 mg of AS-Pd/CeO₂ was placed in the sample holder. The duration time was 10 minutes at 230 °C in this other atmosphere treatment because this was for the demonstration. Hereafter the sample is called Other ST-Pd/CeO₂. After the treatment, the inlet gas composition was changed to 0.9% CH₄, 9% O₂, and Ar balanced at 111 mL/min for the catalytic evaluation and waited for another 10 minutes at 230 °C to reach a steady state. Then, the sample was heated up to 300 °C at 10 °C/min and kept for 5 hours for the catalytic stability test.

CH₄ conversion of Other ST-Pd/CeO₂ showed higher than AS-Pd/CeO₂ without any prior atmosphere treatment so that the Pd/PdO ratio could be optimized by the thermal decomposition of PdC which was formed during the atmosphere treatment for only 10 minutes. But the CH₄ conversion gradually decreased from about 11 % to 9 % during the steady-state reaction. It was reasonable because Pd metal could be oxidized to PdO and Pd/PdO ratio could be gradually out of the optimum range.