Enhanced activity for methane combustion over Pd/Co/Al$_2$O$_3$ catalyst prepared by galvanic deposition method

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Materials

Co(NO$_3$)$_2$·6H$_2$O (98%), 4.5wt% Pd(NO$_3$)$_2$ aqueous and high purity Al$_2$O$_3$ (99%) were purchased/supplied from Kishida Chemical, Cataler Corporation and SASOL, respectively.

Synthesis of Pd/Al$_2$O$_3$-**I** and Co/Al$_2$O$_3$-**I**

Pd/Al$_2$O$_3$-**I** and Co/Al$_2$O$_3$-**I** were prepared by conventional impregnation method with the Pd(NO$_3$)$_2$ and Co(NO$_3$)$_2$·6H$_2$O aqueous, respectively.

Synthesis of Pd/Co/Al$_2$O$_3$-**GD**

Pd/Co/Al$_2$O$_3$-**GD** was prepared using galvanic deposition method as mentioned on previous report and Scheme S1 [1]. First, Co supported on alumina catalyst was prepared by conventional impregnation method (denoted as Co/Al$_2$O$_3$-**I**). Next, Co/Al$_2$O$_3$-**I** was treated by H$_2$ at 600°C. Then, Co species were reduced to Co^0. The existence of Co^0 was confirmed by H$_2$-temperature programmed reduction (H$_2$-TPR) and X-ray absorption fine structure (XAFS) spectroscopy as shown as Fig. S1. After that, the degassed water and Pd(NO$_3$)$_2$ aqueous were dropped into the reduced Co/Al$_2$O$_3$-**I**. Then, Pd^{2+} was reduced to Pd^0 by Co^0, and Co^0 was oxidised to Co^{2+} and Co^{3+} by Pd^{2+}. As a result, Pd^0 nanoparticles (NPs) were deposited on Co particles. Finally, the slurry was centrifuged and dried up at 80°C overnight to get the Pd/Co/Al$_2$O$_3$ catalyst.

Synthesis of Pd/Co/Al$_2$O$_3$-**SI**

Pd/Co/Al$_2$O$_3$-**SI** was prepared using sequential impregnation method. The Co/Al$_2$O$_3$-**I** with 5wt% Co loading and Pd(NO$_3$)$_2$ aqueous were mixed in separable flask. The slurry was evaporated and dried up at 80°C. The powder was calcined at 500°C for 3 h, and Pd/Co/Al$_2$O$_3$-**SI** was obtained.
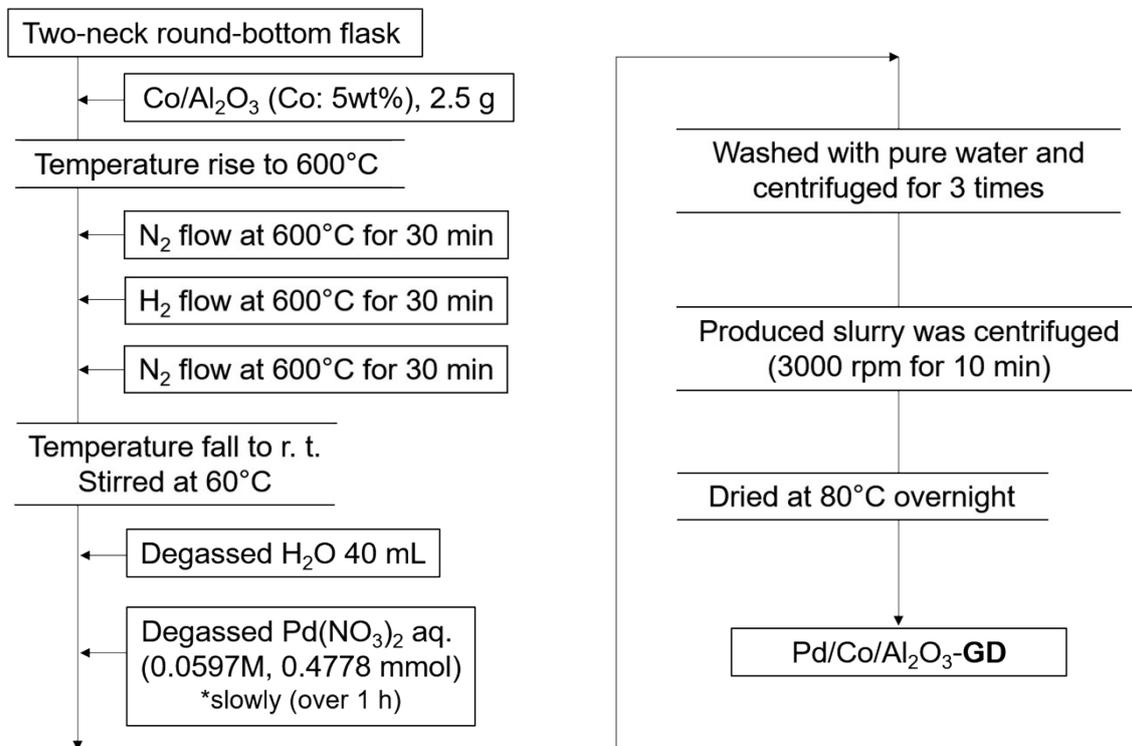
Catalytic activity test

The catalytic activity was evaluated by methane combustion using a conventional fixed-bed flow reactor at atmospheric pressure with a 20 mg of catalyst in a Pyrex glass tube with internal diameter of 4 mm. The catalytic run was carried out under a flow of 0.4% CH_4/10% O_2/He balance at a rate of 100 cm^3/min. The gas hourly space velocity was 300,000 mL/(h·g_{cat}). The effluent gas was analyzed by nondispersive infrared (NDIR) CO/CO_2 analyzer (Horiba VIA510) during stepwise increase in the reaction temperature. The steady state CH_4 conversion was measured after 20 min for each temperature.

Characterization method

The catalysts were characterized by X-ray diffraction (XRD), inductively coupled plasma (ICP), CO chemisorption, the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), energy-dispersive X-ray spectroscopy (EDX), X-ray absorption fine structure (XAFS) spectroscopy, and O_2-temperature programmed desorption (O_2-TPD).

XRD analysis was carried out using Rigaku MiniFlex II/AP diffractometer with Cu Kα radiation. Metal loading of the catalysts were determined by ICP spectroscopy of the filtrate obtained during the centrifugation using Thermo Scientific iCAP7400Duo. CO chemisorption was carried out with BELCAT (Bel Japan Inc.) after oxidation pretreatment by O_2 at 500°C and reduction by H_2 at 50°C. HAADF-STEM images and EDX images were collected using a JEOL JEM-2100F at 200 kV. As the TEM samples, the catalysts used in methane combustion reaction were dispersed in methanol and dropped onto a Cu mesh with a carbon microgrid. The XAFS measurements at the Pd-K and Co-K edge were carried out on the BL01B1 beamline at the SPring-8 synchrotron radiation facility (8 GeV, 100mA) of the Japan Synchrotron Radiation Research Institute (JASRI) in Hyogo, Japan. The catalysts after used in methane combustion were measured without exposure to air. Data analysis was performed using Athena and Artemis including in the Demeter package. The curve-fitting analysis of the EXAFS spectra was performed for inverse Fourier transforms on the single scattering using theoretical parameters calculated by FEFF6. The Pd K-edge and Co K-edge EXAFS data were fitted among 3–12 $Å^{-1}$ and k space and 1–3 Å in R space. O_2-TPD was carried out with BELCAT (Bel Japan Inc.) after oxidation pretreatment by O_2 at 500°C and reduction by H_2 at 50°C.

Two-neck round-bottom flask

└─ Co/Al$_2$O$_3$ (Co: 5wt%), 2.5 g

Temperature rise to 600°C

└─ N$_2$ flow at 600°C for 30 min

└─ H$_2$ flow at 600°C for 30 min

└─ N$_2$ flow at 600°C for 30 min

Temperature fall to r. t.
Stirred at 60°C

└─ Degassed H$_2$O 40 mL

└─ Degassed Pd(NO$_3$)$_2$ aq.
(0.0597M, 0.4778 mmol)
*slowly (over 1 h)

Washed with pure water and
centrifuged for 3 times

Produced slurry was centrifuged
(3000 rpm for 10 min)

Dried at 80°C overnight

Pd/Co/Al$_2$O$_3$-**GD**

Scheme S1 Preparation scheme of Pd/Co/Al$_2$O$_3$-**GD**.
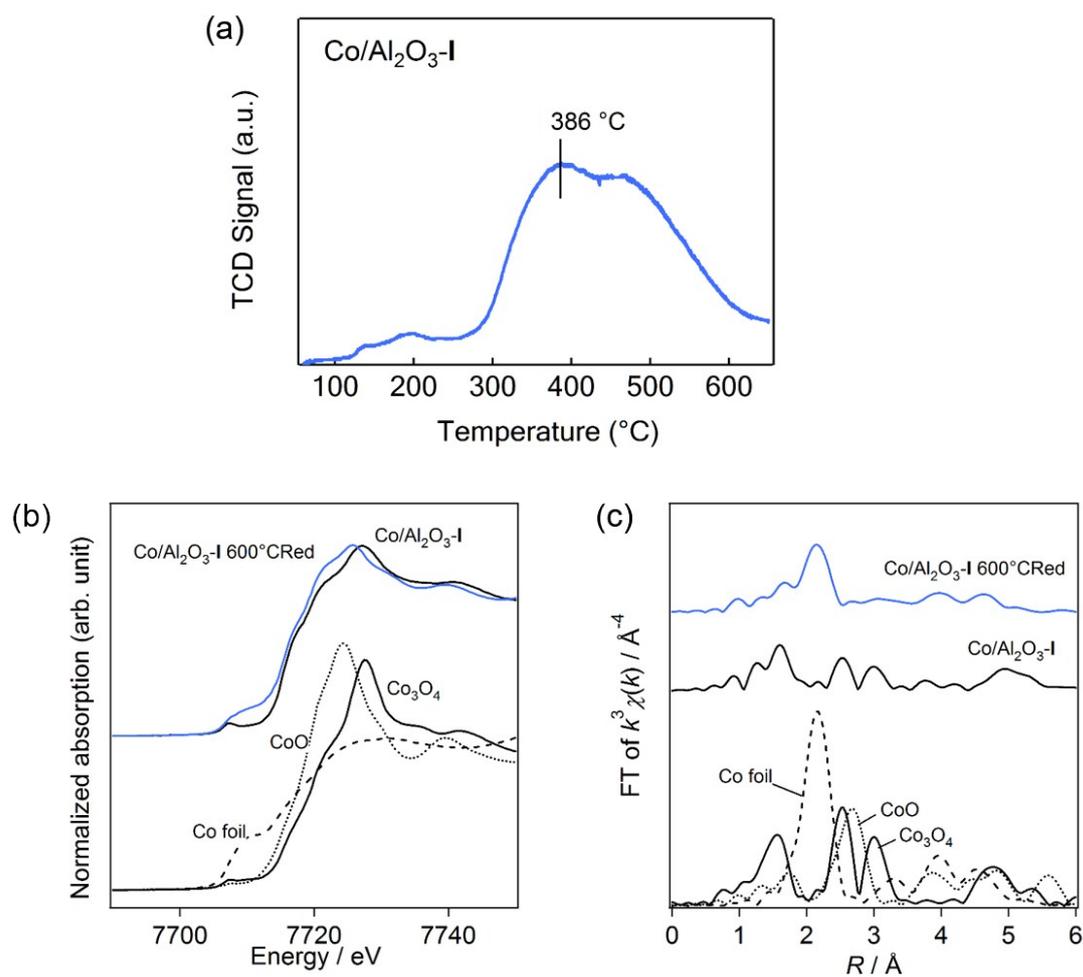
Figure S1 (a) H_2-temperature programmed reduction of Co/Al$_2$O$_3$-**I**. (b) Co K-edge XANES spectra of Co/Al$_2$O$_3$-I reduced by H_2 at 600 °C (blue). (c) FT of k^3-weighted Co K-edge EXAFS of Co/Al$_2$O$_3$-I reduced by H_2 at 600 °C (blue).

Table S1 Summary of preparation method, Pd and Co loading, CO uptake for CO chemisorption and Pd average diameter ($d_{Pd\ MPs}$)

Catalyst	Preparation method	Pd loading (wt%)			Co loading (wt%)			CO uptake	$d_{Pd\ NPs}$
		Int.	ICP[c]	XAS[d]	Int.	ICP[c]	XAS[d]	(μmol/g)[d]	(nm)[e]
Pd/Co/Al$_2$O$_3$-**GD**	Galvanic deposition	0–2[b]	1.99	1.9	4.9–3.9[b]	3.7	4.8	26	8.2
Pd/Co/Al$_2$O$_3$-**SI**	Sequential impregnation	2[a]	-	1.9	4.9[a]	-	5.6	64	3.5
Pd/Al$_2$O$_3$-**I**	Impregnation	2[a]	-	1.9	-	-	-	58	3.8
Co/Al$_2$O$_3$-**I**	Impregnation	-	-	-	5[a]	-	4.8	-	-

a. Introduction amount.
b. Metal loading considered theoretically.
c. Estimated from ICP analysis for a filtrate which we can get by the galvanic deposition method.
d. Estimated from X-ray absorption amount using X-ray absorption spectroscopy (XAS).
e. CO uptake was measured by using CO chemisorption after oxidation pretreatment by O$_2$ at 500°C and reduction by H$_2$ at 50°C.
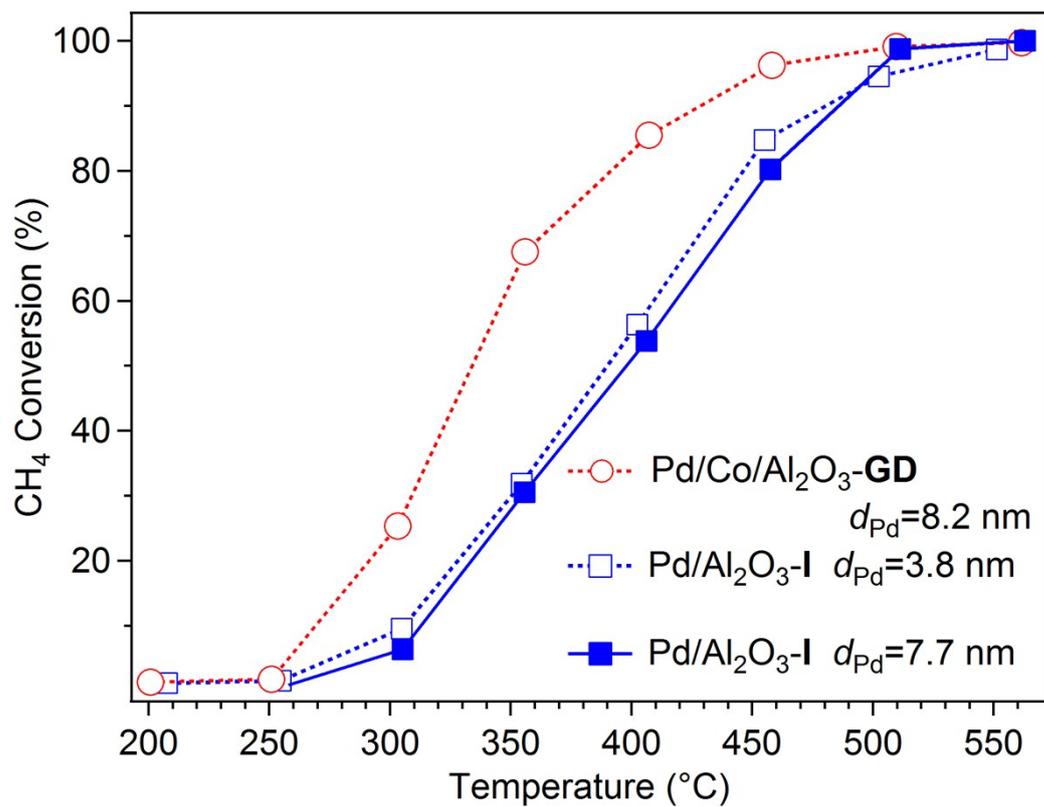f. The particle size of Pd NPs was estimated by assuming a CO to surface metal atom ratio of 1:1.

Figure S2 Methane combustion over Pd/ Al_2O_3 with the Pd particle size equal to that of Pd/Co/Al_2O_3-**GD** (blue solid line).
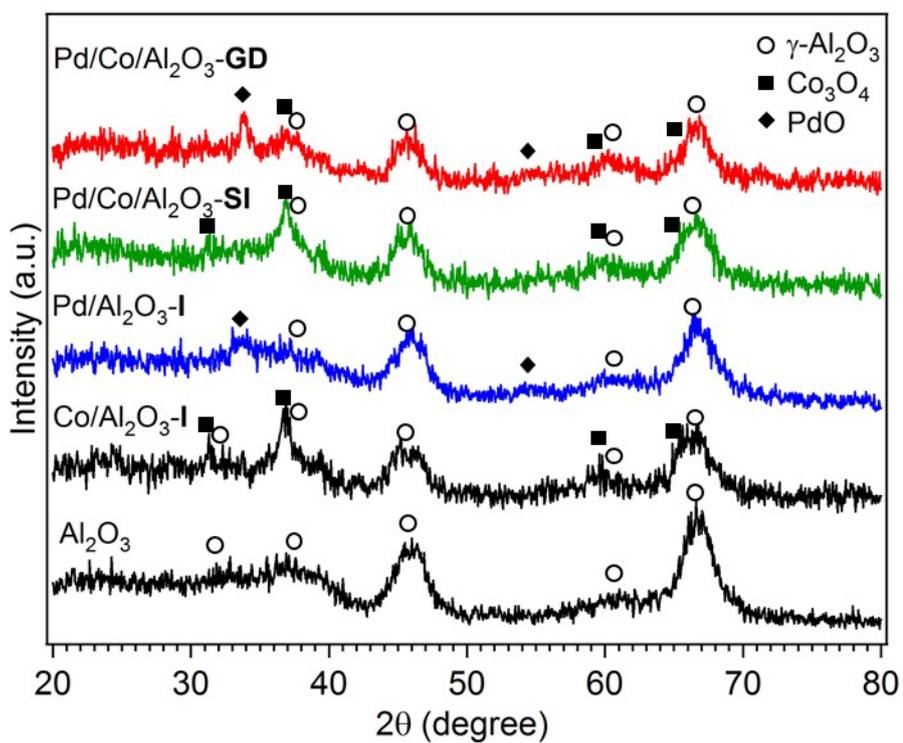
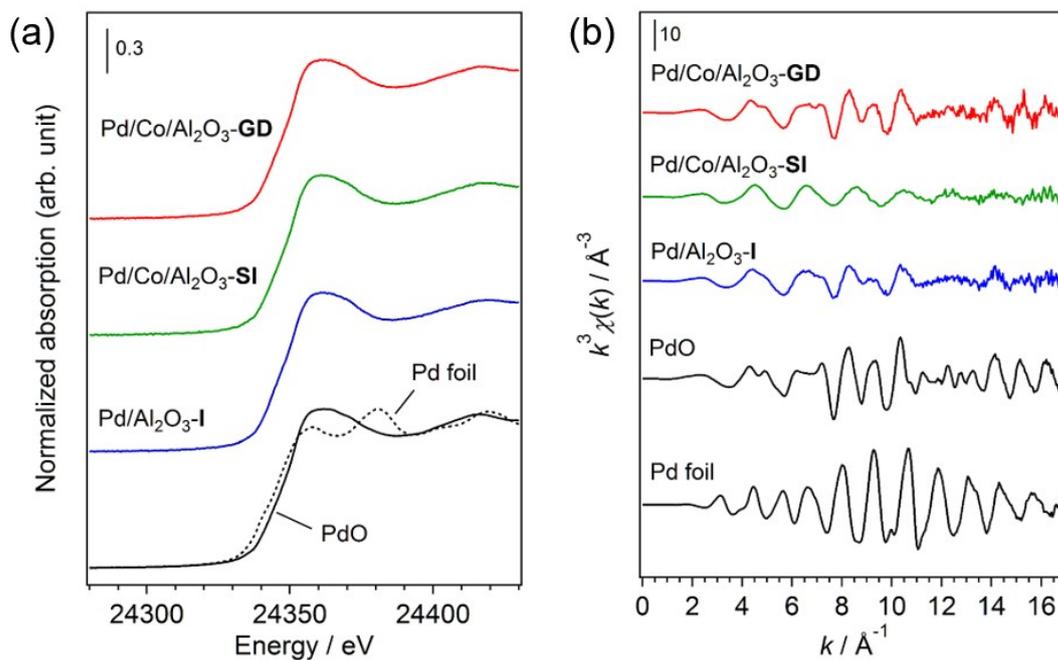Figure S3 XRD spectra of prepared catalysts and Al_2O_3 as a support.

Figure S4 (a) Pd K-edge XANES and (b) k^3-weighted Pd K-edge EXAFS of the series of catalysts. The catalysts were measured after activity tests.
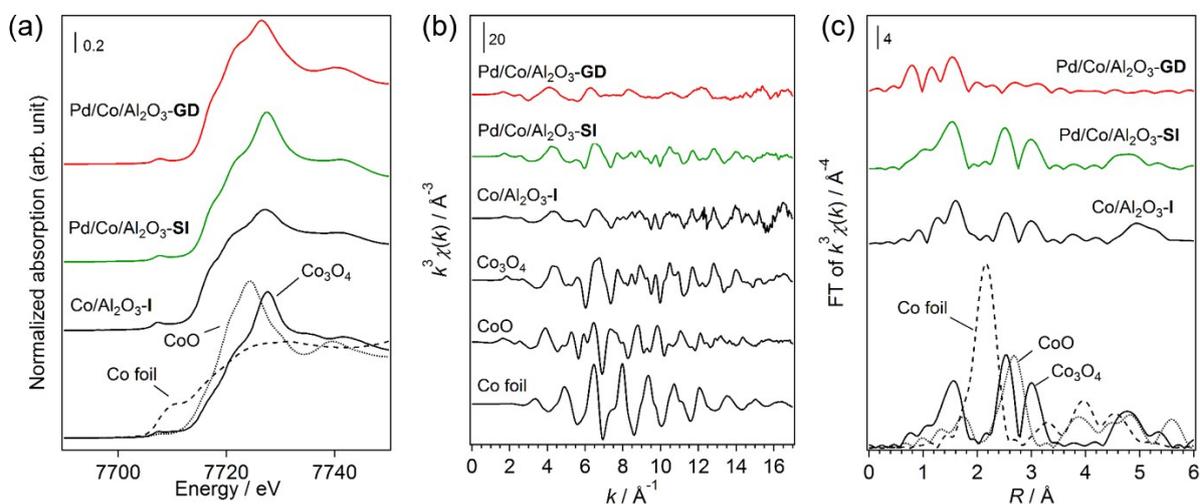

Figure S5 (a) Co K-edge XANES, (b) k^3-weighted Co K-edge EXAFS, and (c) FT of the k^3-weighted Co K-edge EXAFS of the series of catalysts. The catalysts were measured after activity tests.

Table S2 Curve-fitting result of the Pd K-edge EXAFS spectra of prepared catalysts, Pd foil and PdO as a reference.

Catalyst	Shell	C.N.	R/Å	$\sigma^2 \times 10^4$/Å^2	R_f/%
Pd/Co/Al$_2$O$_3$-**GD**	Pd–O	3.9±0.3	2.02±0.01	30±5	0.7
	Pd–Pd1	3.2±0.9	3.05±0.01	58±12	
	Pd–Pd2	4.3±1.2	3.43±0.01	58±12	
Pd/Co/Al$_2$O$_3$-**SI**	Pd–O	3.8±0.3	2.02±0.01	40±5	2.9
Pd/Al$_2$O$_3$-**I**	Pd–O	3.9±0.3	2.02±0.01	35±5	1.3
	Pd–Pd1	1.5±0.5	3.05±0.01	47±14	
	Pd–Pd2	2.1±0.8	3.43±0.01	53±15	
Pd foil	Pd–Pd	12*	2.74	60±3	0.1
PdO	Pd–O	4*	2.01	28±5	1.2
	Pd–Pd1	4*	3.05	49±4	
	Pd–Pd2	8*	3.43	49±4	
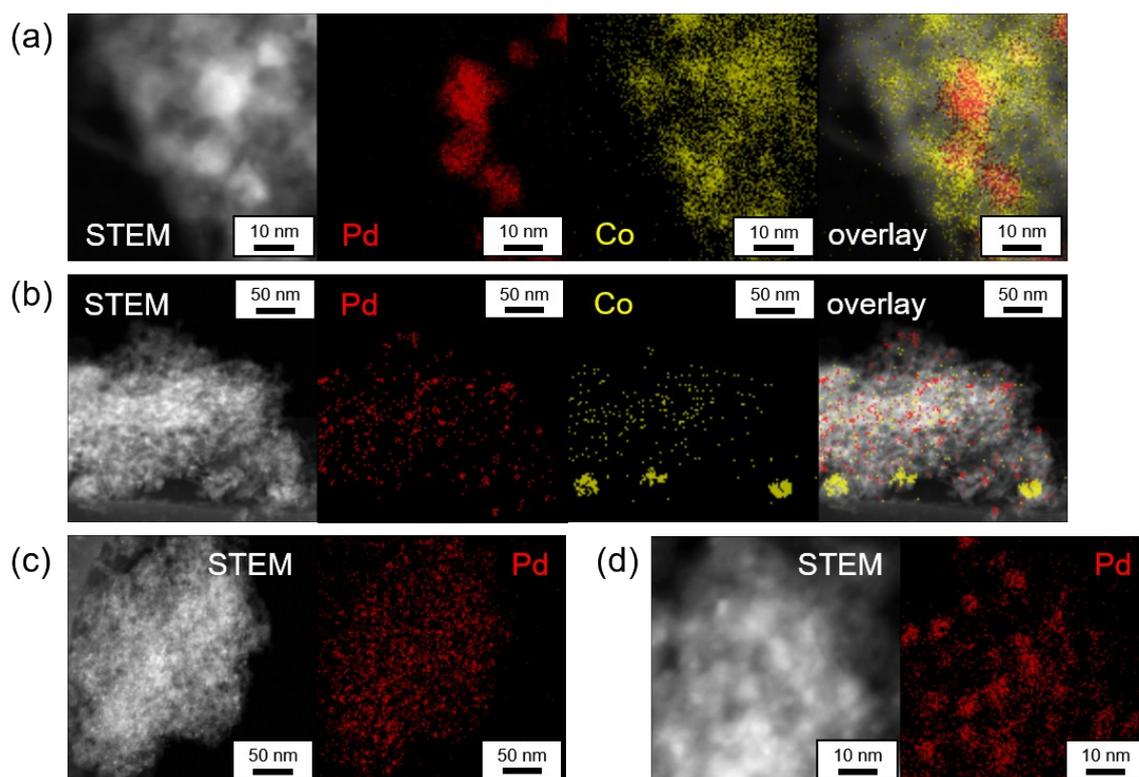
Figure S6 HAADF-STEM and EDX images of (a) Pd/Co/Al$_2$O$_3$-**GD**, (b) Pd/Co/Al$_2$O$_3$-**SI**, and (c,d) Pd/Al$_2$O$_3$-**I** after used for methane combustion reaction. The red and yellow color in EDX mapping correspond to Pd and Co, respectively. The catalysts were observed after activity tests.
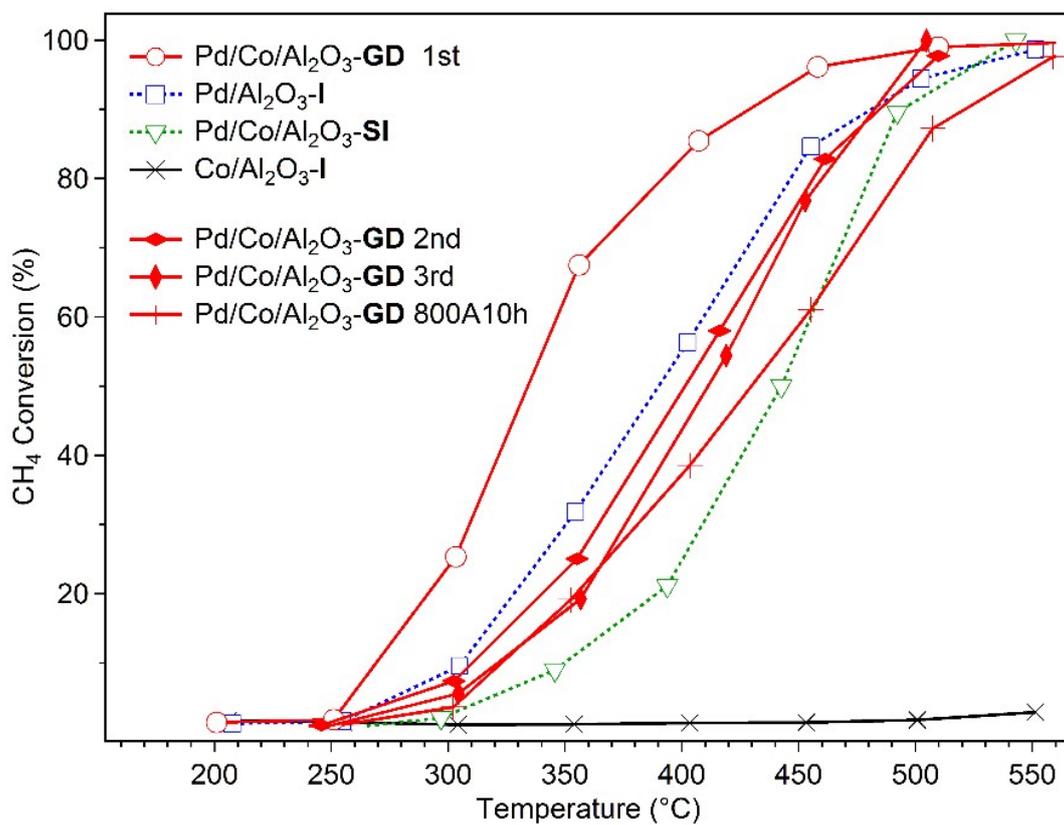
Figure S7 Methane combustion over Pd/Co/Al$_2$O$_3$-**GD** after using for methane combustion from 200°C to 550°C (Pd/Co/Al$_2$O$_3$-**GD** 2nd) and after again (Pd/Co/Al$_2$O$_3$-**GD** 3rd) and after aging in air at 800°C for 10 h (Pd/Co/Al$_2$O$_3$-**GD** 800A 10h).
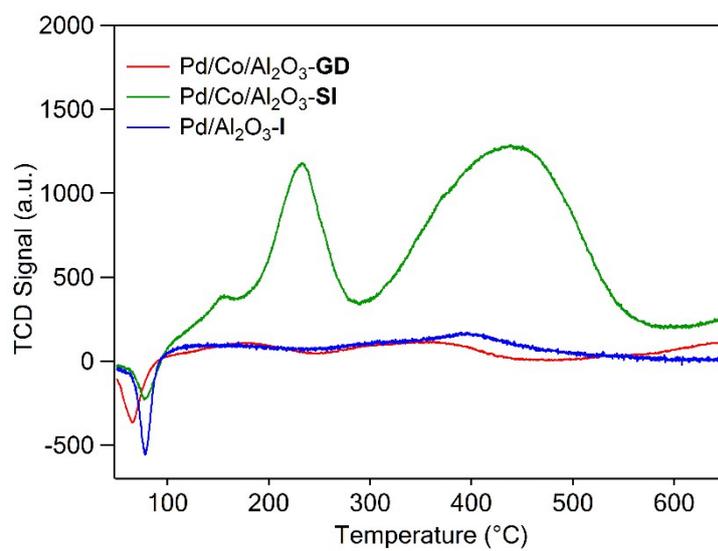
Figure S8 H$_2$-TPR profiles of Pd/Co/Al$_2$O$_3$-**GD**, Pd/Co/Al$_2$O$_3$-**SI**, and Pd/Al$_2$O$_3$-**I**. PdO already reduced to Pd^0 below 50°C.