

Electronic Supplementary Information (ESI)

Methane Combustion over Pd/CoAl<sub>2</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> Catalysts Prepared by Galvanic Deposition.

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Comparison with Previously Reported Catalysts

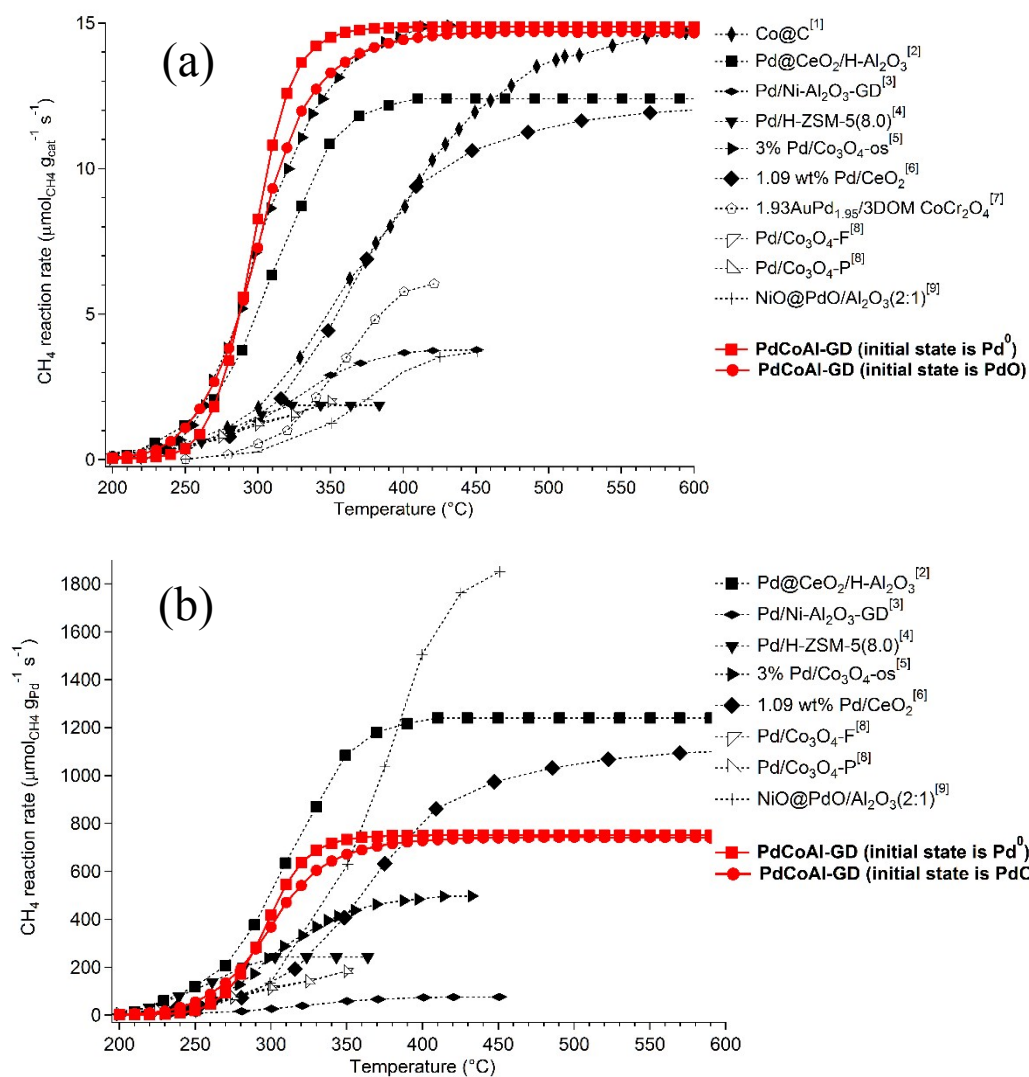


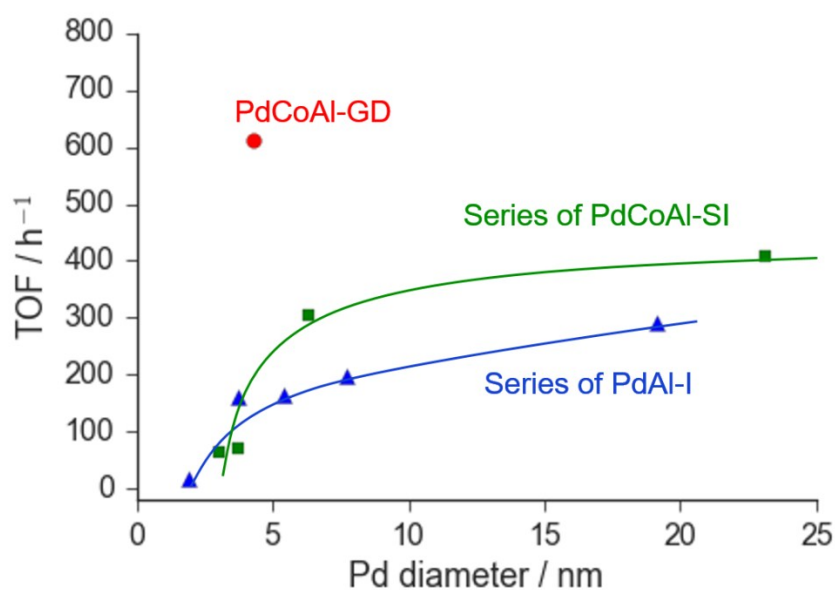
Figure S1. Methane combustion activities for representative catalysts<sup>1-9</sup>. (a) Methane reaction rate per amount of catalyst. (b) Methane reaction rate per amount of Pd.

*Pd particle size effect of TOF of methane combustion*

**Table S1. List of PdCoAl-SI and PdAl-I catalysts with different Pd particle sizes.**

Catalysts	Support	preparation method	Calcination	Pd loading (wt%)	Co loading (wt%)	$d_{Pd-Co}$ (nm)	TOF at 300°C (h <sup>-1</sup> ) <sup>c</sup>
Series of PdCoAl-SI	Al <sub>2</sub> O <sub>3</sub> (sasol)	Sequential Impregnation	500°C for 3 h	0.5 <sup>a</sup>	5 <sup>a</sup>	3	63
	Al <sub>2</sub> O <sub>3</sub> (sasol)	Sequential Impregnation	500°C for 3 h	1 <sup>a</sup>	5 <sup>a</sup>	3.7	71
	Al <sub>2</sub> O <sub>3</sub> (sasol)	Sequential Impregnation	500°C for 3 h	2 <sup>a</sup>	5 <sup>a</sup>	6.3	304
	Al <sub>2</sub> O <sub>3</sub> (sasol)	Sequential Impregnation	900°C for 10 h	2 <sup>a</sup>	5 <sup>a</sup>	23.1	407
Series of PdAl-I	Al <sub>2</sub> O <sub>3</sub> (sasol)	Impregnation	500°C for 3 h	1 <sup>a</sup>	-	1.9	17
	Al <sub>2</sub> O <sub>3</sub> (sasol)	Impregnation	500°C for 3 h	2 <sup>a</sup>	-	3.7	160
	Al <sub>2</sub> O <sub>3</sub> (sasol)	Impregnation	800°C for 10 h	2 <sup>a</sup>	-	5.4	164
	Al <sub>2</sub> O <sub>3</sub> (sasol)	Impregnation	850°C for 10 h	2 <sup>a</sup>	-	7.7	197
	Al <sub>2</sub> O <sub>3</sub> (sasol)	Impregnation	900°C for 10 h	2 <sup>a</sup>	-	19.1	290

<sup>a</sup> Nominal value.

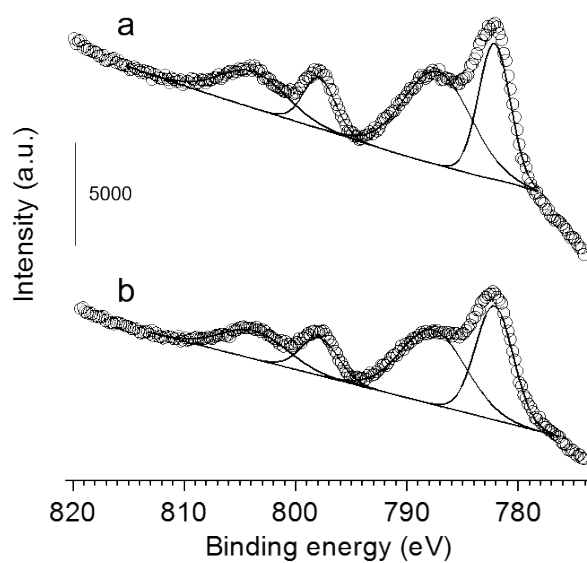


**Figure S2.** Effect of the Pd particle diameter on the methane combustion TOF at 300 °C.

### *X-ray photoelectron spectroscopy (XPS) measurements*

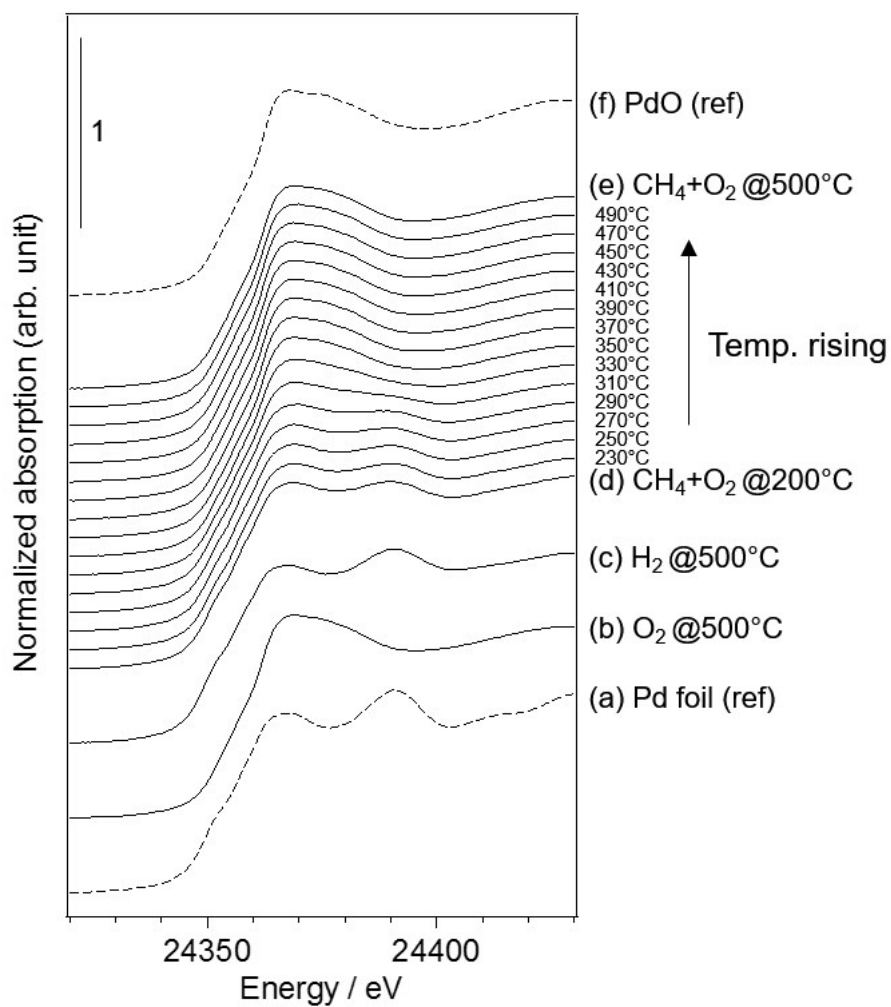
XPS measurements were carried on a JPS-9000MC system (JEOL Ltd.) with a Al  $K\alpha$  radiation. The samples were mounted on a carbon tape. In the analysis, the Shirley equation was used for the background, and the energy position was adjusted with the C 1s XPS spectrum.

As shown in Figure S3, the Co 2p XPS spectra were clearly observed in the PdCoAl-GD and PdCoAl-SI samples. This result indicates that Co species exist near the surface of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

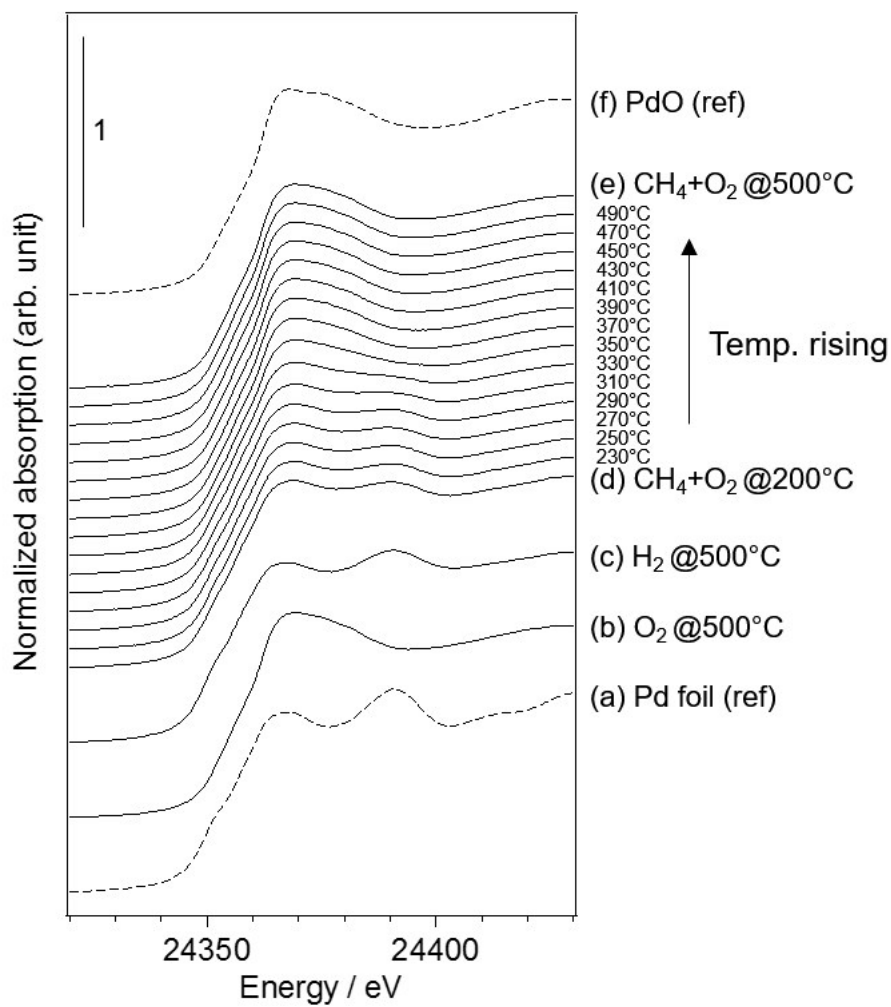


**Figure S3.** Ex situ Co 2d XPS spectra of: (a) PdCoAl-GD and (b) PdCoAl-SI after methane combustion at 600 °C.

*Operando Pd K-edge XAFS measurements*



**Figure S4.** Normalized Pd K-edge XANES spectra of PdCoAl-SI during operando XAFS measurements.



**Figure S5.** Normalized Pd K-edge XANES spectra of PdAl-I during operando XAFS measurements.

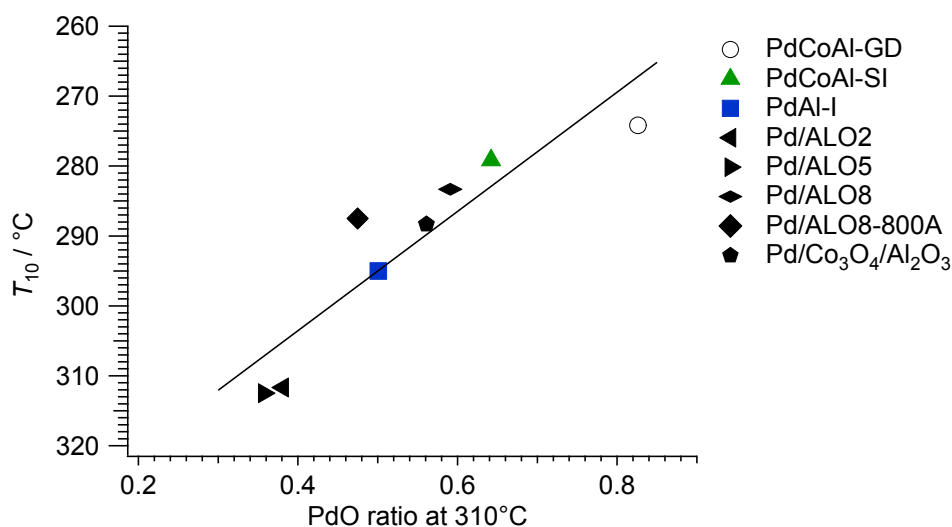
In order to examine more general trends, the operando XAFS experiments were carried out over various Pd catalysts.

Al<sub>2</sub>O<sub>3</sub> (JRC-ALO-2, JRC-ALO-5, and JRC-ALO-8) as a support were supplied from the Catalysis Society of Japan. The four new catalysts (Pd/ALO2, Pd/ALO5, Pd/ALO8, and Pd/ALO8-800A) were prepared by an impregnation method using a Pd(NO<sub>3</sub>)<sub>2</sub> solution and Al<sub>2</sub>O<sub>3</sub>, followed by dryness, and calcination in air at 500 °C for 3 h. Pd/Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> was prepared by a sequential impregnation method as follows. First, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> (Sasol) were mixed and the resulting mixture stirred. After evaporation and drying overnight at 80 °C, the resulting solid was calcined at 500 °C for 3h. The obtained solid and Pd(NO<sub>3</sub>)<sub>2</sub> were mixed and the mixture stirred. After evaporation and drying overnight at 80 °C, the resulting solid was calcined at 500 °C for 3 h, and Pd/Co<sub>3</sub>O<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> was obtained. The prepared catalysts are listed in Table S2.

**Table S2. List of Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/Co/Al<sub>2</sub>O<sub>3</sub> catalysts with different supports.**

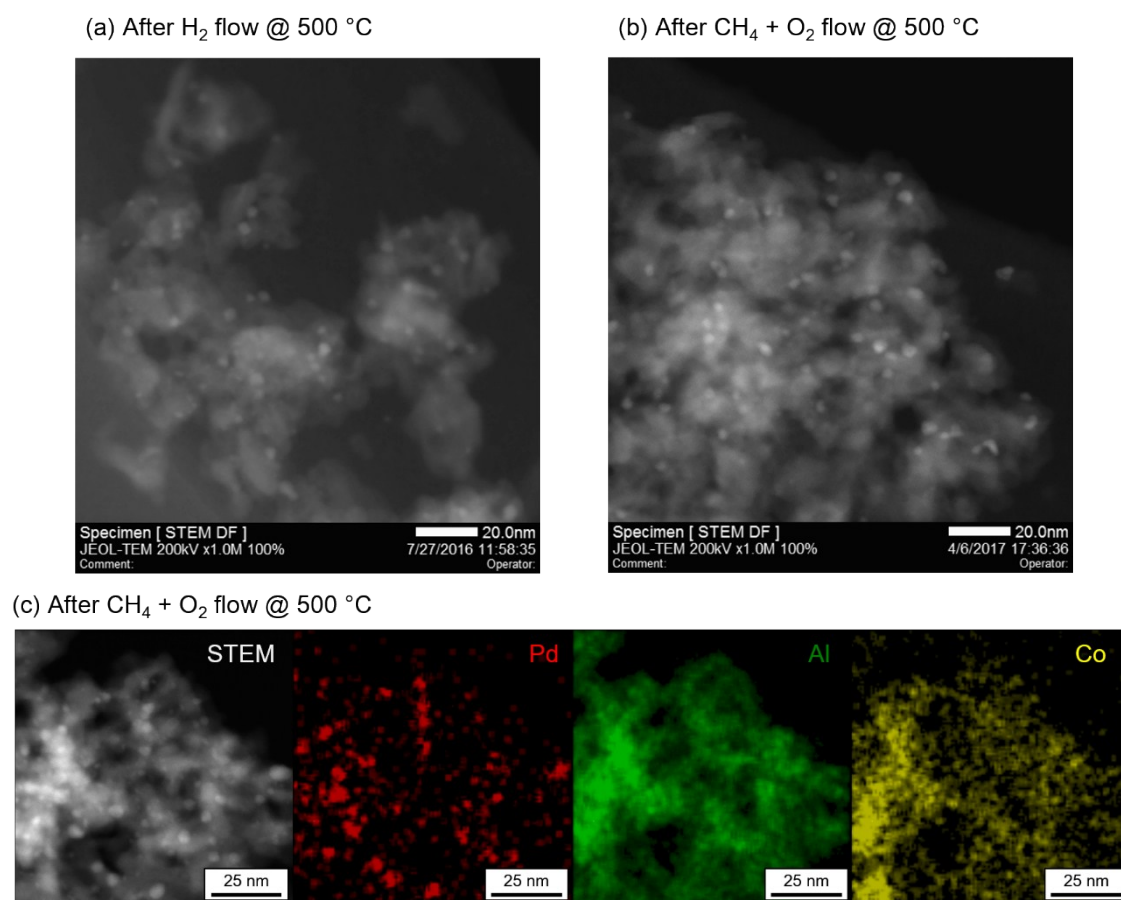
Catalysts	Support	preparation method	Calcination	Pd loading (wt%)	Co loading (wt%)	$d_{\text{Pd-Co}}$ (nm)
Pd/ALO2	JRC-ALO-2	Impregnation	500°C for 3 h	2 <sup>a</sup>	-	2.7
Pd/ALO5	JRC-ALO-5	Impregnation	500°C for 3 h	2 <sup>a</sup>	-	2.8
Pd/ALO8	JRC-ALO-8	Impregnation	500°C for 3 h	2 <sup>a</sup>	-	4.7
Pd/ALO8-800A	JRC-ALO-8	Impregnation	800°C for 10 h	2 <sup>a</sup>	-	7.1
Pd/Co <sub>3</sub> O <sub>4</sub> /Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> (sasol)	Sequential Impregnation	500°C for 3 h	2 <sup>a</sup>	5 <sup>a</sup>	3.7

<sup>a</sup> Nominal value.



**Figure S6.** Correlation between  $T_{10}$  and the PdO ratio for Pd-based catalysts (Figure 9(d)). The catalysts are listed in Table S2.

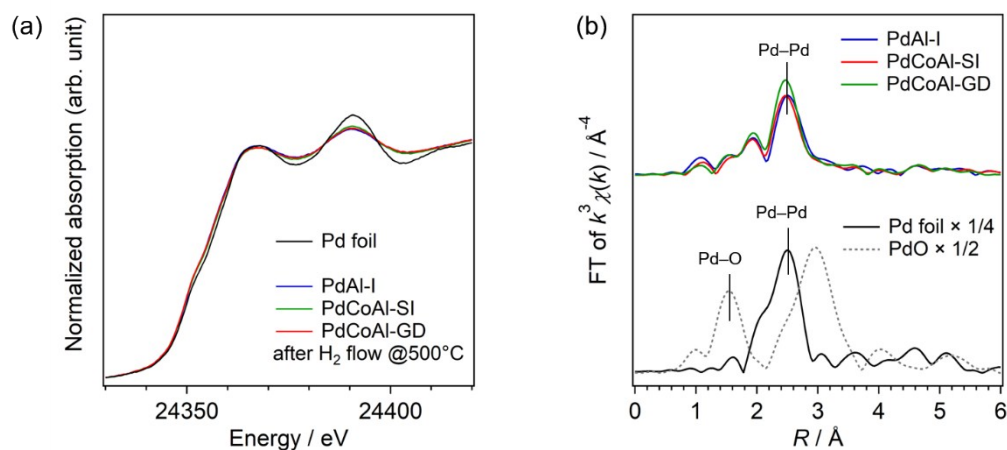
*STEM/EDX images of PdCoAl-GD after combustion*



**Figure S7.** HAADF-STEM images of PdCoAl-GD (a) after reduction by H<sub>2</sub> at 500 °C and (b) after methane combustion at 500 °C. (c) HAADF-STEM image and EDX element mapping of PdCoAl-GD after methane combustion at 500 °C.

PdCoAl-GD after combustion showed a structure in which the PdO particles were dispersed on CoAl<sub>2</sub>O<sub>4</sub>, and the catalyst structure remained unchanged except that Pd was oxidized.

### *Pd K-edge XAFS spectra of the catalysts after H<sub>2</sub> treatment at 500 °C*



**Figure S8.** (a) the Pd K-edge XANES spectra and (b) the Fourier transformed EXAFS spectra of the H<sub>2</sub> treated catalyst at 500 °C.

All XANES spectra were almost in agreement with Pd foil. A peak derived from the Pd–Pd bond of Pd<sup>0</sup> also appeared from Fourier transformed EXAFS. Conversely, since almost no peaks derived from Pd–O bond of PdO was observed, the treatment at 500 °C under H<sub>2</sub> reduced all Pd species to a metallic phase.

### *Pd 3d XPS spectra of the catalysts*

**Table S3.** Pd<sup>n+</sup> 3d<sub>5/2</sub> binding energies for the catalysts.

Samples	Pd <sup>n+</sup> 3d <sub>5/2</sub> B.E. (eV)
PdCoAl-GD	336.1
PdCoAl-SI	336.3
PdAl-I	336.9



## REFERENCE

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