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Enhanced Methane Activation on Diluted Metal–Metal Ensembles under an Electric Field: Breakthrough in Alloy Catalysis

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1. Experimental procedure

Catalyst Preparation.

All chemicals were purchased from Kanto Chemical Co., Inc. and were used as supplied. $Ce_{0.5}Zn_{0.5}O_2$ (CZO) was prepared using a complex polymerization method according to a published procedure.[1] First, 6.9703 g of ethylene glycol and 23.5983 g of citric acid monohydrate were added to a Teflon beaker with 200 mL distilled water and stirred. Next, 8.0871 g of $Ce(NO_3)_3{\cdot}6H_2O$ and 5.0276 g of $ZrO(NO_3)_3{\cdot}2H_2O$ were added to the beaker with 100 mL distilled water into the solution and stirred. The beaker was put in a water bath and heated at 343 K overnight with stirring. After that the gel was heated on a hot plate and stirred until the water was completely removed and light-yellow powder was obtained. The obtained powder was pre-calcined at 673 K for 2 h and then calcined at 1123 K for 10 h under air atmosphere.

Pd–Zn alloy catalysts supported on CZO were prepared using a co-impregnation method with $Pd(NO_3)_2{\cdot}(NH_3)_2$ and $Zn(NO_3)_3{\cdot}6H_2O$ as precursors. The Pd loading amount was 5 wt%; the Pd:Zn atomic ratio was 9:1, 4:1 or 1:1. The prepared catalysts are designated as Pd9Zn1/CZO, Pd4Zn1/CZO and Pd1Zn1/CZO. First, CZO support was added to an aqueous solution of the metal precursors and was stirred for several hours. Then, the water was removed completely using a rotary evaporator. The obtained powder was calcined at 773 K for 1 h. Finally, the powder was reduced by hydrogen (50 mL min^{-1}) at 873 K for 1 h. As reference catalysts, Pd/CZO and Zn/CZO were prepared using an impregnation method with $Pd(NO_3)_3$ and $Zn(NO_3)_2{\cdot}6H_2O$ as precursors.

Catalyst Characterization.

Crystal structures of the prepared catalysts were examined using powder X-ray diffraction (XRD) with an X-ray diffractometer (SmartLab 3; Rigaku Corp.) and Cu $K\alpha$ radiation. Specific surface area and perimeter of supported Pd metal were estimated using CO pulse measurements (BELCAT II; MicrotracBEL Corp.). Before the CO pulse measurements, the catalyst was pre-reduced under 20%H_2 gas flow at 673 K for 30 min.

X-ray absorption fine structures (XAFS) measurements for Pd *K*-edge were taken at the BL14B2 beamline at SPring-8 in Hyogo, Japan to evaluate the local structure of supported Pd. Each sample was milled using an agate mortar. Furthermore, if necessary, the samples were physically mixed with BN (Kojundo Chemical Laboratory Co., Ltd.) using a planetary ball mill (Pulverisette 6; Fritsch GmbH). The obtained powders were then pressed to form a pellet (7 mmϕ). The obtained pellets were reduced at 673 K for 30 min under a reducing gas flow (H_2:Ar = 1:4, total flow rate 100 mL min^{-1}) and were packed into a gas barrier bag with degassing. The measurements were conducted in a transmission mode using Si(311) crystal monochromator at room temperature. Extended X-ray Absorption Fine Structure (EXAFS) data were analyzed using software (Artemis ver. 0.9.25; Bruce Ravel).

FT-IR spectra of adsorbed CO on the catalyst surface were measured using an FT-IR spectrometer (FT/IR-6200; Jasco Corp.) with a MCT detector and ZnSe window. All spectra were recorded with 4 cm^{-1} resolution and 10 scans. About 40 mg of catalysts was charged into a diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) cell and was pre-reduced under a reducing gas flow (H_2:Ar = 1:4, total flow rate 50 mL min^{-1}) at 673 K for 30 min. After pretreatment, the gas was switched to Ar (50 mL min^{-1}) and was cooled to 303 K. Background spectra were recorded at 303 K; then the samples were exposed to CO gas (CO:Ar = 1:90, total flow rate; 50 mL min^{-1}). Spectra were recorded after 10 min.

Catalytic Activity Tests.

Catalytic activity tests were conducted using a fixed bed flow-type reactor with a quartz tube (6.0 mm i.d. and 8.0 mm o.d.). Figure S3 shows a schematic diagram of reactor. Two stainless steel rods (2 mm o.d.) were inserted into the reactor as electrodes. They contacted the top and bottom of the catalyst-bed. Direct current (1–7 mA) was imposed to the catalyst-bed using a high voltage DC power supply. Response voltage waves were observed using an oscilloscope (TDS 2001C with a voltage probe P6015A; Tektronix Inc.). A thermocouple was inserted to the bottom of the catalyst-bed to measure the catalyst-bed temperature. The prepared catalysts were pressed and crushed to obtain particles of 355–500 μm; 100 mg of it was used. Before the activity tests, the catalyst was pre-reduced under a reducing gas flow (H_2:Ar = 1:4, total flow rate 100 mL min^{-1}) at 673 K for 30 min. Activity tests were conducted under a reaction gas flow (CH_4:H_2O:Ar = 1:2:7, total flow rate 100 mL min^{-1}) at various temperatures (423 K for ER and 473–873 K for SR). Product gas was analyzed using a GC-FID (GC-8A; Shimadzu Corp.) with a handmade methanizer and a GC-TCD (GC-2014; Shimadzu Corp.) after removing H_2O using a cold-trap. The CH_4 conversion is calculated using equation (S.1).

$$\mathrm{CH_4\ conv.} = \frac{\text{Carbon moles of products (CO and CO}_2\text{)}}{\text{Carbon moles of input methane}} \times 100 \tag{S.1}$$

Calculation of TOFs

The detailed calculation method of TOF-s and TOF-p over prepared catalysts are shown below. TOFs are calculated using CO adsorption amount measured by CO pulse. Table S3 shows results of calculation of Pd surface area and Pd perimeter of prepared catalysts by CO pulse measurement. TOF-s is TOF that is normalized by Pd atom number at surface (Equation (S.1)), and TOF-p is TOF that is normalized by Pd atom number at perimeter (Equation (S.2)). The reaction rate of CH_4 is calculated from the sum of formation speed of CO and CO_2. In these equations, *Surface area (Pd)* is Pd surface area per catalyst weight, *Perimeter (Pd)* is Pd perimeter per catalyst weight, m_{cat} is catalyst weight, σ_{Pd} is cross-sectional area of Pd and l_{Pd} is bond length of Pd, respectively.

$$\begin{aligned}\text{TOF - s}\left[\mathrm{s}^{-1}\right] &= \frac{\text{Reaction rate of CH}_4\text{ mole number}}{\text{Pd atom number at surface}}\\ &= \frac{r_{CO+CO_2}[\mathrm{mol\ s}^{-1}]\times N_A[\mathrm{mol}^{-1}]}{\text{Surface area (Pd) }[\mathrm{m}^2\mathrm{g}^{-1}]\times m_{cat}[\mathrm{g}]/\sigma_{Pd}[\mathrm{m}^2]}\end{aligned} \tag{S.1}$$

$$\begin{aligned}\text{TOF - p}\left[\mathrm{s}^{-1}\right] &= \frac{\text{Reaction rate of CH}_4\text{ mole number}}{\text{Pd atom number at perimeter}}\\ &= \frac{r_{CO+CO_2}[\mathrm{mol\ s}^{-1}]\times N_A[\mathrm{mol}^{-1}]}{\text{Perimeter (Pd) }[\mathrm{m\ g}^{-1}]\times m_{cat}[\mathrm{g}]/l_{Pd}[\mathrm{m}]}\end{aligned} \tag{S.2}$$

Surface area (Pd) and *Perimeter (Pd)* are calculated as below. In this explanation, *x* denotes the molar ratio of Zn/Pd (x = 0, 1/9, 1/4, 1).

First, V_{CO}, the amount of CO adsorption per catalyst weight is calculated by CO adsorption amount measured using BELCAT (Microtrac-BEL Japan Inc.) using equation (S.3). Here, V_{chem} is adsorption amount and m is sample weight.

$$V_{CO}[cm^3\cdot g^{-1}] = V_{chem}[cm^3]/m[g] \tag{S.3}$$

A_M, which is metal surface area per supported metal weight is calculated by equation (S.4). V_{STP} is the volume of the gas in the standard state (V_{STP} = 22.4 L/mol), N_A is Avogadro constant ($N_A = 6.022 \times 10^{23}$ [mol^{-1}]) and σ_M is cross-sectional area of one atom. In the case of Pd–Zn, because CO adsorbs only on Pd, we calculated σ_{PdZn} as equation (S.5). c is metal weight supported on sample.

$$A_{Pd-Zn}\left[m^2 \cdot g^{-1}\right] = \frac{(V_{chem}[cm^3]/V_{STP}[L \cdot mol^{-1}]) \times N_A[mol^{-1}] \times \sigma_{Pd-Zn}[m^2]}{c[g]} \tag{S.4}$$

$$\sigma_{Pd-Zn}\left[m^2\right] = \sigma_{Pd}\left[m^2\right] + x\sigma_{Zn}\left[m^2\right] \tag{S.5}$$

The diameter of one metal particle assuming that metal particle as sphere is calculated as below. The surface area of metal per metal weight is calculated by equation (S.6) and the volume of metal per metal weight is calculated by equation (S.7). r is radius of metal particle, α is number of metal particle and ρ_{Pd-Zn} is metal density.

$$\frac{4\pi r^2[m^2] \times \alpha[g^{-1}]}{c[g]} = A_{Pd-Zn}[m^2 \cdot g^{-1}] \tag{S.6}$$

$$\frac{4/3\pi r^3[m^3] \times \alpha[g^{-1}]}{c[g]} = 1/(\rho_{Pd-Zn}[g \cdot cm^{-3}] \times 10^6) \tag{S.7}$$

Thus, d_{Pd-Zn}, diameter of metal particle, is calculated by (S.6)/(S.7).

$$3/r = A_{Pd-Zn}\left[m^2 \cdot g^{-1}\right] \times \rho_{Pd-Zn}[g \cdot cm^{-3}] \times 10^6$$

$$\leftrightarrow r[m] = 3/(A_{Pd-Zn}\left[m^2 \cdot g^{-1}\right] \times \rho_{Pd-Zn}[g \cdot cm^{-3}] \times 10^6) \tag{S.8}$$

$$d_{Pd-Zn}[nm] = 2r = 6000/(A_{Pd-Zn}\left[m^2 \cdot g^{-1}\right] \times \rho_{Pd-Zn}[g \cdot cm^{-3}]) \tag{S.9}$$

The volume of one metal particle, $v_{Pd–Zn}$, and the total volume of supported metal per catalyst weight, $V_{Pd–Zn}$, are calculated as equation (S.10), (S.11) respectively, and the number of metal particle per catalyst 1 g, α, is calculated from $v_{Pd–Zn}$ and $V_{Pd–Zn}$. $m_{Pd–Zn}$ is metal loading weight per catalyst m_{cat} g.

$$v_{Pd–Zn}\,[m^3] = \frac{4}{3}\pi\left(\frac{d_{Pd–Zn}[m]}{2}\right)^3 \times \frac{1}{2} \tag{S.10}$$

$$V_{Pd–Zn}[m^3\,g^{-1}] = \left(\frac{m_{Pd–Zn}}{m_{cat}}\right) \div \rho_{Pd–Zn}[g\,cm^{-1}] \tag{S.11}$$

$$\alpha\,[g^{-1}] = V_{Pd-Zn}[m^3\,g^{-1}]/v_{Pd-Zn}\,[m^3] \tag{S.12}$$

Thus, *Surface area (Pd)* and *Perimeter (Pd)* are calculated as below.

$$\text{Surface area (Pd)}\,[m^2 g^{-1}] = \frac{\pi\big(d_{Pd-Zn}[m]\big)^2}{2} \times \alpha[g^{-1}] \times \frac{\sigma_{Pd}[m^2]}{\sigma_{Pd-Zn}[m^2]} \tag{S.15}$$

$$\text{Perimeter (Pd)}\,[m^2 g^{-1}] = \pi d_{Pd-Zn}[m] \times \alpha[g^{-1}] \times \frac{l_{Pd}[m]}{l_{Pd–Zn}[m]} \tag{S.16}$$

Physical properties of Pd–Zn, $l_{Pd–Zn}$ and $\sigma_{Pd–Zn}$ are estimated as following equation. M is molecular weight of metal.

$$l_{Pd–Zn}[m] = l_{Pd}[m] + x l_{Zn}[m] \tag{S.17}$$

$$\sigma_{Pd–Zn}[m^2] = \sigma_{Pd}[m^2] + x\sigma_{Zn}[m^2] \tag{S.18}$$

$$\rho_{\mathrm{Pd-Zn}}[\mathrm{g\ cm^{-1}}] = \frac{1 + x \times \dfrac{M_{\mathrm{Zn}}[\mathrm{g\ mol^{-1}}]}{M_{\mathrm{Pd}}[\mathrm{g\ mol^{-1}}]}}{\dfrac{1}{\rho_{\mathrm{Pd}}[\mathrm{g\ m^{-3}}]} + \dfrac{x}{\rho_{\mathrm{Zn}}[\mathrm{g\ m^{-3}}]} \times \dfrac{M_{\mathrm{Zn}}[\mathrm{g\ mol^{-1}}]}{M_{\mathrm{Pd}}[\mathrm{g\ mol^{-1}}]}}$$

2. Supplementary Tables and Figures

Table S1 Curve fitting analysis for Pd *K*-edge EXAFS of various samples

Catalyst	Scattering path	C.N.	R / Å	ΔE_{j0} / eV	σ^2 / Å^2	R_f
Pd foil	Pd–Pd	12 (fix)	2.74±0.00	4.38±0.26	0.006	0.003
Pd/CZO	Pd–Pd	10.8±0.4	2.74±0.00	0.13±0.26	0.006	0.003
Pd9Zn1/CZO	Pd–Zn	0.8±0.5	2.64±0.05	1.21±6.20	0.003	0.020
	Pd–Pd	9.5±0.8	2.72±0.01	−0.62±0.62	0.001	
Pd4Zn1/CZO	Pd–Zn	1.1±0.5	2.64±0.04	1.33±4.48	0.001	0.004
	Pd–Pd	8.7±0.7	2.71±0.01	−1.31±0.64	0.008	
Pd1Zn1/CZO	Pd–Zn	6.6±0.6	2.61±0.01	−2.48±1.00	0.007	0.004
	Pd–Pd	3.1±0.6	2.90±0.01	−0.78±1.34	0.009	

k range: 2.5-14, FT range: 1.0-2.8 (1.0-3.0 for Pd1Zn1/CZO), S_0^2: 0.899.

C.N.: coordination number, R: interatomic radius, ΔE_{jo}: adsorption edge shift, σ^2: Debye-Waller factor, R_f; R factor.

To evaluate the local structures of the supported Pd–Zn catalysts, XAFS measurement was performed. Figure S2 portray the law EXAFS oscillations and the corresponding Fourier-transforms of the Pd/CZO and Pd–Zn/CZO catalysts. To investigate the coordination environment of Pd, curve fittings of the EXAFS spectra were conducted (Table S1). With increasing Zn content up to 0.2, the coordination number (C.N.) of the Pd–Pd bond decreased, whereas the C.N. of Pd–Zn increased. The Pd–Pd bond length ($R_{\text{Pd–Pd}}$) was also shortened by addition of Zn. These results indicate that some Pd atoms were replaced by Zn to form Pd–Zn solid-solution alloys. The decreased Pd–Pd bond length is consistent with the lattice shrinkage, as observed from XRD results. For Pd1Zn1/CZO, the C.N. and *R* for Pd–Zn and Pd–Pd scatterings were quite different from those of Pd–Zn alloys, but were consistent with those of intermetallic PdZn (P4/mmm, body centered tetragonal: C.N.$_{\text{Pd–Zn}}$ = 8, $R_{\text{Pd–Zn}}$ = 2.64 Å, C.N.$_{\text{Pd–Pd}}$ = 4, and $R_{\text{Pd–Pd}}$ = 2.89 Å).[2] Consequently, the EXAFS measurements demonstrated the formation of Pd–Zn alloy or intermetallic phase and revealed that Pd–Pd ensembles were diluted by Zn.

Table S2 Catalytic activity over various Pd–Zn catalysts with or without EF

Catalyst	Pd loading amount / wt%	CH_4 conversion / %		Reaction rate / mmol min^{-1}		TOF-s (SR 673 K) / s^{-1}	TOF-p (ER 1.5W) / s^{-1}
		SR (673 K)	ER (1.5 W)	SR (673 K)	ER (1.5 W)		
Pd/CZO	1	3.50	8.21	0.0130	0.0325	0.290	32.0
	5	8.74	11.2	0.0367	0.0435	0.310	29.7
Pd9Zn1/CZO	5	6.22	19.6	0.0232	0.0753	0.140	31.9
Pd4Zn1/CZO	5	0.419	13.0	0.00170	0.0525	0.0100	32.7
Pd1Zn1/CZO	1	0.00	9.81	0	0.0391	0	50.3
	3	0.00	9.18	0	0.0386	0	48.1
	5	0.00	5.70	0	0.0256	0	49.6
Zn/CZO	1	0.00	0.39	0	0.0015	No data	No data

CH_4:H_2O:Ar = 1:2:7, total 100 SCCM; preset temperature, 423 K (ER) and 673 K (SR); input power 1.5 W.

Table S3 Calculation of Pd surface area and Pd perimeter of prepared catalysts by CO pulse measurement

□Catalyst	Pd loading amount / wt%	CO adsorption amount / cm^3 g^{-1}	$d_{Pd\text{-}Zn}$ / nm	Pd surface area / m^2 g^{-1}	Pd perimeter / 10^7 m g^{-1}
Pd/CZO	1	0.125	18.8	0.286	2.88
	5	0.332	35.4	0.712	4.02
Pd9Zn1/CZO	5	0.398	27.1	1.00	6.61
Pd4Zn1/CZO	5	0.329	31.8	0.921	4.50
Pd1Zn1/CZO	1	0.085	16.6	0.193	2.30
	3	0.137	28.4	0.340	2.38
	5	0.149	45.6	0.352	1.54

In the case of ER, catalyst-bed temperature measured using a thermocouple increased from 423 K to about 550 K by Joule heat of the imposed electric field (1.5 W). However, at such low temperatures, the reaction did not proceed without the electric field. Therefore, the effect of Joule heating by the electric field is unimportant in the system.

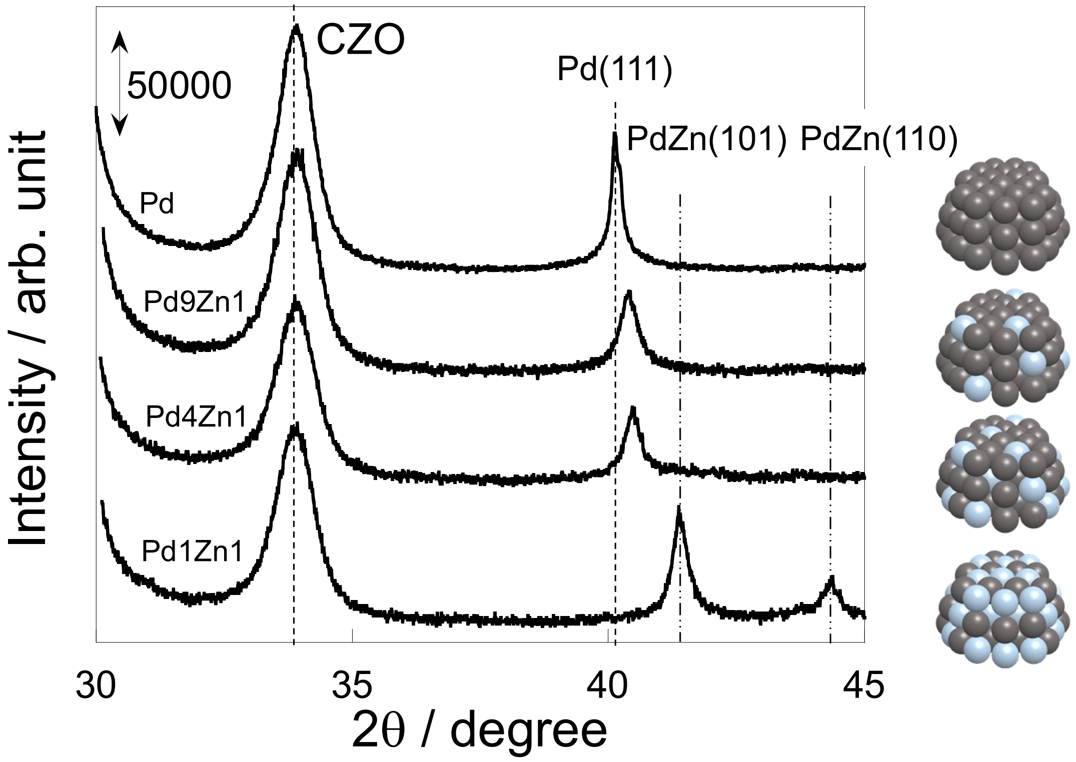

Figure S1. XRD patterns of Pd-Zn alloy supported on CZO with various Pd/Zn ratios: Pd loading amount, 5wt%.

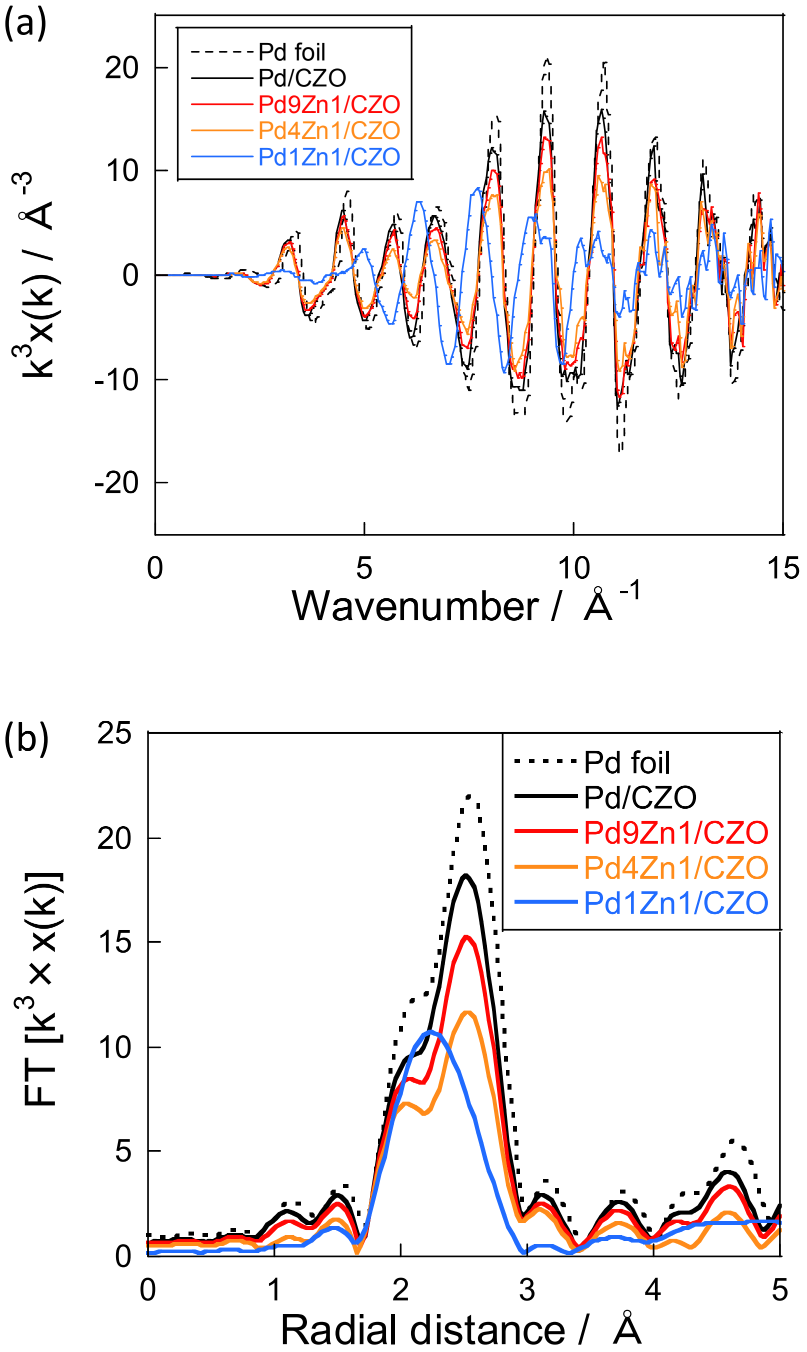

Figure S2. (a) k^3-weighted and (b) Fourier-transformed Pd *K*-edge EXAFS spectra of Pd–Zn/CZO catalysts: Pd loading amount, 5 wt%.

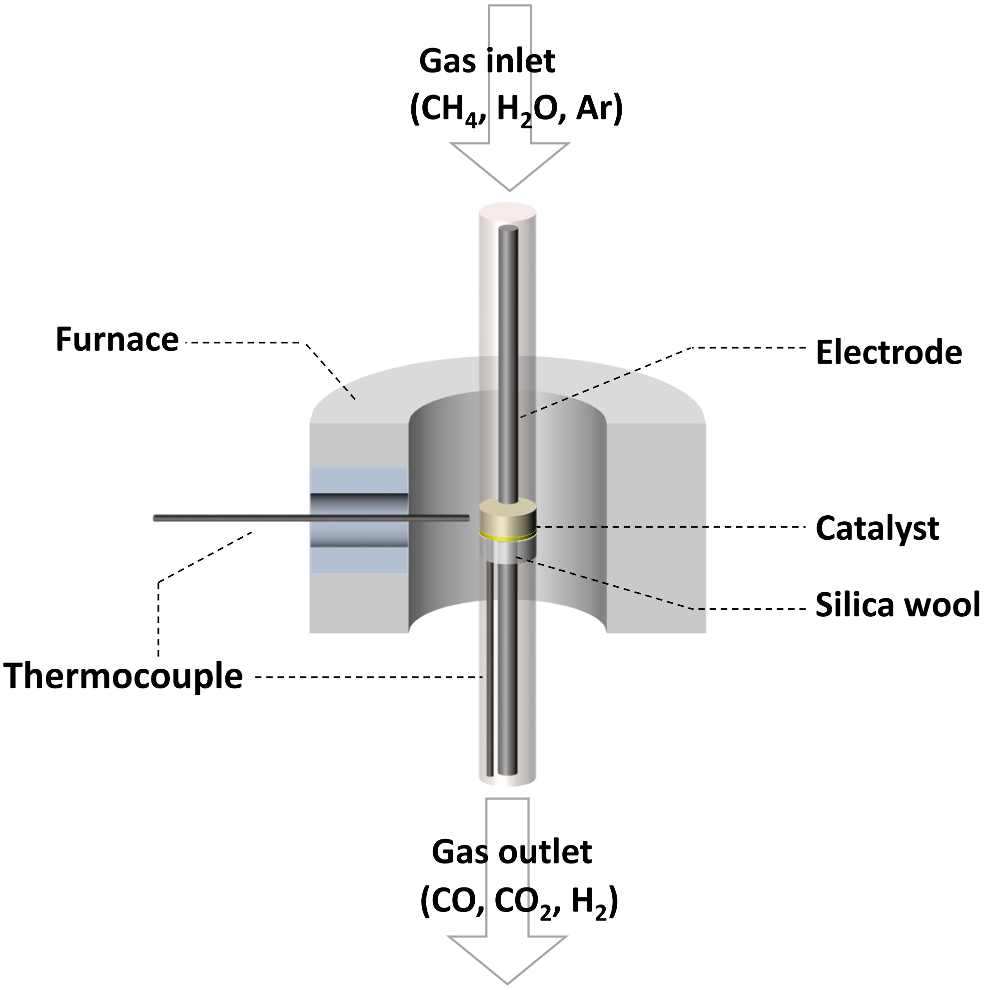

Figure S3. Schematic diagram of reactor.

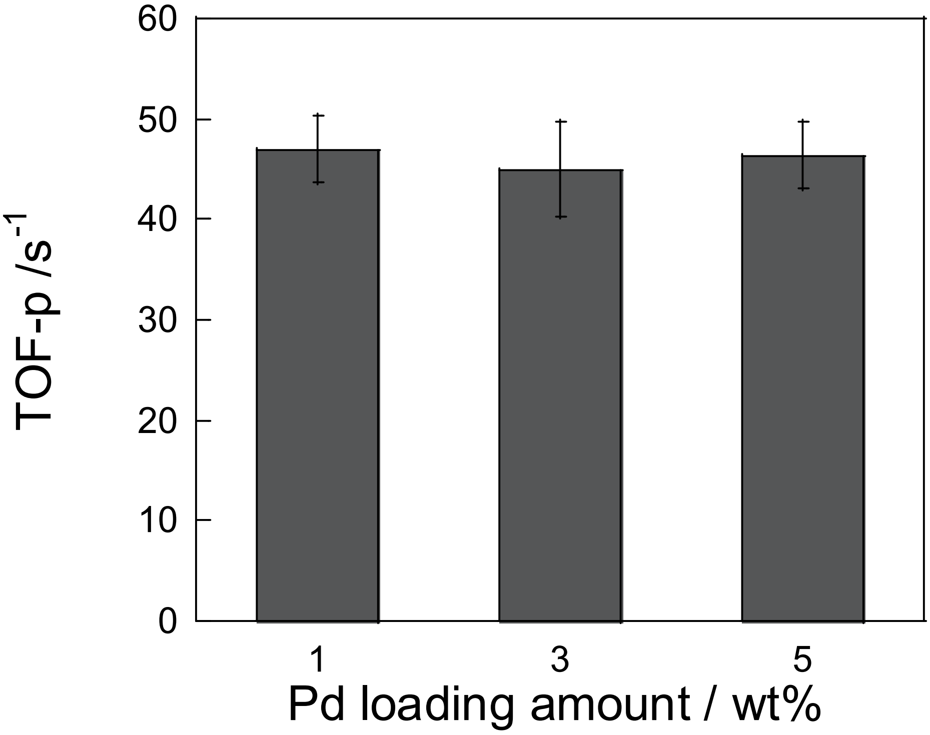

Figure S4 Effects of Pd loading amount of Pd1Zn1/CZO on turnover frequency calculated based on Pd perimeter (TOF-p) in an electric field: Reactant gas, CH_4:H_2O:Ar = 1:2:7, total flow rate 100 SCCM; furnace temperature, 423 K; input power, 1.5 W.

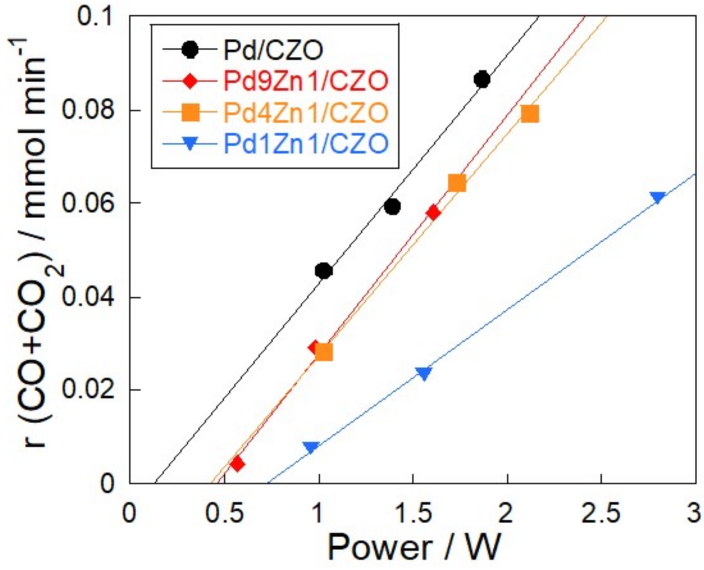

Figure S5. Input power dependence of the catalytic activity with an electric field over 5wt%Pd–Zn/CZO with various Zn/Pd ratios: Reactant gas, CH_4:H_2O:Ar = 1:2:7, total flow rate 100 SCCM; furnace temperature, 423 K; input current, 3-7 mA.

Figure S5 shows the relationship between CO+CO_2 formation rate and input power. As shown in figure S5, the formation rate linearly depends on input power.

ABBREVIATIONS

SR : catalytic steam reforming of methane without an electric field

ER : catalytic steam reforming of methane with an electric field

c : metal weight supported on sample [g]

d_{Pd-Zn} : diameter of metal particle [cm]

r : radius of metal particle [m]

l_M : bond length of metal M [cm]

m : sample weight [g]

m_{cat} : catalyst weight [g]

m_{Pd-Zn} : loading weight of metal supported on catalyst m_{cat} g [g]

M_M : molecular weight of metal M

N_A : Avogadro constant [mol^{-1}] (6.022×10^{23} [mol^{-1}])

V_{CO} : CO adsorption amount on sample m g [cm^3]

V_{chem} : the amount of CO adsorption per catalyst 1 g [cm^3 g^{-1}]

V_{STP} : the volume of the gas in the standard state [L/mol] (22.4 L/mol)

v_{Pd-Zn} : volume of one metal particle [m^3]

V_{Pd-Zn} : total volume of supported metal per catalyst 1 g [m^3 g^{-1}]

α : number of particles per catalysts 1 g [g^{-1}]

ρ_M : density of metal M [g cm^{-3}]

σ_M : cross-sectional area of one atom [m^2]

3. Reference

1 A. Gondo, R. Manabe, R. Sakai, K. Murakami, T. Yabe, S. Ogo, M. Ikeda, H. Tsuneki and Y. Sekine, *Catal. Lett.,* 2018, **148**, 1929–1938.

2 A. P. Tsai, S. Kameoka and Y. Ishii, *J. Phys. Soc. Jpn.,* 2004, **73**, 3270–3273.