Electronic Supplementary Information (ESI)

Ambient-temperature Oxidative Coupling of Methane in an Electric Field by a Cerium Phosphate Nanorod Catalyst

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1. Experimental Procedures

Preparation of monoclinic CePO₄ by a hydrothermal method

$CePO_4$ with a monoclinic structure was prepared by a hydrothermal method according to the published procedure.[1] $Ce(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_2HPO_4$ were dissolved in distilled water and stirred for 1 h at room temperature. The P/Ce molar ratio in the mixed solution was 1. The resulting solution was added into a stainless-steel autoclave with a Teflon vessel liner, and then heated at 453 K for 96 h. After cooling the autoclave to room temperature, the precipitates were collected by filtration and washed with distilled water. Then the resulting solid was calcined at 1173 K for 3 h in air.

Activity test

Activity tests were conducted with a fixed-bed flow type reactor equipped with a quartz tube (4.0 mm i.d.).[2] The catalyst was sieved to 355–500 μm, and then 100 mg of it was charged into the reactor. The reactant gas were methane, oxygen and argon with the ratio of $CH_4:O_2:Ar = 15:12:33$ and the total gas flow rate was 60 SCCM. The contact time (W/F$_{CH4}$) was 2.49 g$_{cat}$ h mol^{-1}. For the reaction in the electric field, two stainless steel electrodes (2.0 mm o.d.) were inserted to each end of the catalyst-bed. A thermocouple was inserted into bottom of the catalyst-bed to measure the catalyst-bed temperature. The electric field was controlled using a constant current (7.0 mA) with a DC power supply. The profiles of the applied voltage and current were monitored using an oscilloscope (TDS 2001C; Tektronix Inc.). The catalytic reaction with the electric field was conducted at ambient temperature. In the reaction without the electric field, the furnace temperature was varied 573–1073 K. The product gas through a cold trap was analyzed by using a GC-FID (GC-2014s; Shimadzu Corp.) with a Porapak N column and a hand-made methanizer (Ru/Al_2O_3) and a GC-TCD (GC-2014s; Shimadzu Corp.) with a molecular sieve 5A packed column. The respective calculation formulae for CH_4 conversion, O_2 conversion, C_2 yield and C_2 selectivity are shown below (eqs. S1–S4):

$$CH_4 \text{ Conversion (\%, C-based)} = \frac{\text{Carbon moles of (CO, CO}_2\text{, C}_2\text{H}_6\text{, C}_2\text{H}_4\text{, and C}_2\text{H}_2\text{)}}{\text{Carbon moles of input methane}} \times 100 \quad \text{(eq. S1)}$$

$$O_2 \text{ Conversion (\%)} = \frac{\text{Consumption moles of O}_2}{\text{Input oxygen moles}} \times 100 \quad \text{(eq. S2)}$$

$$C_2 \text{ Yield (\%, C-based)} = \frac{\text{Carbon moles of (C}_2\text{H}_6\text{, C}_2\text{H}_4\text{, and C}_2\text{H}_2\text{)}}{\text{Carbon moles of input methane}} \times 100 \quad \text{(eq. S3)}$$

$$C_2 \text{ Selectivity (\%, C-based)} = \frac{C_2 \text{ Yield}}{CH_4 \text{ Conversion}} \times 100 \quad \text{(eq. S4)}$$

Periodic Operation Test

Periodic operation test was conducted to investigate the active oxygen species on the catalyst surface in the following four steps.[2] In the first step, oxygen and argon (O_2:Ar = 5:50, total flow rate 55 SCCM) were supplied to the reactor with the electric field for 10 min in order to create the active oxygen species on the catalyst surface. In the second step, oxygen in the gas phase of the reactor was removed by argon purge (total flow rate 100 SCCM) without the electric field. In the third step, methane and argon (CH_4:Ar = 5:50, total flow rate 55 SCCM) was supplied to the reactor with the electric field for 12 min to evaluate the reaction between methane and the active oxygen species on the catalyst surface. As the final step, argon purge (100 SCCM) was conducted for 20 min without the electric field to remove all residual gases. The above four steps were repeated several times. Product gases were analyzed at 5 min after oxygen and argon supply, and at 30 second intervals until 12 min after methane and argon supply. The reaction temperature was 473 K or 1073 K for the reaction with or without the electric field, respectively. The imposed current was set at 3.0 mA. The amount of consumed active oxygen species was calculated based on the following equations (eqs. S5–S9). It was assumed that C_2 hydrocarbons and CO_x were produced accompanying with H_2O and H_2 formations, respectively. It was confirmed that calculated H_2 yield, as estimated from CO_x yield based on equations S8 and S9, was almost identical to observed H_2 yield in the activity tests.

$$2CH_4 + \tfrac{1}{2}O_2 \rightarrow C_2H_6 + H_2O \quad \text{(eq. S5)}$$

$$2CH_4 + O_2 \rightarrow C_2H_4 + 2H_2O \quad \text{(eq. S6)}$$

$$2CH_4 + \tfrac{3}{2}O_2 \rightarrow C_2H_2 + 3H_2O \quad \text{(eq. S7)}$$

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad \text{(eq. S8)}$$

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \quad \text{(eq. S9)}$$
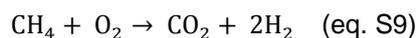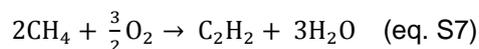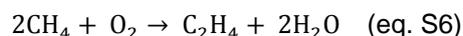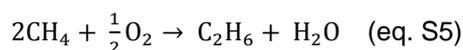
Characterizations

The crystalline structure was characterized using powder X-ray diffraction (Smart Lab III; Rigaku Corp.) operating at 40 kV and 40 mA with Cu $K\alpha$ radiation. HAADF-STEM observations were performed using an aberration-corrected transmission electron microscope (JEM-ARM 200F; JEOL Ltd) operated at 80 kV. Surface oxygen species on $CePO_4$ catalyst was characterized using a Raman spectrometer (NRS-4500; JASCO Corp.). The excitation line (λ) was 532 nm. The resolution was 3.58 cm^{-1}. The Raman spectra were recorded at ambient temperature after O_2 treatment for 10 min at 473 K in the electric field and reaction with CH_4 for 15 min at 473 K in the electric field.

Calculations for surface Ce site

The experimental and structural parameters for monoclinic $CePO_4$ (P_21/n, ICSD 79748) used for the calculation was as follows: specific surface area (S_{BET} = 37 m^2 g^{-1}), Lewis acid site amount measured using pyridine-IR (A_L = 96 μmol g^{-1}),[1] Avogadro constant (N_A = 6.02 ×10^{23} mol^{-1}), a = 6.788 Å, b = 7.0163 Å, c = 6.468 Å, β = 103.43⁰. The surface Ce cations at (110) and (100) facets are assumed to be exposed coordinatively unsaturated Ce cations, and the amounts were estimated according to the following equations (eqs. 10-12).

The amount of surface Ce cations (A_{Ce}/nm^{-2})

Experimental

$$A_{Ce} = \frac{A_L \times 10^{-6} \times N_A}{S_{BET} \times 10^{18}} \times 100 = 1.6 \text{ nm}^{-2} \quad \text{(eq. S10)}$$

Calculated (110) facet

$$A_{Ce} = \frac{1}{(\sqrt{a^2 \sin^2 \beta + b^2} \times c) \times 10^{-2}} = 1.6 \text{ nm}^{-2} \quad \text{(eq. S11)}$$

Calculated (100) facet

$$A_{Ce} = \frac{1}{b \times c \times 10^{-2}} \times 100 = 2.2 \text{ nm}^{-2} \quad \text{(eq. S12)}$$

Areal density of Ce ions: $A_{Ce}[ions/nm^2] = \dfrac{Number\ density\ per\ unit\ surface: \rho_{Ce}[ions]}{Area\ of\ unit\ (hkl)\ surface: S_{hkl}\ [nm^2]}$

Area of parallelogram: $S = a \times b \times \sin\theta$
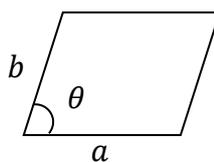
$$S_{110} = \sqrt{a^2 + b^2} \times c \times \sqrt{\frac{a^2 \sin^2 \beta + b^2}{a^2 + b^2}} = \sqrt{a^2 \sin^2 \beta + b^2} \times c$$

$$S_{100} = b \times c \times \sin 90° = b \times c$$
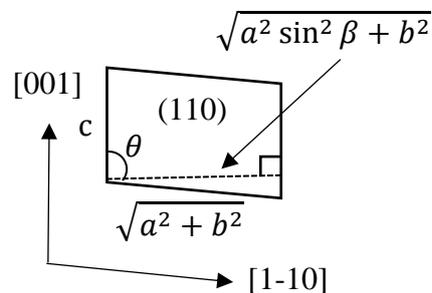
2. Supplementary Tables and Figures

Table S1. Catalytic activity of cerium-based catalysts for oxidative coupling of methane at ambient temperature in an electric field.[a]

Catalyst	Voltage / V	T_{tc} [b] / K	Conversion / %		Selectivity / %					C_2 Selectivity / %	C_2 Yield / %	Field intensity / V mm^{-1}
			CH_4	O_2	C_2H_6	C_2H_4	C_2H_2	CO	CO_2			
$CePO_4$	800	542	62	66	2.1	5.8	21	62	10	29	18	96
$Ce_2(WO_4)_3$	500	480	15	20	2.1	4.3	12	67	15	19	2.8	123
$Ce_2(MoO_4)_3$	700	538	29	36	3.1	5.9	11	71	9	20	5.8	101
$CeVO_4$	800	533	2.1	8.0	1.2	0.8	0.0	73	25	2.0	0.0	123
CeO_2	200	519	37	94	0.3	0.1	0.0	0.4	99	0.4	0.1	39

[a] CH_4:O_2:Ar = 15:12:33, total flow rate 60 SCCM; catalyst weight, 100 mg; furnace temperature, without external heating (299 K); time on stream, 20 min; Current, 7 mA.

[b] T_{tc}: catalyst-bed temperature measured using a thermocouple.

Table S2. Effect of reaction field on catalytic activity of $CePO_4$.[a]

Condition	Furnace temp. / K	T_{tc} [b] / K	Conversion / %		Selectivity / %					C_2 Selectivity / %	C_2 Yield / %
			CH_4	O_2	C_2H_6	C_2H_4	C_2H_2	CO	CO_2		
with EF (7 mA)	Without heating	542	62	66	2.1	5.8	21	62	10	29	18
without EF	573	568	0.0	1.9	0.0	0.0	0.0	64	36	0.0	0.0
	673	669	0.1	3.3	0.0	0.0	0.0	27	73	0.0	0.0
	773	771	0.7	4.9	0.0	0.0	0.0	14	86	0.0	0.0
	873	894	36	91	0.5	0.6	0.0	23	76	1.1	0.4
	973	986	41	99	1.1	1.5	0.0	25	72	2.6	1.1
	1073	1081	47	99	1.5	2.2	0.0	25	71	3.8	1.8

[a] CH_4:O_2:Ar = 15:12:33, total flow rate 60 SCCM; catalyst weight, 100 mg.

[b] T_{tc}: catalyst-bed temperature measured using a thermocouple.
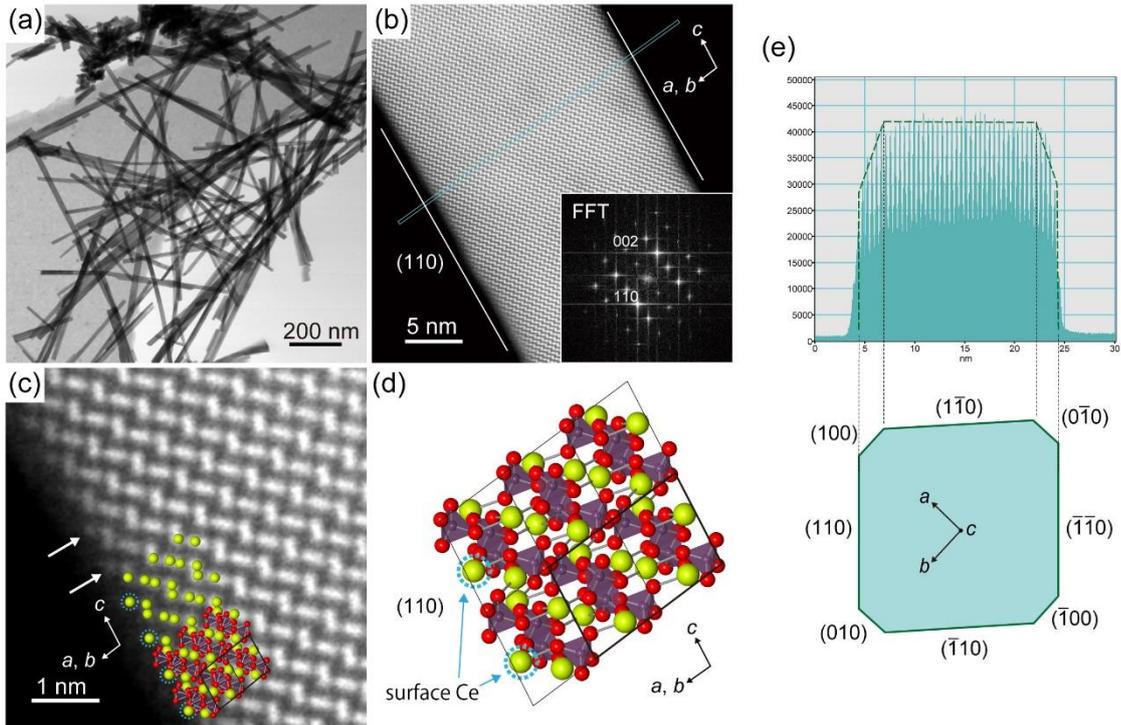
Figure S1. (a) The BF-STEM image of monoclinic CePO$_4$ nanorods and (b) the HAADF-STEM image of the single CePO$_4$ nanorod viewed from [1$\bar{1}$0] direction (the same image of Fig. 1(a)). (c) The magnified image of the (110) side surface in the image (b) with projected monoclinic CePO$_4$ crystal structure from [1$\bar{1}$0] direction (d). The surface Ce ion columns were denoted by white arrows. (e) The intensity profile along the blue line in the image (b) and estimated side facets of the nanorod by the intensity profile.
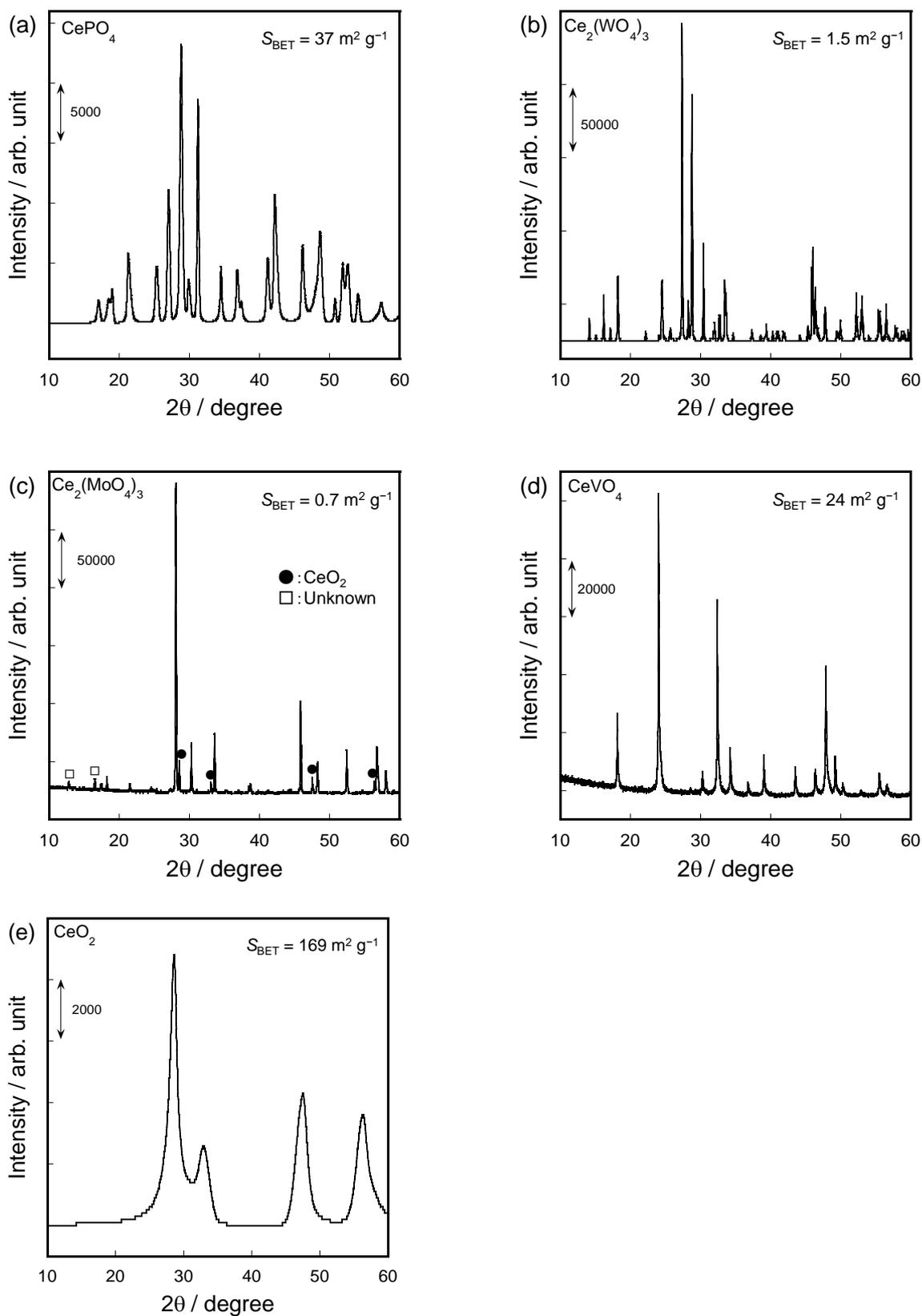
Figure S2. XRD patterns and BET surface area of (a) $CePO_4$, (b) $Ce_2(WO_4)_3$, (c) $Ce_2(MoO_4)_3$, (d) $CeVO_4$ and (e) CeO_2.

Although $Ce_2(MoO_4)_3$ contains small amount of CeO_2 and unknown phase, the other catalysts were the single phase.
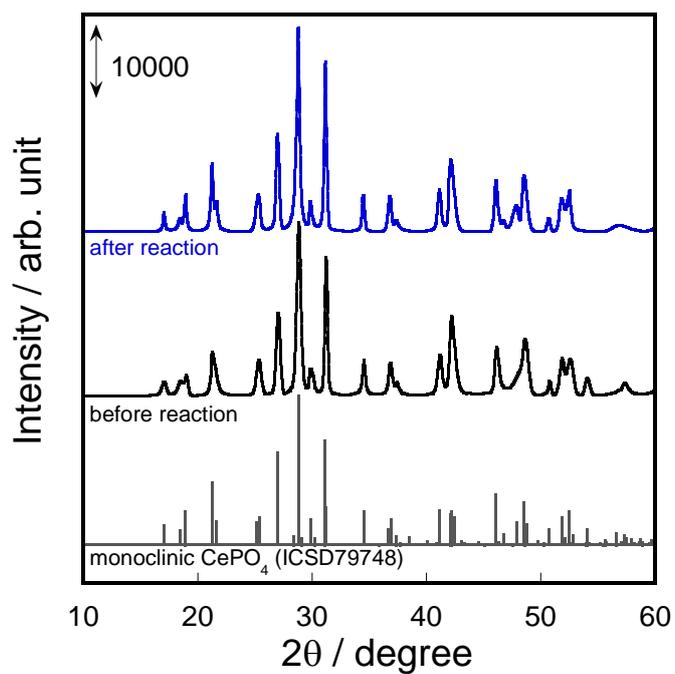
Figure S3. XRD patterns of CePO$_4$ before and after reaction with electric field.
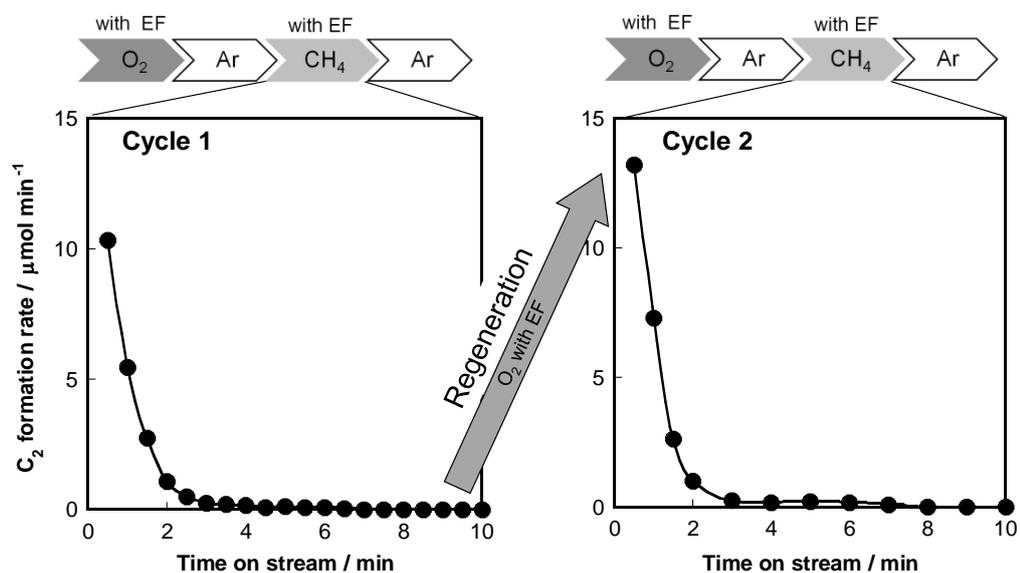
Figure S4. Time course of formation rate of C$_2$ hydrocarbons during methane supply over CePO$_4$ catalyst in the electric field.
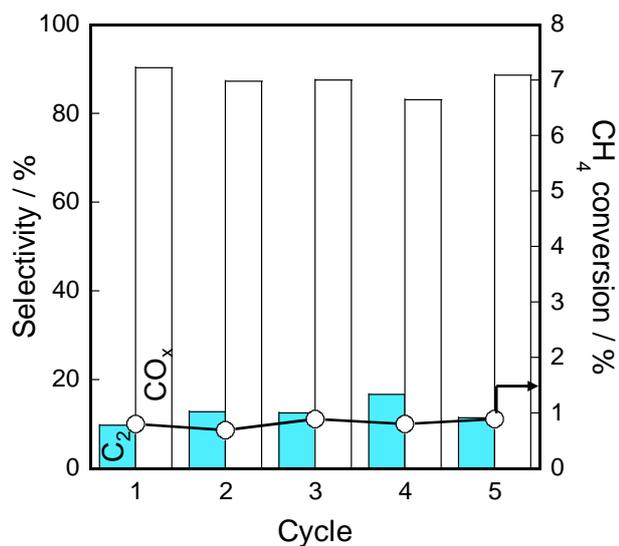
Figure S5. Results of periodic operation tests after 2 min of CH_4 supply over $CePO_4$ catalyst without the electric field at 1073 K: (light blue bar) C_2 selectivity; (white bar) CO_x selectivity; (-○-) CH_4 conversion.
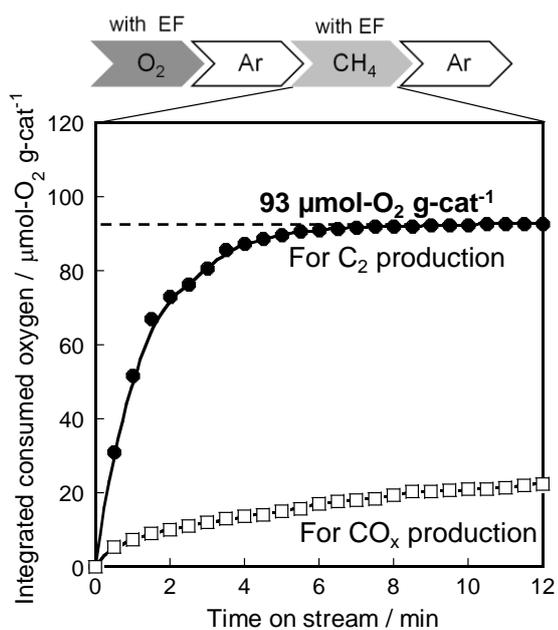
Figure S6. Integrated consumed active oxygen species during methane supply over $CePO_4$ catalyst in the electric field after O_2 pretreatment in the electric field.
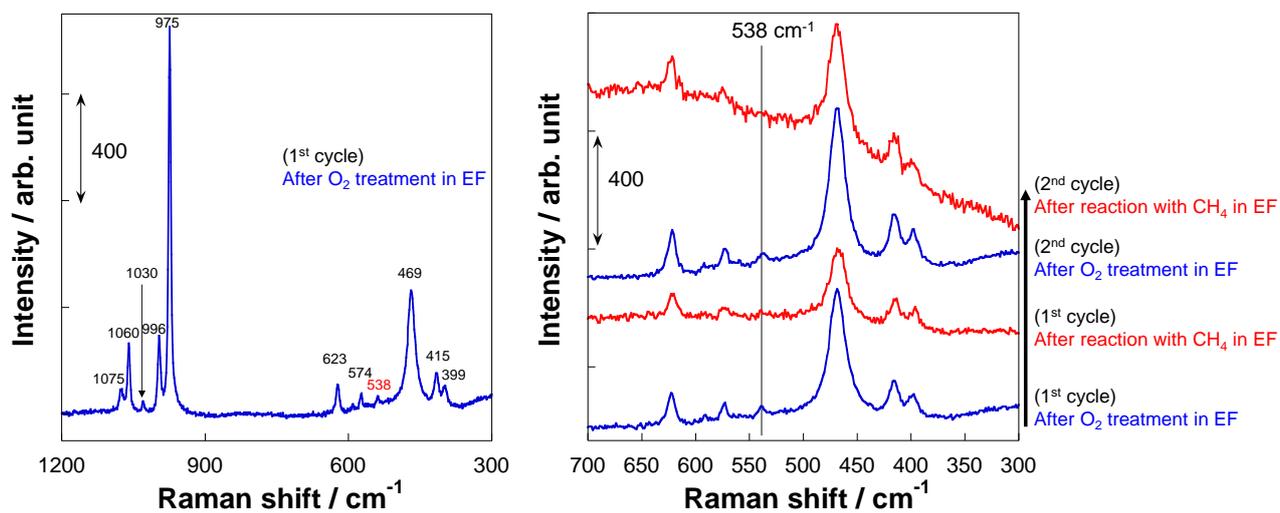
Figure S7. Raman spectra of CePO$_4$ after O$_2$ treatment and reaction with CH$_4$.

The bands at 399, 415, 469, 574 and 623 cm^{-1} were assigned to the bending vibration of PO$_4$ tetrahedral of monoclinic CePO$_4$ structure according to literatures.[3,4] And the bands at 975, 996, 1030, 1060, and 1075 cm^{-1} were assigned to the stretching vibration of PO$_4$ tetrahedral of monoclinic CePO$_4$ structure according to literatures.[3,4] The Raman band at 538 cm^{-1} appeared after the O$_2$ treatment in the electric field while it completely disappeared after the reaction with CH$_4$ in the electric field. It has been reported that the Ce–O bands of active oxygen species on CeO$_2$ are observed in the range of 340–540 cm^{-1}.[3–7] Therefore, the 538 cm^{-1}-band would be related to active oxygen species on CePO$_4$.
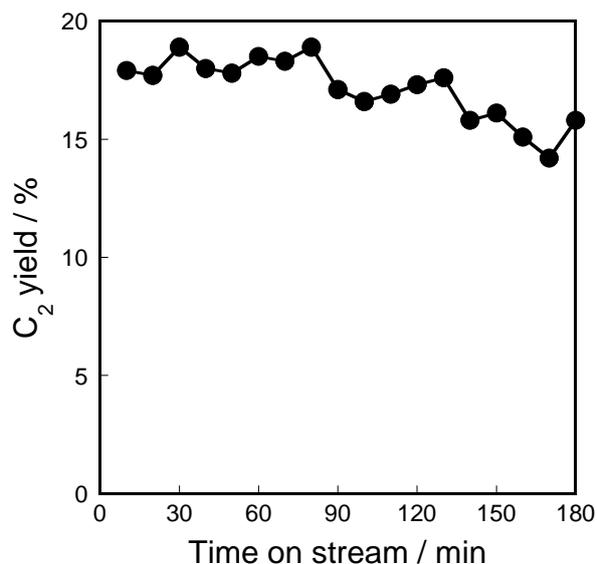
Figure S8. Durability test over CePO$_4$ at ambient temperature in the electric field: CH$_4$:O$_2$:Ar = 15:12:33, total flow rate 60 SCCM; catalyst, 100 mg; current, 7.0 mA; furnace temperature, without heating (299 K).

Figure S8 shows result of durability test over CePO$_4$ for 3 h in the electric field at ambient-temperature. The relative C$_2$ yield ratio at 180 min with respect to the initial stage (Y$_{180}$/Y$_{10}$ = C$_2$ yield at 180 min/C$_2$ yield at 10 min) of CePO$_4$ was 0.89. On the other hand, as shown in Figure 2, C$_2$ hydrocarbon yield over other catalysts became almost zero by 60 min of the reaction. Thus, CePO$_4$ has durability in the electric field at ambient-temperature.

3. References

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