Electronic Supplementary Information

Conversion of methane to C_2 and C_3 hydrocarbons over TiO_2/ZSM-5 core-shell particles in an electric field

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Supplementary experimental procedure

Preparation of silicalite-1

Colloidal silica (Cataloid SI-30, 30.5 wt% SiO_2, JGC Catalysts and Chemicals Ltd.) and de-ionized water were mixed and stirred for 5 min. Then, aqueous NaOH solution (40 wt%) was added to the solution, and stirred for further 5 min. Next, tetrapropylammonium bromide (TPABr) was added into the solution as a structure-directing agent (SDA), and the mixture was stirred gently for 40 min. The mixture with a molar composition 1.0 SiO_2−0.103 NaOH−0.10 TPABr−40.5 H_2O was taken into a 125-mL Teflon®-lined stainless-steel autoclave and kept statically at 175 ºC for 24 h in a convection oven. The autoclave was taken out of the convection oven and cooled in an ice bath for 30 min. The obtained solid was recovered by filtration, washed several times with de-ionized water until the pH of the liquid phase reached around 7 and then dried overnight at 100 ºC in a convection oven.

To remove SDA, the as-synthesized silicalite-1 was calcined at 500 ºC for 5 h in a muffle furnace with 2 ºC min^{-1} of a ramping rate. After cooling to room temperature, the white powder was obtained as calcined silicalite-1.

Isotopic oxygen exchange experiment

The $^{16}O_2$/$^{18}O_2$ isotopic oxygen exchange experiments at 150 °C in an electric field was conducted using a quadrupole mass spectrometer (QGA; Hiden Analytical Ltd.). The TiO_2(mc)/ZSM-5_800 and TiO_2_800 samples were sieved to 355−500 μm and 100 mg of it was inserted into the reactor. The MS signals of m/z = 32($^{16}O_2$), 34 ($^{16}O^{18}O$), and 36 ($^{18}O_2$) were recorded. For the transient isothermal isotopic oxygen exchange experiment in an electric field, the sample was pretreated with $^{16}O_2$-containing gas ($^{16}O_2$: Ar = 5:55; total flow rate, 60 cm^3 (SATP) min^{-1}) at 150 °C with an electric field. After turning off the electric field, $^{18}O_2$-containing gas ($^{18}O_2$: Ar = 5:55; total flow rate, 60 cm^3 (SATP) min^{-1}) was fed until it reached plateau (ca. 10 min). The electric field (6 mA) was imposed (ca. 5 min), and then it was turning off. After that, the reaction gas was switched to the $^{16}O_2$-containing gas and the same procedure was repeated (ON/OFF of the electric field).

Supplementary Figures

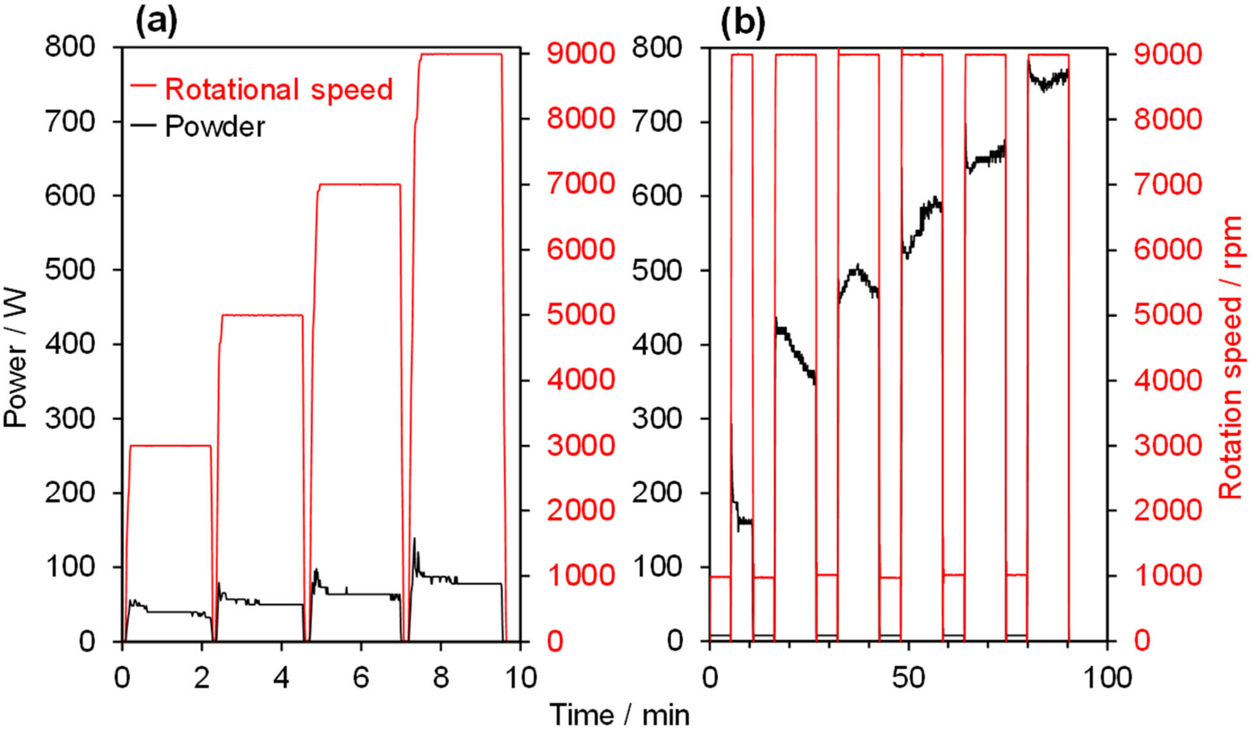

Figure S1. Time courses for the rotational speed of blades in a high performance powder processing machine and the power output (a) without any powders, and (b) with TiO_2 and ZSM-5.

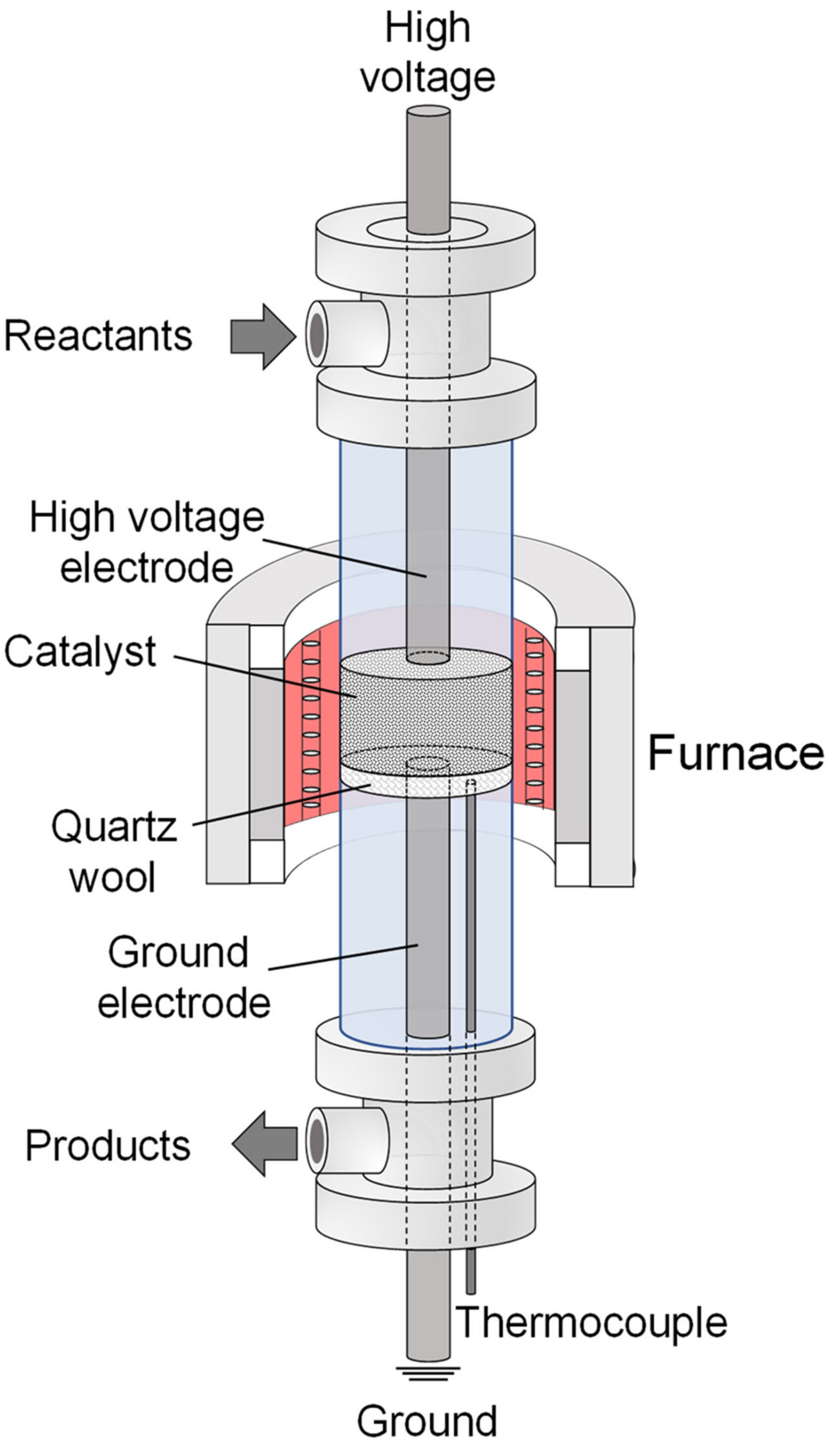

Figure S2. Schematic illustration of the reaction system.

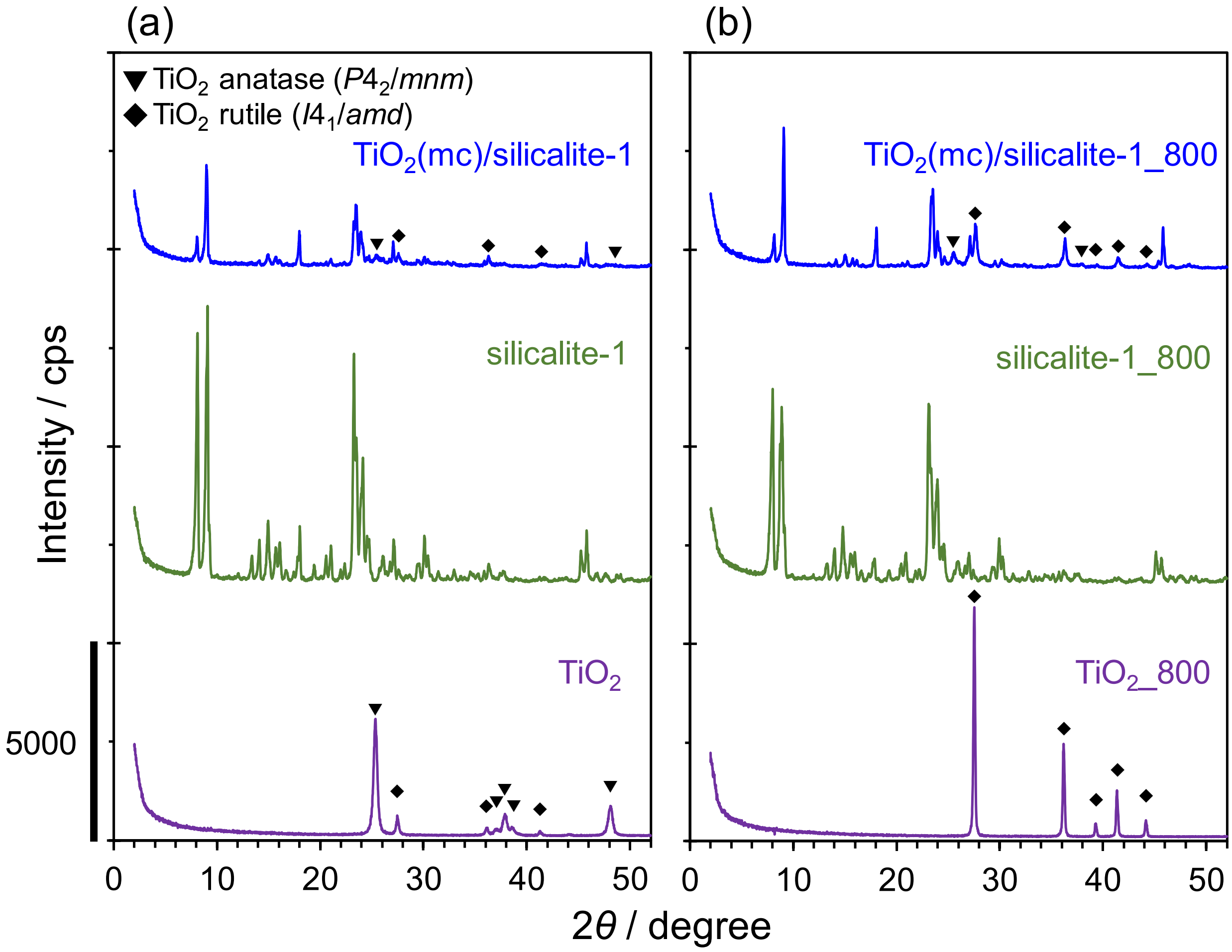

Figure S3. Powder XRD patterns of (a) pristine and (b) thermally-treated samples at 800 °C.

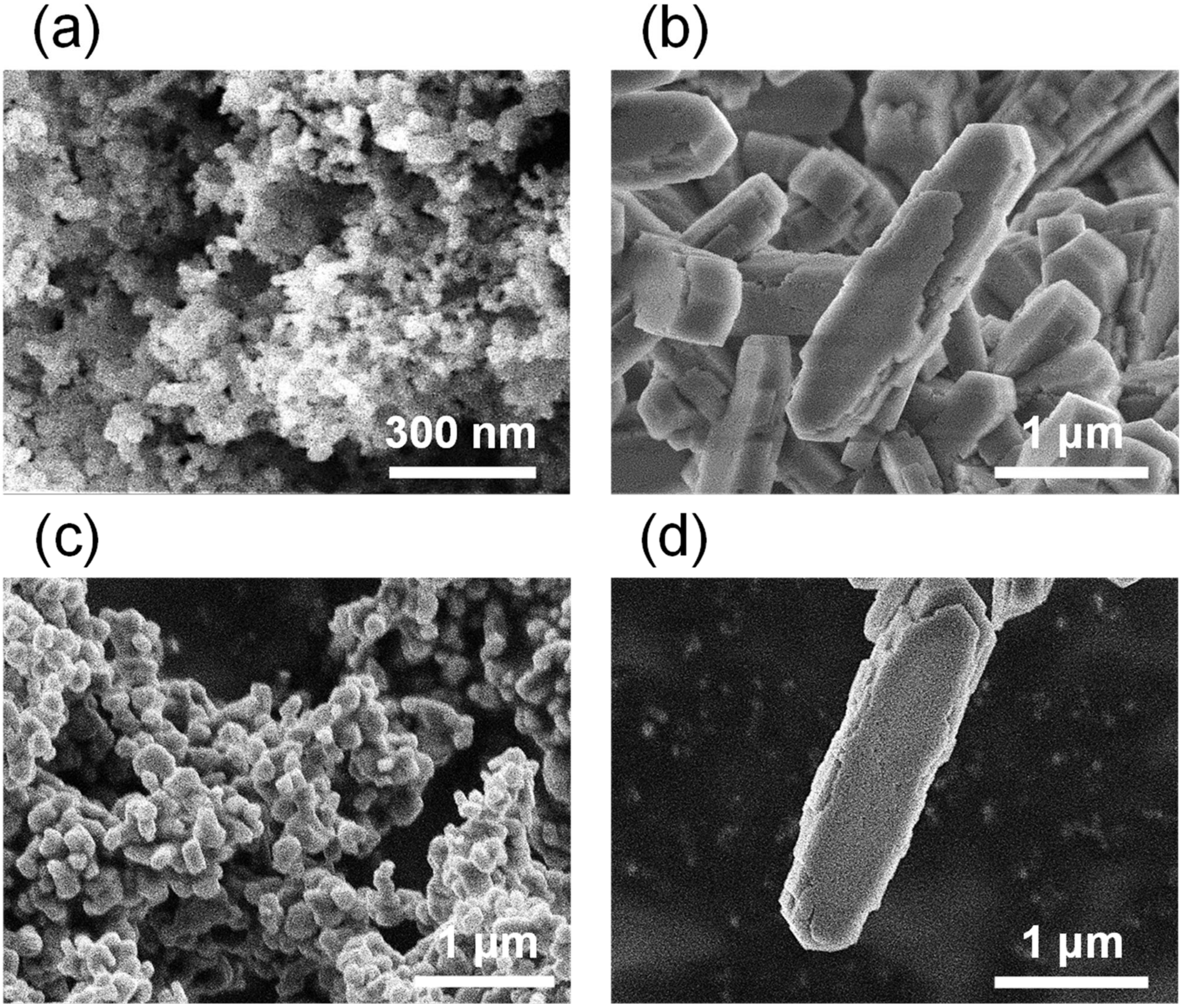

Figure S4. FE-SEM images of (a) TiO_2, (b) ZSM-5, (c) TiO_2_800, and (d) ZSM-5_800.

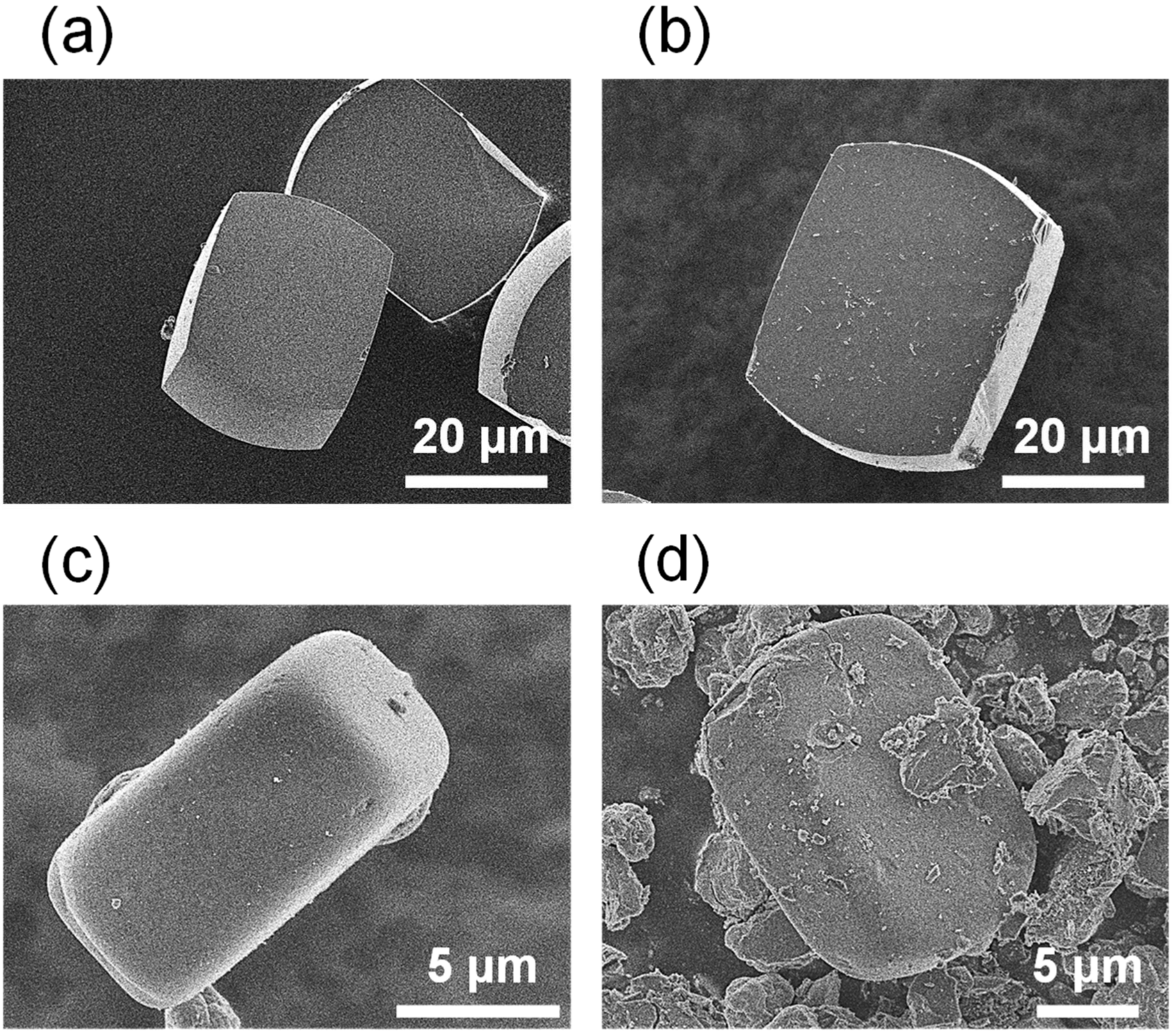

Figure S5. FE-SEM images of (a) silicalite-1, (b) silicalite-1_800, (c) TiO_2(mc)/silicalite-1, and (d) TiO_2(mc)/silicalite-1_800.

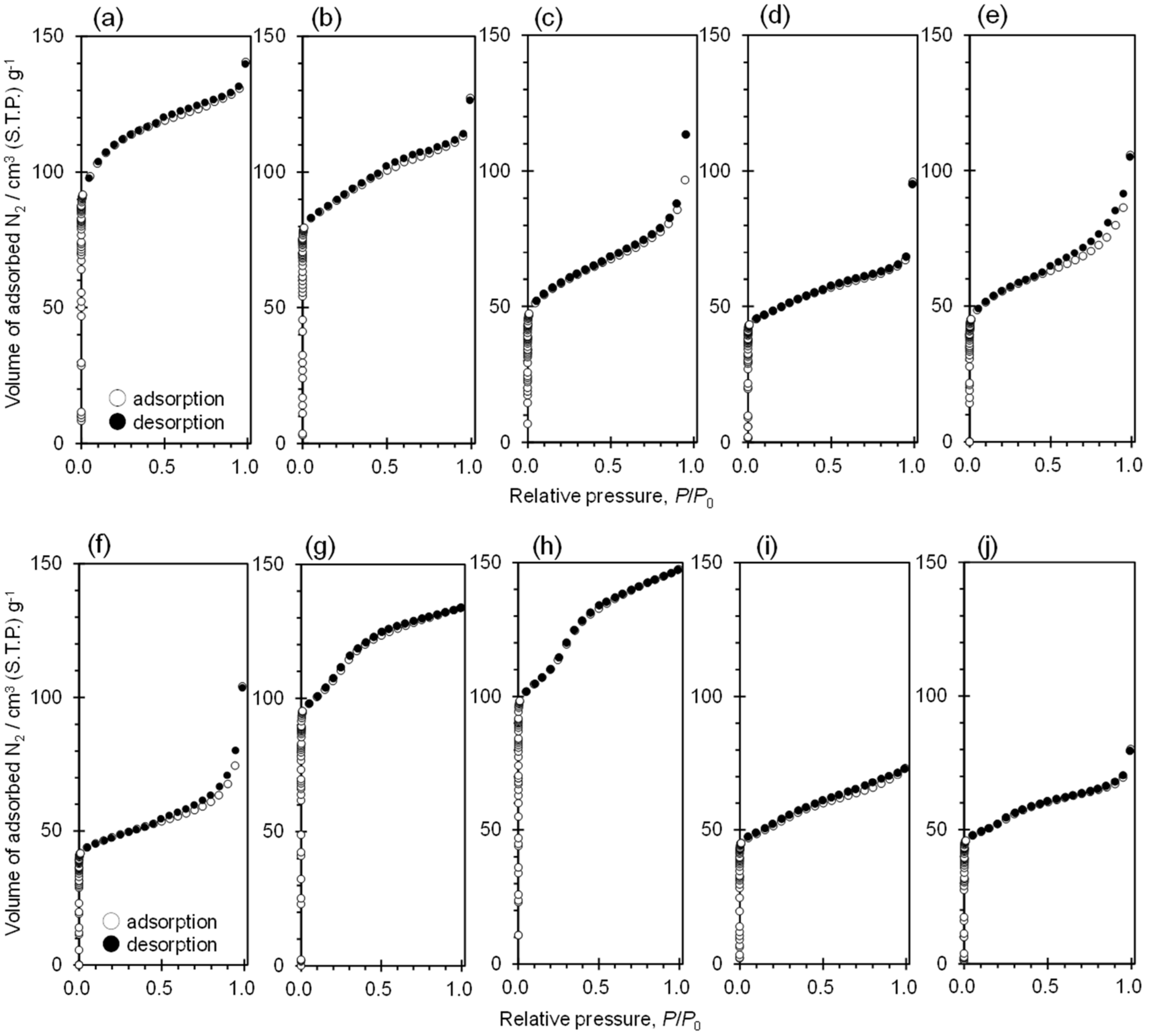

Figure S6. Nitrogen adsorption−desorption isotherms for (a) ZSM-5, (b) ZSM-5_800, (c) TiO_2(pm)/ZSM-5, (d) TiO_2(pm)/ZSM-5_800, (e) TiO_2(mc)/ZSM-5, (f) TiO_2(mc)/ZSM-5_800, (g) silicalite-1, (h) silicalite-1_800, (i) TiO_2(mc)/silicalite-1, and (j) TiO_2(mc)/silicalite-1_800.

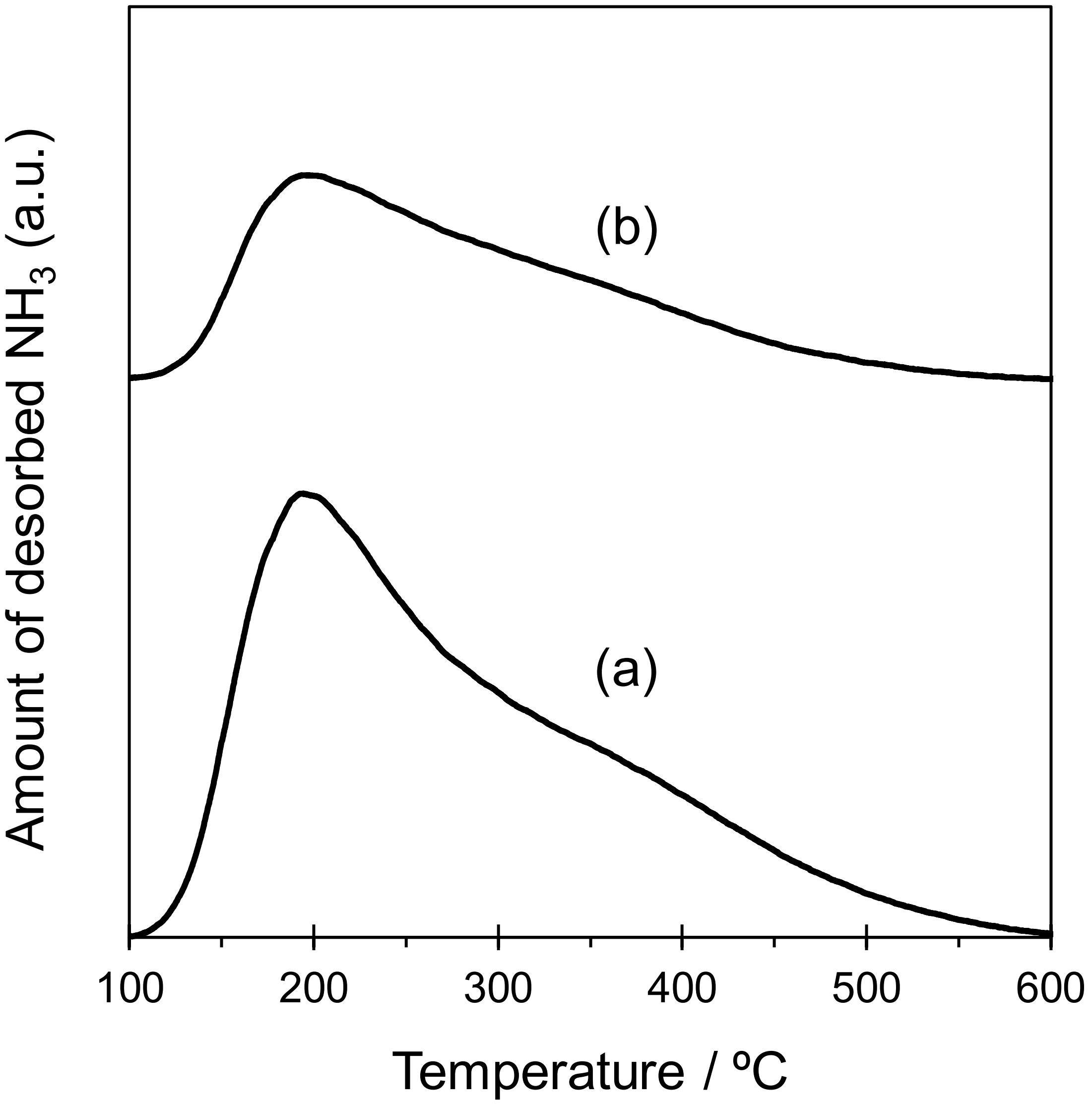

Figure S7. NH_3-TPD profiles of (a) ZSM-5_800 (50 mg) and (b) TiO_2(mc)/ZSM-5_800 (50 mg).

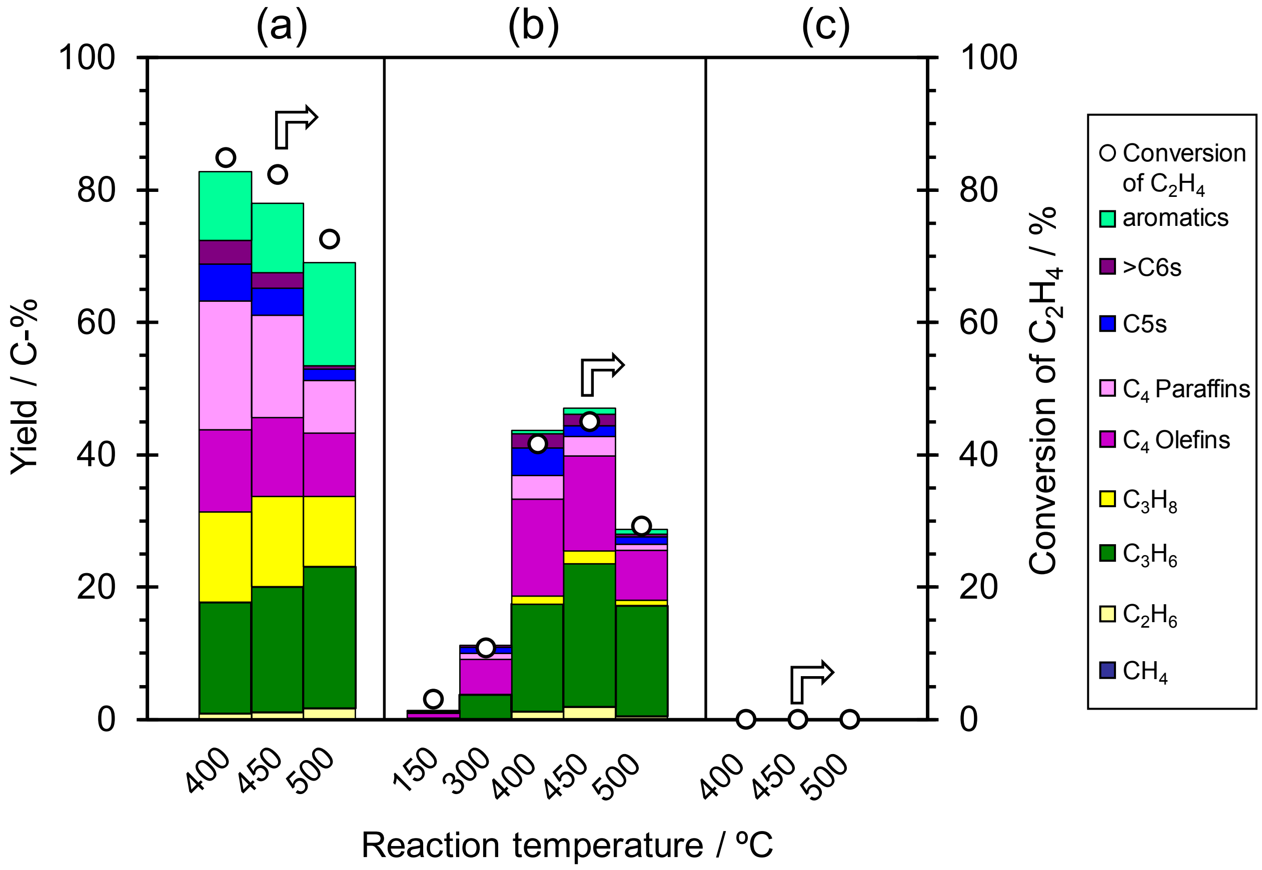

Figure S8. The product yield and conversion of ethylene over (a) ZSM-5, (b) TiO_2(mc)/ZSM-5_800, and (c) TiO_2(mc)/silicalite-1_800 for the ETP reaction at 150, 300, 400, 450 and 500 °C.
Reaction conditions: feed gas, C_2H_4:He = 2.5:27.5 cm^3 (SATP) min^{-1}; $W_{zeolite}/F_{ethylene}$, 16.4 g-cat. h mol^{-1}; time on stream, 5 min.
Pretreatment conditions: temperature, 550 °C; period, 60 min; air flow rate, 30 cm^3 (SATP) min^{-1}.

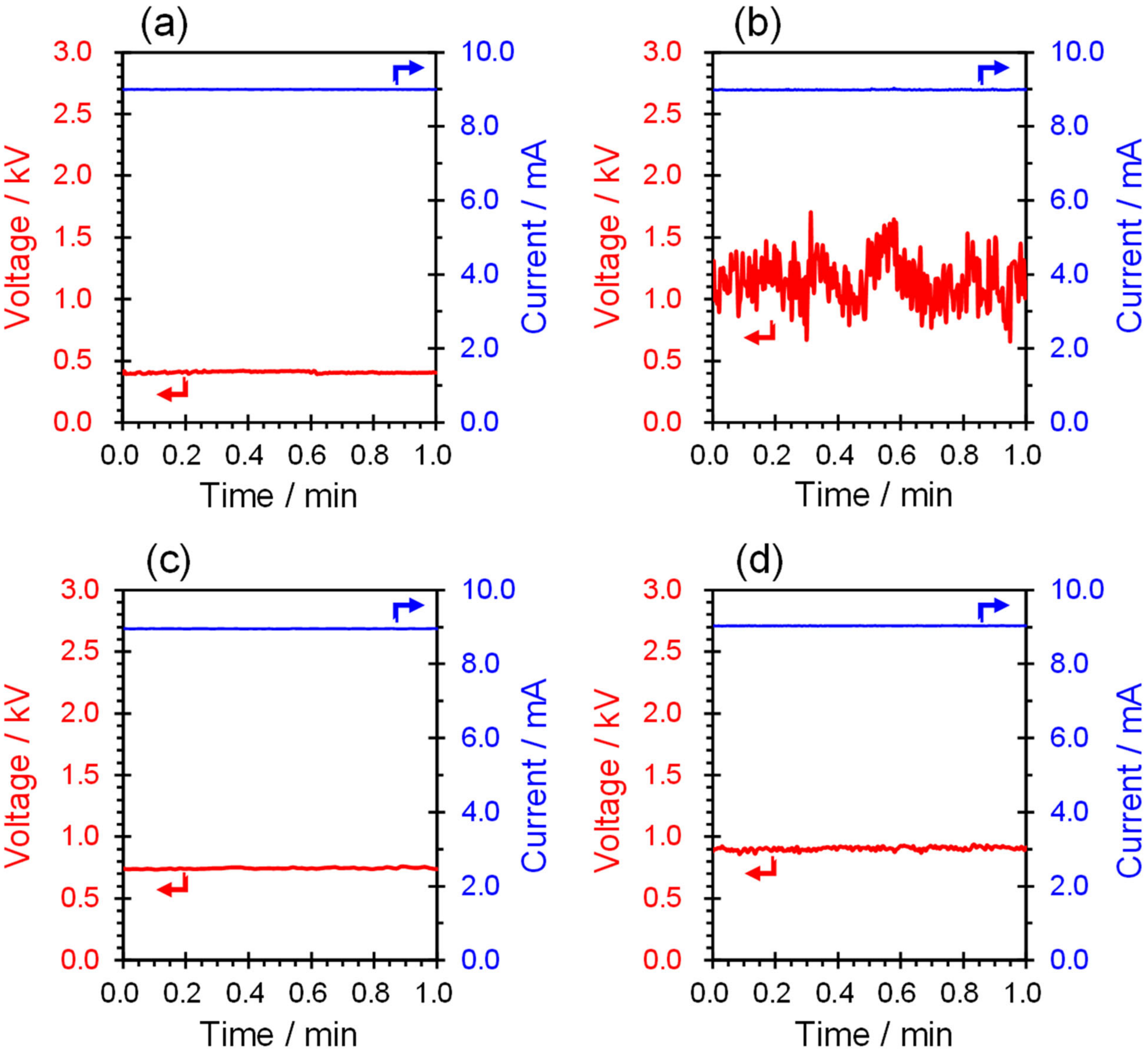

Figure S9. Typical time courses of the voltage and the current for catalyst beds composed of (a) TiO_2, (b) TiO_2(pm)/ZSM-5_800, (c) TiO_2(mc)/ZSM-5_800, and (d) TiO_2(mc)/silicalite-1_800.
Reaction conditions: input current, 9 mA; catalyst, 100 mg; feed gas, CH_4:O_2:Ar = 25:15:60 cm^3 (SATP) min^{-1}; preset furnace temperature, 150 °C.
Pretreatment conditions: temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm^3 (SATP) min^{-1}.

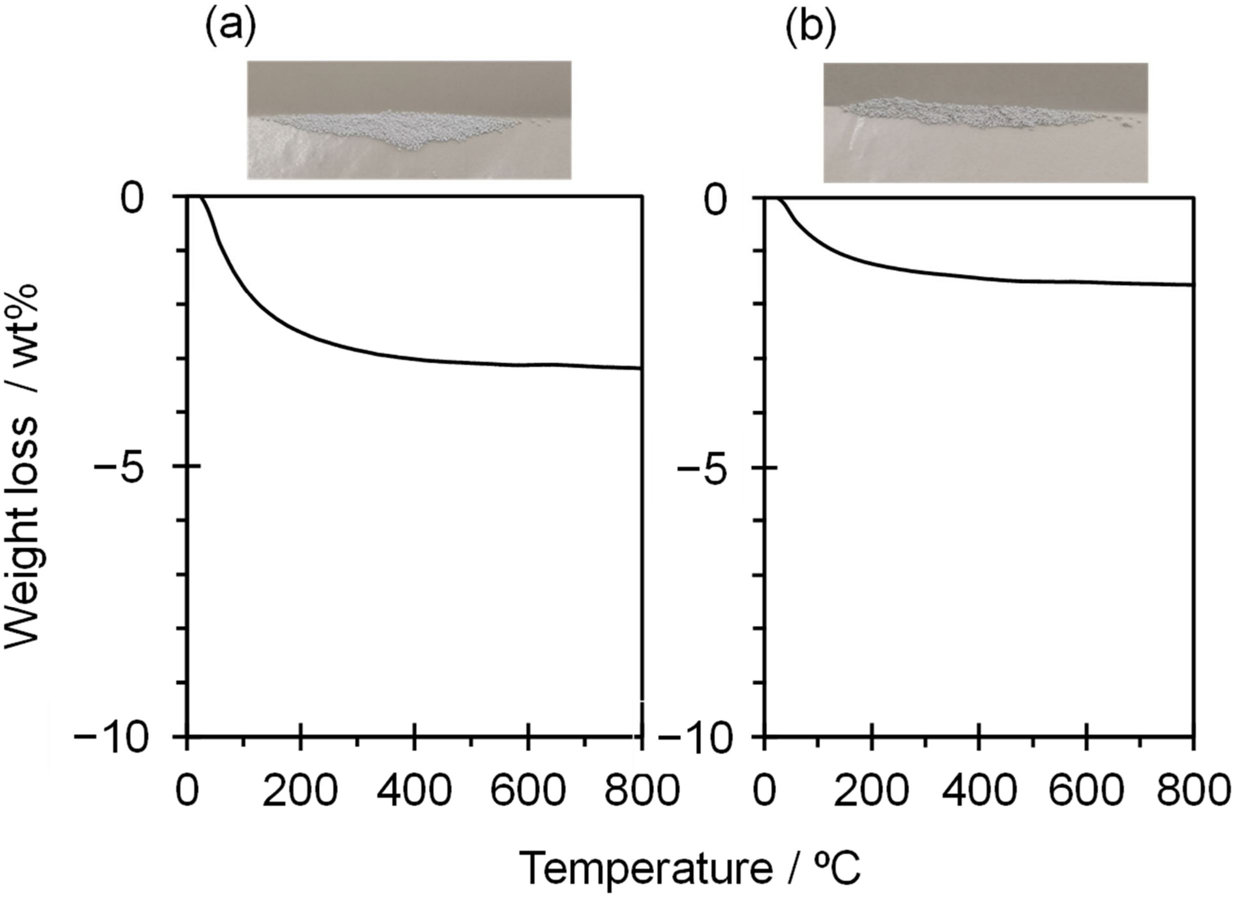

Figure S10. TG-DTA profiles and the photos of TiO_2(mc)/ZSM-5_800 (a) before and (b) after OCM reaction under application of an electric field.

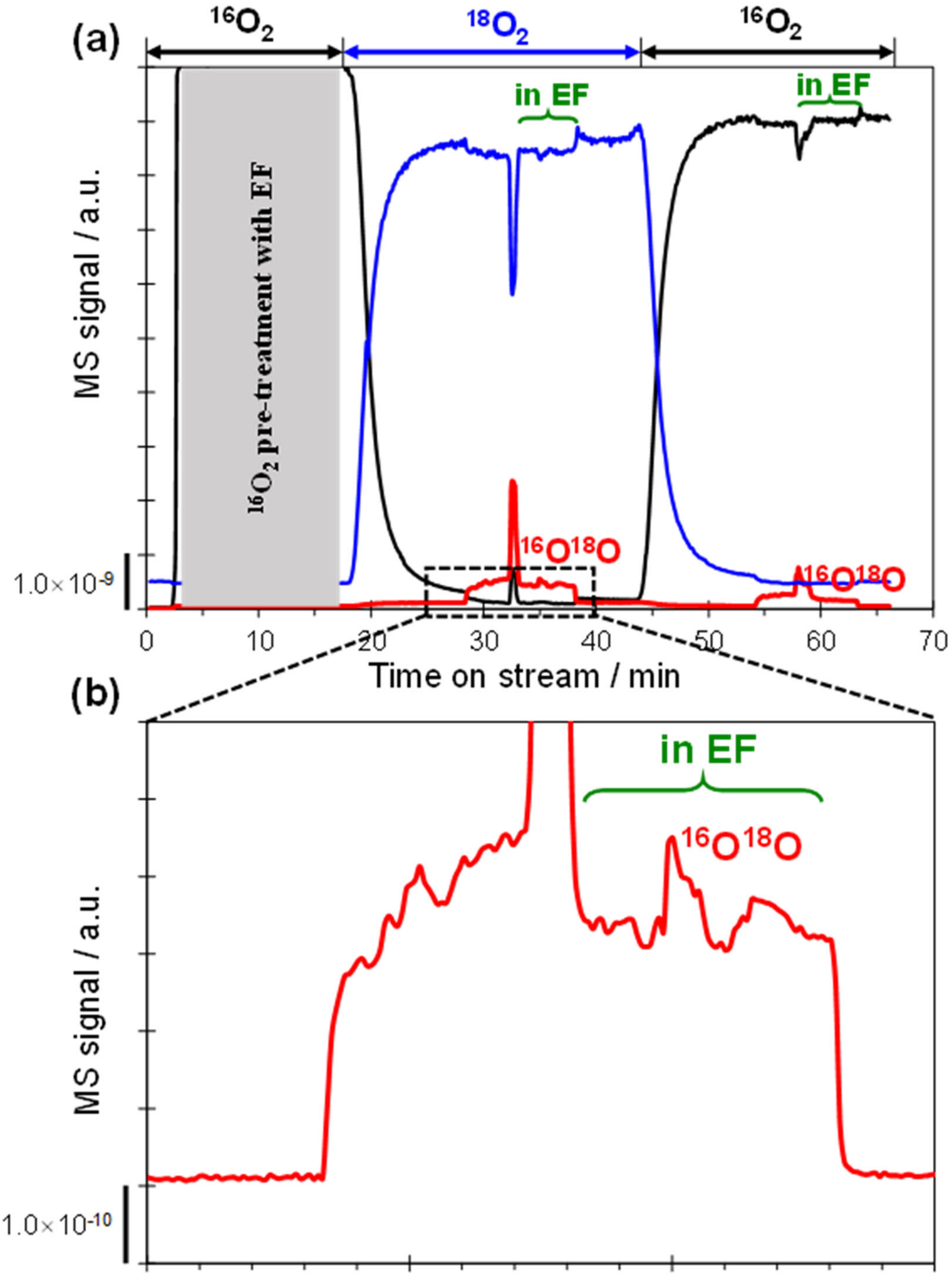

Figure S11A. (a) A full-range view and (b) a magnified view of the changes in MS signals of $^{16}O_2$ (black line), $^{16}O^{18}O$ (red line), and $^{18}O_2$ (blue line) during isotopic oxygen exchange experiments over TiO_2(mc)/ZSM-5_800 at 150 °C in an electric field.

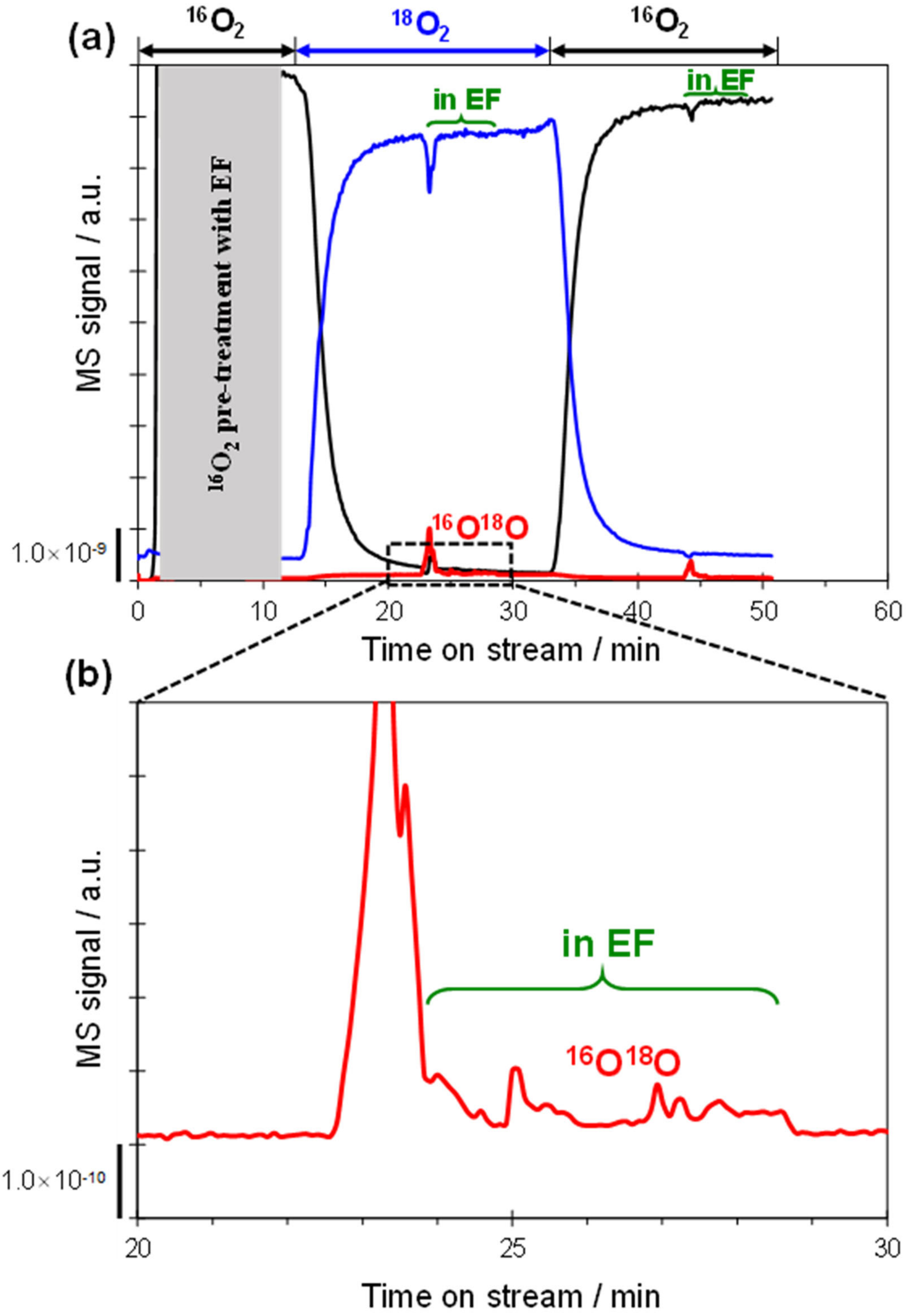

Figure S11B. (a) A full-range view and (b) a magnified view of the changes in MS signals of $^{16}O_2$ (black line), $^{16}O^{18}O$ (red line), and $^{18}O_2$ (blue line) during isotopic oxygen exchange experiments over TiO_2_800 at 150 °C in an electric field.

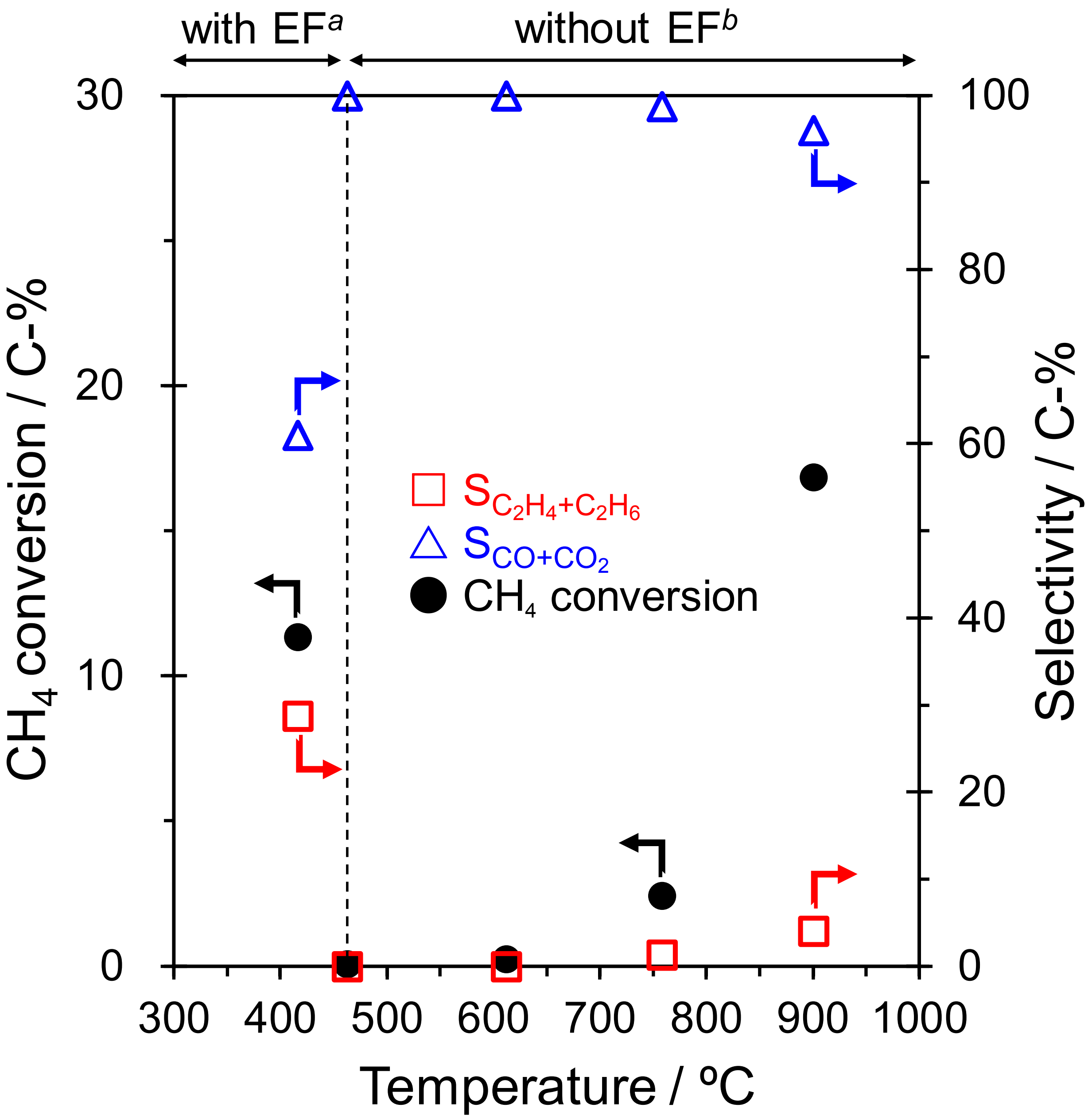

Figure S12. Influence of an electric field on the catalytic activity of TiO_2(mc)/ZSM-5_800. The selectivity of products and conversion of methane in the OCM reaction over TiO_2(mc)/ZSM-5_800 with or without an electric field are plotted.

Reaction conditions:

[a]catalyst, 100 mg; preset furnace temperature, 150 °C; input current, 6.0 mA; feed gas, CH_4:O_2:Ar = 25:15:60 cm^3 (SATP) min^{-1}.

[b]catalyst, 100 mg; preset furnace temperature, 450, 600, 750, 900 °C; feed gas, CH_4:O_2:Ar = 25:15:60 cm^3 (SATP) min^{-1}.

Pretreatment conditions: furnace temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm^3 (SATP) min^{-1}.

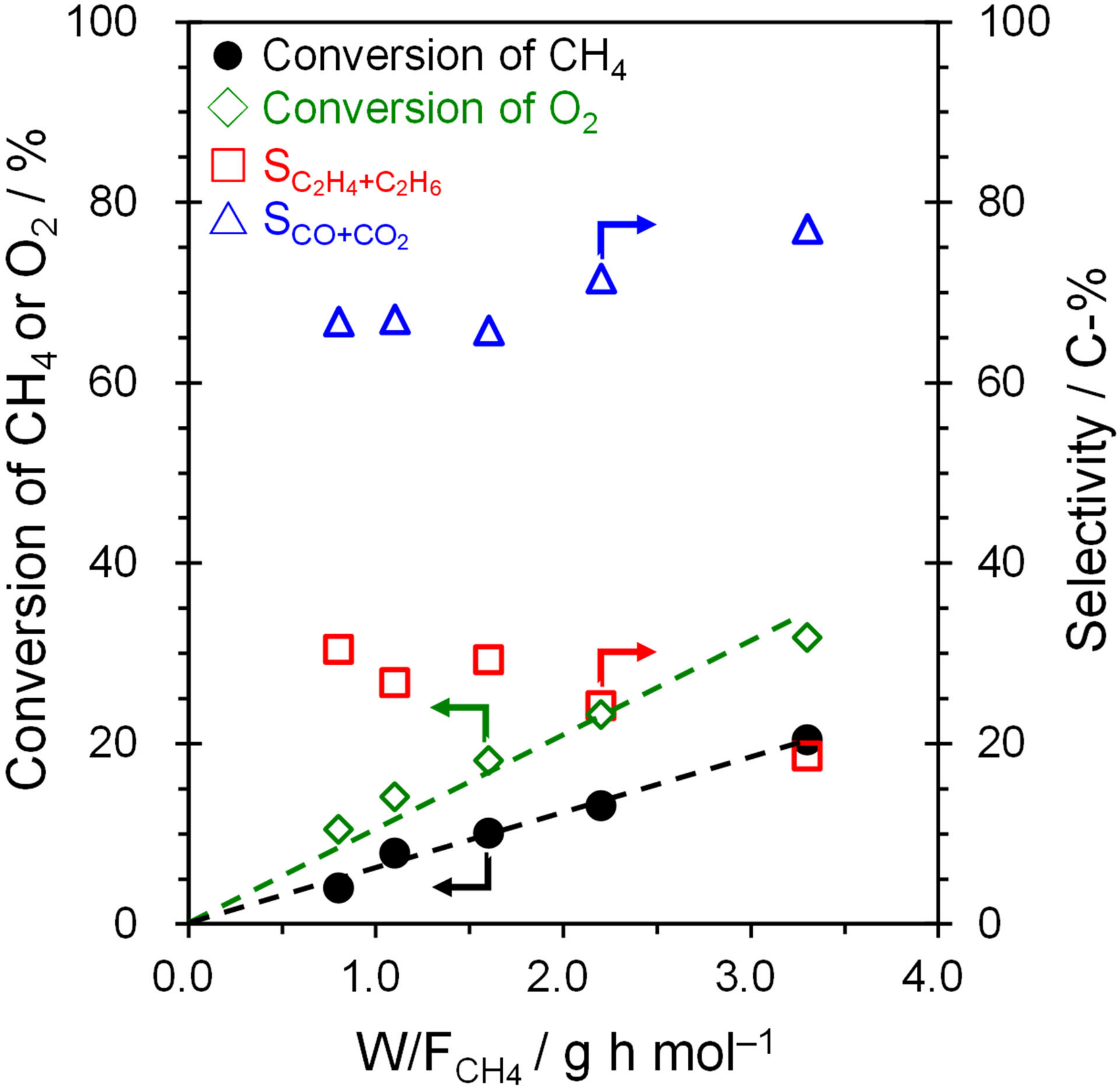

Figure S13. Influence of $W/F_{methane}$ on the catalytic activity for OCM over TiO_2(mc)/ZSM-5_800 under application of an electric field.

Reaction conditions: catalyst, 100 mg; input current, 7.0 mA; feed gas, $CH_4:O_2:Ar = 5x:3x:12x$ (total flow rate: 50, 75, 100, 150, 200 cm^3 (SATP) min^{-1}); preset furnace temperature, 150 °C.

Pretreatment conditions: temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm^3 (SATP) min^{-1}.

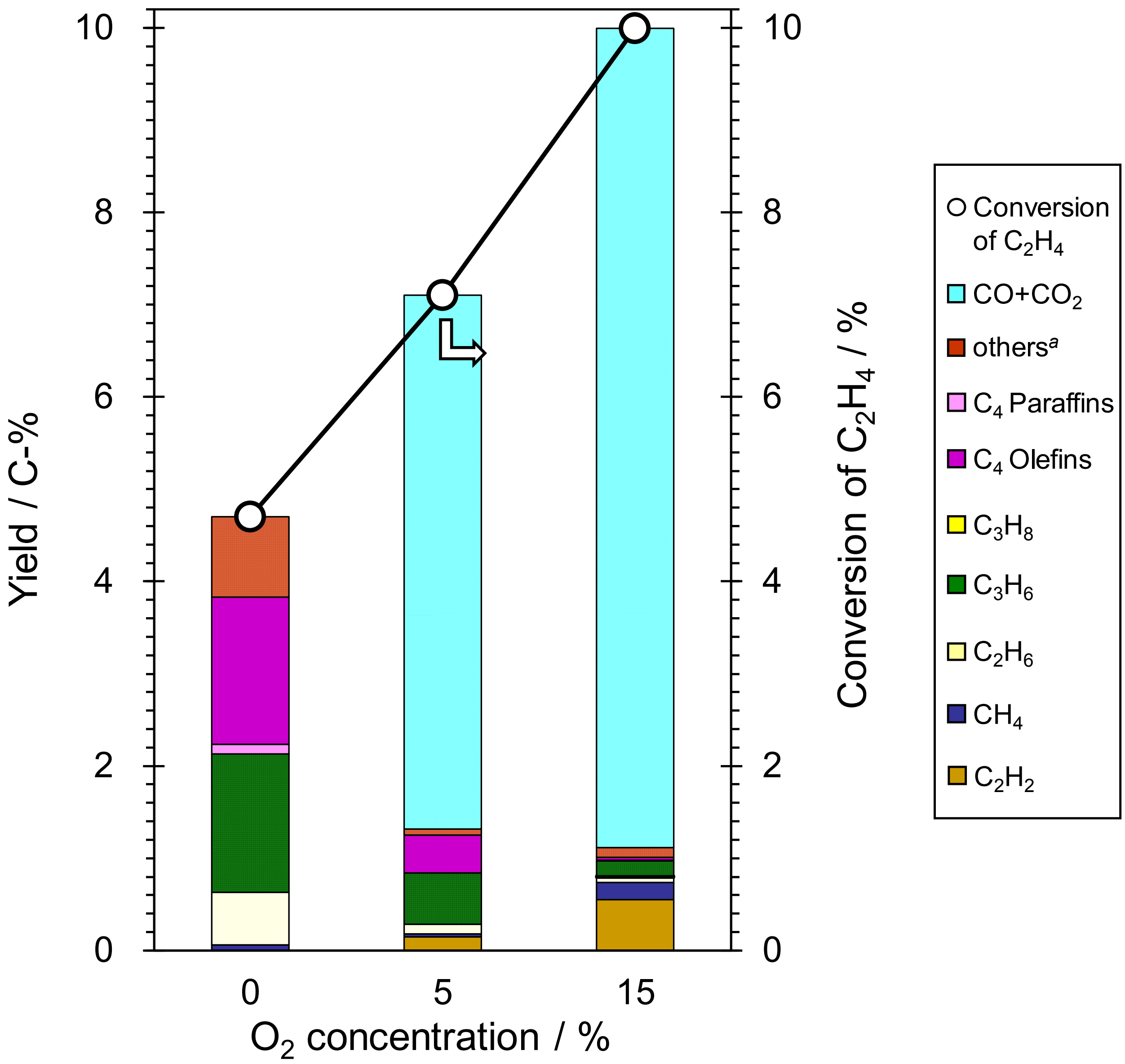

Figure S14. Influence of O_2 partial pressure on the catalytic activity in the ETP reaction over TiO_2(mc)/ZSM-5_800 under application of an electric field.

The catalyst bed temperatures during 0, 5 and 15 vol% of O_2 concentration were 225, 300 and 324 °C, respectively.

[a] The fraction of others indicates the sum of C5s, >C6s, and aromatics produced.

Reaction conditions: catalyst, 100 mg; feed gas, C_2H_4:O_2:Ar = 25: x :(75–x) cm^3 (SATP) min^{-1}; $W_{zeolite}/F_{ethylene}$, 0.75 g-cat. h mol^{-1}; input current, 5.0 mA; preset furnace temperature, 150 °C.

Pretreatment conditions: temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm^3 (SATP) min^{-1}.

Supplementary Tables

Table S1. Product yield in the ethylene-to-propylene (ETP) reaction at 450 °C

Catalyst	Conversion of C_2H_4[a] (%)	Product distribution[b] (C-%)								Material balance[c] (C-%)
		CH_4 + C_2H_6	C_3H_8	C_3H_6	C_4=	C_4	C_5 + C_5=	>C_6	aromatics	
ZSM-5	82	1.4	17.5	24.3	15.2	19.9	5.2	3.1	13.4	96
TiO_2(mc)/ZSM-5_800	45	4.0	4.0	46.2	30.6	6.3	3.5	3.8	1.8	102
TiO_2(mc)/silicalite-1_800	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100

[a] Conversion of C_2H_4 ={(C-atoms of ethylene$_{\text{input}}$) – (C-atoms of ethylene$_{\text{output}}$)}/(C-atoms of ethylene$_{\text{input}}$).

[b] Product distribution = {(C-atoms of each product)/(sum of C-atoms of products)}×100.

[c] Material balance = (total C-atoms of products + ethylene$_{\text{output}}$)/(C-atoms of ethylene$_{\text{input}}$)×100.

Table S2. Influence of W/F$_{methane}$ on the catalytic activity for OCM over TiO_2(mc)/ZSM-5_800 in an electric field

W/F$_{methane}$	Input current	Preset furnace temperature	Temp.$_c$[a]	Conversion (C-%)		Selectivity (C-%)						Yield (C-%)	
(g h mol^{-1})	(mA)	(°C)	(ºC)	CH_4	O_2	CO	CO_2	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_2[b]	C_3H_6
0.8	7	150	433	4.0	10.5	62.5	4.3	17.7	12.7	1.1	1.6	1.26	0.07
1.1			425	7.9	14.1	63.6	3.5	13.4	13.4	3.2	2.6	2.35	0.24
1.6			415	10.1	18.1	62.9	2.9	13.1	16.2	2.5	1.9	3.19	0.25
2.2			395	13.1	23.1	68.0	3.6	10.7	13.5	2.5	1.2	3.51	0.22
3.3			394	20.4	31.8	73.1	4.0	7.7	10.9	4.0	0.3	4.61	0.06

[a] Catalyst bed temperature measured by a thermocouple.

[b] C_2 yield means the sum of C_2H_6, C_2H_4, and C_2H_2 yields.

Reaction conditions: catalyst, 100 mg; feed gas, CH_4:O_2:Ar = $5x$:$3x$:$12x$ (total flow rate: 50, 75, 100, 150, 200 cm^3 (SATP) min^{-1}).

Pretreatment conditions: temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm^3 (SATP) min^{-1}.

Table S3. Influence of W/F$_{\text{ethane}}$ on the catalytic activity for ODH over TiO_2(mc)/ZSM-5_800 in an electric field

W/F$_{\text{ethane}}$	Input current	Preset furnace temperature	Temp.$_{c}$[a]	Conversion (%)		Selectivity[d] (C-%)						Yield[e] (C-%)		
(g h mol^{-1})	(mA)	(°C)	(ºC)	C_2H_6[b]	O_2[c]	C_2H_4	CO	CO_2	CH_4	C_2H_2	C_3H_6	C_2H_4	C_2H_2	C_3H_6
1.5	6	150	306	28.4	25.8	54.7	25.6	2.6	9.6	5.0	1.2	15.6	1.4	0.33
3.0			304	51.0	55.5	48.7	29.6	3.2	10.7	5.9	1.0	24.9	3.0	0.51

[a] Catalyst bed temperature measured by a thermocouple.

[b] C_2H_6 conversion (%) = {(sum of C-atom moles of each product)/(C-atom moles of input C_2H_6)} × 100.

[c] O_2 conversion (%) = {(moles of O_2 consumed}/(input moles of O_2)} × 100.

[d] Product selectivity (C-%) = {(product yield)/(C_2H_6 conversion)} × 100.

[e] Product yield (C-%) = {(C-atom moles of each product)/(C-atom moles of input C_2H_6)} × 100.

Reaction conditions: catalyst, 100 mg; feed gas, C_2H_6:O_2:Ar = $5x$:$3x$:$12x$ (total flow rate: 100, 200 cm^3 (SATP) min^{-1}).

Pretreatment conditions: temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm^3 (SATP) min^{-1}.

Table S4. Evaluation of the reaction through CO and H_2 to C2 hydrocarbons over ZSM-5 zeolite

Reactant gas flow rate (cm^3 (SATP) min^{-1})			Preset furnace temperature[a] (ºC)	Conversion (%)		Selectivity (C-%)			Yield (C-%)
CO/He(10%)	H_2	He		CO	H_2	C_2H_6	C_2H_4	C_2H_2	C_2[b]
29.6	1.6	68.8	400	0.0	0.0	0.0	0.0	0.0	0.0
			500	0.0	0.0	0.0	0.0	0.0	0.0
			600	0.0	0.0	0.0	0.0	0.0	0.0
			700	0.0	0.0	0.0	0.0	0.0	0.0
	3.2	67.2	400	0.0	0.0	0.0	0.0	0.0	0.0
			500	0.0	0.0	0.0	0.0	0.0	0.0
			600	0.0	0.0	0.0	0.0	0.0	0.0
			700	0.0	0.0	0.0	0.0	0.0	0.0
	6.4	64.0	400	0.0	0.0	0.0	0.0	0.0	0.0
			500	0.0	0.0	0.0	0.0	0.0	0.0
			600	0.0	0.0	0.0	0.0	0.0	0.0
			700	0.0	0.0	0.0	0.0	0.0	0.0

[a] Furnace temperature measured by a thermocouple.

[b] C_2 yield means the sum of C_2H_6, C_2H_4, and C_2H_2 yields.

Reaction conditions: catalyst, 100 mg.

Pretreatment conditions: temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm^3 (SATP) min^{-1}.

Table S5. Temperature dependence on product distribution over TiO_2(mc)/ZSM-5_800 in an electric field

Input current	Preset furnace temperature	Temp.$_c$[a]	Conversion (%)	Selectivity (C-%)						Yield (C-%)	
(mA)	(°C)	(°C)	CH_4	CO	CO_2	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_2[b]	C_3H_6
7.0	150	425	13.1	64.0	3.0	11.4	15.7	4.1	1.5	4.10	0.20
	200	436	19.2	71.2	3.7	8.9	12.1	3.1	1.0	4.63	0.19
	300	484	21.7	74.6	5.0	5.9	10.8	2.8	0.8	4.23	0.17
	400	570	22.5	74.6	8.3	5.3	8.0	3.1	0.6	3.69	0.14
	500	611	16.7	76.7	11.4	4.9	6.6	0.2	0.2	1.96	0.03
	600	686	15.2	74.2	13.7	5.9	6.1	0.0	0.1	1.83	0.02
	700	758	14.2	77.9	16.8	2.8	2.5	0.0	0.0	0.76	0.00

[a] Catalyst bed temperature measured with a thermocouple.
[b] C_2 yield means the sum of C_2H_6, C_2H_4, and C_2H_2 yields.
Reaction conditions: catalyst, 100 mg; feed gas, CH_4:O_2:Ar = 25:15:60 cm^3 (SATP) min^{-1}.
Pretreatment conditions: temperature, 300 °C; period, 30 min; Ar flow rate, 60 cm^3 (SATP) min^{-1}.