

Supplementary Information

Study on the unsteady state oxidative coupling of methane: Effects of oxygen species from O₂, surface lattice oxygen, and CO₂ on the selectivity

Table of contents

Fig. S1. (a) Schematic reaction system and (b, c) the manufactured quartz reactors.

Fig. S2. Temperature profile of the catalyst bed at the furnace temperature of 750 °C, 800 °C, and 850 °C. A thermocouple was directly positioned at the top, middle, and bottom of the bed.

Fig. S3. (a, b) Ratios of olefins/paraffins and CO/CO₂, and (c, d) oxygen consumption for the dehydrogenation of ethane (or propane) and the oxidation of CO, depending on the content of N₂ diluent under (a, c) 750 °C and (b, d) 850 °C.

Fig. S4. (a, b) Ratios of olefins/paraffins and CO/CO₂, and (c, d) oxygen consumption for the dehydrogenation of ethane (or propane) and the oxidation of CO, at various GHSV and catalyst bed thickness under (a, c) 750 °C and (b, d) 850 °C.

Fig. S5. (a, b) Ratios of olefins/paraffins and CO/CO₂, and (c, d) oxygen consumption for the dehydrogenation of ethane (or propane) and the oxidation of CO, at various GHSV and total flow rate of the feed gas under (a, c) 750 °C and (b, d) 850 °C.

Fig. S6. (a, b) Ratios of olefins/paraffins and CO/CO₂, and (c, d) oxygen consumption for the dehydrogenation of ethane (or propane) and the oxidation of CO, at 16% CO₂ co-dilution and various GHSV and catalyst bed thickness under (a, c) 750 °C and (b, d) 850 °C.

Fig. S7. C₂₊ yield depending on CH₄ conversion and O₂ conversion. All results with O₂ conversion < 100% reported herein are included.

Fig. S8. (a) XRD and (b) Raman spectra of catalysts depending on the heating temperature. The results of fresh catalysts at room temperature depicted for comparison.

Fig. S9. Activities of various catalysts for the OCM reaction in terms of (a) CH₄ conversion and (b) C₂₊ selectivity. CH₄/O₂ = 3 mol/mol, GHSV = 10,000 h⁻¹.

Fig. S10. XPS results of fresh and spent $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalysts.

Table S1. OCM reaction results at various CH_4/O_2 ratios.

Table S2. OCM reaction results at various contents of N_2 diluent.

Table S3. OCM reaction results at various GHSV adjusted by the catalyst bed thickness.

Table S4. O_2 consumption for the selectivity at various GHSV adjusted by the catalyst bed thickness.

Table S5. OCM reaction results at various GHSV adjusted by the total feed flow rate.

Table S6. O_2 consumption for the selectivity at various GHSV adjusted by the total feed flow rate.

Table S7. OCM results with co-fed CO_2 at various GHSV and catalyst bed thickness.

Table S8. O_2 consumption for the selectivity with co-fed CO_2 at various GHSV adjusted by the catalyst bed thickness.

Table S9. Observed XPS binding energies (eV) and near-surface compositions (atom%) of the $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalysts.

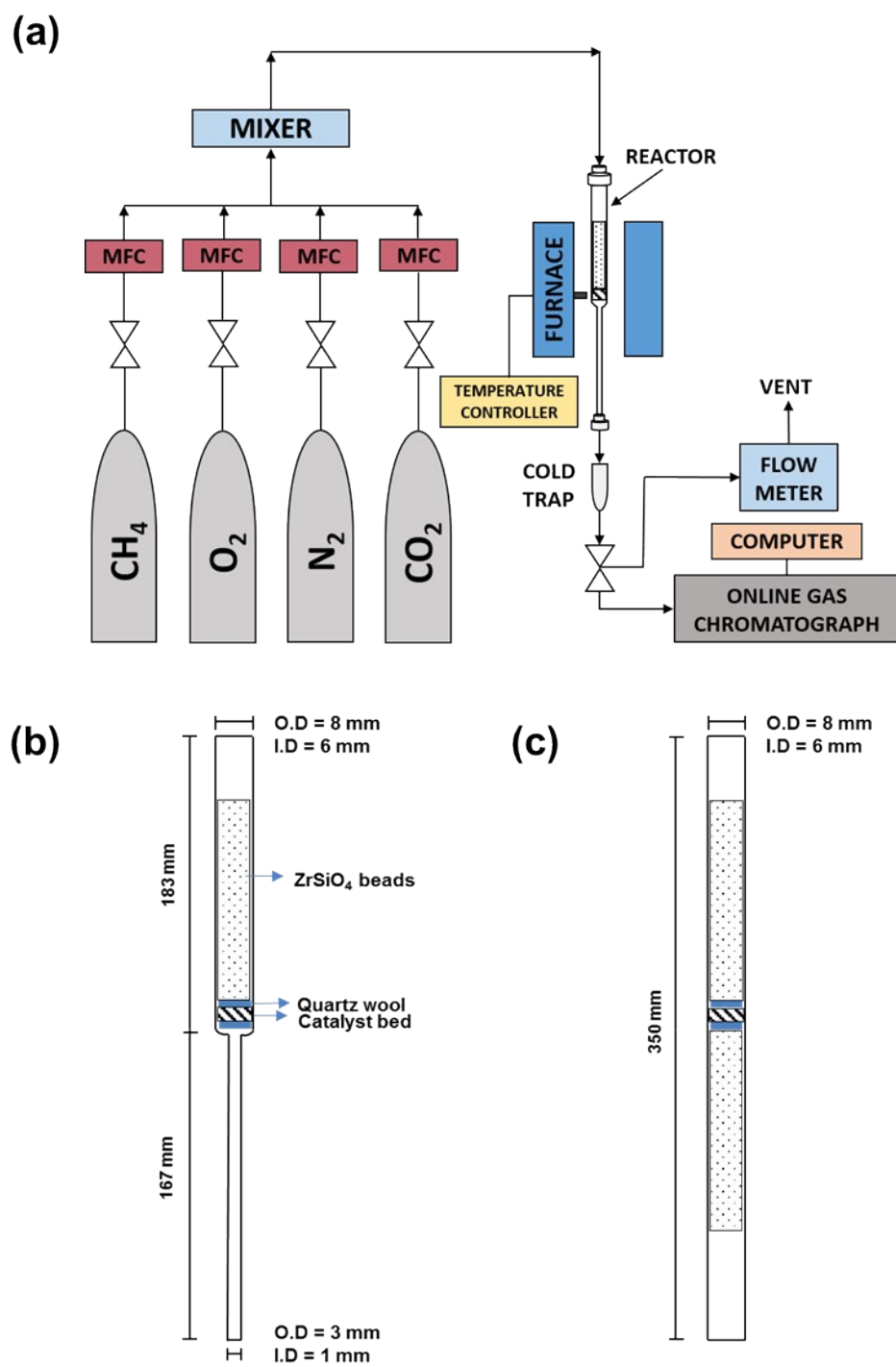


Fig. S1. (a) Schematic reaction system and (b, c) the manufactured quartz reactors.

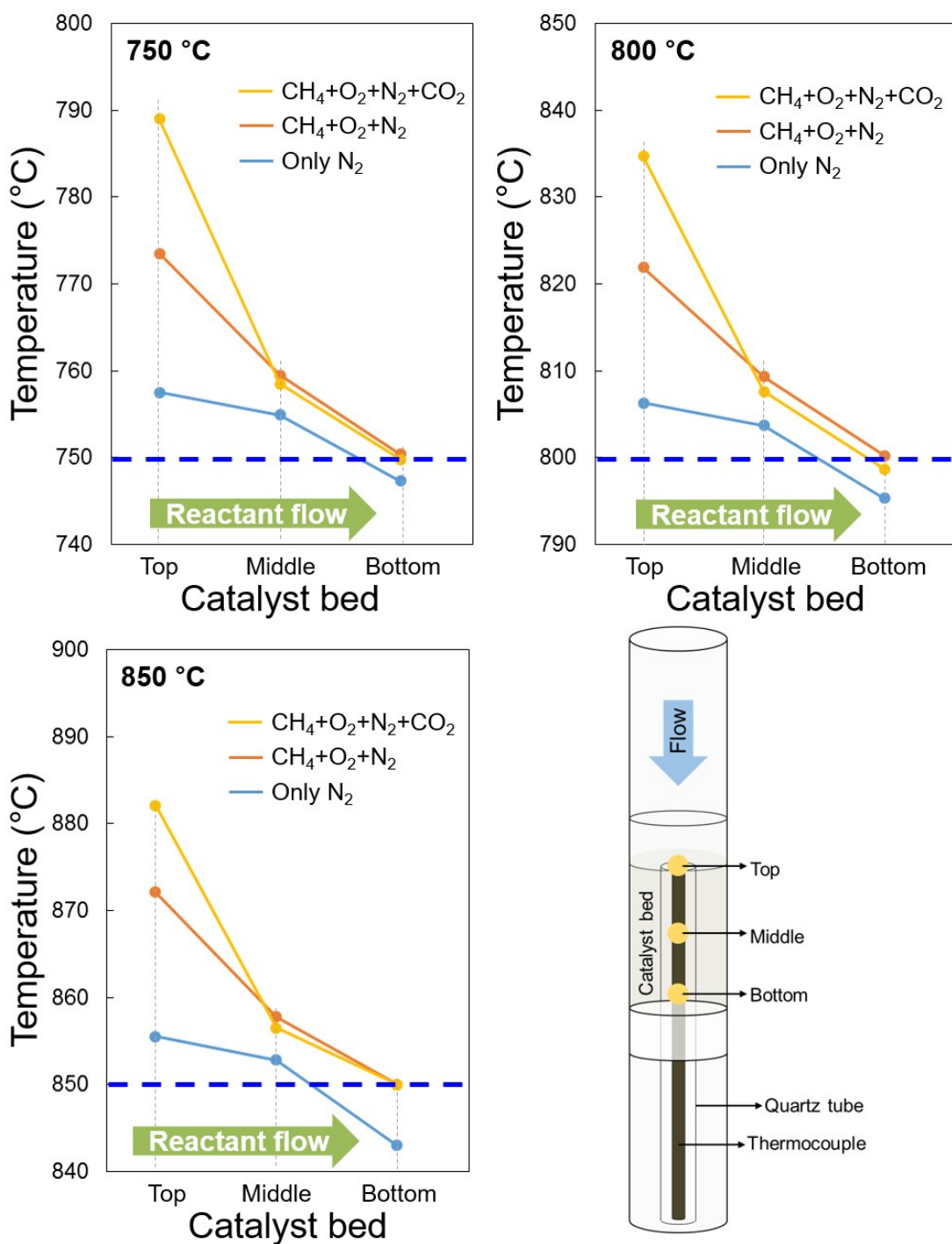


Fig. S2. Temperature profile of the catalyst bed at the furnace temperature of 750 °C, 800 °C, and 850 °C. The blue dotted lines indicate the furnace temperatures. A thermocouple was directly positioned at the top, middle, and bottom of the bed. Catalyst bed thickness = 35.3 mm. CH₄/O₂/N₂/CO₂ = 3/1/1/0 (for CH₄+O₂+N₂), 3/1/0.2/0.8 (for CH₄+O₂+N₂+CO₂).

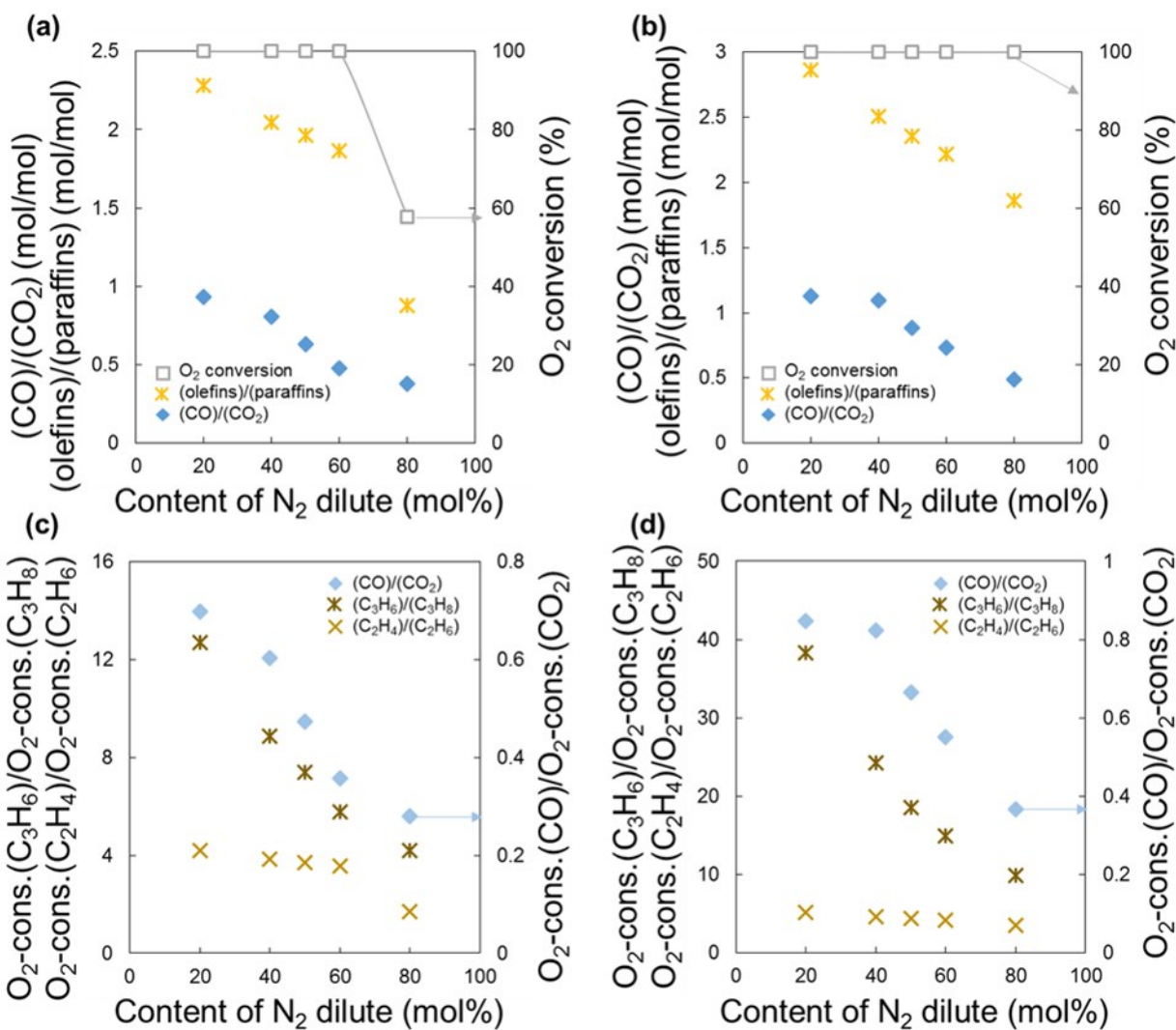


Fig. S3. (a, b) Ratios of olefins/paraffins and CO/CO₂, and (c, d) oxygen consumption for the dehydrogenation of ethane (or propane) and the oxidation of CO, depending on the content of N₂ diluent under (a, c) 750 °C and (b, d) 850 °C.

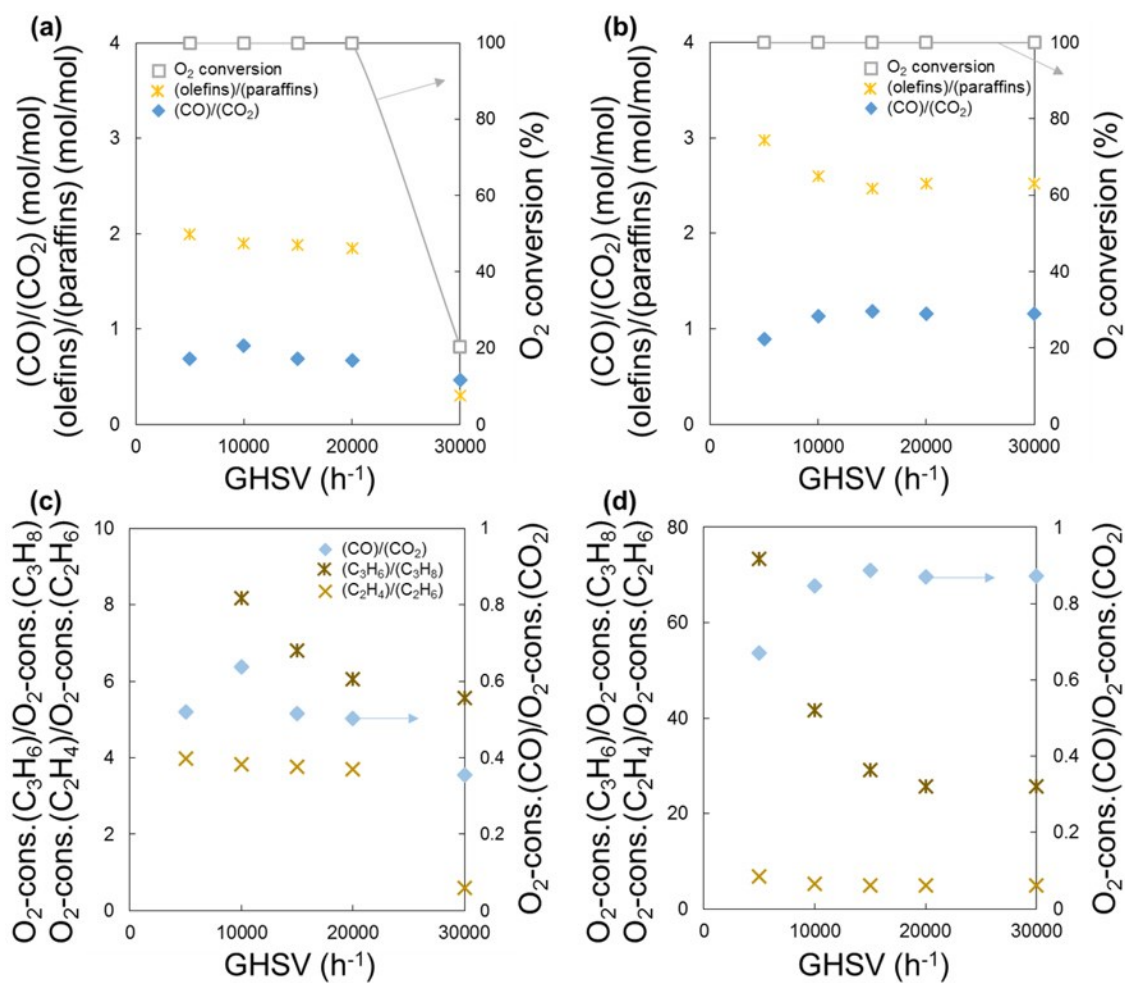


Fig. S4. (a, b) Ratios of olefins/paraffins and CO/CO₂, and (c, d) oxygen consumption for the dehydrogenation of ethane (or propane) and the oxidation of CO, at various GHSV and catalyst bed thickness with a fixed flow rate under (a, c) 750 °C and (b, d) 850 °C.

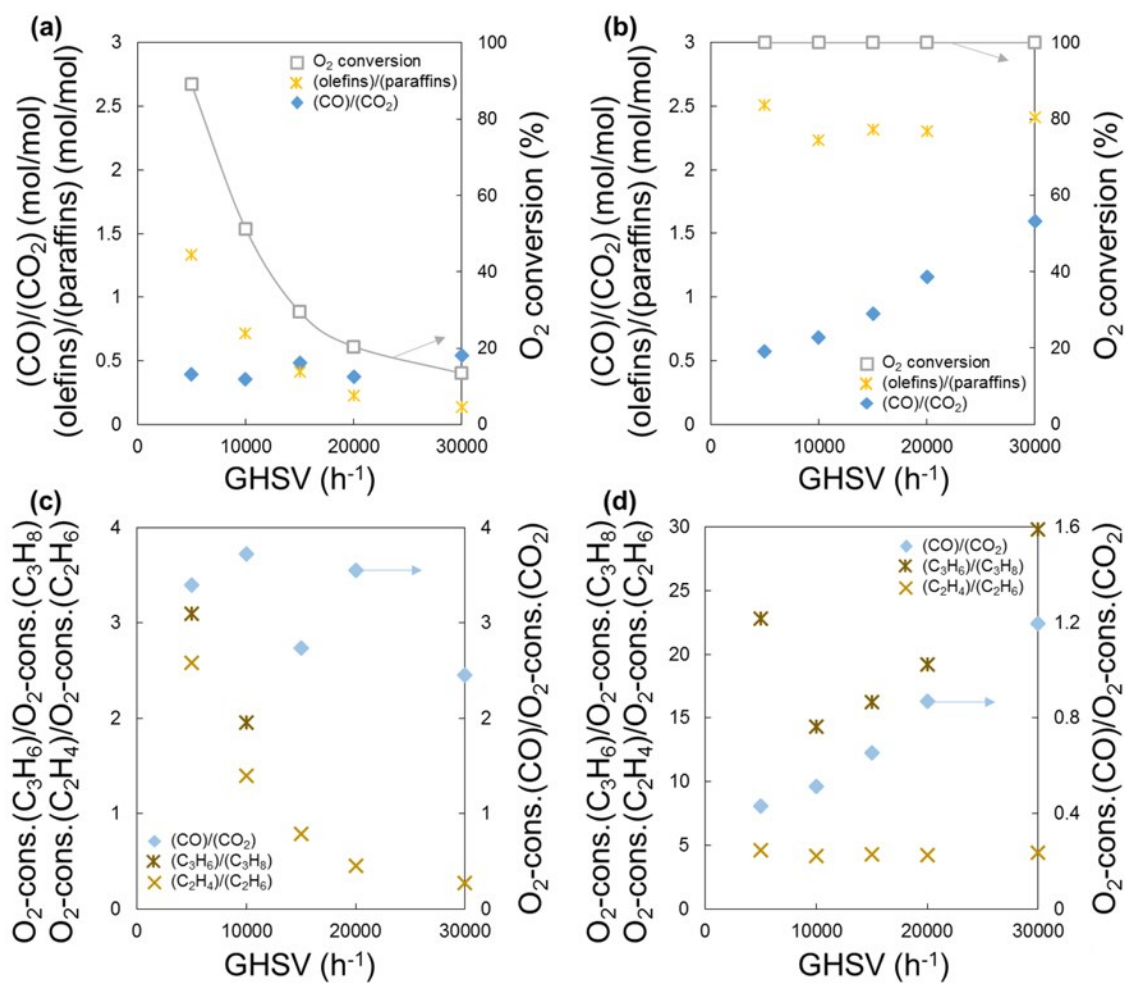


Fig. S5. (a, b) Ratios of olefins/paraffins and CO/CO₂, and (c, d) oxygen consumption for the dehydrogenation of ethane (or propane) and the oxidation of CO, at various GHSV and total flow rate of the feed gas with a fixed catalyst bed thickness under (a, c) 750 °C and (b, d) 850 °C.

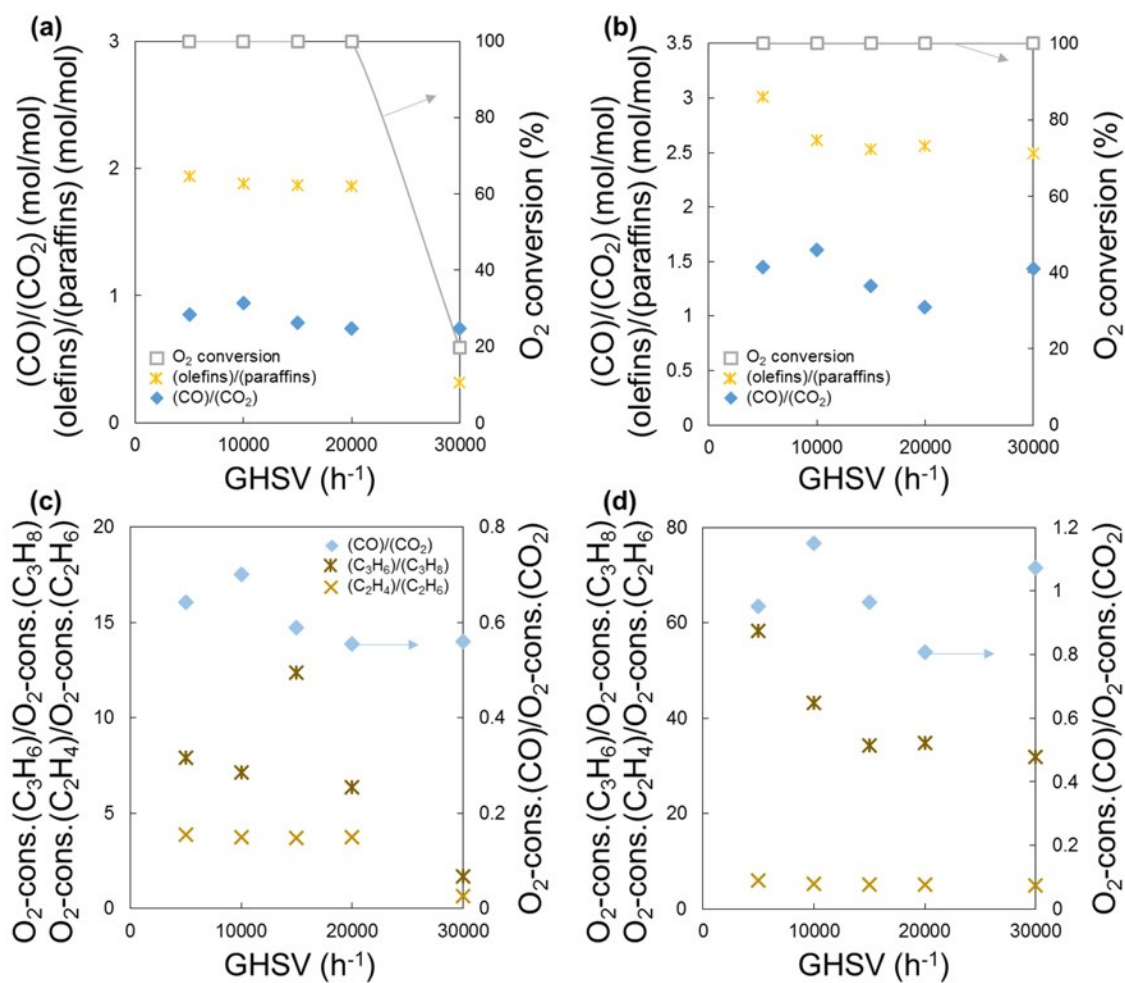


Fig. S6. (a, b) Ratios of olefins/paraffins and CO/CO₂, and (c, d) oxygen consumption for the dehydrogenation of ethane (or propane) and the oxidation of CO, at 16% CO₂ co-dilution and various GHSV and catalyst bed thickness under (a, c) 750 °C and (b, d) 850 °C.

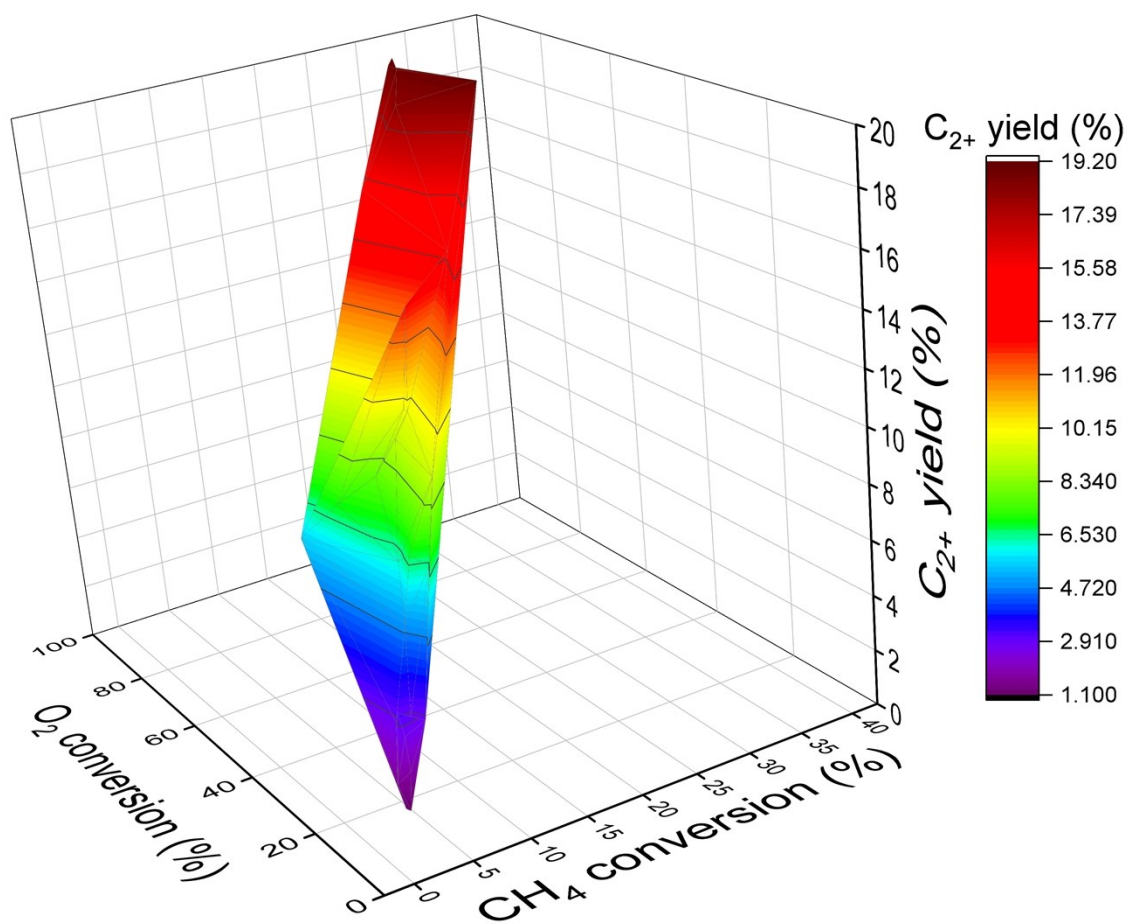


Fig. S7. C_{2+} yield depending on CH_4 conversion and O_2 conversion. All results with O_2 conversion < 100% reported herein are included.

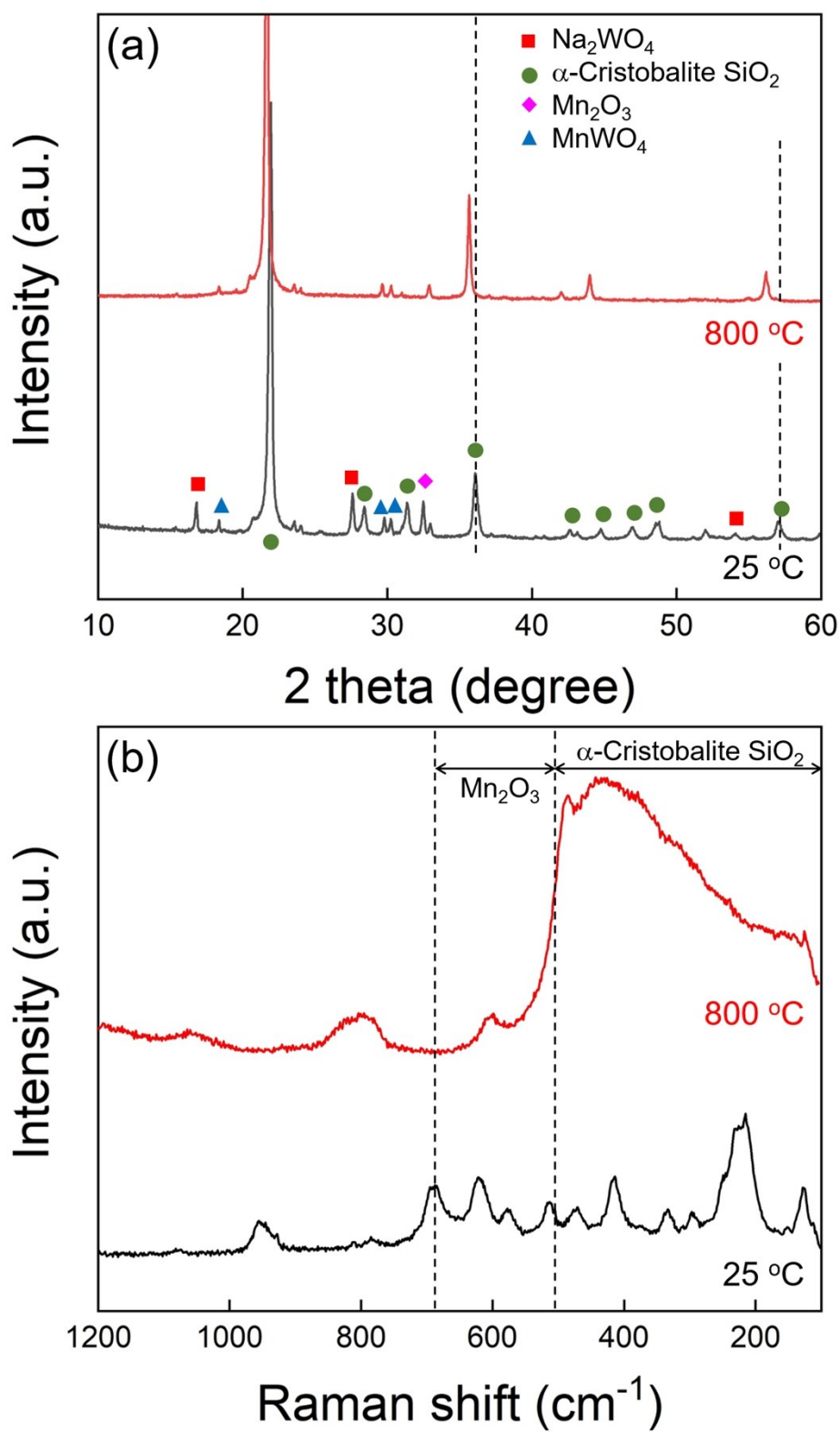


Fig. S8. (a) XRD and (b) Raman spectra of catalysts depending on the heating temperature. The results of fresh catalysts at room temperature depicted for comparison.

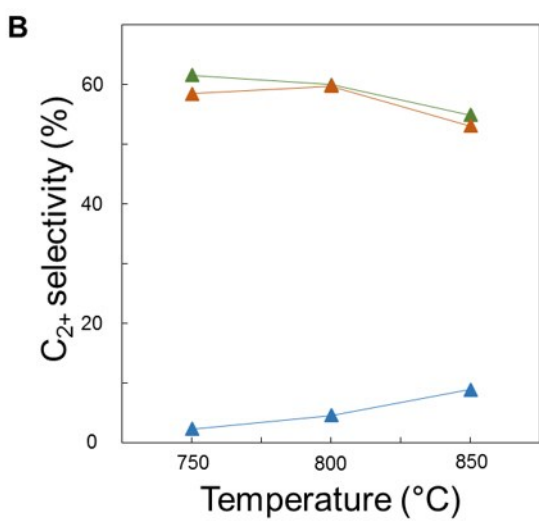
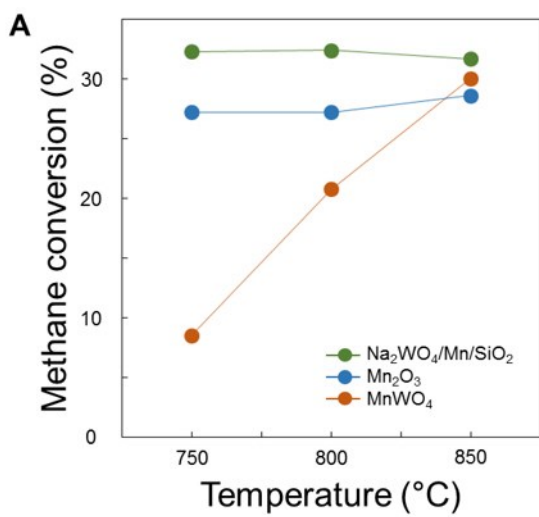


Fig. S9. Activities of various catalysts for the OCM reaction in terms of (a) CH₄ conversion and (b) C₂₊ selectivity. CH₄/O₂ = 3 mol/mol, GHSV = 10,000 h⁻¹.

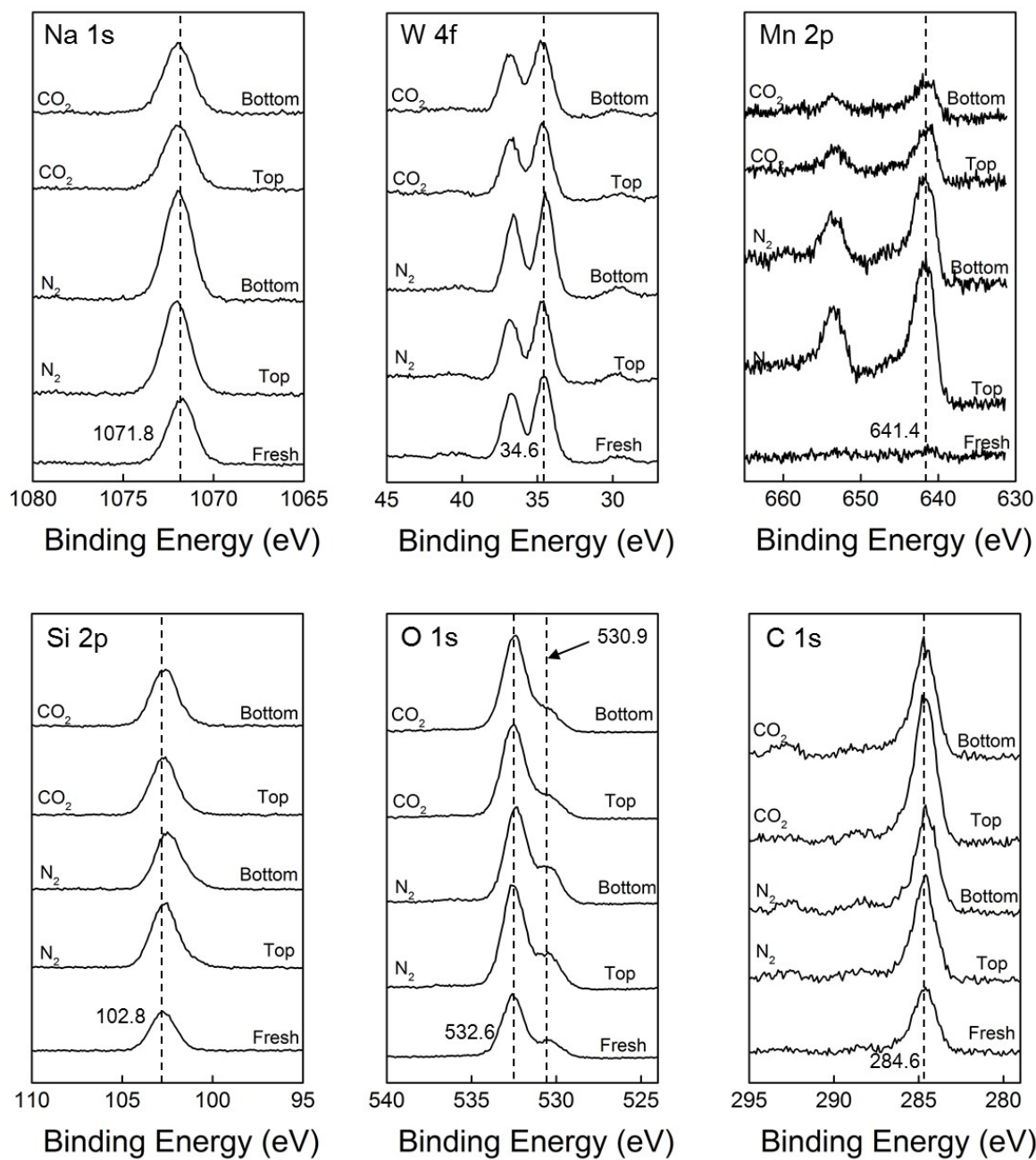


Fig. S10. XPS results of fresh and spent $\text{Na}_2\text{WO}_4/\text{Mn}/\text{SiO}_2$ catalysts.

Table S1. OCM reaction results at various CH₄/O₂ ratios.^a

Temperature (°C)	CH ₄ /O ₂ (mol/mol)	Conversion (%)		Selectivity (%)		Yield (%)		olefins/paraffins (mol/mol)	CO/CO ₂ (mol/mol)
		CH ₄	O ₂	C ₂₊	Olefins	C ₂₊	Olefins		
750	1	66.9	100.0	24.5	18.4	16.4	12.3	3.0	0.63
	1.5	52.6	100.0	41.2	30.0	21.7	15.8	2.7	0.51
	2	35.4	78.8	53.4	33.4	18.9	11.8	1.7	0.52
	2.5	27.1	65.7	51.6	28.4	14.0	7.7	1.2	0.45
	3	18.2	54.1	54.1	24.2	9.8	4.4	0.8	0.68
	4	14.7	53.0	53.0	20.5	7.8	3.0	0.6	0.95
	5	11.5	55.0	60.9	21.4	7.0	2.4	0.5	0.44
6	9.2	60.3	60.3	19.3	5.6	1.8	0.5	0.60	
800	1	66.7	100.0	25.6	20.0	17.1	13.4	3.6	0.74
	1.5	52.7	100.0	39.5	29.6	20.9	15.6	3.0	0.68
	2	44.0	100.0	49.0	35.1	21.5	15.4	2.5	0.60
	2.5	41.3	100.0	50.6	35.4	20.9	14.6	2.3	0.53
	3	34.2	100.0	58.5	38.7	20.0	13.3	2.0	0.51
	4	28.6	100.0	62.6	38.8	17.9	11.1	1.6	0.48
	5	24.5	100.0	66.3	38.7	16.2	9.5	1.4	0.48
6	20.6	100.0	70.8	40.3	14.6	8.3	1.3	0.54	
850	1	66.2	100.0	22.2	18.1	14.7	12.0	4.4	0.92
	1.5	51.8	100.0	35.8	27.9	18.5	14.5	3.5	0.95
	2	42.6	100.0	47.2	35.5	20.1	15.1	3.0	0.83
	2.5	40.9	100.0	46.5	31.3	19.0	12.8	2.1	0.74
	3	33.5	100.0	55.3	38.8	18.5	13.0	2.4	0.70
	4	29.0	100.0	58.0	38.8	16.8	11.2	2.0	0.68
	5	23.3	100.0	67.2	43.4	15.6	10.1	1.8	0.69
6	20.5	100.0	70.0	43.8	14.3	9.0	1.7	0.75	

^aGHSV = 10,000 h⁻¹. CH₄ flow rate was fixed at 18 mL/min, and the flow rates of O₂ and N₂ were adjusted to achieve the total flow rate of 50 mL/min.

Table S2. OCM reaction results at various contents of N₂ diluent.^a

Temperature (°C)	N ₂ dilution (%)	Conversion (%)		Selectivity (%)		Yield (%)		olefins/paraffins (mol/mol)	CO/CO ₂ (mol/mol)
		CH ₄	O ₂	C ₂₊	Olefins	C ₂₊	Olefins		
750	20	34.5	100	59.5	39.8	20.5	13.7	2.02	0.85
	40	29.4	86.1	62.1	36.4	18.2	10.7	1.42	0.48
	50	18.2	52.9	54.1	22.4	9.8	4.1	0.71	0.37
	60	11.8	37.9	52.7	16.5	6.2	2.0	0.46	0.39
	80	7.3	18.2	37.7	7.1	2.8	0.5	0.23	0.30
800	20	34.4	100	56.5	39.3	19.5	13.6	2.28	0.93
	40	34.3	100	59.7	40.1	20.5	13.8	2.05	0.80
	50	35.2	100	59.7	39.6	21.0	14.0	1.97	0.63
	60	35.9	100	60.1	39.1	21.5	14.0	1.87	0.48
	80	20.3	57.7	64.4	30.1	13.1	6.1	0.88	0.37
850	20	31.1	100	53.3	39.5	17.4	12.9	2.86	1.13
	40	32.4	100	58.2	41.6	18.9	13.5	2.51	1.10
	50	34.6	100	56.2	39.5	19.4	13.6	2.35	0.89
	60	35.2	100	56.9	39.2	20.0	13.8	2.22	0.73
	80	34.9	100	61.3	39.9	21.4	13.9	1.86	0.49

^aCH₄/O₂ = 3 mol/mol, GHSV = 10,000 h⁻¹.

Table S3. OCM reaction results at various GHSV adjusted by the catalyst bed thickness.^a

Temperature (°C)	Catalyst bed thickness (mm)	GHSV (h ⁻¹)	Conversion (%)		Selectivity (%)		Yield (%)		olefins/paraffins (mol/mol)	CO/CO ₂ (mol/mol)
			CH ₄	O ₂	C ₂₊	Olefins	C ₂₊	Olefins		
750	2.1	50,000	2.9	9.4	38.8	5.2	1.1	0.2	0.15	0.61
	2.65	40,000	4.4	13.8	40.2	6.8	1.8	0.3	0.20	0.33
	3.5	30,000	5.4	20.4	51.6	11.9	2.8	0.6	0.30	0.47
	4.2	25,000	12.7	31.6	50.8	18.7	6.4	2.4	0.58	0.51
	5.3	20,000	35.9	100.0	55.1	36.3	19.7	13.0	1.94	0.67
	7.1	15,000	35.2	100.0	57.7	38.3	20.3	13.5	1.98	0.69
	10.6	10,000	34.1	100.0	59.7	39.8	20.4	13.6	2.02	0.85
	21.2	5,000	34.3	100.0	59.8	40.6	20.5	14.0	2.12	0.69
	35.3	3,000	34.5	100.0	58.9	39.7	20.4	13.7	2.06	0.72
800	2.1	50,000	14.5	34.0	63.3	28.4	9.2	4.1	0.81	0.81
	2.65	40,000	33.2	99.2	56.6	38.6	18.8	12.8	2.14	1.03
	3.5	30,000	34.4	100.0	57.2	39.9	19.7	13.7	2.30	0.92
	4.2	25,000	33.3	100.0	56.7	39.1	18.9	13.0	2.22	0.92
	5.3	20,000	35.4	100.0	56.0	38.6	19.8	13.7	2.23	0.88
	7.1	15,000	35.5	100.0	55.6	38.3	19.7	13.6	2.21	0.89
	10.6	10,000	33.9	100.0	57.1	39.6	19.3	13.4	2.28	0.93
	21.2	5,000	34.0	100.0	56.9	40.8	19.3	13.9	2.54	0.83
	35.3	3,000	33.1	100.0	59.0	41.5	19.5	13.7	2.37	0.92
850	2.1	50,000	33.9	100.0	52.5	38.3	17.8	13.0	2.69	1.24
	2.65	40,000	32.3	100.0	53.0	38.4	17.1	12.4	2.63	1.28
	3.5	30,000	34.4	100.0	52.3	38.5	18.0	13.2	2.77	1.16
	4.2	25,000	33.0	100.0	50.9	37.4	16.8	12.3	2.77	1.23
	5.3	20,000	34.4	100.0	52.5	38.6	18.0	13.3	2.77	1.16
	7.1	15,000	34.7	100.0	51.0	37.3	17.7	12.9	2.72	1.18
	10.6	10,000	32.3	100.0	53.4	39.6	17.3	12.8	2.86	1.13
	21.2	5,000	32.1	100.0	52.2	41.3	16.8	13.3	3.78	0.89
	35.3	3,000	32.3	100.0	52.2	39.8	16.9	12.8	3.19	1.06

^aCH₄/O₂/N₂ = 3/1/1 mol/mol/mol, total feed flow rate = 50 mL/min.

Table S4. O₂ consumption for the selectivity at various_GHSV adjusted by the catalyst bed thickness.^a

Temperature (°C)	Catalyst bed thickness (mm)	GHSV (h ⁻¹)	Conversion (%)		O ₂ -consumption (%) for					
			CH ₄	O ₂	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈
750	2.1	50,000	2.9	9.4	3.0	6.6	0.2	0.8	0.00	0.00
	2.65	40,000	4.4	13.8	3.6	14.4	0.4	1.1	0.01	0.00
	3.5	30,000	5.4	20.4	4.5	12.8	1.0	1.6	0.00	0.00
	4.2	25,000	12.7	31.6	7.8	20.5	3.4	3.0	0.21	0.10
	5.3	20,000	35.9	100.0	28.4	56.5	17.8	4.8	1.74	0.31
	7.1	15,000	35.2	100.0	29.2	56.6	18.4	4.9	1.84	0.30
	10.6	10,000	34.1	100.0	29.7	47.4	18.5	4.9	1.92	0.28
	21.2	5,000	34.3	100.0	31.0	59.5	18.8	4.8	2.10	0.26
	35.3	3,000	34.5	100.0	31.1	55.4	18.2	4.7	2.00	0.25
800	2.1	50,000	14.5	34.0	21.5	33.0	11.0	4.6	1.03	0.17
	2.65	40,000	33.2	99.2	35.0	45.2	17.3	4.4	1.87	0.16
	3.5	30,000	34.4	100.0	35.4	51.6	18.6	4.4	1.97	0.18
	4.2	25,000	33.3	100.0	33.8	49.2	17.6	4.3	1.95	0.17
	5.3	20,000	35.4	100.0	34.6	52.1	18.5	4.5	2.01	0.19
	7.1	15,000	35.5	100.0	34.2	51.0	18.3	4.5	2.02	0.19
	10.6	10,000	33.9	100.0	35.0	51.3	18.1	4.3	2.08	0.16
	21.2	5,000	34.0	100.0	34.5	55.7	18.5	4.0	2.26	0.13
	35.3	3,000	33.1	100.0	35.7	53.1	18.0	4.1	2.17	0.13
850	2.1	50,000	33.9	100.0	42.2	45.8	17.2	3.6	1.96	0.07
	2.65	40,000	32.3	100.0	41.0	42.6	16.7	3.5	1.94	0.06
	3.5	30,000	34.4	100.0	40.7	46.7	17.8	3.6	2.05	0.08
	4.2	25,000	33.0	100.0	40.5	44.0	16.6	3.3	1.97	0.06
	5.3	20,000	34.4	100.0	41.2	47.4	17.8	3.6	2.07	0.07
	7.1	15,000	34.7	100.0	40.9	46.1	17.4	3.5	2.04	0.07
	10.6	10,000	32.3	100.0	40.9	48.3	17.2	3.3	2.08	0.05
	21.2	5,000	32.1	100.0	38.3	57.1	17.7	2.6	2.20	0.03
	35.3	3,000	32.3	100.0	40.0	53.7	17.2	2.8	2.13	0.02

^aCH₄/O₂/N₂ = 3/1/1 mol/mol/mol, total feed flow rate = 50 mL/min.

Table S5. OCM reaction results at various GHSV adjusted by the total feed flow rate.^a

Temperature (°C)	Feed flow rate (mL/min)	GHSV (h ⁻¹)	Conversion (%)		Selectivity (%)		Yield (%)		olefins/paraffins (mol/mol)	CO/CO ₂ (mol/mol)
			CH ₄	O ₂	C ₂₊	Olefins	C ₂₊	Olefins		
750	90.0	30,000	3.1	13.4	50.1	6.1	1.6	0.2	0.14	0.54
	60.0	20,000	6.7	20.4	41.6	7.8	2.8	0.5	0.23	0.38
	44.9	15,000	9.5	29.5	51.5	15.1	4.9	1.4	0.41	0.49
	30.0	10,000	16.4	51.3	55.8	23.3	9.1	3.8	0.72	0.36
	15.0	5,000	26.1	89.1	58.4	33.3	15.2	8.7	1.33	0.39
800	90.0	30,000	31.1	100	63.6	41.7	19.8	13.0	1.90	1.25
	60.0	20,000	35.5	100	59.2	39.1	21.0	13.9	1.94	0.79
	44.9	15,000	35.4	100	59.3	39.2	21.0	13.9	1.95	0.60
	30.0	10,000	32.6	100	64.2	42.1	20.9	13.7	1.91	0.51
	15.0	5,000	30.1	100	60.7	40.0	18.3	12.1	1.94	0.45
850	90.0	30,000	31.1	100	60.9	43.0	18.9	13.4	2.41	1.60
	60.0	20,000	34.7	100	56.5	39.4	19.6	13.7	2.30	1.16
	44.9	15,000	33.9	100	59.1	41.3	20.0	14.0	2.32	0.87
	30.0	10,000	31.1	100	63.5	43.8	19.7	13.6	2.23	0.68
	15.0	5,000	28.5	100	59.5	42.6	16.9	12.1	2.51	0.57

^aCH₄/O₂/N₂ = 3/1/1 mol/mol/mol, volume of catalyst = 0.18 mL.

Table S6. O₂ consumption for the selectivity at various GHSV adjusted by the total feed flow rate.^a

Temperature (°C)	Feed flow rate (mL/min)	GHSV (h ⁻¹)	Conversion (%)		O ₂ -consumption (%) for					
			CH ₄	O ₂	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈
750	90.0	30,000	3.1	13.4	2.9	7.1	0.3	1.0	-	-
	60.0	20,000	6.7	20.4	4.6	16.2	0.8	1.7	-	-
	44.9	15,000	9.5	29.5	6.8	18.5	2.1	2.6	0.1	-
	30.0	10,000	16.4	51.3	10.2	38.0	5.4	3.9	0.3	0.2
	15.0	5,000	26.1	89.1	14.7	50.1	12.0	4.7	1.0	0.3
800	90.0	30,000	31.1	100	37.9	40.4	17.7	5.0	1.8	0.2
	60.0	20,000	35.5	100	27.4	46.2	19.0	5.2	1.8	0.2
	44.9	15,000	35.4	100	22.5	49.6	19.1	5.1	1.8	0.3
	30.0	10,000	32.6	100	20.4	53.8	18.8	5.2	1.8	0.3
	15.0	5,000	30.1	100	17.7	52.4	16.4	4.5	1.7	0.2
850	90.0	30,000	31.1	100	43.4	36.2	18.2	4.1	1.9	0.1
	60.0	20,000	34.7	100	35.3	40.6	18.6	4.4	1.9	0.1
	44.9	15,000	33.9	100	29.3	44.8	19.0	4.4	2.0	0.1
	30.0	10,000	31.1	100	25.5	49.8	18.5	4.5	2.0	0.1
	15.0	5,000	28.5	100	23.0	53.5	16.3	3.6	1.9	0.1

^aCH₄/O₂/N₂ = 3/1/1 mol/mol/mol, volume of catalyst = 0.18 mL.

Table S7. OCM results with co-fed CO₂ at various GHSV and catalyst bed thickness.^a

Temperature (°C)	Catalyst bed thickness (mm)	GHSV (h ⁻¹)	Conversion (%)		Selectivity (%)		Yield (%)		olefins/paraffins (mol/mol)	CO/CO ₂ (mol/mol)
			CH ₄	O ₂	C ₂₊	Olefins	C ₂₊	Olefins		
750	2.1	50,000	2.4	9.0	52.9	7.4	1.3	0.2	0.16	2.12
	2.65	40,000	5.0	16.6	53.0	11.4	2.7	0.6	0.26	0.98
	3.5	30,000	5.4	19.6	59.8	14.9	3.2	0.8	0.32	0.74
	4.2	25,000	11.6	33.4	58.9	21.1	6.8	2.4	0.54	0.64
	5.3	20,000	34.0	100	59.7	39.5	20.3	13.4	1.86	0.74
	7.1	15,000	33.9	100	59.5	39.9	20.2	13.5	1.87	0.79
	10.6	10,000	33.0	100	61.9	41.2	20.4	13.6	1.88	0.94
	21.2	5,000	34.3	100	60.7	40.8	20.8	14.0	1.94	0.85
	35.3	3,000	34.5	100	58.1	41.9	20.0	14.5	1.95	0.73
800	2.1	50,000	33.0	97.1	57.1	39.3	18.8	13.0	2.06	1.18
	2.65	40,000	33.0	98.3	58.2	40.0	19.2	13.2	2.05	1.23
	3.5	30,000	33.2	100	58.7	40.7	19.5	13.5	2.09	1.03
	4.2	25,000	33.5	100	58.2	40.1	19.5	13.4	2.04	1.00
	5.3	20,000	33.6	100	58.6	40.6	19.7	13.6	2.09	0.95
	7.1	15,000	33.8	100	57.6	39.9	19.5	13.5	2.07	1.00
	10.6	10,000	33.0	100	58.7	40.7	19.4	13.4	2.08	1.15
	21.2	5,000	32.9	100	58.5	41.4	19.2	13.6	2.21	1.11
	35.3	3,000	32.5	100	56.9	40.6	18.5	13.2	2.28	1.08
850	2.1	50,000	32.8	99.2	57.5	41.9	18.9	13.7	2.45	1.63
	2.65	40,000	33.2	99.6	56.3	41.2	18.7	13.7	2.48	1.84
	3.5	30,000	34.4	100	56.1	41.1	19.3	14.1	2.49	1.43
	4.2	25,000	32.4	100	54.5	39.8	17.7	12.9	2.45	1.38
	5.3	20,000	31.8	100	55.7	41.2	17.7	13.1	2.56	1.08
	7.1	15,000	32.1	100	54.4	40.1	17.5	12.9	2.53	1.28
	10.6	10,000	30.8	100	56.0	41.6	17.2	12.8	2.61	1.61
	21.2	5000	31.0	100	53.8	41.5	16.7	12.9	3.01	1.45
	35.3	3000	30.8	100	51.1	40.6	15.7	12.5	3.40	1.23

^aCH₄/O₂/N₂ = 3/1/1 mol/mol/mol, feed flow rate = 50 mL/min.

Table S8. O₂ consumption for the selectivity with co-fed CO₂ at various GHSV adjusted by the catalyst bed thickness.^a

Temperature (°C)	Catalyst bed thickness (mm)	GHSV (h ⁻¹)	Conversion (%)		O ₂ -consumption (%) for					
			CH ₄	O ₂	CO	CO ₂	C ₂ H ₄	C ₂ H ₆	C ₃ H ₆	C ₃ H ₈
750	2.1	50,000	2.4	9.0	3.3	2.1	0.3	0.8	0.00	0.00
	2.65	40,000	5.0	16.6	4.7	11.1	0.7	1.4	0.03	0.00
	3.5	30,000	5.4	19.6	5.2	9.3	1.2	1.8	0.05	0.03
	4.2	25,000	11.6	33.4	8.2	17.1	3.5	3.2	0.20	0.11
	5.3	20,000	34.0	100	28.2	50.9	18.3	4.9	1.84	0.29
	7.1	15,000	33.9	100	28.9	49.1	18.2	4.9	2.10	0.17
	10.6	10,000	33.0	100	31.6	45.1	19.2	5.1	2.00	0.28
	21.2	5,000	34.3	100	30.3	47.2	19.0	4.9	2.06	0.26
	35.3	3,000	34.5	100	31.9	58.0	19.5	5.0	2.20	0.26
800	2.1	50,000	33.0	97.1	36.0	32.6	17.8	5.9	1.78	0.21
	2.65	40,000	33.0	98.3	35.9	43.6	19.0	4.5	1.98	0.19
	3.5	30,000	33.2	100	35.1	45.2	18.8	4.1	2.04	0.18
	4.2	25,000	33.5	100	38.0	50.8	19.3	4.7	2.10	0.17
	5.3	20,000	33.6	100	34.0	47.6	18.4	4.4	2.06	0.16
	7.1	15,000	33.8	100	33.9	45.3	18.2	4.4	2.07	0.16
	10.6	10,000	33.0	100	35.7	40.3	18.6	4.5	2.15	0.16
	21.2	5,000	32.9	100	35.4	44.7	19.0	4.3	2.28	0.14
	35.3	3,000	32.5	100	34.4	49.4	18.3	4.0	2.24	0.12
850	2.1	50,000	32.8	99.2	45.8	35.5	18.5	3.8	2.13	0.07
	2.65	40,000	33.2	99.6	43.9	36.2	18.3	3.7	2.12	0.07
	3.5	30,000	34.4	100	43.8	40.8	19.0	3.8	2.23	0.07
	4.2	25,000	32.4	100	44.0	45.2	18.2	3.7	2.11	0.07
	5.3	20,000	31.8	100	35.9	44.4	17.6	3.4	2.09	0.06
	7.1	15,000	32.1	100	41.1	42.6	17.3	3.4	2.06	0.06
	10.6	10,000	30.8	100	42.4	36.9	17.8	3.4	2.16	0.05
	21.2	5,000	31.0	100	41.6	43.7	18.7	3.1	2.33	0.04
	35.3	3,000	30.8	100	41.0	51.2	17.9	2.6	2.26	0.01

^aCH₄/O₂/N₂ = 3/1/1 mol/mol/mol, feed flow rate = 50 mL/min.

Table S9. Observed XPS binding energies (eV) and near-surface compositions (atom%) of the Na₂WO₄/Mn/SiO₂ catalysts.

Catalysts ^a	Na 1s		W 4f		Mn 2p		Si 2p		O 1s		C 1s		Na/W (atom/atom)
	BE (eV)	atom%	BE (eV)	atom%	BE (eV)	atom%	BE (eV)	atom%	BE (eV)	atom%	BE (eV)	atom%	
Fresh catalyst	1071.8	8.17	34.6	2.19	641.4	0.19	102.8	23.19	532.5	51.72	284.6	14.97	3.7
With N ₂ only (top) ^b	1072.1	7.48	34.7	1.17	641.6	2.55	102.7	24.35	532.5	53.89	284.6	10.56	6.4
With N ₂ only (bottom) ^b	1071.9	8.81	34.4	1.41	641.6	2.03	102.5	22.17	532.4	52.24	284.6	13.34	6.2
With CO ₂ co-fed (top) ^b	1072.0	5.91	34.6	1.24	641.2	1.18	102.7	22.46	532.5	51.38	284.6	17.84	4.8
With CO ₂ co-fed (bottom) ^b	1072.0	6.53	34.7	1.34	641.4	0.61	102.7	23.51	532.5	53.55	284.6	14.46	4.9

^a5 wt% of Na₂WO₄ and 2 wt% of Mn for all catalysts.

^bSpent catalysts.