Supplementary Materials for

Low-temperature oxidative coupling of methane over LaCeZr ternary oxides supported Mn-Na_2WO_4

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Equations:

The CH_4 conversion and products selectivity were calculated based on a carbon atom basis of the inlet and outlet gases.

$$CH_4\,Conv. = \left(1 - \frac{nCH_{4outlet}}{nCH_{4outlet} + \sum x \times n[products]_{outlet}}\right) \times 100\%\#(1)$$

where x is the number of carbon atom in the products.

The products selectivity was calculated on a carbon atom basis of the outlet products (i.e., C_2H_4, C_2H_6, CO, CO_2, C_3H_6 and C_3H_8). C_2 products include both C_2H_4 and C_2H_6.

$$C_2\,Sel. = \frac{2 \times nC_2H_4 + 2 \times nC_2H_6}{2 \times nC_2H_4 + 2 \times nC_2H_6 + 1 \times nCO + 1 \times nCO_2 + 3 \times nC_3H_6 + 3 \times nC_3H_8} \times 100\%\#(2)$$

$$CO\,Sel. = \frac{1 \times nCO}{2 \times nC_2H_4 + 2 \times nC_2H_6 + 1 \times nCO + 1 \times nCO_2 + 3 \times nC_3H_6 + 3 \times nC_3H_8} \times 100\%\#(3)$$

$$CO_2\,Sel. = \frac{1 \times nCO_2}{2 \times nC_2H_4 + 2 \times nC_2H_6 + 1 \times nCO + 1 \times nCO_2 + 3 \times nC_3H_{6}}$$

$$C_2\,Yield = CH_4\,Conv. * C_2\,Sel. * 100\%\#(5)$$

The following formula was used for the calculating of carbon balance, where x is the number of carbon atom in the products. Generally, a >95% carbon balance could be gained.

$$Carbon\ balance = \frac{nCH_{4outlet} + \sum x \times n[products]_{outlet}}{nCH_{4inlet}} \times 100\%\#(6)$$

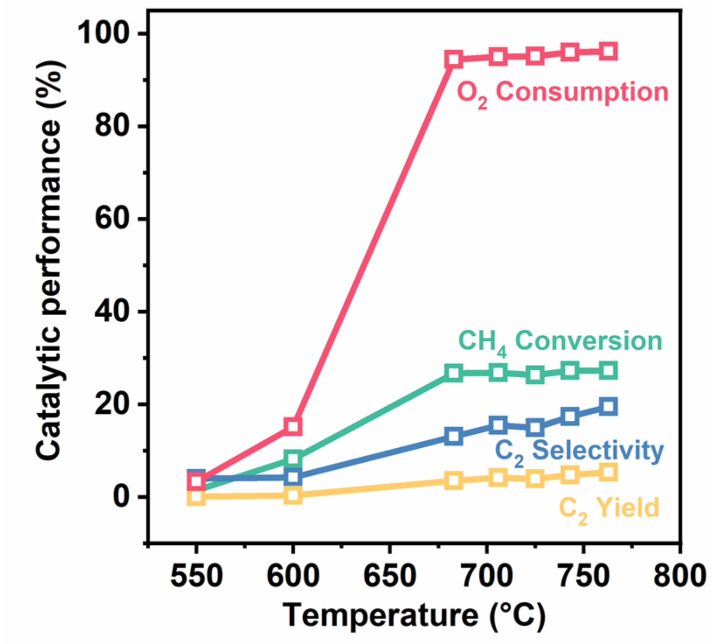

Figure S1. The catalytic performance of the LaCeZr support in OCM.

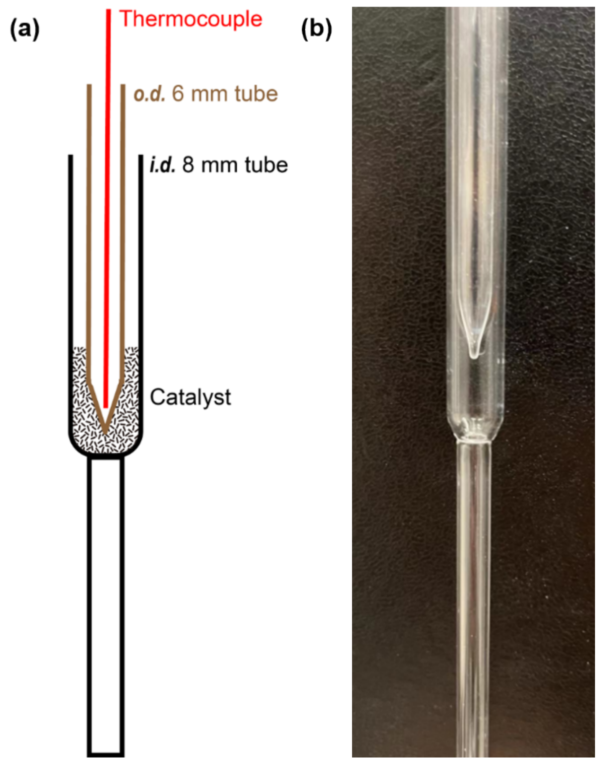

Figure S2. (a) The schematic diagram and (b) the photograph of the quartz fix-bed reactor.

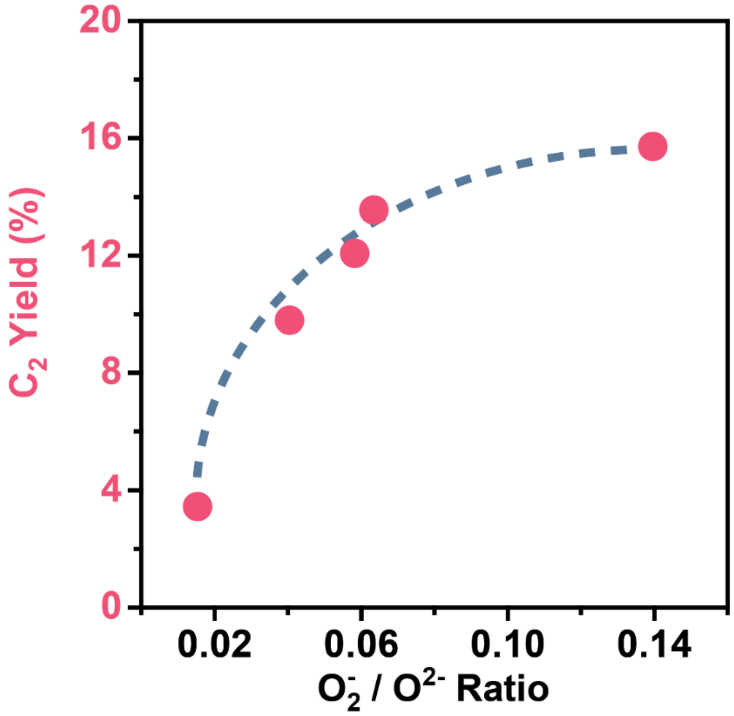

Figure S3. C_2 yields as a function of O_2^-/O^{2-} ratio. Reaction conditions: T = 703 ± °C, CH_4:O_2 = 5:1, total gas flow rate 66 mL min^{-1}.

Table S1: Catalytic performances of Mn-Na_2WO_4/LaCeZr with different CH_4/O_2 ratio.

CH_4/O_2 ratio	T (°C)	CH_4 Conv. (%)	SC_2 (%)	YC_2 (%)	O_2 Conv. (%)	C_2H_4:C_2H_6 molar ratio
6	700	5.3	24.8	1.3	27.9	/
5	701	26.4	59.4	15.7	98.5	1.0
4	700	32.3	58.5	18.9	98.0	1.2
3	700	37.6	55.4	20.9	98.5	1.6

SC_2: C_2 selectivity; YC_2: C_2 yield.

Reaction conditions: $CH_4:O_2$ varied from 6:1 to 3:1, total gas flow rate 66 mL min^{-1}, GHSV 4,000 mL h^{-1} g_{cat}^{-1}.

Table S2. Representative catalysts for low-temperature oxidative coupling of methane.

Entry	T (°C)	Catalyst^a	GHSV^b (mL g_{cat}^{-1} h^{-1})	CH_4:O_2: X^c	CH_4 Conv. (%)	SC_2 (%)	YC_2 (%)	Ref.
1	660	Mn_2O_3-Na_2WO_4/$Ce_{0.15}Zr_{0.85}O_2$	4000	5:1:0	25.0	67.0	16.8	*[30]*
2	680	MnO_x-Na_2WO_4/A-SiO_2	10000	5:1:0	23.0	72.0	16.6	*[18]*
3	650	Mn_2O_3-TiO_2-Na_2WO_4/SiO_2	8000	5:1:4	22.0	62.0	13.6	*[17]*
4	700	TiO_2-modified Mn_2O_3-Na_2WO_4/SiO_2	8000	5:1:4	23.0	73.0	16.8	*[32]*
5	500	La_2O_3	36000	3:1:0	28.0	40.0	11.2	*[33]*
6	500	Sr–La_2O_3	72000	3:1:0	35.0	47.0	16.5	*[34]*
7	570	La_2O_3/5NaWSi	20000	3:1:2.6	31.0	34.2	10.6	*[35]*
8	450	$La_2O_2CO_3$	30000	3:1:0	30.2	48.5	14.7	*[36]*
9	550	$La_2Ce_2O_7$	18000	4:1:5	28.0	52.0	14.6	*[37]*
10	375	$La_{0.8}Ce_{0.2}O_{1.5+\delta}$	30000	3:1:0	29.2	43.0	12.6	*[38]*
11	720	Li/MgO	-	2:1:0	37.8	50.3	19.0	*[39]*
12	500	Sm_2O_3	72000	3:1:0	28.0	42.0	11.8	*[40]*
13	500	Sr-Sm_2O_3	72000	3:1:0	29.0	48.0	13.9	*[40]*
14	720	$LiCa_2Bi_3O_4Cl_6$	-	2:1:7	41.7	46.5	19.4	*[41]*
15	710	Mn-Na_2WO_4/ZrCeLa	4000	3:1:0	37.6	55.4	20.9	*This work*

^{a}Elemental compositions of the catalysts. ^{b}Gas hourly space velocity. ^{c}CH_4/O_2/balance (N_2, He, or Ar in the corresponding references).

Table S3: Catalytic performances of Mn-Na_2WO_4/LaCeZr with different La ratio in support.

La ratio	T (°C)	CH_4 Conv. (%)	SC_2 (%)	YC_2 (%)	O_2 Conv. (%)	C_2H_4:C_2H_6 molar ratio
La = 0	700	20.6	47.5	9.8	96.3	0.6
La = 0.5	700	21.0	57.4	12.1	95.8	0.7
La = 1.0	701	26.4	59.4	15.7	98.5	1.0
La = 2.0	706	23.5	57.6	13.5	97.6	0.8
La = 4.0	699	8.0	43.0	3.4	15.6	/

SC_2: C_2 selectivity; YC_2: C_2 yield.

Reaction conditions: CH_4:O_2 = 5:1, total gas flow rate 66 mL min^{-1}, GHSV 4,000 mL h^{-1} g_{cat}^{-1}.

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