Supplementary information:

Silver enhanced oxidative coupling of methane over Mn-Na_2WO_4/SiO_2 catalyst

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Table S1. Comparison on the performance of Mn-Na_2WO_4/SiO_2 and the modified catalyst.

Catalysts	CH_4 Conversion(%)	C_2 Selectivity(%)	C_2 Yield(%)	*T* (℃)	Data source
Mn-Na_2WO_4/SiO_2	30.3	68.4	20.7	820	[1]
Mn-Na_2WO_4/SiO_2	31.1	64.1	19.9	800	This work
MnO_x-Na_2WO_4/A-SiO_2	23.0	72.0	16.6	680	[2]
Ce/Na_2WO_4/Mn/SiO_2	34	62	21	840	[3]
Na-Mn-Zr-S-P-W/SiO_2	27.5	75.4	20.7	796	[4]
Ge-doped MnO_x-Na_2WO_4/SiO_2	23.2	70.7	16.4	770	[5]
Mn_2O_3-TiO_2-Na_2WO_4/ SiO_2	22.0	62.0	13.6	650	[6]
TiO_2-modified Mn_2O_3-Na_2WO_4/ SiO_2	23.0	73.0	16.8	700	[7]
Ag || Mn-Na_2WO_4/SiO_2	35.3	58.4	20.6	750	This work

Table S2. Catalytic performances of various catalysts in OCM. Reaction conditions: $CH_4/O_2/N_2$ = 30/10/27, total gas flow rate 67 mL min^{-1}.

Catalysts	T_b (°C)	CH_4 Conv. (%)	O_2 Conv. (%)	SC_2H_4 (%)	SC_2H_6 (%)	SC_2 (%)	SCO_2 (%)	SCO (%)	YC_2 (%)
Mn-Na_2WO_4/SiO_2	700	3.4	6.3	4.0	18.8	22.8	65.2	9.3	0.8
	750	13.9	34.9	20.7	35.9	56.6	33.9	8.7	7.9
	800	31.1	97.5	39.8	24.3	64.1	21.7	13.8	19.9
Ag || Mn-Na_2WO_4/SiO_2	700	7.3	17.2	3.3	37.4	40.7	58.8	0.5	3.0
	750	34.1	98.3	27.1	28.7	55.8	40.4	2.6	19.0
	800	35.7	98.9	29.1	25.8	54.9	39.0	4.3	19.6
AgCl || Mn-Na_2WO_4/SiO_2	700	11.4	24.9	25.9	37.1	63.0	34.3	2.0	7.1
	750	30.5	88.5	39.3	17.0	56.3	35.8	6.0	17.2
	800	33.2	98.9	37.2	14.9	52.1	37.2	8.6	17.3
$AgNO_3$ || Mn-Na_2WO_4/SiO_2	700	5.5	12.8	1.4	29.6	31.0	67.6	1.4	1.7
	750	20.5	46.4	19.0	40.6	59.6	37.5	1.9	12.2
	800	35.6	99.0	31.5	26.2	57.7	35.9	5.3	20.5

T_b: bed temperature; SC_2H_4: C_2H_4 selectivity; SC_2H_6: C_2H_6 selectivity; SC_2: C_2 selectivity; SCO_2: CO_2 selectivity; SCO: CO selectivity; YC_2: C_2 yield.

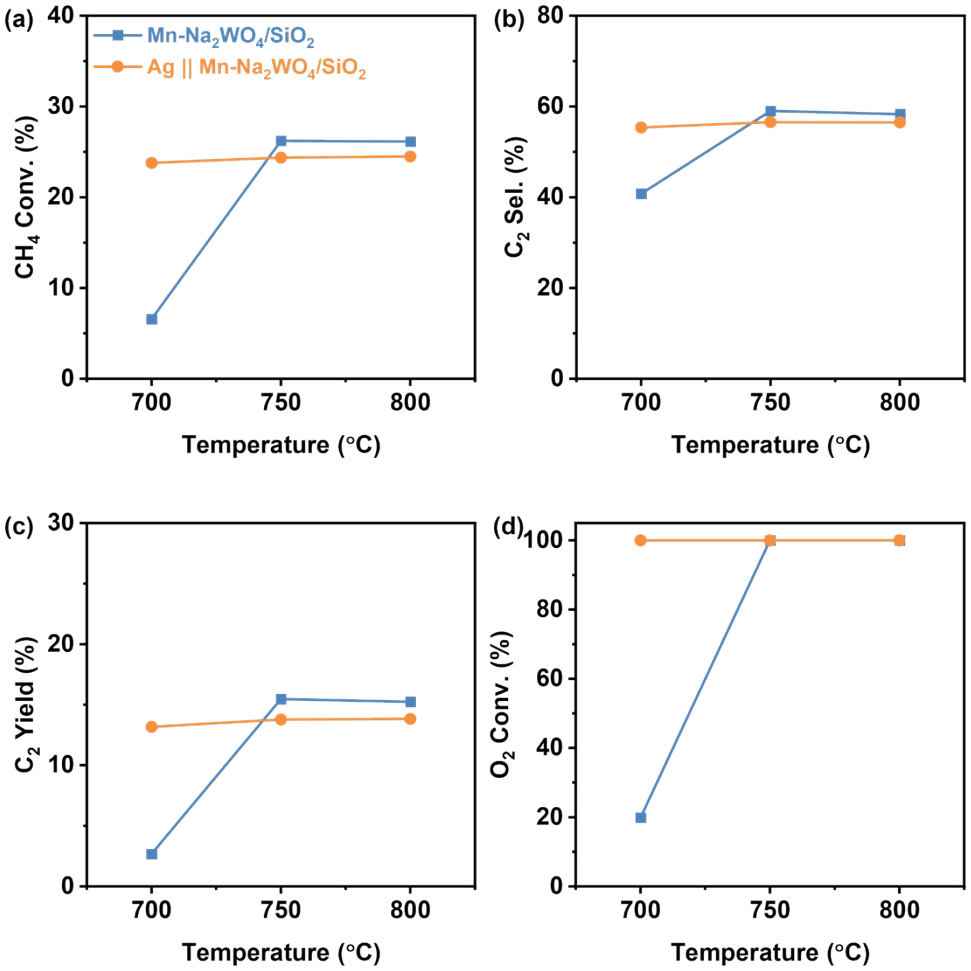

Figure S1. OCM performance of the $Mn\text{-}Na_2WO_4/SiO_2$ and Ag || $Mn\text{-}Na_2WO_4/SiO_2$ catalyst.

Reaction conditions: $CH_4:O_2:N_2$=45:15:7

Table S3. Catalytic performances of various catalysts in OCM. Reaction conditions: CH_4:O_2:N_2=45:15:7, total gas flow rate 67 mL min^{-1}

Catalysts	T_b (°C)	CH_4 Conv. (%)	O_2 Conv. (%)	SC_2H_4 (%)	SC_2H_6 (%)	SC_2 (%)	SCO_2 (%)	SCO (%)	YC_2 (%)
Mn-Na_2WO_4/SiO_2	700	6.6	19.9	8.5	32.3	40.8	39.5	19.8	2.7
	750	26.2	100.0	37.4	21.6	59.0	20.7	20.7	15.5
	800	26.1	100.0	37.4	20.9	58.3	20.1	21.1	15.2
Ag || Mn-Na_2WO_4/SiO_2	700	23.8	100.0	25.5	29.9	55.4	38.4	6.3	13.2
	750	24.4	100.0	29.1	27.5	56.6	34.3	9.1	13.8
	800	24.5	100.0	31.1	25.4	56.5	31.0	12.5	13.8

T_b: bed temperature; SC_2H_4: C_2H_4 selectivity; SC_2H_6: C_2H_6 selectivity; SC_2: C_2 selectivity; SCO_2: CO_2 selectivity; SCO: CO selectivity; YC_2: C_2 yield.

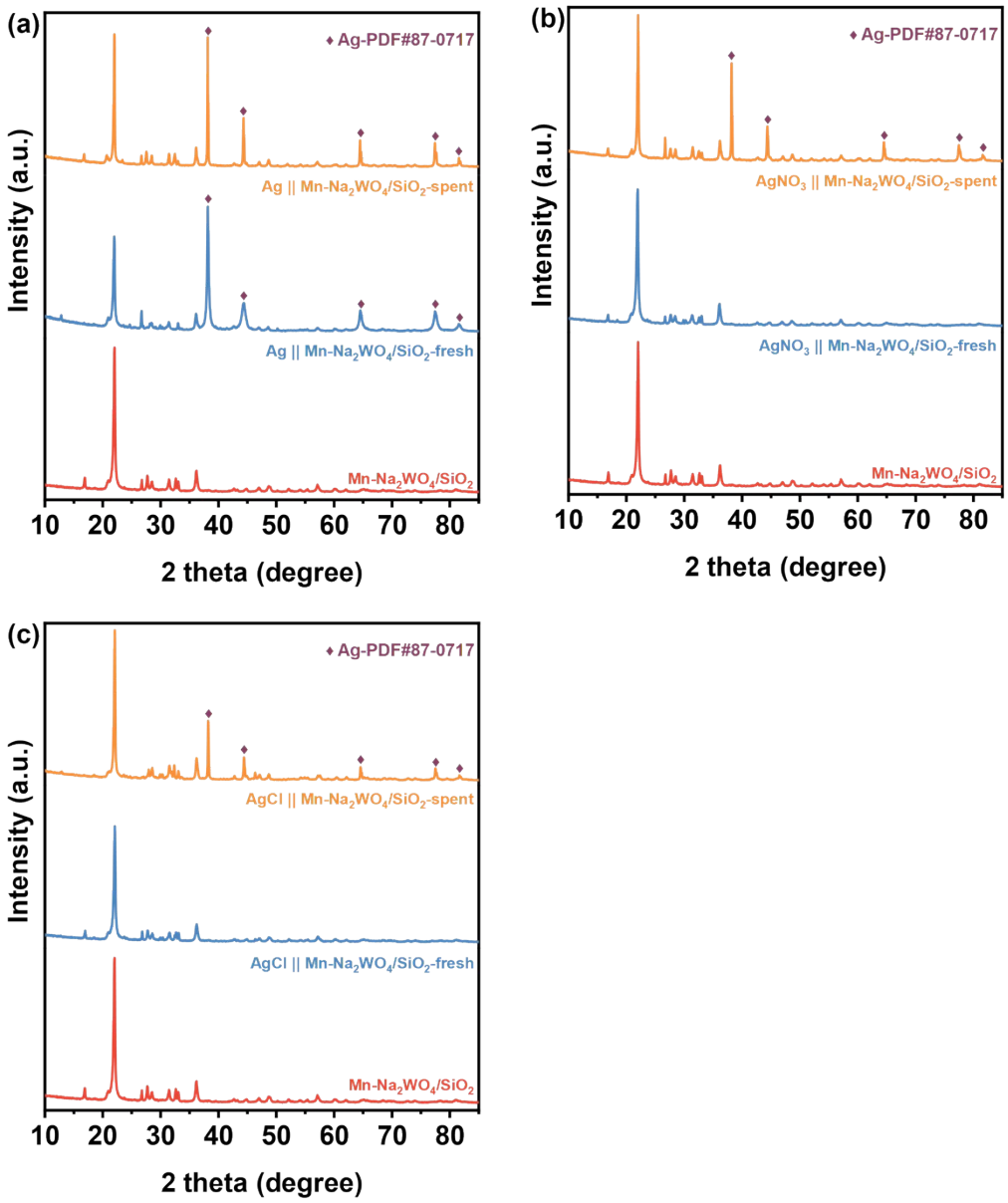

Figure S2. XRD patterns for the fresh catalyst and spent sample of (a) Ag || Mn-Na_2WO_4/SiO_2, (b) $AgNO_3$ || Mn-Na_2WO_4/SiO_2, (c) AgCl || Mn-Na_2WO_4/SiO_2 catalyst

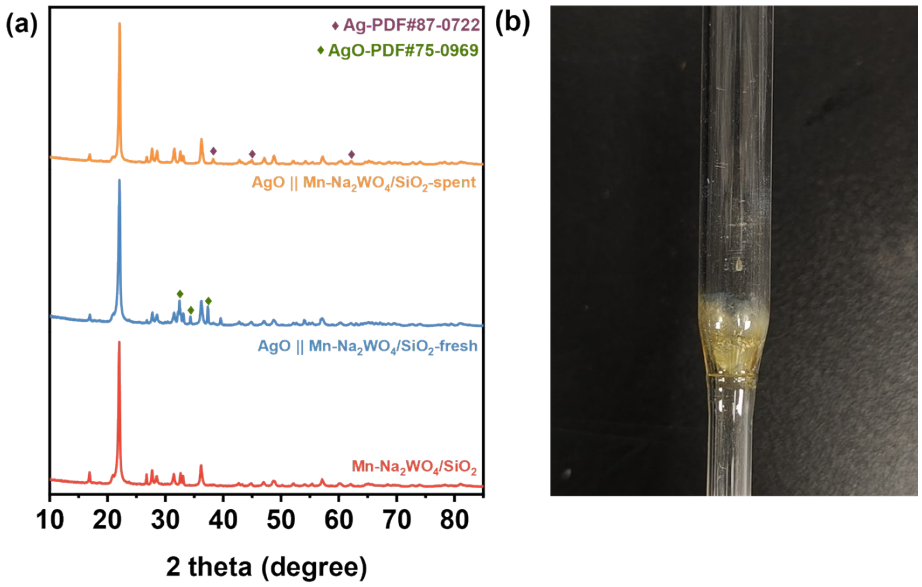

Figure S3. (a) XRD patterns for the fresh catalyst and spent sample of AgO || Mn-Na_2WO_4/SiO_2; (b) Quartz tube picture of AgO after reaction.

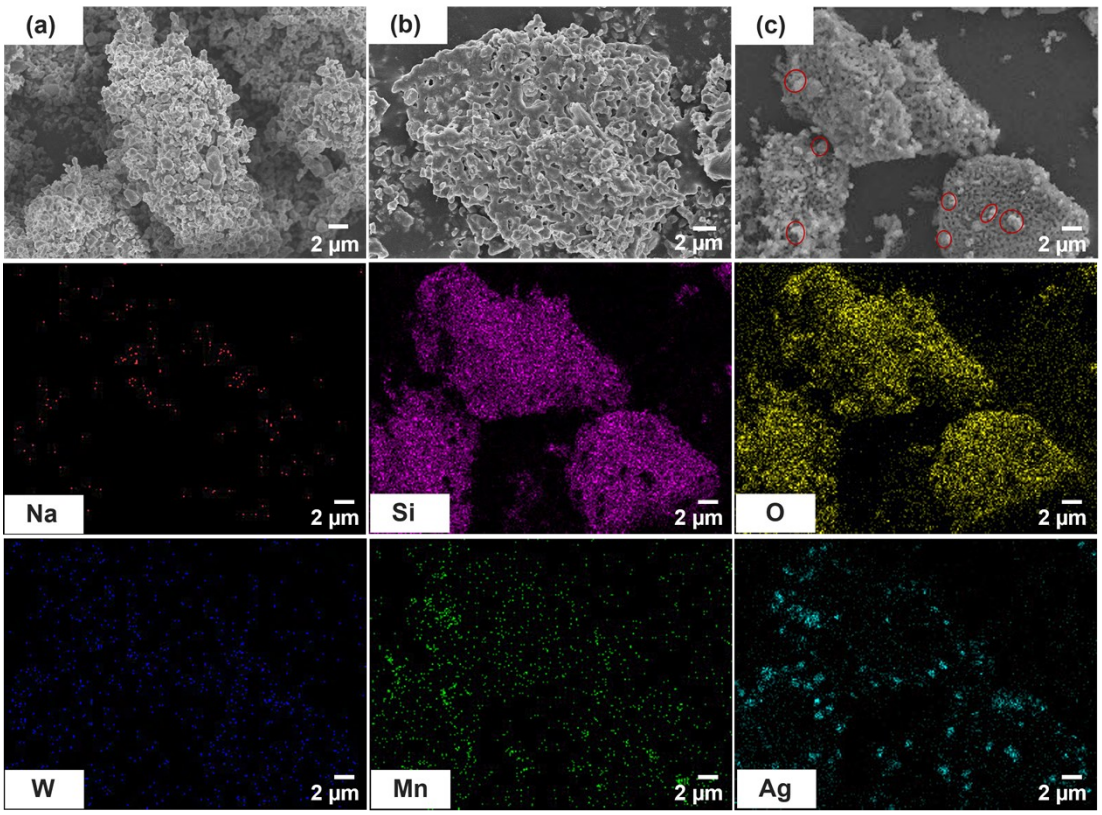

Figure S4. SEM images of the sample before (a) and after (b) the OCM reaction; (c) energy dispersive spectroscopy mapping images.

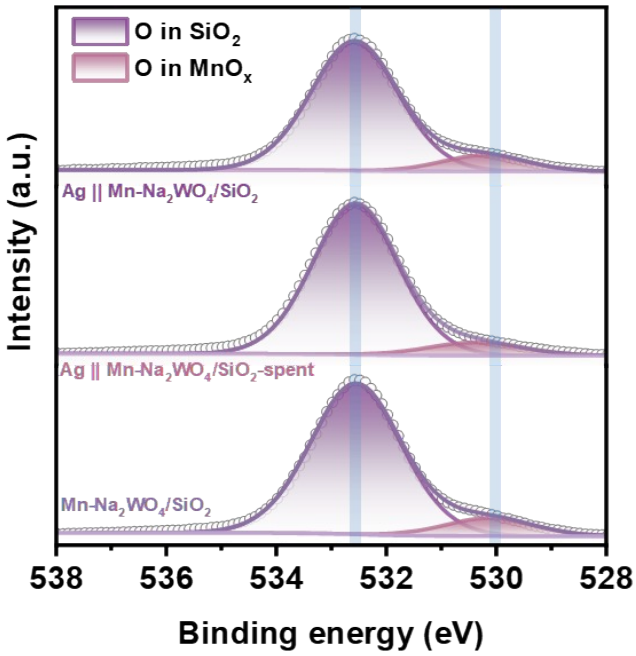

Figure S5. XPS O_{1s} spectra for (a) the fresh catalyst and (b)spent sample of Ag || Mn-Na_2WO_4/SiO_2 and (c) Mn-Na_2WO_4/SiO_2 catalyst

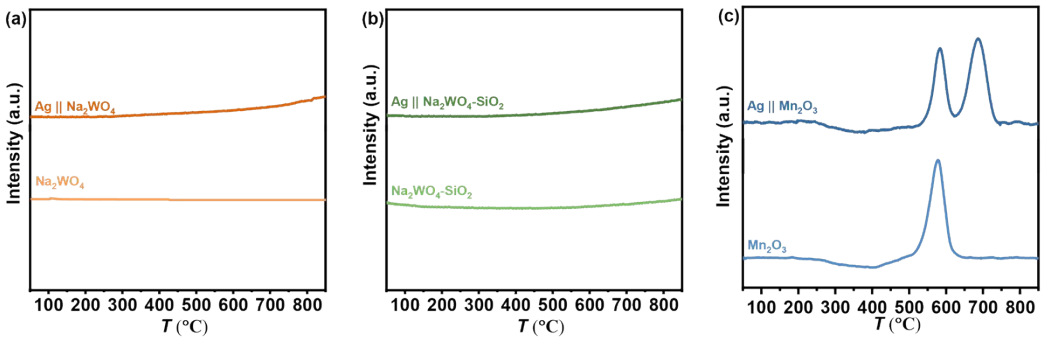

Figure S6. O_2-TPO profiles of different samples.

References:

[1] J. Wang, L. Chou, B. Zhang, H. Song, J. Zhao, J. Yang, S. Li, Comparative study on oxidation of methane to ethane and ethylene over Na_2WO_4–Mn/SiO_2 catalysts prepared by different methods, Journal of Molecular Catalysis A: Chemical 245 (2006) 272-277.

[2] J. Si, G. Zhao, W. Sun, J. Liu, C. Guan, Y. Yang, X.R. Shi, Y. Lu, Oxidative Coupling of Methane: Examining the Inactivity of the MnO_x-Na_2WO_4 /SiO_2 Catalyst at Low Temperature, Angew Chem Int Ed Engl 61 (2022) e202117201.

[3] S.M.K. Shahri, A.N. Pour, Ce-promoted $Mn/Na_2WO_4/SiO_2$ catalyst for oxidative coupling of methane at atmospheric pressure, Journal of Natural Gas Chemistry 19 (2010) 47-53.

[4] F.Q.C. K. Huang, D.W. Lü, Artificial neural network-aided design of a multi-component catalyst for methane oxidative coupling, Appl. Catal. A: Gen 219 (2001) 61-68.

[5] N.S. Hayek, G.J. Khlief, F. Horani, O.M. Gazit, Effect of reaction conditions on the oxidative coupling of methane over doped MnOx-Na_2WO_4/SiO_2 catalyst, Journal of Catalysis 376 (2019) 25-31.

[6] P. Wang, G. Zhao, Y. Wang, Y. Lu, $MnTiO_3$-driven low-temperature oxidative coupling of methane over TiO_2-doped Mn_2O_3-Na_2WO_4/SiO_2 catalyst, Sci. Adv. 3 (2017) e1603180.

[7] P. Wang, X. Zhang, G. Zhao, Y. Liu, Y. Lu, Oxidative coupling of methane/MO_x- modified (M =Ti, Mg, Ga, Zr) Mn_2O_3-Na_2WO_4/SiO_2 catalysts and effect of MO_x modification, Chin. J. Catal. 39 (2018) 1395–1402.