Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

Enhanced production of C_2-C_4 alkanes from syngas via the metal sulfides-support interaction over Ni-MoS_2/$Ce_{1-x}La_xO_{2-\delta}$

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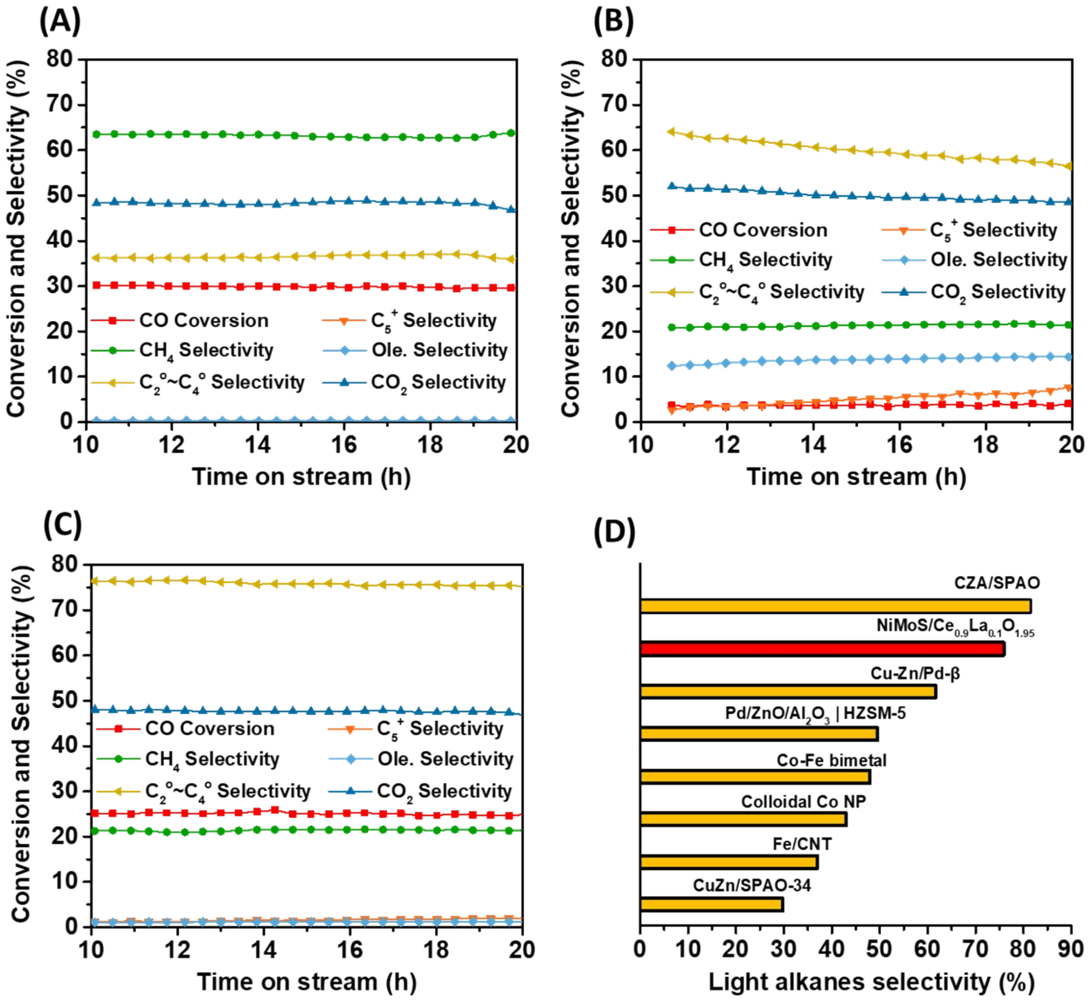

Fig. S1: The variation of CO conversion and product selectivity with time on stream over $MoS_2/Ce_{0.9}La_{0.1}O_{0.05}$-250 (A), $NiS_x/Ce_{0.9}La_{0.1}O_{0.05}$-250 (B), and Ni-$MoS_2/Ce_{0.9}La_{0.1}O_{0.05}$-250 (C). Reaction condition: T = 380 °C, P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h). And the light alkanes selectivities in the CO conversion reaction published in the previous studies[1-7].

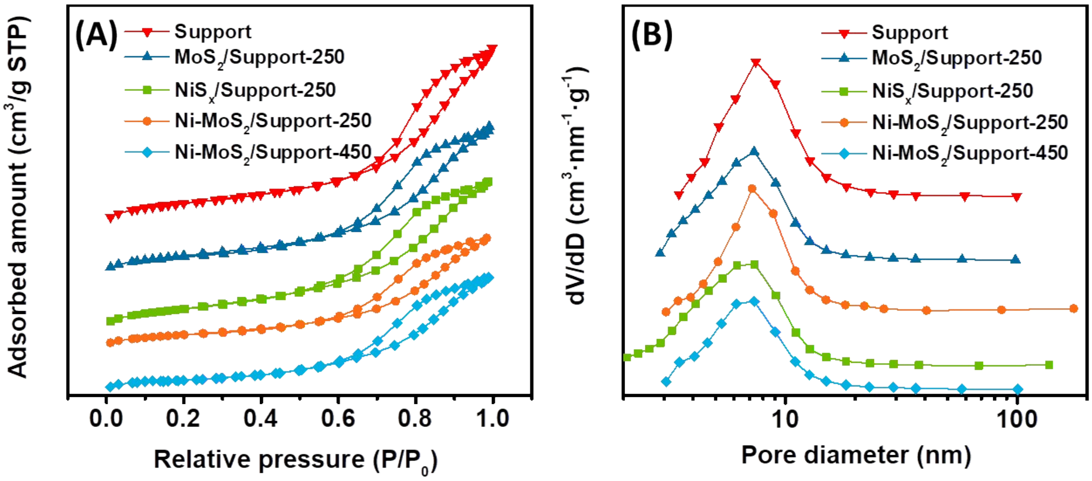

Fig. S2: N_2 adsorption-desorption isotherms (A) and pore size distributions (B) of the $Ce_{0.9}La_{0.1}O_{0.05}$ support, $MoS_2/Ce_{0.9}La_{0.1}O_{0.05}$-250, $NiS_x/Ce_{0.9}La_{0.1}O_{0.05}$-250, Ni-$MoS_2/Ce_{0.9}La_{0.1}O_{0.05}$-250, and the Ni-$MoS_2/Ce_{0.9}La_{0.1}O_{0.05}$-450.

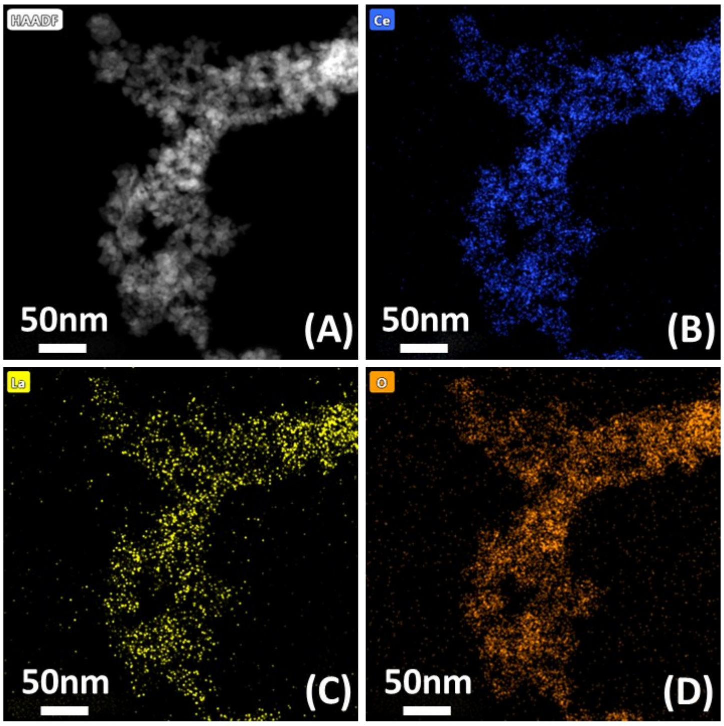

Fig. S3: HAADF TEM image of Ni-$MoS_2/Ce_{0.9}La_{0.1}O_{1.95}$-250 (A), and EDX mapping of Ce (B), La (C), and O (D).

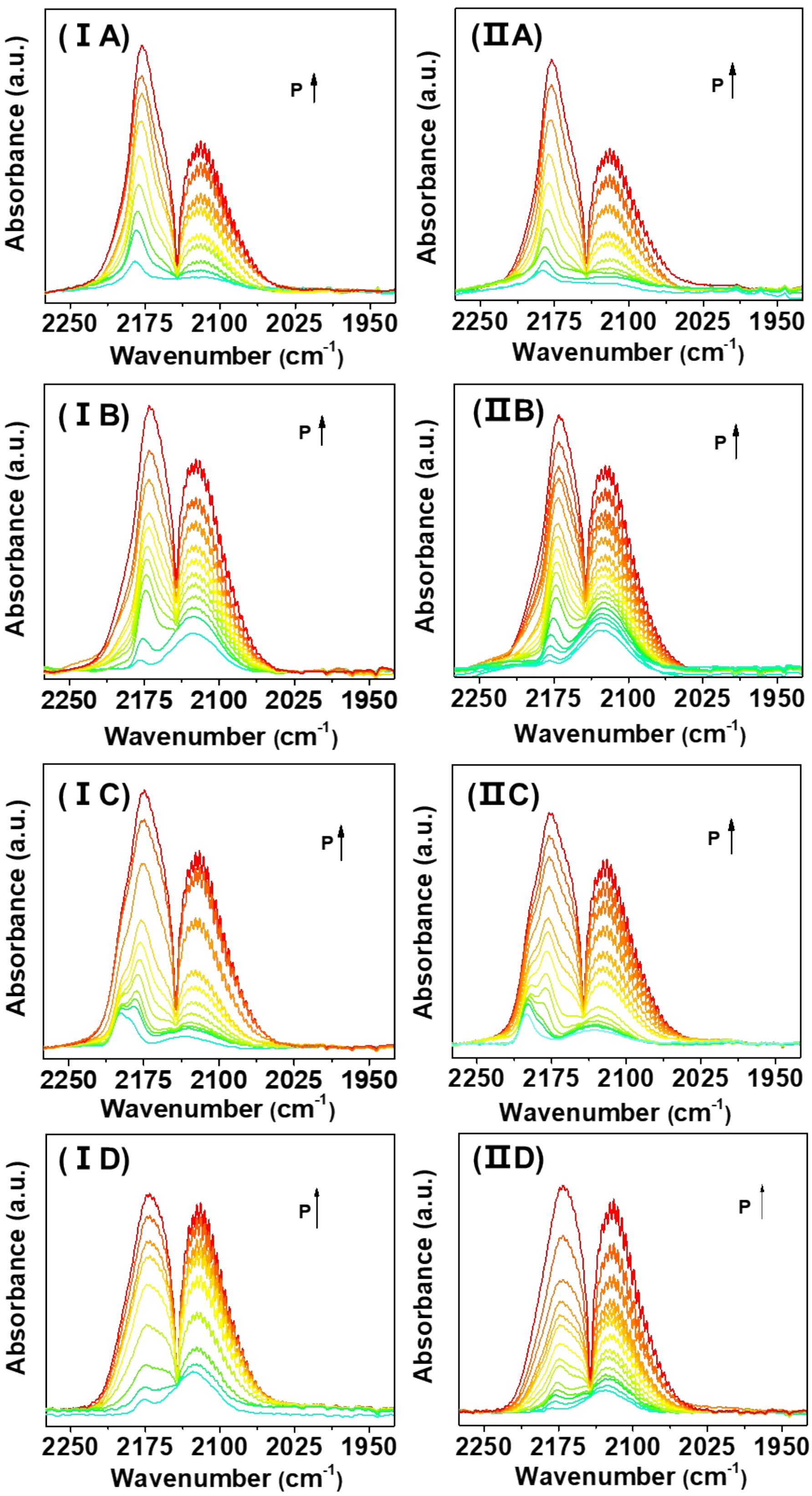

Fig. S4: The DRIFT spectra of CO adsorption (I) and desorption (II) over $NiS_x/Ce_{0.9}La_{0.1}O_{1.95}$-250 (A), $MoS_2/Ce_{0.9}La_{0.1}O_{1.95}$-250 (B), Ni-$MoS_2/Ce_{0.9}La_{0.1}O_{1.95}$-250 (C), and Ni-$MoS_2/Ce_{0.9}La_{0.1}O_{1.95}$-450 (D).

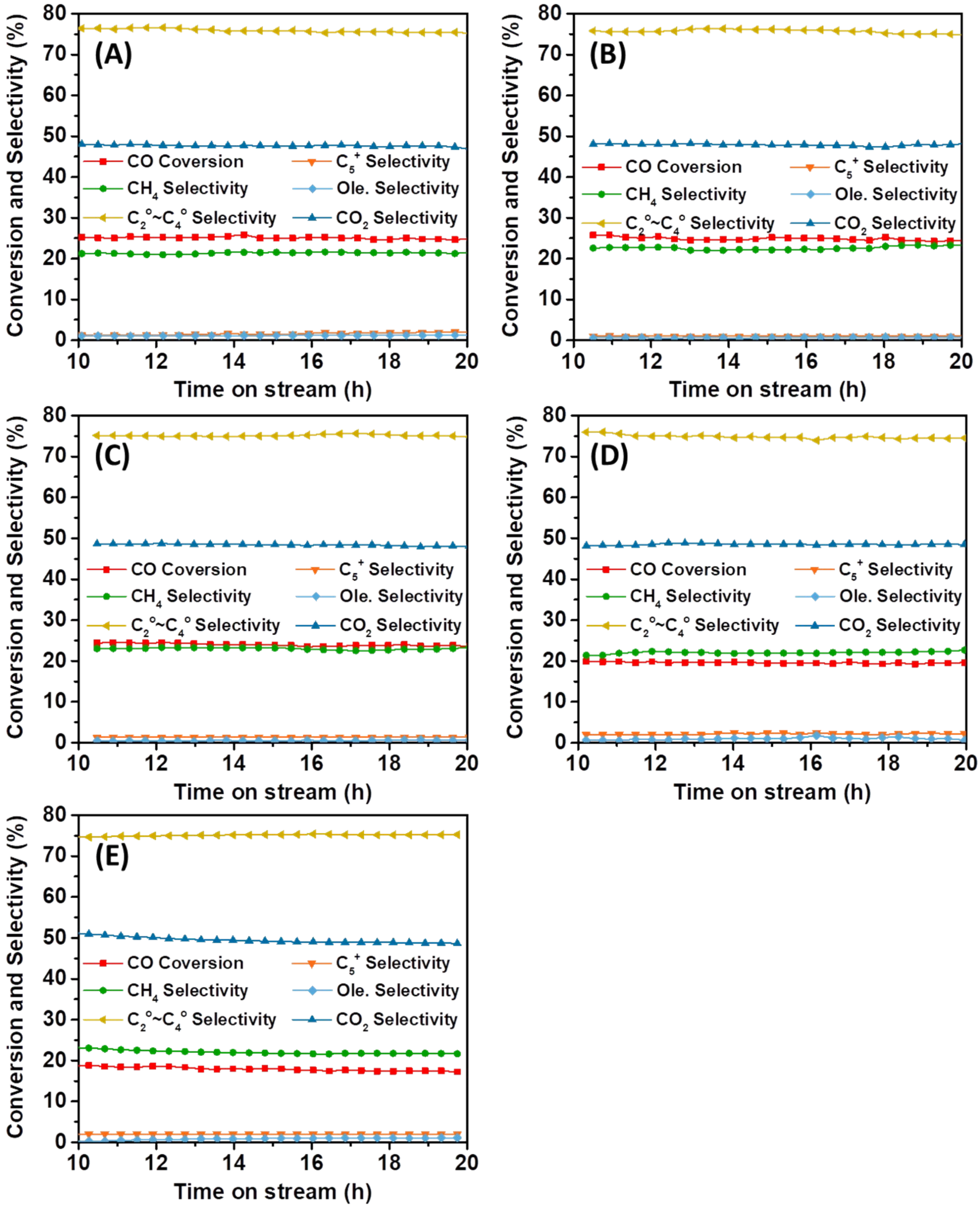

Fig. S5: The effect of sulfidation temperature (A: 250 °C, B: 300 °C, C: 350 °C, D: 400 °C, E: 450 °C) on the time on-stream conversion of CO and product selectivity over Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{0.05}$. Reaction condition: T = 380 °C, P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h).

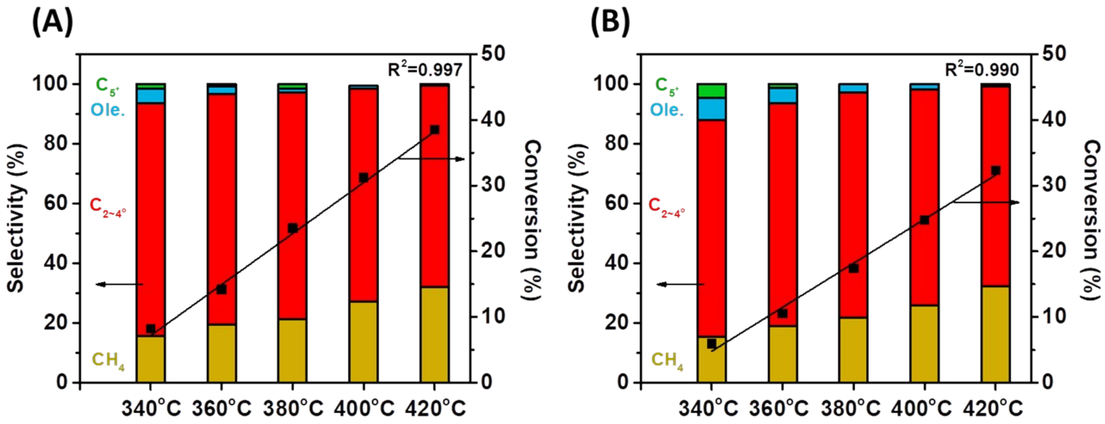

Fig. S6: The hydrocarbon selectivities (yellow bar: CH_4, red bar: C_2~C_4 light alkanes, blue bar: olefins, green bar: C_5^+ hydrocarbons) and CO conversions as a function of reaction temperatures (340-420 °C) over Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-250 (A) and Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-450 (B). Reaction condition: P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h).

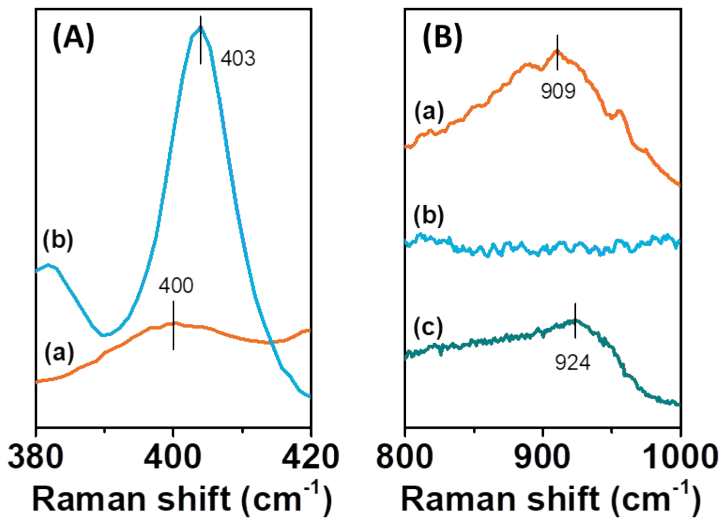

Fig. S7: Raman spectra ranging from 380 to 420 cm^{-1} (A) and 800 to 1000 cm^{-1} (B) over the Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-250 (a), the Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-450 (b) catalysts, and the NiMo-oxide/$Ce_{0.9}La_{0.1}O_{1.95}$ precursor (c).

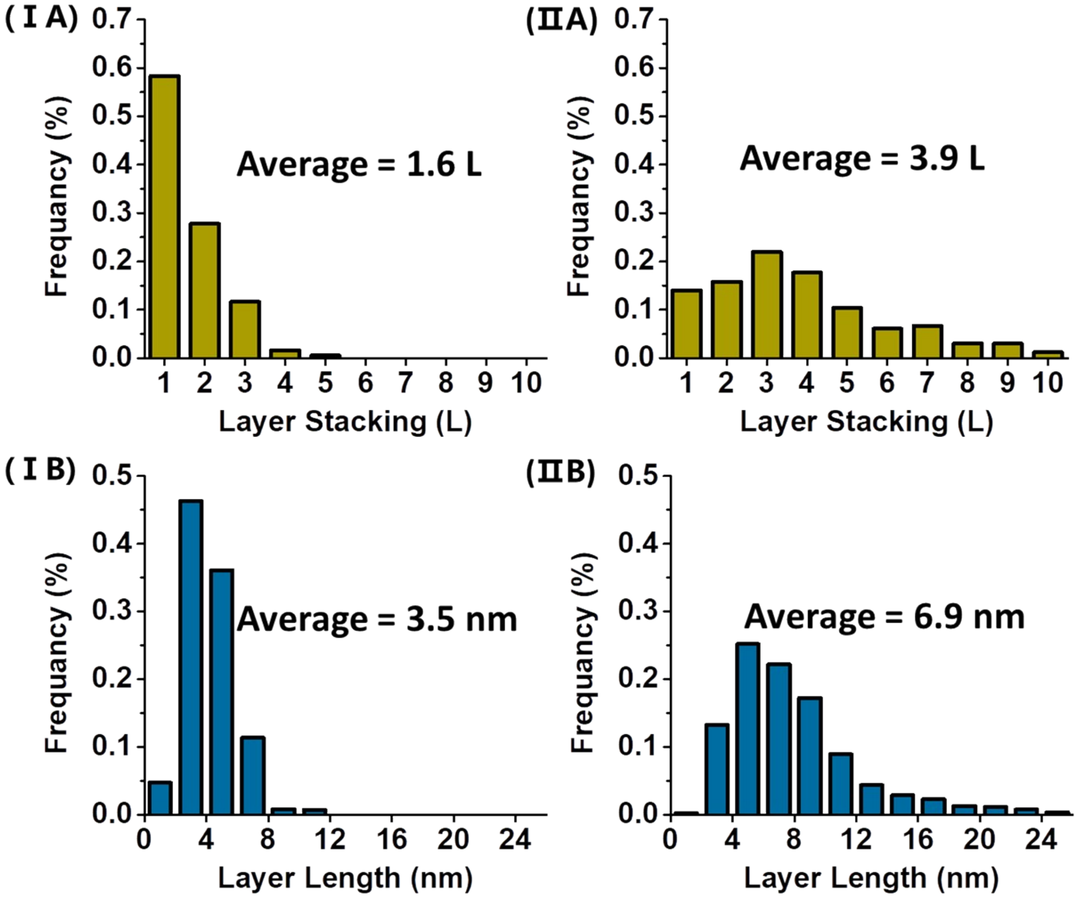

Fig. S8: Histograms of the layer stacking (Ⅰ) and length (Ⅱ) over Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-250 (A) and Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-450 catalysts (B).

Table S1: The support effect on the catalytic performance in the reaction over the supported MoS_2. Reaction condition: T = 380 °C, P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h).

Catalysts[(1)]	X_{CO} (%)	Hydrocarbon selectivity (%)							CO_2 (%)	R_{CO} (h^{-1})
		CH_4	C_2^o	C_3^o	C_4^o	C_2^o-C_4^o	Ole.	C_5^+		
MoS_2/MgO	7.4	56.7	32.3	9.1	1.5	42.9	0.4	0	48.0	7.4
MoS_2/MgO-Al_2O_3	14.4	64.1	29.0	5.7	0.6	35.3	0.4	0.3	48.2	14.5
MoS_2/Al_2O_3	14.3	62.5	30.0	6.7	0.7	37.4	0.1	0	47.2	14.4
MoS_2/CeO_2	10.3	59.4	34.9	3.8	0.3	39.0	1.6	0	48.5	10.3
$MoS_2/Ce_{0.9}La_{0.1}O_{0.05}$	17.3	57.1	37.5	4.2	0.4	42.0	0.8	0	48.4	17.4
MoS_2/La_2O_3	8.5	64.1	29.4	3.1	0.5	33.0	2.5	0.5	48.2	8.6

(1) Sulfidation condition: 450 °C for 300 min.

Table S2: Catalytic performances over $Ce_{0.9}La_{0.1}O_{1.95}$ supported NiS_x, MoS_2 and Ni-MoS_2. Reaction condition: T = 380 °C, P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h).

Catalysts[(1)]	X_{CO} (%)	Hydrocarbon selectivity (%)							CO_2 (%)	R_{CO} (h^{-1})
		CH_4	C_2^o	C_3^o	C_4^o	C_2^o-C_4^o	Ole.	C_5^+		
$NiS_x/Ce_{0.9}La_{0.1}O_{1.95}$-250	3.7	21.3	39.4	16.3	4.0	60.0	13.8	5.2	49.8	-
$MoS_2/Ce_{0.9}La_{0.1}O_{1.95}$-250	29.9	63.2	33.0	3.3	0.2	36.5	0.3	0	48.2	53.2
Ni-$MoS_2/Ce_{0.9}La_{0.1}O_{1.95}$-250	25.1	21.4	42.0	27.6	6.2	75.9	1.2	1.6	47.7	45.4

(1) Sulfidation condition: 450 °C for 300 min.

Table S3: H_2 consumption in the H_2-TPR analysis of the oxide precursors

Samples	Support(1)	MoO_3/Support(1)	NiO/Support(1)	NiMo oxide/Support(1)
H_2 consumption (mol/g)	111.7	144.9	509.7	363.9

(1) Support: $Ce_{0.9}La_{0.1}O_{1.95}$

Table S4: The effect of support composition (Ce and La content) on the catalytic performance over the supported Ni-MoS_2. Reaction condition: T = 380 °C, P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h).

Catalysts(1)	X_{CO} (%)	Hydrocarbon selectivity (%)							CO_2 (%)	R_{CO} (h^{-1})
		CH_4	C_2^o	C_3^o	C_4^o	C_2^o-C_4^o	Ole.	C_5^+		
Ni-MoS_2/$Ce_{0.95}La_{0.05}O_{1.975}$	10.7	20.5	31.0	29.5	10.1	70.4	5.6	3.5	49.1	11.0
Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$	10.6	18.1	30.0	31.0	11.2	72.2	6.1	3.7	49.3	10.9
Ni-MoS_2/$Ce_{0.8}La_{0.2}O_{1.9}$	8.7	22.1	31.3	27.6	8.9	67.9	6.9	3.1	49.1	8.9

(1) Sulfidation condition: 450 °C for 300 min.

Table S5: An optimization of the loading of Mo and Ni for the reaction over Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-450. Reaction condition: T = 380 °C, P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h).

NiO(1)	MoO_3(1)	X_{CO} (%)	Hydrocarbon selectivity (%)							CO_2 (%)	R_{CO} (h^{-1})
			CH_4	C_2^o	C_3^o	C_4^o	C_2^o-C_4^o	Ole.	C_5^+		
10 %	5 %	10.9	18.6	31.4	27.7	9.4	68.4	8.9	4.1	48.2	39.0
10 %	10 %	12.6	19.9	31.3	31.5	11.1	73.9	5.0	1.2	49.3	23.6
10 %	15 %	11.3	18.0	29.4	30.1	10.5	70.0	8.4	3.7	49.3	14.8
10 %	20 %	9.1	20.8	31.2	28.8	10.0	70.0	7.7	1.6	49.5	9.3
1.0 %	10 %	17.2	30.5	43.4	21.3	2.8	67.5	2.0	0	48.3	30.7
2.5 %	10 %	17.8	22.4	34.5	30.9	9.5	74.8	2.8	0	49.8	32.2
5.0 %	10 %	14.8	20.9	34.1	28.6	8.8	71.5	5.6	2.1	48.9	27.1
7.5 %	10 %	14.3	19.4	32.4	32.4	11.1	75.9	4.7	1.2	49.7	26.5

(1) Sulfidation condition: 450 °C for 300 min.

Table S6: The effect of sulfidation time on the catalytic performance for the reaction over Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-450. Reaction condition: T = 380 °C, P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h).

Sulfidation time	X_{CO} (%)	Hydrocarbon selectivity (%)							CO_2 (%)	R_{CO} (h^{-1})
		CH_4	C_2^o	C_3^o	C_4^o	C_2^o-C_4^o	Ole.	C_5^+		
200 min	17.0	21.4	34.7	28.4	8.9	72.0	4.3	2.8	48.3	30.6
300 min	17.9	22.1	34.5	32.1	8.6	75.1	2.8	0	49.5	32.5
400 min	17.8	22.4	34.5	30.9	9.5	74.8	2.8	0	49.7	32.2

(1) Sulfidation temperature: 450 °C.

Table S7: The effect of sulfidation temperature on the catalytic performance for the reaction over Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$. Reaction condition: T = 380 °C, P = 3.5 MPa, CO/H_2 = 2 and WHSV = 5000 mL/(g·h).

Catalysts(1)	X_{CO} (%)	Hydrocarbon selectivity (%)							CO_2 (%)	R_{CO} (h^{-1})
		CH_4	C_2^o	C_3^o	C_4^o	C_2^o-C_4^o	Ole.	C_5^+		
Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-250	25.1	21.4	42.0	27.6	6.2	75.9	1.2	1.6	47.7	45.4
Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-300	24.8	22.6	41.3	27.6	6.7	75.7	0.7	1.0	47.9	45.0
Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-350	24.0	23.0	39.4	28.6	7.1	75.1	0.5	1.3	48.4	43.3
Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-400	19.6	22.1	35.8	29.6	9.4	74.8	1.0	2.2	48.5	35.7
Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-450	17.9	22.1	34.5	32.1	8.6	75.1	0.8	2.0	49.5	32.5

(1) Sulfidation time: 300 min.

Table S8: The effect of CO/H_2 and pressure on the catalytic performance for the reaction over Ni-MoS_2/$Ce_{0.9}La_{0.1}O_{1.95}$-250. Reaction condition: T = 380 °C and WHSV = 3125-5000 mL/(g·h).

Pressure (MPa)	CO/H_2	X_{CO} (%)	Hydrocarbon selectivity (%)							CO_2 (%)	R_{CO} (h^{-1})
			CH_4	C_2^o	C_3^o	C_4^o	C_2^o-C_4^o	Ole.	C_5^+		
3.5	0.5	28.9	33.3	41.2	19.9	3.9	65.0	0.92	0.7	47.3	52.4
3.5	1	32.6	33.7	41.9	20.1	3.4	65.3	0.9	0.1	47.4	59.1
3.5	2	25.1	21.4	42.0	27.6	6.2	75.9	1.2	1.6	47.7	45.4
2.5	2	21.5	23.7	44.2	27.6	3.1	74.8	1.5	0	49.0	38.9
3.5	2	25.1	21.4	42.0	27.6	6.2	75.9	1.2	1.6	47.7	45.4
4.5	2	24.8	21.5	41.6	28.8	5.8	76.2	1.0	1.35	48.9	44.8

Reference

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