Construction Inverse NiCoCeAl-LDO/Ni Catalyst for Effective CO_2 Methanation in Low Temperature

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Synthesis of CoCeAl-LDO

3.28 g $Co(NO_3)_2 \cdot 6H_2O$ (11.2 mmol), 1.22 g $Ce(NO_3)_3 \cdot 6H_2O$ (2.80 mmol) and 1.05 g $Al(NO_3)_3 \cdot 9H_2O$ (2.79 mmol) were dissolved in 50 mL deionized water to obtain solution C. 1.19 g Na_2CO_3 (11.20 mmol) and 1.07 g NaOH (26.70 mmol) were dissolved in 50 mL deionized water to obtain solution D. Then solution C and solution D were simultaneously dropped into a three-necked flask using a peristaltic pump, maintaining a pH of 9-10 at 60 ℃, followed by aging at 60 ℃ for 12 h. The mixed solution was cooled to room temperature, filtered, washed with deionized water and alcohol. Subsequently, dried at 60 ℃ for 24 h, denoted as CoCeAl-LDH. The CoCeAl -LDH were calcinated at 500 ℃ in a muffle furnace for 3 h, denoted as CoCeAl -LDO. The obtained sample was reduced in H_2 at 400 ℃ for 3 h to obtain the final catalyst, denoted as CoCeAl -LDO-R

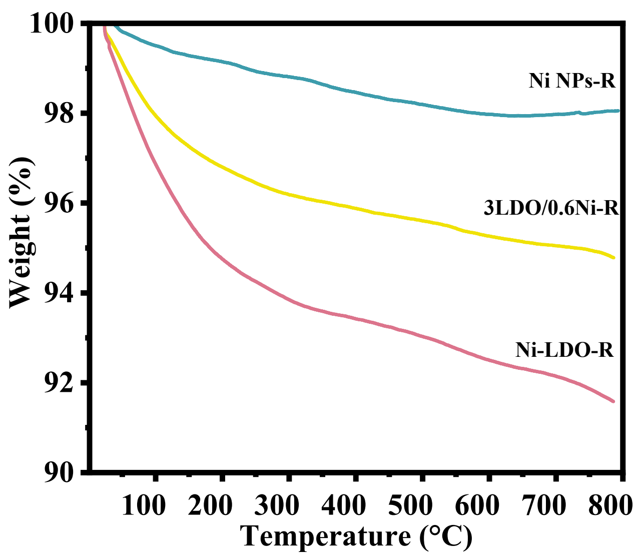

Fig. S1 TG profiles of the catalysts.

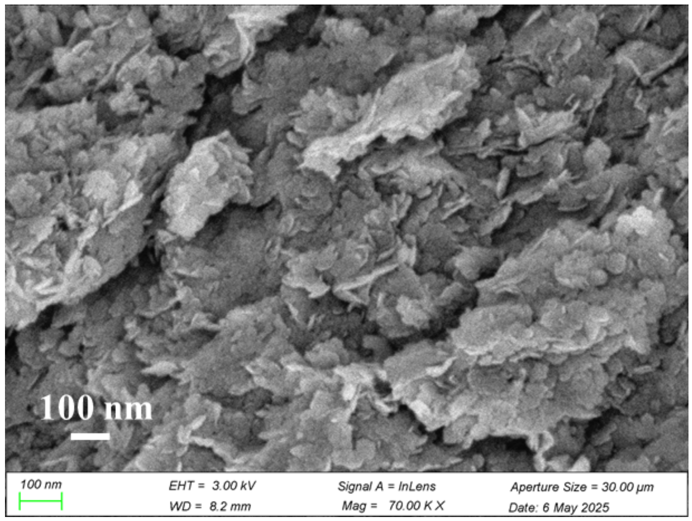

Fig. S2. SEM images of $Ni(OH)_2$.

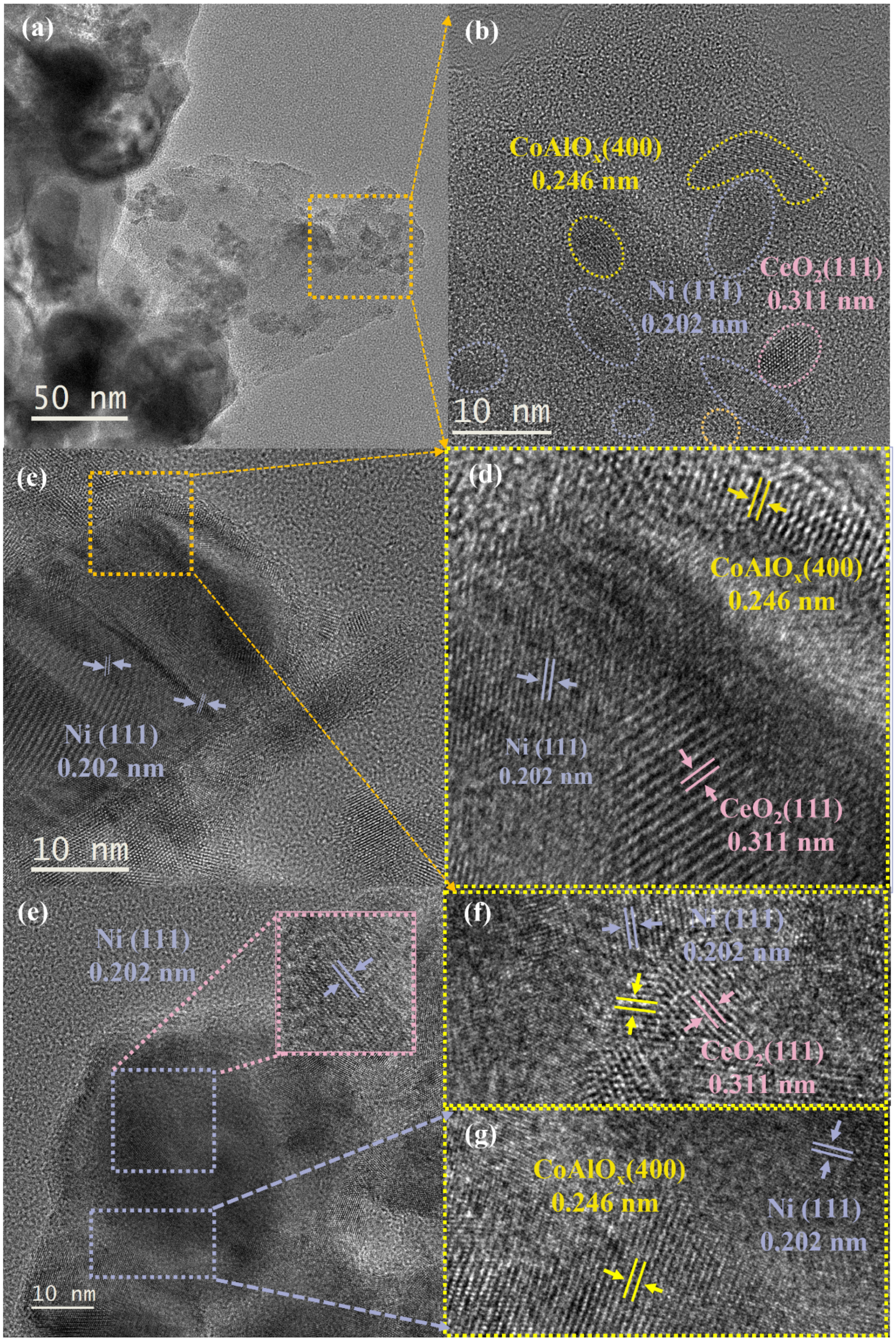

Fig. S3 (a-f) TEM and HRTEM images of 3LDO/0.6Ni-R.

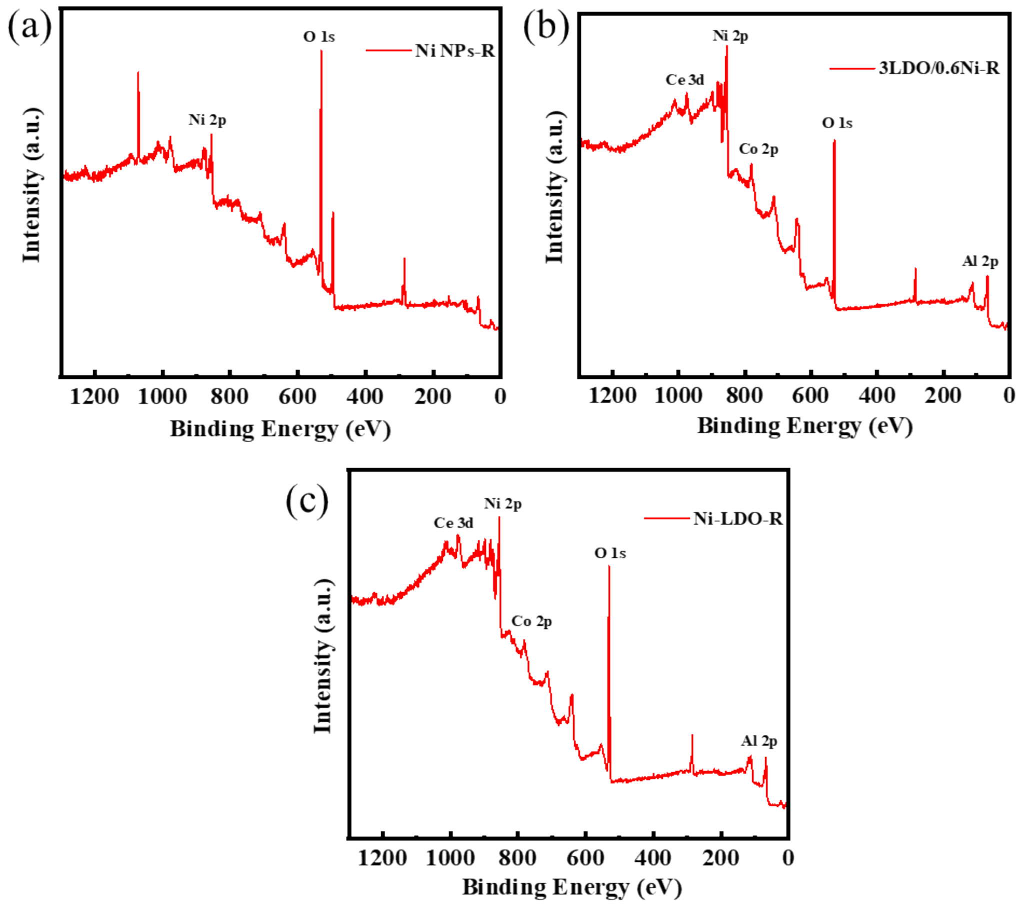

Fig. S4 XPS survey spectra of the catalysts.

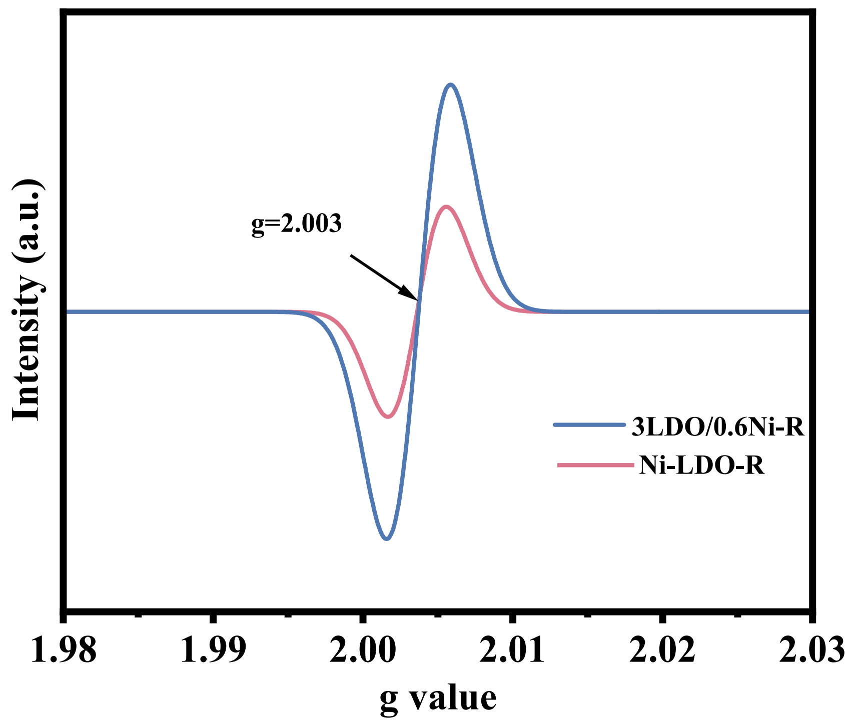

Fig. S5 EPR signals of LDO/0.6Ni-R and Ni-LDO-R samples.

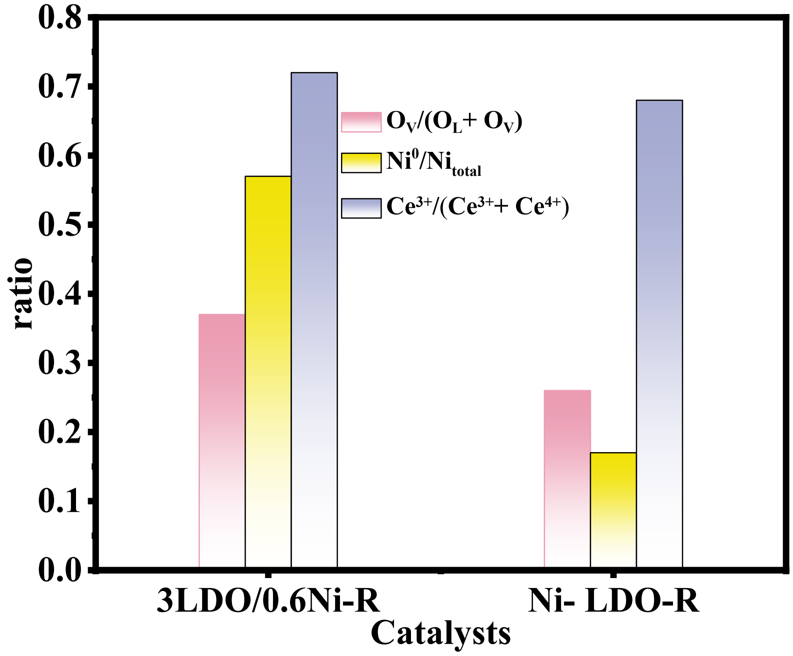

Fig. S6 The ratios of OV/(OL+ OV), Ni^0/Ni_{total}, and $Ce^{3+}/(Ce^{3+}{}_{+}\ Ce^{4+})$ for LDO/0.6Ni-R and Ni-LDO-R samples.

Tab. S1 The compositions of the catalysts

Catalysts		Ni loading (wt %)	Co loading (wt %)	Ce loading (wt %)	Al loading (wt %)
3LDO/0.6Ni-R	Actual	58.55	4.53	11.11	2.15
	Theoretical	60.05	4.81	11.42	2.20
Ni- LDO-R	Actual	31.59	10.41	24.63	4.55
	Theoretical	34.12	11.46	26.24	5.24

Obtained based on the ICP-OES results.

Tab. S2 The carbon equilibrium data of the catalysts sample under the conditions of 260 ℃, 2 MPa, and WHSV=15000 mL·g·h^{-1}.

Catalysts	$V_{CO2, in}$ (mL·min^{-1})	$V_{CO2, out}$ (mL·min^{-1})	$V_{CH4, out}$ (mL·min^{-1})	Carbon balance coefficient
Ni NPs-R	27.00	25.52	1.12	0.98
3LDO/0.6Ni-R	27.00	0.77	26.05	0.99
Ni-LDO-R	27.00	6.52	20.45	0.99

Note: $V_{CO2, out}$ and $V_{CH4, out}$ are calculated based on the exhaust gas flow rate at the outlet and the concentrations of each component in the GC.

$$Carbon\ balance\ coefficient = \frac{V_{CO_2, out} + V_{CH_4, out}}{V_{CO_2, in}}$$

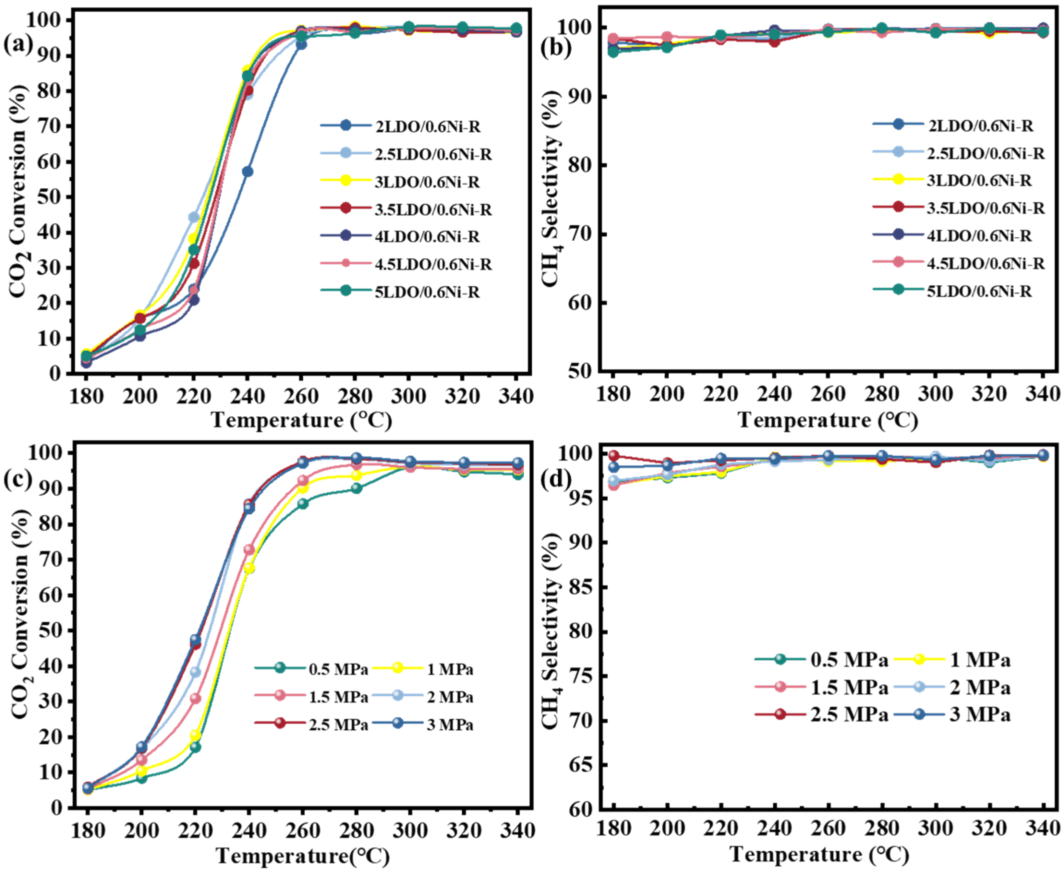

Fig. S7 The effect of different Ni:Co:Ce:Al mole ratio of LDO on (a) CO_2 conversion and (b) CH_4 selectivity; the effect of different pressure on (c) CO_2 conversion and (d) CH_4 selectivity over 3LDO/0.6Ni-R at various reaction temperature.

Note: y is the mole ratio of Ni:Co:Ce:Al = y:1:1:1 in LDO.

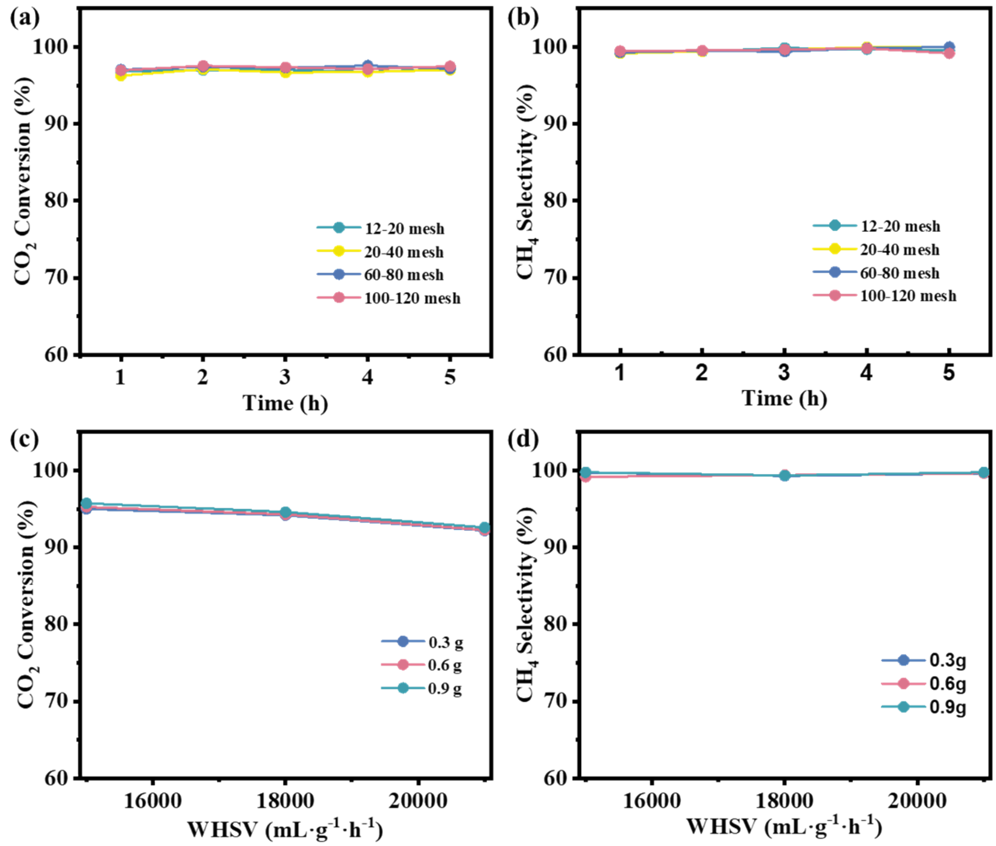

Fig. S8 (a-b) CO_2 conversion and CH_4 selectivity over catalysts with different particle sizes. (2 MPa, 260 ℃, H_2/CO_2 mole ratio of 4:1, WHSV=15000 mL·g^{-1}·h^{-1}); (c-d) CO_2 conversion and CH_4 selectivity over catalysts with different catalyst quality and different WHSV. (2 MPa, H_2/CO_2 mole ratio of 4:1, 260 ℃, 20-40 mesh)

Tab. S3 Conversion and R_{CO2} over various reaction temperature

Temperature (℃)	Conversion (%)		R_{CO2} (mol/g·h)	
	3LDO/0.6Ni-R	Ni-LDO-R	3LDO/0.6Ni-R	Ni-LDO-R
220	38.27	22.93	0.047	0.027
230	60.55	40.14	0.074	0.048
240	82.51	54.18	0.099	0.068
250	94.75	67.96	0.114	0.082

Tab. S4 Comparison of catalysts performance of CO_2 methanation over different catalysts in the literature.

Catalyst	H_2/CO_2	CO_2 Con. (%)	WSHV ($mL\cdot g_{cat}^{-1}\cdot h^{-1}$)	Temperature (℃)	Ref.
3LDO/0.6Ni-R	4:1	97.2	15000	260	This work
NiZrAl-LDH	4:1	93.3	15000	310	1
5Ni/NPs	4:1	85.0	12000	350	2
Co_3O_4-Al_2O_3	3:1	42.5	8000	250	3
Ru/CeO_2	4:1	86.0	36000	300	4
Co (3)-N/CA2	4:1	83.1	18000	450	5
Ni15C10	4:1	62.1	21500	375	6
0.16Ni/0.15Co/CeO_2	4:1	84.3	11000	300	7
3Mg10Ni5Co/MS	4:1	72.0	12000	400	8
NiCe EISA	4:1	68.5	15000	300	9
13Ni5MgO-BEA	4:1	78.0	7500	350	10

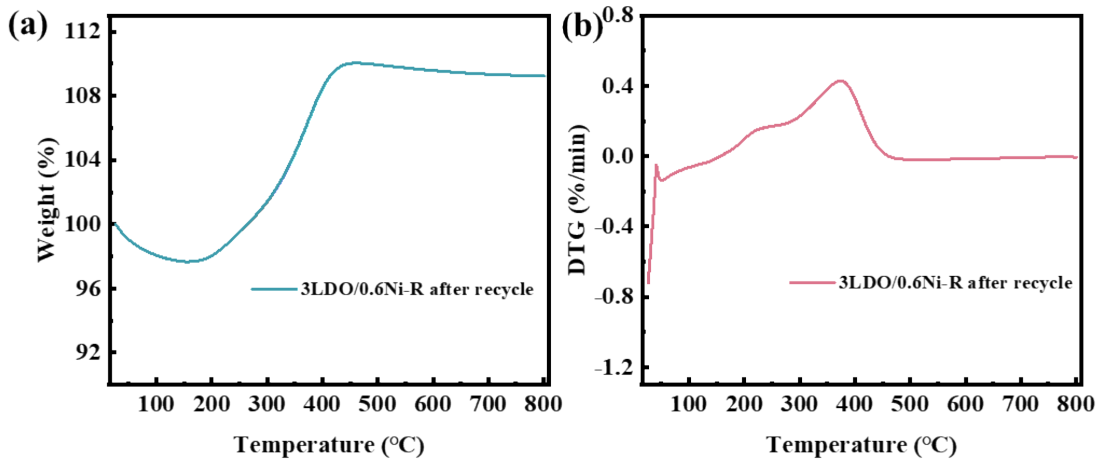

Fig. S9 (a) TG and (b) DTG spectra of 3LDO/0.6Ni-R after recycle in air atmosphere

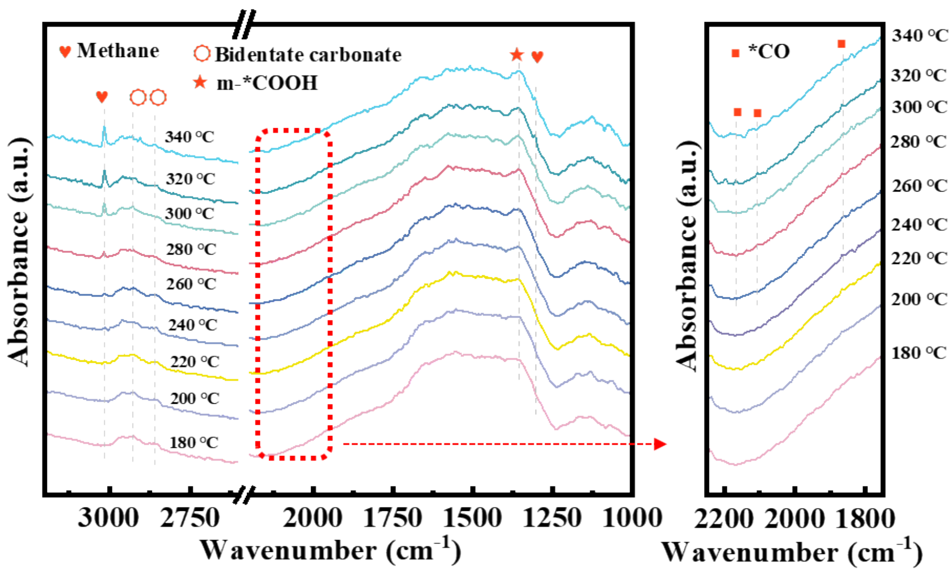

Fig. S10 DRIFTS spectra recorded at different temperature in 72% H_2/18% CO_2/10% N_2 on 3LDO/0.6Ni.(1800-2200 cm^{-1})

Tab. S5 Infrared band assignments of the surface species for CO_2 methanation.[1,11–15]

Wavenumber (cm^{-1})	Surface species
1511	monodentate carbonate
1584	bidentate carbonate
1370	monodentate formate
1548	bidentate formate
2850, 2923	methoxy
1306, 3012	methane
1733, 1740	formyl
1863, 2105, 2168	carbonyl

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