

Supplementary Information

Directed thermocatalytic CO₂ reduction over NiAl₄ layered double hydroxide precursors – activity and selectivity control using different interlayer anions

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Analytical study of the CO₂ hydrogenations

The missing description has been added to the *Analytical study of the CO₂ hydrogenations* section in the Supporting Information. The CO₂ consumption and the CH₄/CO formation rates were calculated according to the carbon dioxide, methane and carbon monoxide content of the samples taken at regular intervals, normalized to 1 second reaction time and 1 gram of catalyst. The turnover frequency values were calculated by the number of molecules of CO or CH₄ produced at 500 or 700 °C and after 0.5 or 14 h reaction in relation to the total basicity or acidity values normalised to a reaction time of 1 hour and 1 gram of catalyst. The values of the CO₂ conversion and selectivity of CO or CH₄ formations were calculated based on the CO₂ concentrations of the inlet (CO_{2in}) and outlet (CO_{2out}) and the concentration of the CH₄ (CH_{4out}) and CO (CO_{out}) molecules in the outlet using the following equations:

$$\text{CO}_2 \text{ conversion}(\%) = \frac{\text{CO}_{2\text{in}} - \text{CO}_{2\text{out}}}{\text{CO}_{2\text{in}}} \times 100$$
$$\text{CH}_4 \text{ selectivity}(\%) = \frac{\text{CH}_{4\text{out}}}{\text{CO}_{2\text{in}} - \text{CO}_{2\text{out}}} \times 100$$
$$\text{CO selectivity}(\%) = \frac{\text{CO}_{\text{out}}}{\text{CO}_{2\text{in}} - \text{CO}_{2\text{out}}} \times 100$$

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Characterization techniques

The normalized powder X-ray diffraction patterns in the $\Theta = 5 - 80^\circ$ range using $\text{CuK}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation with $2^\circ/\text{min}$ scan speed was recorded by a Rigaku Miniflex II powder X-ray diffractometer. The diffractometer worked with Ni foil $K\beta$ filter and scintillation detector operating in continuous mode with step width of $0.02^\circ 2\theta$ at 30 kV and 15 mA. JCPDS–ICDD (Joint Committee of Powder Diffraction Standards – International Centre for Diffraction Data) database was used for the interpretation of the reflections obtained. The average crystallite sizes of the spinel phases were calculated from the full width at half maximum (FWHM) of the (311) reflections applying Scherrer equation with shape factor of 0.9 and Gaussian distribution fit.

Fourier-transform infrared spectra of the calcined hydroxides were registered on a JASCO FT/IR-4700 spectrophotometer accumulating 128 scans at 2 cm^{-1} resolution with ZnSe ATR accessory and DTGS detector. On the normalized spectra, the structural features of the solids were investigated in the $4000 - 600 \text{ cm}^{-1}$ wavenumber range.

The composition of the solids were analyzed by a Thermo Scientific iCAP 7400 ICP-OES (Inductively coupled plasma - optical emission spectrometry) DUO spectrometer. The solids were dissolved in sulfuric acid (assisted by microwave digestion) and ICP Multielement standard solution IV (CertiPUR) was applied with manganese internal standard.

The acid, basic sites, the specific surface area and the reducibility of the samples were probed by a BELCAT-A catalyst analyzer operated with a thermal conductivity detector. For the N_2 adsorption-desorption isotherms, the solids were degassed at $300 \text{ }^\circ\text{C}$ for 1 h and the Brunauer-Emmett-Teller equation was applied on the adsorption branches. The NH_3 and CO_2 temperature programmed desorption measurements were done up to $800 \text{ }^\circ\text{C}$ with $10 \text{ }^\circ\text{C}/\text{min}$ heating rate. Before the measurements, $\sim 50 \text{ mg}$ of the calcined solids were degassed at $300 \text{ }^\circ\text{C}$ for 1 h in He flow and quartz cell. The CO_2 and NH_3 saturation were achieved at 40 and $90 \text{ }^\circ\text{C}$, respectively. For the temperature programmed reduction analysis, parameters similar the above ones were set; the heat derivatives ($\sim 50 \text{ mg}$) were pretreated in pure oxygen for 1 h at $300 \text{ }^\circ\text{C}$ and the H_2 consumption profiles were recorded also up to $800 \text{ }^\circ\text{C}$ with $10 \text{ }^\circ\text{C}/\text{min}$ heating rate applying N_2 containing 10% H_2 ($50 \text{ cm}^3/\text{min}$ flow).

The thermogravimetric and differential thermal analysis of the spent catalysts were performed applying a Setaram Labsys TGA-DTA 1600 derivatograph with constant flow ($60 \text{ ml}/\text{min}$) of synthetic air. The samples ($30\text{-}40 \text{ mg}$) were taken into high-purity alpha alumina crucibles and heated up to $1000 \text{ }^\circ\text{C}$ with $10 \text{ }^\circ\text{C}/\text{min}$ rate.

Spatially-resolved elemental analysis and mapping of the solids was performed using energy dispersive X-ray spectroscopy (EDX, Röntec QX2 spectrometer with Be window) coupled to the scanning electron microscopy (SEM, Hitachi S-4700) at various magnifications and 20 kV acceleration voltages.

The *in situ* diffuse reflectance infrared Fourier-transform spectroscopy analysis were done applying an Agilent Cary-670 FTIR spectrometer using Harrick Praying Mantis diffuse reflectance cell with two BaF₂ windows. Prior to the measurements, the samples were pretreated at 500 °C for 1 h in O₂ flow and then they were purged by He at 500 °C for 0.5 h. The spectra of the as-prepared catalysts were used as background. The solids were warmed linearly up to 500 °C with a 10 °C/min heating rate. The spectra were recorded in the 4000–800 cm⁻¹ wavenumber range, accumulating 32 scans at 2 cm⁻¹ resolution. The purging gas was He and the mixture of the CO₂, H₂ and He gas (2 cm³/min CO₂, 8 cm³/min H₂ and 30 cm³/min He) was introduced in the cell.

For the characterization of the binding forms of the Ni, O, Al, Cl, and S elements in the solids, *quasi in situ* X-ray photoelectron spectroscopy measurements were executed by a Kratos Analytical XSAM800 instrument operated with Mg K α radiation source at 120 W and 12 kV. The samples (~150 mg) were pressed into round pellets with 1 cm diameter, oxidized at 500 °C and/or exposed by CO₂:4H₂ gas mixture for 30 min. Before the measurements, all materials were placed in a modified pre-chamber of the instrument, purified by Ar flow the necessary pre-treatments were performed. The chamber was then purged again with Ar, and pumped down to insert the sample into the main ultra-high vacuum chamber for spectra acquisition thus avoiding the removal of samples from the instrument and their contact with oxygen and moisture in the air. Survey spectra were collected with 80 eV pass energy and 1 eV step size. The high-resolution spectra were collected using 20 eV pass energy and 0.1 eV step size. Charge accumulation on the sample surface was observed, for this compensation, electron flood gun was applied. The spectra were charge corrected for the aliphatic component of the C 1s spectrum at 284.8 eV and background corrected using Shirley baseline subtraction. All peaks were fit employing a Gauss-Lorentzian (70%-30%) product function by CasaXPS software version 2.3.22PR1.0.

Table S1 Crystallite sizes, surface areas and total H₂ consumption of heat-treated samples.

Initial solids	Calcined derivatives (500 °C)			Calcined derivatives (1000 °C)		
	Average crystallite sizes of spinels (nm)	Specific surface area (m ² /g)	Total H ₂ consumption (mmol/g)	Average crystallite sizes of spinels (nm)	Specific surface area (m ² /g)	Total H ₂ consumption (mmol/g)
NiAl ₄ -Cl-LDH	3	163	2.35 (70.5%) ^a	8	94	1.34 (37.8%) ^a
NiAl ₄ -Br-LDH	4	180	2.57 (77.7%)	9	112	1.68 (48.7%)
NiAl ₄ -I-LDH	5	156	1.95 (55.8%)	7	93	0.62 (17.5%)
NiAl ₄ -NO ₃ -LDH	3	152	2.77 (79.7%)	9	92	0.95 (26.4%)
NiAl ₄ -ClO ₄ -LDH	3	176	3.79 (107%)	9	96	1.39 (39.4%)
NiAl ₄ -SO ₄ -LDH	–	22	10.57 (373%)	11	59	2.94 (82.7%)
NiAl ₄ -NH ₂ SO ₃ -LDH	–	56	16.29 (664%)	9	102	2.72 (75.9%)
NiAl ₂ -OH	4	203	6.02 (111%)	8	63	2.82 (49.7%)
NiAl ₄ -OH	<3	364	3.03 (88.2%)	10	64	0.48 (13.4%)

^aThe percent of the reduced Ni(II) to Ni(0) compared to the total amount of nickel atoms in the solids measured until 800 °C.

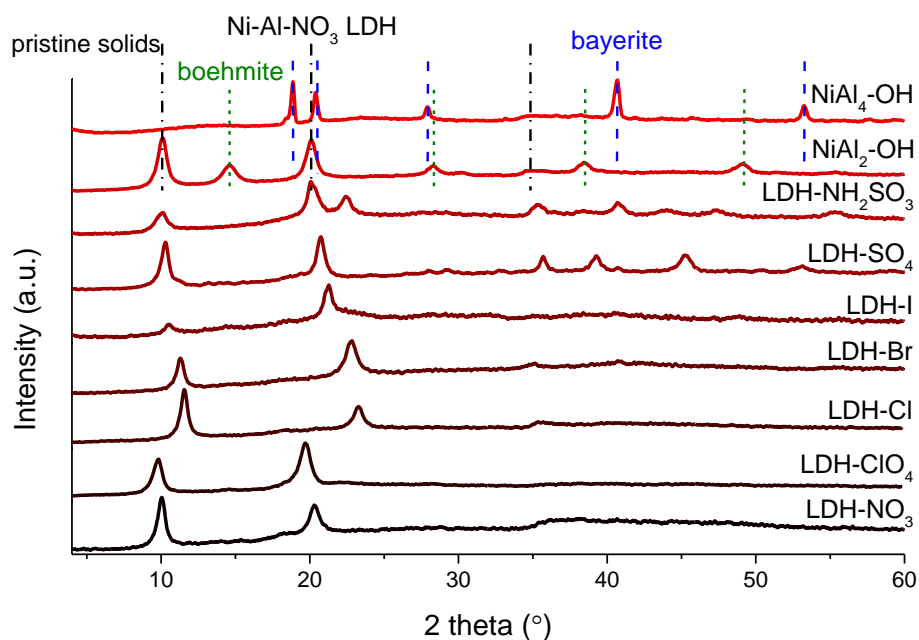
**Fig. S1** XRD patterns of the pristine NiAl₄-LDHs with varied interlayer anions and the hydroxide control materials.

Table S2 Composition, acidity and turnover frequency (TOF) parameters of the catalyst precursors derived from calcination at 1000 °C.

Initial solids	Ni content (wt.%)	Total acidity (mmol NH ₃ /g)	TOF _{CH₄} (acid site ⁻¹ h ⁻¹) at 500°C ^b	TOF _{CO} (acid site ⁻¹ h ⁻¹) at 500°C ^b	TOF _{CH₄} (acid site ⁻¹ h ⁻¹) at 700°C ^b	TOF _{CO} (acid site ⁻¹ h ⁻¹) at 700°C ^b
NiAl ₄ -Cl-LDH	20.8	0.38	1.23	20.9	14.6	81.4
NiAl ₄ -Br-LDH	20.2	0.34	1.16	61.7	84.7	423
NiAl ₄ -I-LDH	20.9	0.25	0.08	0	1.18	104
NiAl ₄ -NO ₃ -LDH	21.1	0.28	1.76	19.5	5.12	243
NiAl ₄ -ClO ₄ -LDH	20.7	0.21	0.76	39.8	167	994
NiAl ₄ -SO ₄ -LDH	20.9	0.16	0.30	61.1	386	756
NiAl ₄ -NH ₂ SO ₃ -LDH	21.0	0.27	14.0	137	45.7	633
NiAl ₂ -OH	33.3	0.10	1036	716	67.5	1522
NiAl ₄ -OH	21.1	0.08	0.21	81.2	90.6	950

^aThe formation values of the methane and carbon monoxide after 0.5 h reaction time.

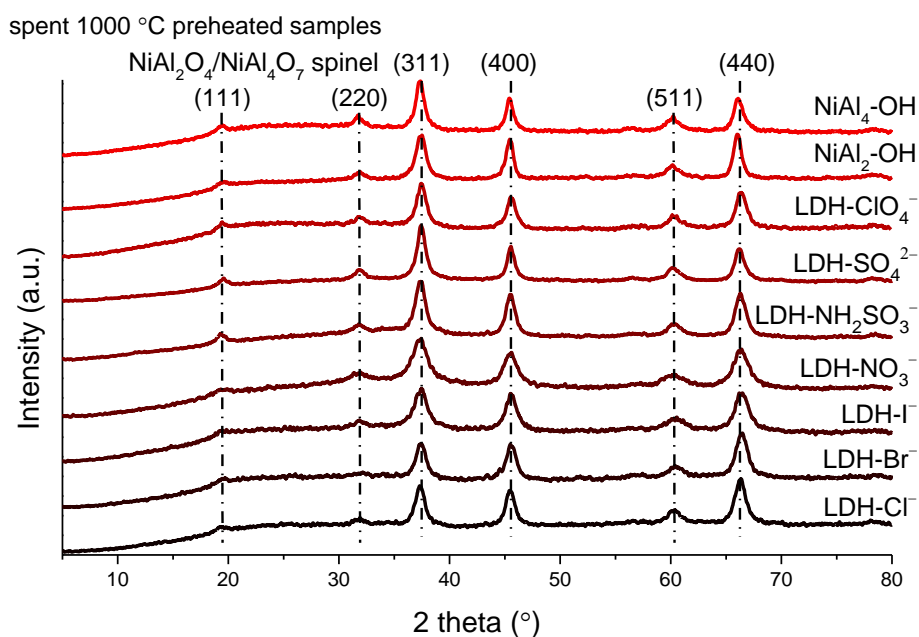


Fig. S2 XRD traces of the spent NiAl₄-LDHs (pre-calcined at 1000 °C) with varied interlayer anions and hydroxide control materials after the catalytic methanation reactions up to 700 °C.

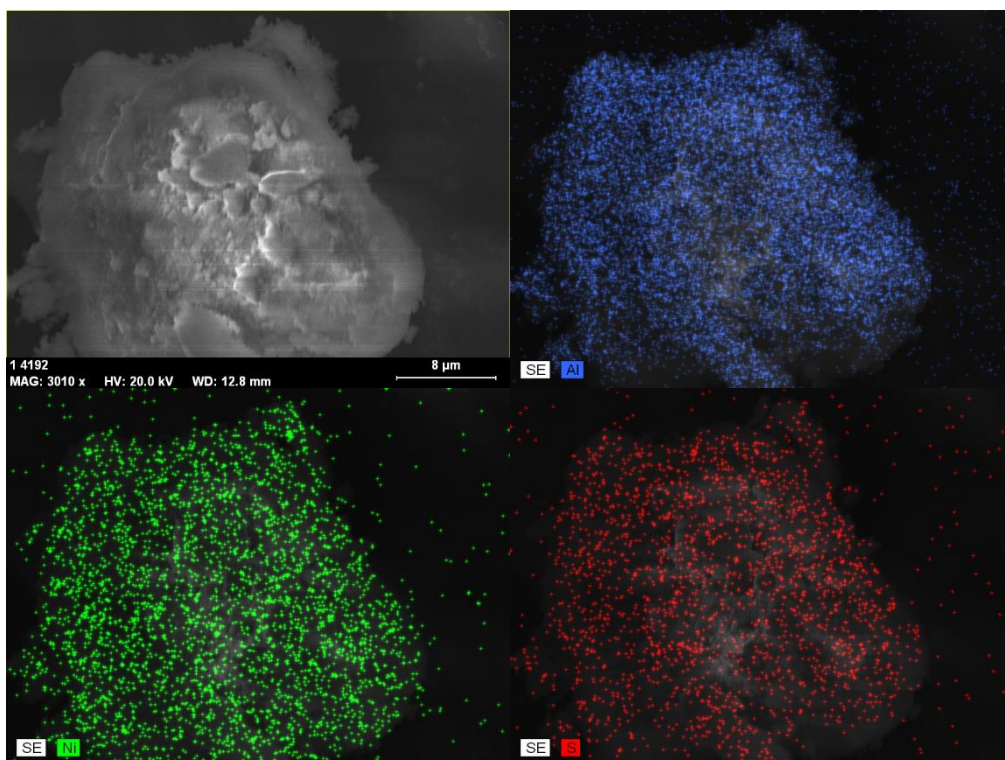


Fig. S3 SEM images and the corresponding elemental distribution maps derived from the energy dispersive X-ray analysis of the calcined LDH-SO₄ precursor.

Table S3 Basicity, reducibility and turnover frequency (TOF) parameters of the catalyst precursors derived from calcination at 1000 °C.

Initial solids	Total basicity (mmol CO ₂ /g)	TOF _{CH₄} (basic site ⁻¹ h ⁻¹) at 500°C ^a	TOF _{CO} (basic site ⁻¹ h ⁻¹) at 500°C ^a	TOF _{CH₄} (basic site ⁻¹ h ⁻¹) at 700°C ^a	TOF _{CO} (basic site ⁻¹ h ⁻¹) at 700°C ^a	H ₂ consumption until 500°C (mmol/g)	H ₂ consumption until 700°C (mmol/g)
NiAl ₄ -Cl-LDH	0.41	1.14	19.4	13.5	75.4	0.32 (9.03%) ^b	0.56 (15.8%) ^b
NiAl ₄ -Br-LDH	0.32	1.23	65.6	90	450	0.30 (8.72%) ^b	0.70 (20.3%) ^b
NiAl ₄ -I-LDH	0.21	0.09	0	1.41	124	0.29 (8.71%) ^b	0.38 (10.7%) ^b
NiAl ₄ -NO ₃ -LDH	0.36	1.37	15.2	3.98	189	0.31 (8.62%) ^b	0.45 (12.5%) ^b
NiAl ₄ -ClO ₄ -LDH	0.29	0.55	28.8	121	720	0.71 (20.1%) ^b	0.79 (22.4%) ^b
NiAl ₄ -SO ₄ -LDH	0.20	0.24	48.9	309	605	0.23 (6.46%) ^b	0.59 (16.6%) ^b
NiAl ₄ -NH ₂ SO ₃ -LDH	0.30	12.6	123	41.1	570	0.32 (8.94%) ^b	0.67 (18.7%) ^b
NiAl ₂ -OH	0.19	545	377	35.5	801	0.45 (7.93%) ^b	0.72 (12.7%) ^b
NiAl ₄ -OH	0.09	0.19	72.2	80.5	844	0.32 (8.90%) ^b	0.38 (10.6%) ^b

^aThe formation values of the methane and carbon monoxide after 0.5 h reaction time.

^bThe percent of the reduced Ni(II) to Ni(0) compared to the total amount of nickel atoms in the solids.

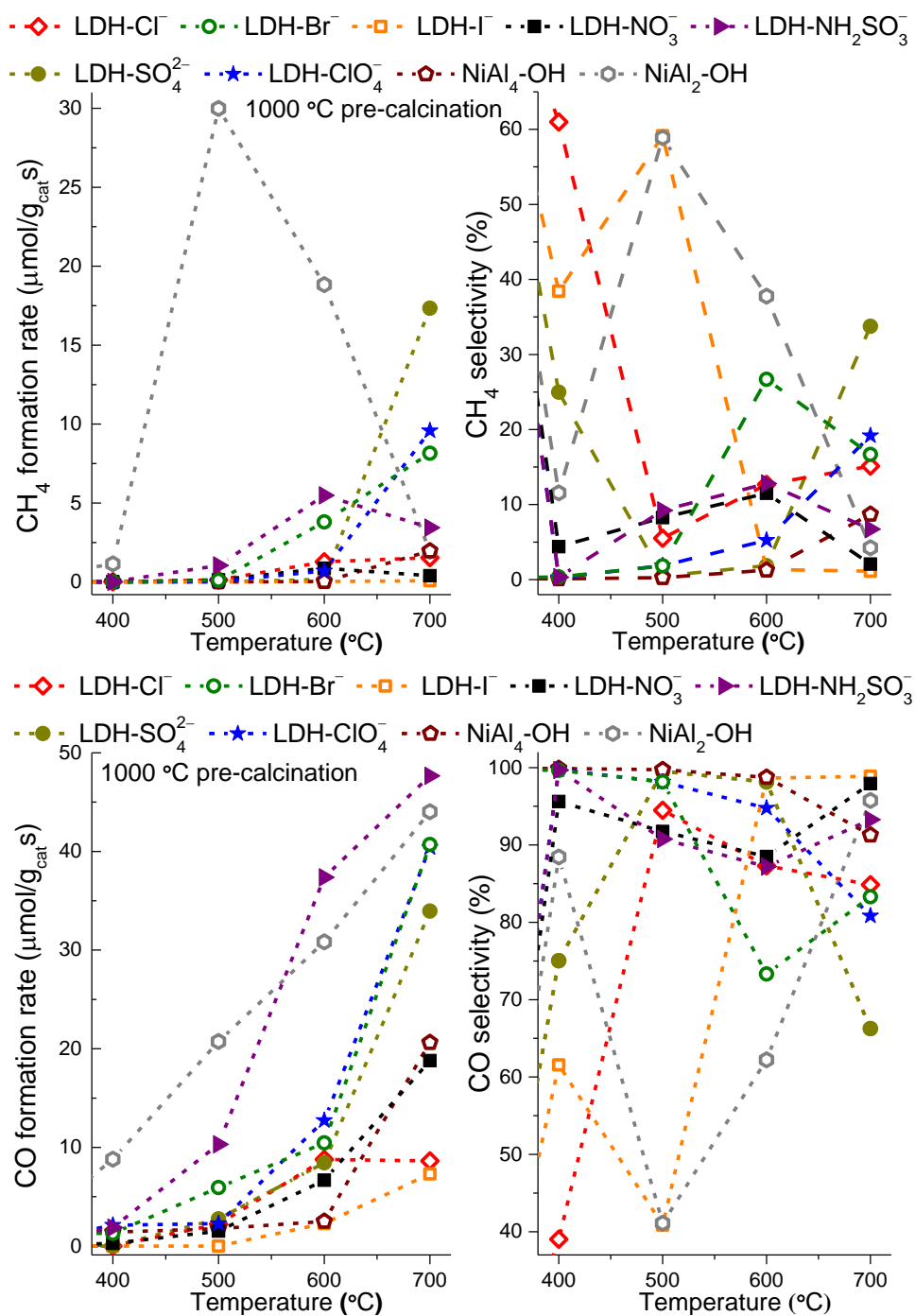


Fig. S4 The evolution of the CH₄/CO formation rates and selectivity values over the heat-treated (1000 °C) LDH and the control precursors between 400 and 700 °C reaction temperature.

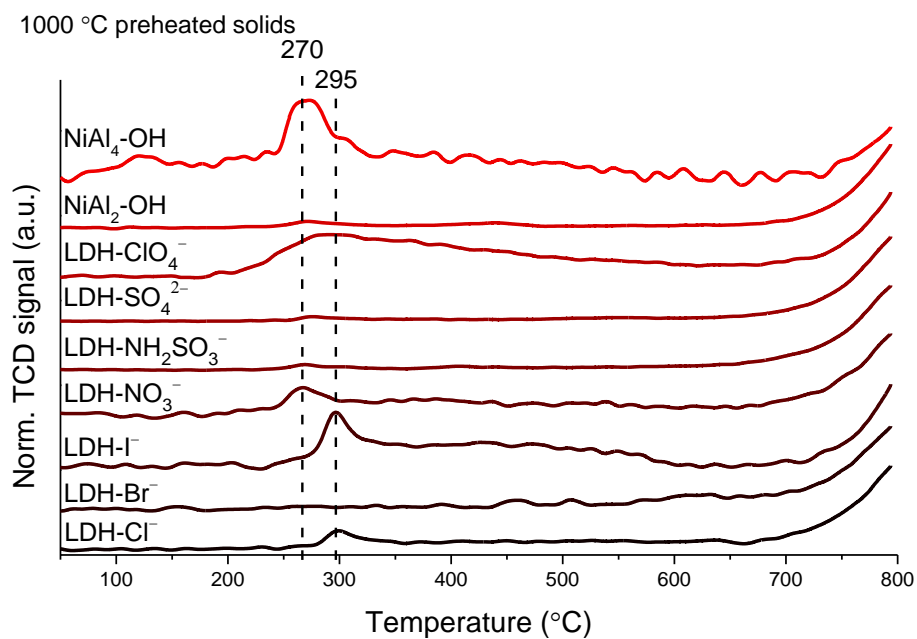


Fig. S5 H₂-TPR curves of the heat-treated (1000 °C) NiAl₄-LDH and hydroxide control materials.

Table S4 Acid to base centres ratio of catalyst precursors obtained by calcination at 1000 °C.

Initial solids	Weak acid to weak base ratio	Moderate acid moderate to base ratio	Strong acid to strong base ratio	Total acid to total base ratio
NiAl ₄ -Cl-LDH	0.64	0.71	1.67	0.93
NiAl ₄ -Br-LDH	0.39	1.18	2.68	1.06
NiAl ₄ -I-LDH	1.01	1.03	1.88	1.19
NiAl ₄ -NO ₃ -LDH	0.35	0.68	1.73	0.78
NiAl ₄ -ClO ₄ -LDH	0.33	0.83	1.48	0.72
NiAl ₄ -SO ₄ -LDH	0.39	0.75	1.44	0.8
NiAl ₄ -NH ₂ SO ₃ -LDH	0.44	0.77	1.99	0.9
NiAl ₂ -OH	0.23	0.86	1.23	0.53
NiAl ₄ -OH	0.66	1.07	1.56	0.89

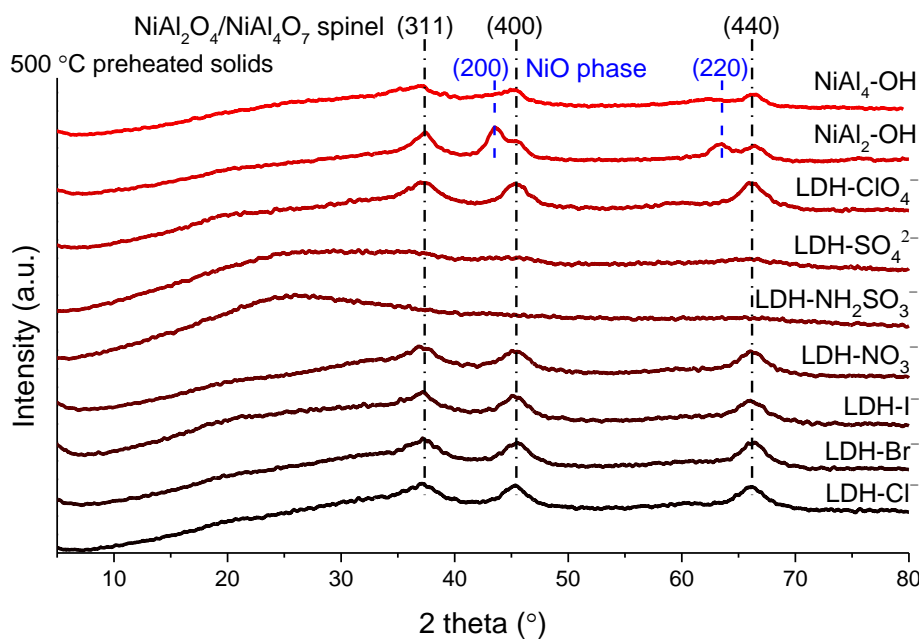


Fig. S6 Powder X-ray diffraction curves of the calcined (500 °C) NiAl₄-LDH and hydroxide control materials.

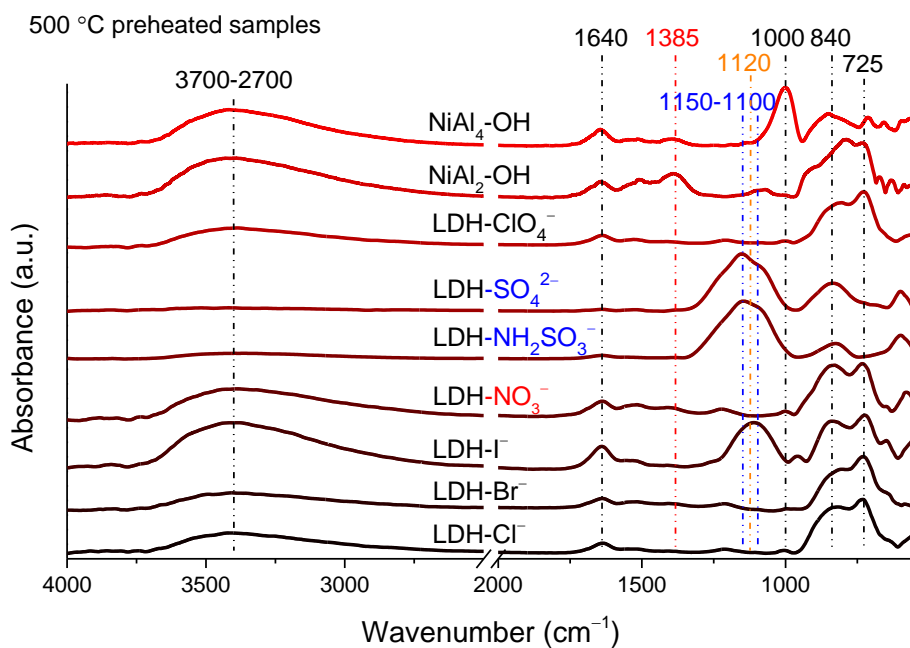


Fig. S7 Infrared spectra of the heat-treated (500 °C) NiAl₄-LDH and hydroxide control solids.

Table S5 Composition, acidity and turnover frequency (TOF) parameters of the catalysts derived from calcination at 500 °C.

Initial solids	Ni content (wt.%)	Total acidity (mmol NH ₃ /g)	TOF _{CH₄} (acid site ⁻ h ⁻¹) at 500°C ^a	TOF _{CO} (acid site ⁻ h ⁻¹) at 500°C ^a	TOF _{CH₄} (acid site ⁻ h ⁻¹) at 500°C ^b	TOF _{CO} (acid site ⁻ h ⁻¹) at 500°C ^b
NiAl ₄ -Cl-LDH	19.5	0.84	57.3	0	107	19.5
NiAl ₄ -Br-LDH	19.4	1.53	9.2	0	47.6	5.42
NiAl ₄ -I-LDH	20.3	0.62	13.7	11.1	138	24.2
NiAl ₄ -NO ₃ -LDH	20.4	1.07	36.7	17.9	82.1	12.5
NiAl ₄ -ClO ₄ -LDH	19.1	0.77	53.3	0	113	21.5
NiAl ₄ -SO ₄ -LDH	16.6	2.41	0.005	9.8	0.47	6.2
NiAl ₄ -NH ₂ SO ₃ -LDH	14.4	4.78	0.002	0.37	0.02	2.3
NiAl ₂ -OH	31.7	0.74	102	21.6	156	18.1
NiAl ₄ -OH	20.6	1.40	75.5	7.6	89.4	9.1

^aThe formation values of the methane and carbon monoxide after 0.5 h reaction time.^bThe formation values of the methane and carbon monoxide after 14 h reaction time.**Table S6** Basicity, reducibility and turnover frequency (TOF) parameters of the catalysts derived from calcination at 500 °C.

Initial solids	Total basicity (mmol CO ₂ /g)	TOF _{CH₄} (basic site ⁻ h ⁻¹) at 500°C ^a	TOF _{CO} (basic site ⁻ h ⁻¹) at 500°C ^a	TOF _{CH₄} (basic site ⁻ h ⁻¹) at 500°C ^b	TOF _{CO} (basic site ⁻ h ⁻¹) at 500°C ^b	H ₂ consumption until 500°C (mmol/g)
NiAl ₄ -Cl-LDH	0.43	112	0	209	38.1	0.41 (12.3%) ^c
NiAl ₄ -Br-LDH	0.26	53.9	0	281	31.9	0.40 (12.1%) ^c
NiAl ₄ -I-LDH	0.34	25.0	20.3	251	44.2	0.13 (3.72%) ^c
NiAl ₄ -NO ₃ -LDH	0.13	302	147	676	103	0.19 (5.47%) ^c
NiAl ₄ -ClO ₄ -LDH	0.19	216	0	457	87.2	0.63 (17.8%) ^c
NiAl ₄ -SO ₄ -LDH	0.69	0.23	51.9	2.05	33.0	8.64 (305%) ^c
NiAl ₄ -NH ₂ SO ₃ -LDH	0.78	0.12	22.7	0.14	14.2	13.36 (545%) ^c
NiAl ₂ -OH	0.27	279	59.2	427	49.7	0.37 (6.85%) ^c
NiAl ₄ -OH	0.15	705	70.5	834	84.5	0.67 (19.5%) ^c

^aThe formation values of the methane and carbon monoxide after 0.5 h reaction time.^bThe formation values of the methane and carbon monoxide after 14 h reaction time.^cThe percent of the reduced Ni(II) to Ni(0) compared to the total amount of nickel atoms in the solids.

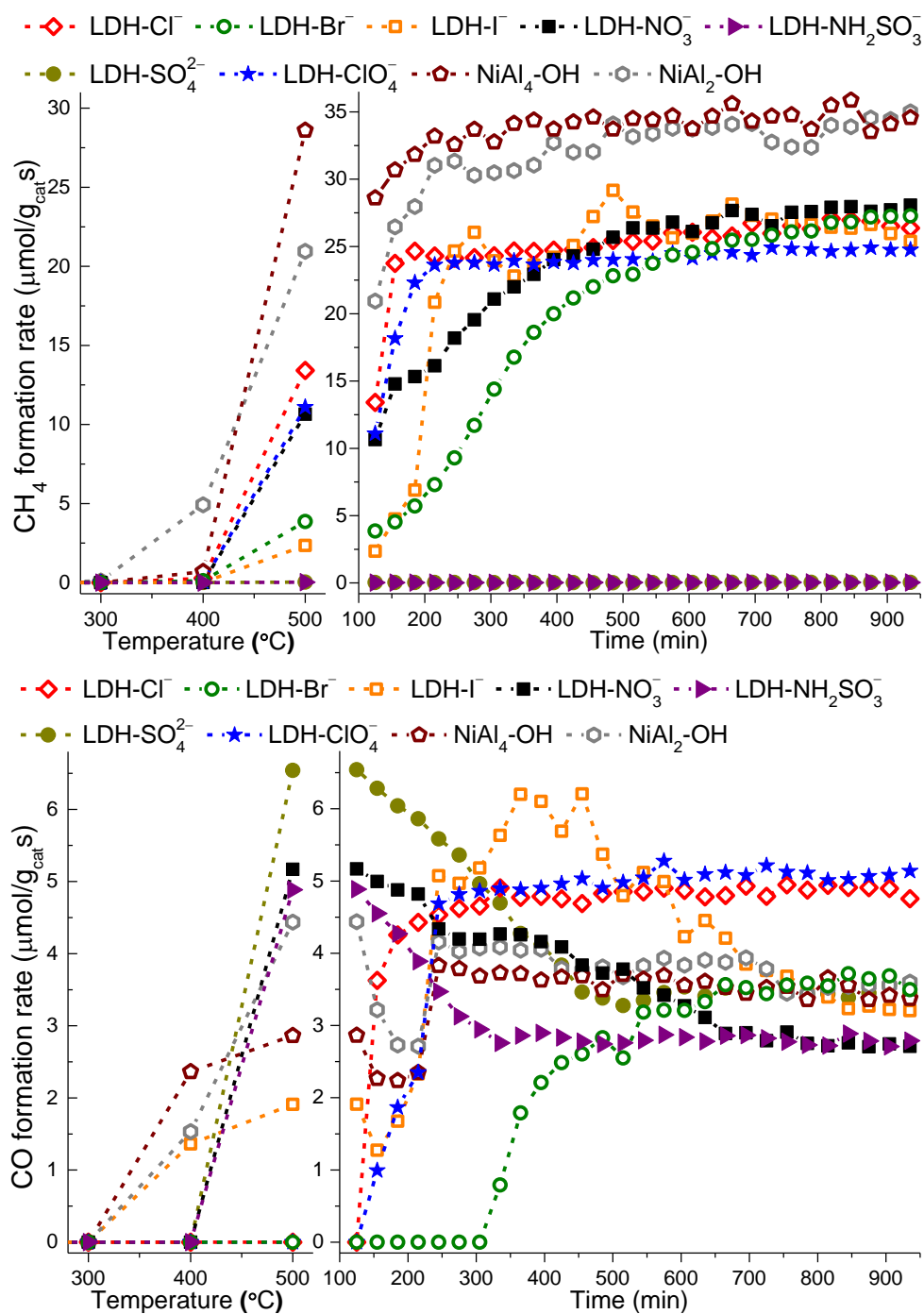


Fig. S8 CH₄/CO formation rates and long-term stability tests (at 500 °C) over the calcined (500 °C) LDH and the hydroxide control precursors at various reaction temperatures.

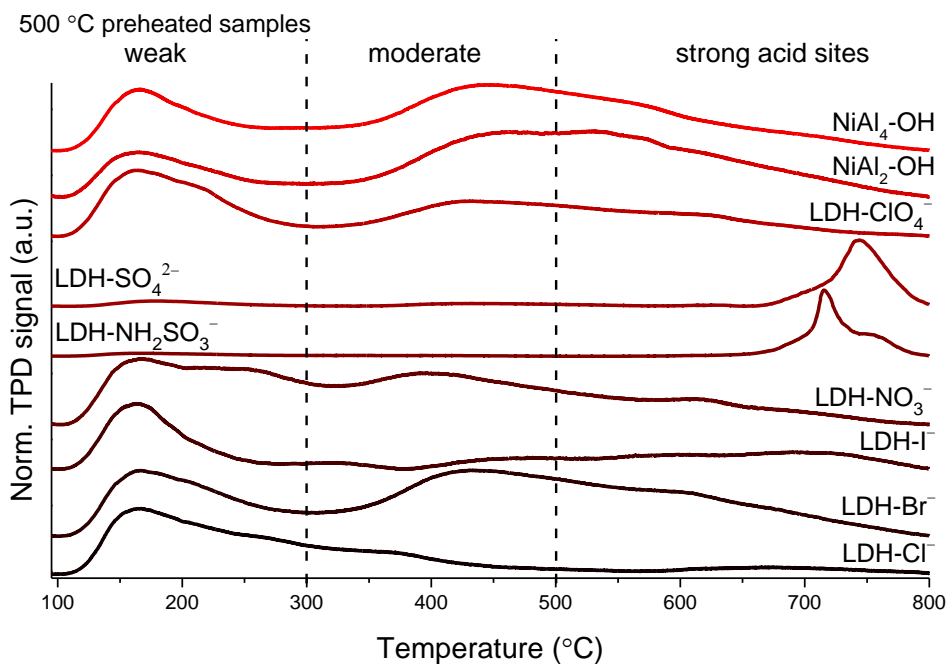


Fig. S9 NH_3 -TPD profiles of the calcined (500 °C) NiAl_4 -LDH and hydroxide control materials.

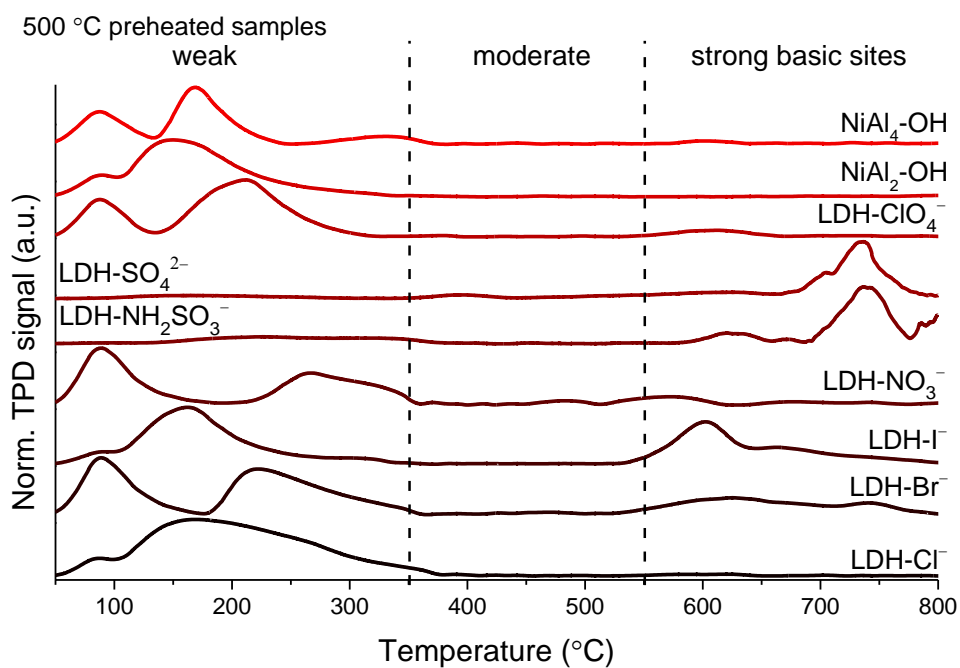


Fig. S10 CO_2 -TPD profiles of the calcined (500 °C) NiAl_4 -LDH and hydroxide control materials.

Table S7 Acid to base centres ratio of catalyst precursors obtained by calcination at 500 °C.

Initial solids	Weak acid to weak base ratio	Moderate acid to moderate base ratio	Strong acid to strong base ratio	Total acid to total base ratio
NiAl ₄ -Cl-LDH	1.29	25.9	15.4	1.95
NiAl ₄ -Br-LDH	2.36	118	8.03	5.88
NiAl ₄ -I-LDH	1.55	56.9	1.67	1.82
NiAl ₄ -NO ₃ -LDH	4.04	40.3	15.5	8.23
NiAl ₄ -ClO ₄ -LDH	1.91	230	15.7	4.05
NiAl ₄ -SO ₄ -LDH	6.68	1.98	7.85	3.50
NiAl ₄ -NH ₂ SO ₃ -LDH	2.59	0.84	7.12	6.13
NiAl ₂ -OH	0.58	151	114	2.74
NiAl ₄ -OH	2.81	14.9	6.84	9.33

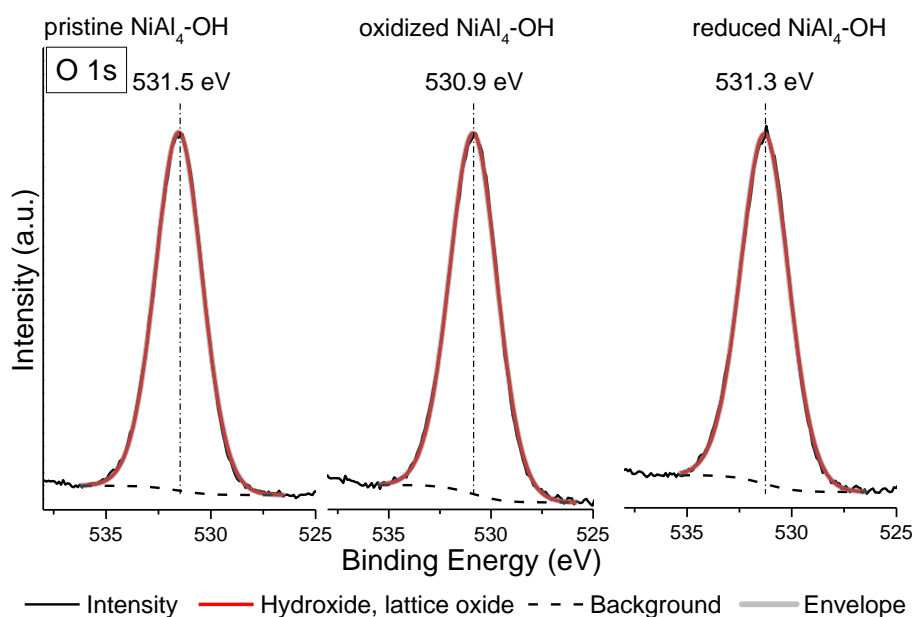
Table S8. Carbon deposition of the spent catalysts measured by thermogravimetric analysis.

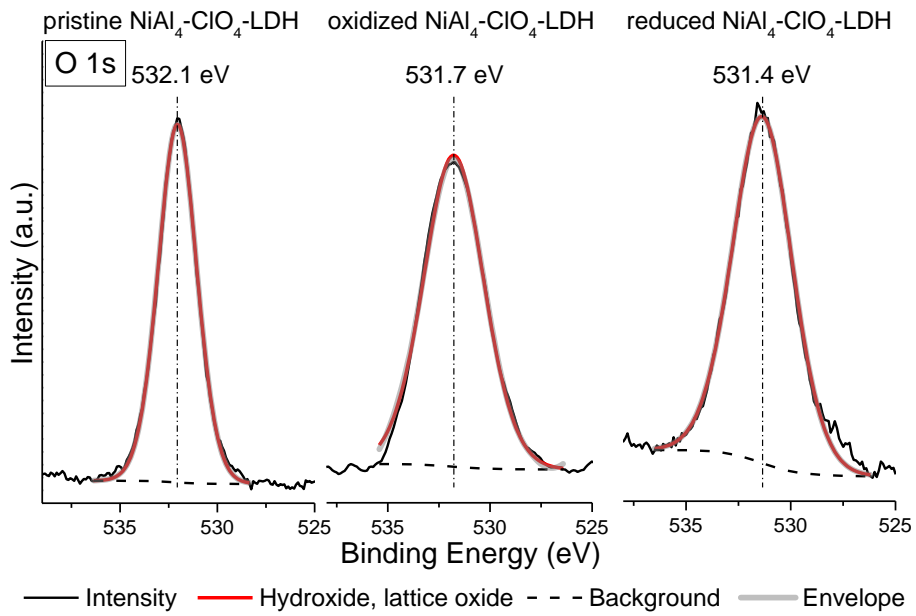
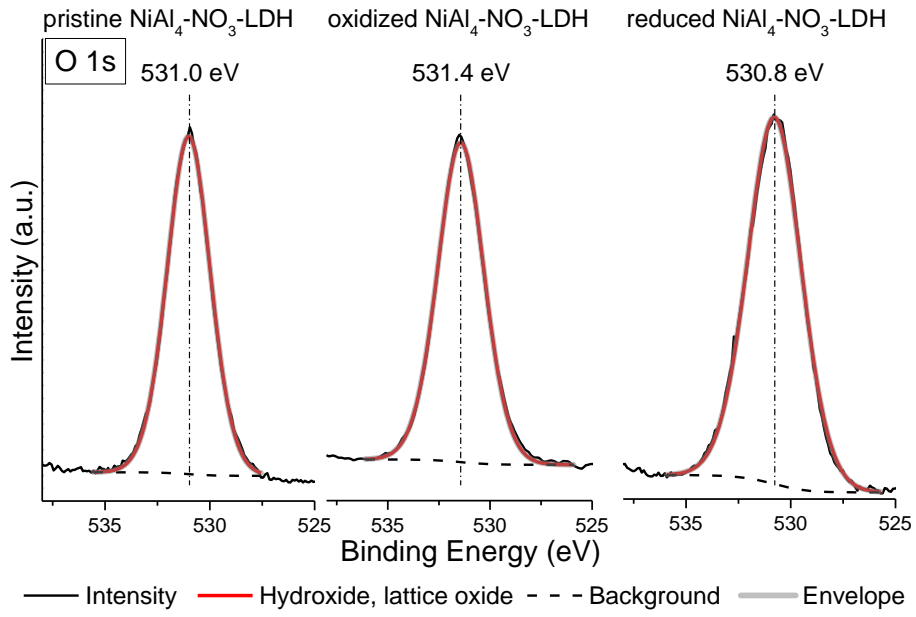
Catalyst precursors	Carbon deposition (wt. %)	
NiAl ₄ -Cl-LDH	1.6	<0.5
NiAl ₄ -Br-LDH	<0.5	<0.5
NiAl ₄ -I-LDH	<0.5	<0.5
NiAl ₄ -NO ₃ -LDH	2.4	3.1
NiAl ₄ -ClO ₄ -LDH	<0.5	<0.5
NiAl ₄ -SO ₄ -LDH	<0.5 ^a	<0.5
NiAl ₄ -NH ₂ SO ₃ -LDH	1.4 ^a	0.9
NiAl ₂ -OH	0.7	2.2
NiAl ₄ -OH	<0.5	<0.5

^aCorrected by the thermogravimetric losses of the sulphamate and sulphate containing LDHs between 700 and 1000 °C (pre-calcination at 700 °C, 0.5 h and air atmosphere).

Table S9. Composition of the various surface Ni(II) species in the pristine and treated catalysts obtained by XPS analysis.

Catalyst forms	Atomic concentration [%]							
	Ni-Al solid solution	Ni(II) hydroxide	Ni(II) oxide	Ni(0) metallic	Ni(II) perchlorate	Ni(II) chloride	Ni(II) sulphate	Ni(II) sulphide
Control solid								
pristine NiAl ₄ -OH	30.8	69.2	–	–	–	–	–	–
oxidized NiAl ₄ -OH	29.8	26.5	43.7	–	–	–	–	–
reduced/spent NiAl ₄ -OH	–	–	71.2	28.8	–	–	–	–
LDH materials								
pristine NiAl ₄ -NO ₃	31.3	68.7	–	–	–	–	–	–
oxidized NiAl ₄ -NO ₃	52.6	–	47.4	–	–	–	–	–
reduced/spent NiAl ₄ -NO ₃	–	–	61.7	38.3	–	–	–	–
pristine NiAl ₄ -ClO ₄	26.9	68.6	–	–	4.5	–	–	–
oxidized NiAl ₄ -ClO ₄	36.2	–	35.7	–	–	28.1	–	–
reduced/spent NiAl ₄ -ClO ₄	–	–	52.4	33.6	–	14.0	–	–
pristine NiAl ₄ -SO ₄	58.3	34.5	–	–	–	–	7.2	–
oxidized NiAl ₄ -SO ₄	34.6	–	58.1	–	–	–	7.3	–
reduced/spent NiAl ₄ -SO ₄	–	–	49.6	30.9	–	–	9.4	10.1





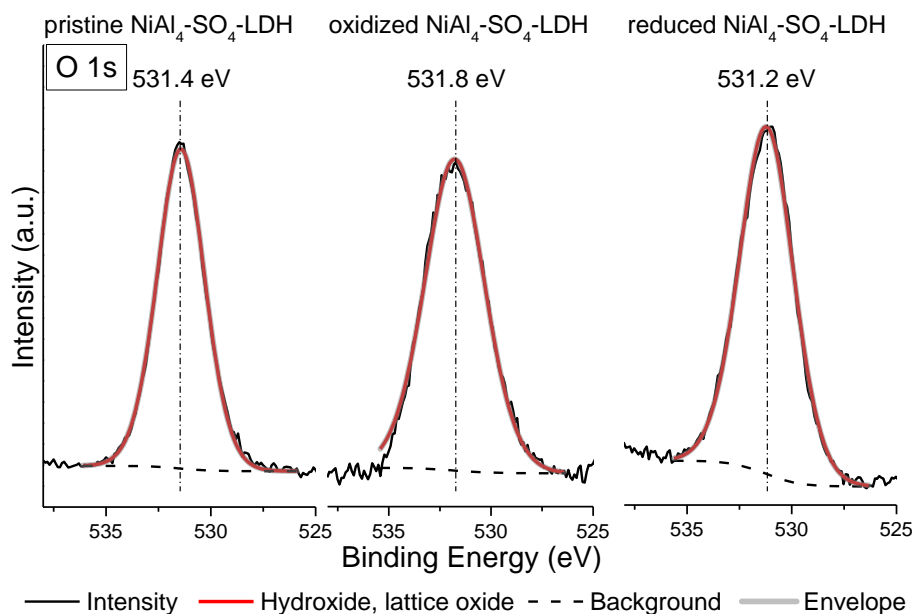
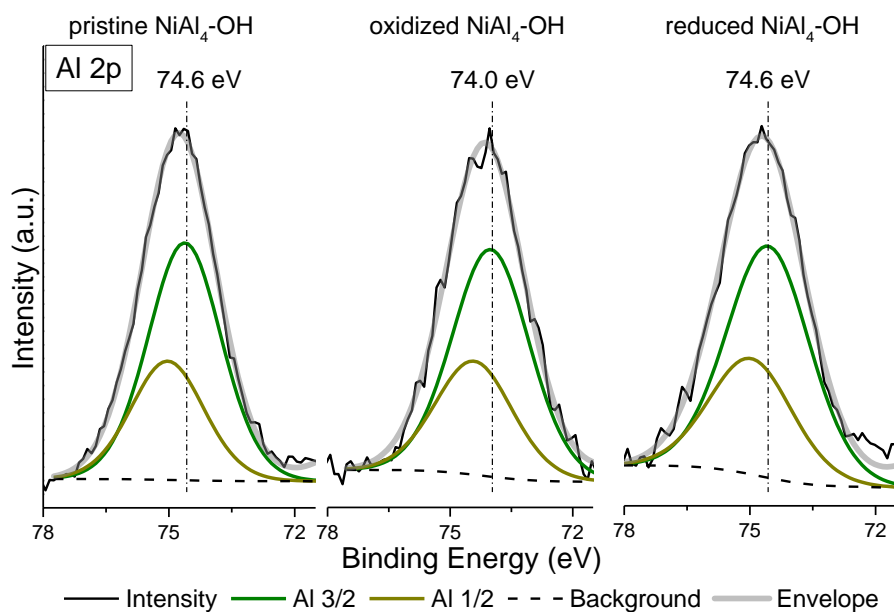
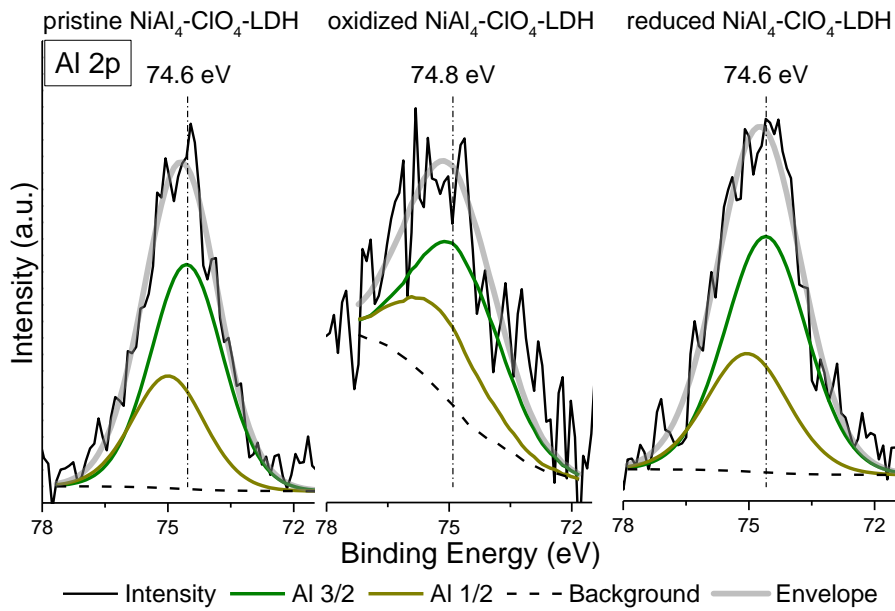
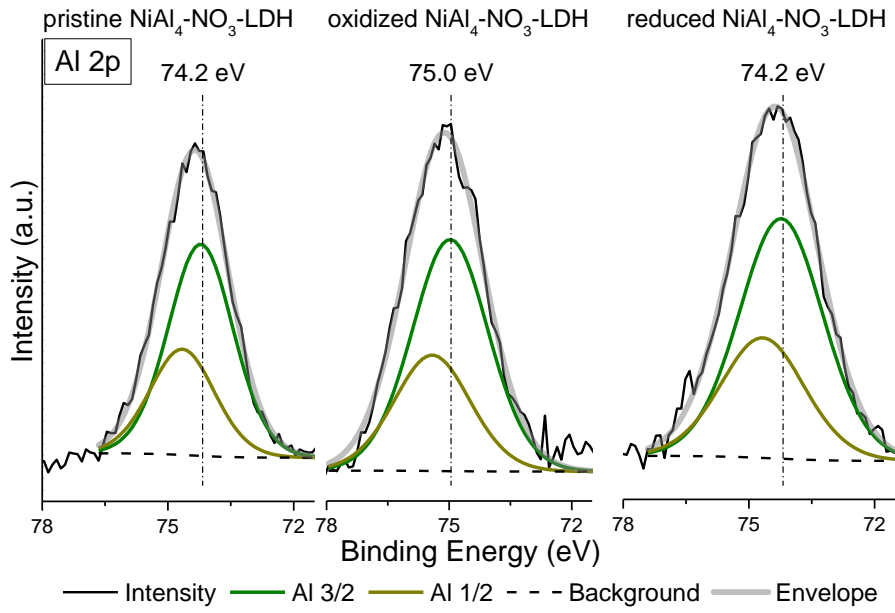


Fig. S11 High-resolution O 1s *quasi in situ* XPS spectra of the NiAl₄-OH control sample, NiAl₄-LDHs intercalated with nitrate, perchlorate and sulphate anions collected from the pristine solids, after oxidation (500 °C, 1 h, O₂ flow, oxidized forms) and reduction (in CO₂:4H₂ flow, oxidized samples heated up from 200 to 500 °C for 0.5 h and kept at 0.5 h, 500 °C, reduced/spent forms).





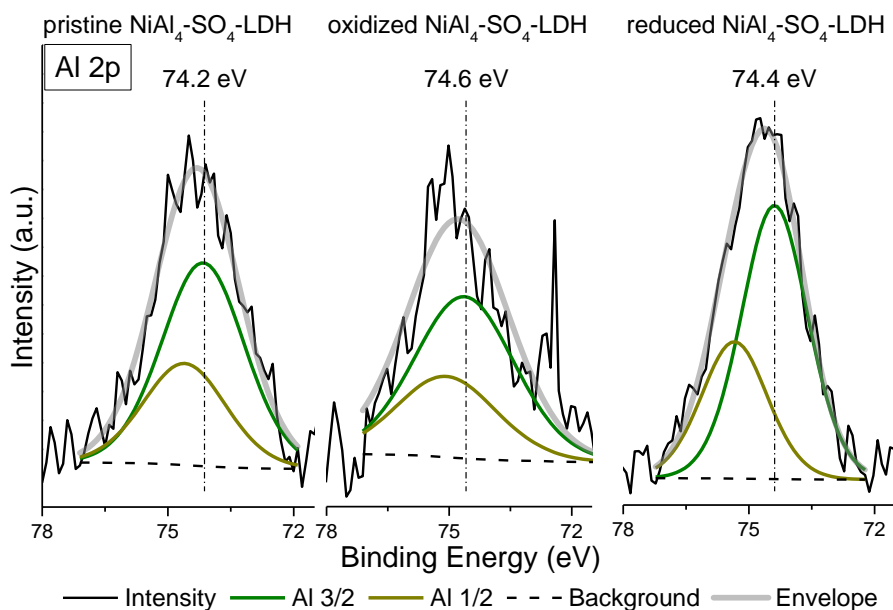


Fig. S12 High-resolution Al 2p *quasi in situ* XP spectra of the NiAl₄-OH control sample, NiAl₄-LDHs intercalated with nitrate, perchlorate and sulphate anions collected from the pristine solids, after oxidation (500 °C, 1 h, O₂ flow, oxidized forms) and reduction (in CO₂:4H₂ flow, oxidized samples heated up from 200 to 500 °C for 0.5 h and kept at 0.5 h, 500 °C, reduced/spent forms).

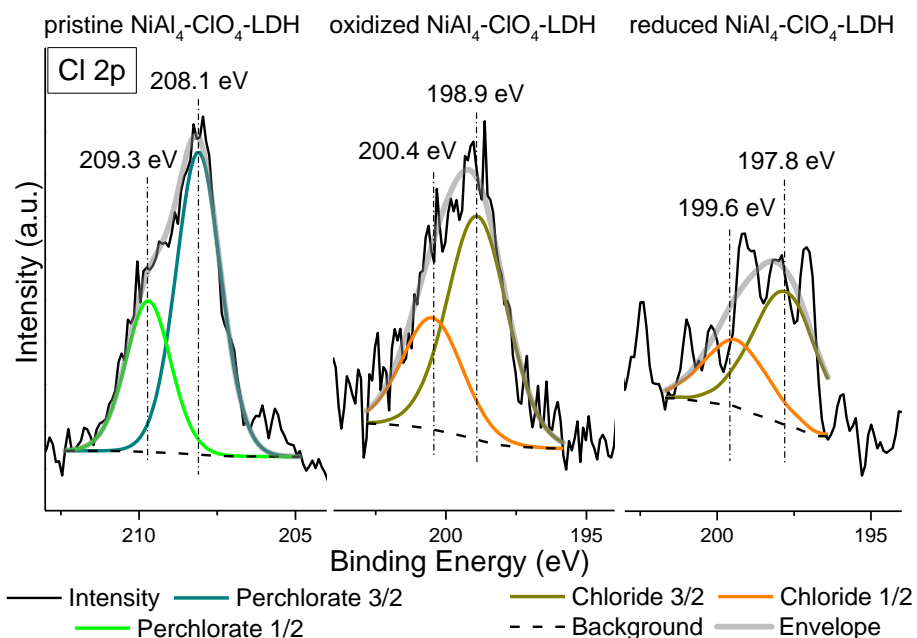


Fig. S13 High-resolution Cl 2p *quasi in situ* X-ray photoelectron spectra of the NiAl₄-LDH intercalated with perchlorate anions collected from the pristine LDH, after (500 °C, 1 h, O₂ flow, oxidized form) and reduction (in CO₂:4H₂ flow, oxidized samples heated up from 200 to 500 °C for 0.5 h and kept at 0.5 h, 500 °C, reduced/spent form).

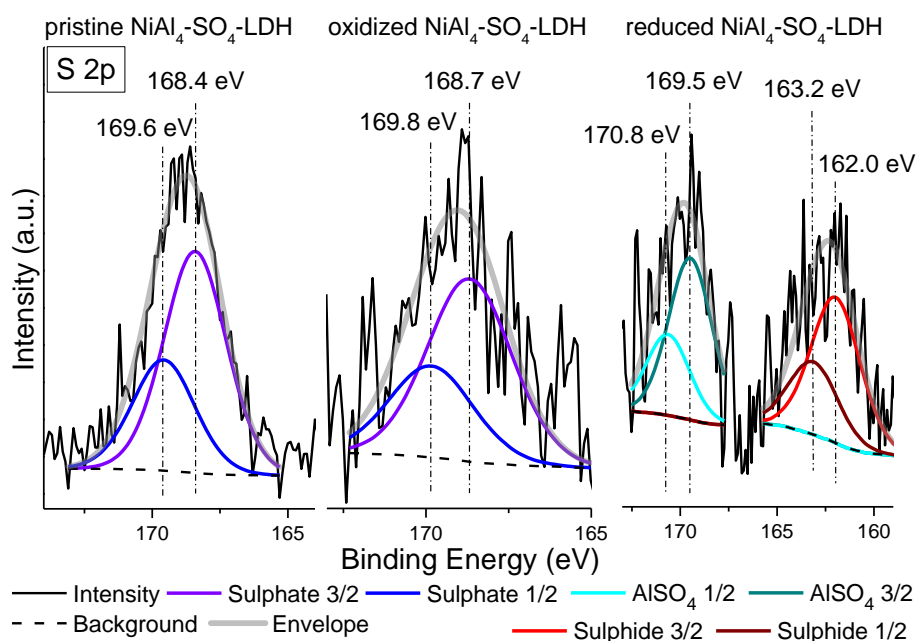


Fig. S14 High-resolution S 2p *quasi in situ* X-ray photoelectron spectra of the NiAl₄-LDH intercalated with sulphate anions collected from the pristine LDH, after oxidation (500 °C, 1 h, O₂ flow, oxidized form) and reduction (in CO₂:4H₂ flow, oxidized samples heated up from 200 to 500 °C for 0.5 h and kept at 0.5 h, 500 °C, reduced/spent form).

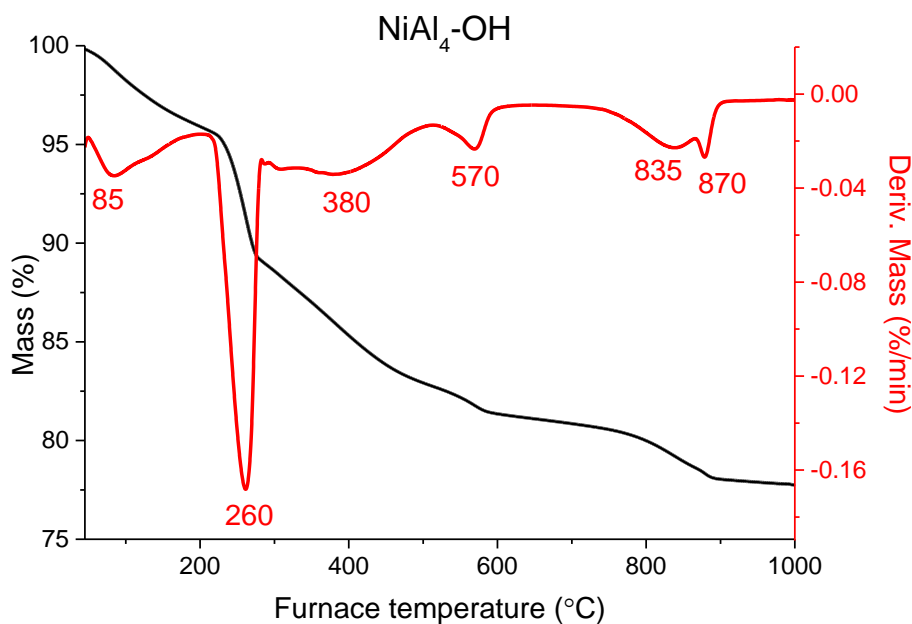


Fig. S15 Thermogravimetric curves of the NiAl₄-OH control solid under air atmosphere.

Table S10. Summary with comparison of previous catalytic results.

Catalyst or precursor forms	Reaction temperature (°C)	CO ₂ consumption rate (μmol/g _{cats})	CH ₄ selectivity (%)	CO selectivity (%)	Ref.
NiAl ₄ -NO ₃ LDH	300	6	100	0	This work
	350	19	92	8	
	400	49	91	9	
	450	69	91	9	
	500	83	88	12	
NiAl ₄ -ClO ₄ LDH	450	14	52	48	This work
	500	32	61	39	
FeCo ₂ O ₄	300	1.5	59	41	[39]
	400	4	44	56	
Ni _{0.4} Co _{2.6} O ₄	300	0	–	–	[39]
	400	5	80	20	
MnCo ₂ O ₄	300	2.5	77	23	[39]
	400	5	78	22	
NiAl ₂ O ₄	350	1	6	94	[83]
	400	2	11	89	
	450	7	53	47	
	500	13	80	20	
ZnAl ₂ O ₄	350	1	0	100	[83]
	400	2	0	100	
	450	3	0	100	
	500	6	0	100	
ZnO/NiAl ₂ O ₄	350	1	0	100	[83]
	400	1	0	100	
	450	2	5	95	
	500	12	12	88	
MnOx	350	0	–	–	[84]
	400	2	1	99	
	450	7	1	99	
	500	13	1	99	
Pt/MnOx	300	5	0	100	[84]
	350	9	2	98	

	400	12	15	85	
	450	13	9	81	
	500	17	2	98	
Cu/MnOx	400	3	3	97	[84]
Pt/ZSM-5	450	2	5	95	[85]
	300	18	100	0	
5Ni/CeO ₂	350	27	100	0	[86]
	400	33	100	0	
	300	2	0	100	
10Cu/CeO ₂	350	6	0	100	[86]
	400	10	0	100	
	300	10	90	10	
10Co/CeO ₂	350	12	84	16	[86]
	400	16	81	19	
	300	12	23	77	
4 mol% Ni/CeO ₂ (pre-reduced at 300 °C)	350	25	49	51	
	400	32	61	39	[87]
	450	31	60	40	
	500	30	59	41	
	300	3	100	0	
4 mol% Ni/CeO ₂ (pre-reduced at 600 °C)	350	15	80	20	
	400	26	90	10	[87]
	450	29	90	10	
	500	30	84	16	
	300	12	98	2	
Pt/NiO	350	12	–	–	[88]
	400	12	95	5	
	300	10	98	2	
Pt/Co ₃ O ₄	350	13	–	–	[88]
	400	13	95	5	
	300	3	98	2	
Pt8@NiO	350	9	94	6	[89]
	400	10	93	7	
	450	10	88	12	

	500	10	75	25	
Pt/m-Co ₃ O ₄	310	22	89	11	
	350	24	95	5	[90]
	400	23	95	5	
Pt/c-Co ₃ O ₄	310	20	92	8	
	350	21	93	7	[90]
	400	22	92	8	

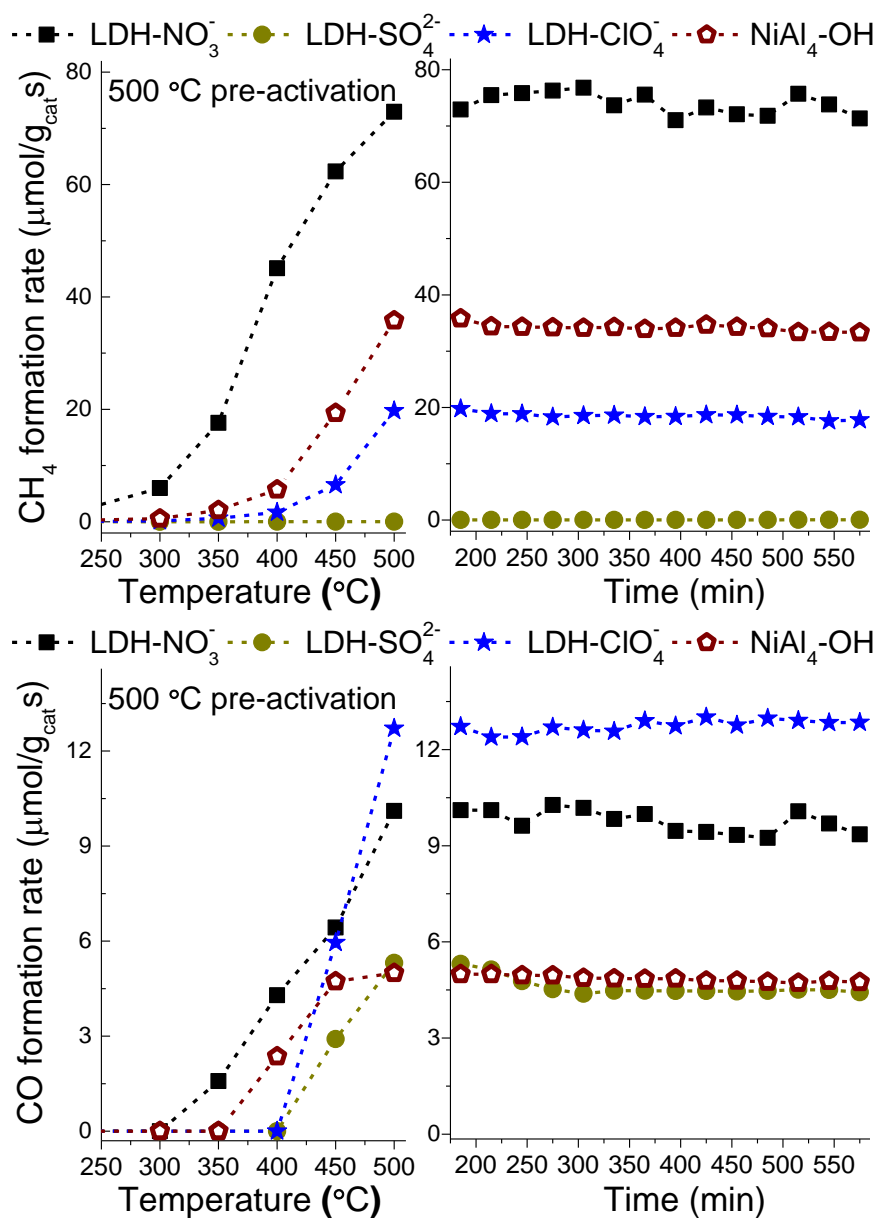


Fig. S16 CH₄/CO formation rates and long-term stability tests (at 500 °C) over the pre-activated LDH and the hydroxide control precursors at various reaction temperatures.