Supporting information

From Ethene to Propene (ETP) on Tailored Silica-Alumina Supports with Isolated Ni(II) Sites: Uncovering the Importance of Surface Nickel Aluminate Sites and the Carbon-Pool Mechanism

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Table S5. Weightings employed in fit for GC-MS spectrum of ethane (Figure S40).

Table S6. Weightings employed in fit for GC-MS spectrum of propene (Figure S41).
Experimental Details

Materials. Al-SiO$_2$-500 supports were prepared by atomic layer deposition (ALD) using a reported method.$^{[1]}$ In brief, silica dehydroxylated at 500 °C (SiO$_2$-500) was subjected to alternating pulses of trimethylaluminum (TMA) and ozone at 300 °C. The as-prepared materials were subsequently calcined in synthetic air at 500 °C for 4 h (5 °C min$^{-1}$). This gave supports denoted as Al1-, Al5-, Al10-SiO$_2$-500 that contain an OH density of 0.67, 0.58 and 0.47 mmol g$^{-1}$, respectively, according to titration with benzyl magnesium bromide. The Ni precursor, [Ni(OSi(OBu)$_3$)$_2$], was prepared following a literature method.$^{[2]}$ A solution of [Ni(OSi(OBu)$_3$)$_2$] (100 mg, 0.08 mmol) in 10 mL of dry toluene was added to Al1-, Al5-, Al10-SiO$_2$-500 supports (1 g) that were suspended in 10 mL of toluene. The purple-brown suspension was stirred at room temperature under N$_2$ for 3 h. Then, the solid material was washed with toluene (3 × 5 mL), and dried overnight under high vacuum (10$^{-5}$ mbar) to give 1 g of the grafted material denoted as Ni$_4$graffted-Al1-, Al5-, Al10-SiO$_2$-500. These materials were further calcined under 50 mL min$^{-1}$ of synthetic air (20 mol% O$_2$ in N$_2$) at 300 °C (5 °C min$^{-1}$, 1 h) and then at 400 °C (5 °C min$^{-1}$, 1 h). The calcined materials are denoted as Ni-Al1, Ni-Al5, Ni-Al10-SiO$_2$-500. Elemental analysis yielded for Ni-Al1-SiO$_2$-500: 1.67% Al, 0.73% Ni; for Ni-Al5-SiO$_2$-500: 8.63% Al, 1.03% Ni; and for Ni-Al10-SiO$_2$-500: 17.3% Al, 1.09% Ni.

Methods. ALD of TMA (Pegasus Chemicals) onto SiO$_2$-500 using ozone as an oxidant was performed on a Picosun R-200 system enclosed within an MBraun glovebox (O$_2$, H$_2$O < 1 ppm). N$_2$ (99.999%) was used as the carrier and purge gas in the ALD experiments. The ozone concentration expected at the power used is 10% w/w (140 g Nm$^{-3}$). Fourier-transform infrared spectroscopy (FTIR) was performed on an Alpha II spectrometer (Bruker) operated inside an MBraun glovebox (O$_2$ and N$_2$). elemental analysis was performed by the Mikroanalytisches Labor Pascher, Remagen, Germany. X-ray powder diffraction (XRD) data was obtained using a PANalytical Empyrean diffractometer with a Cu Ka radiation source set at 45 kV and 40 mA and a Bragg-Brentano HD optic. The detector used was an ultrafast line X'Celerator Scientific. The diffractograms were acquired between 5 and 100° (2θ; the step size was 0.0167° using an acquisition time of 0.4 s step$^{-1}$). The samples were measured on a zero-background sample holder (made of Si wafers). The microstructure of the materials (opened to air) was probed by TEM (FEI Talos F200X) equipped with a high-brightness field-emission gun, a high-angle annular dark field (HAADF) detector, and a large collection-angle EDX detector. The operation voltage of the instrument was set to 200 kV in scanning transmission electron microscopy (STEM) mode. The samples for electron microscopy were prepared by dipping the Cu grids coated with carbon (TedPella, 300 mesh) into the powder. X-ray absorption spectroscopy (XAS) was performed at the BM31 station of the Swiss-Norwegian beamline (SNBL) at the European Synchrotron Radiation Facility (ESRF). All spectra were collected at the Ni K-edge using continuous scanning in transmission mode with a double-crystal Si(111) monochromator. The spectral energy was calibrated using a Ni foil (8333 eV). To avoid contact with air, all sample pellets were sealed in two aluminized plastic bags using an impulse sealer inside the glovebox. The outside sealing layer was removed just before the measurement. Data processing and analysis were carried out using the Demeter software. EXAFS spectra were fitted in R space between 1 and 3.5 Å with a k-weight of 3. The Fourier transform (FT) of the EXAFS oscillations were obtained for a k-space range 3 - 12 Å$^{-1}$. The value of S$_0^2$ = 0.85 was obtained from fitting a Ni foil reference and was fixed for all the fittings. The initial F$_{eff}$ paths (Ni–O and Ni–Al/Si) were generated using a Ni aluminosilicate phase model.$^{[3]}$

$^{27}$Al MAS NMR. Direct one-pulse excitation $^{27}$Al NMR spectra were acquired using a wide bore 20.0 T Bruker Neo spectrometer. All samples were packed in 1.3 mm zirconia rotors inside an argon-filled glovebox. The rotor was spun at 60.0 kHz under pure nitrogen gas. A pulse of 0.5 μs has been used at
a radio-frequency field of 10 kHz (i.e. less than π/16 for quantitative purposes) and recycle delays were 100 ms (spin-lattice relaxation times estimated ≤ 400 ms). 432000, 86400 and 43200 transients were accumulated for Ni-Al1-, Ni-Al5 and Ni-Al10-SiO2-500 respectively. 27Al chemical shift is referenced to a nitric 1M solution of Al(NO3)3. Baseline corrections due to dead-time truncation were performed using an automated iterative procedure. All spectra were simulated using DMFit based on the so-called Czjzek (or Gaussian Isotropic) model rendering both the central <1/2,-1/2> as well as the external <1/2,±3/2> and <1/2,±5/2> transitions, the latter being included in the fit by taking into account up to their ±3 spinning sidebands.

Py-FTIR experiments. Calcined materials were evacuated (10⁻⁵ mbar) and then exposed to the vapor pressure of dry pyridine (Py) at room temperature for ca. 1 min, followed by outgassing (at RT or 150 °C, for 3 h or 1 h, respectively, using a heating ramp of 5 °C min⁻¹ at ca. 10⁻⁵ mbar). The IR spectra of the outgassed specimen were collected on an Alpha II spectrometer (Bruker) operated inside the N2 glovebox using self-supporting pellets.

Raman spectroscopy. Coke deposits on spent catalysts were analyzed utilizing a DRX 2 Raman microscope (Thermo Fischer). All samples were shortly exposed to air before the measurements and the spectra were collected at room temperature using a 455 nm excitation laser with a full range grating (100-3500 cm⁻¹, 1200 lines mm⁻¹). The baseline correction and fitting were carried out with the Fityk v 0.9.8 data analysis software.

TGA tests. Thermogravimetric analyses (Mettler Toledo, DSC 1) were performed by placing ca. 30 mg of the material in a 150 μL TGA platinum crucible followed by calcination (400 °C, 50 mL min⁻¹, synthetic air), ETP test (350 °C; 50 mL min⁻¹, 5% C2H4 in N2) and regeneration (500 °C; 50 mL min⁻¹, synthetic air). Changes in the specimen weight were monitored during the entire experiment.

NMR analysis of strongly bound surface adsorbates.

13C2H4/12C2H4 batch reaction. In an argon filled glovebox, Ni-Al5-SiO2-500 (57 mg, light yellow) was loaded into a glass reactor (volume: 64 mL). The reactor was evacuated (ca. 10⁻⁵ mbar), a 1:1 gas mixture of 13C2H4/C2H4 (approximately 1:1) was introduced (48 mbar), and the reactor additionally charged with 328 mbar of Ar, to give a total pressure of ca. 375 mbar. The reactor was then closed and heated to 350 °C (300 °C h⁻¹, 12 h). After 12 h, the reaction vessel was cooled to ~78 °C, evacuated at 10⁻⁵ mbar and the gas phase was collected for further GC analysis. The resulting black solid that was retained in the reactor was transferred to an argon-filled glovebox prior to NMR analysis.

13C and 1H ssNMR of strongly-bound surface adsorbates. Solid-state NMR spectra of 13C and 1H were recorded on a Bruker 400 MHz spectrometer using double resonance 3.2 mm CP-MAS probe. Samples were packed in 3.2 mm zirconia rotors inside an Ar-filled glovebox, and spectra were recorded at 298 K. In all cases, the downfield 13C resonance of adamantane (38.5 ppm) was used as an external secondary reference to calibrate chemical shifts. The MAS frequency was set to 16 kHz.

Gas chromatography mass spectrometry (GC-MS) analysis of the gas phase. Identification and analysis of the isotopic distribution of the gas-phase products (C1-C3) was performed using GC-MS (Agilent Technologies 7890 gas chromatograph coupled to an Agilent Technologies 5977B MSD mass spectrometer). The line fed a split-splitless port that injected in the split mode with He carrier gas on a GS-Carbonplot capillary column (30 m x 0.30 mm, 3.0 μm stationary phase) plugged to a mass selective detector (MSD) operated in the scan mode in the m/z range 0–100. Elution was realized using the following temperature program: 40 °C for 2 min, then ramp to 150 °C at 55 °C min⁻¹ and 150 °C for 11 min. The distribution of isotopologues was assessed using fragmentation patterns obtained
performed to investigate the distribution of Ni sites in high complete disappearance of C bands and recovery of the grafted materials in synthetic air at 400 °C. The decrease of IR bands at 3018 cm⁻¹ accompanied by the appearance of IR bands at 2850 cm⁻¹ indicates the successful removal of isolated silanols partially remains in Ni(grafted-Al10-SiO2-500) but disappears in Ni(grafted-Al5-SiO2-500 and Ni(grafted-Al10-SiO2-500). The complete removal of the bands due to the organic ligands was achieved by calcination of the grafted materials in synthetic air at 400 °C. The IR spectra of calcined Ni-Al1,5,10-SiO2-500 reveal a complete disappearance of C-H bands and recovery of the hydroxyl bands (Figures S1-S3).

High-angle annular dark-field imaging (HAADF) and energy-dispersive X-ray spectroscopy (EDX) were performed to investigate the distribution of Ni sites in the prepared catalysts. Here, the materials were exposed to ambient air shortly before the electron microscopy measurements. No Ni-containing
nanoparticles were observed; instead, Ni sites are found homogenously distributed in Ni-Al1,5,10-SiO2-500 catalysts, based on the EDX mapping (Figure S4–S6). This observation is consistent with XRD results where only a halo of amorphous silica is seen, suggesting a lack of crystalline phases and consistent with the high dispersion of supported Ni sites (Figure S7).

X-ray absorption spectroscopy (XAS) at the Ni K-edge was performed to assess the oxidation state and the local environment of Ni sites in Ni-Al1,5,10-SiO2-500 catalysts. The qualitative comparison of the X-ray absorption near-edge structure (XANES) spectra of the Ni-Al1,5,10-SiO2-500 catalysts and the reference materials [Ni(OSi(O′Bu))3]2 and NiO shows that the edge energy is nearly identical in all these materials (ca. 8339 eV) while Ni foil has a lower edge energy of 8333 eV, suggesting Ni(II) oxidation state in Ni-Al1,5,10-SiO2-500 catalysts (Figure S8). However, the catalysts show distinct XANES features that are different from those of NiO. Notably, the white line is broadened in Ni-Al1,5,10-SiO2-500 relative to NiO and shifted to lower energies, while the characteristic feature of bulk NiO at ca. 8367 eV is absent in all three Ni-Al1,5,10-SiO2-500 catalysts. This result is consistent with the absence of NiO nanoparticles in the HAADF-EDX images.

To provide further evidence for the absence of NiO crystallites in the Ni-Al1,5,10-SiO2-500 catalysts, a Ni–Ni path was also used to fit the experimental data. However, the obtained R factors are higher than the ones obtained considering Ni–Al(Si) paths, suggesting the fitting of Ni–Ni path is not justified (Table S1). Note that we introduced two subshells to fit the second coordination sphere of the Ni-Al1,5,10-SiO2-500 catalysts in order to account for the likely mono-grafting of [Ni(OSi(O′Bu))3]2 onto Al1,5,10-SiO2-500 supports, which after calcination may feature Ni–O–Si and Ni–O–Al paths. In addition, Al surface sites could be either tetra- or pentacoordinated, further justifying the introduction of two subshells for fitting the second coordination sphere. These observations are consistent with the formation of isolated surface Ni(II) sites in all three Ni-Al1,5,10-SiO2-500 catalysts.

IR spectroscopy of a pyridine probe molecule (Py-FTIR) adsorbed on oxide surfaces is one of the most frequently used techniques for characterizing the nature (Lewis or Brønsted) and strength of the acid sites.11–14 We probed the Lewis acid sites (LAS) and Brønsted acid sites (BAS) in Ni-Al1,5,10-SiO2-500 by Py-FTIR. The pyridinium ion (PyH+) formed upon protonation of pyridine by strong BAS, gives bands at ca. 1640 cm−1 and 1545 cm−1 while pyridine on LAS is associated with the bands between 1630 cm−1 and 1600 cm−1.15

Py on Ni-Al1-SiO2-500, desorbed at 150 °C, displays clear bands due to PyH+ (strong BAS) at 1639 cm−1 and 1545 cm−1 (Figure S12). These strong BAS are also found in Ni-Al5 and Ni-Al10-SiO2-500, but the intensities of the corresponding IR bands for these two materials are notably lower, especially for Ni-Al10-SiO2-500. This is consistent with a decreasing abundance of strong BAS in the order Al1- > Al5- > Al10-SiO2-500.1 The IR bands due to Py on LAS are found at ca. 1622 cm−1 and 1614 cm−1 in all three catalysts. Comparison of the Py-FTIR spectra of Al1,5,10-SiO2-500 reported by us previously and of Ni-Al1,5,10-SiO2-500 developed in this work reveals that the band at ca. 1614 cm−1 is only present in Ni-Al1,5,10-SiO2-500 and is absent in Al1,5,10-SiO2-500 (150 °C desorption temperature).1 At the same time, the band at 1622 cm−1 is present in Al1,5,10-SiO2-500.1 Therefore, the band at 1614 cm−1 can be assigned to the Py-Ni(II) interaction. An alternative explanation is the appearance of a new Al-based LAS in Ni-Al1,5,10-SiO2-500, however, this hypothesis is not supported by the 27Al NMR data of Ni-Al1,5,10-SiO2-500, which shows a similar distribution of Al sites between Al1,5,10-SiO2-500 and Ni-Al1,5,10-SiO2-500 (Figure S36). In addition, it is worthy to note that the intensity of the band at 1622 cm−1 is higher than the band at 1614 cm−1 in Ni-Al1-SiO2-500 but lower than the band at 1614 cm−1 in Ni-Al5,10-SiO2-500, which can be related to the higher amounts of Ni aluminate sites in Ni-Al5,10 than in Ni-Al1. To summarize, the surface acidity of Ni-Al1,5,10-SiO2-500 catalysts is consistent with the acidity of their supports,11 that is, Ni-Al1-SiO2-500 with an aluminosilicate shell has strong BAS with the highest abundance. With the growth of an amorphous alumina layer on top of the aluminosilicate
shell, the relative fraction of strong BAS with respect to that of other LAS and BAS in Ni-Al5 and Ni-Al10-SiO2-500 decreases.

In the batch labelling experiments, ethane and propylene were the only species detected by GC-MS of the gas-phase after reaction. On the basis of isotopic distributions, concentration of unlabeled, mono-, di- and tri-labelled propene reflect the isotopic distributions of the gas mixture prior to reaction (Figure S40, Table S5), suggesting that the distribution of isotopologues is best described as statistical. For ethane, best fit of isotopologues was obtained when ≤5% of mixed 13C-13C ethane was incorporated in the fit (Figure S41, Table S6), suggesting that scrambling due to self-metathesis of ethene is not significant for the catalyst – an observation that is consistent with previous reports on ETP over Ni-based Al-SiO2 catalysts. Notably, neither ethene nor propane were present in detectable quantities.

The spent Ni-Al catalysts were collected and stored in a N2-filled glovebox (O2, H2O < 1 ppm) without exposing to air. Figure S23 compares FTIR spectra for as-prepared and activated catalysts collected at TOS = 90 min, when the highest catalytic activity was reached during the ETP test after regeneration. Two characteristic bands at 1596 and 1482 cm\(^{-1}\), which are more intense in Ni-Al5- and Ni-Al10-SiO2-500 but notably weaker in Ni-Al1-SiO2-500, are assigned to surface carbonates which can be fully removed via calcination at 700°C for 2h (Figure S24).

Thermogravimetric analysis experiments (TGA) were performed to assess the coke deposition on Ni-Al catalysts: a platinum crucible with ca. 30 mg of the catalyst was kept at 350°C in 5% C2H4 in N2 for 5 h followed by calcination (regeneration) at 500°C in synthetic air for 1 h, and the weight change owing to coke deposition and removal was determined. The weight increase after 5 h of the ETP test decreases in the order: Ni-Al10-SiO2-500 > Ni-Al5-SiO2-500 > Ni-Al1-SiO2-500, which is also consistent with the order of the weight loss observed in the 1 h regeneration experiment (Figure S31).

Raman spectroscopy was carried out to further analyze the nature of the carbon deposits on spent catalysts (Figure S30). Based on the previous reports, deconvolution of the spectra obtained from spent Ni-Al catalysts identifies four first-order Raman bands, i.e. D\(_s\) (∼1200 cm\(^{-1}\)), D\(_1\) (∼1350 cm\(^{-1}\)), D\(_3\) (∼1500 cm\(^{-1}\)), and G (∼1580 cm\(^{-1}\)). While the D\(_s\) and G bands are fitted using Lorentzian peak shapes, Gaussian functions were used to fit the D\(_1\) and D\(_3\) bands. D\(_1\) and G bands corresponding to disordered graphic lattice (\(\text{A}_{1g}\) symmetry) and the ideal graphic lattice, respectively, are dominating in Raman spectra of all three spent Ni-Al catalysts (Figure S29). The D\(_3\) band is presented in spent-Ni-Al1-SiO2-500 and spent-Ni-Al5-SiO2-500, suggesting the formation of amorphous carbon. Here, in order to evaluate the degree of disorder in the carbon deposits, the ratio of the areas D\(_3\)/G are utilized. The D\(_3\)/G values obtained for spent-Ni-Al1-SiO2-500 and spent-Ni-Al5-SiO2-500 show a similar ratio of 1.5, while spent-Ni-Al10-SiO2-500 has a much lower ratio of 0.3 (Table S3).
Figure S1. FTIR spectra of Al1-SiO2-500, Ni\textsubscript{grafted}-Al1-SiO2-500 and Ni-Al1-SiO2-500 (black, dark red and blue, respectively).

Figure S2. FTIR spectra of Al5-SiO2-500, Ni\textsubscript{grafted}-Al5-SiO2-500 and Ni-Al5-SiO2-500 (black, dark red and blue, respectively).
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Figure S7. XRD patterns of Ni-Al1,5,10-SiO2−500.

Figure S8. Ni K-edge XANES spectra of Ni-Al1,5,10-SiO2−500 (black, dark red and dark blue traces, respectively) along with the [Ni(OSi(O^tBu)3)2]2 (green), NiO (yellow) and Ni foil (light blue) references.
Figure S9. EXAFS fittings of Ni-Al1-SiO2-500 at Ni K-edge: magnitude (top) and imaginary (bottom) parts of the FT in R space.
Figure S10. EXAFS fittings of Ni-Al5-SiO2−500 at Ni K-edge: magnitude (top) and imaginary (bottom) parts of the FT in R space.
Figure S11. EXAFS fittings of Ni-Al10-SiO2−500 at Ni K-edge: magnitude (top) and imaginary (bottom) parts of the FT in R space.
Figure S12. EXAFS fittings of NiO at Ni K-edge: magnitude (top) and imaginary (bottom) parts of FT in R space.
**Table S1.** Structural parameters obtained from Ni K-edge EXAFS data fitted with Ni-O and Ni-Ni paths.

| Material         | Neighbour | CN | r (Å)  | σ²(Å²) | E₀ (eV) | R-factor |
|------------------|-----------|----|--------|--------|---------|----------|
| Ni-Al1-SiO₂-500  | O         | 5.4(9) | 2.00(4) | 0.010(2) | ~5(2)   | 0.018    |
|                  | Ni        | 1.8(6) | 2.94(9) | 0.010(2) |         |          |
| Ni-Al5-SiO₂-500  | O         | 5.3(8) | 1.99(6) | 0.010(2) | ~8(2)   | 0.013    |
|                  | Ni        | 1.5(4) | 2.93(7) | 0.010(2) |         |          |
| Ni-Al10-SiO₂-500 | O        | 5.0(8) | 1.99(5) | 0.009(1) | ~5(2)   | 0.017    |
|                  | Ni        | 1.3(5) | 2.92(7) | 0.009(1) |         |          |

All samples were measured at ambient temperature. S₀² was fixed to 0.85 obtained by fitting a Ni foil reference. CN stands for the coordination number. Debye-Waller factor σ² were constrained to the same value for all paths in each sample. The larger R-factors compared with those obtained in Table 1 suggests that the model (representing NiO) is inappropriate.

**Table S2.** Structural parameters for NiO obtained from Ni K-edge EXAFS data.

| Material | Neighbour | CN | r (Å)  | σ²(Å²) | E₀ (eV) | R-factor |
|----------|-----------|----|--------|--------|---------|----------|
| NiO      | O         | 6(1) | 2.01(1) | 0.006(1) | ~4.2(8) | 0.002    |
|          | Ni        | 12(1) | 2.95(5) | 0.007(1) |         |          |

All samples were measured at ambient temperature. S₀² was fixed to 0.85 obtained by fitting a Ni foil reference.
**Figure S13.** FTIR spectra of pyridine adsorbed on Ni-Al1-(black), Ni-Al5-(red) and Ni-Al10-SiO$_2$-500 (blue) after evacuation at ca. $10^{-5}$ mbar at ambient temperature (3 h) and then at 150 °C (1 h).

**Figure S14.** (a) Conversion of ethene and (b) propene productivity with time on stream on Ni-Al1-, Ni-Al5-, and Ni-Al10-SiO$_2$-500 (black, red and blue symbols, respectively).

Conditions: 5mL min$^{-1}$ (total flow), 10% C$_2$H$_4$ in N$_2$, 350 °C, GHSV = 0.2 L$_{C_2H_4}$ h$^{-1}$ g$_{cat}^{-1}$. 
Figure S15. Productivity to propene, benzene, toluene, C₈ aromatics (ethylbenzene and o-, m-, p-xylanes) and 1-butene on Ni-Al1-(black-and-white), Ni-Al5-(red), Ni-Al10-SiO₂-500 (blue) over 30 h of TOS including five regeneration cycles after every 5 h.
Figure S16. Productivity (left Y-axis) to propene (black), trans-butene (blue), cis-butene (green), isobutene (yellow), 1-butene (navy), C_1-C_4 alkanes (orange) and carbon balance (black open squares, right Y-axis) with TOS for Ni-Al1-SiO_2−500.

Here and in experiments presented in Figures S17-S21, and in Figures S30, S31, a total flow of 5 mL min^{-1} of 10% C_2H_4 in N_2, at 350°C and GHSV = 200 mL C_2H_4 h^{-1} g_{cat}^{-1}, was used.

Figure S17. Productivity (left Y-axis) to propene (black), trans-butene (blue), cis-butene (green), isobutene (yellow), 1-butene (navy), C_1-C_4 alkanes (orange) and carbon balance (black open squares, right Y-axis) with TOS for Ni-Al5-SiO_2−500.
Figure S18. Productivity (left Y-axis) to propene (black), trans-butene (blue), cis-butene (green), iso-butene (yellow), 1-butene (navy), C₁₋₄ alkanes (orange) and carbon balance (black-and-white open squares, right Y-axis) with TOS for Ni-Al₁₀-SiO₂−500.

Figure S19. Productivity to (a) benzene, (b) toluene and (c) xylenes with TOS for Ni-Al₁₋₅, Al₁₅₋₁₀, Al₁₀₋₁₉-SiO₂−500.
Figure S20. Productivity to $\text{H}_2$ (left) and $\text{C}_1$-$\text{C}_4$ alkanes (right) with TOS for Ni-Al1-, Al5-, Al10-SiO$_2$-500.

Figure S21. Initial partial selectivity to alkanes for Ni-Al1-, Ni-Al5-, Ni-Al10-SiO$_2$-500.
Figure S22. (a) HAADF and (b) EDX imaging of spent catalyst Ni-Al1-SiO2−500 after 20 h on stream in the ETP reaction.

Figure S23. (a) HAADF and (b) EDX imaging of spent catalyst Ni-Al5-SiO2−500 after 20 h on stream in the ETP reaction.

Figure S24. (a) HAADF and (b) EDX imaging of spent catalyst Ni-Al10-SiO2−500 after 20 h on stream in the ETP reaction.
Figure S25. Comparison of the FTIR spectra of the calcined Ni-Al1,5,10-SiO2−500 materials and the respective materials after 90 min of TOS after the 6th regeneration.

Activated samples were collected after five ETP-regeneration cycles and the activation period, i.e. at the maximum of the catalytic performance.

Figure S26. FTIR spectra of activated Ni-Al10-SiO2−500 (grey) and Ni-Al10−SiO2−700 (black trace).

Calcination at 700 °C removes bands in Ni-Al10-SiO2−500 that likely belong to carbonate species.
Figure S27. (a) HAADF and (b) EDX imaging of activated Ni-Al1-SiO2−500.

Figure S28. (a) HAADF and (b) EDX imaging of activated Ni-Al5-SiO2−500.

Figure S29. (a) HAADF and (b) EDX imaging of activated Ni-Al10-SiO2−500.
Figure S30. Conversion of ethene on (a) Al1-SiO2-500, (b) Al5-SiO2-500 and (c) Al10-SiO2-500 over 2 h on stream.

Figure S31. Productivity to propene (black), trans-butene (blue), cis-butene (green), iso-butene (yellow), 1-butene (navy) and C1-C4 alkanes (orange) with TOS for Ni-Al5-SiO2-500 calcined prior to the catalytic test at (a) 400 °C (temperature used for the material synthesis) and (b) 500 °C.
Figure S32. Raman spectra of carbon deposits on spent catalysts after 20 h on stream for (a) Ni-Al1-SiO$_2$-500 (b) Ni-Al5-SiO$_2$-500 (c) Ni-Al10-SiO$_2$-500.

Table S3. Results of the Raman fitting.

| Sample         | D$_4$ | Position | FWHM | Area | D$_1$ | Position | FWHM | Area | D$_3$ | Position | FWHM | Area | G    | Position | FWHM | Area | Area Ratio D$_1$/G |
|----------------|-------|----------|------|------|-------|----------|------|------|-------|----------|------|------|------|----------|------|------|-----------------|
| Spent-Ni-Al1   |       | 1171     | 159.8| 14.3 |       | 1346     | 163.8| 37.1 |       | 1520     | 185.8| 24.2 |     | 1588     | 62.1 | 24.3 | 1.5             |
| Spent-Ni-Al5   | 1348  | 222.9 | 55.2 |       | 1521  | 78.2     | 8.8  |       | 1599  | 64.1     | 36.0 |       |     | 1602     | 83.7 | 78.7 | 1.5             |
| Spent-Ni-Al10  | 1375  | 142.5 | 21.3 |       |       | 1602 | 83.7 | 78.7 |       | 1602     | 83.7 | 78.7 | 0.3 |          |      |      |                 |

* Position is given in cm$^{-1}$. 


Figure S33. TGA coke deposition profiles for Ni-Al1,5,10-SiO2−500. ETP test: T = 350 °C; 50 mL min⁻¹ of 5% C3H4 in N2.

Regeneration: 500 °C; 50 mL min⁻¹ in synthetic air.

Figure S34. Comparison of the propene productivity after regeneration in synthetic air at 400 °C (hollow symbols) and 500 °C (solid symbols) on Ni-Al1-(a), Ni-Al5-(b), Ni-Al10-SiO2−500 (c).
Figure S35. Comparison between the Py-FTIR spectra of fresh (red) and regenerated (pink) Ni-Al5-SiO$_2$-500.

Figure S36. $^{27}$Al MAS NMR spectra for (a) Ni-Al1-SiO$_2$-500 (b) Ni-Al5-SiO$_2$-500 (c) Ni-Al10-SiO$_2$-500. Left: Czjzek-type simulations taking into account AlO$_4$ (green), AlO$_5$ (purple) and AlO$_6$ (yellow) environments; the sub-layer being accounted for Ni-Al5-SiO$_2$-500 and Ni-Al10-SiO$_2$-500 by the experimental Ni-Al1-SiO$_2$-500 spectra (grey). Right: comparison between the Ni-loaded samples (blue) and the Ni-free materials (black, taken from ref. [1]).
Table S4. Results of the $^{27}$Al NMR fittings.

| Site* | % ± 0.5 | $\delta_{150}$ (ppm) ± 0.2 | $\Delta \delta_{150}$ (ppm) ± 1 | $\tilde{C}_Q$ (MHz) ± 0.1 |
|-------|---------|-----------------|-----------------|-----------------|
| Ni-Al1-SiO$_2$-$500$ | | | | |
| [4]Al | 46.1 | 56.1 | 18.3 | 10.6 |
| [5]Al | 38.8 | 32.5 | 16.9 | 8.71 |
| [6]Al | 15.1 | 10.2 | 15.7 | 8.54 |
| Ni-Al5-SiO$_2$-$500$ | | | | |
| [4]Al | 43.1 | 64.2 | 24.1 | 10.2 |
| [5]Al | 30.6 | 39.4 | 14.2 | 9.83 |
| [6]Al | 5.3 | 9.8 | 34.3 | 3.82 |
| Ni-Al11-SiO$_2$-$500$ | 21.0 | | | |
| Ni-Al10-SiO$_2$-$500$ | | | | |
| [4]Al | 33.6 | 67.6 | 19.9 | 7.86 |
| [5]Al | 31.7 | 39.8 | 15.5 | 7.50 |
| [6]Al | 4.3 | 8.5 | 17.4 | 4.18 |
| Ni-Al15-SiO$_2$-$500$ | 30.4 | | | |
| Al5-SiO$_2$-$500$-regen | | | | |
| [4]Al | 53.7 | 65.7 | 18.9 | 12.02 |
| [5]Al | 38.5 | 38.0 | 15.0 | 9.21 |
| [6]Al | 7.7 | 10.4 | 13.6 | 8.37 |
| Ni-Al5-SiO$_2$-$500$-regen | | | | |
| [4]Al | 52.9 | 67.5 | 15.6 | 11.86 |
| [5]Al | 39.2 | 38.2 | 13.3 | 8.50 |
| [6]Al | 7.9 | 9.7 | 12.1 | 7.07 |
| Ni-Al5-SiO$_2$-$500$ | | | | |
| [4]Al | 61.3 | 64.7 | 23.3 | 12.3 |
| [5]Al | 34.8 | 38.2 | 15.8 | 9.7 |
| [6]Al | 4.0 | 6.5 | 19.0 | 4.8 |

*The spectrum of Ni-Al1-SiO$_2$-$500$ was used as a fitting component for Ni-Al5-SiO$_2$-$500$ and Ni-Al10-SiO$_2$-$500$ (top part entries). A three-site simulation was used in the bottom part entries.
**Figure S37.** $^{27}$Al MAS NMR spectra for Al$_5$SiO$_2$-500 (red, from ref. [1]), regenerated Al$_5$SiO$_2$-500 (purple), Ni-Al$_5$SiO$_2$-500 (blue), regenerated Ni-Al$_5$SiO$_2$-500 (cyan).

**Figure S38.** $^{13}$C CP-MAS NMR spectrum of Ni-Al$_5$SiO$_2$-500 after exposure to $^{13}$C$_2$H$_4$/C$_2$H$_4$ (1:1) at 350 °C for 12 h. Asterisks indicate spinning sidebands. Spinning rate: 16 kHz; NS = 49152; d1 = 1 s.
Figure S39. $^1$H MAS NMR spectrum of (a) Ni-Al5-SiO$_{2-500}$ after exposure to $^{13}$C$_2$H$_4$/C$_2$H$_4$ (1:1) at 350 °C for 12 h, and (b) fresh Ni-Al5-SiO$_{2-500}$. Spinning rate: 16 kHz; NS = 64; d1 = 1 s (a), and 1.3 s (b).

Figure S40. Mass spectrum (EI) for ethane obtained using GC-MS. Fractional composition of isotopologues given in Table S5.
Table S5. Weightings employed in fit for GC-MS spectrum of ethane (Figure S40).

| Isotopologue | Fractional composition |
|--------------|------------------------|
| Unlabeled    | 0.42                   |
| Mono-labeled | 0.05                   |
| Di-labelled  | 0.53                   |
| Sum          | 1.00                   |
| RMSE         | 0.017                  |

Figure S41. Mass spectrum (EI) for propene obtained using GC-MS. Fractional composition of isotopologues given in Table S6.

Table S6. Weightings employed in fit for GC-MS spectrum of propene (Figure S41).

| Isotopologue | Fractional composition |
|--------------|------------------------|
| Unlabeled    | 0.2                    |
| Mono-labeled | 0.27                   |
| Di-labeled   | 0.305                  |
| Tri-labeled  | 0.225                  |
| Sum          | 1.00                   |
| RMSE         | 0.017                  |
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