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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Experimental Details

Materials. Al-SiO₂₋₅₀₀ supports were prepared by atomic layer deposition (ALD) using a reported method.^[1] In brief, silica dehydroxylated at 500 °C (SiO₂₋₅₀₀) 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-SiO₂₋₅₀₀ 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(O^fBu)₃)₂]₂, was prepared following a literature method.^[2] A solution of [Ni(OSi(O^fBu)₃)₂]₂ (100 mg, 0.08 mmol) in 10 mL of dry toluene was added to Al1-, Al5-, Al10-SiO₂₋₅₀₀ supports (1 g) that were suspended in 10 mL of toluene. The purple-brown suspension was stirred at room temperature under N₂ 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 ca. 1 g of the grafted material denoted as Ni_{grafted}-Al1-, Al5-, Al10-SiO₂₋₅₀₀. These materials were further calcined under 50 mL min⁻¹ of synthetic air (20 mol% O₂ in N₂) 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-SiO₂₋₅₀₀. Elemental analysis yielded for Ni-Al1-SiO₂₋₅₀₀: 1.67% Al, 0.73% Ni; for Ni-Al5-SiO₂₋₅₀₀: 8.63% Al, 1.03% Ni; and for Ni-Al10-SiO₂₋₅₀₀: 17.3% Al, 1.09% Ni.

Methods. ALD of TMA (Pegasus Chemicals) onto SiO₂₋₅₀₀ using ozone as an oxidant was performed on a Picosun R-200 system enclosed within an MBraun glovebox (O_2 , $H_2O < 1$ 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 , $H_2O < 1$ ppm). Elemental analysis was performed by the Mikroanalytisches Labor Pascher, Remagen, Germany. X-ray powder diffraction (XRD) data was obtained using a PANalytical Empyrean diffractometer provided with a Cu Kα 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° (2 θ ; 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 Feff paths (Ni–O and Ni–Al/Si) were generated using a Ni aluminosilicate phase model.^[3]

²⁷Al MAS NMR. Direct one-pulse excitation ²⁷Al 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 $\pi/16$ 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.^[4] 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 <±3/2,±5/2> transitions, the latter being included in the fit by taking into account up to their ±3 spinning sidebands.^[5]

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.^[6]

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.^[7]

TGA tests. Thermogravimetric analyses (Mettler Toledo, DSC 1) were performed by placing ca. 30 mg of the material in a 150 μ L 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.

 ${}^{13}C_{2}H_{4}/{}^{12}C_{2}H_{4}$ 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 ${}^{13}C_{2}H_{4}/C_{2}H_{4}$ (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 (C_1 - C_3) 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

from the NIST WebBook for both ethane and propylene.^[8] For the purpose of fitting, the sum of fractional contributions from all isotopologues was fixed to a value of 1.

Catalytic tests. The ETP tests were performed in a fixed-bed quartz reactor (13 mm ID, PID Eng&Tech). In a typical catalytic test, 150 mg of catalyst was diluted with SiC up to the total weight of 4.0 g and loaded between two plugs of quartz wool. The reactor was sealed inside a N₂ glovebox and purged with N₂ via a bypass prior to the catalytic test. After equilibration of the reaction temperature to 350 °C under a flow of N₂ (20 mL min⁻¹), a stream of 10 % of C₂H₄ in N₂ (5 mL min⁻¹, ambient pressure) was introduced into the reactor. The gas flow rate was controlled by mass flow controllers, which were calibrated for the desired gases. The temperature was controlled by a thermocouple immersed into the catalyst bed. The products at the outlet of the reactor were analyzed by a 4-channel compact gas chromatography (CompactGC 4.0, Global Analyser Solutions) equipped with two thermal conductivity detectors (TCD) and two flame ionization detectors (FID). An Rt-Al₂O₃/MAPD column was utilized to separate C₁-C₅ hydrocarbon products (T ranged from 190 to 210 °C during measurements) and an Rt-WAX column was used to separate aromatic products. The data points were collected every 7 min. For the reaction-regeneration tests, a regeneration step was introduced after every 5 h of time on stream, by flowing synthetic air (50 mL min⁻¹ at 400 °C or 500 °C) for 1 h, followed by flushing with N₂ (50 mL min⁻¹) while decreasing the temperature to 350 °C.

The outlet gas fractions ($C_{x,out}$) were determined by calibrating the GC with gas mixtures of respective known gases diluted in N₂ except that to quantify *n*-butane, the calibration for isobutane was used. The formation rate of products ($F_{x,out}$, mol min⁻¹) was calculated based on the gas fractions in the outlet flow (Eq. 1). The ethene conversion ($X_{C_2H_4}$), productivities (P_x , g h⁻¹ g_{Ni}⁻¹) and carbon balance was calculated according to equations 2-4, respectively.

$$F_{x,out}[\operatorname{mol} \operatorname{min}^{-1}] = \frac{C_{x,out}F_{N_2,in}}{C_{N_2,out}}$$
Eq.1

$$X_{C_2H_4} = \frac{F_{C_2H_4,in} - F_{C_2H_4,out}}{F_{C_2H_4,in}} \times 100\%$$
 Eq.2

$$P_x = \frac{F_{x,out} \times M \times 60}{m_{Ni}}$$
, where *M* is the molar weight of the product Eq.3

$$Carbon \ balance = \frac{\sum F_{x,out} \times N_x + F_{C_2H_4,out} \times N_{C_2H_4}}{F_{C_2H_4,in} \times N_{C_2H_4}}$$
Eq.4

Detailed Characterization of Prepared Materials

Grafting of $[Ni(OSi(O^{T}Bu)_{3})_{2}]_{2}$ onto Al1-, Al5- and Al10-SiO₂₋₅₀₀ supports was monitored by IR spectroscopy. The decrease of the intensity of the hydroxyl band at 3741 cm⁻¹ accompanied by the appearance of IR bands at 3018-2850 cm⁻¹ (v_{CH} stretching modes) and 1510-1370 cm⁻¹ (δ_{CH} bending modes) indicates the successful grafting of $[Ni(OSi(O^{T}Bu)_{3})_{2}]_{2}$ (Figure S1-3).^[2] The band due to isolated silanols partially remains in Ni_{grafted}-Al1-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- SiO_{2-500} 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^tBu)₃)₂]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 $[Ni(OSi(O^tBu)_3)_2]_2$ 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,^[1] 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 $\leq 5\%$ of mixed $^{12}C^{-13}C$ 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.^[16] 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_4 (~1200 cm⁻¹), D_1 (~1350 cm⁻¹), D_3 (~1500 cm⁻¹), and G (~1580 cm⁻¹).^[17] While the D_4 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 (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_1/G are utilized.^[18-19] The D_1/G values obtained for spent-Ni-Al1-SiO₂₋₅₀₀ and spent-Ni-Al5-SiO₂₋₅₀₀ has a much lower ratio of 0.3 (Table S3).



Figure S1. FTIR spectra of Al1-SiO₂₋₅₀₀, Ni_{grafted}-Al1-SiO₂₋₅₀₀ and Ni-Al1-SiO₂₋₅₀₀ (black, dark red and blue, respectively).



Figure S2. FTIR spectra of AI5-SiO₂₋₅₀₀, Ni_{grafted}-AI5-SiO₂₋₅₀₀ and Ni-AI5-SiO₂₋₅₀₀ (black, dark red and blue, respectively).



Figure S3. FTIR spectra of Al10-SiO₂₋₅₀₀, Ni_{grafted}-Al10-SiO₂₋₅₀₀ and Ni-Al10-SiO₂₋₅₀₀ (black, dark red and blue, respectively).



Figure S4. (a) HAADF and (b) EDX images of Ni-Al1-SiO₂₋₅₀₀.



Figure S5. (a) HAADF and (b) EDX images of Ni-A5-SiO $_{2-500}$.



Figure S6. (a) HAADF and (b) EDX images of Ni-A10-SiO₂₋₅₀₀.



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.

Material	Neighbour	CN	r (Å)	σ²(Ų)	E ₀ (eV)	R-factor
Ni-Al1-SiO ₂₋₅₀₀	0	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-SiO ₂₋₅₀₀	0	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-SiO ₂₋₅₀₀	0	5.0(8)	1.99(5)	0.009(1)	-5(2)	0.017
	Ni	1.3(5)	2.92(7)	0.009(1)		

Table S1. Stuctural parameters obtained from Ni K-edge EXAFS data fitted with Ni-O and Ni-Ni paths.

All samples were measured at ambient temperature. S_0^2 was fixed to 0.85 obtained by fitting a Ni foil reference. CN stands for the coordination number. Debye-Waller factor σ^2 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. Stuctural	parameters for NiO	obtained from	Ni K-edge EXAFS data.
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Material	Neighbour	CN	r (Å)	σ²(Ų)	E ₀ (eV)	R-factor
NiO	0	6(1)	2.01(1)	0.006(1)	-4.2(8)	0 002
	Ni	12(1)	2.95(5)	0.007(1)		0.002

All samples were measured at ambient temperature. S_0^2 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-SiO₂₋₅₀₀ (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-SiO₂₋₅₀₀ (black, red and blue symbols, respectively).

Conditions: 5mL min⁻¹ (total flow), 10% C₂H₄ in N₂, 350 °C, GHSV = 0.2 L_{C2H4} h⁻¹ g_{cat}⁻¹.



Figure S15. Productivity to propene, benzene, toluene, C_8 aromatics (ethylbenzene and *o*-, *m*-, *p*-xylenes) 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), *iso*-butene (yellow), 1-butene (navy), C_1 - C_4 alkanes (orange) and carbon balance (black open squares, right Y-axis) with TOS for Ni-Al1-SiO₂₋₅₀₀.

Here and in experiments presented in Figures S17-S21, and in Figures S30, S31, a total flow of 5 mL min⁻¹ of 10% C₂H₄ in N₂, at 350°C and GHSV = 200 mL_{C2H4} h^{-1} g_{cat}⁻¹, was used.



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



Figure S18. Productivity (left Y-axis) to propene (black), *trans*-butene (blue), *cis*-butene (green), *iso*-butene (yellow), 1-butene (navy), C_1 - C_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-, Al5-, Al10- SiO_{2-500} .



Figure S20. Productivity to H₂ (left) and C₁-C₄ alkanes (right) with TOS for Ni-Al1-, Al5-, Al10-SiO₂₋₅₀₀.



Figure S21. Initial partial selectivity to alkanes for Ni-Al1-, Ni-Al5-, Ni-Al10-SiO₂₋₅₀₀.



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-SiO $_{\rm 2-500}$.



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 C_1 - C_4 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-SiO₂₋₅₀₀ (c) Ni-Al10-SiO₂₋₅₀₀.

		D_4			D_1			D_3			G		
Sample	Position*	FWHM	Area	Position	FWHM	Area	Position	FWHM	Area	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	1.5
Spent- Ni-Al10	-	_	-	1375	142.5	21.3	-	-	-	1602	83.7	78.7	0.3

Table S3. Results of the Raman fitting.

* 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% C_2H_4 in N_2 .

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. ²⁷Al MAS NMR spectra for (a) Ni-Al1-SiO₂₋₅₀₀ (b) Ni-Al5-SiO₂₋₅₀₀ (c) Ni-Al10-SiO₂₋₅₀₀. Left: Czjzek-type simulations taking into account AlO₄ (green), AlO₅ (purple) and AlO₆ (yellow) environments; the sub-layer being accounted for Ni-Al5-SiO₂₋₅₀₀ and Ni-Al10-SiO₂₋₅₀₀ by the experimental Ni-Al1-SiO₂₋₅₀₀ spectra (grey). Right: comparison between the Ni-loaded samples (blue) and the Ni-free materials (black, taken from ref. [1]).

Site*	%	$ar{\delta_{iso}}$ (ppm)	$\Delta\delta_{iso}$ (ppm)	$ar{C}_Q$ (MHz)
	± 0.5	± 0.2	± 1	± 0.1
		Ni-Al1-SiO ₂₋₅₀₀		
^[4] AI	46.1	56.1	18.3	10.6
^[5] AI	38.8	32.5	16.9	8.71
^[6] AI	15.1	10.2	15.7	8.54
		Ni-AI5-SiO ₂₋₅₀₀		
^[4] AI	43.1	64.2	24.1	10.2
^[5] AI	30.6	39.4	14.2	9.83
^[6] AI	5.3	9.8	34.3	3.82
Ni-Al1-SiO ₂₋₅₀₀	21.0			
		Ni-Al10-SiO ₂₋₅₀₀		
^[4] AI	33.6	67.6	19.9	7.86
^[5] AI	31.7	39.8	15.5	7.50
^[6] AI	4.3	8.5	17.4	4.18
Ni-Al1-SiO ₂₋₅₀₀	30.4			
		AI5-SiO _{2-500-regen}		
^[4] AI	53.7	65.7	18.9	12.02
^[5] AI	38.5	38.0	15.0	9.21
^[6] AI	7.7	10.4	13.6	8.37
		Ni-AI5-SiO _{2-500-regen}		
^[4] AI	52.9	67.5	15.6	11.86
^[5] AI	39.2	38.2	13.3	8.50
^[6] AI	7.9	9.7	12.1	7.07
		Ni-AI5-SiO ₂₋₅₀₀		
^[4] AI	61.3	64.7	23.3	12.3
^[5] AI	34.8	38.2	15.8	9.7
^[6] AI	4.0	6.5	19.0	4.8

Table S4. Results of the ²⁷Al NMR fittings.

*The spectrum of Ni-Al1-SiO₂₋₅₀₀ was used as a fitting component for Ni-Al5-SiO₂₋₅₀₀ and Ni-Al10-SiO₂₋₅₀₀ (top part entries). A three-site simulation was used in the bottom part entries.



Figure S37. ²⁷Al MAS NMR spectra for Al5-SiO₂₋₅₀₀ (red, from ref. [1]), regenerated Al5-SiO₂₋₅₀₀ (purple), Ni-Al5-SiO₂₋₅₀₀ (blue), regenerated Ni-Al5-SiO₂₋₅₀₀ (cyan).



Figure S38. ¹³C CP-MAS NMR spectrum of Ni-Al5-SiO₂₋₅₀₀ after exposure to ${}^{13}C_2H_4/C_2H_4$ (1:1) at 350 °C for 12 h. Asterisks indicate spinning sidebands. Spinning rate: 16 kHz; NS = 49152; d1 = 1 s.



Figure S39. ¹H MAS NMR spectrum of (a) Ni-Al5-SiO₂₋₅₀₀ after exposure to ${}^{13}C_2H_4/C_2H_4$ (1:1) at 350 °C for 12 h, and (b) fresh Ni-Al5-SiO₂₋₅₀₀. 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).

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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