Supporting Information

Nature of active nickel sites and initiation mechanism for ethylene oligomerization on heterogeneous Ni-beta catalysts

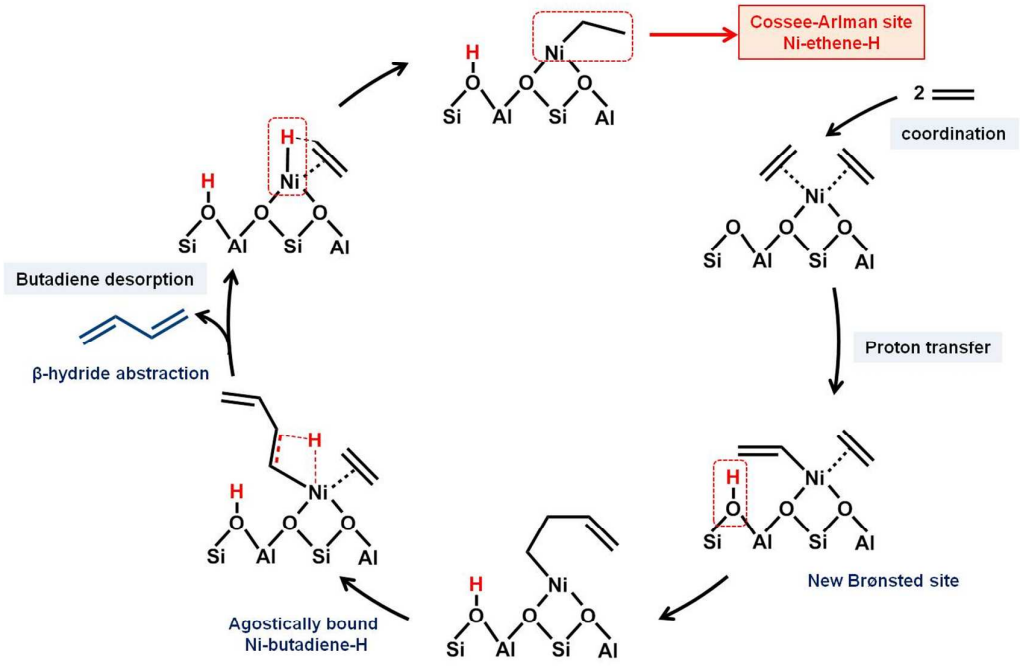
Sara Moussa, Patricia Concepción, María A. Arribas, and Agustín Martínez*

Instituto de Tecnología Química, Universitat Politècnica de València – Consejo Superior de Investigaciones Científicas (UPV-CSIC), Avda. de los Naranjos s/n, 46022 Valencia, Spain

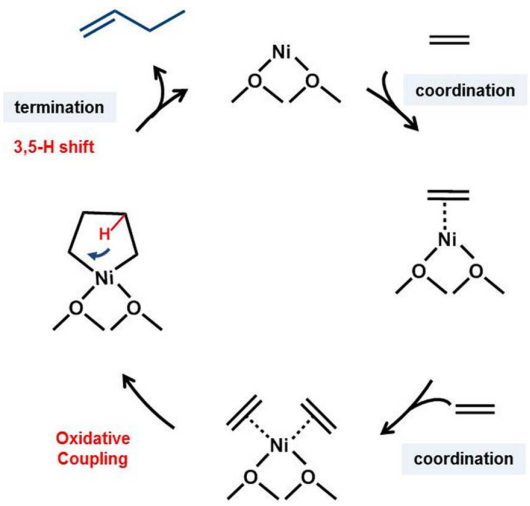
* Corresponding author: Prof. A. Martínez

E-mail address: amart@itq.upv.es

Scheme S1. Simplified route proposed for the generation of Cossee-Arlman centers (Ni-H or Ni-ethene-H) in nickel-aluminosilicate catalysts initiated by proton transfer[1]. According to this pathway, the heterolytic cleavage of a C-H bond of ethylene coordinated at a charge-balancing Ni^{2+} site leads to a nickel-vinyl species and H that generates a new Brønsted acid site on a nearby lattice O atom. Insertion of a second ethylene molecule into the Ni-C bond of the Ni-vinyl species forms Ni-butenyl which releases butadiene through β-hydride abstraction to the same Ni ion, creating the Ni-H Cossee-Arlman site[1].



Scheme S2. Metallacycle mechanism proposed for the oligomerization of ethylene catalyzed by nickel.



The metallacycle route, originally proposed for the selective trimerization of ethylene on Phillips (Cr/SiO_2) catalysts[2-5], involves the formation of a metallacyclopentane intermediate via oxidative coupling of two ethylene molecules coordinated to the metal site. Chain propagation then occurs by insertion of additional ethylene molecules into any of the two metal-C bonds forming larger metallacycles, while chain termination can take place through a direct hydrogen shift or via stepwise β-hydride elimination to the metal site followed by reductive elimination releasing the corresponding linear α-olefin. More recently, the metallacycle mechanism has been suggested in order to account for the product distribution during the heterogeneous oligomerization of ethylene over Ni-Al-SBA-15 catalysts[6].

Table S1. Characteristic mass fragmentations (m/z signals) and relative peak intensities, taking the most intense m/z peak for each compound as 100, for ethylene and relevant reaction products. The specific m/z values used in the identification of each compound during the acquisition of the online MS spectra are highlighted in bolt.

	m/z values										
	26	27	28	29	30	43	55	56	58	69	84
Ethylene	**55**	62	100	5	-	-	-	-	-	-	-
Ethane	22	35	100	21	**30**	-	-	-	-	-	-
Butenes	10	25	30	15	1	6	50	**100**	5	-	-
Butane	10	40	35	45	3	100	2	1	**15**	-	-
Hexenes	5	35	5	20	3	60	65	100	10	25	**30**

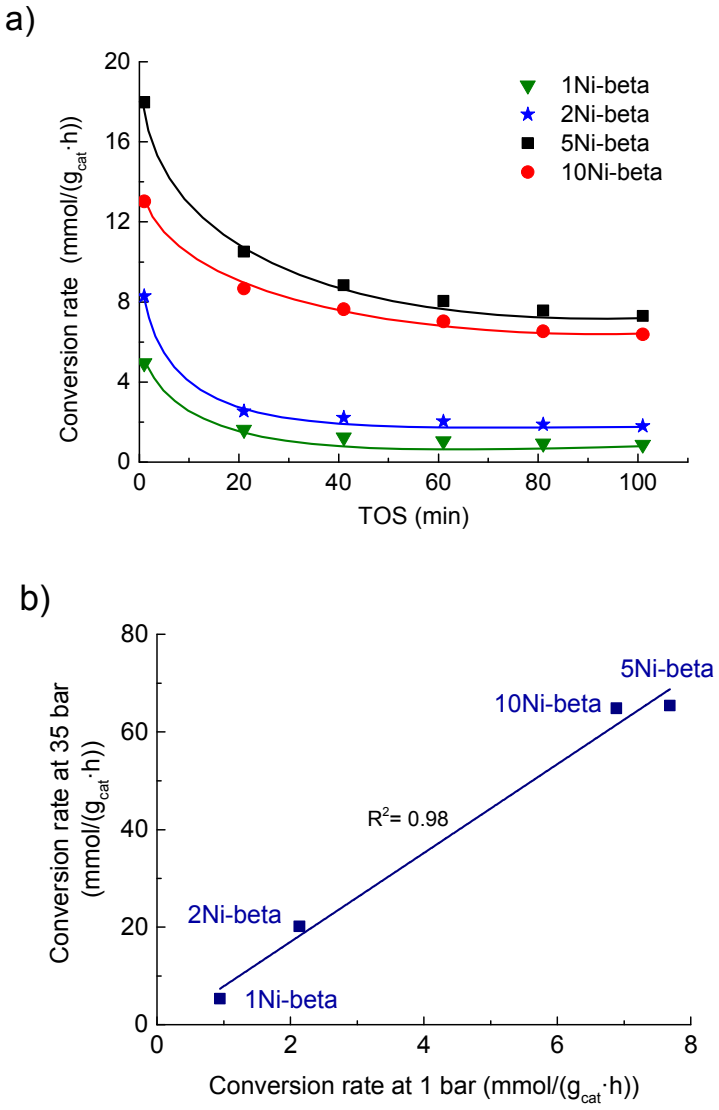


Figure S1. a) Ethylene conversion rates at 120 ºC, 1 bar, and WHSV of 33 h^{-1} as a function of time-on-stream (TOS) for Ni-beta catalysts loaded with different amounts of nickel (1-10 wt%); b) Correlation between the steady state ethylene conversion rates at the reaction pressure of 1 bar (120 ºC, 33 h^{-1}) and 35 bar (120 ºC, 2.1 h^{-1}).

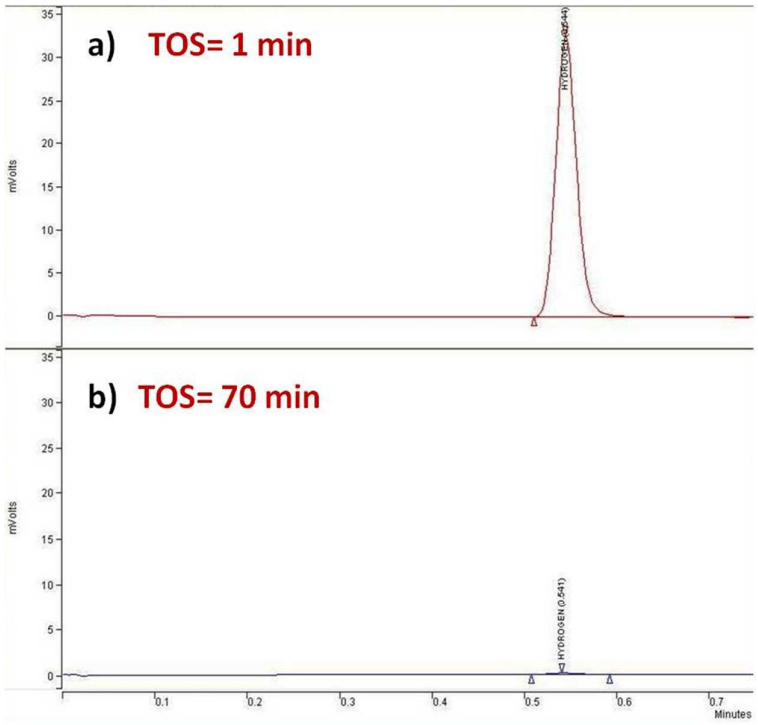


Figure S2. Chromatograms evidencing the initial formation of H_2 upon reacting 5Ni-beta with ethylene at 120 ºC and 1 bar for 1 min (a) and its practical absence after 70 min of reaction (b). The analyses were performed by manually injecting a representative sample of the gaseous effluent in a Varian 3800 GC specially equipped for H_2 detection (5Å Molecular Sieve column, TCD-type detector, Ar as carrier gas).

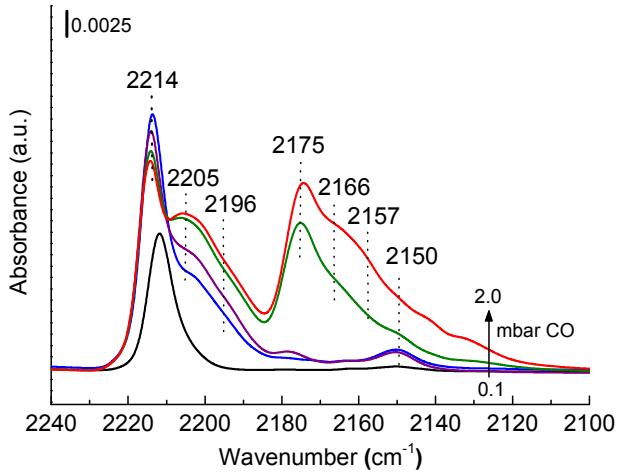


Figure S3. FTIR spectra of CO adsorption recorded at -176 ºC for pre-reacted (i.e. after in situ pretreatment in flowing N_2 at 300 ºC) 5Ni-beta sample at increasing CO pressures (0.1→2.0 mbar).

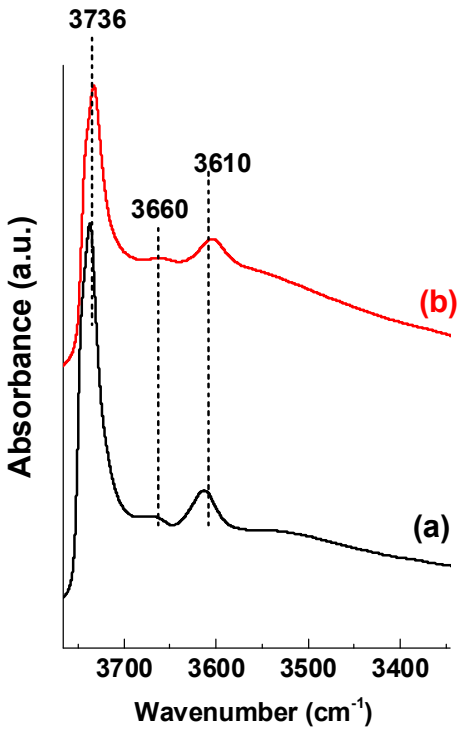


Figure S4. Normalized FTIR spectra in the OH stretching region of a) pristine H-beta zeolite, and b) 5Ni-beta sample after *in situ* pretreatment in flowing N_2 at 300 ºC.

The FTIR spectrum of activated pristine H-beta zeolite in the OH stretching region (spectrum a) showed three distinct features with maxima at ca. 3736, 3660, and 3610 cm^{-1} assigned to the ν(O-H) vibration modes of silanols, extraframework aluminium species, and Brønsted acid sites, respectively. After nickel incorporation (spectrum b), a reduction in the intensities of the peaks at 3736 and 3610 cm^{-1} is observed due to the replacement of some acidic protons by nickel ions. Furthermore, no additional peak in the 3630–3650 cm^{-1} region attributable to Ni-OH species[7] could be detected in the activated 5Ni-Beta sample.

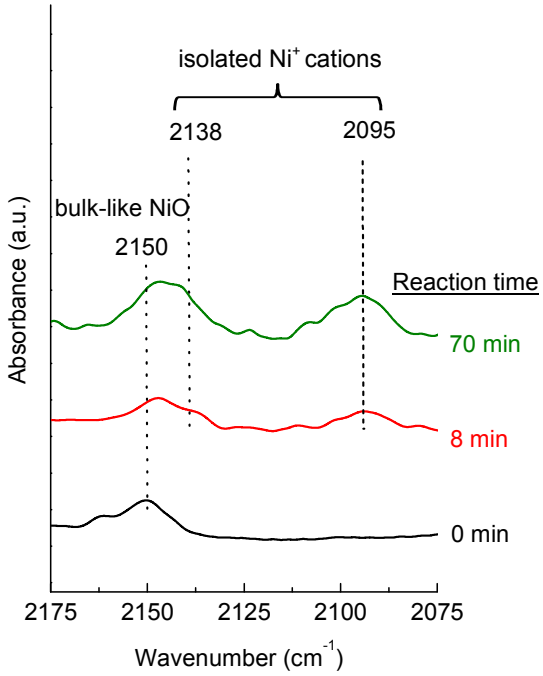


Figure S5. Low temperature FTIR-CO spectra at low CO coverage (0.1 mbar) for the 5Ni-beta catalyst showing the development of dicarbonyl Ni^{+} bands at 2138 and 2095 cm^{-1} upon reaction with ethylene at 120 ºC and 1 bar for selected reaction times. The component at 2150 cm^{-1} of CO coordinated to unsaturated Ni^{2+} species on the surface of bulk-like NiO particles (reported as inactive in ethylene oligomerization) remains almost unaffected during the catalytic reaction. Spectra are up-shifted for better visualization.

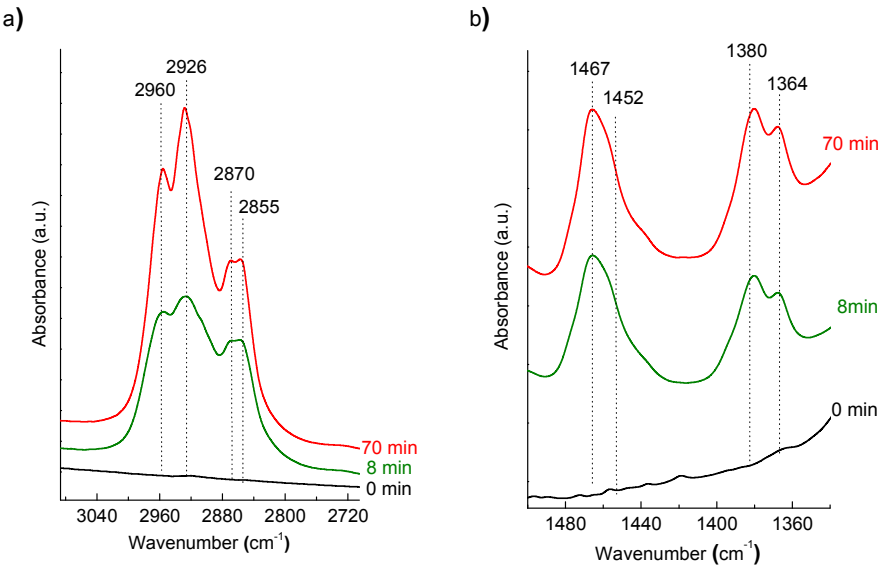


Figure S6. FTIR spectra (normalized by overtone area) in the C-H stretching (a) and bending (b) vibration regions for 5Ni-beta in its pre-reacted state (spectrum at 0 min) and after reaction with ethylene at 120 ºC and 1 bar for 8 and 70 min and subsequent evacuation of the cell at 120 ºC for 1 h under dynamic vacuum of 10^{-5} mbar. The characteristic sp3 C-H stretching and bending IR bands of CH_3 (ν_{as}= 2960 cm^{-1}, ν_s= 2870 cm^{-1}, δ_s= 1364-1380 cm^{-1}, δ_{as}= 1440-1470 cm^{-1}) and CH_2 (ν_{as}= 2926 cm^{-1}, ν_s= 2855 cm^{-1}, δ= 1440-1470 cm^{-1}) groups[8-11] are clearly perceived.

From the intensities of the peaks assigned to CH_2 and CH_3 asymmetric stretches, a CH_2/CH_3 ratio of ca. 1.14 and 1.24 is obtained for the irreversibly adsorbed hydrocarbons (spectators) after 8 and 70 min of reaction, respectively, evidencing a minor increase in chain length with reaction time. Considering that a CH_2/CH_3 ratio of 2 and 3 has been reported for the asymmetric C-H stretches of *n*-hexane and *n*-octane, respectively[12], we infer that those spectators are mainly short-chain aliphatic acyclic hydrocarbons.

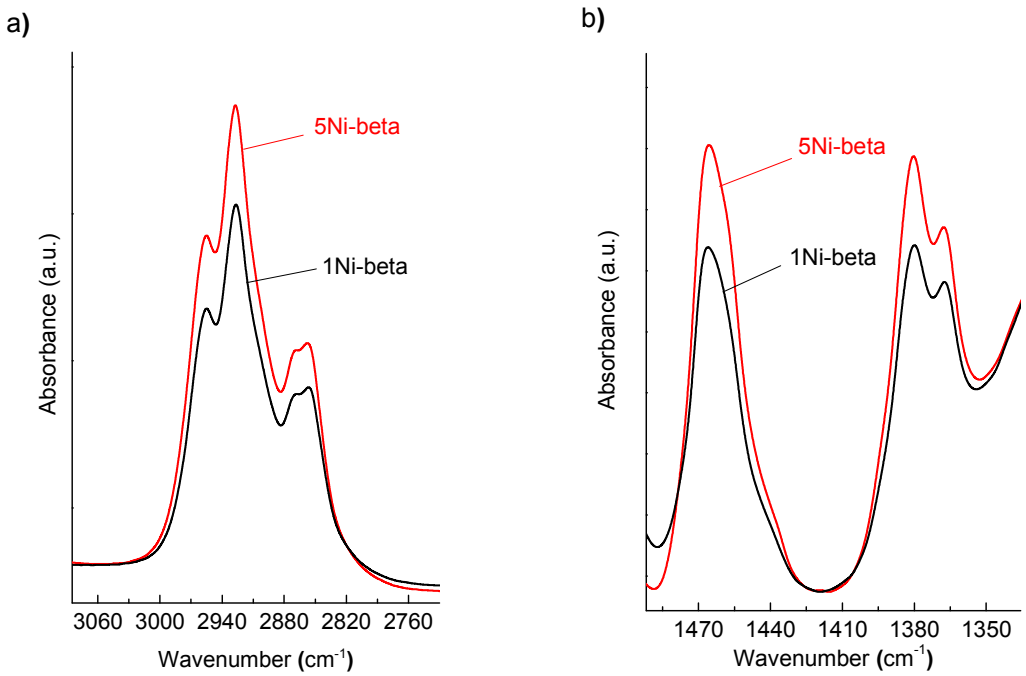


Figure S7. Normalized FTIR spectra in the C-H stretching (a) and bending (b) vibration regions for Ni-beta samples loaded with 1 and 5 wt% Ni after in situ reaction with ethylene for 70 min at 120 ºC and 1 bar followed by evacuation at this temperature for 1 h under dynamic vacuum of 10^{-5} mbar. The higher concentration of hydrocarbon species irreversibly adsorbed on the surface of the highly-loaded 5Ni-beta catalyst exhibiting a 2.5-fold lower amount of Brønsted acid sites than 1Ni-beta[13] is an indication that they predominantly form at the cationic nickel centers.

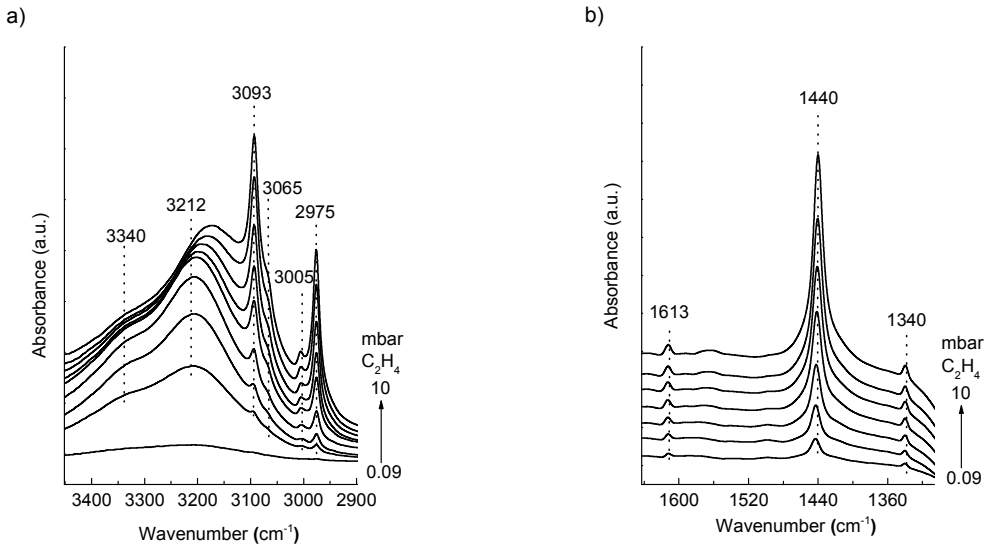


Figure S8. FTIR spectra in the C-H stretching (a) and bending (b) regions of ethylene adsorbed at -100 ºC on pristine H-beta zeolite at increasing ethylene doses (from 0.09 to 10 mbar). Spectra have been up-shifted for clarity.

Ethylene adsorbs only physically on the surface OH groups of Ni-free H-beta zeolite, as inferred from the presence of IR bands of CH_2 groups in the C-H stretching (3093, 3065, 3005, and 2975 cm^{-1}, left graph) and bending (1440 and 1340 cm^{-1}) regions and the ν[C=C] stretching band at 1613 cm^{-1}. Broad IR bands peaking at around 3340 and 3210 cm^{-1} correspond to the shift towards lower frequencies of the O-H stretching bands of the zeolite perturbed by ethylene.

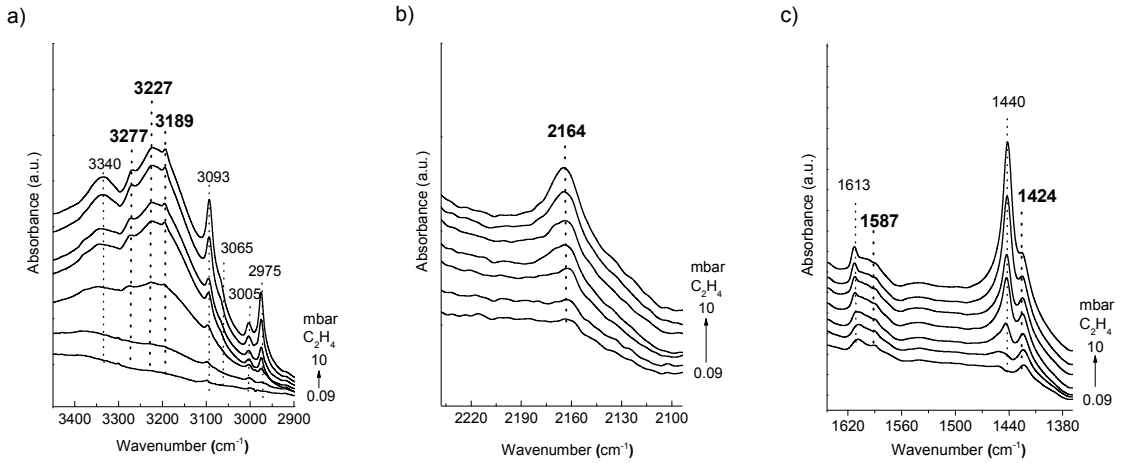


Figure S9. FTIR spectra recorded in different IR regions (a-c) upon adsorption of ethylene at -100 ºC on 5Ni-beta catalyst at increasing ethylene doses from 0.09 to 10 mbar. Spectra have been up-shifted for clarity. The bands related to ethylene π-bonded to Ni^{2+} cations and acetylenic species (see main text) are highlighted in bold.

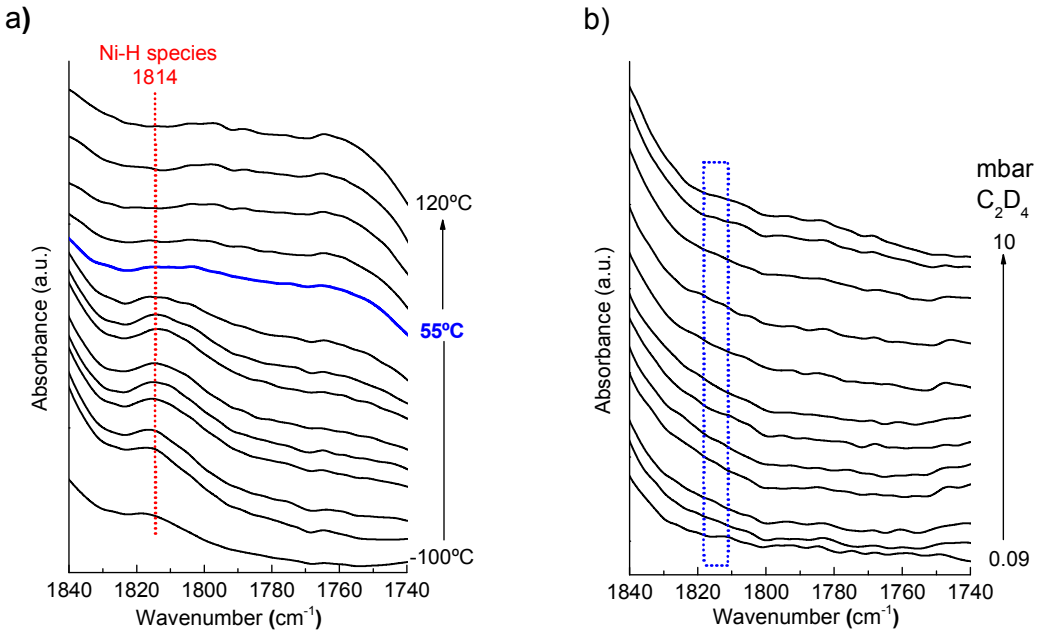


Figure S10. FTIR spectra acquired in the Ni-H region for 5Ni-beta upon adsorption of ethylene from -100 ºC to 120 ºC (a) and of deuterated ethylene at -100 ºC and increasing coverage from 0.09 to 10 mbar (b). Spectra have been up-shifted for clarity.

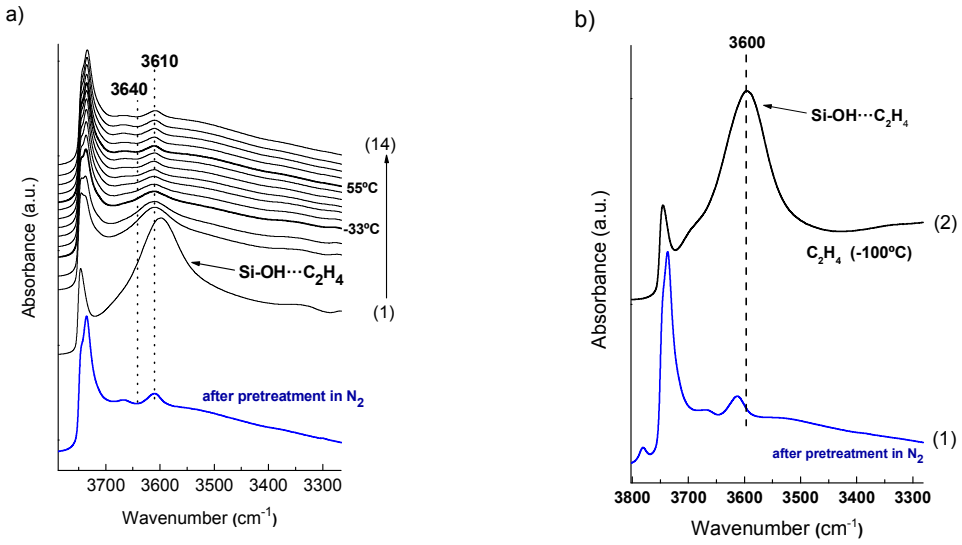


Figure S11. a) Temperature-resolved FTIR spectra for 5Ni-beta in the OH stretching region after in situ pretreatment in flowing N_2 at 300ºC (blue bold line) and during in situ reaction of ethylene (black lines) at a constant pressure of 1.5 mbar in the temperature range of : (1) -100ºC, (2) -58ºC, (3) 48ºC, (4) -33ºC, (5) -25ºC, (6) -15ºC, (7) -4ºC, (8) 5ºC, (9) 26ºC, (10) 55ºC, (11) 66ºC, (12) 88ºC, (13) 107ºC, (14) 120ºC. Spectra have been up-shifted for the sake of clarity; b) FTIR spectra in the OH stretching region of pristine H-beta zeolite after in situ pretreatment in flowing N_2 at 300ºC (1), and upon ethylene adsorption (10 mbar) at -100 ºC (2).

As seen in Figure S11a, when ethylene is contacted with 5Ni-Beta catalyst at -100ºC, it physisorbs on the catalyst surface resulting in a pronounced decrease of the silanol band at ca. 3736 cm^{-1} that shifts to lower frequencies producing an intense broad band with maxima at ca. 3605 cm^{-1}.[10] Indeed, the perturbed OH band (Si-OH···C_2H_4 molecular complex) is also detected when ethylene was adsorbed over pristine H-beta zeolite at -100ºC (Figure S11b). As observed in Figure S11a, the IR spectra in the OH region is dominated from -100 ºC to -33 ºC by the broad perturbed OH band vibrating in the region where the formation of new OH groups would be observed (ca. 3610 and 3640 cm^{-1})[14,15]. This makes an unequivocal conclusion on the possible formation of new OH groups in this temperature range unfeasible. However, at temperatures above ca. -33ºC (at which vinyl intermediates start to be detected),

where the perturbed OH band at 3605 cm^{-1} does no longer disturb the peaks in this region, there are no spectroscopic signs evidencing the formation of new OH groups.

References

1. Brogaard, R. Y.; Olsbye, U. Ethene Oligomerization in Ni-Containing Zeolites: Theoretical Discrimination of Reaction Mechanisms. *ACS Catal.* **2016,** *6*, 1205-1214.

2. McGuinness, D. S. Olefin Oligomerization via Metallacycles: Dimerization, Trimerization, Tetramerization, and Beyond. *Chem. Rev.* **2011,** *111*, 2321-2341.

3. Briggs, J. R. Selective trimerization of ethylene to hex-1-ene. *J. Chem. Soc., Chem. Commun.* **1989,** 674-675.

4. Nenu, C. N.; Weckhuysen, B. M. Single-site heterogeneous Cr-based catalyst for the selective trimerization of ethylene. *Chem. Commun.* **2005,** 1865-1867.

5. Ruddick, V. J.; Badyal, J. P. S. Early stages of ethylene polymerization using the Phillips CrO_x/silica catalyst. *J. Phys. Chem. B* **1998,** *102*, 2991-2994.

6. Andrei, R. D.; Popa, M. I.; Fajula, F.; Hulea, V. Heterogeneous oligomerization of ethylene over highly active and stable Ni-AlSBA-15 mesoporous catalysts. *J. Catal.* **2015,** *323*, 76-84.

7. Hall, D. S.; Lockwood, D. J.; Poirier, S.; Bock, C.; MacDougall, B. R. Raman and Infrared Spectroscopy of α and β Phases of Thin Nickel Hydroxide Films Electrochemically Formed on Nickel. *J. Phys. Chem. A* **2012**, *116*, 6771−6784.

8. Tanaka, M.; Itadani, A.; Kuroda, Y.; Iwamoto, M. Effect of Pore Size and Nickel Content of Ni-MCM-41 on Catalytic Activity for Ethene Dimerization and Local Structures of Nickel Ions. *J. Phys. Chem. C* **2012,** *116*, 5664-5672.

9. Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Zecchina, A. The Structure of Active Centers and the Ethylene Polymerization Mechanism on the Cr/SiO_2 Catalyst: A Frontier for the Characterization Methods. *Chem. Rev.* **2005,** *105*, 115-183.

10. Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Damin, A.; Zecchina, A. FTIR Investigation of the H_2, N_2, and C_2H_4 Molecular Complexes Formed on the Cr(II) Sites in the Phillips Catalyst: a Preliminary Step in the understanding of a Complex System. *J. Phys. Chem. B* **2005**, *109*, 15024-15031.

11. Groppo, E.; Lamberti, C.; Bordiga, S.; Spoto, G.; Zecchina, A. In situ FTIR spectroscopy of key intermediates in the first stages of ethylene polymerization on the Cr/SiO2 Phillips catalyst: Solving the puzzle of the initiation mechanism?. *J. Catal.* **2006**, *240*, 172-181.

12. Smith, B.C. How to Properly Compare Spectra, and Determining Alkane Chain Length from Infrared Spectra. *Spectroscopy* **2015**, *30*, 40-46.

13. Martinez, A.; Arribas, M. A.; Concepcion, P.; Moussa, S. New bifunctional Ni-H-Beta catalysts for the heterogeneous oligomerization of ethylene. *Appl. Catal., A* **2013**, *467*, 509-518.

14. Delley, M. F.; Núñez-Zarur, F.; Conley, M. P.; Comas-Vives, A.; Siddiqi, G.; Norsic, S.; Monteil, V.; Safonova, O. V.; Copéret, C. Proton transfers are key elementary steps in ethylene polymerization on isolated chromium(III) silicates. *PNAS.* **2014***, 111*, 11624-11629.

15. Conley, M. P.; Delley, M. F.; Siddiqi, G.; Lapadula, G.; Norsic, S.; Monteil, V.; Safonova, O. V.; Copéret, C. Polymerization of ethylene by silica-supported dinuckear Cr(III) sites through an initiation step involving C-H bond activation. *Angew. Chem. Int. Ed.* **2014**, *53*, 1872-1876.