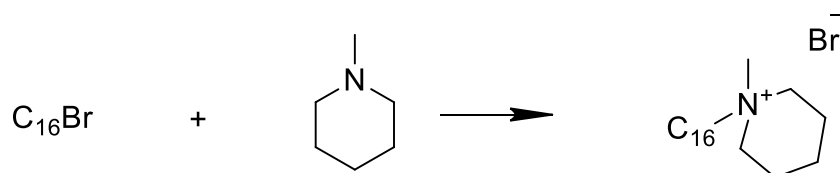


Supporting Information

Synthesis of modified surfactant



Cetyltrimethylammonium bromide ($C_{16}MPip$, $M_w = 404.51$ g/mol) was prepared by mixing 0.1 mol of 1-Bromohexadecane (Acros Organics, 97%, $M_w = 305.34$ g/mol) and 0.12 mol of N-methylpiperidine (Sigma-Aldrich, 99%, $M_w = 99.18$ g/mol) in 400 mL of acetonitrile. The solution was heated at $80^\circ C$ for 24 hours. After reaction, solution was concentrated by rotavapour and the product was precipitated with diethylether, filtrated and washed with more diethylether. The white solid was dried under vacuum at $50^\circ C$ during 4 hours to remove completely the solvents. Yield was 92%.

Synthesis of nano-ferrierites (N-FER)

N-FER(15) zeolite was prepared adding 9.429 g of doubly distilled water to 3.200 g of NaOH (10%, $8 \cdot 10^{-3}$ mol) prepared previously. Then 3.005 g of colloidal silica (Sigma-Aldrich, Ludox AS-40, 0.02 mol) was added under magnet stirring followed by 0.405 g of the surfactant $C_{16}MPip$ ($1 \cdot 10^{-3}$ mol). When surfactant was completely dissolved, 0.444g of $Al_2(SO_4)_3 \cdot 18H_2O$ (Panreac, $6.67 \cdot 10^{-4}$ mol) were added and stirred until the product was dissolved. 0.341 g of piperidine (Sigma-Aldrich, $4 \cdot 10^{-3}$ mol) were added dropwise and the gel was stirred vigorously during 4 hours at room temperature. Final gel with composition $0.2 Na_2O : 1 SiO_2 : 0.033 Al_2O_3 : 0.1 H_2SO_4 : 0.2$ Piperidine : $0.05 C_{16}MPip : 40 H_2O$, was transferred to a 35 mL PTFE-Lined stainless-steel autoclave and keep at

temperatures ranging from 120 to 150°C under rotation at 60 rpm at different times as specified in Table S1. After quenching the reaction mixture with cold water, the product was filtered, washed with distilled water until pH<9, and dried at 100°C overnight. The organic material was removed by calcination in air at 550°C for 10 h. Calcined sample was exchanged with 2.5 M solution of NH₄Cl during 2 h at 80°C in the ratio 10:1 (liquid - solid) to remove the Na⁺. After washing with distilled water until absence of Cl⁻, the solid was dried at 100°C and calcined again to obtain the acidic form of the zeolite. N-FER(30) has been synthesized following the same procedure but adjusting the gel composition to 0.2 Na₂O : 1 SiO₂ : 0.016 Al₂O₃ : 0.05 H₂SO₄ : 0.2 Piperidine : 0.05 C₁₆MPip : 40 H₂O.

Synthesis of conventional reference ferrierite (R-FER)

R-FER zeolite was prepared adding 8.795 g of doubly distilled water to 3.888 g of NaOH (10%, 0.0972 mol) prepared previously. Then 3.005 g of colloidal silica (Sigma-Aldrich, Ludox AS-40, 0.02 mol) was added under magnet stirring followed by 0.444g of Al₂(SO₄)₃·18H₂O (Panreac, 6.67·10⁻⁴ mol). 0.760 g of piperidine (Sigma-Aldrich, 0.0089 mol) were added dropwise and the gel was stirred vigorously during 4 hours at room temperature. Final gel with composition 0.243 Na₂O : 1 SiO₂ : 0.033 Al₂O₃ : 0.1 H₂SO₄ : 0.446 Piperidine : 40 H₂O, was transferred to a 35 mL PTFE-Lined stainless-steel autoclave and keep at 150°C under rotation at 60 rpm during 5 days. After quenching the reaction mixture with cold water, the product was filtered, washed with distilled water until pH<9, and dried at 100°C overnight. The organic material was removed by calcination in air at 550°C for 10 h. Calcined sample was exchanged with 2.5 M solution of NH₄Cl during 2 h at 80°C in the ratio 10:1 (liquid - solid) to remove the Na⁺. After washing with distilled water until absence of Cl⁻, the solid was dried at 100°C and calcined again to obtain the acidic form of the zeolite.

Characterization

Crystallinity of the samples was determined by X-ray powder diffraction (XRD) with a Panalytical CUBIX diffractometer with monochromatic $\text{CuK}\alpha_{1,2}$ radiation ($\lambda = 1.5406, 1.5444 \text{ \AA}$; $\text{K}\alpha_2/\text{K}\alpha_1$ intensity ratio = 0.5). The chemical analyses were carried out on a Varian 715-ES ICP-Optical Emission Spectrometer, after solid dissolution in $\text{HNO}_3/\text{HCl}/\text{HF}$ aqueous solution. TG/DTG were carried out with a METTLER TOLEDO TG/SDTA 851^e thermogravimetric analyzer using a ramp of $10^\circ\text{C}\cdot\text{min}^{-1}$ up to 800°C . Textural properties were determined by N_2 adsorption isotherms measured at 77 K with a Micrometrics ASAP 2020. Infrared spectra were measured with a Nicolet 710 FT IR spectrometer. Pyridine adsorption-desorption experiments were made on self-supported wafers ($10 \text{ mg}\cdot\text{cm}^{-1}$) of original samples previously activated at 400°C and 10^{-2} Pa for 2 hours. After wafer activation, the base spectrum was recorded and pyridine vapor ($6.5 \times 10^2 \text{ Pa}$) was admitted into the vacuum IR cell and adsorbed onto the zeolite. Desorption Pyridine was performed under vacuum over three consecutive one-hour periods of heating at 150, 250 and 350°C , each of them followed by an IR measurement at room temperature. The spectra were scaled according to the sample weight.

Crystal morphology was determined by a Field Emission Scanning Electron Microscopy (FESEM) using a ZEISS ULTRA 55, Transmission Electron Microscopy (TEM) using a PHILIPS CM10 and a High Resolution Transmission Electron Microscopy (HRTEM) using a JEOL JEM 2100F operating with an accelerator voltage of 200kV. The electron diffraction spectra corresponding to a certain crystal is calculated from the HRTEM image by means of the Gatan Digital Micrograph software (GMS3), and applying the FFT (Fast Fourier transform) to a section of the crystal appearing in the image. The inverse of the distance measured from the center to the spots can be associated to an hkl index and, therefore, to the orientation of the crystals.

Solid NMR spectra were recorded at room temperature with a BRUKER AVANCE III HD WB 400 spectrometer. ^{27}Al MAS NMR spectra were recorded at 104.2 MHz with spinning rate of 10 kHz and 9° pulse length of 0.5 μs with a 1 s repetition time. ^{27}Al chemical shift was in reference to $\text{Al}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$. ^{13}C MAS NMR cross-polarization (CP) spectrum was recorded at a simple spinning rate of 5 kHz. ^{13}C chemical shift was referenced to adamantane. ^1H and ^{13}C NMR were recorded in a BRUKER AV 300 instrument using MeOD as solvent containing TMS as internal standard.

Catalytic tests: 1-pentene oligomerization

The 1-pentene oligomerization experiments were performed in a 10-mm internal diameter down-flow stainless-steel fixed-bed reactor at 200°C, 4.0 MPa, and WHSV in the range of 3 to 50 h^{-1} . Under these conditions, the reaction occurs in the liquid phase, as determined by means of the process simulation software package Aspen Plus v8.2. The zeolites were pelletized, crushed and sieved to recover the particles with sizes in the 0.25-0.42 mm fraction. Then the pelletized samples were diluted with SiC (0.6-0.8 mm) to obtain a bed volume of 4.0 cm^3 . The temperature in the catalyst bed was controlled by two independent heating zones, with the corresponding thermocouples properly placed inside the catalytic bed. Before reaction, the catalysts were activated in situ by increasing temperature to 520°C in N_2 flow (200 $\text{ml}\cdot\text{min}^{-1}$) at a rate of 2.0°C $\cdot\text{min}^{-1}$ and further calcining in air flow (200 $\text{ml}\cdot\text{min}^{-1}$) at 520°C for 5 h. Then, the reactor was cooled to the reaction temperature in a flow of N_2 (200 $\text{ml}\cdot\text{min}^{-1}$). The olefinic mixture was fed to the reactor as a liquid by means of a Gilson piston pump, and the pressure was controlled during the reaction by means of a back pressure regulator. 1-pentene was co-fed (in the liquid phase) with n-heptane in a 60:40 1-pentene/n-heptane molar ratio. The full reactor outlet stream was vaporized and analyzed with an online Varian 3800 gas chromatograph. The unconverted reactants and products were separated in a 25 m, 0.25 mm x 1.2 μm CP-Sil 5CB column and

quantified by means of a FID detector. n-Heptane was used as internal standard for mass balance quantification. Finally, the C₅₊ mixture was condensed for further analysis by simulated distillation, excluding n-heptane from the naphtha fraction. For discussion, the selectivity results are referred to as the naphtha, diesel, and heavy product fractions, determined by simulated distillation according to the following cut points:

- Naphtha: C₅–173.9°C.

- Diesel: 173.9–391.1°C.

- Heavy fraction: 391.1–1000°C.

Mass transfer effects were studied as described in *Perego et al., Catal. Today 52 (1999) 133-145*. Absence of interphase (external) concentration gradients were ensured for total feed mass flows of 3.5 g/h or higher. The absence of intraphase (internal) gradients was determined by changing the particle size in the ranges of 0.1-0.25, 0.25-0.42 and 0.6-0.83 mm. Varying the particle size in this range under our experimental conditions (T=200°C, P=40 bar and WHSV=30 h⁻¹) has no effect on the conversion variation vs. TOS.

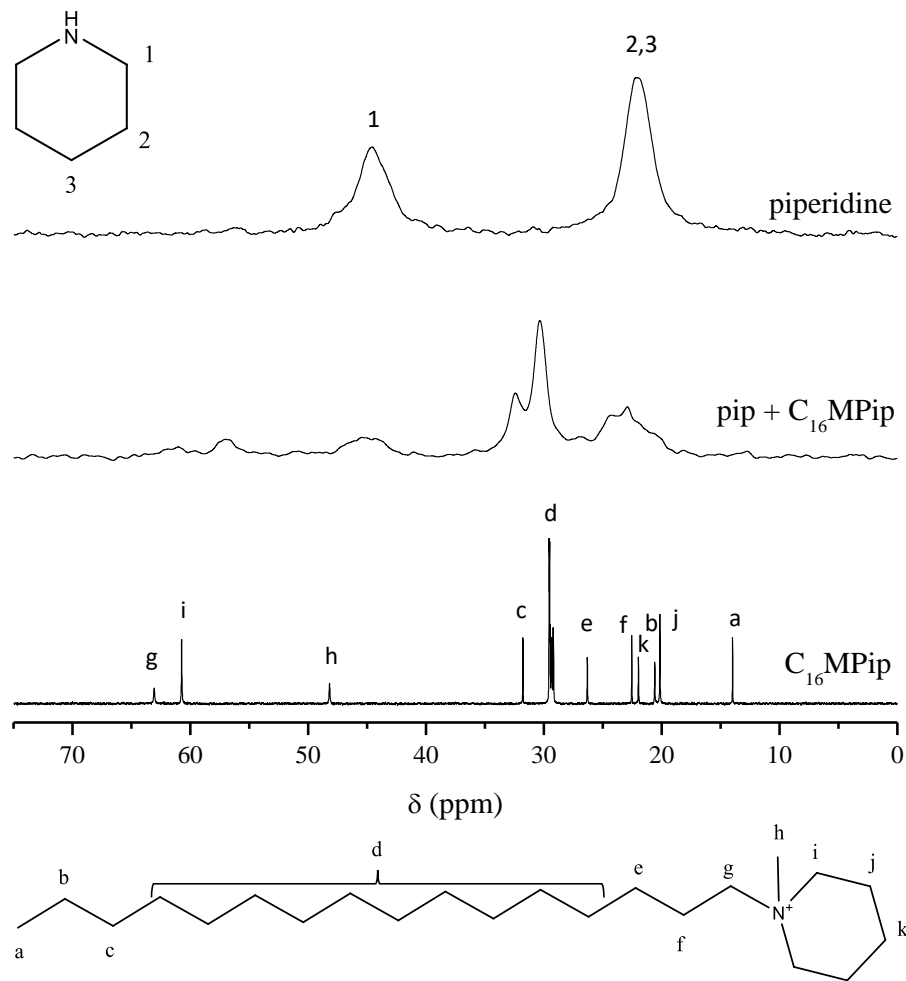


Figure S1. Liquid ^{13}C -NMR spectrum of C_{16}MPip in CDCl_3 (bottom) and solid ^{13}C -MAS-NMR spectra of piperidine into R-FER (top) and of the mixture of both organic molecules into the N-FER (middle).

Both OSDAs, piperidine and the modified surfactant, were stable within the zeolite structure under the synthesis conditions, according to the solid state ^{13}C -MAS-NMR spectrum (see Figure S1).

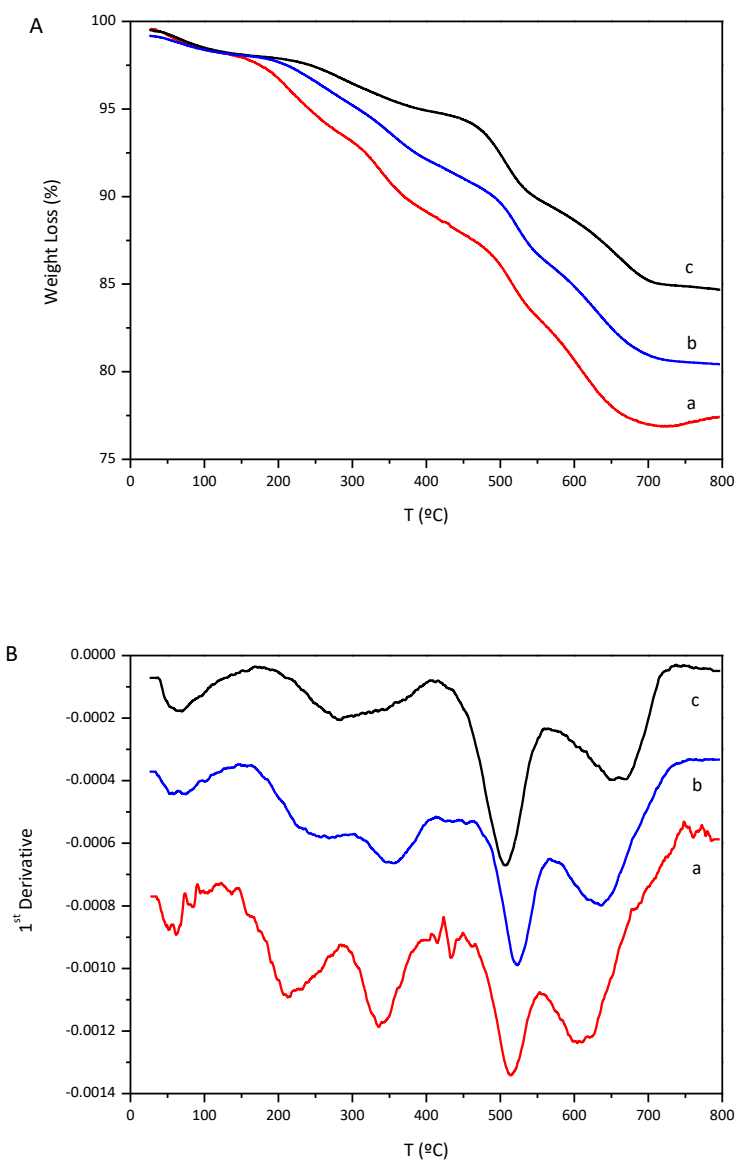


Figure S2. TG (A) and DTG (B) curves of N-FER(15)-120 (a), N-FER(15)-150 (b) and R-FER (c).

Thermogravimetric and differential thermogravimetric analysis (TG and DTG respectively) did not only confirm the presence of the surfactant within the crystals, but also showed a higher weight loss at lower temperatures in the case of the N-FER (see Figure S2), again pointing out to a reduced crystal size of the nanosized zeolite.

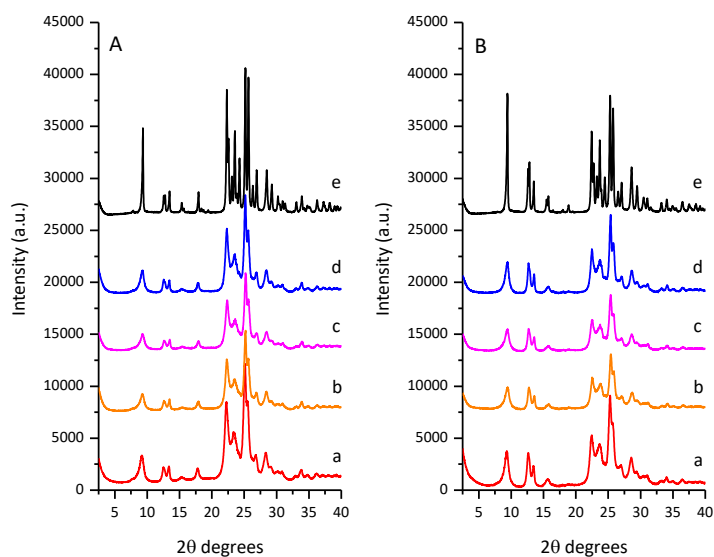


Figure S3. XRD patterns of ferrierites as synthesized (A) and in their final acid form after calcination-ion exchange-calcination (B) of N-FER(15)-120 (a), N-FER(15)-125 (b), N-FER(15)-140 (c), N-FER(15)-150 (d) and R-FER (e). The presence of amorphous material in the final solids was discarded based on the absence of a broad peak in the 15 to 35 2θ range.

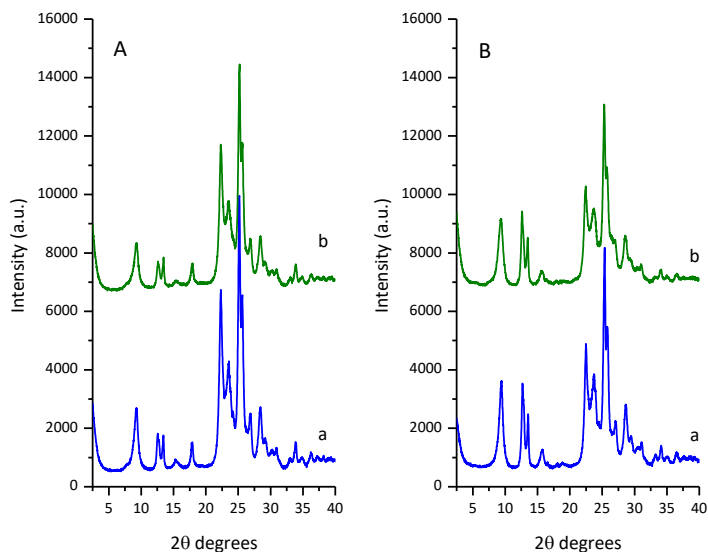


Figure S4. XRD patterns of ferrierites as synthesized (A) and in their final acid form after calcination-ion exchange-calcination (B) of N-FER(15) (a) and N-FER(30) (b) synthesized at 150°C. The presence of amorphous material in the final solids was discarded based on the absence of a broad peak in the 15 to 35 2θ range.

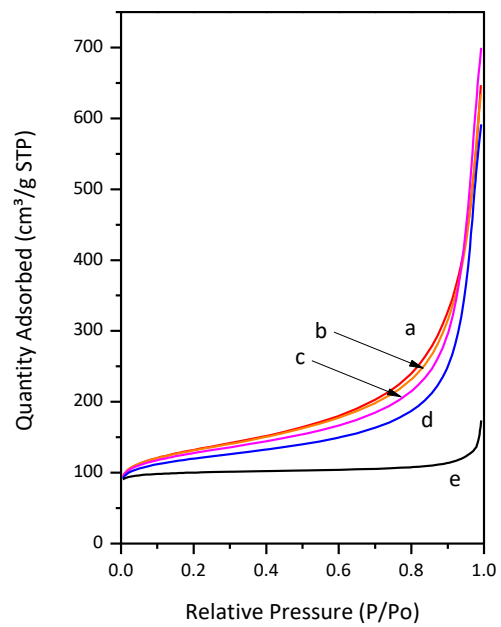


Figure S5. Nitrogen adsorption isotherms of the calcined samples: N-FER(15)-120 (a), N-FER(15)-125 (b), N-FER(15)-140 (c), N-FER(15)-150 (d) and R-FER (e).

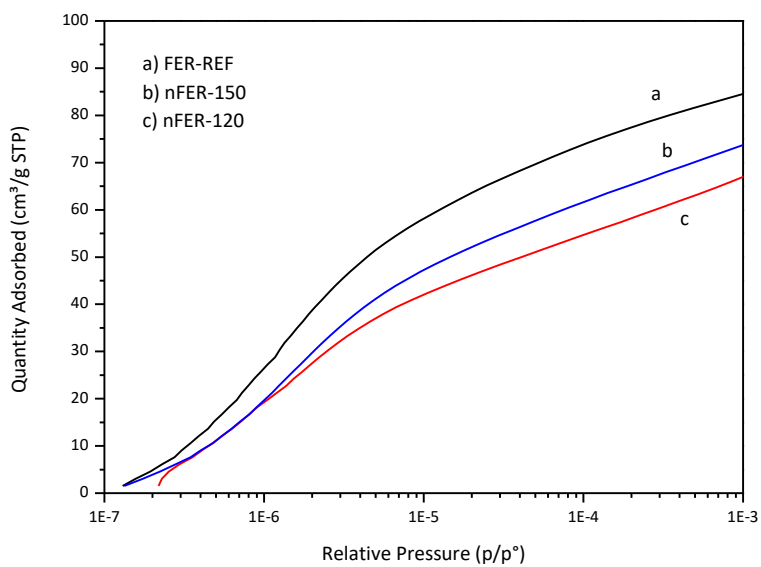
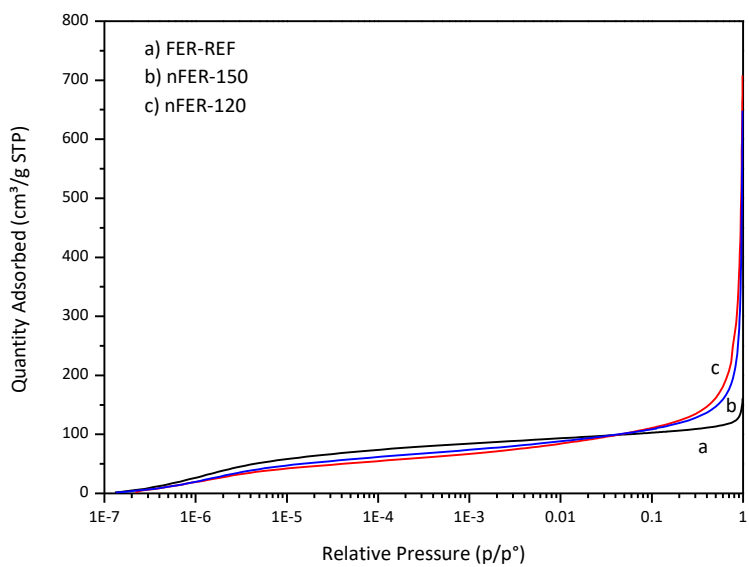


Figure S6. Argon adsorption isotherms of the calcined samples: R-FER (a), N-FER(15)-150 (b), N-FER(15)-120 (c). Relative pressure IS given in logarithmic scale.

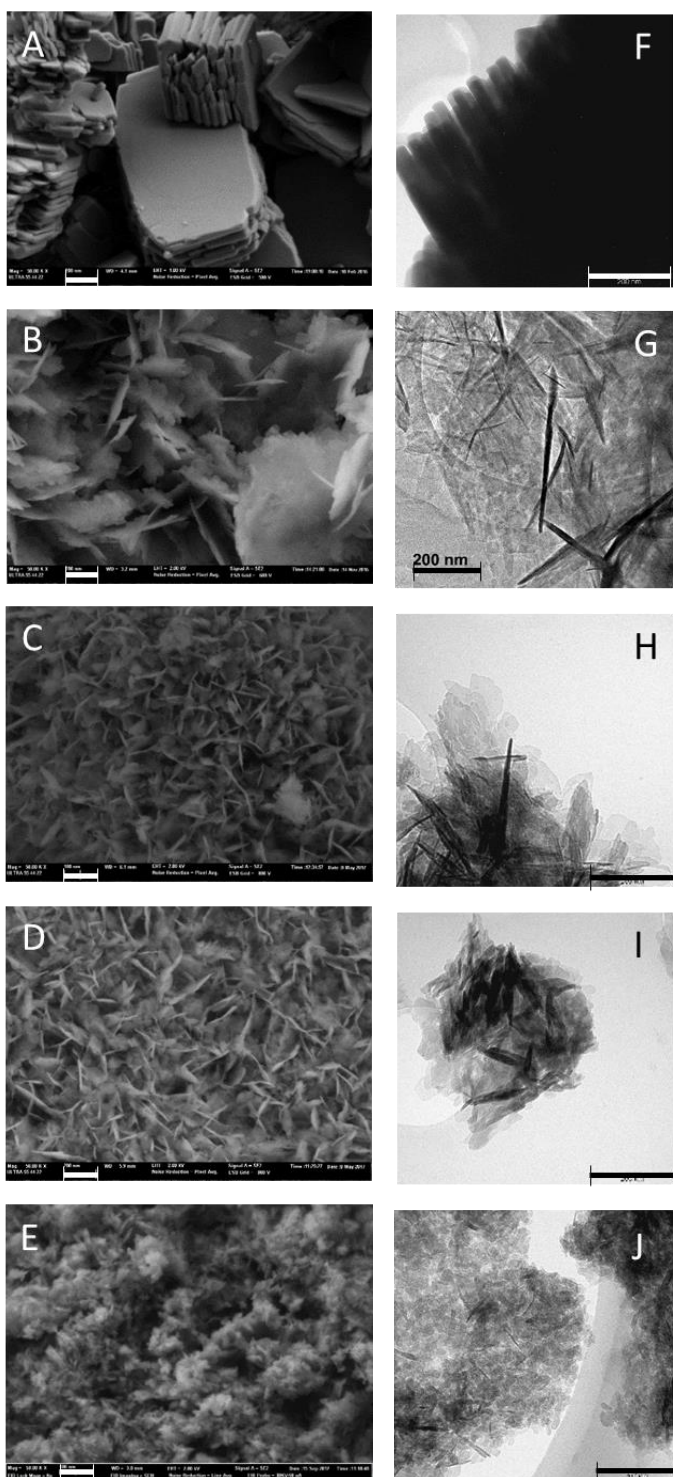


Figure S7. FESEM (A-E) and TEM (F-J) images corresponding to zeolites R-FER(15) (A,F), N-FER(15)-150 (B,G),N-FER(15)-140 (C,H), N-FER(15)-125 (D,I) and N-FER(15)-120 (E,J). Scale bar corresponds to 200 nm in all images.

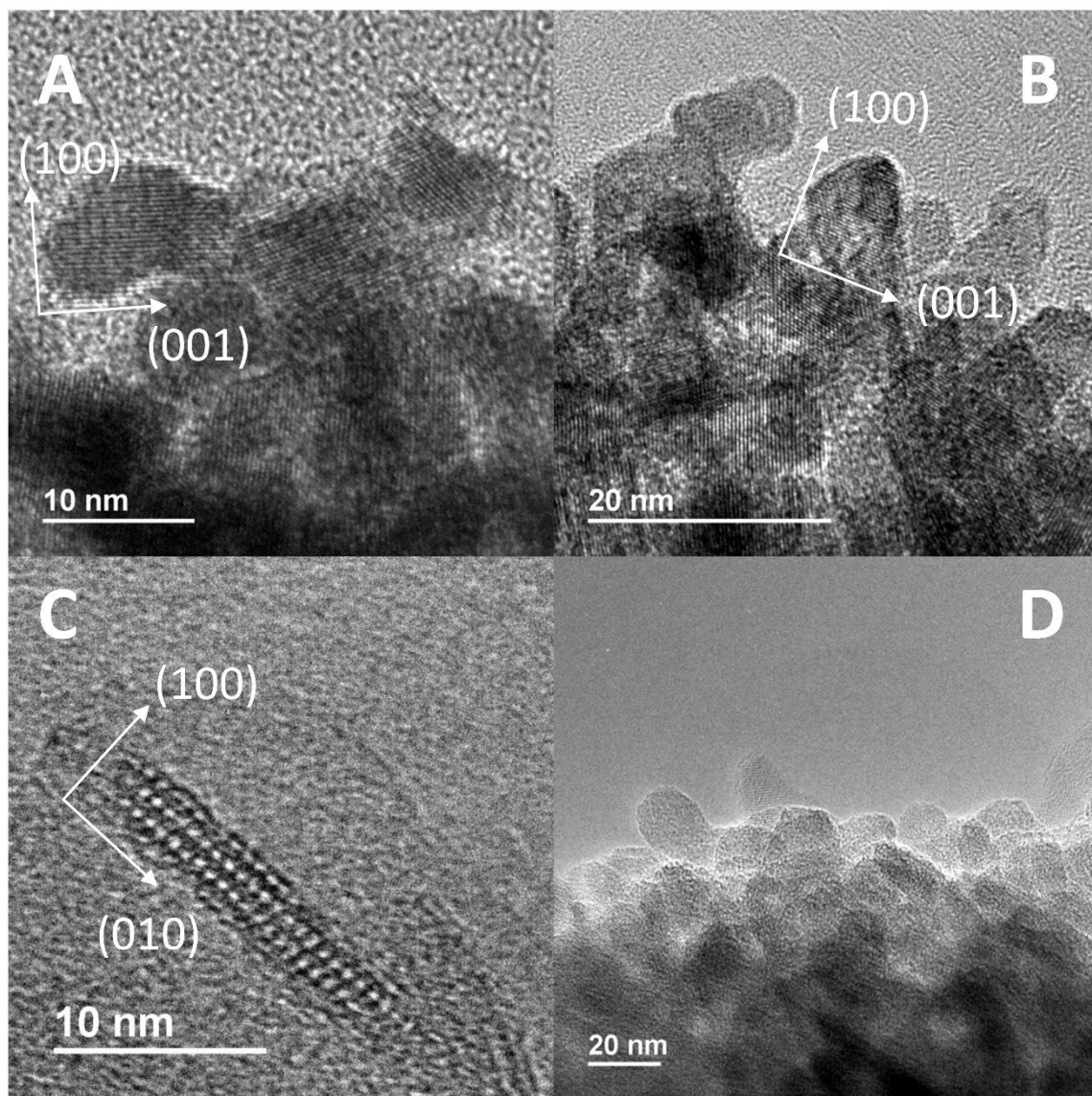


Figure S8. HRTEM images of N-FER(15)-150 (A, B) and of N-FER(15)-120 (C,D).

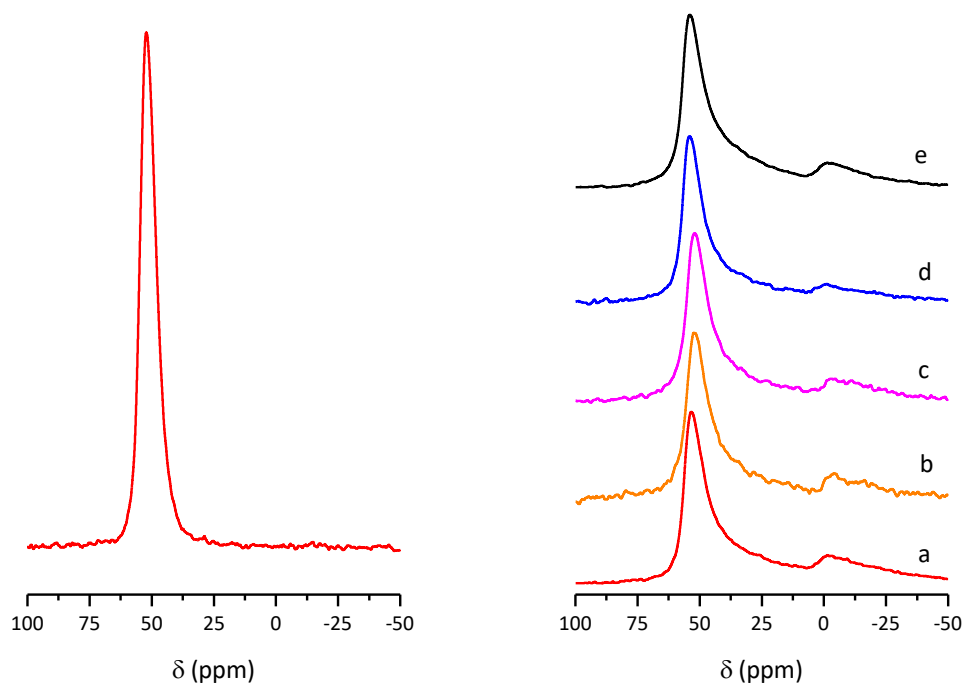


Figure S9. ^{27}Al -MAS-NMR spectra of as-prepared N-FER(15)-120 (A) and acidic samples (B) N-FER(15)-120 (a), N-FER(15)-125 (b), N-FER(15)-140 (c), N-FER(15)-150 (d) and R-FER (e), with 80%, 85%, 87%, 85% and 84% respectively of the aluminum in tetrahedral coordination (50 ppm).

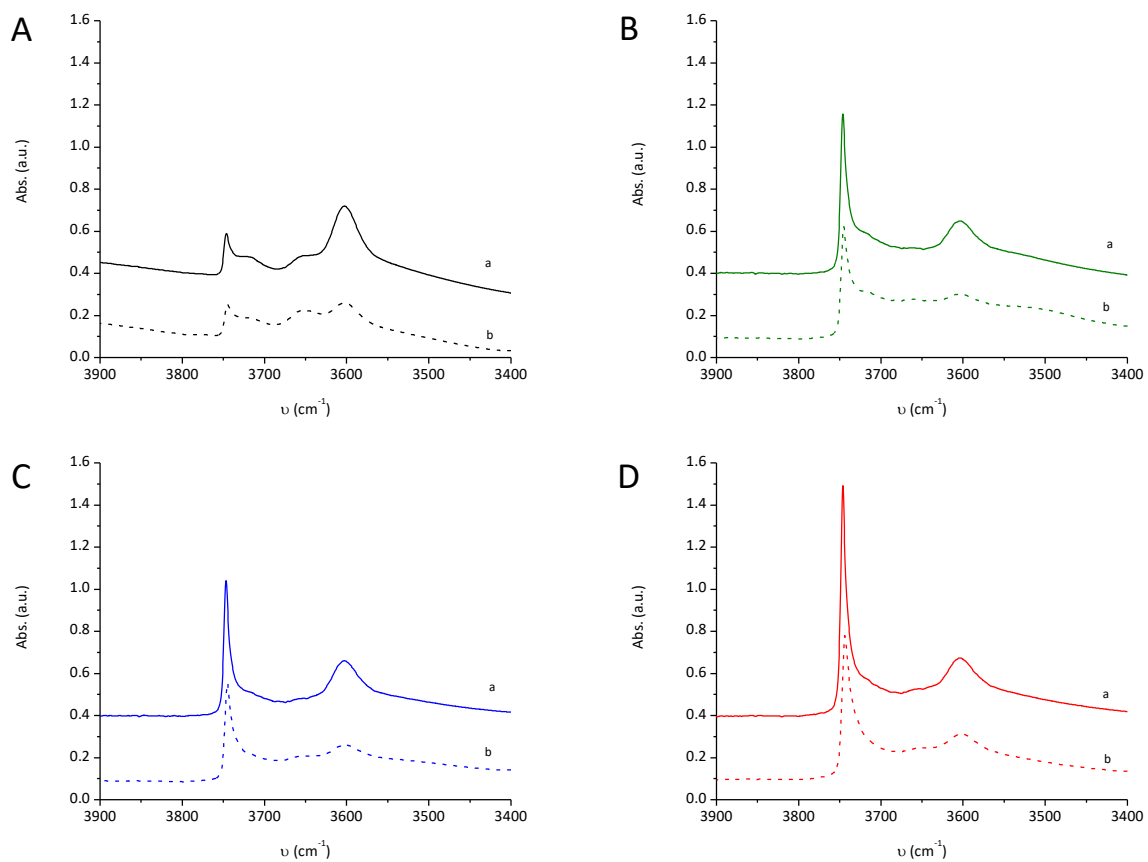


Figure S10. FT-IR spectra of the calcined materials pretreated at 400°C under vacuum (a) and after adsorption of the pyridine (b). R-FER (A), N-FER(30)-150 (B), N-FER(15)-150 (C) and N-FER(15)-120 (D).

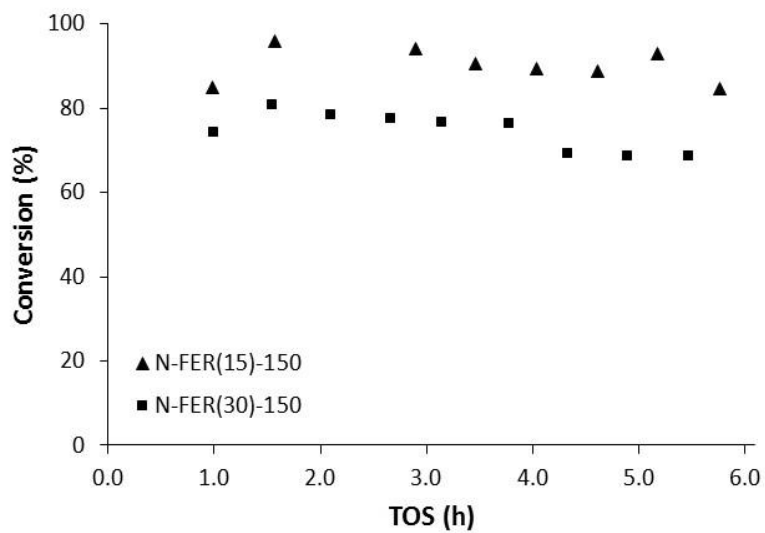


Figure S11. 1-pentene conversion for N-FER(15)-150 and N-FER(30)-150 at WHSV=8 h⁻¹, T=200°C, P = 4.0 MPa, 60% mol olefin in the feed.

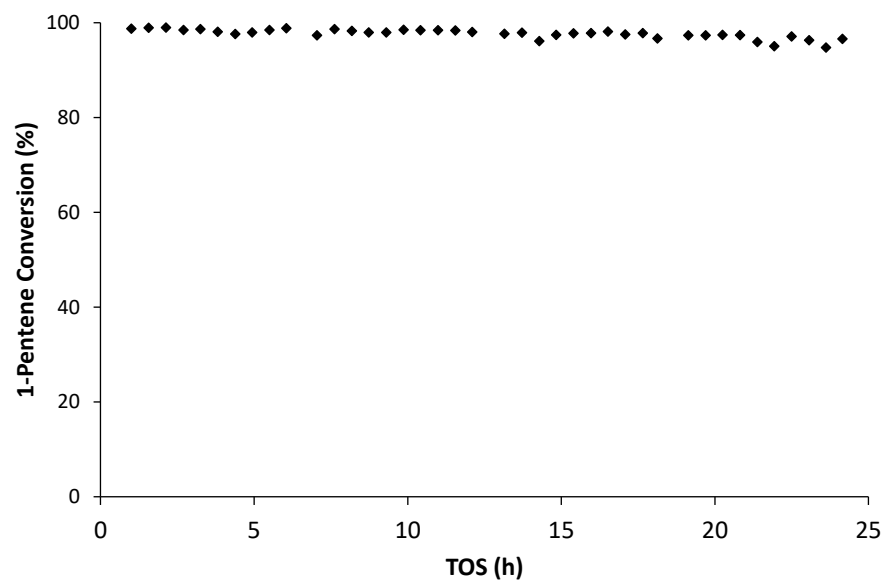


Figure S12. 1-pentene conversion for N-FER(15)-120 at WHSV=3.3 h⁻¹, T=200°C, P = 4.0 MPa, 60% mol olefin in the feed.

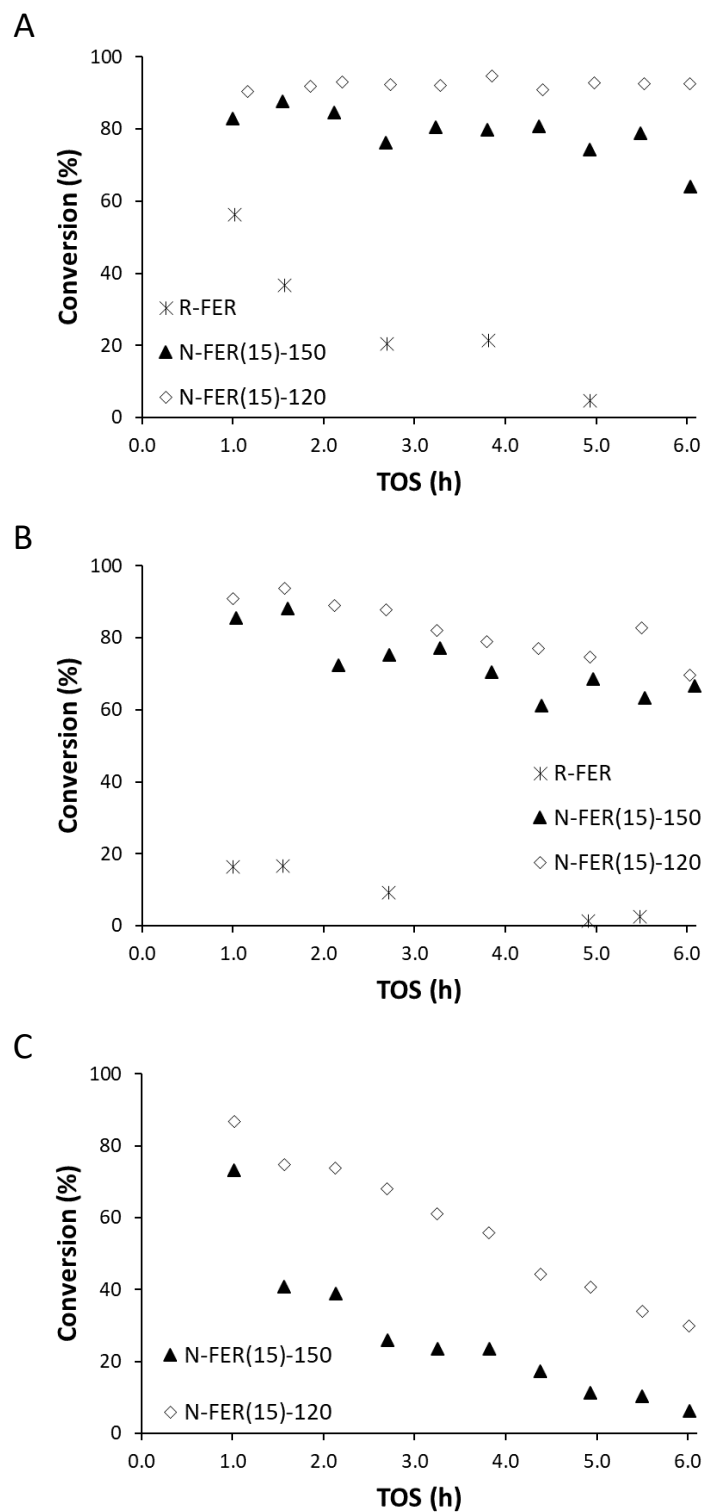


Figure S13. 1-pentene conversion for N-FER(15) at higher WHSV. (A) $WHSV = 15 \text{ h}^{-1}$, (B) $WHSV = 25 \text{ h}^{-1}$ and (C) $WHSV = 50 \text{ h}^{-1}$.

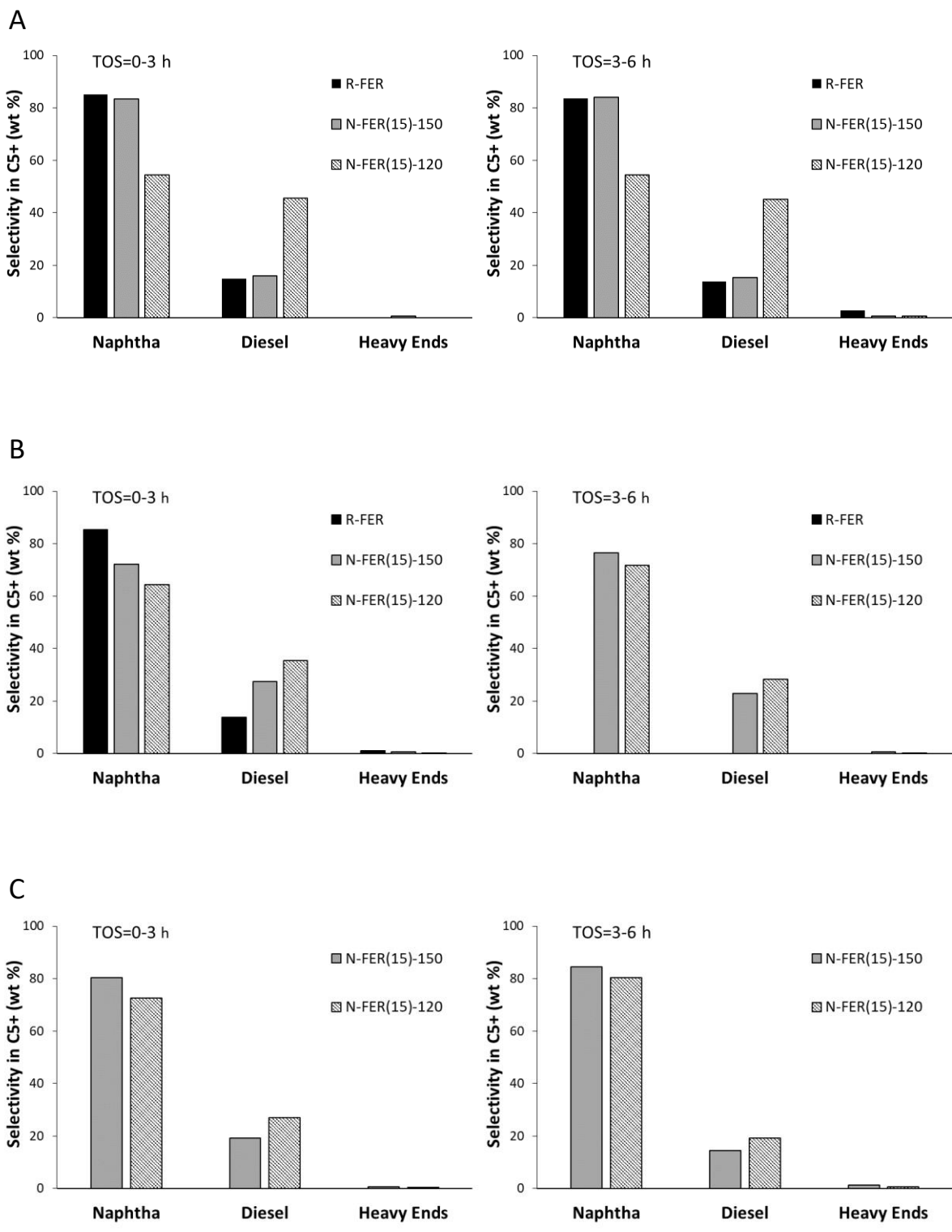


Figure S14. Selectivity within the accumulated C_{5+} liquid fractions for the ferrierite zeolites at $T=200^{\circ}\text{C}$, $P = 4.0 \text{ MPa}$, 60% mol olefin in the feed. (A) $\text{WHSV}=15 \text{ h}^{-1}$, (B) $\text{WHSV}=25 \text{ h}^{-1}$ and (C) $\text{WHSV}=50 \text{ h}^{-1}$.

Table S1. Gel compositions (moles) for reference ferrierite (R-FER) and nano-ferrierites (N-FER) with Si/Al molar ratio of 15 and 30

	Na₂O	SiO₂	Al₂O₃	H₂SO₄	Pip	C₁₆MPip	H₂O
R-FER	0.24	1	0.033	0.1	0.446	---	40
N-FER(15)	0.20	1	0.033	0.1	0.200	0.05	40
N-FER(30)	0.20	1	0.016	0.05	0.200	0.05	40

TABLE S2. Physicochemical properties of the samples in their acid form.

Sample	Temp. (°C)	Time (days)	Si/Al^a ICP	Area_{BET} (m² g⁻¹)	A._{micro} (m² g⁻¹)	A._{Ext} (m² g⁻¹)	Vol._{Tot} (cm³ g⁻¹)	Vol._{micro} (cm³ g⁻¹)	Vol._{Meso} (cm³ g⁻¹)
R-FER	150	5	8.9	319	302	17	0.269	0.145	0.030
N-FER (30)	150	7	18.2	366	231	135	0.859	0.111	0.245
N-FER (15)	150	7	11.9	398	241	157	0.915	0.116	0.283
N-FER (15)	140	7	10.7	428	223	205	1.082	0.106	0.380
N-FER (15)	125	14	11.6	441	193	248	0.981	0.091	0.406
N-FER (15)	120	17	10.5	447	187	262	1.001	0.085	0.427

^a Si/Al ratio was determined from zeolites after processes of calcination, exchange and calcination.

Table S3. Acidic properties of the different ferrierites.

Sample	Brönsted (a.u. x 10 ³)				Lewis (a.u. x 10 ³)		
	Si/Al	150°C	250°C	350°C	150°C	250°C	350°C
R-FER	8.9	346	341	254	32	65	92
N-FER (15)-150	11.9	305	285	181	77	82	81
N-FER (15)-120	10.5	229	192	125	108	104	92
N-FER (30)-150	18.2	225	189	119	87	81	81