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Exploring Brønsted Acids Confined In the 10-ring Channels of the Zeolite Ferrierite

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Experimental Section

Synthesis of FER zeolite

FER: $AlCl_3$•$6H_2O$ (Sinopharm Chemical Reagent) solution and fumed silica (CAB-O-SIL M-5) were mixed with vigorous stirring. Sodium hydroxide (Sinopharm Chemical Reagent), pyridine and required amount of deionized water were then sequentially added. After manual stirring, a thick gel with final molar ratio: 30 SiO_2/ 0.5 Al_2O_3/ 5.25 NaOH/ 18 Pyridine / 600 H_2O was obtained. After the gel became homogenous, it was transferred to a 35 mL autoclave and crystallized at 433 K for 96 h under the rotation condition of 50 r/min. The final product was recovered by centrifugation and washing with deionized water to a neural pH. The product was then dried at 373 K in air overnight, and calcined at 873 K in air for 6 h.

Ion exchange of the aluminosilicate zeolite

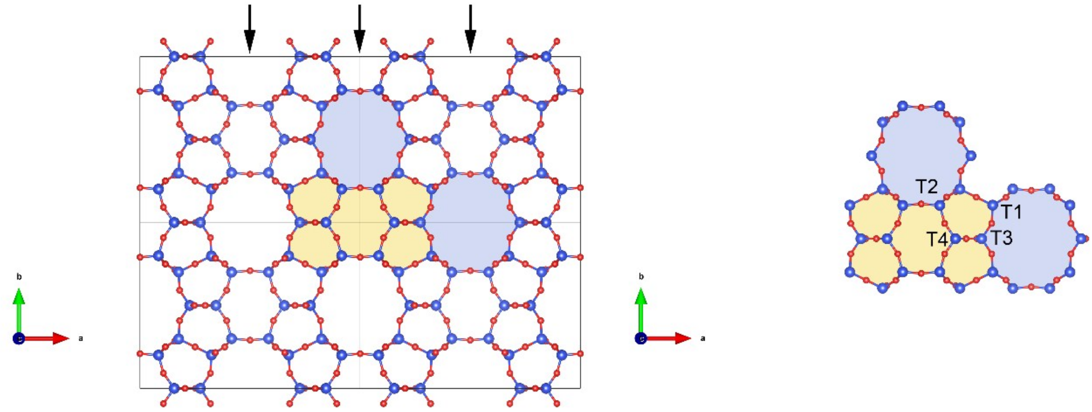
The proton form of the prepared sample was acquired by three rounds of ion-exchange processes with 1 M NH_4NO_3 at 353 K for 4 h, followed by a calcination process at 873 K for 6 h.

Pyridine adsorption of H-FER zeolite

The proton form zeolite (H-FER) was loaded into a quartz sample tube connected to a pyridine cell. Prior to the adsorption, the zeolite was activated at 773 K for 1 h under nitrogen gas flow to remove residual water. The zeolite sample was then exposed to pyridine gas and heated to 573 K for 240 min (denoted as H-FER-Py). After the adsorption process, the sample was cool down to room temperature under nitrogen flow and sealed in a sample cell for further measurements.

Materials Characterization

The powder X-ray diffraction (PXRD) data used for phase identification was collected on a STOE STADI P X-ray diffractometer with pure Cu Kα_1 radiation (λ=1.5406 Å) in a transmission mode. Field emission scanning electron microscopy (FESEM) was performed on a Hitachi SU8020 with low accelerating voltage 2 kV, working distance 6 mm. Elemental analysis for Si, Al, O and Na of the samples was carried out by a Philips Magix-601 X-ray fluorescence spectroscopy (XRF). Thermogravimetric (TG) analyses were performed on a TA Q-600 analyzer with a heating rate of 10 °C /min under an air flow of 100 mL/min, where the weight loss due to the loss of water (before 433K) and the decomposition of the SDA were further verified by differential analyses (DTA) with the same analyzer. PXRD data for Rietveld refinement was acquired on STOE STADI P X-ray diffractometer with pure Cu Kα_1 radiation (λ=1.5406 Å) in a transmission mode (capillary: 0.1 mm, angle range: 5-120°, step size: 0.015°, total counting time: 63 h, room temperature). Rietveld refinements were performed with commercial program DIFFRAC. TOPAS V5.0. The nitrogen in the pyridine ring was treated to be evenly distributed at all six sites. The hydrogen bonding is identified by assuming that the atom in pyridine closest to a framework oxygen atom is nitrogen.[1] FT-IR was carried out on a Bruker Tensor27 spectrometer in the frequency range 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. Prior to the measurements, the H-FER-Py sample tablet was activated at 573 K under vacuum for 1 h. Consequently, the temperature was slowly decreased to 423 K. The solid-state MAS NMR experiments were recorded on a Bruker Avance III 600 spectrometer equipped with a 14.1 T field using a 4mm WVT probe. The resonance frequencies for ^{29}Si, ^{13}C, ^{27}Al, and ^{1}H were 119.2, 150.9, 156.4 and 600.13 MHz, respectively. ^{1}H-^{13}C CP MAS NMR spectra were recorded with a contact time of 4 ms and a recycle delay of 2 s at the spinning rate of 12 kHz. 400 scans were accumulated in order to obtain data of good signal-to-noise ratio. The chemical shifts were referenced to adamantane with the upfield methine peak at 29.5 ppm. ^{27}Al MAS NMR experiments were performed with a spinning rate of 12 kHz using one pulse sequence. 600 scans were accumulated with a 2 s recycle delay and a $\pi/8$ pulse width of 0.75 us. Chemical shifts were referenced to $(NH_4)Al(SO_4)_2.12H_2O$ at -0.4 ppm. ^{29}Si MAS NMR spectra were recorded with a spinning rate of 8 kHz using high-power proton decoupling. 1000 scans were accumulated with a 10 s recycle delay. Chemical shifts were referenced to 4,4-dimethyl-4-silapentane sulfonate sodium salt (DSS) at 0 ppm.



Scheme S1. Channel systems of **FER** framework (arrow indicates the 8-ring channels, blue: 10-ring channel, yellow: ferrierite cage) are shown on the left and different T sites in the **FER** framework are illustrated on the right (blue: Al or Si atom, red: O atom).

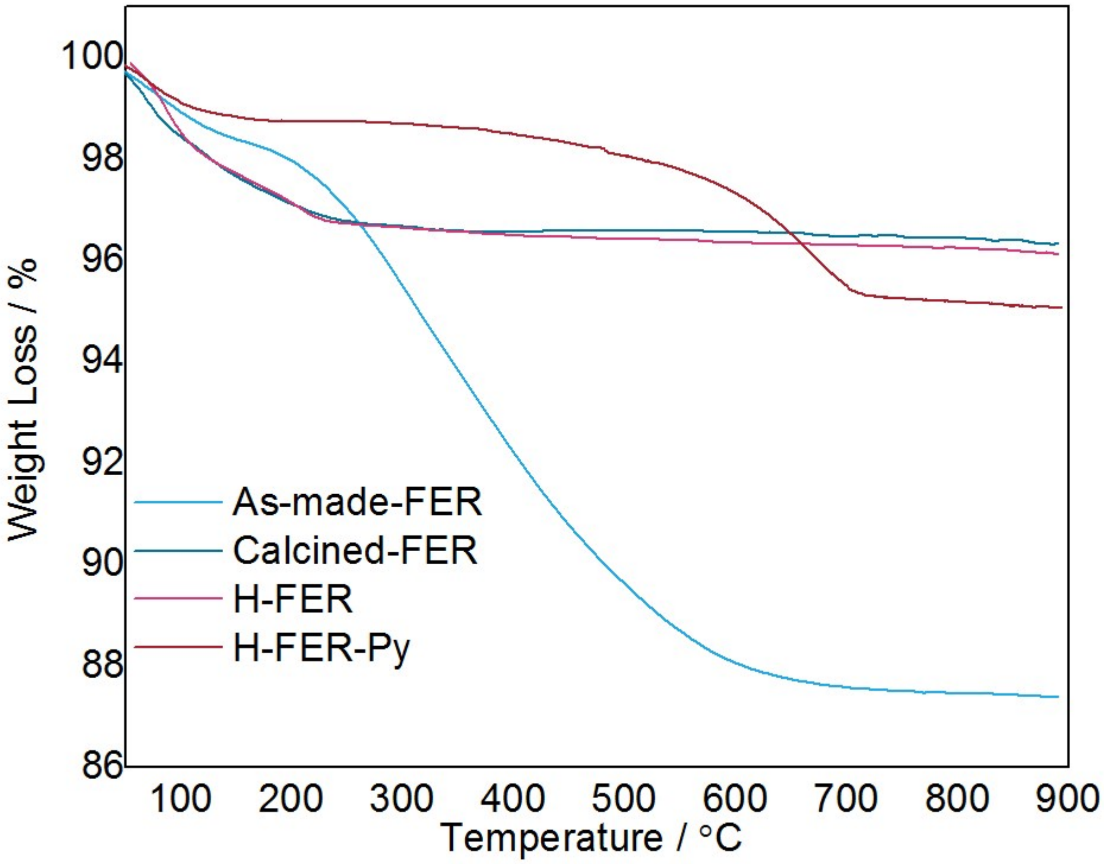


Figure S1. Thermogravimetric profiles of the as-made-**FER**, calcined-**FER**, H-**FER**, H-**FER**-Py samples.

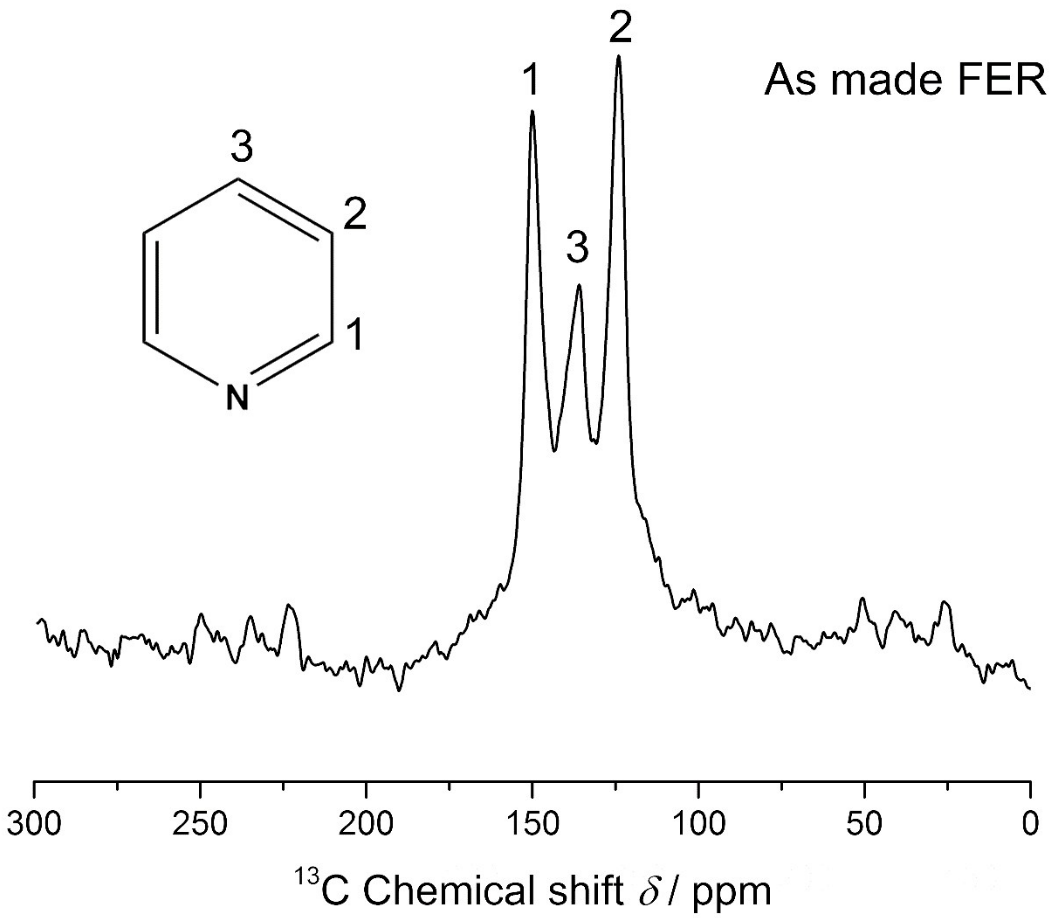


Figure S2. Solid-state ^{13}C MAS NMR spectra of the as-made-**FER** zeolite.

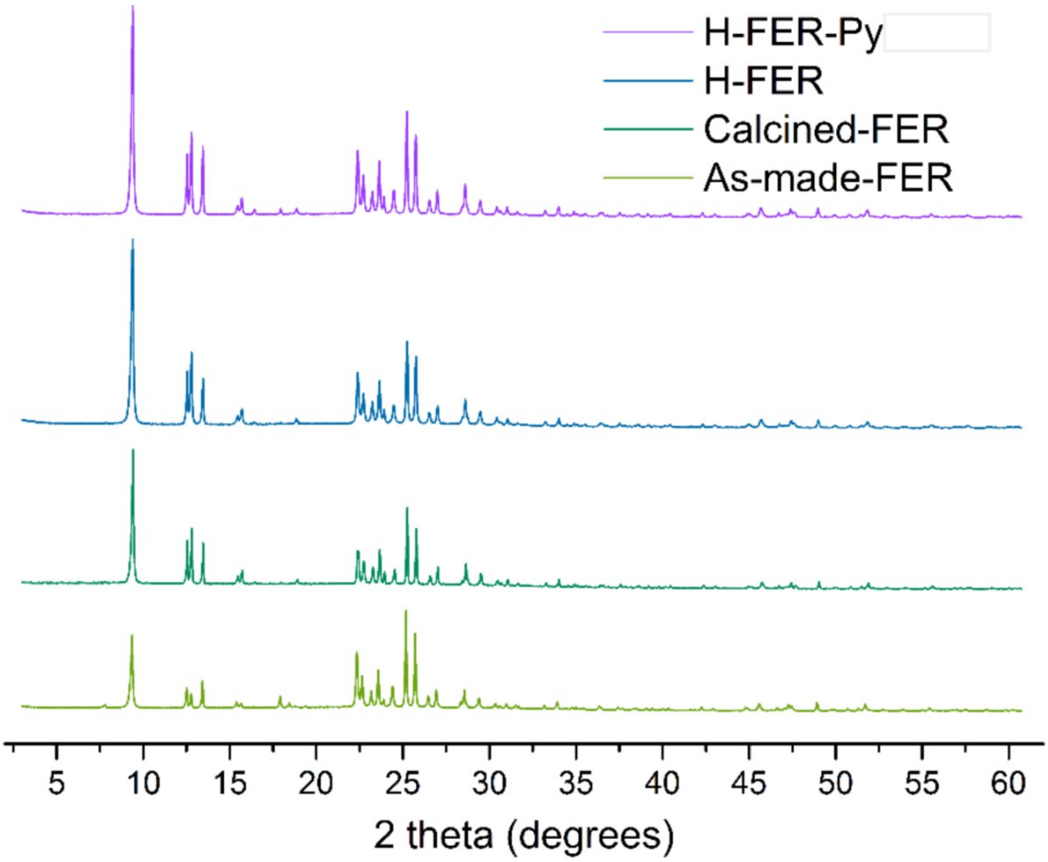


Figure S3. PXRD of the as-made and post-treated **FER** zeolite samples.

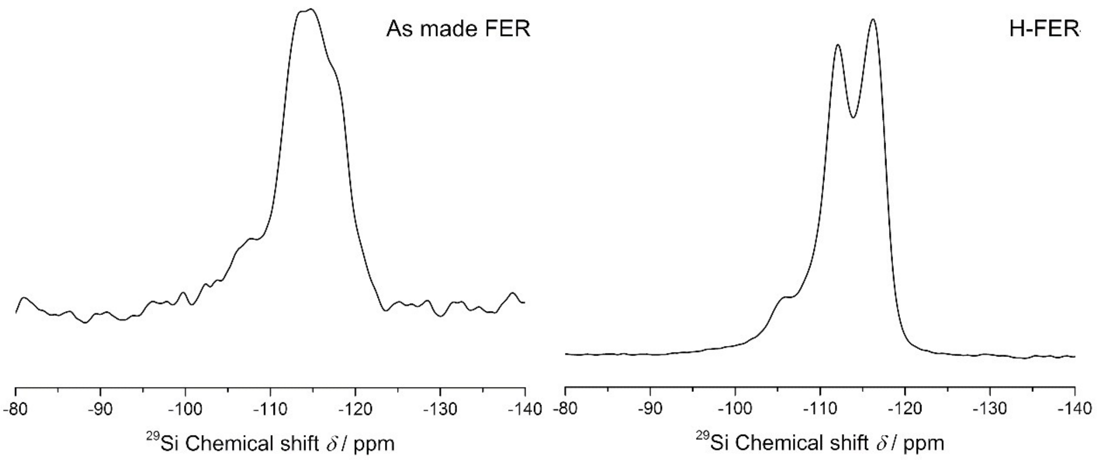


Figure S4. ^{29}Si MAS NMR spectra of as-made and H-FER zeolite.

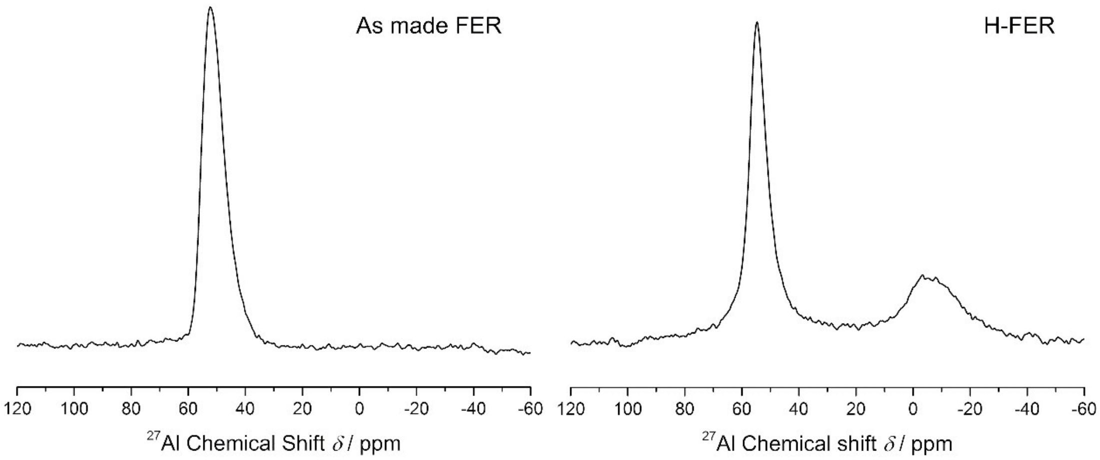


Figure S5. ^{27}Al MAS NMR spectra of as made and H-FER zeolite.

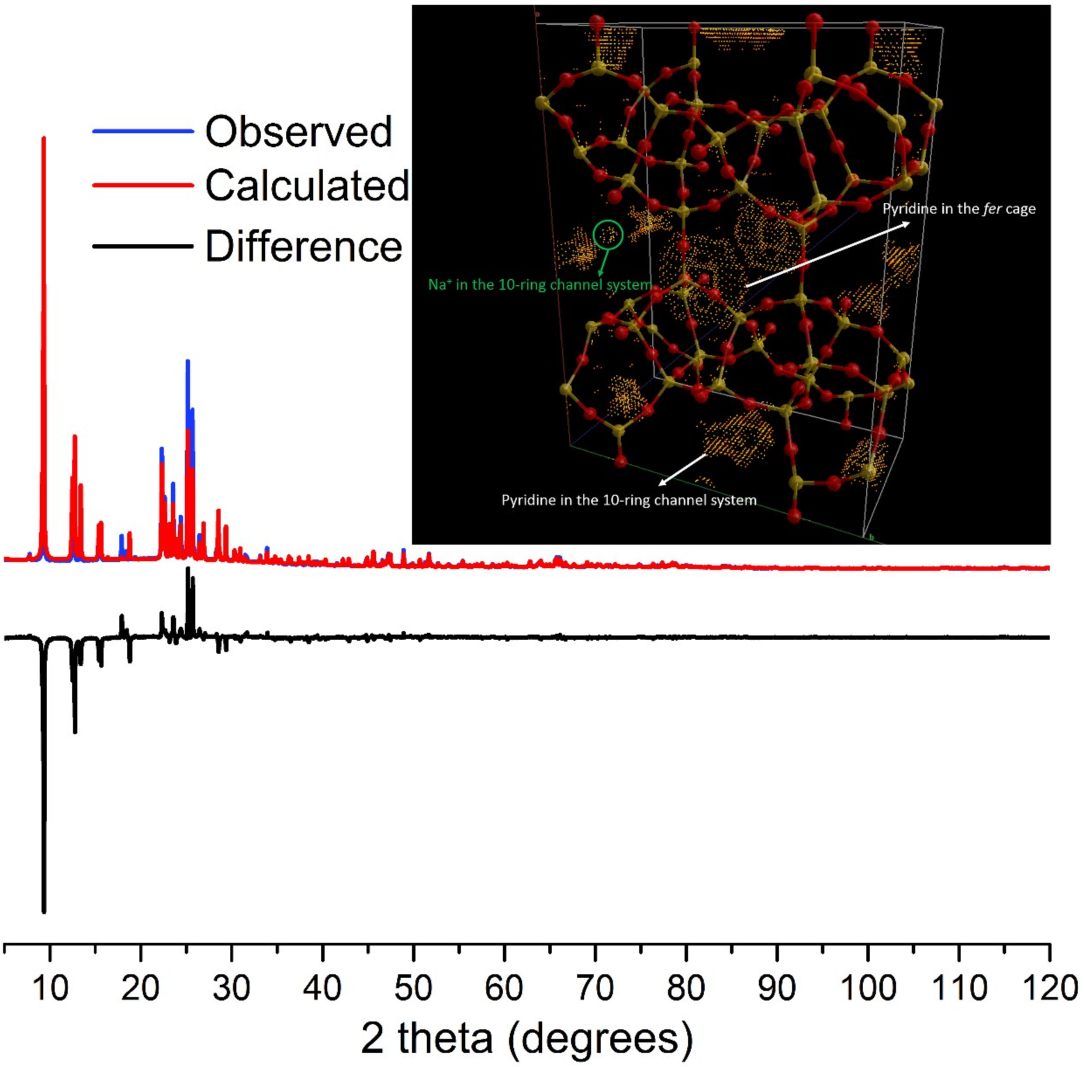
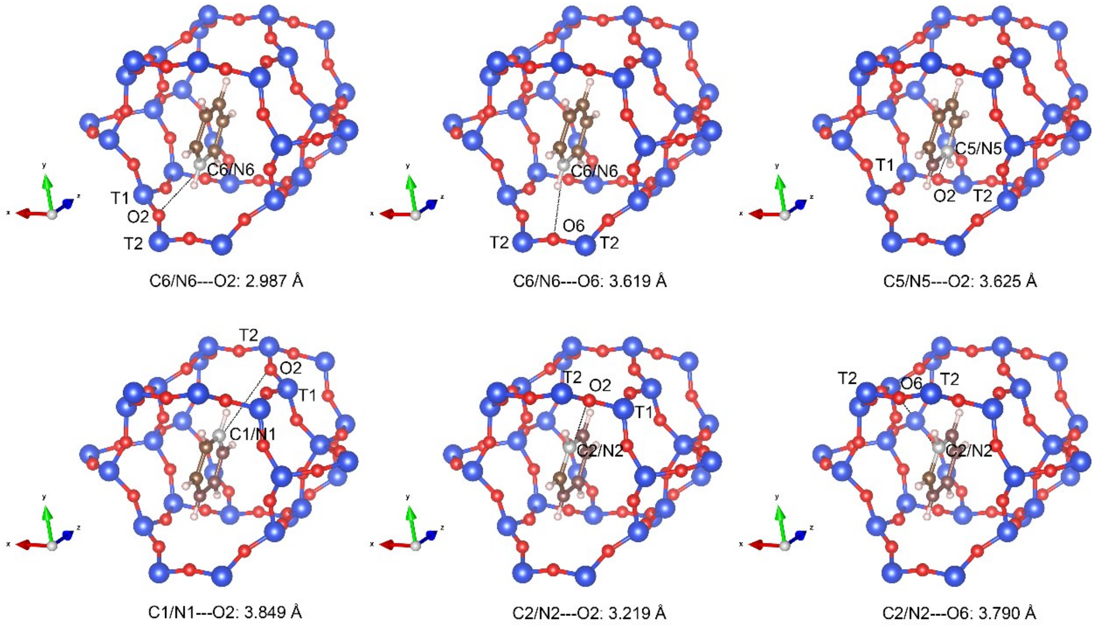


Figure S6. Identification of SDAs through Rietveld refinement. Difference electron density map (insert) clearly indicates the location and the orientation of the organic pyridine molecules and inorganic sodium cations.



C6/N6---O2: 2.987 Å

C6/N6---O6: 3.619 Å

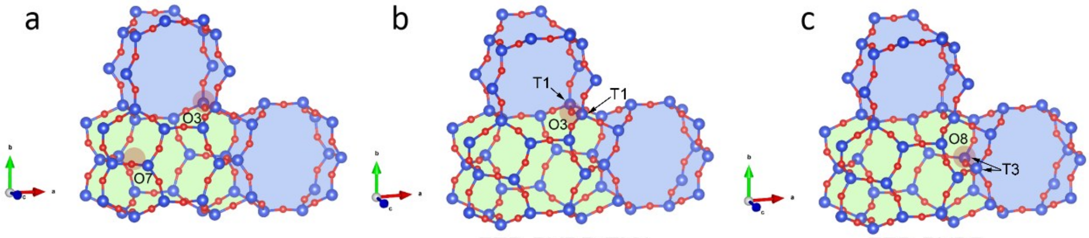
C5/N5---O2: 3.625 Å

C1/N1---O2: 3.849 Å

C2/N2---O2: 3.219 Å

C2/N2---O6: 3.790 Å

Figure S7. Distances between atoms in the pyridine and framework oxygen (blue: Al or Si atom, red: O atom).



FER-PYRR-TMA FER-PYRR

Figure S8. Catalytic sites in the **FER** framework determined by neutron diffraction (a, in Ref. 2) and PXRD (b-c, in Ref. 1) (blue: Al or Si atom, red: O atom).

Table S1. General composition of **FER** zeolites

Sample	Composition	Number of OSDA / *u.c.*
As-made-FER	$|Na_{1.33}(Pyridine)_{3.36}(H_2O)_{2.79}|[Al_{1.33}Si_{34.67}O_{72}]$	3.36
H-FER	$(H_2O)_{2.81}[H_{1.33}Al_{1.33}Si_{34.67}O_{72}]$	0
H-FER-Py	$|(HPyridine)_{1.05}(H_2O)_{1.51}|[\ H_{0.28}Al_{1.33}Si_{34.67}O_{72}]$	1.05

Note: The composition is calculated by XRF and TG results.

Table S2. Rietveld refinement profiles of as-made-FER and H-FER-Py samples.

	As-made-FER	**H-FER-Py**
Crystal system	Orthorhombic	Orthorhombic
Space group	*Immm*	*Immm*
Chemical Formula	$\vert Na_{1.33}(Pyridine)_{3.36}(H_2O)_{2.79}\vert[Al_{1.33}Si_{34.67}O_{72}]$	$\vert(HPyridine)_{1.05}(H_2O)_{1.51}\vert[H_{0.28}Al_{1.33}Si_{34.67}O_{72}]$
Formula Weight	2505.25	2270.23
Py / *u.c.*	3.36	1.05
2θ range refinement / º	5-120	5-110
Refinement method	Rietveld	Rietveld
Detector	MYTHEN2 R 1K	MYTHEN2 R 1K
Sample holder	spinning 0.1 mm capillary	spinning 0.1 mm capillary
Wavelength / Å	1.540598	1.540598
2θ Zero shift / º	-0.00556	-0.00284
Number of parameters	73	86
Number of hkls	870	752
***a* / Å**	18.8501(4)	18.7891(5)
***b* / Å**	14.1221(3)	14.0936(3)
***c* / Å**	7.43866(15)	7.43266(17)
***V* / Å^3**	1980.19(7)	1968.22(8)
Rwp/Rp/Rexp (%)	5.836/4.261/ 1.792	8.258/5.529/3.172
GoF	3.256	5.215

Table S3. General composition and the location of Bronsted acid sites reported by references

General Composition	Si/Al	BAS	Temperature	Method	Ref
$\|K_{2.7}Na_{1.1}12H_2O\|[Al_{3.8}Si_{32.2}O_{72}]^{\cdot}$	8.4	O3（10-ring channel and O7 (*fer* cage)	2 K	Neutron diffraction	2
Not given (made in F^- media)	15.0-16.0	*fer* cage	423K	IR	3
Not given (made in OH^- media)	15.8	10-ring channel	423K	IR	3
$\|((CH_3)_4N)_{0.4}((CH_2)_4NH)_{3.6}H_{1.7}\|$ $[Al_{2.1}Si_{33.9}O_{72}]$	16.1	O3 (10-ring channel)	RT	PXRD	1
$\|((CH_2)_4NH)_{4.2}H_{2.2}\|[Al_{2.2}Si_{33.8}O_{72}]$	15.4	O8 (*fer* cage)	RT	PXRD	1
$\|Na_{1.33}(Pyridine)_{3.36}(H_2O)_{2.79}\|[Al_{1.33}Si_{34.67}O_{72}]$	26.0	O2 (10-ring channel)	RT	PXRD	This work

Note: The coordinates and labels of T and O atoms described above have been unified according to the **FER** framework deposited in the IZA-Structure Database.

Reference:

1. A. B. Pinar, L. Gómez-Hortigüela, L. B. McCusker and J. Pérez-Pariente, *Chemistry of Materials*, 2013, **25**, 3654-3661.
2. A. Martucci, A. Alberti, G. Cruciani, P. Radaelli, P. Ciambelli and M. Rapacciulo, *Microporous and Mesoporous Materials*, 1999, **30**, 95-101.
3. A. B. Pinar, C. Márquez-Álvarez, M. Grande-Casas and J. Pérez-Pariente, *Journal of Catalysis*, 2009, **263**, 258-265.