

Supplementary Information

Synthesis and further treatment of FER samples.

The same molar composition was used for the sample prepared in the presence of pyrrolidine as the only SDA but using a molar ratio pyrr:(Si+Al) = 0.54, thus maintaining the organic compounds/T atoms ratio constant. Gels were prepared by adding the silicon and aluminium sources, tetraethylorthosilicate (TEOS, Merck, 98 wt%) and aluminium isopropoxide (Fluka, 97 wt%), respectively, to an aqueous solution containing the SDAs employed in each case. The solution was stirred at room temperature until all the ethanol from the hydrolysis of TEOS was evaporated. Subsequently, HF (Panreac, 48 wt.%) was added drop-wise. The resulting thick gel was homogenized with a spatula, introduced into 20-mL Teflon-lined stainless steel autoclaves, and heated statically at 150 °C under autogeneous pressure for different periods of time. The samples selected for this study were heated for 10 days (sample prepared with pyrrolidine) and 83 days (sample prepared with bmpOH and TMAOH). The solid products were separated by filtration, washed first with water, then with ethanol and finally with water again, and dried at room temperature overnight.

Both samples underwent a post-synthesis treatment in order to get their proton form. They were heated in nitrogen flow up to 200 °C and kept at this temperature for 2 h, followed by a treatment with a flow of oxygen enriched in ozone (60 mL/min, ca. 2 vol.% ozone) at 200 °C to remove, in mild conditions, the organic molecules employed as SDAs. An ECO-5 ozone generator (Salveco Proyectos, S.L.) was employed to produce the ozone-enriched oxygen stream. In the final step, the samples were heated in an air flow for 2 h up to 550 °C and kept at this temperature for additional 2 h.

Hereafter, the FER samples will be denoted making reference to the organic species employed as SDAs in their synthesis, separated by a dash: FER-bmp-TMA (synthesised with 1-benzyl-1-methylpyrrolidinium and TMA) and FER-pyrr (with pyrrolidine). The Si/Al ratio of the solids, as measured by chemical analysis (ICP-AES), was 15.6 for the sample FER-bmp-TMA and 15.0 for the sample FER-pyrr.

The replacement of protons by sodium cations in the acid-form of the zeolites was carried out in two steps. First, ammonia was adsorbed to form NH₄⁺ as charge compensating cation and after that NH₄⁺ cations were exchanged by Na⁺. To obtain the ammonium form, the samples were placed in a tubular reactor, dried at 450 °C in a nitrogen flow and then kept under an ammonia stream at 35 °C for 30 minutes. In order to remove physically adsorbed ammonia, the samples were subsequently heated in a nitrogen flow in two steps: first the temperature was increased up to 80 °C at 5 °C/min and maintained at 80 °C for 20 minutes, and then it was increased up to 100 °C at the same rate and maintained for 60 minutes. Finally, ammonium cations were replaced by sodium by two-fold ion-exchange with a 1 M solution of NaCl (1 g zeolite/100 mL solution) at 80°C under reflux, first for 8 h and then for 20 h. The ion-exchanged samples were thoroughly washed with water and dried overnight at room temperature. Full ion exchange of ammonium by sodium was confirmed by FTIR, which showed complete removal of the characteristic ammonium bending band in the 1400-1500 cm⁻¹ wavenumber range.

Characterization of FER samples.

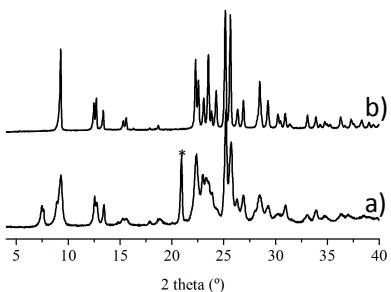


Figure S1. X-ray diffraction patterns of calcined FER samples FER-bmp-TMA (a) and FER-pyrr (b). The peak highlighted with an asterisk (*) corresponds to a dense phase, probably α -quartz.

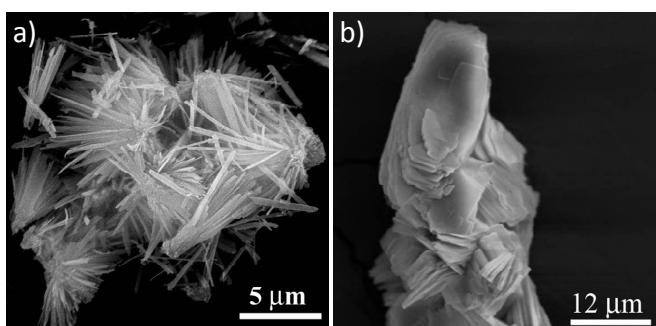


Figure S2. SEM images of the calcined FER samples FER-bmp-TMA (a) and FER-pyrr (b). The former is constituted by needle-like crystals of *ca.* 7 μm in length, whereas the latter contains plate-like crystals (*ca.* 22 \times 13 μm) which are indeed aggregates of smaller crystals (*ca.* 7 μm width).

Sorption measurements.

In order to attain a sufficient accuracy in the accumulation of the adsorption data, the ASAP 2020 was equipped with pressure transducers covering 1 torr, 10 torr and 1000 torr ranges. Before adsorption experiments the sample was outgassed under turbomolecular pump vacuum using a special heating program allowing for a slow removal of most preadsorbed water at low temperatures. This was done to avoid potential structure damage of the sample due to surface tension effects and hydrothermal alteration. Starting at ambient temperature the sample was outgassed at 383 K (temperature ramp of 0.5 K/min) until the residual pressure of 0.01 torr was obtained. After further heating at 383 K for 1 h

the temperature was increased (temperature ramp of 1 K/min) until temperature of 623 K was achieved. This temperature was maintained for 8 h.

Before each measurement of carbon dioxide isotherm the sample was outgassed at 473 K overnight. Adsorption isosteres were calculated from adsorption isotherms in coordinates a vs. $\log p$ using a polynomial interpolation procedure. Isosteric adsorption heats q_{st} were then determined from the slope of adsorption isosteres using the equation

$$[d(\log p)/d(1/T)]a = -q_{st}/2.303R$$

where a is amount adsorbed and R the gas constant. As adsorption isosteres in coordinates $\log p$ vs. $1/T$ were linear, isosteric adsorption heats did not depend on temperature.

CALCULATIONS

The DFT/CC correction scheme for the CO₂..zeolite interaction

Recently, the DFT/CC method has been proposed for the accurate description of weakly interacting systems.¹⁻² The method is based on the pairwise representability of the DFT error, $\Delta E_{DFT/CC}$, defined as the difference between the CCSD(T) and DFT interaction energies. The above assumption leads to the following equation

$$\Delta E_{DFT/CC} = \sum_{ij} \varepsilon_{ij}(R_{ij}),$$

where ε_{ij} are the DFT/CC correction functions and R_{ij} are the interatomic distances. The pairwise correction functions are obtained by means of the Reciprocal Power Reproducing Kernel Hilbert Space Interpolation (RP-RKHS); no a priori functional form of correction functions is assumed except for the asymptotic behavior given by the RKHS kernel ($R^{-6} + R^{-8}$). A more detailed description of DFT/CC can be found in Refs.¹⁻².

Correction functions are evaluated from the potential energy surfaces (PES) obtained at the CCSD(T) and DFT levels for a suitable reference set of molecular complexes. For the description of CO₂ interaction with zeolites, the pairwise corrections function ε_{ij} were obtained, where i stands for C or O atoms of CO₂ molecule and j stands for framework O and Si atoms. The framework Al atoms where not explicitly considered, instead correction functions derived for framework Si atoms were used also for Al. The following correction functions where obtained: ε_{CO} , ε_{CSi} , ε_{CH} , ε_{OO} , ε_{OSi} , ε_{OH} .

The DFT calculations (employing PBE exchange-correlation functional) where performed with the augmented correlation-consistent valence-quadruple- ζ basis set with polarization functions³ (AVQZ). The CCSD(T)/CBS estimate was obtained using a simple correlation energy dependence on the cardinal number, employing basis sets from Ref. ³ (details given below). All interaction energies were corrected

for the basis set superposition error.⁴ More details about calculations, including the transferability checks, can be found in Supporting Information of Ref.⁵

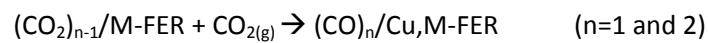
CO₂ interaction with Na-FER

Calculations were performed using a fixed-volume UC (cell parameters $a=19.1468$, $b=14.3040$, and $c=7.5763$ Å), optimized previously for all-silica FER.⁶ Two periodic models of alkaline-metal exchanged FER (M-FER, M = Li, Na, and K) have been used, corresponding to: (i) Si/Al=35, denoted as M-FER(35), having UC composition [AlSi₃₅O₇₂] and (ii) Si/Al=8, named M-FER(8), with UC composition [Al₄Si₃₁O₇₂]. Calculations with UC doubled along c direction were also performed to check the convergence of the model.

The alkali-metal cation sites are classified using the nomenclature introduced for Cu-FER⁶ and adopted for Na-FER⁷ where cation sites are denoted as Xn/Ti, where X refers to the main channel (M), perpendicular channel (P), or intersection (I), n specifies a particular site within the channel system, and Ti designates the tetrahedral position of framework Al (Figure S3). Preferred sites of Na⁺ cations in FER were investigated previously⁷ for all four distinguishable framework Al positions. Note that (contrary to Ref.⁷) framework atom numbering scheme from Atlas of Zeolite Structures is adopted. When framework Al is in T1, T2, T3, and T4 position Na⁺ cations are preferably located in I2/T1, I2/T2, M7/T3, and P6/T1 sites, respectively (see Figure S3).

3.2. Methods.

Calculations were performed at the periodic DFT level, employing the PBE functional,⁸ a projector-augmented-wave method (PAW) of Blöchl⁹ as adopted by Kresse and Joubert,¹⁰ and the plane-wave basis set with a kinetic energy cut-off of 400 eV. Brillouin-zone sampling was restricted to the gamma-point. The calculations were performed using the VASP program.¹¹⁻¹² CO₂ adsorption enthalpies in the M-FER zeolite (M=Li, Na, and K) were evaluated for the process:



CO₂ adsorption enthalpies (at 0 K), ΔH_{ads}^0 , were calculated as

$$\Delta H_{ads}^0 = \Delta E_{int}^{DFT} + \Delta E^{DFT/CC} + \Delta ZPVE,$$

where $\Delta E_{\text{int}}^{\text{DFT}}$ is electronic interaction energy obtained with PBE functional and periodic model, $\Delta E^{\text{DFT/CC}}$ is the DFT/CC correction accounting for a dispersion interaction between adsorbate and adsorbent, and $\Delta ZPVE$ is the correction for the zero-point vibrational energy. The latter contribution was evaluated at the periodic PBE level within harmonic approximation and considering 9 degrees of freedom for each CO₂ molecule; the second derivatives were calculated numerically, using ±0.005 Å displacement for C and O atoms of CO₂.

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