

Structure Influence on High-Pressure Water Intrusion in Pure Silica Zeolites

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Supporting Information

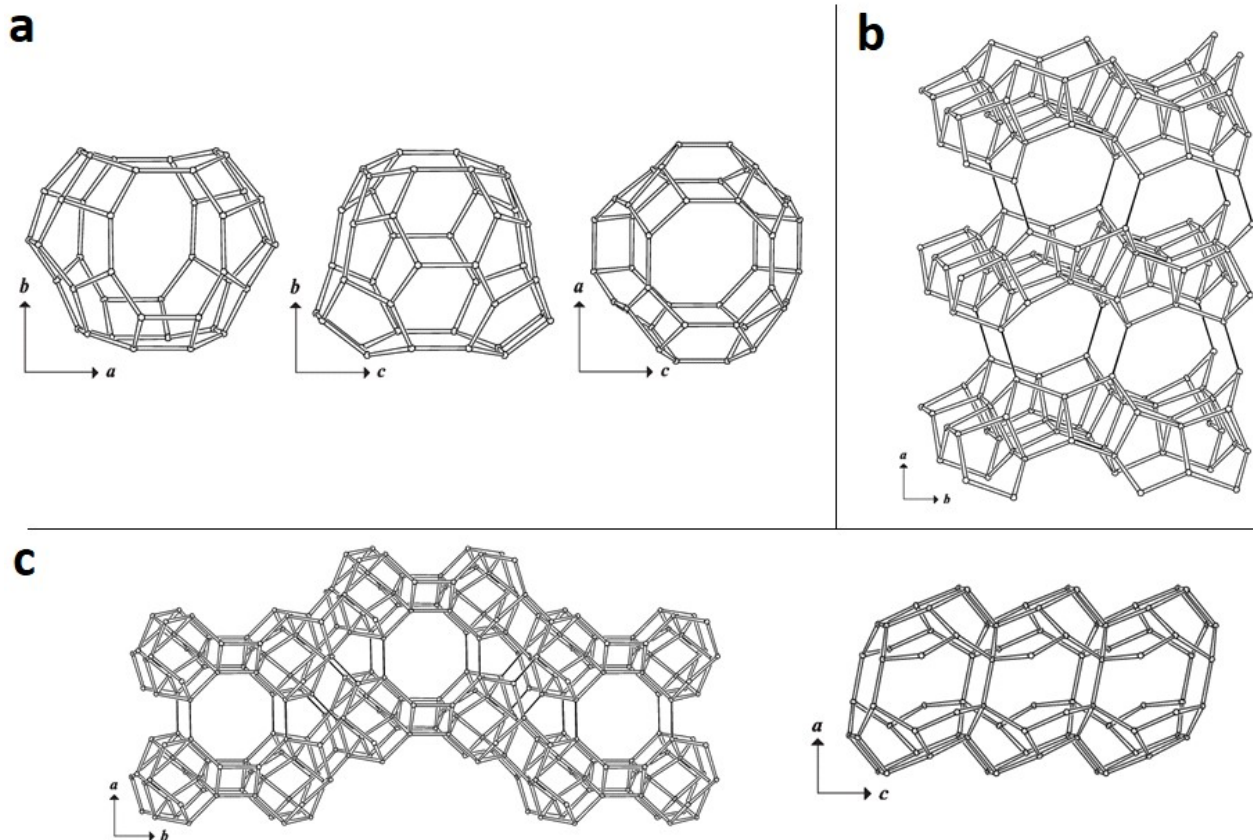


Figure S1. a). Cavity of ITE structure viewed (from left to right) along c , a and b . b). CDO framework viewed along $[001]$ direction. c). MTF framework along $[001]$ direction and fusion of of cavities of 8 MR channels viewed along $[010]$ direction. In these representations, the silicon atoms of the framework are located at the intersection of the edges, while oxygen atoms are located in the middle of the edges [1].

Characterization techniques

The samples were analyzed by powder X-ray diffraction recorded on a STOE STADI-P diffractometer in the transmission scan mode equipped with a curved germanium (111), primary monochromator and a linear position-sensitive detector ($6^\circ 2\theta$) using $\text{CuK}\alpha_1$ radiation ($\lambda = 0.15406$

nm). Measurements were performed for 2θ angle values in the $3\text{--}50^\circ$ range, step 0.2° 2θ and time/step = 10 or 80 s.

The size and the morphology of the crystals were determined by scanning electron microscopy (SEM) using a Philips XL 30 FEG microscope.

Thermogravimetric (TG) analyses were carried out on a Mettler Toledo STARE apparatus, under air flow, with a heating rate of $5^\circ\text{C}/\text{min}$ from 30 to 800°C . The resulting weight loss curve was obtained by subtracting of the curve of an empty pan from the one of the sample in order to remove the mass variations due to the modifications related to the pan.

Nitrogen adsorption–desorption isotherms were performed at -196°C using a Micromeritics ASAP 2420 apparatus. Prior to the adsorption measurements, the nonintruded samples were outgassed at 90 or 300°C overnight under vacuum while the samples after intrusion-extrusion tests were only outgassed at 90°C to avoid the dehydroxylation process. The specific surface area (S_{BET}) and the microporous volume (V_{micro}) were calculated using the BET and t-plot methods, respectively.

The samples before and after intrusion-extrusion tests were also characterized by solid-state nuclear magnetic resonance spectroscopy (NMR). Two different techniques were adopted: ^{29}Si MAS (Magic Angle Spinning) NMR (quantitative technique) and $^1\text{H}\text{--}^{29}\text{Si}$ CPMAS (Cross Polarization, Magic Angle Spinning) NMR. In the former the polarization of silicon atoms is directly recorded, while in the latter the polarization of a copious element (^1H) is transferred to a rarer one (^{29}Si in this work). Transfers are better if the concerned atoms are close to each other, particularly if chemically bonded. This technique allows to reduce the signal/noise ratio and to better observe the defects in zeosil structure (e.g., Q_3 and Q_2 groups: $(\text{HO-Si}(\text{OSi})_3$ and $(\text{HO})_2\text{-Si}(\text{OSi})_2$, respectively).

The spectra were recorded with a short contact time (8 ms, the time in which the transfer of polarization occurs) in order to enhance the signal of silicon atoms that bear protons and consequently to get evidence of the presence of silanol groups. $^1\text{H}\text{--}^{29}\text{Si}$ CPMAS NMR does not provide quantitative results, however, it allows a relative comparison of the spectra if they were registered under the same conditions. During this work, ^{29}Si MAS and $^1\text{H}\text{--}^{29}\text{Si}$ CPMAS NMR spectra were recorded at room temperature on a Bruker Advance II 300 MHz spectrometer, with a double-channel 7 mm Bruker MAS probe. An example of the recording conditions is given in Table S1. These conditions are similar for every sample analyzed during this work.

Table S1. Recording conditions of the ^{29}Si MAS and ^1H - ^{29}Si CPMAS NMR spectra.

	^{29}Si MAS	^1H - ^{29}Si CPMAS
Chemical Shift Standard	TMS ^a	TMS ^a
Frequency (MHz)	59.6	59.6
Pulse width (μs)	2.17	5.00
Flip angle	$\pi/6$	$\pi/2$
Contact time (ms)	/	8
Recycle time (s)	80	^(*) 1.5
Spinning rate (kHz)	4	4
Scans number	1700	10000

^a = Tetramethylsilane; ^(*) = the relaxation time t_1 was optimized

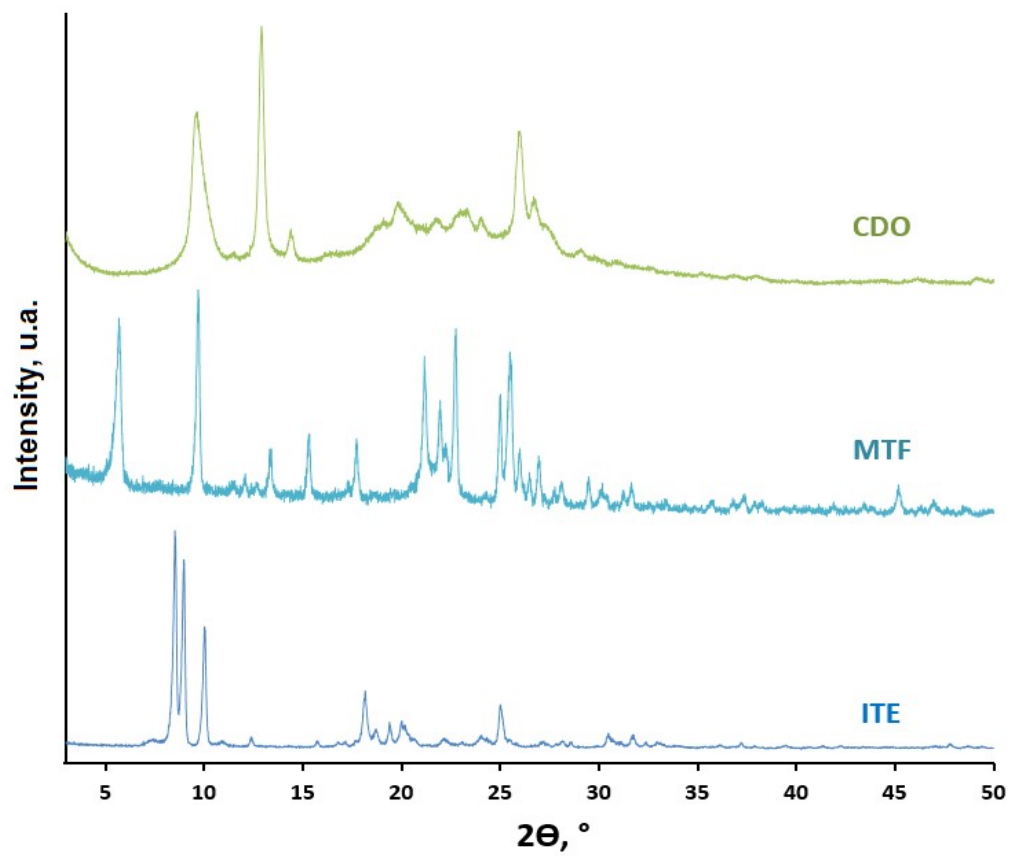


Figure S2. XRD patterns of synthesized ITE-, MTF- and CDO-type zeolites.

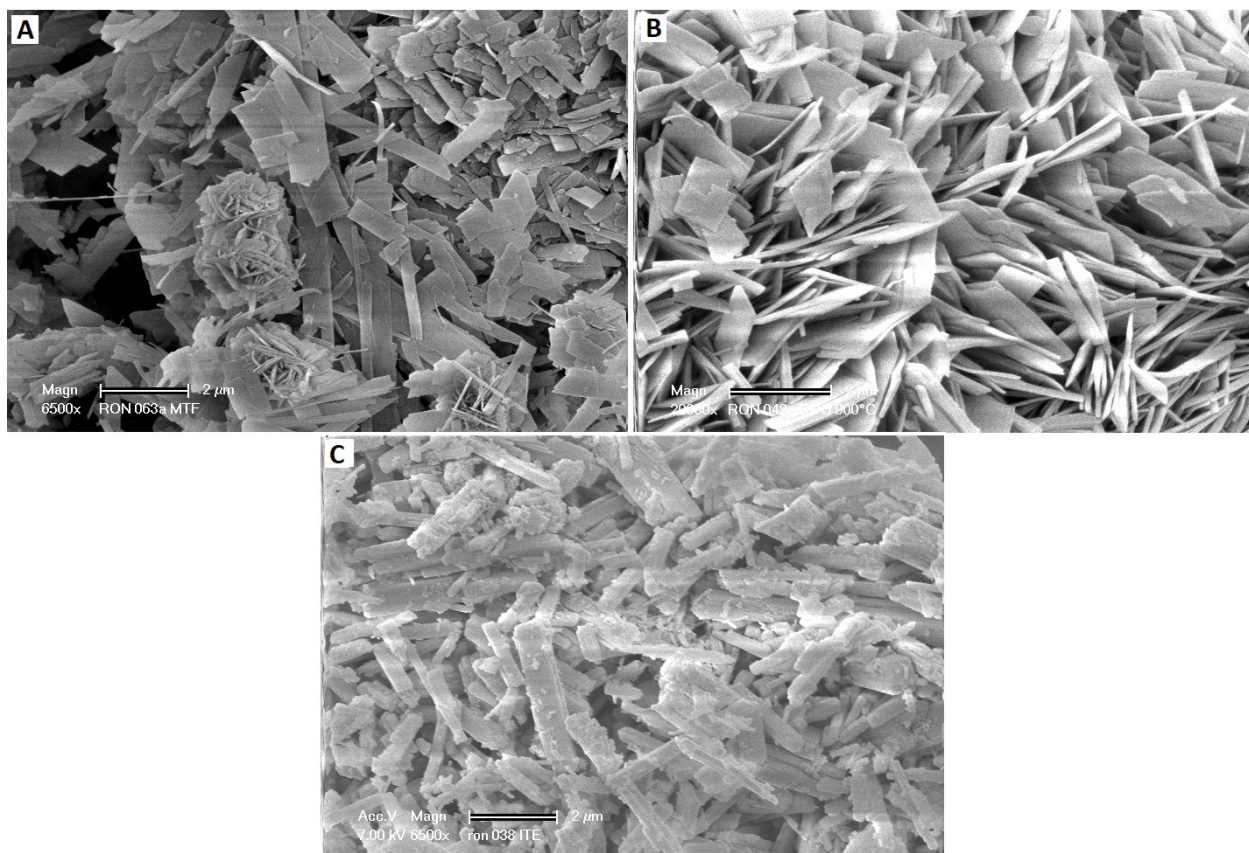


Figure S3. SEM images of MTF- (A), CDO- (B) and ITE-type (C) zeolites. Scale bar = 2 μm .

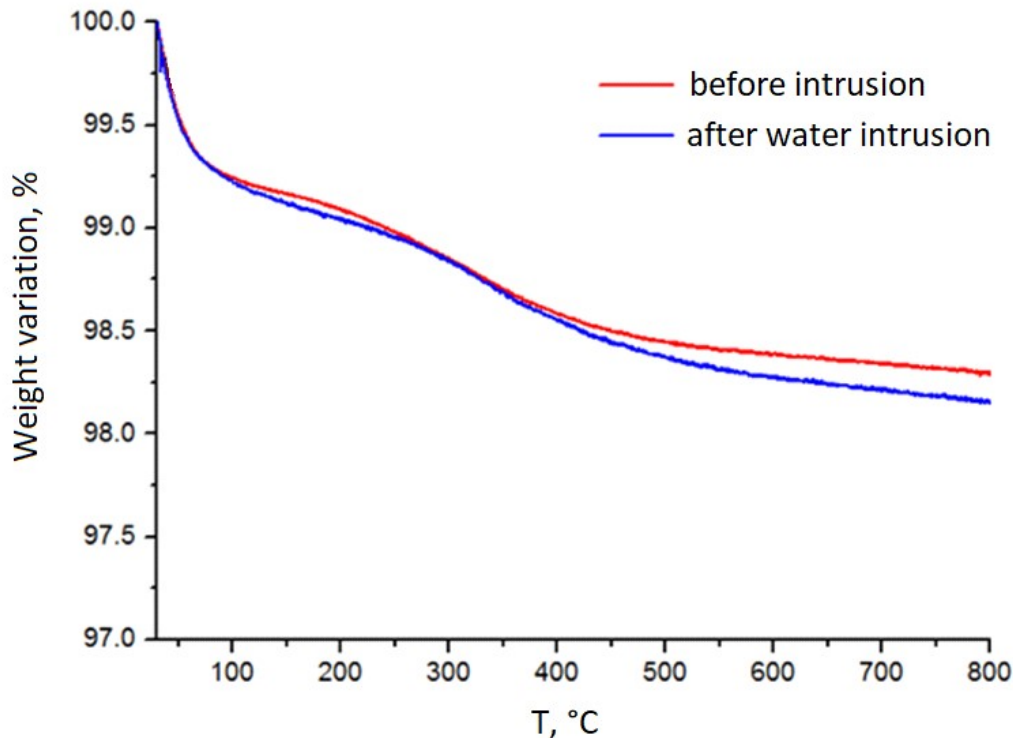


Figure S4. Thermogravimetric curves of CDO-type zeosil before and after water intrusion-extrusion. The first weight loss step between 30° and 200°C corresponds to the desorption of physisorbed water molecules, the second one between 200° and 600°C is attributed to the desorption of water molecules issued from the condensation of silanol groups.

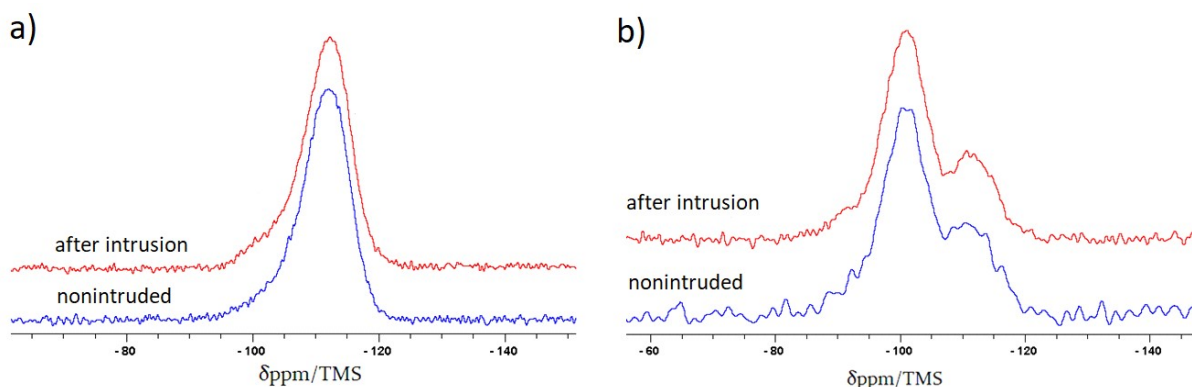


Figure S5. ^{29}Si -MAS (a) and ^1H - ^{29}Si -CPMAS (b) NMR spectra of the samples of CDO-type zeosil before and after water intrusion-extrusion. A very broad resonance on ^{29}Si -MAS NMR spectra between -95 and -123 ppm corresponds to Q_3 and Q_4 ($\text{Si}(\text{SiO})_4$) groups and can indicate that the CDO structure is not fully condensed. The amount of Q_3 sites could be estimated at $\sim 6\%$ of the total ^{29}Si signal, corresponding to approximately two silanol groups per unit cell. The ^1H - ^{29}Si CPMAS NMR spectra show the presence of a resonance corresponding to Q_3 groups between -93 and -107 ppm and a small resonance at -86 ppm which indicates the presence of Q_2 species.

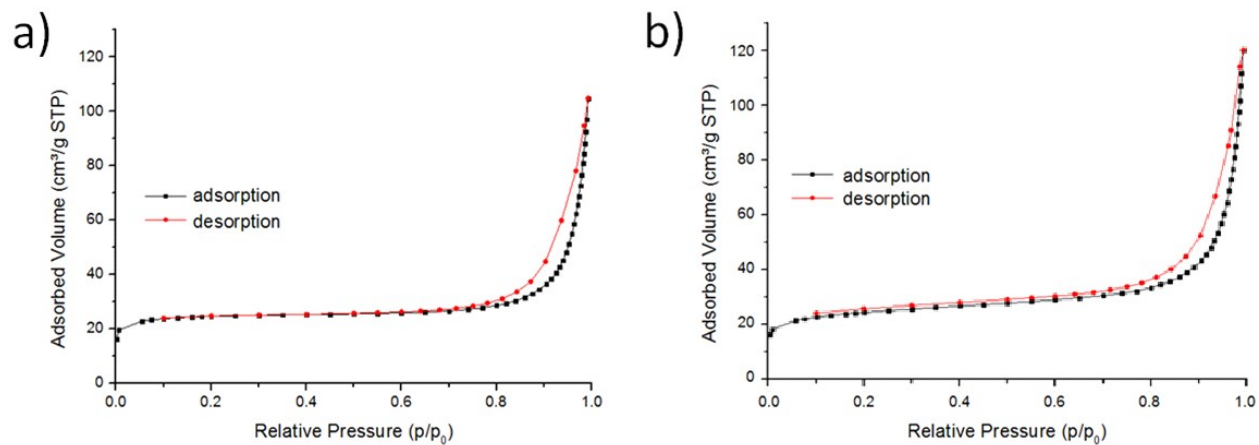


Figure S6. N_2 adsorption-desorption isotherms at -196°C of CDO-type zeosil samples before (a) and after water intrusion-extrusion experiments (b).

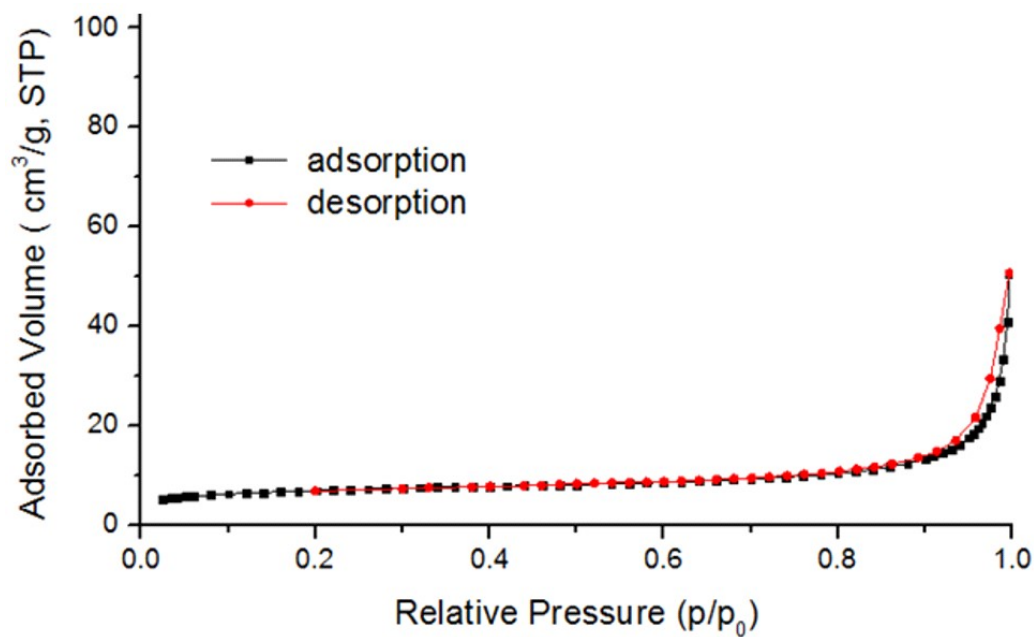


Figure S7. N_2 adsorption-desorption isotherms at -196°C of MTF-type zeosil.

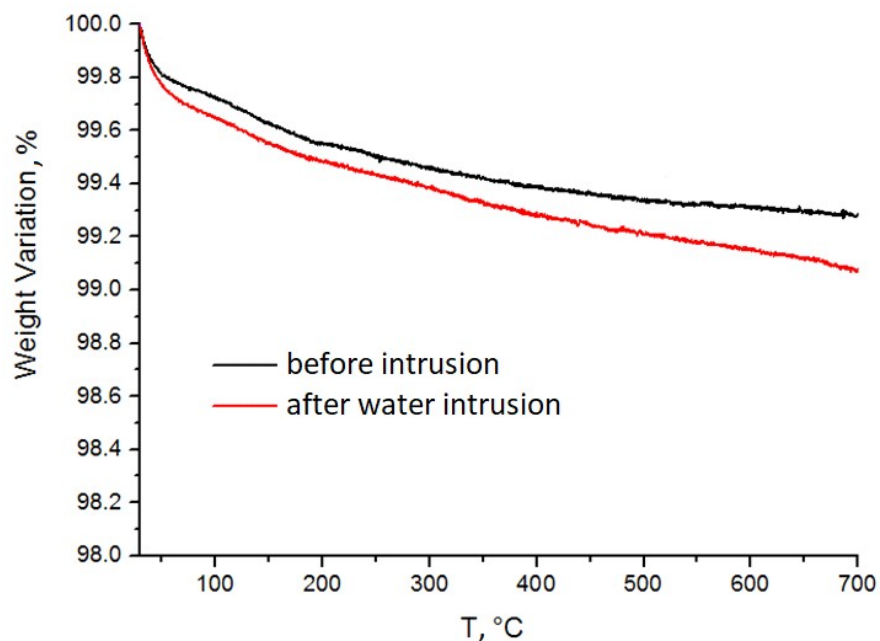


Figure S8. Thermogravimetric curves of MTF-type zeosil before and after water intrusion-extrusion.

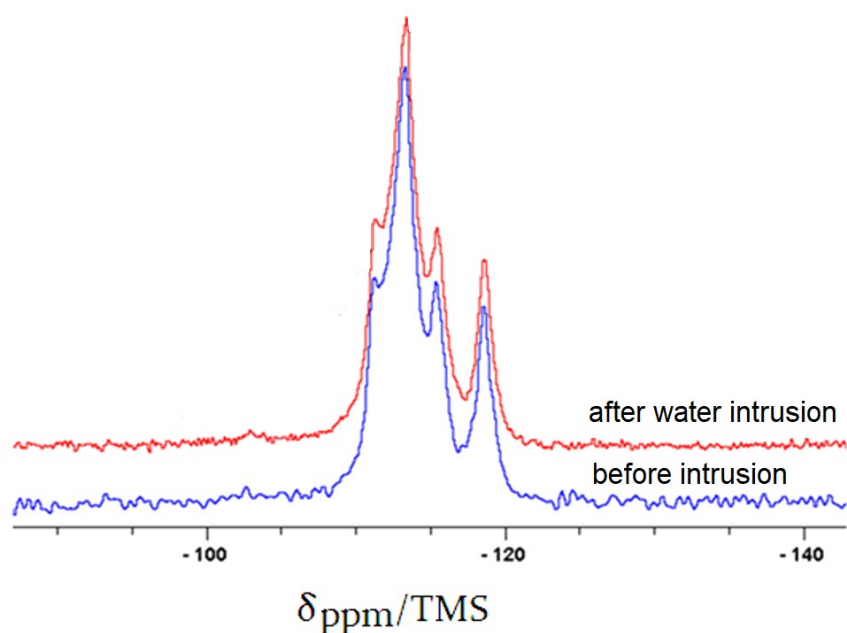


Figure S9. ^{29}Si MAS NMR spectra of MTF-type zeosil before and after water intrusion-extrusion. The resonances at -111.3, -113.4, -115.5 and -118.6 ppm correspond to Q_4 groups that can be ascribed to the six non-equivalent crystallographic silicon sites of the MTF framework in agreement with the literature (five resonances found by deconvolution of the spectrum with approximate relative intensities of 2 : 2 : 3 : 2 : 2).

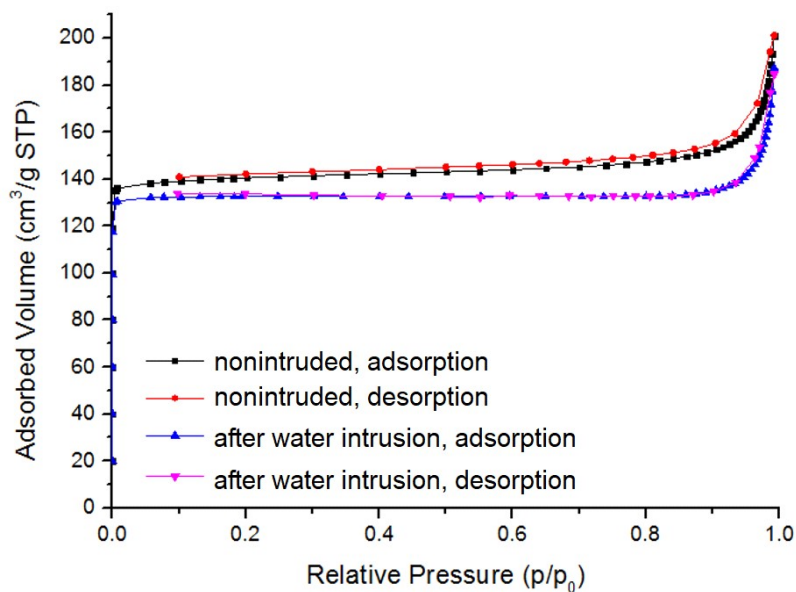


Figure S10. N₂ adsorption-desorption isotherms at -196°C of ITE-type zeosil before and after water intrusion-extrusion.

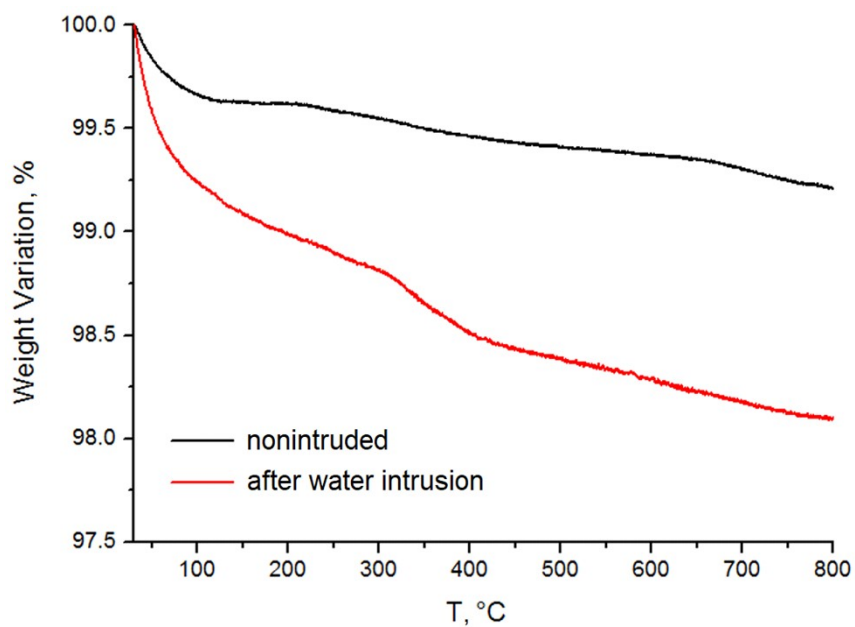


Figure S11. Thermogravimetric curves of ITE-type zeosil samples before and after water intrusion-extrusion.

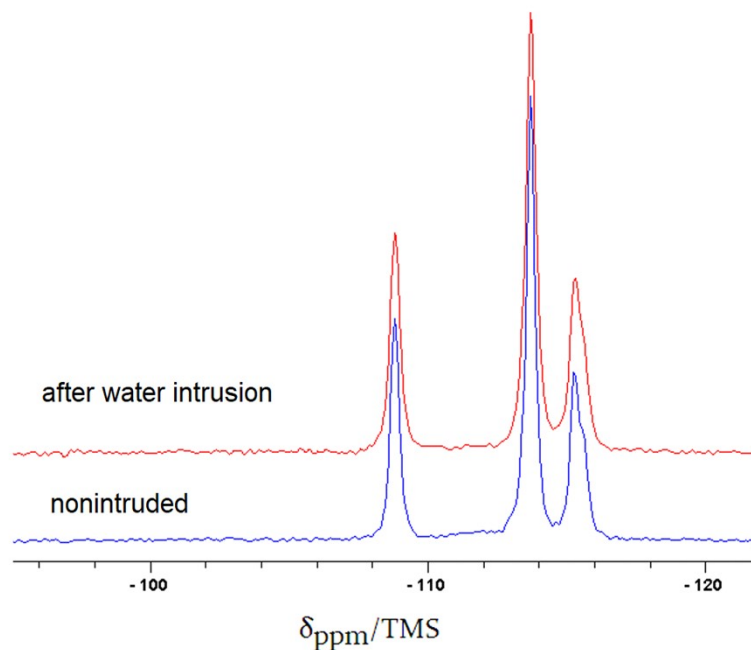


Figure S12. ^{29}Si -MAS NMR spectra of the ITE-type zeosil before and after water intrusion-extrusion. Four resonances in Q_4 region at -108.8, -113.7, -115.3 and -115.6 ppm corresponding to the four distinct crystallographic silicon sites of ITE unit cell are observed.

References

- [1] Database of Zeolite Structures. Available online: <http://www.iza-structure.org>