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Intrusion–extrusion spring performance of –COK-14 zeolite enhanced by structural changes

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–COK-14 zeolite, the variant of COK-14 (OKO topology) with a systematically interrupted framework, exhibits unusual behaviour in high pressure intrusion–extrusion cycles of 20 M LiCl solution. After the first cycle with deviating behaviour and partially irreversible intrusion, subsequent cycles show stable reversible behaviour. The system behaves like a spring with unique progressive intrusion in the range of 10–120 MPa followed by enhanced uptake before saturation. While the intrusion–extrusion cycling leads to fragmented crystals, powder diffraction reveals high crystallinity of the fragments. Based on the detailed characterisation of the zeolite samples with XRD, Rietveld refinement, N₂ adsorption, TGA and ²⁹Si MAS NMR before and after intrusion–extrusion experiments, a model of the structure of the intruded –COK-14 samples is proposed. Intrusion–extrusion of LiCl solution systematically breaks the most strained bonds in the structure which results in a new framework connectivity with enhanced stability, which persists during the harsh intrusion–extrusion conditions.

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Introduction

Zeolites, which are crystalline microporous solids, have a wide range of applications in adsorption, separation, ion-exchange heterogeneous catalysis, and other desired functions.¹ Since fifteen years, a new field of application which concerns mechanical energy storage and dissipation has been developed particularly by our group.^{2–4} The basic idea focuses on the intrusion of water into a hydrophobic porous material. Among microporous solids, especially pure silica zeolites (zeosils), well known for their

hydrophobic character, are highly promising for this novel application. To penetrate water in such microporous matrices, high pressure must be applied.⁵ During this forced penetration (intrusion), the mechanical energy can be converted into interfacial energy by dividing the aqueous phase over the large internal surface area of the zeolite. Depending on the various physical parameters related to the pore system (cavities or channels), its dimensionality (1, 2, or 3-D) or pore size, when the pressure is released (extrusion) the “zeosil–water” system is able to restore, dissipate or absorb the supplied mechanical energy during the compression step with a more or less significant hysteresis, displaying a spring, shock-absorber or bumper behaviour.

Several “zeosil–water” systems have already been studied.^{6–15} Water intrusion–extrusion is quite detrimental for zeolites’ structural integrity, and fragmentation of zeolite crystals and even structural collapse are often observed.

Recently this research field was extended to the intrusion of aqueous solutions of electrolytes.^{16–18} Solutions of salts, such as LiCl, were demonstrated to improve the energetic performances of the “zeosil–liquid” systems by a considerable increase of the intrusion pressure. Thus, the intrusion of a 20 M LiCl solution in pure silica MFI-type zeolite led to an increase of the intrusion pressure by a factor of three in comparison to pure water.^{16,17} Most zeosils are prepared by hydrothermal synthesis from a silicate gel in the presence of organic molecule species as a structure-directing agent (SDA). In the past 10–20 years, a considerable effort has been paid to innovative synthesis pathways to form new zeosils. One of the most attractive synthesis strategies consists in the use of layered silicates as starting materials

(also called layered zeolite precursor, LZP¹⁹) which are transformed by a topotactic solid-state dehydration–condensation reaction into a perfect porous 3D silicate framework structure upon calcination. By this way known or new zeosils were obtained. This was the case for instance for the pure silica FER-type zeolite and the RRO-type zeosil (RUB-41) prepared by calcination of the layered materials PREFER²⁰ and RUB-39,²¹ respectively. A related synthesis route was recently developed to prepare layered zeolite precursors. It consists in the removal of germanium species from certain microporous germanosilicates. One of the most popular cases is the use of the IM-12 zeolite with UTL topology,²² which displays a two-dimensional channel system with 12- and 14-membered rings (MRs). Its 3D-structure can be described as the stacking of silicate layers connected by double four ring (D4R) units, the latter being suggested to consist of a germanate and a silicate four ring. Roth *et al.*^{23,24} demonstrated that the 3D framework of the UTL-type zeolite can be selectively disassembled into layered subunits and Verheyen *et al.*²⁵ discovered that removal of germanium atoms by treatment with strong acid directly converts IM-12 zeolite into pure silica –COK-14 material which is an interrupted framework with dangling OH groups.^{25,26} The –COK-14 structure displays a two-dimensional channel system with interconnected 10- and 12-MRs and is composed of exactly the same silicate layers, which originally were present in the UTL topology. These layers are connected no longer by a cube-like double four-ring but rather by silicate pairs, whereof each silicon atom is linked to the top and bottom layer, the second silicon atom and a hydroxyl. The latter are found to strongly interact with hydrogen bonded water molecules and high temperatures are necessary to remove this chemisorbed water and to close the interrupted –COK-14 structure into a fully connected COK-14 with OKO zeolite topology, where the UTL-layers are now connected by single four rings.^{25,26}

In the present work, the energetic performance of –COK-14 during water and electrolyte (20 M LiCl aqueous solution) intrusion–extrusion experiments is studied. The samples, before and after these experiments, were characterised by powder X-ray diffraction SEM, thermogravimetric analysis, N₂ porosimetry, and ²⁹Si MAS NMR spectroscopy. A Rietveld refinement was also performed to elucidate the structural changes caused by the intrusion and extrusion process.

Experimental section

Synthesis of –COK-14

The –COK-14 sample was synthesised using an earlier published protocol.^{25,26} The starting material, the silicogermanate IM-12 (UTL-structure type), was leached with concentrated HCl for eliminating germanium and thoroughly washed until it was free from chloride and germanium. The obtained –COK-14 was dried at 60 °C and stored at ambient temperature.

Intrusion–extrusion experiments

The intrusion–extrusion experiments of water and 20 M LiCl aqueous solution in the –COK-14 sample in the form of

compressed and preliminary degassed pellets were performed at room temperature using a modified mercury porosimeter (Micromeritics Model Autopore IV), as described previously.¹⁴ The experimental intrusion–extrusion curves were obtained after subtraction of the curve corresponding to the compressibility of pure water or LiCl aqueous solution. The values of the intrusion (P_{in}) and extrusion (P_{ex}) pressures correspond to that of the half volume total variation. Pressure is expressed in megapascals (MPa) and volume variation in millilitres (mL) per gram of calcined samples. The experimental error on the pressure and on the volume is estimated to be α . 1%.

After intrusion–extrusion experiments, the samples intruded with LiCl aqueous solution were washed with water to remove traces of LiCl. The absence of chloride in the filtrate was verified by the absence of silver chloride precipitate upon addition of a few drops of 1 M silver nitrate aqueous solution. Then the samples were dried at 60 °C overnight, and hydrated in an 80% relative humidity atmosphere for 24 h to restore the hydration state.

Powder X-ray diffraction

X-ray diffraction patterns of the different samples were recorded in a Debye–Scherrer geometry on a STOE STADI-MP diffractometer equipped with a curved germanium (111) primary monochromator and a linear position-sensitive detector ($6^\circ 2\theta$) using Cu K α_1 radiation ($\lambda = 0.15406$ nm). Measurements were recorded between 3 and 80° 2θ , with a resolution of 0.01°. Before measurements the samples were gently dried at 110 °C. TG measurements (*vide infra*) indicated that at this temperature all physisorbed, but not hydrogen-bonded chemisorbed, water is removed. Rietveld refinement was performed using the GSAS software package.^{27,28} A number of different framework interruptions were tested, whereof the starting configurations for refinement were generated by forcefield optimisation in the GULP program, using the well-established Catlow forcefield.^{29,30}

Scanning electron microscopy

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

Nitrogen adsorption–desorption measurements

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 300 °C overnight under vacuum. The intruded–extruded samples but also the nonintruded samples were outgassed at 90 °C overnight under vacuum to eliminate physisorbed water and to avoid the dehydroxylation process. The specific surface area (S_{BET}) and microporous volume (V_{micro}) were calculated using the BET and t -plot methods, respectively.

Thermal analysis

Thermogravimetric (TG) analyses were carried out on a Mettler-Toledo TG/DSC Star[®] System apparatus, under air flow, with a heating rate of 5 °C min^{–1} from 30 to 800 °C.

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

	^{29}Si	
	MAS	CP MAS
Chemical shift standard	TMS ^a	TMS ^a
Frequency (MHz)	59.6	59.6
Pulse width (μs)	1.87	4
Flip angle	$\pi/6$	$\pi/2$
Contact time (ms)	—	1
Recycle time (s)	80	8 ^b
Spinning rate (kHz)	4	4
Scan number	1070	8000

^a TMS: tetramethylsilane. ^b The relaxation time T_1 was optimised.

Solid-state NMR spectroscopy

^{29}Si MAS (magic angle spinning) and ^1H - ^{29}Si CPMAS (cross polarisation) NMR spectra were recorded at room temperature on a Bruker Advance II 300 MHz spectrometer, with a double-channel 7 mm Bruker MAS probe. The recording conditions are given in Table 1.

Results and discussion

Intrusion–extrusion isotherms: pressure–volume diagrams

The pressure–volume diagrams of the “–COK-14–water” and the “–COK-14–LiCl aqueous solution (20 M)” systems at ambient temperature are shown in Fig. 1. For each system, three intrusion–extrusion cycles were performed. With both water and concentrated LiCl solution, the behaviour was reproducible in different experiments.

As shown in previous studies, the volume variation observed at low pressure (<0.1 MPa) corresponds to the compressibility of the particle bed (pellets) and filling of its interparticular porosity.^{13,17} However, for the “–COK-14–water” system, a large water uptake was observed near atmospheric pressure corresponding

Fig. 1 Pressure–volume diagrams of the “–COK-14–water” and “–COK-14–20 M LiCl” systems for the 1st, 2nd and 3rd intrusion–extrusion cycles. For clarity, the water intrusion–extrusion isotherms were shifted along the Y axis by 0.09 mL g^{−1}.

to spontaneous intrusion of water, indicating –COK-14 to be, to some extent, hydrophilic. The presence of silanol groups in the interrupted framework of –COK-14, which are actively involved in strong hydrogen bonding with water,²⁶ readily explains this behaviour. According to the intrusion isotherms (Fig. 1) no intrusion step is observed at higher pressure.

In the case of the 20 M LiCl solution, the system behaves completely different. A clearly pronounced volume variation, corresponding to intrusion and extrusion, is observed. The first intrusion proceeds gradually from 10 to ca. 120 MPa. Then, a marked intrusion step is observed in the range of 120–180 MPa, and thereafter a plateau is reached upon saturation of the pores. For the first intrusion–extrusion cycle the intrusion pressure is 162 MPa with a total intruded volume of 0.12 mL g^{−1}. Such an intruded volume is quite in agreement with the pore volume determined from N₂ physisorption ($V_p = 0.16 \text{ mL g}^{-1}$, see below) assuming a lower density of the intruded liquid compared to its bulk state, as shown by Desbiers *et al.*³¹ The extrusion pressure is shifted to a lower pressure ($P_{\text{ext}} = 131 \text{ MPa}$) with an extruded volume slightly lower than the intruded one. Hence, part of the liquid (0.015 mL g^{−1}) remains trapped in the solid. This is in accordance with a mixed shock absorber and bumper performance of the “–COK-14–20 M LiCl” system during the first cycle. For the second and third cycles the intrusion curves (with $P_{\text{int}} = 143 \text{ MPa}$) and the extrusion curves (with $P_{\text{ext}} = 131 \text{ MPa}$) are almost identical, indicating a spring behaviour with a small hysteresis. The intruded volume is close to 0.10 mL g^{−1}. In the second and third cycles all the intruded liquid is expelled from the solid during extrusion, indicating that the volume of the trapped liquid in the sample remains the same.

It should be noticed that drastic differences in systems’ responses when comparing water to electrolyte intrusion have been observed before. For example, in the case of high-silica *BEA- and FAU-type zeolites, spontaneous intrusion of water was observed, whereas these systems showed a shock-absorber performance with electrolyte solutions.^{32–35} For pure silica zeolites the change of system behaviour was demonstrated for *BEA- and LTA-type zeolites.^{18,36} In the case of LTA-type zeolite, the bumper behaviour with water changed to mixed shock-absorber/bumper behaviour in the case of LiCl solutions, quite similar to the here reported case of –COK-14. However, it should be noticed that continuous intrusion in the range of 10–120 MPa is characteristic exclusively for the “–COK-14–20 M LiCl” system, which was never observed for other “zeosil–aqueous solution” systems.

The samples after intrusion–extrusion cycles with LiCl were carefully washed before further characterisation. ICP AES analysis confirmed that the samples did not contain any residual Li⁺ or Cl[−] from intrusion–extrusion cycling.

SEM characterization

The crystal morphology of the –COK-14 samples before and after intrusion–extrusion experiments was examined by scanning electron microscopy. Before intrusion, the –COK-14 sample displays a lamellar morphology with a typical crystal size of $5 \times 5 \times 0.2 \mu\text{m}^3$ (see Fig. S1a, ESI†). After intrusion experiments, whatever the nature

of the liquid (water or LiCl solution), most of the crystals are fragmented (see Fig. S1b, ESI†).

TG analysis and N₂ adsorption-desorption measurements

The TG curves of the -COK-14 samples before and after intrusion-extrusion experiments are shown in Fig. 2. For the non-intruded sample three weight losses are observed. The first one, from room temperature to 100 °C, as mentioned by E. Verheyen *et al.*²⁶ corresponds to an arbitrary amount of physisorbed water. The second one (2.8 wt%) occurs between 100 and 340 °C and could be attributed to water molecules tightly bound to the dangling OH groups in the interrupted -COK-14 structure. According to the idealised unit cell formula of this material (Si_{6.8}O_{13.2}(OH)₈(H₂O)₄, the expected weight loss should be close to 1.7 wt% (4 water molecules). Therefore 2.6 additional water molecules are present per unit cell, in close interaction with the silanol functions. The third weight loss occurring between 340 and 600 °C is close to expectation (2 wt% instead of 1.7 wt%). It corresponds to the condensation of the dangling OH groups (dehydroxylation reaction) leading to the condensed OKO topology.²⁵ Whatever the nature of the liquid (water or 20 M LiCl aqueous solution), the TG curves of the intruded-extruded samples display only two main losses. The first one, assigned to an arbitrary amount of physisorbed water molecules, is similar to the one observed for the nonintruded sample. The second one, which corresponds to the removal of water arising from dehydroxylation reactions, occurs in the range of 220–550 °C and 280–650 °C for the 20 M LiCl and water intruded-extruded samples, respectively, and in both cases is close to 2.8 wt%. Surprisingly, it appears that the dehydroxylation reaction occurs at a higher temperature for the water intruded-extruded sample. However, after intrusion-extrusion experiments and as shown below (¹H-²⁹Si CPMAS NMR section) silanol defects resulting from breaking of siloxane bounds are created in both cases. According to the weight loss, this number is close to 4 OH groups per unit cell. It is worth noting that no water molecules bridging the dangling OH groups in the -OKO

Fig. 2 TG curves under air of the -COK-14 samples before and after intrusion-extrusion experiments with water and 20 M LiCl aqueous solutions.

material are evidenced after intrusion experiments. Such a result might indicate a different site for framework disruption (see Rietveld refinement, below), leading to a silanol configuration, which does not allow easy trapping of water molecules.

The textural properties of the different -COK-14 samples were determined by N₂ adsorption-desorption measurements. To avoid a dehydroxylation process, the samples were outgassed at 90 °C under vacuum. Nevertheless, for comparison the nonintruded sample was also outgassed at 300 °C under vacuum. The isotherms are reported in Fig. 3 with the corresponding data in Table 2. They are mainly of type I characteristic of microporous materials with a H4-type hysteresis which, according to the IUPAC recommendation,³⁷ reveals the presence of mesopores (mesoporous zeolite). At high relative pressures ($p/p^\circ = 0.9$) an increase of the adsorbed volume corresponding to interparticular porosity is also observed. Comparison of samples outgassed at 90 and 300 °C shows an increase of pore volume from 0.12 mL g⁻¹ to 0.16 mL g⁻¹. This is in full agreement with the removal of the water molecules, strongly hydrogen-bonded to the systematic silanol functions in -COK-14, at the higher outgassing temperature. For both intruded-extruded samples, the micropore volume is quite similar (0.14–0.15 mL g⁻¹). It is larger compared to the nonintruded sample (0.12 mL g⁻¹) outgassed at the same temperature (90 °C) and quite close to the micropore

Fig. 3 N₂ adsorption-desorption isotherms at -196 °C of the -COK-14 samples outgassed at 90 °C under vacuum: before and after three intrusion-extrusion cycles with water, and with 20 M LiCl aqueous solutions. For comparison the N₂ adsorption-desorption isotherms at -196 °C of the -COK-14 sample outgassed at 300 °C under vacuum before intrusion are also reported. (Filled symbols: adsorption curves; empty symbols: desorption curves.)

Table 2 Textural properties of -COK-14 samples

Sample (outgassing temperature, °C)	S_{BET} (m ² g ⁻¹)	V_{micro} (mL g ⁻¹)
Nonintruded sample (90)	342	0.12
Nonintruded sample (300)	438	0.16
Water intruded-extruded sample (90)	421	0.15
20 M LiCl intruded-extruded sample (90)	392	0.14

volume of the nonintruded sample outgassed at 300 °C (0.16 mL g⁻¹). This observation confirms the suspicion that after intrusion–extrusion cycling no hydrogen-bonded water remains in the structure, which reinforces the hypothesis of a new configuration of silanol-groups in the intruded–extruded –COK-14 materials.

²⁹Si MAS and CP MAS NMR spectra

The ²⁹Si MAS NMR spectra of the nonintruded and intruded–extruded –COK-14 samples are depicted in Fig. 4. All spectra display two components at –102 and –114 ppm (TMS) corresponding to Q₃ (HO–Si–[(OSi)₃] or [–O–Si–[(OSi)₃]]) and Q₄ (Si–[(OSi)₄]) groups, respectively. According to the idealised formula (Si₆₈O₁₃₂(OH)₈(H₂O)₄), the Q₃/Q₄ molar ratio in the –OKO structure is equal to 8/60 = 0.133. For the nonintruded sample this value (0.16) is a little bit higher than the theoretical one. For the intruded–extruded samples the Q₃/Q₄ ratios are significantly higher (0.20–0.22) revealing the creation of defect sites. The defect sites correspond probably to the breaking of siloxane bonds as already observed for RRO¹⁰ and CHA⁷-type zeolites after intrusion experiments.

The whole of these results was confirmed by ¹H–²⁹Si CPMAS NMR experiments. The ¹H–²⁹Si CPMAS NMR spectra of the nonintruded and intruded samples are reported in Fig. S2 (ESI†). These spectra were collected to enhance the sensitivity of those silicon atoms that bear protons and thus highlight the presence of silanol groups. Though the ¹H–²⁹Si CPMAS technique does not provide quantitative results, it still allows a relative comparison of the spectra, when collected under the same conditions. The spectrum of the nonintruded sample (Fig. S2, ESI†) displays a Q₃ component, revealing, as expected, the presence of silanol groups (HO–Si–(OSi)₃). After water and 20 M LiCl intrusion–extrusion experiments (Fig. S2, ESI†), the Q₃ component increases, and even a small signal corresponding to Q₂ sites ((HO–)₂Si–(OSi)₂ groups) is detected at –92 ppm.

Powder diffraction and structure refinement

The XRD patterns of the –COK-14 samples before and after intrusion–extrusion experiments are reported in Fig. 5. They are

Fig. 4 ²⁹Si MAS NMR spectra of the –COK-14 samples before and after intrusion–extrusion experiments with water and 20 M LiCl aqueous solutions.

quite similar, which reveals that long range order is present after intrusion–extrusion experiments. However, after intrusion the reflections are slightly shifted indicating small changes of the lattice constants. This is best shown for the (200) reflection, with the highest intensity located at 7.6° (2θ) which shifts from 7.61 to 7.65° (2θ). In the work of Verheyen *et al.*²⁵ a shift from 7.60 to 7.77° (2θ) was also observed when the interrupted form of –COK-14 was heated and led to the condensed COK-14 with OKO topology. The position of the reflections and the resulting lattice constants for both intruded samples indeed were found between the values of the open and the closed state of COK-14 (see Table 3).

For both samples the powder diffraction patterns appeared well resolved with sharp reflections, so that Rietveld refinement appeared feasible (see Fig. S3, ESI†). However, the attempt to refine the data with the known opened structure of –COK-14, in its typical state at ambient humidity, resulted in low goodness of fit and very high temperature factors for the atoms.

Furthermore, a clear electron density in the region between the opened 4Rs indicated that at least a part of these 4Rs are

Fig. 5 XRD patterns of the –COK-14 samples before and after intrusion–extrusion experiments with water and 20 M LiCl aqueous solution. The inset shows the low angle region.

Table 3 Unit-cell parameters of the different –COK-14 samples and the reliability factors of the Rietveld refinements

	–COK-14	Water intruded sample	LiCl intruded sample
Percentage of intralayer breaks (substructure 2)	0	45	63
<i>a</i> /Å	24.645(4)	24.541(8)	24.404(7)
<i>b</i> /Å	13.9270(3)	13.9186(20)	13.8785(18)
<i>c</i> /Å	12.2644(6)	12.2635(19)	12.2669(15)
Beta/°	109.280(3)	109.351(24)	109.323(16)
GOF	1.42	1.61	1.57
<i>R_p</i> /%	3.30	3.76	3.83
<i>R_{wp}</i> /%	3.92	4.33	5.89
<i>R_F²</i> /%	6.8	8.5	9.7

closed in the materials intruded with either water or aqueous LiCl. A superposition of the closed and opened structure was tried as a model for refinement and led to improved results. However, in the closed substructure still very high temperature factors of atoms in the vicinity of T6 were encountered. This atom is one of those connecting the closed 4Rs to the rest of the layers on top and below (see Fig. 6). Considering also the increased number of Q₃ silicon atoms as observed by NMR, the models were tested for possible breaks in the layer rather than in the connecting 4Rs. The best result was obtained for disconnecting T atoms T6 and T5. This model, a superposition of the known –COK-14 structure with disrupted interlayer 4Rs (substructure 1) with the structure containing a systematic intralayer disruption (substructure 2), led to excellent refinement results for both samples, intruded by either water or LiCl solution. The only difference between these two materials is in the amount of disrupted layers and slight variations in the unit

cell parameters. Indeed the sample intruded by 20 M LiCl solution contained a higher content of intralayer disruption (substructure 2) compared to the water intrusion experiment (63% vs. 45%). As mentioned above, the lattice constants of both materials were found to be situated between the ideal opened and ideal closed COK-14 structures, with the sample containing a lower number of closed 4Rs being closer to the ideal opened structure –COK-14. This result is also in accordance with the observation of a stronger breakdown of the plate-morphology after 20 M LiCl intrusion as increased number of breaks within the layers should easily lead to their fracturing. Furthermore, it stands to reason that the T6 atom, when broken, also is susceptible to leaching, which not only would lead to an increase in the Q₃ number but also can result in Q₂ species, should T6 on both sides of T12 be removed, which might explain the slight Q₂ signal discerned by NMR. The different weight loss behaviour of the intruded samples also can be explained by the found models. The weight loss between 100° and 200 °C in intact –COK-14 results from the removal of water molecules which are strongly hydrogen-bonded between neighbouring opened 4Rs. In the intruded samples, this loss is much less pronounced due to the presence of closed 4Rs and a much lower number of neighbouring opened 4Rs.

Conclusion

The intrusion of water and electrolyte solution in all silica –COK-14 zeolite with an interrupted framework was studied. The zeolite is hydrophilic and demonstrates spontaneous intrusion of water. However, when using 20 M LiCl solution, intrusion–extrusion steps are observed at high pressure. In the first cycle the “–COK-14–20 M LiCl” system shows mixed shock-absorber and bumper behaviour, where part of the liquid (0.015 mL g^{−1}) remains trapped in the solid. In the following cycles the system is completely reversible and demonstrates a spring behaviour with intrusion and extrusion pressure of 143 and 131 MPa, respectively. A particularity of the system is a continuous intrusion in the range of 10–120 MPa, which was never observed previously for other “zeolite–electrolyte solution” systems. While many zeolite structures are degraded upon high pressure intrusion–extrusion cycling, –COK-14 exhibits unusual high stability, owing to structural changes caused by the first intrusion. Based on the structural characterisation, the following model for structural transformations under intrusion–extrusion experiments is proposed. Under high pressure intrusion the fully interrupted –COK-14 structure is partially condensed with closing of interlayer 4Rs. At the same time intralayer disruptions close to the forming 4Rs occur. The resulting structure consists of a mixture of two substructures, whereof one corresponds to an interlayer disrupted state, as observed in the non-intruded –COK-14 material, while the other shows an intralayer disruption which increases the total number of structural OH groups. This model is quite in agreement with the changes of chemical water content determined gravimetrically, textural changes probed with N₂ adsorption and changes in ²⁹Si solid-state NMR spectra.

Fig. 6 Structures of –COK-14 (top) and the refined structure model after intrusion/extrusion cycles (bottom). Left: View along *c*. Right: View along *b*. In pink: substructure 1 corresponding to non-intruded –COK-14. In green: substructure 2 showing structural break between T6 and T5. Large spheres symbolise silanol functions. The structure of non-intruded –COK-14 also shows the labelling of tetrahedron sites as well as the strongly hydrogen-bonded water molecule (W) in blue.

In particular, the much lower number of neighbouring opened interlayer 4Rs can explain the absence of strongly hydrogen bonded water molecules in the intruded samples.

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