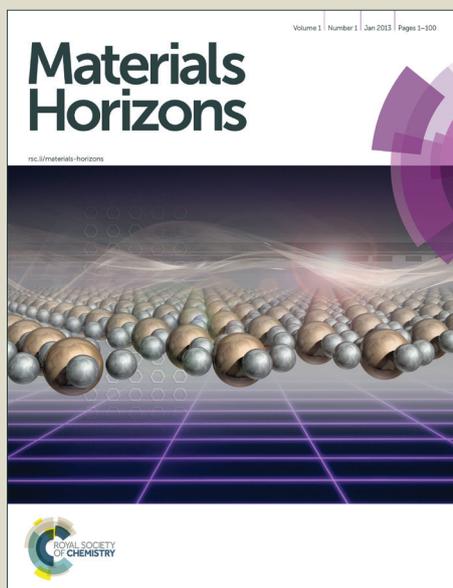


# Materials Horizons

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### Conceptual Insights

Outstanding stability of zeolites is one of the reasons for their success as porous materials in industry. However, the assessment whether or not a hypothetical zeolite topology is stable and accessible to synthesis up to now largely neglected the impact of entropy and framework flexibility. Now, the newly discovered zeolites, -COK-14 and COK-14 with OKO topology, allow a detailed study of entropic and flexibility effects on framework stability. COK-14 is the first zeolite which exists in its fully connected as well as in its systematically interrupted form and can be reversibly transformed between these states. This not only allows rational tuning of porosity and hydrophilicity of this unique material but clearly highlights the importance of framework flexibility. Fully connected siliceous COK-14 is demonstrated as very rigid structure in siliceous form. This renders it unstable at room temperature in presence of humidity. An opening of Si-O-Si bonds occurs spontaneously, resulting in systematically arranged silanol groups and framework flexibility. Only at high temperatures the entropic disadvantage of the rigid, closed structure can be overcome through release of water molecules by re-condensation. The hypothesis that entropic effects are essential to determine the feasibility of a zeolite framework is further highlighted by the observation that the presence of heteroatoms, like Al, with larger bond distances to oxygen compared to silicon, results in perfectly stable, fully closed COK-14 zeolites. It is not surprising that these heteroatoms lend flexibility to the structure as has been determined by theoretical analysis which explains the observation of the heteroatom containing OKO frameworks in fully closed state.

## ARTICLE

# Flexibility versus rigidity: what determines the stability of zeolite frameworks? A case study

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All silica COK-14/-COK-14 with OKO topology is the first case of a zeolite which reversibly transforms from systematically interrupted to fully connected state and back. Analysis of the opening/closing behavior allowed the study of entropy and framework flexibility as determinants for stability of zeolite topologies, which up to now was experimentally inaccessible. Interconversion of all-silica COK-14 zeolite with fully connected OKO topology and its -COK-14 variant with systematic framework interruption was investigated using high-temperature XRD, thermogravimetric analysis, <sup>29</sup>Si MAS NMR, nitrogen adsorption and a range of modelling techniques. Specific framework bonds in OKO framework can be reversibly hydrolyzed and condensed. Structural silanols of the parent -COK-14, prepared by degermanation of IM-12 zeolite, were condensed by heating at 923 K, and hydrolyzed again to the initial state by contacting the zeolite with warm water. Molecular modelling revealed an inversion of the relative stabilities for both variants depending on temperature and hydration. Condensation of the structural silanols in -COK-14 to COK-14 is entropy driven, mainly resulting from the release of water molecules. Framework reopening in presence of water is spontaneous due to the high rigidity of the fully connected OKO framework. Isomorphous substitution was demonstrated as a viable option for stabilization of the fully connected OKO framework as this renders the closed framework flexible.

## Introduction

Idealized zeolite frameworks exclusively contain fourfold connected T-atoms (T = Si, Al, P, etc.). In a fully connected zeolite framework all T-atoms share bridging oxygen atoms with neighboring T-sites. Real zeolites, however, may contain defect sites, lowering the T-atom connectivity. While these

broken links are often statistically distributed, an interruption in four-connected frameworks can also occur periodically. Framework type codes assigned to such periodically interrupted frameworks are indicated by a leading dash, and are encountered in both naturally occurring zeolites (-CHI<sup>1</sup>, -LIT<sup>2</sup>, -PAR<sup>3</sup>, -RON<sup>4</sup>, -WEN<sup>5</sup>) and synthetic materials (-CLO<sup>6,7</sup>, -ITV<sup>8</sup>, -IRY<sup>9</sup>, -SRV<sup>10</sup>). The -COK-14 zeolite, having a systematically interrupted OKO framework, is a recent addition to the interrupted framework zeolite family (Figure 1, top).<sup>11</sup>

-COK-14 materials can be obtained by degermanation of IM-12 zeolite<sup>11</sup> (UTL topology<sup>12,13</sup>). The structure of germanosilicate IM-12 can be described as silicate layers connected by double four-ring (D4R) units. IM-12 with UTL topology has an intersecting two-dimensional channel system circumscribed by 12-membered rings (12-MRs) and 14-MRs. The D4R in IM-12 contains a germanate four-ring (Ge-4R) connected to a silicate four-ring (Si-4R)<sup>11</sup>. Acidic treatment converts IM-12 zeolite to the -COK-14 material by selective removal of the Ge-4R, thereby creating a two-dimensional channel system with interconnecting 8-, 10- and 12-MRs (Figure 1). While Ge removal leaves the silicate layers intact, the 4Rs connecting the layers split symmetrically into T-atom pairs carrying silanol groups, pointing into the 12-MRs of the -COK-14 structure (Figure 1, top). These silanols can be reoriented and condensed resulting in COK-14 (Figure 1, bottom). We investigated these framework annealing and disruption processes with X-ray diffraction, <sup>29</sup>Si MAS NMR, thermal analysis and nitrogen adsorption porosimetry. Theoretical modelling assisted to rationalize the observations based on the stability differences of the interrupted zeolite framework and its fully connected analogue.

## Experimental section

The synthesis of -COK-14 was performed according to the original publication.<sup>11</sup> In short, the parent -COK-14 sample, denoted -COK-14(H1), was obtained by slurrying freshly calcined IM-12 zeolite in concentrated hydrochloric acid (1 g IM-12 in 42.4 mL HCl, 12 M, from VWR) in a 60 mL polypropylene bottle for 2 days at 363 K.

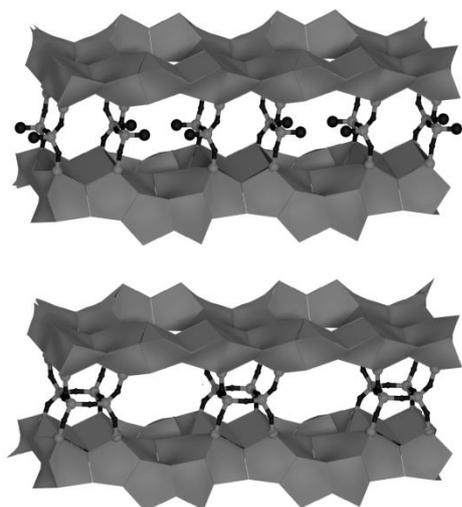


Figure 1 : Top: Framework of -COK-14 and bottom: COK-14 (OKO framework type code), viewed along the 12-MR pores. Structural silanol groups in -COK-14, depicted with balls and sticks, protrude into the 12-MR channels (top).

-COK-14(H1) was recovered by centrifugation and washed till the water reached pH 6, and dried overnight at 333 K.

First time condensed COK-14 sample, denoted as **COK-14(C1)**, was obtained by heating -COK-14(H1) at 923 K under nitrogen flow for 6 h using a temperature ramp of 1 K min<sup>-1</sup>. To prevent back transformation to -COK-14, rehydration was carefully avoided during cooling, sample storage and manipulation.

COK-14(C1) was hydrolyzed to the interrupted **-COK-14(H2)** by suspending the powder in water at 333 K for 1 day.

**COK-14(C2)** was obtained by heating -COK-14(H2) again at 923 K, similar as done for COK-14(C1).

A detailed description of X-ray diffraction, <sup>29</sup>Si MAS NMR, nitrogen adsorption, thermogravimetric analysis and computational approaches is available in Supporting Information.

## Results and discussion

Parent -COK-14, denoted -COK-14(H1), and the fully connected COK-14 obtained by heating -COK-14(H1) at 923 K, denoted COK-14(C1), have distinct XRD patterns (Figure 2). Indexing of the powder XRD pattern of COK-14(C1) in spacegroup C2/m resulted in a unit cell of  $a = 24.13$  Å,  $b = 13.79$  Å,  $c = 12.30$  Å and a monoclinic angle of 109.60° compared to  $a = 24.64$  Å,  $b = 13.94$  Å,  $c = 12.26$  Å and  $\beta = 109.22^\circ$  for -COK-14(H1). A listing of all h k l reflections, and corresponding 2theta positions, d spacings and relative intensities, of -COK-14 and COK-14 in the 2 – 30° 2theta range is provided in Table S1 in Supplementary Information.

The transformation of -COK-14 to COK-14 is revealed by the altered diffraction pattern, and is most clearly visible by the shift of the 2 0 0 reflection from 7.60 to 7.77° 2theta (Figure 2). Near to the 2 0 0 reflection in the 7.2 to 8° 2theta range, the 0 0 1 and 1 1 0 reflections are present (Figure 2).

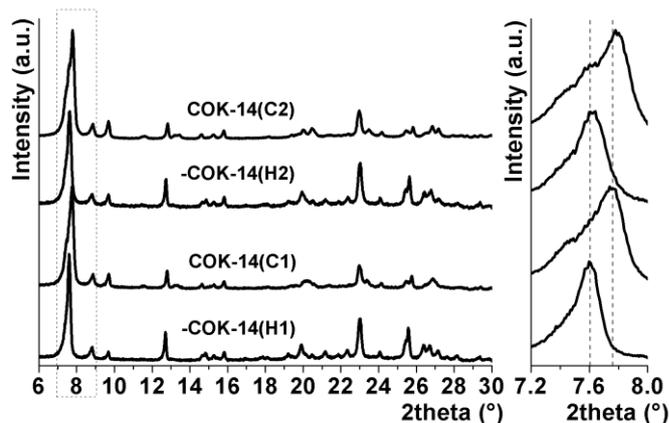


Figure 2 : X-ray diffraction patterns of -COK-14(H1), COK-14(C1), -COK-14(H2) and COK-14(C2) zeolites. Magnification of the 7.2 - 8° 2theta range highlights the shifting of the 2 0 0 reflection between 7.60 and 7.77° 2theta (dashed lines) during transformation.

The shift of both reflections, resulting from the framework transformation, is documented in Figure S1 and Table S1 in Supplementary Information. COK-14(C1) was slurried in warm water (333 K) to provoke transformation to -COK-14, denoted -COK-14(H2), through hydrolysis of the layer-connecting 4Rs (Figure 1). X-ray diffraction patterns of the original -COK-14(H1) sample and -COK-14(H2), obtained after condensation of -COK-14(H1) at 923 K and subsequent hydrolysis in water, were almost identical (Figure 2), showing the reversibility of the transformation.

-COK-14(H2) was heated a second time at 923 K. The XRD patterns of the resulting sample, denoted COK-14(C2), and the first time condensed sample, COK-14(C1), strongly resembled each other (Figure 2). The 2 0 0 reflection was fully shifted to 7.77° 2theta. The remaining signal around 7.62° 2theta resulted from the 0 0 1 reflection (Figure S1, Table S1). It was observed that the diffraction pattern of COK-14(C2), obtained after condensation, hydrolysis and second condensation, improved in quality and resolution. This can be seen as indication that cycling between both states has a positive influence on the integrity of the overall structure.

Using a high temperature reaction chamber allowed to follow this framework transformation in situ and record XRD patterns at 50 K intervals while heating the sample from room temperature to 1073 K under a continuous flow of dry nitrogen. The structural transformation of -COK-14(H1) to COK-14(C1) was probed by monitoring the shift of the 2 0 0 reflection (Figure 3). At temperatures up to 573 K, the 2 0 0 reflection was at 7.6° 2theta, characteristic of the systematically interrupted framework. From 573 K onwards, the transformation gradually proceeded, as traced by the 2 0 0 reflection (Figure 2). At 923 K, the fully connected framework was obtained and no changes were detected while further heating up to 1073 K. The position of the 2 0 0 reflection in function of temperature for all recorded X-ray diffraction patterns is shown in Figure S2 in Supplementary Information.

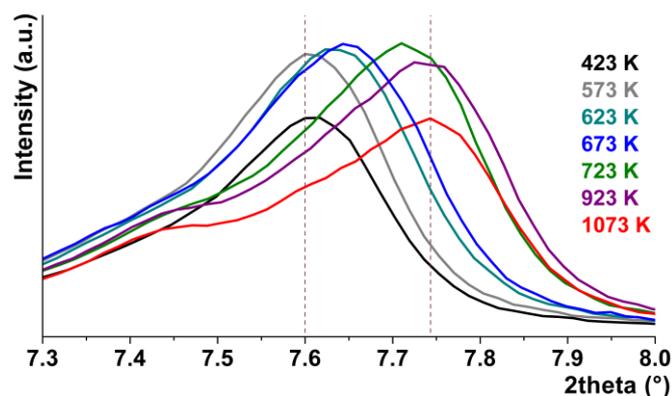


Figure 3 : X-ray diffraction patterns at the 2 0 0 reflection recorded at stepwise increased temperature, revealing transformation of -COK-14(H1) to COK-14(C1) in the temperature range 573 – 923 K.

While XRD reflected the global state of the structure,  $^{29}\text{Si}$  MAS NMR allowed observation of the bonding state of the silicon atoms in the frameworks. The spectra of -COK-14(H1), COK-14(C1), and -COK-14(H2) are reported in Figure 4. Chemical shifts and signal intensities of the quantitative  $^{29}\text{Si}$  MAS NMR spectra of -COK-14(H1) and COK-14(C1) are given in Table S2 in Supplementary Information. All spectra show signals in the regions of 4-fold and 3-fold connected silicon atoms ( $\text{Q}^4$  and  $\text{Q}^3$ , respectively). In the broadened  $\text{Q}^4$  region of COK-14(C1) two maxima can be discerned, at  $\delta = -109$  and  $\delta = -114$  ppm, respectively. The interrupted frameworks -COK-14(H1) and -COK-14(H2) show a main signal centered at -111 ppm, which confirms the reversibility of the transformation.

The  $\text{Q}^3$  regions allow quantitative determination of the content of silanol groups in the zeolites. The idealized unit cell composition of -COK-14 corresponds to  $\text{Si}_{68}\text{O}_{132}(\text{OH})_8$ <sup>11</sup>, resulting in a concentration of 11.7%  $\text{Q}^3$  silicon atoms carrying an OH group ( $\text{Q}^3$  silicon atoms;  $\delta \sim -101$  ppm). The experimental content of  $\text{Q}^3$  silicon atoms in -COK-14(H1), determined with  $^{29}\text{Si}$  MAS NMR, was 13%, slightly exceeding this theoretical value (Table S2). Heating at 923 K, which according to XRD leads to the condensed COK-14(C1) with unit cell composition  $\text{Si}_{68}\text{O}_{136}$ , removed the majority of  $\text{Q}^3$  silicon atoms down to 4%. The residual  $\text{Q}^3$  silicon atoms could be due to defect sites already present in -COK-14(H1) before heating, or disruption of some bonds in the layers upon heating resulting in additional silanol groups, or to incomplete condensation of the systematic silanol groups. Exposure to water at 333 K to form the interrupted -COK-14(H2), increases the  $\text{Q}^3$  silicon atom concentration at the expense of  $\text{Q}^4$ , reaching a value of 16%, slightly exceeding the value of 13% for -COK-14(H1). The  $^{29}\text{Si}$  MAS NMR spectrum of -COK-14(H2) can be fitted as a linear combination of 77% -COK-14(H1), 21% COK-14(C1) and 2%  $\text{Q}^3$  silanols, as shown in Figure S3 in Supplementary Information. -COK-14(H2) is therefore nearly fully reopened according to  $^{29}\text{Si}$  MAS NMR.

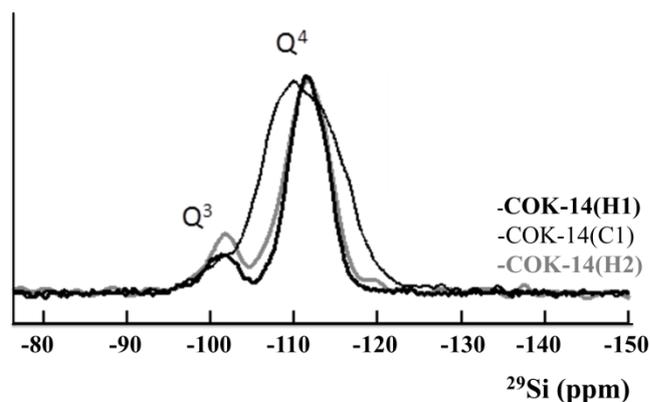


Figure 4 :  $^{29}\text{Si}$  MAS NMR spectra of -COK-14(H1), COK-14(C1) and -COK-14(H2).

The structural changes associated with the reversible transformation of -COK-14 to COK-14 zeolite are mirrored in the microporosity of the samples, as characterized by nitrogen adsorption (Figure S4). The specimen with structural hydroxyls, -COK-14(H1) and -COK-14(H2), have similar micropore volume (0.146 and 0.145 mL/g, respectively) and pore size (0.67 and 0.68 nm, respectively), substantially different from the fully connected sample COK-14(C1) having a pore volume of 0.160 mL/g and a pore size of 0.78 nm. The differences can be explained by silanol groups systematically pointing into the 12-MR channels of the interrupted framework (Figure 1, top)

The physical and chemical water content of -COK-14 samples was quantified by thermogravimetric analysis (TGA) (Figure 5). Upon heating of -COK-14 samples three weight loss steps could be discerned. In a first step till ca. 350 K, an arbitrary amount of physisorbed water molecules was removed. Subsequent weight loss in the temperature range 350-475 K on -COK-14(H1) and 350-600 K on -COK-14(H2) represented ca. 1.6 weight-%, while the third, more gradual loss also represented a weight fraction of 1.6%. Transformation of the -COK-14(H1) and -COK-14(H2) samples to the condensed form of COK-14 after TGA was confirmed with XRD. The TGA pattern is consistent with the presence of 4 tightly bound water molecules per unit cell, bridging the structural silanol groups (Figure 6). DFT calculations indicated the adsorption energy of such bridging water molecules to be as high as  $152 \text{ kJ mol}^{-1}$  for the first water molecule, hence explaining the high temperature necessary for desorption.<sup>11</sup> The weight loss in the temperature range 350-475 K on -COK-14(H1) and 350-600 K on -COK-14(H2) of about 1.6 weight-% corresponds to the desorption of these 4 tightly bound water molecules per unit cell. The additional further weight loss can be explained by the release of 4 water molecules per unit cell stemming from condensation of the structural silanols. When loosely held water is discarded, the idealized unit cell composition of interrupted and fully condensed OKO zeolites correspond to  $\text{T}_{68}\text{O}_{132}(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ , and  $\text{T}_{68}\text{O}_{136}$ , respectively, corresponding to a content of ca. 3.2 weight-% of strongly physisorbed and chemical water. The TGA analysis of -COK-14(H1) and -COK-14(H2) revealed such water contents.

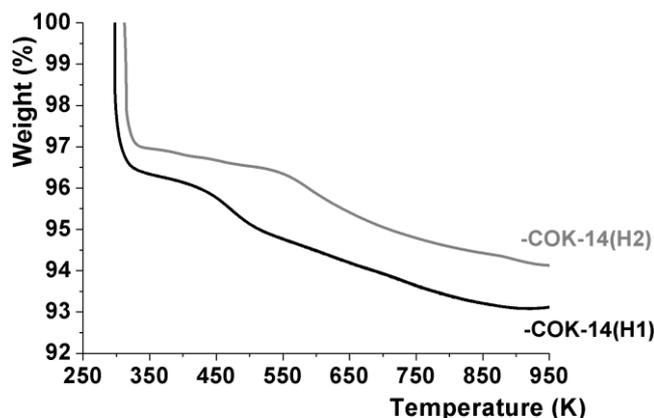


Figure 5 : Thermogravimetric analysis of -COK-14(H1) and -COK-14(H2).

At ambient conditions, hydration of COK-14(C1) causes spontaneous interruption of the structure, but the process is slow. After 1 month, a partially reopened sample called -COK-14(H2-43%) was formed. The  $^{29}\text{Si}$  MAS NMR spectrum and XRD pattern are shown in Figures S3 and S5 in Supplementary Information. -COK-14(H2-43%) was only partially converted as evidenced by the 2 0 0 reflection at  $7.69^\circ 2\theta$ . The  $^{29}\text{Si}$  MAS NMR spectrum could be fitted as a linear combination of 43% -COK-14(H1) and 57% COK-14(C1).

Until the discovery of -COK-14, SSZ-74 zeolite (-SRV topology) was the only example of a purely siliceous framework with systematic framework interruption. While calcination of -SRV leads to irreversible loss of crystallinity<sup>10</sup>, the interrupted framework of -COK-14 can thermally be transformed to the highly crystalline and fully connected COK-14 with OKO framework type code<sup>11</sup> (Figure 1, bottom). This contrasting behavior can be explained by the distribution of the silanol groups. In -COK-14, structural silanols are located pairwise, suitable for condensation reaction, while in SSZ-74 they are isolated. The large distance between nearest silanol sites in the latter explains why this zeolite cannot be calcined beyond the stability temperature of its silanol groups. A range of modelling techniques was applied to gain more insight in this remarkable structural transformation.

A set of DFT calculations was performed to obtain quantitative insight to the various contributions of the free energy determining the framework transformation from -COK-14 to COK-14. The methodology is outlined in the computational section in Supplementary Information. Figure 7 provides a summary of the energetic ( $\Delta H$ ) and entropic ( $T\Delta S$ ) contributions to the free energy ( $\Delta G$ ). Since framework condensation involves the release of four water molecules per unit cell upon silanol condensation, energetic comparisons are made between the interrupted framework and the condensed state enclosing four water molecules. At 0 K (Figure 7 a), the electronic energy difference ( $\Delta E_0$ ) including zero-point-energies reveals a  $161 \text{ kJ mol}^{-1}$  lower energy for the interrupted framework. Such an energy difference per unit cell is substantial and correlates to the high temperature required for framework condensation. Including thermal effects, however, is essential for the evaluation of the free energy profile during condensation. Since both enthalpy (Figure 7,  $\Delta H$ ) and entropy (Figure 7,  $T\Delta S$ ) terms are significantly contributing to the overall free energy (Figure 7,  $\Delta G$ ) of the

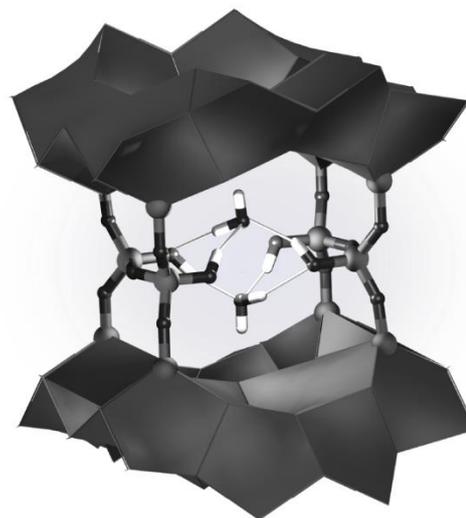


Figure 6 : Framework fragment of -COK-14, illustrating the bridging of 4 silanol groups with 2 water molecules (DFT calculation at 0 K).

interrupted framework releasing water molecules upon condensation, full vibrational analysis was essential for calculating the various thermal contributions and entropy term contributing to the free energy. At 300 K (Figure 7 b), the interrupted framework appears slightly less stable according to its free energy ( $4 \text{ kJ mol}^{-1}$  higher energy compared to the condensed framework) including thermal corrections and the entropy term. The release of four water molecules upon framework condensation is entropically favored ( $T\Delta S < 0$ ) and at 300 K, this contribution ( $T\Delta S = -148 \text{ kJ mol}^{-1}$ ) is enough to achieve an overall more stable condensed state. Inspecting the entropy terms of the framework itself revealed the interrupted framework has a slightly higher entropy resulting from its higher degree of flexibility. The additional stabilization of the interrupted -COK-14 due to the four tightly bound water molecules per unit cell (Figure 5, Figure 6) has not been taken into account in the DFT calculations. Including these bridging water molecules would probably demonstrate the thermodynamical preference of the periodically interrupted -COK-14 at 300 K, as experimentally observed. At 700 K (Figure 7 c), the entropy contribution ( $T\Delta S = -312 \text{ kJ mol}^{-1}$ ) exceeds the enthalpic contribution ( $\Delta H = 121 \text{ kJ mol}^{-1}$ ) thus favoring framework condensation ( $\Delta G = -191 \text{ kJ mol}^{-1}$ ). The results indeed explain the observation that the framework can be annealed at elevated temperatures. Although this analysis contains some simplifying approximations, such as the harmonic oscillator approach and full recovery of all degrees of freedom, it allows assignment of the different factors determining the energetic evolution upon framework condensation. As shown in Figure 7, the enthalpic term always favors the interrupted state, while the entropic contribution increases with temperature and favors the condensed framework. The framework transformation from the interrupted to the condensed framework is thereby entropy driven.

In addition to the energetic approach discussed above, the potential of a zeolite for reversible framework condensation can be linked to framework flexibility in combination with the systematic presence of vicinal silanol groups. Framework flexibility is essential to allow accommodation of small shifts in the T-atom positions resulting from the condensation of the silanol pairs.

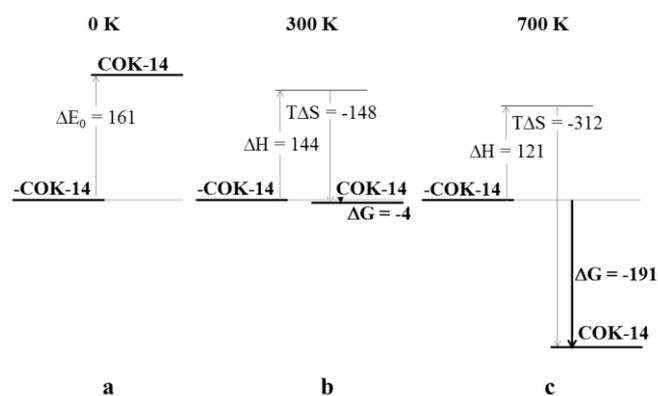


Figure 7 : Energy profiles of the condensed OKO framework enclosing four water molecules per unit cell ( $T_{68}O_{136} + 4 H_2O$ ) compared to the interrupted state of  $-COK-14$  ( $T_{68}O_{132}(OH)_8$ ) at (a) 0 K, (b) 300 K and (c) 700 K. Energies are reported in  $\text{kJ mol}^{-1}$  per unit cell and with respect to the energy of the interrupted  $-COK-14$  structure.

Geometrically, the flexibility window of a zeolite can be assessed by representing the framework as a periodic assembly of rigid, regular  $SiO_4$  tetrahedra that have force-free 'spherical' joints at the tetrahedral corners where the oxygen atoms reside.<sup>14-16</sup> Such idealized models allow to represent all known zeolite frameworks within a limited density range, called the flexibility window, wherein strain is removed by rotation of the T-O-T linkages (T = Si, Ge, or Al). Although the Si-O bond length, and the O-Si-O angle are strongly constrained in pure silicates, the variability of the Si-O-Si angles<sup>17</sup> provides flexibility to 97% of the known frameworks. The remaining 3% can be obtained only when larger tetrahedra (such as  $AlO_4$  and  $GeO_4$ ) are incorporated at some sites. Compared to pure aluminosilicates, germanosilicates tend to be more flexible because germanates exhibits slightly 'softer', or less-rigid, tetrahedra, thereby allowing Ge-O-Ge angles in the range  $116^\circ - 135^\circ$ .

This geometric flexibility analysis reveals that the interrupted framework of  $-COK-14$  is flexible when represented as an idealized pure silicate in its full symmetry,  $C2/m$ . In contrast, oxygen-neighbor overlap prevents flexibility in the fully 4-coordinated all-silica **OKO** framework of  $COK-14$ , even when its symmetry is reduced to  $P1$ . This result explains the observation that the siliceous fully condensed  $COK-14$  is not stable and spontaneously transforms to  $-COK-14$  upon contact with humidity. As an idealized, pure germanate however,  $COK-14$  becomes flexible in  $C2$  symmetry, although one of the Ge-O-Ge angles drops to  $108.7^\circ$ , which is small even for a germanate material. This observation provided an indication that flexibility can be restored to the silica-rich  $COK-14$  framework by partial isomorphous substitution of Si by Ge. Indeed, the minimal requirement to restore flexibility in  $COK-14$  is a reduction of the unit cell symmetry to  $P1$  in combination with substitution of Si for Ge at either site 1 or site 9 to give a nominal unit cell composition of  $Si_{32}Ge_2O_{68}$  with Si/Ge ratio of 16. The increased Ge-O distance relative to Si-O at these sites is sufficient to avert oxygen atom overlaps in the framework.

Framework energy calculations (GULP, SLC potential) not only support the conclusions of the geometric flexibility analysis, but also explain why the broken framework  $-COK-14$  is the most stable geometry for this material in siliceous form. The calculations indicate a lower energy ( $0.1435 \text{ eV/SiO}_2$  relative to quartz) for the

pure silicate form of  $COK-14$  when optimized in  $C2$  space group symmetry, as compared to  $C2/m$  symmetry ( $0.1518 \text{ eV/SiO}_2$  relative to quartz). Even in the lower  $C2$  symmetry, the structure can only be relaxed by substituting Si for Ge in more than 50 percent of the T6 sites (as labeled in the higher  $C2/m$  symmetry), which would indicate a maximum Si/Ge ratio of 16. The experimentally determined Si/Ge ratio of 110 for as made  $-COK-14$  consequently is too high to render enough flexibility to the **OKO** framework.

This also implies that stabilization of  $COK-14$  requires the introduction of heteroelements such as  $GeO_4$  or  $AlO_4$ , thereby providing flexibility. Experimental evidence demonstrating this strategy for stabilization of  $COK-14$  was recently reported.<sup>18</sup> In contrast with the all-silica zeolite  $COK-14$ , the aluminosilicate version of this zeolite, obtained by framework condensation of Al-ALD aluminated  $-COK-14$ , did not return to its interrupted form upon hydration and remained stable in ambient conditions for at least 6 months.

## Conclusions

$COK-14/-COK-14$  is the first reversible transformation encountered between a fully connected zeolite framework and an interrupted analogue, influencing hydrophilicity and porosity. Experimental evidence in combination with two unrelated theoretical analysis methods evaluating respectively energetic and framework flexibility aspects, not only demonstrate and document the mechanism of the framework condensation, but also explain the high temperature requirements for condensation of  $-COK-14$  and the experimentally observed instability of all-silica, condensed framework zeolite  $COK-14$ . This information was exploited for formulating a strategy for stabilization of such frameworks by incorporation of suitable heteroelements and allowed to interpret and confirm recently published experimental results involving Al-ALD modified  $COK-14$ . These results show that introduction of trace amounts of germanium or aluminum provides stability to the condensed **OKO** framework by introduction of flexibility thereby broadening the potential for application of this recently discovered large pore zeolite in industrial applications. This work also demonstrates that the impact of entropy, including framework flexibility, need to be considered in assessment of framework feasibility and development of new zeolite syntheses.

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## Notes and references

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