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Design of zeolite by inverse sigma transformation

Elke Verheyen[1], Lennart Joos[2], Kristof Van Havenbergh[3], Eric Breynaert[1], Nataliia Kasian[1,4], Elena Gobechiya[1], Kristof Houthoofd[1], Charlotte Martineau[5], Manuel Hinterstein[6], Francis Taulelle[5], Veronique Van Speybroeck[2], Michel Waroquier[2], Sara Bals[3], Gustaaf Van Tendeloo[3], Christine E. A. Kirschhock[1]* and Johan A. Martens[1]

Although the search for new zeolites has traditionally been based on trial and error, more rational methods are now available. The theoretical concept of inverse σ transformation of a zeolite framework to generate a new structure by removal of a layer of framework atoms and contraction has for the first time been achieved experimentally. The reactivity of framework germanium atoms in strong mineral acid was exploited to selectively remove germanium-containing four-ring units from an UTL type germanosilicate zeolite. Annealing of the leached framework through calcination led to the new all-silica COK-14 zeolite with intersecting 12- and 10-membered ring channel systems. An intermediate stage of this inverse σ transformation with dislodged germanate four-rings still residing in the pores could be demonstrated. Inverse σ transformation involving elimination of germanium-containing structural units opens perspectives for the synthesis of many more zeolites.

Since their discovery, the synthesis of zeolite frameworks has boosted the development of sustainable chemical technology. Following the first synthetic aluminium-rich zeolites in the 1940s, successive waves of zeolites have emerged, including silicon-rich and transition metal-substituted silicate zeolites, aluminophosphates and substituted specimens. The key requirements for application of a zeolite are the accessibility of catalytic and adsorptive centres and the ability to withstand reaction and regeneration conditions. So far about 200 zeolite frameworks have been synthesized, but only about a dozen of these topologies are applied in industrial processes[1]. Zeolites are needed to tackle catalytic and adsorptive challenges in the transition from fossil to renewable raw materials.

Where traditionally the search for zeolites mainly was based on trial and error, now more rational approaches are available. One promising path to expand the number of zeolites is the development of layered zeolite structures. Although the description of interconnected layers originally was a purely structural concept, in some instances precursor materials with not yet fully connected layers have been reported. The first zeolite with such a layer growth mechanism was MCM-22 (MWW topology)[2]. Laminar precursors designated MCM-22(P), have been manipulated to yield several new materials. Swelling of layered precursors by intercalation of organic molecules enables molecular engineering of the connectivity of the layers. Pillaring of the layers with tetraethylorthosilicate yields the MCM-36 structure[3]. Alternatively, some zeolite crystals can be split into layers that are forced apart via so-called delamination processes. Delamination of MCM-22 yields ITQ-2 material[4]. MCM-56 (ref. 5) intermediate, presenting a disordered collection of MWW monolayers, has been converted into MCM-49 (ref. 6). Likewise, a layered PREFER (ref. 7) has been pillared into ITQ-36 zeolite[8] and delaminated into ITQ-6 (ref. 9). Recently, layered nanosheets with MFI framework type have been synthesized by application of bifunctional surfactants[10,11]. The cited examples illustrate the potential of zeolite layers obtained by direct synthesis or delamination of a fully formed framework as versatile building units for designing materials with new frameworks.

Zeolite frameworks are conveniently described as three-dimensional nets of four connected nodes representing the framework tetrahedra. Systematic insertion and elimination of nodes, called σ and inverse σ transformation, respectively, is a handy tool to classify topologies and to propose hypothetical framework types[12,13]. In contrast to zeolite synthesis approaches involving connection of layers, systematic removal of T-atom layers and framework reconnection has not previously been achieved. This Article describes the synthesis and characterization of a zeolite material through inverse σ transformation (Fig. 1). Figure 1 depicts how germanate 4-rings (Ge-4Rs) are dislodged from an IM-12 zeolite by acid leaching, shifted into the channels of the contracted framework (Ge-COK-14) and eliminated, thereby resulting in an interrupted framework (-COK-14) that can be fully closed on calcination (COK-14). This topology presents a two-dimensional channel system with 10Rs and 12Rs attractive for catalysis. An inverse σ transformation, until now only known as a theoretical concept, best describes this transformation.

Key to our success was the instability of germanosilicate zeolites, especially the extra-large pore specimen[14–16]. Germanium shows a marked affinity for octahedral next to tetrahedral coordination[17] resulting in a much wider range of bonding angles, and allowing the release of strain in a 4-coordinated network with larger pores. Germanium, with its higher coordination flexibility, has been suggested to specifically occupy T-atom positions within double 4Rs (D4Rs; refs 18,19). The germanosilicate zeolite with UTL topology can be described as individual layers interconnected by D4Rs and presents extra-large pores delineated with 14Rs next to 12Rs (refs 15,16,20,21; Fig. 1). ITQ-15 (ref. 15) and IM-12 (ref. 16) are UTL zeolites synthesized with a different organic template. Recently

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[1]Center for Surface Chemistry and Catalysis, KU Leuven, 3001 Heverlee, Belgium, [2]Center for Molecular Modelling, Ghent University, 9052 Zwijnaarde, Belgium, [3]Electron Microscopy for Materials Science, University of Antwerp, 2020 Antwerp, Belgium, [4]L. V. Pisarzhevsky Institute of Physical Chemistry, National Academy of Sciences of Ukraine, 03028 Kyiv, Ukraine, [5]Tectospin, Institut Lavoisier, UMR 8180, Université de Versailles st. Quentin en Yvelines 45, Avenue des Etats Unis, 78035 Versailles, Cedex, France, [6]Institut für Werkstoffwissenschaft, Technische Universität Dresden, 01062 Dresden, Germany. *e-mail: Christine.Kirschhock@biw.kuleuven.be.

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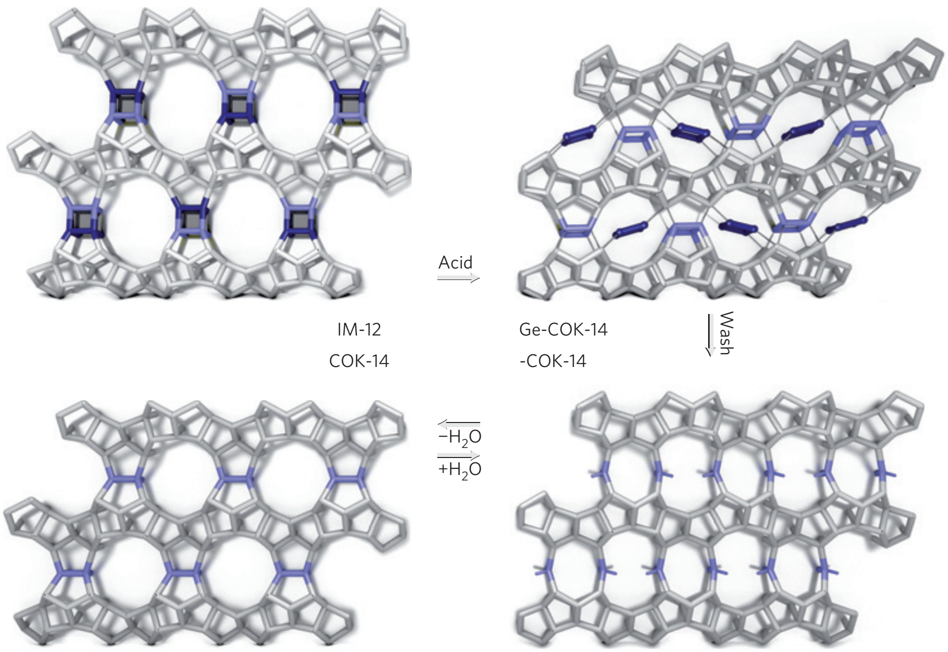

Figure 1 | Acid leaching of IM-12 zeolite (UTL topology) dislodges germanate four-rings (Ge-4Rs, dark blue), allowing a framework contraction whereby the Ge-4R units are shifted into the channels of Ge-COK-14. Further leaching fully eliminates the Ge-atoms, resulting in a Ge-free interrupted framework (-COK-14) that can be annealed on calcination (550 °C). Si-atoms in layers are presented in grey, Si-atoms in layer-connecting Si-4Rs in light blue.

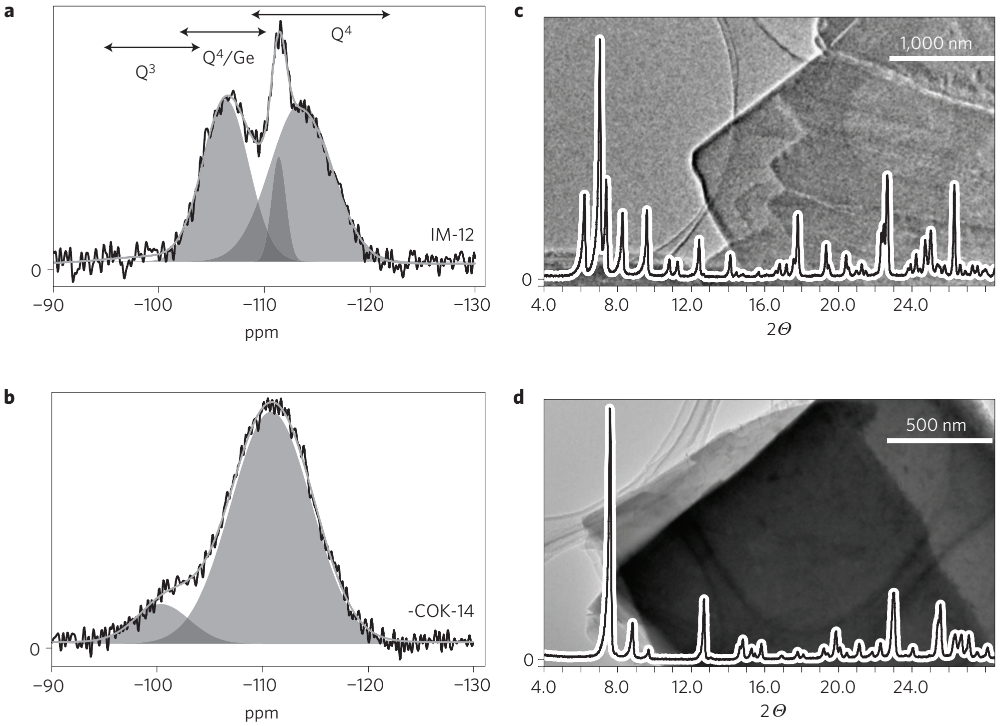

Figure 2 | Comparison of IM-12 and -COK-14. a–d, ^{29}Si-NMR spectra (**a**,**b**) and XRD patterns (**c**,**d**) of the parent IM-12 (**a**,**c**) and -COK-14 (**b**,**d**). The TEM images inserted on **c**,**d** show both materials have similar sheet-like morphology.

it has been shown that the bond between the layers and the D4R, the preferential location of germanium, is very sensitive and can be hydrolysed in the presence of water, even at ambient conditions, leading to isolated zeolite layers[22,23]. We exploited this reactivity of germanium in the UTL lattice and succeeded in the systematic removal of the germanium and annealing to form a zeolite.

-COK-14 was obtained by heating a suspension of calcined IM-12 zeolite in strongly acidic solution. Using 12 M HCl solution at 95 °C, the phase transformation from IM-12 to -COK-14 was achieved within two days, as demonstrated by the markedly different X-ray diffraction (XRD) pattern of -COK-14 when compared with the parent calcined IM-12 zeolite (Fig. 2).

Wet-chemical analysis and EDX revealed -COK-14 contained very little germanium. The Si to Ge atomic ratio was 110, as compared to 5.3 for the IM-12 zeolite used for synthesis of -COK-14.

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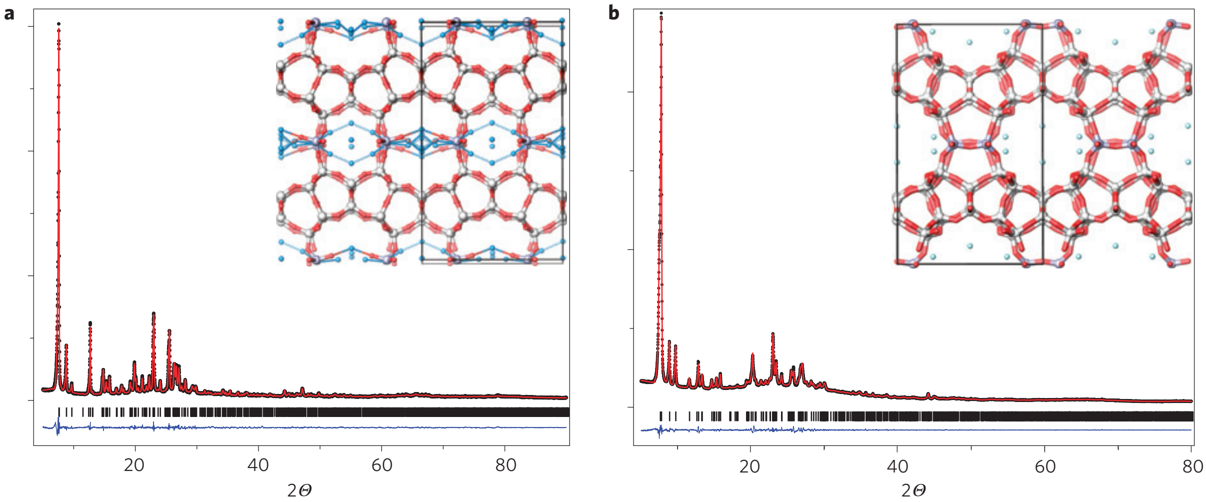

Figure 3 | Rietveld refinement of X-ray powder patterns. a, -COK-14 dried at 60 °C, recorded on a STOE Stadi MP diffractometer ($\lambda = 1.54056$ Å). **b**, COK-14 dried at 550 °C, measured on a STOE Stadi MP diffractometer ($\lambda = 1.54056$ Å). Experimental (black) and calculated (red) XRD patterns as well as the difference profile are shown (blue). The short tick marks below the patterns give the position of the Bragg reflections. The insets show the refined structures with framework O atoms in red and networks of hydrogen bonded water molecules in the pores in blue.

The acid treatment successfully leached out the germanium from the IM-12 framework, resulting in an almost pure-silica zeolite.

^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded and the signals fitted with Gaussians[24] (Fig. 2 and Supplementary Table S1). A chemical shift between −90 and −102 ppm is commonly assigned to Q^3 silicon atoms (with 3 siloxane bridges and one hydroxyl). Q^4 silicon atoms with at least one link to a Ge atom as a direct neighbour (Q^4-nGe) show a chemical shift in the range of −100 to −110 ppm. Signals at −110 ppm to −120 ppm result from Q^4 silicon atoms surrounded by silicon atoms only[19,23,25]. The intense Q^4-nGe signal of IM-12 was much weaker in -COK-14, confirming the extraction of germanium (Fig. 2). A key observation was the large concentration of Q^3 environments (11%) in -COK-14 associated with silanol groups, as confirmed by ^{1}H-NMR (Supplementary Fig. S2). This suggested the presence of incompletely connected tetrahedral sites.

-COK-14 exhibited a type I nitrogen adsorption isotherm, characteristic of a zeolite (see Supplementary Fig. S5 and Table S3). The diffraction pattern of -COK-14 retained several reflections of the IM-12 parent material (Fig. 2) but could not be indexed in the same unit cell. This clearly marked it as a phase structurally related to IM-12. Indexing of the powder pattern resulted in a unit cell with space group C 2/m with parameters $a = 24.64$ Å, $b = 13.92$ Å, $c = 12.26$ Å and a monoclinic angle of 109.20°. Although the b and c lattice parameters of -COK-14 very closely resembled the corresponding constants of the IM-12 structure ($a = 29.00$ Å, $b = 13.98$ Å $c = 12.45$ Å, $\beta = 104.91°$; ref. 26), the a direction was found to be significantly shorter. As the bc-planes in IM-12 are parallel to the layers, the structure obviously contains a more condensed stacking of the same layers (partially or fully preserved). Comparison of the lattice constants with the layer thickness observed in IM-12, revealed the interlayer distance in -COK-14 could accommodate only one layer of T atoms as compared to two in the parent material. (Fig. 1: IM-12 ⇒-COK-14). The structure of the parent material suggested this layer consisted formally of 4Rs, but their connectivity was not yet clear. The silanol content of 11% (Fig. 2) revealed these 4Rs in -COK-14 were not fully connected. Force field calculations accounting for the potential presence of framework disruptions resulted in one probable model, which was used as a starting geometry for Rietveld refinement of the XRD pattern. According to the refined structure (Fig. 3a), -COK-14 has an idealized unit cell composition of $T_{68}O_{132}(OH)_8$. The feasibility of this model containing IM-12-like layers linked by broken 4Rs was also confirmed by high-level density functional theory (DFT) calculations (see Supplementary Information). DFT geometry optimization not only resulted in a structure closely reflecting the experimental lattice constants (DFT: $a = 25.1$ Å, $b = 14.2$ Å $c = 12.5$ Å, $\beta = 109°$; Rietveld refinement: $a = 24.64$ Å, $b = 13.92$ Å, $c = 12.26$ Å, $\beta = 109.20°$.), but also confirmed the feasibility of structural hydroxyl groups pointing outwards into the 12 membered rings (Fig. 1), qualifying -COK-14 as a systematically interrupted framework zeolite.

Transmission electron microscopy (TEM) analysis revealed -COK-14 to consist of flat, stacked sheets (Fig. 2). Electron diffraction patterns indicated the presence of three different zone axes in the flat, stacked phase, thereby supporting the XRD results and confirming the proposed space group (see Supplementary Fig. S1). The space groups of IM-12 and -COK-14 were found to be identical, but again the unit cell parameters differed in a direction, suggesting the presence of a similar layer structure in both materials.

The presence of physisorbed and constitutive water in -COK-14 was manifested in thermogravimetric analysis (see Supplementary Fig. S7). Physisorbed water was evacuated below 100 °C. Further heating to 300 °C led to a weight loss of about 1.8 wt%. This quantity corresponds to the release of about four water molecules per unit cell and was assigned to water molecules that systematically hydrogen bridge two opposing silanol groups. The adsorption energy of such bridging water molecule was estimated by DFT calculations and found to be remarkably high (152 kJ mol^{-1} for the first water molecule). This is reflected by the high temperature necessary for release, as observed with thermogravimetric analysis. Between 300 and 900 °C, a further weight loss (1.8 wt%) corresponds to a release of another four water molecules per unit cell. This was ascribed to systematic silanol condensation and the formation of the fully connected framework of COK-14 (Fig. 1).

To verify the existence of the fully connected framework COK-14, a sample of -COK-14 was calcined at 550 °C and transferred into a capillary for XRD, avoiding contact to humidity. Unit cell dimensions and coordinates for a fully developed tetrahedral framework of COK-14 were obtained by force field calculation (ref. 27) in combination with the Catlow force field[28]) and used as a starting model for Rietveld refinement. The refinement very quickly converged (Fig. 3b), supporting the existence of the fully connected framework with intersecting 10R and 12R channels (Fig. 1) and the conversion of IM-12 to COK-14 corresponding to an inverse σ

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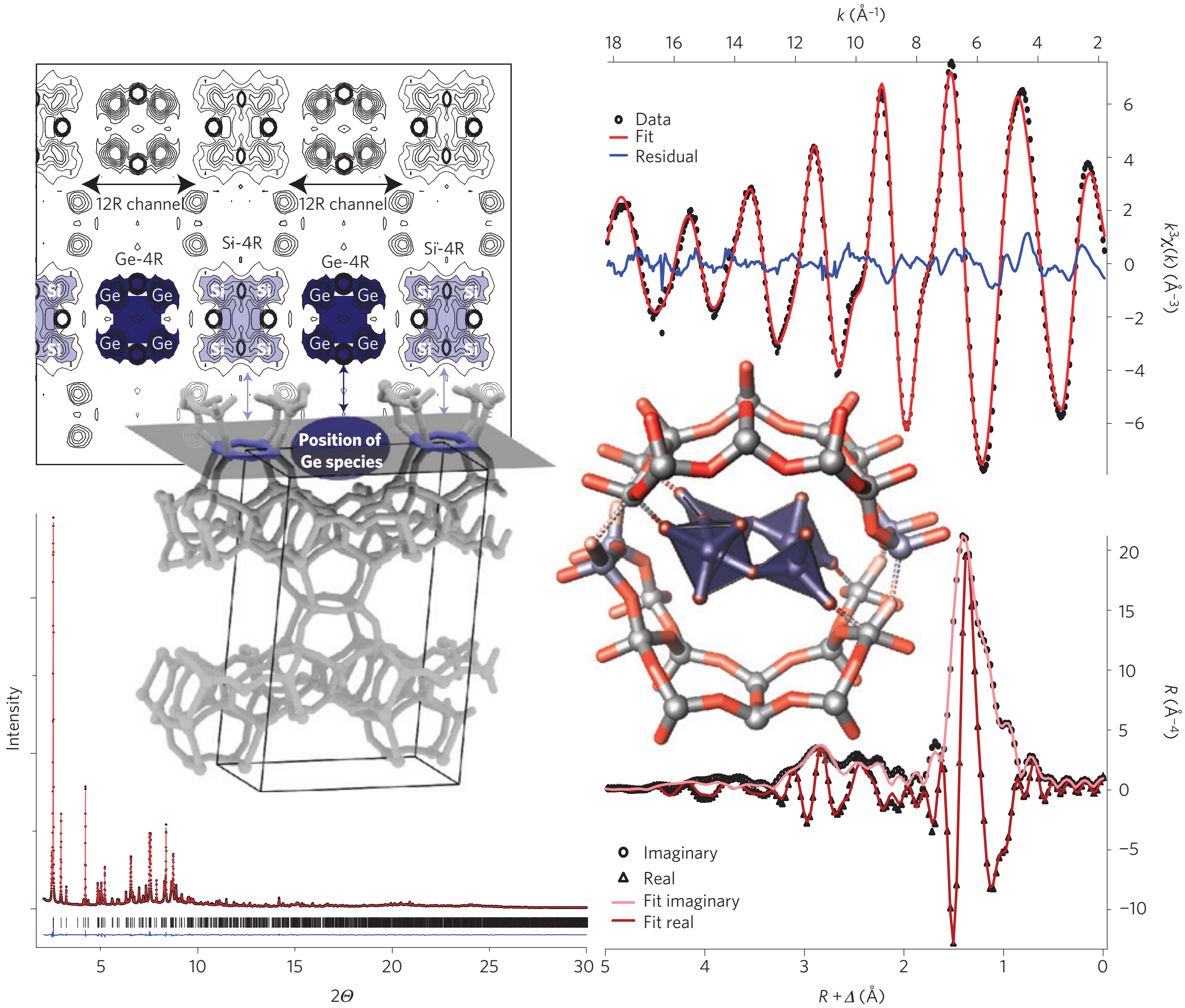

Figure 4 | Rietveld refinement (bottom left), observed electron density (upper left) and fitted EXAFS data (right)[33,34] of Ge-COK-14. EXAFS analysis was based on the inserted fragment from Rietveld refinement. Inset on the left indicates the shown plane of observed electron density.

transformation (Fig. 1). COK-14 spontaneously converted back to -COK-14 on rehydration in ambient air.

To further investigate the transformation mechanism, a further sample was prepared to capture intermediate states. Treatment of calcined IM-12 in 12 M HCl solution for only 4 h at 95 °C and limited washing yielded a sample retaining approximately half of its original Ge content, referred to as Ge-COK-14. ^{29}Si and ^{1}H-NMR revealed this sample already contained Q^3 Si centres, while still containing Si–O–Ge bonds (see Supplementary Fig. S2 and Table S1). Nonetheless, XRD revealed a highly ordered structure that already had the interlayer spacing of -COK-14. Thus the combination of NMR and XRD provided a strong indication that the framework contraction had already occurred without complete removal of germanium. Ge K-edge extended X-ray absorption fine structure (EXAFS) spectra revealed the local environment and coordination of Ge in Ge-COK-14 (Fig. 4). Each Ge atom had two Ge neighbours at 3.2 Å distance, which indicated the presence of either a closed oxide ring or an infinite germanium oxide chain. Therefore, framework 4R fragments consisting of germanium were considered as the most likely candidates for the dislodged species. Fourier analysis of the X-ray data revealed the electron density in the 12R channel between two Si-4Rs (Fig. 4). As the electron density maxima were located on the corners of a square with an edge in accordance with the EXAFS derived Ge-Ge distance, the corresponding species was identified as a Ge-4R. Interestingly, EXAFS analysis of the parent IM-12 structure revealed that this material already contained germanate 4Rs. Although it may seem as if these 4Rs are simply cut from the IM-12 structure and moved into the pores, the underlying chemistry is most probably quite complex. Topologically, in terms of an inverse σ transformation of IM-12 into COK-14, the D4Rs collapse to single 4Rs (Fig. 1). Formally, these 4Rs open on opposite sides to release strain, as observed in -COK-14 (Fig. 1). This transformation is reminiscent of the reverse process of the swelling and pillaring procedure of layered zeolite materials[2,3,7,8].

The COK-14 zeolite family is a valuable addition to the all-silica large-pore zeolite types. -COK-14 has a 2D channel system with 12Rs and 10Rs (Fig. 1). All-silica zeolites with 10R and 12R intersecting channel systems are quite unique and previously encountered in the IWR framework[29] and ITQ-39 (refs. 30,31) only. In the Atlas of Zeolite Framework Types there is only one example of a silicate framework with systematic interruption, viz. SVR, encountered in SSZ-74 zeolite, presenting a 3D 10R channel system with an ordered framework vacancy[32]. The -COK-14 material is expected to be locally hydrophilic owing to the presence of structural hydroxyls in the 12R channels but also presents hydrophobic regions devoid of silanols in the 10R channels. The crossing of hydrophilic and hydrophobic pores is expected to give rise to special adsorption behaviour and to

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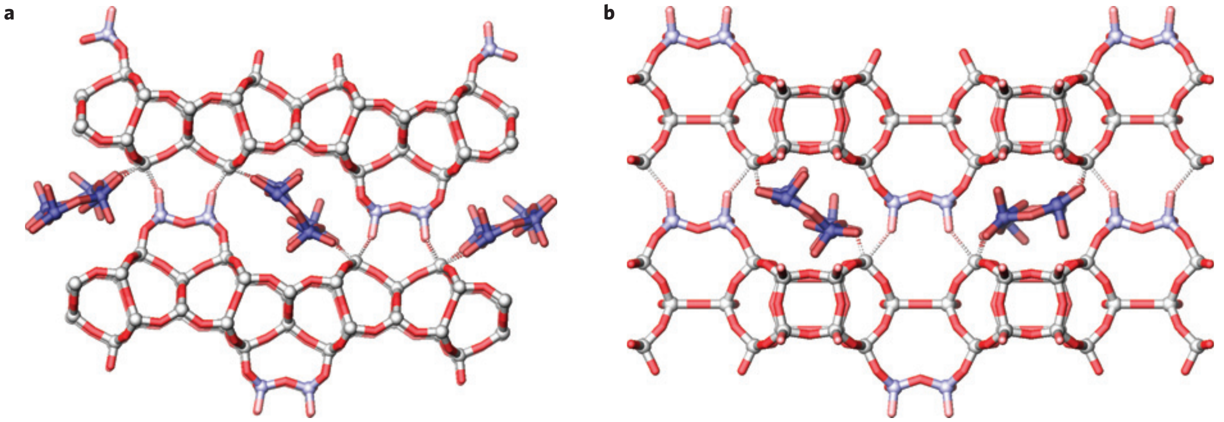

Figure 5 | Two postulated intermediate structures during inverse σ transformation, obtained by simple geometric considerations. a, IWV topology with 14R and 12R channels resulting in a 12R and 10R pore system. **b**, BEC topology with 12R channels in three dimensions resulting in two perpendicular 10R channels with one remaining perpendicular 12R channel.

be beneficial in catalytic conversion with molecules of different polarity. We speculate that -COK-14 will be particularly attractive in organic reactions in aqueous media such as in biorefineries where adsorption competition between organic molecules and water is critical. The availability of hydroxyl groups in -COK-14 at specific locations invites the incorporation of chemical functions via post-synthesis modification.

Our degermanation method is expected to be generic and to lead to the formation of further zeolite framework types via inverse σ transformation. Potential parent materials should contain mostly siliceous layers connected via structural units incorporating heteroelements such as germanium that can be selectively removed. Connecting units could be D4Rs with approximately 50% heteroelement, which already preferably resides in a 4R. Inspection of different germanosilicate zeolite structures (ITQ-7, ITQ-13, IM-12/ITQ-15, ITQ-22, ITQ-24, ITQ-27 and ITQ-34) led to the observation that D4Rs often act as a common building unit to expand the framework and assume the structural role of linking layers. Alternatively, single-ring structures, such as 4Rs or 3Rs, entirely consisting of heteroelements also could lead to success. The intermediate broken structure should contain sufficiently large pores or channels to allow accommodation of the removed fragment. Although Ge-coordination is highly flexible in terms of bond distances and angles, simple geometrical inspection of topologies indicates the finally formed materials should contain a ring size of at least 10 T-atoms. Two examples of postulated intermediates in σ transformations of interest are shown in Fig. 5.

Methods

-COK-14 was synthesized by suspending freshly calcined IM-12 powder in hydrochloric acid (HCl) in a closed polypropylene bottle, minimizing exposure to ambient air. In the standard preparation the weight ratio of calcined IM-12 powder to HCl (12 M, VWR) was 1:50. The IM-12 suspension was heated at 95 °C for two days. The solids were recovered by filtration, extensively washed with deionized water until the wash water reached pH 5, then dried overnight at 60 °C (partially dried sample). Part of the sample was kept at ambient conditions before characterization (hydrated sample). The synthesis yield was 83 wt%.

COK-14 was obtained by heating -COK-14 at 550 °C for 6 h using a temperature ramp of 1 °C min^{-1} under continuous oxygen flow. A 0.5 mm glass capillary was filled and sealed off in a glove box under nitrogen atmosphere. At all times rehydration through exposure to ambient air was avoided.

Ge-COK-14 was synthesized by suspending freshly calcined IM-12 in 12 M HCl solution with a weight ratio of IM-12 powder to HCl solution of 1:50. This suspension was heated at 95 °C for 4 h only. The solids were recovered by filtration with limited rinsing and dried overnight at 60 °C. Comparison of XRD data of freshly prepared Ge-COK-14 with the same sample after one year proved the material to be stable. High-resolution powder X-ray diffraction and Ge K-edge X-ray absorption data were obtained at the DUBBLE and SNBL (BM01B) beamlines at ESRF[33,34].

The synthesis procedure of the structure-directing agent, (6*R*,10*S*)-6,10-dimethyl-5-azoniaspiro[4,5]decane hydroxide, and IM-12 zeolite can be found in the Supplementary Information, together with all experimental procedures and computational details.

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Author contributions

J.A.M. and C.E.A.K. conceived and directed the project. E.V. synthesized -COK-14, COK-14 and Ge-COK-14 and performed the characterization. N.K. synthesized IM-12 and initiated the degermanation work. C.E.A.K., E.G. and E.B. solved crystal structures and performed data fitting. L.J., V.V.S. and M.W. carried out the DFT calculations. K.V.H., S.B. and G.V.T. performed the TEM measurements. K.H. carried out the ^{29}Si magic angle spinning nuclear magnetic resonance. M.H. measured XRD using synchrotron radiation. C.M. and F.T. conducted the ^{1}H-NMR experiments and contributed to their interpretation. All authors participated in the writing of the publication.

Additional information

Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to C.E.A.K.

Competing financial interests

The authors declare no competing financial interests.

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