Zeolites

# The Topotactic Conversion of a Novel Layered Silicate into a New Framework Zeolite**

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Zeolites have been widely used, among others, as catalysts, ion exchangers, detergents, and adsorbents, and their range of applications continues to grow. Thus, there is a large demand for new types of zeolites with high thermal and chemical stability. However, new zeolites are still mainly synthesized by trial and error, and molecular engineering in their synthesis has been underdeveloped. Here we report that a thermostable zeolite with a novel framework is obtained by molecular manipulation, that is, topotactic dehydration–

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condensation between the layers of face-sharing pentagon cylinders in a new silicate.

Peculiar properties of zeolites arise as a result of the framework structure. This framework structure has been understood as the combination of ringed silicate building blocks,[1–3] and some of the corresponding silicate oligomers have been detected and/or isolated.[4,5] Therefore molecular engineering can be used to design zeolite frameworks by assembling block oligomers or appropriate precursors which dehydration–condensation. However, there has been no example for this kind of molecular manipulation in zeolite synthesis so far, although some syntheses were carried out with this intent.

For instance, we have investigated the transformation of the layered silicates kanemite and HLS (helix layered silicate) into the zeolites MFI (zeolite socony mobil five, ZSM-5) and SOD (sodalite), respectively.[6–9] However, these conversions did not proceed with dehydration–condensation only, that is, they were not perfect block condensation polymerizations. In the case of kanemite→MFI a different type of bond breaking and recombination took place, and for HLS→SOD the presence of aluminum hydroxide or gallium hydroxide was essential. This means that the transformation to SOD is not a simple block condensation–polymerization, although the structures of HLS and SOD are very similar.

Schreyeck et al.[10,11] have reported that the layered aluminosilicate PREFER was converted into an FER-type zeolite[12] by dehydration–condensation. Since the crystal structure of PREFER has not been clearly determined, it is unknown if the conversion is a simple block condensation–polymerization. Furthermore, although not yet proven, such conversions were suggested for the transformation of EBR-1[13] into MWW-type zeolites such as MCM-22 and ITQ-1 and the formation of RUB-24 from an intercalated layered material based on RUB-18.[14] Here we show a concrete example of zeolite synthesis by complete block condensation–polymerization, which can be a guiding principle for the molecular engineering of zeolites.

A novel layered silicate was crystallized by the hydrothermal treatment of a mixture of $SiO_2$, $H_2O$, KOH, tetramethylammonium hydroxide (TMAOH), and 1,4-dioxane at 423 K. As observed in the X-ray crystal structure (see below), the silicate adopts a structure with shared faces of pentagon cylinders made up of five-membered silicon rings, or pentasil rings. Thus, it was named pentagonal cylinder-layered silicate (PLS-1). When PLS-1 was heated above 673 K under vacuum, a novel framework zeolite with a cylindrically double saw edged structure (CDS-1) was obtained as the result of dehydration–condensation between the pentasil layers. The as-synthesized PLS-1 contains TMAOH molecules between the layers (see below), and during the conversion into CDS-1 most of the TMAOH can be recovered by trapping the volatile components with liquid nitrogen.

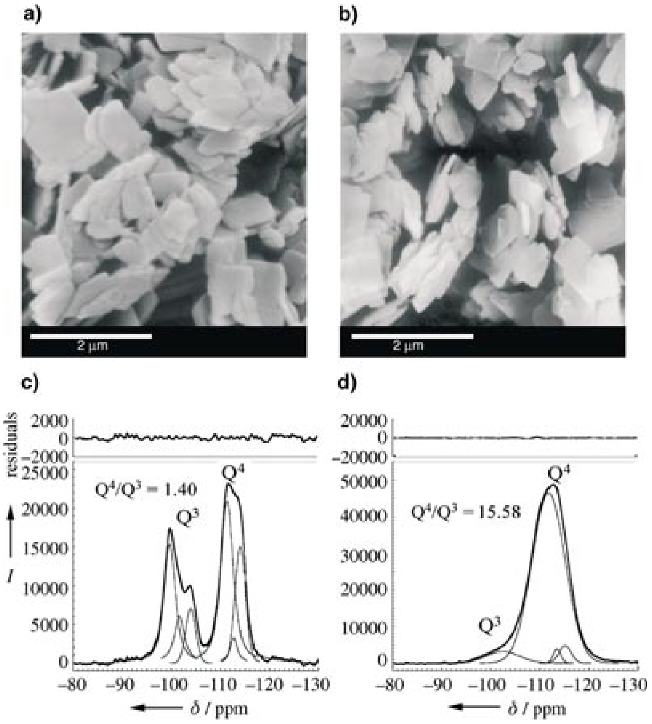

***Figure 1.*** Top: SEM images of purified samples of PLS-1 (a) and CDS-1 (b) showing platelike microcrystals. Bottom: $^{29}$Si-MAS NMR spectra of PLS-1 (c) showing three resonances and of CDS-1 (d) showing one broad resonance. The chemical shifts are given with respect to tetramethylsilane.

Figure 1 shows the scanning electron microscope (SEM) images and $^{29}$Si magic angle spinning (MAS) NMR spectra of powdered crystals of PLS-1 and CDS-1. In the SEM images, the two crystal morphologies are quite similar in the thin plate, suggesting that the conversion of PLS-1 into CDS-1 is a topotactic condensation–polymerization with simple dehydration (strictly speaking, removal of $H_2O$ and TMAOH). In the NMR spectra, PLS-1 exhibits resonances around $\delta = -102$ and $-113$ that are characteristic of $HOSi(OSi)_3$ ($Q^3$) and $Si(OSi)_4$ ($Q^4$) silicon sites, respectively. On the other hand, CDS-1 displays only a broad peak around $\delta = -112$ that is mostly due to $Q^4$ structures and possibly contains a small amount of $Q^3$. This indicates that during the conversion of PLS-1 into CDS-1, the $Q^3$ sites lose their terminal silanol groups upon dehydration–condensation to become $Q^4$ structures.

If layered silicates are converted into three-dimensional microporous crystals with pores large enough to accommodate gas molecules, the amount of gas adsorbed after the conversion should increase. Figure 2 shows the nitrogen

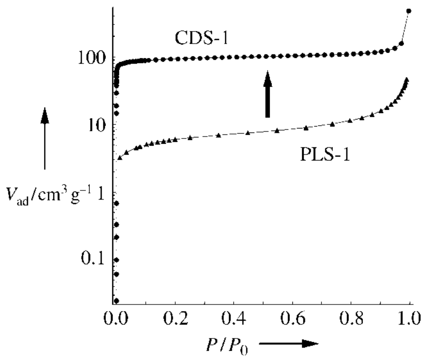

***Figure 2.*** Nitrogen adsorption isotherm plots for PLS-1 and CDS-1.

adsorption isotherm curves for PLS-1 and CDS-1. Silicate CDS-1 adsorbs a much higher volume of nitrogen than PLS-1, and its curve exhibits the adsorption pattern characteristic of microporous crystals. The multipoint Brunauer–Emmett–Teller (BET) surface area and the Saito–Foley (SF) cumulative pore volume were calculated from the argon adsorption isotherm curve to be 301 $m^2 g^{-1}$ and 0.13 $cm^3 g^{-1}$, respectively, for CDS-1. These values are equal to or higher than those of typical zeolites such as FER and silicalite. The total pore volume was calculated to be 0.60 $cm^3 g^{-1}$ at the maximum $P/P_0$. In addition, the minimum of the pore size distribution calculated from the argon adsorption isotherm data with nonlocal density functional theory[15] was 4.83 Å. This is in good agreement with the pore diameter (ca. 4.8 Å) of the main window of CDS-1 (a silicate eight-membered ring, 8MR), which was calculated on the basis of structural parameters, the ionic radius of an oxygen atom, and lattice constants obtained by the Rietveld refinement.

Figure 3 provides views of the crystal structures of PLS-1 and CDS-1. The structure of PLS-1 was elucidated from the preliminary X-ray structure determination (see the Supporting Information), and then the positions of the interlayer potassium ions and TMAOH molecules were estimated by the maximum entropy method (MEM).[16,17] It was determined that PLS-1 is a three-dimensional layered silicate—the structure is similar to that proposed for PREFER and MCM-47[18]—with different types of layer stacking. The X-ray diffraction data for CDS-1 did not directly give the structure because the crystals were poor in crystallinity and contained various distortions and small domains of crystallites. Therefore, with molecular dynamics (MD) simulations, preliminary structural models for CDS-1 were derived from the layer structure of PLS-1, and then the most probable model was determined by structure analyses.[19]

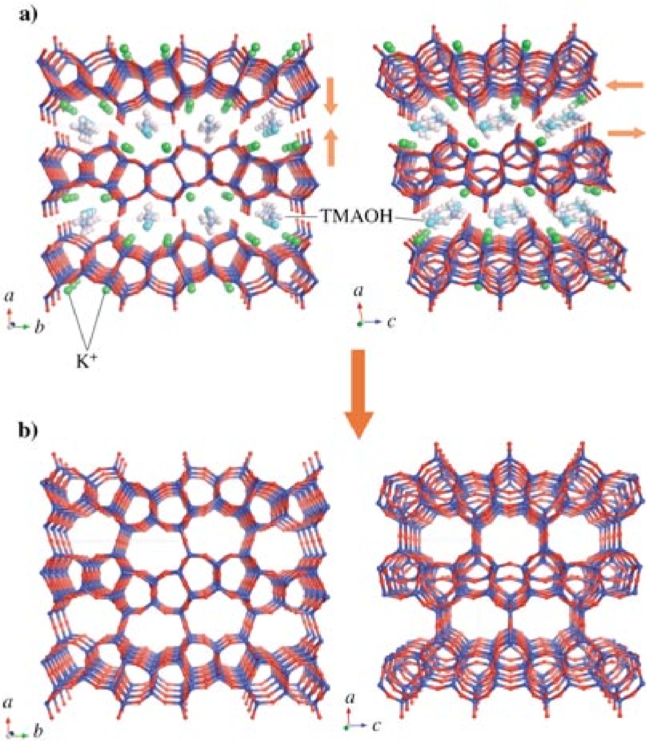

*Figure 3.* Perspective view of the crystal structure of a) PLS-1 along the [001] (left) and [010] directions (right) as well as b) CDS-1 along the [001] (left) and [010] directions (right). Color coding: blue = Si, red = O, green = K, white = C, cerulean = N, sky blue = OH. CDS-1 consists of silicates layers based on a framework of PLS-1 with 5MRs and forms 8MRs in the [001] and [010] directions.

The crystal system of PLS-1 is a monoclinic phase with the space group $P2_1/m$ and lattice parameters $a = 10.5710(5)$, $b = 14.0064(3)$, $c = 7.4220(2)$ Å, $\beta = 98.014(4)°$, and $V = 1088.21(7)$ $Å^3$. The framework contains a pair of high-density silicate sheets made up of five-membered rings, and the porelike interlayer space is occupied by TMAOH molecules and $K^+$ ions that are distributed with partial disorder (Figure 3 a). The chemical composition was estimated to be $Si_{18}O_{34}(OH)_4{\cdot}K_{1.3}{\cdot}1.7\,(CH_3)_4NOH$ by the Rietveld refinement.

For CDS-1, indexing of the reflections gave an orthorhombic unit cell with $a = 18.355(3)$, $b = 13.779(2)$, $c = 7.3674(6)$ Å, and $V = 1863.3(4)$ $Å^3$; these values are very close to the corresponding values of zeolites FER. The reflection conditions afforded the space groups *Pnma*, *Pnnm*, and *Pbcm* as well as *Cmcm* on the assumption that CDS-1 has a centrosymmetric space group. Three preliminary models constructed on the basis of the MD calculation results[20] were evaluated by the Rietveld method taking into account geometrical considerations. Finally, we adopted the highest symmetry model with space group *Pnma*. The framework obtained shows a novel type of topology, which has straight channels consisting of 8MRs along the [010] and [001] directions (Figure 3 b). The chemical composition was calculated to be $Si_{36}O_{72}$, but the positions of the $K^+$ ions could not be determined because of insufficient resolution of the X-ray data. The comparison of the frameworks of PLS-1 to CDS-1 shows that the sheets of PLS-1 condense and polymerize along the [100] direction by dehydration to form CDS-1. The TMAOH molecules are removed along the [001] direction.

The X-ray diffraction patterns were then used for structure refinement by the MEM-based pattern fitting (MPF) technique at the electron density level.[21] The MEM electron density distribution map of PLS-1 ($R_F = 0.0142$ after MPF refinement) shows that the TMAOH molecules and potassium ions exist in the interlayer (Figure 4 a). Localized electron densities between $TMA^+$ and $OH^-$ are clearly observed, and the chemical bonding is directed parallel to [001]. Small amounts of $K^+$ seem to be closely located to the silicate sheets; however, the ion sites could be replaced by water molecules. After a revision based on the electron density, the MPF refinement dramatically improved and the $R_F$ of the final MPF became 0.0093.

On the other hand, the final electron densities of CDS-1 obtained by MEM ($R_F = 0.0267$) reveal the three-dimensional microporous structure composed of 5MRs and 8MRs (Figure 4 b). No electron densities arising from water molecules and/or other adsorbed atoms or molecules are observed in the straight channels. Electron densities of oxygen atoms at the points connecting the sheets are anisotropically elongated, which means that the framework structure of CDS-1 has considerable lattice distortion and internal stress in comparison with other zeolite frameworks.

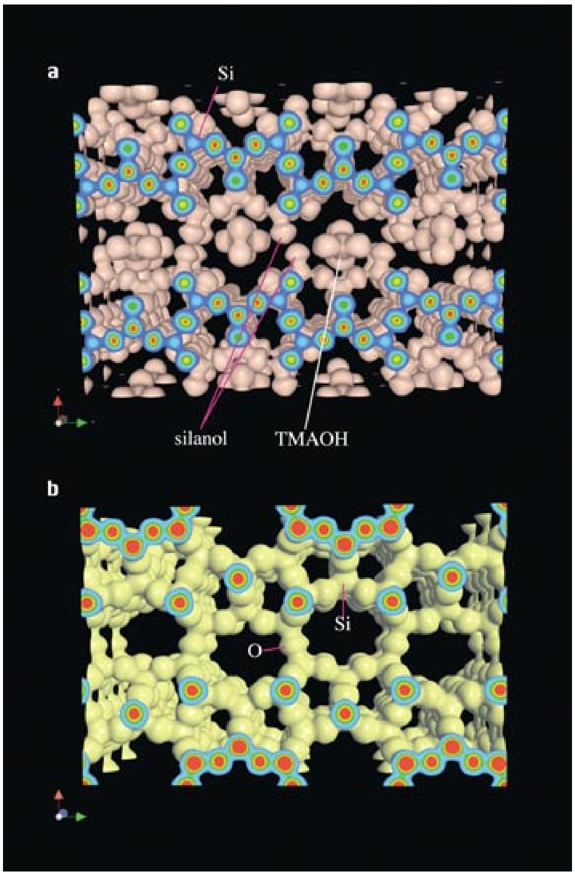

*Figure 4.* Electron-density images of PLS-1 (a) and CDS-1 (b) along the [001] direction. The equidensity level was set at 0.7 e$\text{Å}^{-3}$ in both images.

Organic amines are effective for the formation of zeolite frameworks, and various types of zeolites have been synthesized so far.[22] However, the amines are often difficult to synthesize and expensive to buy, and only several types of zeolites show sufficient thermal and chemical stability to be employed in industry. This stability generally increases with increasing silica content. Silicate CDS-1, with straight two-dimensional channels, is pure silicate and thermally stable. Furthermore, the TMAOH used in the synthesis of the CDS-1 precursor, PLS-1, is inexpensive and can be recovered. The Si atom defects, which are homogeneously distributed in the CDS-1 crystals, could be active sites for catalytic reactions or different metal ions could be incorporated to make new active sites. Thus, CDS-1 is expected to find wide application as a catalyst, adsorbent, separator, or ion exchanger for various industrial uses.

## Experimental Section

PLS-1: Silica powder (Cab-O-Sil M5, 10.0 g), TMAOH (22.0 g, 15 wt%), 0.5 N KOH (5.0 g), and 1,4-dioxane (50.0 g) were consecutively suspended in distilled water (25.0 g). The sol mixture was vigorously stirred for 1 h at room temperature with a magnetic stirrer, and then heated at 423 K under autogenous pressure for 10 d in a stable PTFE-lined stainless-steel autoclave with an internal volume of 300 mL. The crystalline product was filtered and washed with acetone and distilled water, then dried at 70 °C in a drying oven for 12 h.

CDS-1: Silicate PLS-1 was heated (range 673 to 1173 K) under vacuum ($10^{-3}$ to $10^{-8}$ torr). Thus, the conversion was carried out reproducibly.

General: KOH and 1,4-dioxane were purchased from Wako chemical, and TMAOH was purchased from Tokyo Kasei Kogyo Co. Ltd. Cab-O-Sil M5 (CABOT Co.) was employed as a silica source. The SEM observations with a HITACHI S-800 microscope showed the samples to be thin microcrystals with a length of less than 1 µm and a thickness of about 0.1 µm. Solid-state $^{29}$Si-MAS NMR spectra were obtained on a Bruker AMX-500 spectrometer. The recycle delay was 300 s for PLS-1 and 30 s for CDS-1 with the sample rotor spinning at 4 kHz. Nitrogen adsorption isotherm plots of all materials were obtained by using a Shimazu ASAP-2010 instrument, and the argon adsorption isotherm plot of CDS-1 was measured with a Quantachrome Autosorb-1MP instrument. The X-ray diffraction data were collected at room temperature on a MAC Science MXP-3TA HR powder diffractometer in a Bragg–Brentano geometry for PLS-1 and a Debye–Scherrer geometry using a capillary specimen for CDS-1. The conditions of the diffraction experiments for both specimens were as follows: $\text{Cu}_{\text{K}\alpha1}$ radiation using a Ge(111) primary monochromator, output 40 kV and 50 mA, scan range $6° \leq 2\theta \leq 90°$, step width 0.02°, counting time per step 120 s.

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[1] C. Baerlocher, W. M. Meier, D. H. Olson, *Atlas of zeolite structure types*, *Structure Commission of the International Zeolite Association*, 5th rev. ed., Elsevier, London, **2001**.
[2] C. S. Cundy, P. A. Cox, *Chem. Rev.* **2003**, *103*, 663–701.
[3] M. Ogura, Y. Kawazu, H. Takahashi, T. Okubo, *Chem. Mater.* **2003**, *15*, 2661–2667.
[4] P. Bussian, F, Sobott, B. Brutschy, W. Schrader, F. Schüth, *Angew. Chem.* **2000**, *39*, 4065–4069; *Angew. Chem. Int. Ed.* **2000**, *39*, 3901–3905.
[5] C. E. A. Kirschhhock, S. P. B. Kremer, P. J. Grobet, P. A. Jacobs, J. A. Martens, *J. Phys. Chem. B* **2002**, *106*, 4897–4900.
[6] S. Shimizu, Y. Kiyozumi, K. Maeda, F. Mizukami, G. Pál-Borbély, R. M. Mihályi, H. Beyer, *Adv. Mater.* **1996**, *8–9*, 759–762.
[7] M. Salou, Y. Kiyozumi, F. Mizukami, P. Nair, K. Maeda, S. Niwa, *J. Mater. Chem.* **1998**, *8*, 2125–2132.
[8] T. Ikeda, Y. Akiyama, F. Izumi, Y. Kiyozumi, F. Mizukami, T. Kodaira, *Chem. Mater.* **2001**, *13*, 1286–1295.
[9] Y. Kiyozumi, F. Mizukami, A. Akiyama, T. Ikeda, T. Nishide, *Stud. Surf. Sci. Catal.* **2001**, *135H*, 191.
[10] L. Schreyeck, P. Caullet, J. C. Mougenel, J. L. Guth, B. Marler, *Microporous Mater.* **1996**, *6*, 259–271.
[11] L. Schreyeck, P. Caullet, J. C. Mougenel, J. L. Guth, B. Marler, *Stud. Surf. Sci. Catal.* **1997**, *105*, 1949–1956.
[12] P. A. Vaughan, *Acta. Crystallogr.* **1966**, *17*, 983–990.
[13] R. Millini, G. Perego, W. O. Parker, Jr., G. Bellussi, L. Carluccio, *Microporous Mater.* **1995**, *4*, 221–230.
[14] B. Marler, N. Ströter, H. Gies, *Recent Research Reports of the 14th International Zeolite Conference*, **2004**, pp. 15–16.
[15] R. Evans, *J. Phys. Condens. Matter* **1990**, *2*, 8989–9007.
[16] D. M. Collins, *Nature* **1982**, *298*, 49–51.
[17] M. Sakata, M. Sato, *Acta. Crystallogr. Sect. A* **1990**, *46*, 263–270.
[18] A. Burton, R. J. Accardi, R. F. Lobo, M. Falcioni, M. W. Deem, *Chem. Mater.* **2000**, *12*, 2936–2942.
[19] The structure was solved with the EXPO package,[23] refined with the RIETAN-2000 package[24] combined with the MEM

program PRIMA,[25] and visualized with the VENUS package.[25] The final number of structural parameters (fractional atomic coordinates, lattice, and isotropic atomic displacement parameters) was 68 for PLS-1 and 40 for CDS-1. Including the profile, scaling, and zero shift factors, the total number of refinable parameters was 155 for PLS-1 and 78 for CDS-1. The numbers of contributing *hkl* reflections are 929 (PLS-1) and 800 (CDS-1), the numbers of geometric restraints of type $d$(Si–O), $\phi$(O-Si-O), $d$(C–N), and $\phi$(C-N-C) are 21, 30, 3, and 4, respectively, for PLS-1; 24 and 36 restraints of $d$(Si–O) and $\phi$(O-Si-O) are adopted, respectively, for CDS-1. The MEM electron density distributions were calculated from "observed" structure factors based on the Rietveld refinement, using the program PRIMA and visualized by the program VEND built into the VENUS package.

[20] Silicate CDS-1 was modeled by MD methods with the CRYSTAL Builder module in the Cerius2 program developed by Accelrys Inc., USA. The MD calculations were carried out with the MXDTRICL program developed by Kawamura et al.[26] The Verlet algorithm was used to calculate the atomic motions, while the Ewald method was applied to calculate the electrostatic interactions.[27,28] Temperature and pressure were controlled by means of scaling the atom velocities and unit cell parameters under three-dimensional periodic boundary conditions. The calculations were performed for 10000 steps with a time step of $2\times10^{-15}$ s at 300 K.

[21] F. Izumi, S. Kumazawa, T. Ikeda, T. Ida, *Powder Diffraction* (Ed.: S. P. Sen Gupta), Allied Publication, New Delhi, **1998**, pp. 24–36.

[22] *Introduction to Zeolite Science and Practice* (Eds.: H. van Bekkum, E. M. Flanigen, P. A. Jacobs, J. C. Jansen), 2nd rev. ed., Elsevier, London, **2001**.

[23] A. Altomare, M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Rizzi, *J. Appl. Crystallogr.* **1999**, *32*, 339–340.

[24] F. Izumi, T. Ikeda, *Mater. Sci. Forum* **2000**, *321–324*, 198–203.

[25] F. Izumi, R. A. Dilanian, *Recent Research Developments in Physics*, *Vol. 3*, *Part II*, Transworld Research Network, Trivandrum, **2002**, pp. 699–726.

[26] K. Kawamura in *Molecular Dynamics Simulations* (Ed.: K. Kawamura), Springer, Berlin, **1990**.

[27] L. Verlet, *Phys. Rev.* **1967**, *159*, 98–103.

[28] P. Ewald, *Ann. Phys.* **1921**, *64*, 253–287.