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Self-Limiting Distortion by Antirotating Hinges Is the Principle of Flexible but Noncollapsible Frameworks

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Microporous frameworks formed by TO_4 coordination tetrahedra (with T = Si or Al) in zeolites are systems composed of rigid parts, the tetrahedra, and of joint oxygen atoms serving as flexible hinges between the tetrahedra. It is known that these frameworks can be flexible or inflexible (or even rigid). Some of the most open tetrahedral frameworks display a pronounced resistance to collapse, even when undergoing radical changes in the chemistry of their embedded guests (ions or molecules). A study of empirically observed angular distortions in zeolite A (LTA) and a computer simulation show that this property is due to a self-regulating mechanism which allows changes in the dimensions of the framework only within limits set by chemically possible values of the T–O–T angles of the joint bridging oxygen atoms and which depends solely on the topological, symmetrical, and geometrical properties of the three-dimensional nets underlying the frameworks. In collapsible frameworks the hinges corotate, and compression or tension at all hinges is exerted simultaneously in the same sense. In noncollapsible frameworks the hinges antirotate, and compression at one hinge necessitates tension at another hinge and vice versa.

The cell volume of orthorhombic K-natrolite (*1*), $K_2Al_2Si_3O_{10} \cdot 2H_2O$, is larger by 43% than that of dehydrated Na-natrolite (*2*), $Na_2Al_2Si_3O_{10}$. When we view this in the linear dimension (to the power of $\frac{1}{3}$) there is still a difference of 12.7%. The cell constant of the largest known unit cell of a zeolite RHO (*3*), $D_9Al_9Si_{39}O_{96}$, is 8.1% larger than that in the case of the smallest zeolite RHO (*4*), $Ca_6Al_{12}Si_{12}O_{48}$. It has been generally accepted (*3, 4*) that RHO and natrolite are exceptionally flexible zeolites. However, their frameworks are also collapsible, which means they can reduce their volume until the framework wraps itself around the embedded guests (exchangeable cations or molecules) or until the lower limit of chemically possible T–O–T angles (where T might be tetrahedrally coordinated Si or Al atoms) is reached. This is very different in many apparently inflexible or rigid zeolites, most of them of cubic symmetry, such as zeolites A, X, Y, or ZK-5 (*5*). For example, even hydrogenated and evacuated faujasite (zeolite Y) with no cations present, except for hydrogen ions and otherwise empty pores, maintains its large cell volume and its cubic symmetry (*6*). Similarly, the largest reported cell constant of zeolite A, 12.42 Å (*7*), see Fig. 1, is only 3.8% larger than the smallest reported value, 11.96 Å (*8*). Similar observations can be made for the faujasite-related zeolites and for zeolite ZK-5 (*9, 10*). These frameworks are called here noncollapsible. What property provides some of these zeolites with such remarkable geomet-

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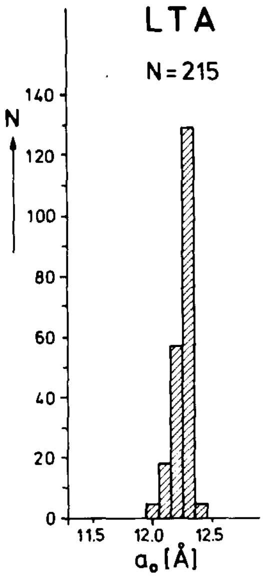

FIG. 1. Histogram of unit cell constants determined for zeolite A (LTA) in space group $Pm\bar{3}m$. Cell constants of zeolites A described in space group $Fm\bar{3}c$ have been halved. Data are taken from ZeoBase (*9*) and have been used even if a crystal structure determination was not performed on the sample.

rical stability and allows others to change their cell constants and cell volumes by so much?

Zeolite A (LTA) is used as an example to show how the two classes of zeolites differ from each other. In the crystal structure of topology LTA (*5*) in space group $Pm\bar{3}m$ (*11*) the *T* and O3 atoms are in special 24-fold positions located on mirror planes, while atoms O1 and O2 are in 12-fold positions located on 2-fold symmetry axes at the intersection of two mirror planes. When the bridging angles *T*–O–*T* are plotted against the unit cell constants *a* for LTA, the angles around the O2 atoms vary with the cell constants, while the angles around the O1 atoms change in the opposite direction (the *T*–O–*T* angles around the O3 atoms increase in the same sense as around O2, but their increase with *a* is much less than for *T*–O2–*T*). Thus the changes in angle around O1 and O2 compensate each other. They distort in an opposite sense; this is called here an *antirotation* of the two hinges. The change in the *T*–O3–*T* angle is not compensated and thus supplies most of the contribution to whatever volume change is observed for the LTA framework. In contradistinction to LTA, all angles around the coordination tetrahedra in natrolite and in zeolite RHO vary in the same sense when cell constants and volumes change (*1, 3*); that is, all *T*–O–*T* hinges *corotate* there. As a consequence, the frameworks of natrolite and of zeolite RHO can collapse until the smallest chemically possible value of the angle *T*–O–*T* (around 124° to 128°, see Refs. (*1, 12, 13*)) is reached for all oxygen atom hinges (or until the framework is stopped from further collapse by contact with guest ions or molecules), while in the LTA framework either the angle *T*–O1–*T* reaches a value of close to 180° and *T*–O2–*T* assumes a value of about 128°, or vice versa (see Fig. 2). The size and shape of the aperture of the eight-member ring is almost the same in the two extreme configurations of LTA (Fig. 3), but rotated by 45°. The maximum diameter of this opening would be reached with an in-between arrangement where the ring could become as circular as possible and the angles *T*–O1–*T* and *T*–O2–*T* would both have values close to 155°. This shape is realized in some of the cation-exchanged forms of zeolite A.

The same picture emerges from a computer simulation (Fig. 4) of zeolite A in which the variation of *T*–O–*T* angles is obtained as a function of the preset unit cell size. The crossover point of *T*–O1–*T* and *T*–O2–*T* is at a value of *a* of about 12.3 Å and at angles between 150° and 160°. More than one-half of all cell constants of zeolite A were found to lie in this range between 12.25 and 12.35 Å (Fig. 1). From Fig. 2 we see that the empirical *T*–O1–*T* and *T*–O2–*T* distributions both flatten out at around a = 12.3 Å, and in this range *T*–O1–*T* can assume values from about 128° to about 155°,

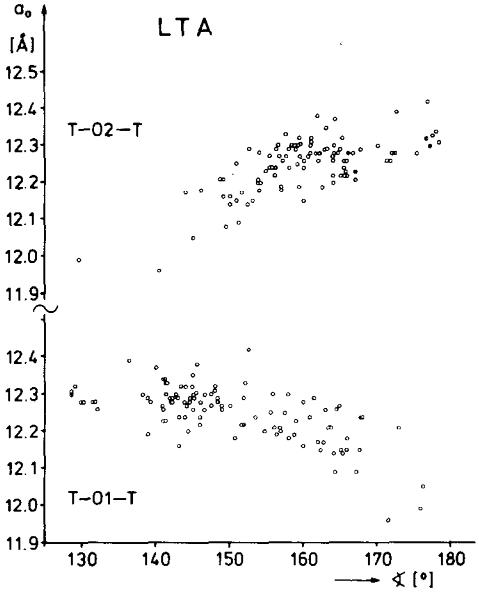

FIG. 2. Plots of angles T–O1–T (bottom) and T–O2–T (top) against the unit cell constants of 108 zeolites A in cases where the crystal structure was determined by single crystal methods or by neutron powder diffraction. As T–O2–T increases, T–O1–T tends to decrease in value. Numerical data from ZeoBase (*9*).

while T–O2–T can range from about 155° to close to 180°. This is an indication of a considerable softness of the framework at values of the cell constant around 12.3 Å: it can deform easily. What this means is that within a given overall size of the framework (fixed unit cell constant) the eight-member rings can deform locally with ease from a square shape to a more rounded shape, with a larger free aperture. Thus, a cation or molecule which is slightly larger than the pore size would allow can still move through the framework which deforms like a boa constrictor around it. Because of this property, frameworks such as LTA or faujasite might perhaps be particularly useful as molecular sieves or catalysts.

All attempts to simulate zeolite A with a = 11.4 in lower symmetries (including space group $P1$) have failed. This was attempted to allow the framework to find an arrangement without strained T–O–T angles. Instead, the simulated structure always returned to the symmetry of the original space group $Pm\bar{3}m$. This seems to indicate that the high symmetry of LTA is inherent in the topology of its connectivity.

Frameworks should be described as collapsible or as noncollapsible. Collapsible frameworks are those in which, upon a change in volume, all hinges corotate, while the framework distorts. Noncollapsible frameworks are those where the hinges anti-

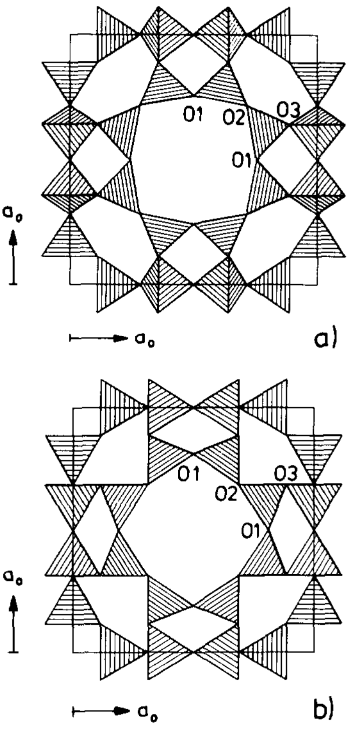

FIG. 3. The two extremes of possible distortions of zeolite A in tetrahedral representation (T atoms at centers of the tetrahedra, oxygen atoms at vertices of the tetrahedra): projections parallel [100] of (a) dehydrated K-exchanged zeolite A (Ref. (*14*), $KAlSiO_4$, a = 12.31 Å, T–O1–T 128.5°, T–O2–T 178.4°, T–O3–T 153.7°) and of (b) dehydrated Li-exchanged zeolite A (Ref. (*7*), $LiAlSiO_4$, a = 11.96 Å, T–O1–T 171.6°, T–O2–T 140.4°, T–O3–T 133.4°). The unit cell is outlined. The plot was made using STRUPLO90 (*19*).

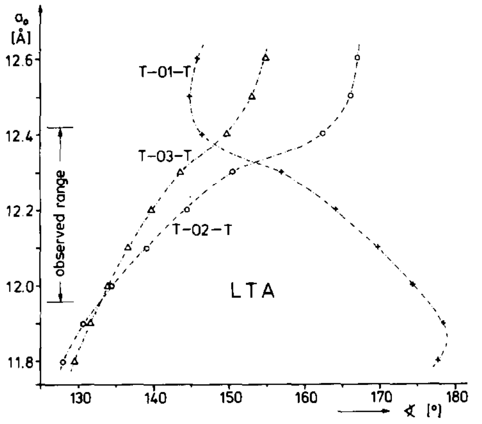

FIG. 4. Plot of angles T–O1–T (crosses), T–O2–T (circles), and T–O3–T (triangles) against the cell constant of zeolite A. This is the result of a computer simulation by distance least squares, DLS (*20*), of zeolite A at preset different values of the cell constants. The arrows and bars indicate the range in a for which zeolites A have been observed. Input values (and weights in simulation) for T–O: 1.665 Å (1.0); for O–O: 2.719 Å (0.5); for T–T: 3.129 Å (0.1). The latter value corresponds to an angle T–O–T of 140°. This means the simulation assumed essentially rigid tetrahedra TO_4 and very flexible hinges T–O–T.

rotate when the volume is changed. Both types are flexible in responding to changes in angle at the hinges. However, the absolute amount of change at the hinges is actually larger for the noncollapsible than for the collapsible frameworks. Individual oxygen atoms can be displaced without change in cell constant by up to 0.5 Å. The difference between collapsible and noncollapsible frameworks lies in the topology involving the symmetry and the geometry of the connections between the rigid parts (in our case the tetrahedra). If the arrangement (the topology) of the flexible connections (the hinges) between the rigid parts is such that one hinge can only open up when another closes, the framework cannot collapse, because the opening angle cannot open beyond being straight, and the closing angle must have a limit before its two sides interpenetrate. Or to put it differently: a framework is noncollapsible if parts of it must be stretched while other parts are compressed and vice versa. Thus a subtle equilibrium is reached in this self-limiting framework topology. How well this balancing operates is shown by the small thermal expansion observed for zeolite A (*15*). It is smaller by a factor of 5 than the thermal expansion of the collapsible framework of zeolite RHO (*16*). In collapsible frameworks the hinges corotate, and compression or tension at all hinges is exerted simultaneously in the same sense. Thermal expansion then depends on the changing interactions between the exchangeable cations and the framework.

Thus, frameworks should be classified into rigid (or inflexible) and flexible, and the latter further subdivided into collapsible, with corotating hinges, and noncollapsible frameworks with antirotating hinges.

Nothing in this discussion limits the results to porous tetrahedral frameworks. Denser tetrahedral frameworks are also classifiable as collapsible or noncollapsible; so are octahedral or mixed frameworks. For example, the tetrahedral frameworks on which quartz, tridymite, and cristobalite are based are collapsible (all angles corotate), while the framework of the feldspar structures is noncollapsible. Actually, the same principle must apply to frameworks with flexible hinges on a macroscopic scale. Many aesthetically pleasing graceful examples of noncollapsible frameworks, albeit not three-dimensionally periodic, are provided by the type of sculpture invented by Kenneth Snelson (*17*). These also are based on the interplay of compression elements (in that case provided by steel pipes) and tension elements (the wire ropes). Fuller would call them tensegrity structures (*18*).

Computer programs used for this work were mainly STRUPLO90 (*19*), DLS-76 (*20*), and SADIAN90 (*21*). I thank Dr. Ammann, director of the Museum für Moderne Kunst, Frankfurt am Main, for providing me with Ref. (*17*), and R. X. Fischer for

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References

1. W. H. Baur, D. Kassner, C.-H. Kim, and N. H. W. Sieber, *Eur. J. Mineral.* **2,** 761 (1990).
2. A. Alberti and G. Vezzalini, *Neues Jahrb. Mineral. Monatsh.* 135 (1983).
3. W. H. Baur, R. X. Fischer, and R. D. Shannon, *in* "Innovation in Zeolite Materials Science" (P. Grobet, W. J. Mortier, E. F. Vansant, and G. Schulz-Ekloff, Eds.) p. 281, Elsevier, Amsterdam (1988).
4. D. R. Corbin, L. Abrams, G. A. Jones, M. M. Eddy, W. T. A. Harrison, G. D. Stucky, and D. E. Cox, *J. Am. Chem. Soc.* 4821 (1990).
5. W. M. Meier and D. H. Olson, "Atlas of Zeolite Structure Types," 2nd ed., Butterworths, London (1987).
6. D. H. Olson and E. Dempsey, *J. Catal.* **13,** 221 (1969).
7. K. Seff and D. P. Shoemaker, *Acta Crystallogr.* **22,** 162 (1969).
8. Z. Jirak, V. Bosacek, S. Vratislav, H. Herden, R. Schöllner, W. J. Mortier, L. Gellens, and J. B. Uytterhoeven, *Zeolites* **3,** 255 (1983).
9. W. H. Baur and R. X. Fischer, "ZeoBase," Frankfurt and Mainz (1991).
10. R. X. Fischer, W. H. Baur, R. D. Shannon, R. H. Staley, A. J. Vega, L. Abrams, and E. Prince, *Zeolites* **6,** 378 (1987).
11. T. Hahn, Ed., "International Tables for Crystallography," Reidel, Dordrecht (1983).
12. A. Bieniok and W. H. Baur, *J. Solid State Chem.* **90,** 173 (1991).
13. W. H. Baur, *Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem.* **36,** 2198 (1980).
14. J. J. Pluth and J. V. Smith, *J. Phys. Chem.* **83,** 741 (1979).
15. J. M. Bennett, C. S. Blackwell, and D. E. Cox, *J. Phys. Chem.* **87,** 3783 (1983).
16. J. B. Parise, L. Abrams, T. E. Gier, D. R. Corbin, J. D. Jorgensen, and E. Prince, *J. Phys. Chem.* **88,** 2303 (1984).
17. K. Snelson, "Skulpturen," Catalogue of the Nationalgalerie, Berlin (1977).
18. R. B. Fuller, "Synergetics," MacMillan, New York (1975).
19. R. X. Fischer, A. le Lirzin, D. Kassner, and B. Rüdinger, *Z. Kristallogr. Suppl. Issue* **3,** 75 (1991).
20. C. Bärlocher, A. Hepp, and W. M. Meier, "DLS-76 Manual," Zürich (1977).
21. W. H. Baur and D. Kassner, *Z. Kristallogr. Suppl. Issue* **3,** 15 (1991).