The Density of Silicon-Rich Zeolite Frameworks

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Abstract

Many low-density frameworks containing channel networks (such as zeolites) are related to periodic minimal surfaces of well characterized surface area. This observation allows a direct connection to be made between the framework density and the average size of rings in the framework that lie on the hyperbolic surface. The analysis exploits the observation that the area per vertex on the surfaces is the same as that for related uncurved sheet silicates, which implies that the density of the framework can be inferred from the average ring size alone. The relation between density and bond lengths and angles is also discussed. A lower bound for the density of open-framework silicates and hydrophobic zeolites is suggested that is consistent with the preferred bonding geometry of SiO_2 networks.

Introduction

The design and synthesis of new crystalline sieve materials depends on our capacity to tune pore size and morphology. Elucidation of the relation between density and structure of the atomic framework would improve that capacity. Apart from empirical correlations between ring size and framework density (FD, the number of Si/Al T atoms in alumino-silicates per 1000 Å^3) in zeolites (Brunner & Meier, 1989), the geometrical factors that set the density of crystalline frameworks are not known. Such three-dimensional crystalline frameworks can always be fitted onto a periodic curved surface that contains all the edges of the framework. The framework is then viewed as a tessellation of a non-Euclidean two-dimensional object whose geometry is hyperbolic. In many cases, the surface contains self-intersections. We confine our analysis to so-called 'open' frameworks, which lie on surfaces that are free of self-intersections, forming open-tunnel labyrinths on either side of the surface. Such surfaces are often well described by infinite periodic minimal surfaces (IPMS) (Andersson, Hyde, Larsson & Lidin, 1988), although our analysis is easily generalized to any hyperbolic surface.

Framework density

The framework density of any three-dimensional network can be expressed in terms of the surface area per unit cell (A) of a hyperbolic surface that contains all vertex atoms in the framework, the cell volume, V, and the surface area per vertex atom, Ω, as FD $(= 10^3 N/V) = 10^3 (A/\Omega V)$, where N denotes the number of vertices per (framework) unit cell. The area of a curved surface defines the average Gaussian curvature, $\langle K \rangle$, $\iint_{\text{unit cell}} K \, da = \langle K \rangle A$. The global Gauss–Bonnet theorem (do Carmo, 1976) yields

$$\text{FD} = 10^3 2\pi |\chi| / (|\langle K \rangle| \, \Omega V),$$

where χ is the Euler–Poincaré characteristic of that portion of the hyperbolic surface in a unit cell of the network. (In general, the unit cell of the framework differs from that of the hyperbolic surface.) In terms of a dimensionless constant, $C = [(A^3)/2\pi |\chi| V^2)]^{1/2}$, the density has the alternative forms

$$\text{FD} = 10^3 C\Omega^{-1} |\langle K \rangle|^{1/2}$$

or

$$\text{FD} = 10^3 C\Omega^{-3/2} (2\pi |\chi| / N)^{1/2}. \tag{1}$$

The connection between the surface topology and the average ring size on the surface follows from Euler's relation (Coxeter, 1969), *viz* $\chi / N = [z + (1 - z/2)n]/n$. Here, z denotes the connectivity (number of edges per vertex) of the framework and n the average ring size (counting only those rings that are spanned by the hyperbolic surface). Hence, the density of a four-connected framework is simply related to the average ring size,

$$\text{FD} = 10^3 C\Omega^{-3/2} [2\pi(n-4)/n]^{1/2}. \tag{2}$$

Bonding geometry

It is intuitively clear that the density is also related to the magnitudes of bond angles and lengths. The connection can be drawn from consideration of the complementary rings to those whose interior contains the hyperbolic surface, namely the 'collar' rings that surround tunnels of the surface. The curvature of the

latter rings is a measure of the normal curvature of any surface that shrouds the network. If all edges of the network describe geodesics of the hyperbolic surface, the curvature of the latter rings is equal to the normal curvature of the surface in the vicinity of the edges. For an arbitrary edge geometry, we can decompose the bending of the edge into two components: the normal curvature and the geodesic torsion. The normal curvature is the curvature of the edge projected onto the plane containing the surface normal vector and the instantaneous tangential direction of the edge. The geodesic torsion is the curvature of the edge projected onto the tangent plane to the surface (do Carmo, 1976).

For a minimal surface, the (average value of the) Gaussian curvature, $\langle K \rangle$, is related to the normal curvature, k_n and the geodesic torsion, τ_g, in a simple way,

$$-\langle K \rangle = k_n^2 + \tau_g^2.$$

The normal curvature of curves on the surface linking adjacent T atoms is set by the Euclidean distances (l) between these atoms and the angles (Δ) subtended by the straight lines joining adjacent T atoms. The magnitude of this curvature is equal to the reciprocal of the radius of a circle that contains three vertices spanned by two adjacent bonds. The average value of the normal curvature of the surface over the region of surface sampled by the two bonds is

$$k_n = 2(\cos \Delta/2)/l. \tag{3}$$

The framework density on a minimal surface can then be estimated with the help of (1),

$$FD = 10^3 C \Omega^{-1} \{[(\cos \Delta/2)2/l]^2 + \tau_g^2\}^{1/2}. \tag{4a}$$

If the (curved) edges are along the lines of curvature on the surface, the geodesic torsion of the network vanishes ($\tau_g = 0$). In this case, the density can be written as

$$FD = 10^3 C\Omega^{-1} |(\cos \Delta/2)2/l|. \tag{4b}$$

At the other extreme, if the edges lie along the asymptotic directions, they are straight ($k_n = 0$) and the framework is torsional only (do Carmo, 1976).

Equations (2) and (4) relate the framework density to the average ring geometry in the framework. The former equation admits calculation of the density as a function of the average ring size of those rings spanned by surface, while the latter describes the density in terms of the bonding dimensions of collar rings. To proceed further, C and Ω must also be specified.

For intersection-free triply periodic minimal surfaces, C is approximately equal to $\frac{3}{4}$ (Hyde, 1990). The vertex density on the surface (Ω^{-1}) depends on the choice of surface, which is not unique. Surfaces of differing topology can be fitted to a framework, which depends on the rings chosen to lie on the

Table 1. *Density data for framework (alumino-) silicates, with lowest-genus periodic minimal surfaces consistent with tunnel morphologies*

Zeolite/ silicate	Si/Al ratio	FD (T atoms $\times 1000$ Å^3)[ref]	Surface[ref]	$|\chi|/N$	n
Zeolite X	1–1.5	12.4[1]	D[5]	0.08	4.36
Faujasite	2.31	12.7[2]	D	0.08	4.36
Zeolite Y	1.5–3	12.7[1]	D	0.08	4.36
Hexagonal faujasite	>3	12.7[3]	T-WP[6]	0.08	4.36
Hydrophobic zeolite Y	>5	13.3[4]	D	0.08	4.36
Rho	3	14.3[2]	P	0.08	4.36
ZK5	2	14.6[2]	I-WP	0.12	4.57
Gismondine	1.00	15.4[2]	T	0.12	4.57
Linde A	1.00	12.9[2]	P[5]	0.17	4.80
Gmelinite	2.00	14.6[2]	H[5]	0.17	4.80
Sodalite	1.00	17.2[2]	D	0.17	4.80
ZSM5	8.00	17.9[2]	Genus 9 surface[7]	0.17	4.80
Melanophlogite	∞	18.9[2]	–	0.20	5.00

$|\chi|/N$ denotes the ratio of the Euler-Poincaré characteristic (per zeolite unit cell) to the number of T atoms in the unit cell. n is the average T-atom ring size on the surface. The choice of lowest-genus surface is discussed in the main text.

The surfaces for hexagonal faujasite and melanophlogite are unknown. In the former case, ring sizes and surface topology must be the same as those for zeolite Y. In the latter, all six-rings define tunnels of the clathrate structure so that the average ring size is five.

References: (1) Breck (1974); (2) Meier & Olson (1987); (3) Annen, Young, Arhancet & Davis (1991); (4) Thomasson, Lidin & Andersson (1987); (5) Andersson, Hyde, Larsson & Lidin (1988); (6) Karcher (1989); (7) Hyde (1991).

surface and on those chosen to surround a tunnel (forming a collar). The two-dimensional nature of the frameworks becomes apparent by focusing on those contiguous faces bounded by smaller rings. (Larger rings then define the tunnels.) Accordingly, we choose the surface that minimizes the value of the average ring size on the surface, n (and maximizes Ω^{-1}). By this convention, its Euler–Poincaré characteristic (χ) and the genus attain the least magnitudes possible for the framework fitted onto a hyperbolic surface.

To check the validity of these equations for silicate frameworks, the magnitude of Ω must be set. The simplest assumption is that this value is equal to that of flat-sheet silicates. In other words, we assume that the surface density is independent of the surface curvature. Under this assumption, surface densities in silicate frameworks can be estimated from unit-cell dimensions of (flat-) sheet silicates, viz $\Omega = 12.0$ Å^2 per SiO_2 group for talc (Brindley & Brown, 1980).

Table 1 lists framework (alumino-) silicate data consistent with the convention for surface topology described above. Fig. 1 shows the plot of measured framework densities for a range of open-framework alumino-silicates compared with the values expected from (2).

We were surprised to find that our twin assumptions, of constant surface density and hyperbolic surfaces close to minimal surfaces, hold, to a reasonable

approximation. The framework densities for silicon-rich zeolites Y, hexagonal faujasite, rho, ZSM5 and the silicate melanophlogite are close to the theoretical curve based on the surface density of talc. The area per SiO_2 group is apparently unchanged from that in the flat state, regardless of topology. Thus, the density is dependent only on the average ring size.

We note that the FDs of zeolites containing aluminium fall below the silicate curve. This is expected because of the larger area required for aluminium atoms as well as the variable influence of interstitial templating species. A general trend of increasing area with aluminium content is discernible, although further quantification is marred by the presence of the templating species.

Given this apparent conservation of surface density in silicate networks, a number of disparate observations can be reconciled. Brunner & Meier (1989) have observed that the minimum FD in zeolites is related to the size of the smallest ring in the framework. We have established that the framework density increases monotonically with the average ring size, n. Our convention for the surface topology ensures that larger rings do not contribute to n. Hence, the smallest rings are a crude measure of the average ring size, whose value determines the FD. Consequently, the least-dense zeolite frameworks will contain a large proportion of three- and four-rings, in accord with an earlier hypothesis of Brunner (1979).

We turn now to the bonding geometry in silicate frameworks. The T-T distance is related to the T-O bonding parameters by the equation $l = 2d(\sin \alpha_0/2)$, where d is the T-O bond length and α_0 is the T-O-T bond angle. Recall that Δ denotes the (vertex) angle of collar rings about a T atom formed by connecting adjacent T atoms with straight lines. In total, six

angles occur at each vertex of four-connected nets. Four of these angles lie in the hyperbolic surface and two define the vertex angles of the collar rings (Δ). Δ is related to the O-T-O angle (α_T) and the T-O-T angle (α_0) by $\alpha_T - \pi + \alpha_0 \le \Delta \le \alpha_T + \pi - \alpha_0$. The bounds are achieved for torsionless frameworks ($\tau_g = 0$), in which case the bound reached depends on the location of the two O atoms bonded to the three T atoms (which subtend the angle Δ) relative to the ring containing the T atoms. The upper limit is realized if the O atom lies inside the ring; the lower bound requires all O atoms to lie outside the ring.

It is clear from (4a) that the density is minimized when the geodesic torsion of the framework vanishes. This occurs when the net edges are parallel to the principal directions. If all O atoms lie inside rings formed by connecting adjacent T atoms ($\Delta = \alpha_T + \pi - \alpha_0$), the density is further reduced. If the bond angles and lengths are constrained, (4b) provides an estimate of the most open framework that can be realized in SiO_2 networks. The Si-O bond length is typically equal to 1.61 Å, the O-T-O angle is 109.5° and the T-O-T angle is 140° (Liebau, 1985). These data yield a minimum FD for silicon-rich zeolites of 10.7 T atoms per 1000 Å^3 (average ring size 4.2), compared with 13.3 for the least-dense open-framework silicate synthesized to date, hydrophobic zeolite Y. Meier (1986) has designed a number of hypothetical frameworks containing three-rings whose densities are close to this minimum value. The stability of three-rings is, however, questionable. More recently, O'Keeffe (1991) proposed a 'rare' four-connected net whose smallest rings are four-rings (his net #15) whose density is also close to this limiting value. Such a low value of the FD can only be achieved when all the (coplanar) O atoms lie within the silicon rings, which may be a sterically unfavourable configuation.

Four-connected nets of lower framework density than the minimum density derived here have been proposed as hypothetical zeolite frameworks. Such nets can only be realized at the expense of the usual bond angles.

Lower bounds on the FD of other materials can likewise be determined. A number of reports suggest that sieve materials of lower density than open-framework silicates can be made by substitution of Al and P (Wilson, Lok, Messina, Cannon & Flanigen, 1982) or Ga and P (Estermann, McCusker, Baerlocher, Merrouche & Kessler, 1991) in the T-atom positions. If so, the relation between the surface density and bonding dimensions embodied in (3) must reflect this expectation. The anticipated lower surface densities ($\Omega > 12.0$ Å^2), together with the smaller T-O-T angles in cristobalite-related structures for Al-O-P and Ga-O-P compared with Si-O-Si (O'Keeffe & Hyde, 1976), account for the low FDs. The low value of the Ge-O-Ge angle in cristobalites
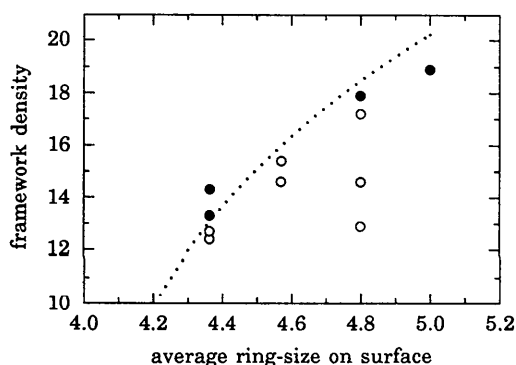

Fig. 1. Plot of framework density *versus* the average ring size of the hyperbolic net (n) for zeolites (and the open-framework silicate melanophlogite, see Table 1). The curve is calculated from equation (2), which is valid for a four-connected network on a minimal surface occupying an area of 12.0 Å^2 per vertex on the surface (corresponding to the area per SiO_2 group in talc). The filled circles denote high-silica structures whose Si : Al ratio exceeds three.

suggests that low-density-framework germanates should be particularly stable.

The recent announcement of ultralarge pores (~ 50 Å) in 'zeolites' (Kresge, Leonowicz, Roth, Vartuli & Beck, 1992) clearly violates the expected lower bound on the framework density of zeolites derived in this paper. We expect the atomic frameworks of these large-pore materials to differ from the zeolites considered here: *viz* hyperbolic alumino-silicate monolayers. Our calculations suggest that these structures are probably related to double-layer silicates, which lie on hyperbolic 'mesh' surfaces (Hyde, 1993).

The analysis does not take into account the variations of Gaussian curvature over the tessellating surface and is therefore most accurate for low-density structures, such as those included here. Furthermore, the value of the variable C in the equations has been derived for minimal surfaces. Admittedly, many framework structures do not form geodesic nets on periodic minimal surfaces; in many cases, parallel surfaces to minimal surfaces offer better descriptions. For example, the T atoms in the faujasite framework are displaced approximately $\frac{1}{6}$ of a typical tunnel radius from the D surface. Using the standard formulae for parallel surfaces, we estimate the area of the parallel surface to be less than 3% smaller than that of the D surface, in which case the constant C is overestimated by less than 5%. Clearly then, at this stage, the assumption of homogeneous minimal surfaces is adequate to describe the faujasite framework.

This approach, which views three-dimensional silicate frameworks as non-Euclidean two-dimensional structures, reveals a striking universality. The constancy of surface density suggested by this analysis is a novel constraint on the geometries of open-framework structures, in addition to the usual requirements of preferred bonding dimensions. Indeed, density/ring-size data for a number of other clathrate frameworks (water, silicides, germanides) suggests that the constancy of surface density – irrespective of the framework curvature – may be a more general structural requirement (Hyde, 1993). The areas per C atom in the sp^2 carbon polymers graphite and C_{60} fullerene are 2.62 and 2.64 Å^2, respectively. Note that the predicted surface densities of hypothetical hyperbolic sp^2 carbon polymers (dubbed 'schwarzites') (Mackay & Terrones, 1991; Lenosky Gonze, Teter & Elser, 1992; Vanderbilt & Tersoff, 1991; O'Keeffe, Adams & Sankey, 1992) do not exhibit this univer-

sality. Clearly, then, the constraint is not a trivial one, automatically satisfied by standard interatomic potentials.

We have excluded so-called 'dense' framework silicates from our analysis. We expect these structures to be related to self-intersecting surfaces, for which surface-area data are less certain. However, in these cases too, it seems that this two-dimensional picture of frameworks holds: analyses of dense silicates (tridymite and quartz) (Hyde, 1993) reveals the same surface density as that found here.

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