INTERSTITIAL NANOSTRUCTURES IN ENGINEERED SILICATES

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ABSTRACT

Interstices in silicates play an important role in various technologies such as gas transport in glasses and catalysis in zeolites. The interstices are generally in the nanometer-range and, in non-crystalline silicates, are important components of “medium-range” structure (larger than the tetrahedral building blocks). The atomic structures of crystalline silicas such as quartz and cristobalite are analogs of vitreous silica and can be described as a packing of filled oxygen polyhedra (SiO$_4$ tetrahedra) and empty ones (interstices of various shapes). Computer simulation software has been used to describe the interstices quantitatively. In addition, the energetics of high-silica zeolites is directly related to the internal surface area of these interstices. Computer simulation also allows the interstitial surface area in vitreous silica to be compared to that for the common silica polymorphs (quartz and cristobalite) as well as a wide-range of the high-silica zeolites.

INTRODUCTION

Silicate glasses are known for their permeability to various gases [1], and zeolites are widely used as catalysts and molecular sieves [2]. These material applications depend on nano-scale interstitial structure, which is in turn a useful structural descriptor. As in Bernal’s canonical hole model of liquids [3], interstitial voids are defined by connecting the centers of adjacent atoms. Amorphous metals [4] and metallic grain boundaries [5, 6] have been modeled in this way. An advantage of the stacking of polyhedra as a structural descriptor is that the technique does not “break down” as one goes from crystalline to defective to completely non-crystalline structures.

The interstitial structure of cristobalite helped to illustrate the nature of gas transport in vitreous silica [7]. Oxygen polyhedra (edge-shared CaO$_6$ octahedra) defined medium-range ordering in calcium silicate glass, for which wollastonite is a crystalline analog [8]. A wide range of silicates has silica tetrahedra intricately linked to non-silicon metal-oxide polyhedra, often assembled as planar sheets of edge-shared octahedra (e.g., wollastonite) [9]. In identifying crystalline analogs
of silicate glasses, one can identify the shapes of the unfilled polyhedra (interstices) as well as the filled ones (e.g., SiO₄ and CaO₆). The interstitial structure of wollastonite (distorted tetrahedra, square pyramids, and triangular prisms) has been identified as part of a general description of the canonical hole set for non-metallic solids, such as silicates [11]. Based on the constructable, convex polyhedra identified by Zalgaller [12], the canonical hole set for silicates [11] consists of 44 simple polyhedra. This number is larger than the eight simple, Bernal holes for metals [5] due to the different bonding. (Some covalent, directional bonding in ceramics allows more open, cage-like structures in contrast to the densely packed nature of metallic, non-directional bonding).

INTERIOR NANOSTRUCTURES IN CRYSTALLINE SILICAS – ANALOGS FOR VITREOUS SILICA

Images of silica polymorphs and associated interstitial structure were created using software from Accelrys (formerly known as Molecular Simulations Inc. [MSI] and BIOSYM Inc.) on Silicon Graphics workstations [10]. Interstitial polyhedral volume calculations were performed using simple vector analysis. The process involved calculating an interstitial polyhedron volume as the sum of tetrahedral volume elements. To confirm the accuracy of the method, the sum of volumes of SiO₄ tetrahedra and the interstitial polyhedra were shown to be equivalent to the total volume of the corresponding unit cells.

Figure 1 shows three adjacent interstitial polyhedra (truncated tetrahedra) in high cristobalite, the simplest of the silica polymorphs. In this crystalline analog for vitreous silica, there are eight interstitial polyhedra along with eight SiO₄ tetrahedra in the cristobalite unit cell [7]. Figure 1 illustrates the utility of this approach for monitoring diffusional paths in relatively open network silicates. Six-membered rings (hexagons) serve as doorways between adjacent truncated tetrahedra.

Although cristobalite is an appropriate crystalline analog for vitreous silica [7], the range of ring sizes in the non-crystalline material requires that some smaller interstices also exist. The interstices in the common, higher-density polymorph low quartz provide some indication of the nature of the smaller polyhedra expected in silica glass [10]. The linkage of SiO₄ tetrahedra in low quartz follows a double helix when viewed along the c-axis [13]. It is interesting to note that the interstices found in low quartz are of the same type found in wollastonite [11], viz. distorted tetrahedra, square pyramids, and triangular prisms. Of course, the exact nature of the distortion is somewhat different in the two cases. Quartz, like wollastonite, is a relatively tight structure with interstitial space represented by a limited number of relatively small oxygen polyhedra. These relatively small interstices shown in Figure 2 are part of the complete set of polyhedra for non-metallic solids given in Table 1.
Figure 1. A diffusional path in high cristobalite illustrated by three, adjacent interstices (each being a truncated tetrahedron). The doorway between adjacent polyhedra is a six-membered, hexagonal ring.
Figure 2 With the c-axis in the plane of the page, one can see how a set of interstices (two distorted tetrahedra and two distorted square pyramids) packs into the space between two adjacent silica tetrahedra along the quartz double helix. Also, the interstitial space along the c-axis is filled with distorted triangular prisms.

Table I. Polyhedra sets for interstices in metals and nonmetals [1]

<table>
<thead>
<tr>
<th>Metals</th>
<th>Nonmetals</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 polyhedra (with up to 20 triangular faces)</td>
<td>44 polyhedra</td>
</tr>
<tr>
<td>28 simple, convex regular polyhedra</td>
<td></td>
</tr>
<tr>
<td>8 prisms</td>
<td></td>
</tr>
<tr>
<td>8 antiprisms</td>
<td></td>
</tr>
</tbody>
</table>

*Ref. [5], #Ref. [11], &Ref. [12]

In Table II, the sizes of the interstices found in the crystalline analogs of vitreous silica are compared with the distribution of interstitial solubility site sizes determined by the analysis of gas transport in vitreous silica [14]. Assuming an oxygen radius corresponding to a 50 - 75% covalent nature of the Si-O bond [15], the inscribed sphere diameters for regular polyhedra and the "doorways" into those polyhedra are the appropriate comparison for the "sizes" of interstices determined by gas probe atoms. The values of the doorway sizes in Table II are in good agreement with the range of interstitial sizes determined by gas transport (0.1 to 0.4 nm) [14].

Table II. Size of interstices and their distribution in metals and nonmetals [10]

<table>
<thead>
<tr>
<th>Interstice</th>
<th>Inte</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedron</td>
<td>0.14</td>
</tr>
<tr>
<td>Square pyramid</td>
<td>0.19</td>
</tr>
<tr>
<td>Triangular prism</td>
<td>0.22</td>
</tr>
<tr>
<td>Truncated tetrahedron</td>
<td>0.44</td>
</tr>
</tbody>
</table>

*Using an oxygen radius of 0.067 nm, corresponding to a 50% covalent nature of the Si-O bond [15].

The next phase of the current study involved a detailed analysis of all interstices in a vitreous silica framework density, the number of interstitial sites, and the distribution of interstitial site sizes. Garofalini [16]. The linkage of interstices illustrated in Figure 3, for which the linkage of interstices is evident. The Fueston and Garoff basis of an independent study by Garofalini [16]. The linkage of interstices illustrated in Figure 3, for which the linkage of interstices is evident. The Fueston and Garoff basis of an independent study by Garofalini [16].

INTERIOR NANOSTRUCTURES: COMPARISON WITH VITREOUS SILICA

The Cerius² modeling environment allows the complex interior surfaces to be mapped out by a wide range of internal surfaces. It is interesting to apply the Cerius² modeling environment to the complex interior surfaces of the zeolites, as well as to the framework density, the number of interstitial sites, and the distribution of interstitial site sizes. Garofalini [16]. The linkage of interstices illustrated in Figure 3, for which the linkage of interstices is evident. The Fueston and Garoff basis of an independent study by Garofalini [16].

In Figure 5, the interior surfaces of the zeolites are mapped out by a 0.096 nm diameter. Moloy, et al. In Figure 5, the interior surfaces of the zeolites are mapped out by a 0.096 nm diameter. Moloy, et al.

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Table II. Size of interstices and their doorways (as inscribed spheres\(^*\)) for quartz and cristobalite [10]

<table>
<thead>
<tr>
<th>Interstice</th>
<th>Interstice dia. [\text{nm}]</th>
<th>Doorway</th>
<th>Doorway dia. [\text{nm}]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tetrahedron</td>
<td>0.147 - 0.190</td>
<td>Triangle</td>
<td>0.128 - 0.172</td>
</tr>
<tr>
<td>Square pyramid</td>
<td>0.197 - 0.241</td>
<td>Square</td>
<td>0.197 - 0.241</td>
</tr>
<tr>
<td>Triangular prism</td>
<td>0.227 - 0.271</td>
<td>Square</td>
<td>0.197 - 0.241</td>
</tr>
<tr>
<td>Truncated tetrahedron</td>
<td>0.442 - 0.486</td>
<td>Hexagon</td>
<td>0.275 - 0.319</td>
</tr>
</tbody>
</table>

\(^*\)Using an oxygen radius of 0.067 - 0.089 nm corresponding to 50 - 75\% covalent nature of the Si-O bond [15].

The next phase of the current research will focus on systematically cataloging all interstices in a vitreous silica model equivalent to that of Fueston and Garofalini [16]. The linkage of tetrahedra for the Fueston-Garofalini model is illustrated in Figure 3, for which a wide variety of interstitial geometries are evident. The Fueston and Garofalini model is especially interesting as it is the basis of an independent study by Chan and Elliott [17] who showed that the distribution of interstitial site sizes closely follows a log-normal distribution consistent with that based on gas solubility data [7].

**INTERIOR NANOSTRUCTURES IN HIGH-SILICA ZEOLITES – A COMPARISON WITH VITREOUS SILICA**

The Cerius\(^2\) modeling environment is an Accelrys simulation product that allows the complex interior surface area of interstitial regions to be mapped, as illustrated for a zeolite structure in Figure 4. Moloy, \textit{et al.} have shown that the formation enthalpy of a wide range of high-silica zeolites displays a linear relationship with this internal surface area [2]. The slope of the regression line through the data corresponds to an internal surface enthalpy with a value of 0.093 ± 0.009 \text{J/m}^2, in good agreement with the experimental value for external silica surfaces.

It is interesting to apply the technique used by Moloy, \textit{et al.} [2] to vitreous silica. Figure 5 shows the interior surface area of the structure in Figure 3 mapped out by a 0.096 nm diameter probe atom, the same size as used in the study by Moloy, \textit{et al.} In Figure 6, one can see that the interior surface area of vitreous silica follows the same general trend shown by the relatively open, cage structures of the zeolites, as well as the common (and more dense) silica polymorphs quartz and cristobalite. The horizontal axis in Figure 6 is the framework density, the number of tetrahedra per unit volume.
Figure 3 The linkage of tetrahedra in a vitreous silica model equivalent to that of Fueston and Garofalini [16].

Figure 4 Example of (a) a zeolite defined by tracing out accessible

Figure 7 shows that the enthalpy area for a wide range of silica. Moloy, et al. [2]. The enthalpy between the given silica and the vitreous silica is consistent with crystalline silicas reported by Moloy.

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We thank T.E. Allis of the Un N. Khosrovari, and A. Amiri of experimental help. Professor provided numerous useful discussions corresponding to Figure 3. Pr Thermochemistry Facility at the especially helpful discussions regarding us (LPD) was supported by the U Fellowship (SEGRF) Program.

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Figure 4 Example of (a) a zeolite structure for which (b) an interior surface area is defined by tracing out accessible space by a probe sphere of radius $= 0.05$ nm.

Figure 7 shows that the enthalpy of transition ($\Delta H_{\text{trans}}$) versus internal surface area for a wide range of silica structures follows a linear trend, as noted by Moloy, et al. [2]. The enthalpy of transition is defined as the enthalpy difference between the given silica and that of $\alpha$-quartz. One can note that the value for vitreous silica is consistent with this linear trend exhibited by the wide range of crystalline silicas reported by Moloy, et al.

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Figure 5 The interior surface area of the structure in Figure 3 mapped out by a 0.096 nm diameter probe atom.

Figure 6 Interior surface area in silica zeolites, along with quasi framework density (the number of interior surface area of vitreous silica of crystalline silicas.


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Figure 6 Interior surface area in a wide variety of silica structures (mostly high-silica zeolites, along with quartz, cristobalite, and vitreous silica) versus framework density (the number of tetrahedra per unit volume). Note that the interior surface area of vitreous silica follows the overall trend for the wide range of crystalline silicas.


Figure 7 Enthalpy of transition in a wide variety of silica structures (mostly high-silica zeolites, along with quartz, cristobalite, and vitreous silica) versus internal surface area. Note that the datum for vitreous silica follows the overall trend for the wide range of crystalline silicas reported by Moloy, et al. [2].