Ab Initio Computer Modelling of Basic Units in Zeolite Frameworks

Mitsuo Sato* and Hirofumi Uehara
Department of Chemistry, Gunma University, Kiryu, Gunma 376

(Received July 17, 1996)

A new computer modelling system for derivation of basic units in zeolite frameworks was developed on the basis of graph theory and molecular simulation. In the first step, all the kinds of concentric clusters(CCL) were derived on the basis of graph theory, and in the second step, three dimensional models of them were constructed by means of molecular mechanics simulation. In the 2nd CCLs, all the combinations of 4- and 5-membered rings in zeolite frameworks were realized systematically.

Several concepts such as SBU(secondary building unit)[1] or SSU(structural subunit)[2] have been introduced for modelling as well as characterizing of zeolite frameworks. All these units have been derived from the known structural frameworks, not from any mathematical basis. A mathematical concept which is termed as consecutive Concentric Cluster(CCL) has been introduced on the basis of graph theory.[3] The CCL is a kind of graph which propagates concentrically around a framework node. The extension of it is regulated in terms of the topological distance. The CCL of topological distance n=0 is the framework node itself, while the CCL of n=1 a graph of one central node and 4 neighboring nodes. Both of them are common in any kind of zeolite frameworks. When extending the distance n=2,3,4,.. , various kinds of CCLs can be formed. Among them, the CCLs of n=2 are the least criteria for framework characterization and the minimum basic units for framework construction. In this paper, ab initio modelling of them in 3-dimensional space are shown.

A given CCL consists of both front and inner nodes. The front nodes in the nth CCL are defined as nodes located at topological distance n, while the inner nodes as those of less than n. The valences of the inner nodes are all 4, while those of the front nodes are either 1,2,3 or 4, depending on the connectivity relation between the front nodes. It has been shown that the topological characteristics of the CCLs are realized on the valence type and the frequency of the front nodes. A four digit symbol which is called degree sequence is introduced for characterizing them, in which the number of nodes are arranged in the order of their valences 1,2,3,and 4. The distinct degree sequences can be easily derived by using some mathematical relationships holding for graph generation. Total number of 869 is obtained for the case of n=2. However, for a given degree sequence, there are much more graphical representations. For example, a degree sequence (8,2,0,0) has three different CCLs, and (6,3,0,0) six different CCLs. An algorithm for deriving all the connectivity graphs for a given

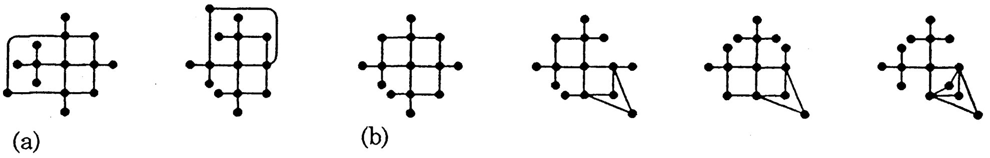

Figure 1. All the 2nd CCLs derived for a degree sequence (6,3,0,0).

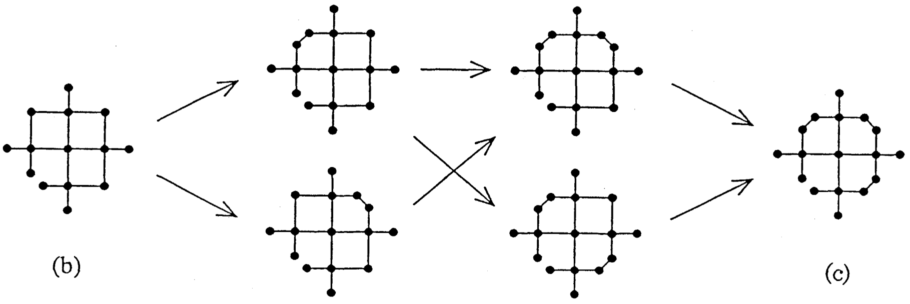

Figure 2. Systematic derivation of 5-membered rings from a 4-memberd ring.

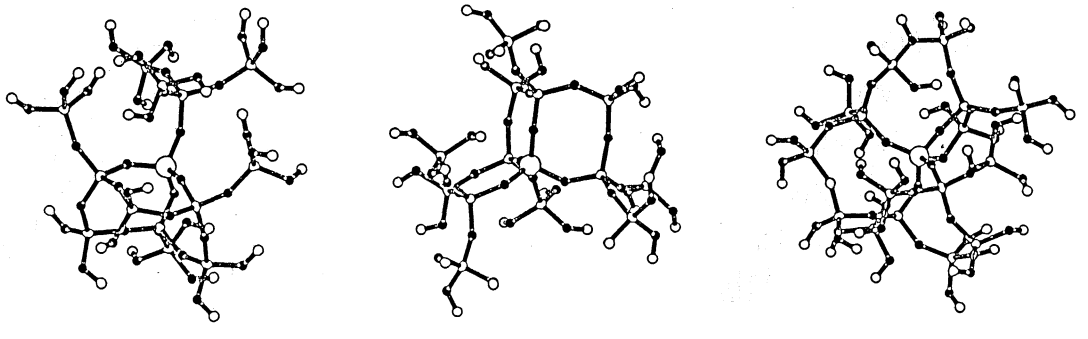
(a) -114.82 (b) -114.55 (c) -155.25

Figure 3. Some of examples of simulated basic units. Numerals show their potential energies in kcal/mol. Four-connected open circles denote Si atoms, terminal open ones H atoms and black ones O atoms. The obtained models (a),(b),(c) correspond to the graphs (a),(b),(c) in Figure 1 and Figure 2.

degree sequence has not been yet presented. In this paper, this can be achieved by use of Hendrickson's maximum adjacency matrix method,[4] which was originally proposed for the canonical numbering of the molecular graph. All the kinds of combinations of point coalescence and edge sharing can be realized in an $m \times m$ matrix representation, m denoting the total number of graph nodes. In the representation, the point coalescence is localized in the restricted region, which gives us all the combinations of 4-membered rings in zeolite frameworks. The isomorphism of graph can be identified by introduction of characteristic polynomial of matrix. The result shows the number of topologically different combinations of them to be 95 in total. On the contrary, the edge sharing, which creates 5-memberd ring, takes more extended region of matrix. To avoid the difficulty of matrix operation in the extended region, a new composite operation is introduced. The operation, which is defined as that of separation of coalesced point followed by edge addition, is based on the fact that the point coalescence to form 4-membered ring is topologically equivalent to the edge addition to form 5-membered ring. This results in the formation of 5-membered ring by replacing the the 4-membered ring. Figure 1 shows all the CCLs derived for a degree sequence (6,3,0,0), and Figure 2 the process of derivation of related 5-membered rings from a given 4-membered ring.

In the construction of 3-dimensional CCLs on the basis of these graphs, the molecular mechanics can be available, which are widely used in the filed of organic molecules. The modelling included only SiO_4 and $Si(OH)_4$ tetrahedrons, not including AlO_4 and $Al(OH)_4$. The force field V is represented by a sum of potential energy terms,

$$V = V_{\text{bond}} + V_{\text{angle}} + V_{\text{torsion}} + V_{\text{van der Waals}} + V_{\text{elect}}$$

where V_{bond} indicates the Si-O bond stretching with a harmonic function, V_{angle} the O-Si-O and Si-O-Si bond angle bending with a harmonic function, V_{torsion} the Si-O-Si-O angle dihedral angle torsion, $V_{\text{van der Waals}}$ van der Waals function, and V_{elect} electrostatic interactions. The force field parameters are taken from Mabilia et al.,[5] and Nicholas et al.[6] Computer simulation is performed on the program HyperChem MM+.[7] The equilibrium values adopted are 1.61 Å for Si-O distance, 109.5° for O-Si-O angle, and 149.5° for Si-O-Si angle.

In this modeling, Si atoms are set on the nodes of the connective graph, while oxygen atoms in the midpoints of them to form SiO_4 tetrahedron. In the front nodes, additional H atoms are set to form $Si(OH)_4$. Some of results are shown in Figure 3 in association with their calculated potential energies. In the Figure, (a) is a known basic unit of CLO(Cloverite) and LTA(Linde A), and (b) that of FAU(Faujasite), EMT (Hexagonal Faujasite), PHI(Phillipsite), CHA(Chabazite) etc., while (c) including 5-membered ring is unknown. In the cluster (a), the neighboring 4-memberd rings are perpendicular to one another, resulting in the formation of double 4-membered ring D4R in the SBU criterion. In the cluster (b), the neighboring 4-membered rings make angle of 120° each other, resulting in the formation of double 6-membered ring D6R in the SBU criterion. These results strongly suggest that the system presented here could realize completely both of SBU and SSU criteria in the extension process of its topological distance.

References

1 W.M.Meier and D.H.Olson, Atlas of zeolite Structure types, Butterworth(1992).
2 J.V.Smith, *Chem.Rev.*, **88**,149(1988).
3 M.Sato, *J.Phys.Chem.*, **91**,4675(1987).
4 J.B.Hendrickson and A.G.Toczko, *J.Chem. Inf.Comput. Sci.*, **28**,171(1983).
5 M.Mabilia, R.A.Pearlstein and A.J.Hopfinger, *J.Am. Chem. Soc.*, **109**,7960(1987).
6 J.B.Nicholas, A.J.Hopfinger, F.R.Trouw, L.E.Iton, *J.Am. Chem. Soc.*, **113**,4792 (1991).
7 HyperChem, Release4.0, Hypercube, Inc. Canada.