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Similarity of Zeolite Micropore Structures

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ABSTRACT. Similarity indexes for six loop configurations of zeolitic T-atoms are calculated on the basis of n-dimensional vectors with the procedure of normalization taking into account the unitary self-similarity of each configuration as well as the possibility of "sliding" for the low-dimensional vectors that topologically is considered as an addition of apexes not connected with the graphs of loop configuration. Complicacy of loop configurations and similarity of zeolite structures characterized by two loop configurations are considered in the frame of the proposed approach. © *2007 Bull. Georg. Natl. Acad. Sci.*

Key words: *zeolite, loop configuration, adjacency matrix, similarity index, complicacy.*

Zeolites and zeolite-like materials do not comprise an easily definable family of crystalline solids [1], and description of zeolite structure includes loop configuration of T-atoms (atoms of Si, Al, P, Ge, etc.). The loop configuration is a simple graph showing how many 3- or 4-membered rings a given T-atom is involved in. In all known structure types of zeolites and zeolite-like materials, including interrupted frameworks, 16 loop configurations are observed. Figure 1 shows 6 loop configurations of highest frequency of occurrence in natural and synthetic zeolites; black dots represent T-atoms, solid lines show T-O-T linkages with rings.

The adjacency matrix having unitary non-diagonal elements for connected apexes is an invariant of the loop configuration graph. Structure type codes for zeolites characterized by only one type of loop configuration, the frequency of their occurrence, and results of calculations - characteristic polynomial $P_G=a_0+a_1x+a_2x^2+...+a_{n-1}x^{n-1}+x^n$ of the corresponding adjacency matrix represented as vectors (a_0, a_1, a_2,...,a_{n-1}, 1) are given in the Table 1.

Characteristic polynomial P_G can be applied for comparison of similarity of loop configurations in the same way as it is proposed for quantitative assessment of the structural similarity of organic molecules [2].

A known algorithm [4] of evaluation of the similarity index SI(A-B) for two graphs A and B (characterized by $P_A=a_0+a_1x+a_2x^2+...+a_{n-1}x^{n-1}+x^n$ and $P_B=b_0+b_1x+b_2x^2+...+b_{m-1}x^{m-1}+x^m$) including construction of positive fractions from equivalent polynomial coefficients ($|a_0/b_0|$, $|a_1/b_1|$, $|a_2/b_2|$, etc., with bigger coefficient in denominator and smaller coefficient in nominator), and summing up of the obtained fractions have been used, but normalization was carried out in a different manner, taking into

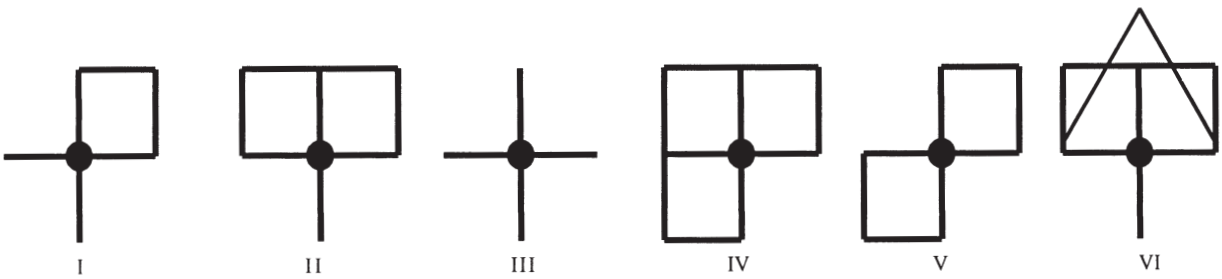

Fig. 1. Loop configurations frequently occurred in zeolite and zeolite-like structures

Table 1

Characterization of loop configurations

Graph	Structure type code	Frequency	P_G
I	MON	38	(0,0,4,0,-2,0,1)
II	CAN, MAZ	34	(0,3,0,7,0,-3,0,1)
III	BIK, FER, MEP, TON, VET	31	(0,0,0,-4,0,1)
IV	CHA, FAU, GIS, GME, MER, PAU, PHI, PHO	30	(3,0,-10,0,9,-2,-8,0,1)
V	LTA	23	(0,8,0,12,0,-6,0,1)
VI	ANA, LAU, SOD	9	(0,4,3,-6,7,2,-3,0,1)

consideration the self-similarity of each graph. In the frame of an approach applied for quantitative assessment of structural similarity of organic molecules [5] the normalization by max{n,m} has been taken into account; such procedure for loop configurations gives fractional indexes of self-similarity (e.g., SI(I-I) = SI(II-II) = $^1/_2$, SI(III-III) = $^1/_3$, SI(IV-IV) = $^5/_9$, etc.), which is not good for quantitative measures and causes several difficulties. It is possible to consider the unitary self-similarity for each graph during their comparison taking into account max{$n_{\neq 0}$, $m_{\neq 0}$}, where $n_{\neq 0}$ is the number of $a_i \neq 0$, and $m_{\neq 0}$ is the number of $b_i \neq 0$. For example, the sum of positive fractions for graphs I and IV, ($^4/_{10}+^2/_9+^1/_8$) = 0.7472, is normalized by 6, the maximum number of non-zero coefficients in the characteristic polynomial of P_{IV}. The results obtained are given in Table 2.

The highest indexes characterize the similarity between loop configurations II and V, graphs IV and VI are characterized by rather high similarity also; it is to be mentioned that graphs in both pairs have the same dimensions. Comparison of graph I with graphs II, III, and V shows an absence of similarity between the aforesaid loop configurations - all fractions and, correspondingly, SI(I-II), SI(I-III), and SI(I-V) are equal to zero. Such result is not connected with the difference in dimensions, because graphs II and III having rather different dimensions (7 and 5 apexes) are characterized by a rather high similarity index SI(II-III)=0.2262.

In spite of different dimensions, visually and intuitively, graph I can be considered as intermediate between graphs II and III, and an absence of similarity between such loop configurations excites perplexity. Taking into account that operation with vectors includes shifts, it is possible to change the "position" of a "short" vector III relatively to a "long" vector I (see Figure 2), as a result, the similarity index increases from zero to a rather high value of 0.5.

Shift of the vector III=(0,0,0,-4,0,1) shown in Figure 2 may be considered as its transformation to a vector III'=(0,0,0,0,-4,0,1) characterized by higher dimension, or as an addition to an apex not bonded with the initial graph G_{III} (see Figure 3). The same procedure may be carried out for the "short" vector I to compare it with the "long" vector II (see Figure 3), again resulting in the increase of the similarity index to 0.5595. Comparing graphs II and III, a single-step shift (addition of one apex) give no result - the similarity index remains the same value of zero, but second shift (addition of two apexes as shown in Figure 3) gives the similarity index of 0.4375.

I	0	0	4	0	–2	0	1	SI=0
III	0	0	0	–4	0	1		
I	0	0	4	0	–2	0	1	SI=0.5000
III'	0	0	0	–4	0	1		

Fig. 2. Shifting of vector III along "long" vector (IV) and corresponding SI's

Addition of apexes not connected with the graphs of loop configuration is always possible in zeolite structures even in interrupted frameworks. Similarity indexes different from the values listed in Table 2 and obtained taking into consideration the sliding of a short vector (addition of apexes) are given in the Table 3. Graphs in

Table 2

Similarity indexes of loop configurations I - VI

Graph	I	II	III	IV	V	VI
I	1	0	0	0.1245	0	0.1956
II	0	1	0.2262	0.1111	0.6146	0.3248
III	0	0.2262	1	0.0833	0.1250	0.1667
IV	0.1245	0.1111	0.0833	1	0.0555	0.4932
V	0	0.6146	0.1250	0.0555	1	0.1905
VI	0.1956	0.3248	0.1667	0.4932	0.1905	1

Table 3

"Sliding" similarity indexes

	I	II	III	IV	V	VI
I	1	0.5595	0.5	0.1667 0.2824	0.4583	0.2381 0.3197
II	0.5595	1	0 0.4375	0.4088		0.5714
III	0.5	0 0.4375	1	0.0949 0.0833 0.2500	0 0.4167	0.1292 0.07143 0.2500
IV	0.1667 0.2824	0.4088	0.0949 0.0833 0.2500	1	0.4167	
V	0.4583		0 0.4167	0.4167	1	0.3512
VI	0.2381 0.3197	0.5714	0.1292 0.07143 0.2500		0.3512	1

Table 4

Complicacy of loop configurations

Graph	I	II	IV	V	VI
SI	0.5	0.4375	0.25	0.4167	0.3197
D	0.602	1.09	2.4	1.14	1.88

pairs II-V and IV-VI have the same dimensions and sliding is not possible.

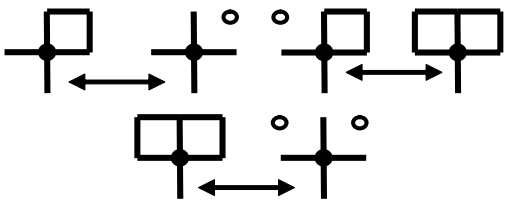

Fig. 3. Comparison of graphs with additon of apexes for smaller ones

Consideration of the results obtained reveals several peculiarities. As a rule, shift (addition of apex) results in higher similarity indexes, and highest values correspond to the utmost shift, when the (..., 1) "tails" of two vectors are in coincidence. For example, similarity indexes for vector III sliding along vector IV are as follows: 0.0833, 0.0949, 0.0833 again, and 0.25000, the highest value. Sliding of vector III sliding along vector V results in the following indexes: 0.1250 - 0 - 0.4167, so addition of one apex in graph III results in deprivation of similarity with graph V, but addition of two apexes gives the rather high similarity. At the same time, single shift of a short vector gives the possibility to remove above-mentioned incompatibility of graphs I, II, and III - SI'(I=II)=0.5595, and SI'(I-III)=0.5000.

Similarity indexes the give possibility of quantitative evaluation of the structural complicacy of the organic molecules D=lgn/SI, where n is the number of apexes in graph, and methane is considered as a simplest reference structure with D=0 [GNL]. From the aforesaid loop configurations of T-atoms graph III, having the lowest number of apexes can be considered as a "zeolite methane" and used as a reference. Quantitative assessement of complicacy for loop configurations is given in Table 4 for the condition of D(III)=0.

Graph IV is characterized by the highest complicacy, whereas graph VI, having the same number of apexes, is characterized by lower complicacy. The comparatively short graph I is characterized by the lowest complicacy; graphs II and V having the same number of apexes are characterized by nearly the same complicacy.

In several zeolite structures different T-atoms are characterized by different loop configurations. In the MOR type structures (mordenite and other isotypic

Table 5

Similarity indexes between constructions (P_{GI}*P_{GIII}, P_{GI}+P_{GIII}) and loop configurations I-VI

Graph	I	II	III	IV	V	VI
P_{GI}+ P_{GIII}	1	0.2262 0.5595	1 0.75	0.2494 0.3139 0.4389	0.125 0.4167	0.5071 0.5143 0.5476
P_{GI}*P_{GIII}	0 0.0521 0 0.1458 0 0.4167	0.06771 0 0.2135 0 0.5677	0.01562 0 0.08333 0 0.125 0 0.4167	0.0521 0.3490 0.04167 0.7812	0.1146 0 0.3542 0 0.875	0.03125 0.2135 0.1354 0.5677

frameworks) two T-atoms ($T_{1,2}$) are characterized by graph III, whereas the other two T-atoms ($T_{3,4}$) are characterized by graph I. At first sight, it is logical to consider loop configurations I and III as non-connected graphs and to use combined loop configuration described by characteristic polynomial P_C=P_{GI}*P_{GIII} and sliding procedure for assessement of similarity indexes, but application of such an approach results in inexplicable high similarity indexes with graphs V and IV whereas similarity with the initial graphs is characterized by lowest indexes (see Table 5).

A more conformed result is achieved by application of the "enclosure" of graph I in graph III, P_{GI}+P_{GIII}; such construction is similar to the initial graphs I and III, its similarity index with graph II is the same (0.2262) as for the initial graphs, and in comparison with graph V it is characterized by the lowest similarity index.

The enclosure of graph II in graph IV, (3,3,-10,7,9,-5,8,1,1), applied for the description of the loop configuration of T-atoms in ERI type zeolite structures (erionite, $AlPO_4$-17, etc.) is characterized by high values of the similarity index with all graphs from I to VI (see Table 6), but the highest values of 0.9 are obtained for similarity indexes with the initial graphs II and IV and with the simplest graph III.

The proposed approach gives a base for quantitative assessement of similarity for microporous structures of zeolites and zeolite-like materials.

Table 6

Similarity indexes of enclosure II+IVand loop configurations I - VI

Graph	I	II	III	IV	V	VI
II+IV	0.2491 0.6571 0.5648	0.9 0.6132	0.3857 0.2847 0.9 0.75	0.9	0.6979 0.825	0.6371

ფიზიკური ქიმია

ცეოლითების მიკროფორული სტრუქტურების მსგავსება

ვლადიმერ ციციშვილი

აკადემიის წევრი, პეტრე მელიქიშვილის ფიზიკური და ორგანული ქიმიის ინსტიტუტი

განხილულია T-ატომების ექვსი მარყუჟისებრი კონფიგურაცია (მარტივი გრაფი, რომელიც გვიჩვენებს, რამდენ, სამ- თუ ოთხწევრიან რგოლებთანაა დაკავშირებული მოცემული T-ატომი), რაც ცეოლითური მასალების რეალურ სტრუქტურებში ყველაზე უფრო ხშირად გვხდება. მომიჯნავეობის შესაბამისი მატრიცების დამახასიათებელი პოლინომების $P_{G(A)}=a_0+a_1x+a_2x^2+...a_{n-1}x^{n-1}+x^n$ გაანგარიშებით გრაფები წარმოდგენილია n-განზომილებიანი ვექტორების $(a_0,a_1,a_2,...a_{n-1},1)$ სახით, რაც გამოყენებულია მათი მსგავსების რაოდენობრივი შეფასებისათვის ცნობილი ალგორითმის საფუძველზე, თუმცა დამატებით შემოღებულია ნორმირება თვითმსგავსების ხარისხის ერთეულად მიღების გათვალისწინებით. შემოთავაზებული მიდგომის მეორე სიახლეს წარმოადგენს "მოკლე" ვექტორის "სრიალის" განხილვა უფრო მაღალი განზომილების მქონე ვექტორის გასწვრივ, რაც ტოპოლოგიურად გრაფში ერთი ან რამდენიმე დაუკავშირებელი წვეროს დამატებას ნიშნავს, ეს კი ცეოლითურ მასალებში, დაწყვეტილი სტრუქტურების ჩათვლით, ყოველთვის შესაძლებელია. ამავე მიდგომის ფარგლებში განხილულია კონფიგურაციული მარყუჟების სირთულე და ორი კონფიგურაციული მარყუჟის მქონე ცეოლითური სტრუქტურების დახასიათების საკითხები.

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