THEORY OF CRYSTAL STRUCTURES

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Computer Modeling of Self-Assembly of the Crystal Structure of Zeolite Na384[Al384Si384O1536] (H2O)422 (LTN, cF4080) from Suprapolyhedral Cluster Precursors AB2 (A-K48, B-K24)

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Abstract—Combinatorial and topological analyses and a simulation of the self-assembly of zeolite crystal structure Na384Al384Si384O1536 ⋅ 422H2O (LTN, sp. gr. Fd3) have been performed using computer methods (TOPOS program package). A cubic cell with the parameters a = 36.95 Å and V = 50 449 Å3 contains 768 framework-forming AlO4- and SiO4 tetrahedra (T tetrahedra). The method of complete expansion of a 3D factor graph in nonintersecting cluster substructures in the tetrahedral T framework was used to reveal nanocluster precursors: A composed of 48 T tetrahedra (A-K48) and B composed of 24 T tetrahedra (B-K24). The nanocluster precursors A and B correspond to the polyhedral T clusters (tiles) 48T-grc and 24T-toc; they are involved in the matrix self-assembly of the crystal structure within the supracluster AB2. The centers of clusters A and B occupy the positions of Mg and Cu atoms in the Laves net AB2 = MgCu2; i.e., the zeolite structure is a suprapolyhedral analog of an intermetallic compound. The self-assembly code of a 3D structure from complementary bound nanocluster precursors is completely reconstructed in the following form: supracluster → primary chain → microlayer → microframework → ...framework. The localization of the Na+ template cations in the 6T- and 8T rings of nanocluster precursors A and B and Na+ spacer cations in the 28T-Lin tile with the formation of tetrahedral configuration and in the center of 6-ring, which arises as a result of bonding two B nanoclusters, is established.

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INTRODUCTION

The most complex crystal structures of inorganic compounds include structures of the following zeolites: mineral paulingite (Na13Ca36K68Ba1.5)[Al152Si520O1344] ⋅ wH2O (PAU) with a = 35.093 Å, V = 43 217 Å3, and sp. gr. Im3m [1–7] and the synthetic phase Na384Al384Si384O1536 ⋅ 422H2O (LTN) with a = 36.95 Å, V = 50 449 Å3, and sp. gr. Fd3 [6–10]. Zeolites have a framework structure composed of vertex-sharing AlO4- and SiO4 tetrahedra (T tetrahedra); the PAU [2–4] and LTN [7, 8] unit cells contain 672 and 768 T tetrahedra, respectively.

The method of the complete decomposition of a 3D factor graph to nonintersecting cluster substructures was applied to PAU in [11] to reveal three types of nanocluster precursors, K6, K16, and K20 (composed of 6, 16, and 20 T tetrahedra, respectively), in the tetrahedral T framework; these precursors are involved in the matrix self-assembly of the crystal structure. The nanocluster precursors of a crystal structure are considered the main types of nanoclusters, which are interlinked to form the primary chain of the crystal structure and determine the moduli of translation vectors [11–16].

The topological type of the tetrahedral framework of LTN was found in [7]. The complete model of the crystal structure, including the positions of extraframework Na cations and H2O molecules, was established in [8].

Two models of the LTN framework structure have been developed: the Baur–Fischer model [10] and the Königsveld model [7], in which different cluster substructures were selected (of the sodalite SOD, LTA, cancrinite CAN, and D6R types), but without indicating the criterion for their selection.

In [10], the LTN framework was presented in the form of two substructures: one was composed of SOD-type clusters and the other was composed of LTA-type clusters.

Van Königsveld [7] presented a model of framework assembly based on two structural units: BU1, containing 120 T tetrahedra (in the form of an ensemble of four CAN-type clusters and dual D6R rings), and BU2, composed of 72 T tetrahedra (an ensemble of four CAN-type clusters).
The fundamental difference in the models considered in [7] and [10] is that the model [10] uses mutually intersecting clusters of the SOD type, which share hexagonal faces. In this context, the aggregation of these clusters requires the removal of the $T$ tetrahedra with shared faces.

The model proposed in [7] describes the LTN structure as an ensemble of CAN-type clusters and dual D6R rings, which have no common $T$ tetrahedra, i.e., form a packing. Accordingly, the aggregation of these clusters does not lead to the removal of $T$ tetrahedra.

The formation model of SOD-type clusters ($K_{24}$ composed of 24 $T$ tetrahedra) in the form of self-folding nets based on 6$T$ rings and different types of packings of suprapolyhedral $K_{24}$ clusters were considered previously when modeling the self-assembly of Na-containing zeolite structures of the FAU and LTA types [12].

In this paper we report the results of the computer modeling of the self-assembly of the Na-containing zeolite structure from cluster precursors, which is selected in the automatic mode of data processing using the previously developed algorithm [11] for selecting combinations from nonintersecting nanocluster precursors. The cluster modeling of the macrostructure was performed using the principle of maximally filled space and, correspondingly, the requirement of maximum complementary bonding nanocluster precursors during crystal-structure self-assembly with the successive formation of the primary chain, microlayer, and microframework [12].

This work continues the studies [11–16] in the field of geometrical and topological analysis of the structure of crystalline phases and modeling of the self-organization processes in chemical systems; the application of modern computer methods of structural analysis [17, 18] is also considered.

Basic definitions. As was noted above, nanocluster precursors of crystal structure are the main types of nanoclusters, which, being bonded with each other, form the primary chain of the crystal structure and determine the moduli of translation vectors.

There may be two versions of structure formation. One of them is simple and the most widespread for zeolites. Here, the structure is formed of nanoclusters of the same type [12, 13]. In the second, more complex, case, the structure is formed by nanoclusters of two or more types [11]. Both cases allow for a version where nanoclusters form supraclusters: ensembles of several bound nanoclusters (of one or two types); here, supraclusters determine the moduli of the translation vectors of a periodic structure.

In addition, when modeling the formation of framework zeolite structures of complex chemical composition, it is necessary to take into account the effect of cation templating. Within this model cations perform two typical structural functions: they play the role of templates (which stabilize the local structure of nanocluster precursors) and spacers (which fill the framework voids between nanocluster precursors).

TECHNIQUES USED IN THE COMPUTER ANALYSIS

The geometrical and topological analysis of zeolites was performed using the TOPOS program package [17], which makes it possible to carry out a multipurpose automatic study of the structure of crystal using a representation of structures in the form of "reduced graphs" (factor graphs).

The algorithm of automatic geometric and topological analysis with the aid of the TOPOS package included the following stages:

(i) a calculation of the adjacency matrix and the analysis of zeolites of arbitrary complexities based on the complete decomposition of the 3D graph of the structure (3D factor graph) in cluster substructures according to the principles reported in [11]. The algorithm was implemented within the TOPOS program package [17].

RESULTS

Using the tiling method, we selected five topological types of clusters in the framework (Fig. 1): 48$T$-groc ($8b$, $\bar{4}3m$), 28$T$-lnm ($48f$, mm2), 24$T$-toc (16c, $\bar{3}m$ and $8a$, $\bar{3}m$), 18$T$-can (32e, $3m$), and 12$T$-hpr (16d, $\bar{3}m$). We applied the topological model of a 4-connected 3D-$T$ net of LTN with four crystallographically independent $T$ sites (Table 1), which corresponds to its maximum symmetry, described by the sp. gr. $Fd\bar{3}m$, the order of which is 192.

The combinatorial and topological analysis of the $T$ framework was performed with not five but six geometrically different clusters, with the number of tetrahedra ranging from 12 to 48, because there are two crystallographically independent 24$T$-toc clusters in the structure (Table 1).

It was established that the framework of the LTN structure can be constructed as a result of self-assembly from a minimum set composed of two nonintersecting nanoclusters and in only two ways.