Perceiving zeolite self-assembly within the natural tiling model

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Zeolites represent a unique class of inorganic compounds, which have a simple idealized composition TO_2 and uniform tetrahedral and bridge coordination of the T and O atoms. However, such simplicity gives rise to extremal diversity in the topologies of the zeolite frameworks, which is comparable with the variety of organic compounds: theoretically, the number of the framework topologies is infinite and the databases of hypothetical frameworks generated by computer procedures contain hundreds of thousands of entries. All the more surprising that the number of zeolites existing in nature or obtained in the laboratory is quite modest: currently, in the database produced by the International Zeolite Association there are only 248 topologically distinct zeolite frameworks, which compose less than 0.1% of the known low-energy hypothetical frameworks. Many efforts were undertaken to explain this phenomenon, as well as to predict new zeolite topologies. Paradoxically, most of the proposed explanations of this topological scarcity were based on geometrical or energetic properties of the frameworks, but not on their topological properties. However, low energy of the zeolite framework is not the sufficient proof of its feasibility; no less important are the kinetic factors that drive the framework assembly. While the framework energy is reflected to some extent by the geometrical parameters, which characterize the framework distortion, the assembly of the framework is encoded in its topological parameters. Thus geometry and topology meet to feature the thermodynamics and kinetics of the framework formation.

We explain the feasibility of the zeolite frameworks within the topological model of natural tiling, which represents covering of the crystal space by non-crossing minimal cages (natural tiles) built from the nodes and edges of the framework. We show that the assembling of the framework from natural tiles reflects kinetic factors, which complement the thermodynamic criteria, and explains the inconsistency in the number of hypothetical and realized framework motifs [1]. Moreover, the model of natural tiling enables one to predict more thoroughly new robust zeolite frameworks. We have extended this model and included parts (halves) of tiles into consideration. This extension allowed us to find many hidden relations in the zeolite topological motifs and particularly to interpret and predict the intergrowth phenomena in the zeolite minerals and synthetic phases [2]. Natural tiles can also be considered as building units in modelling crystal growth by Monte Carlo methods [3]. We have implemented the natural tiling model in the *ToposPro* program package (https://topospro.com) and developed a database of all natural tiles that occur in known zeolite frameworks (*TTT* collection), which is now available online at https://topcryst.com. This enabled us to explore the natural tilings in hypothetical zeolites and find those of them that could be easily assembled and hence obtained in the experiment. We also apply the tiling model for the purposeful sampling of organic structure directing agents and propose a list of them for a target synthesis of the hypothetical zeolite frameworks.

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