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PROPERTIES OF THE FORMS AND STRUCTURES OF METAL-ORGANIC FRAMEWORK MATERIALS

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Abstract: The article discusses the size of the MOF (Metal-Organic Frame) cavity and the peculiarities of its composition and structure. The main methods of synthesis and application of MOF systems, which have begun to be widely used in such important areas as oil and gas, medicine, and ecology, are described. The importance of colloidal chemical research for mastering the development of innovative materials was also analyzed.

Keywords: organometallic framework, selectivity, spherical pore, synthesis, adsorption, cell, SBU, MIL-100, MIL-101, ZIF-8, spatial structure, heterogeneous catalyst, phenylendicarboxylate.

It is advisable to consider in more detail the structure of three-dimensional frame structures of MOFs. The structure of porous 3D-coordination polymers can be visualized using the example of the well-known and well-studied MOF-5 system, in which inorganic clusters $[Zn_4O]^{+6}$ are linked with solid organic phenylendicarboxylate (1,4-benzoldicarboxylate) ligands, forming a three-dimensional cubic lattice similar to a zeolite[1]. Figure 1 shows various methods of depicting the frame structure of MOK-5.

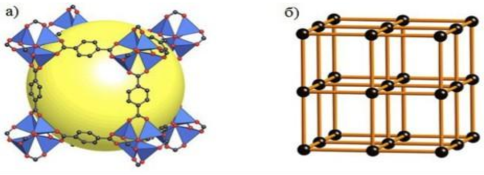


Figure 1. Various versions of the MOF-5 structure: a) - in the form of a MOF-5 cell consisting of Zn_4O tetrahedra connected to the cubic frame by phenylendicarboxylate bonds. b) - in the form of a simple cubic lattice [2].

Figure 1-a depicts the structure of MOF-5 in the form of tetrahedra $[Zn_4O]$, which are connected by phenylendicarboxylate links to a cubic frame with small pores of size 8 E and large spherical pores of diameter 12 (15) E inscribed in the cube. Figure 1b depicts the structure of MOF-5 in the form of a ball-rod model, which is essentially a classical cubic lattice [3].

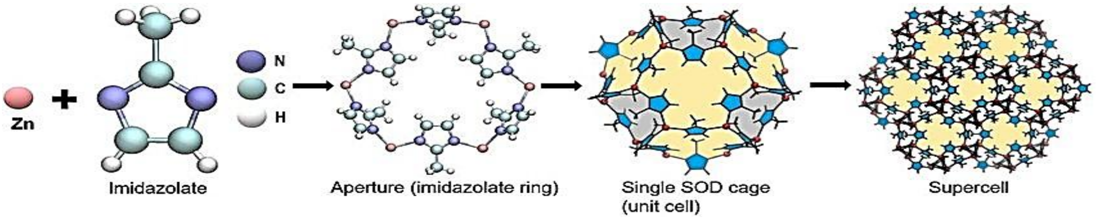


Figure 2. Schematic representation of the structure and topology of ZIF-8

An important feature of MOF is that the size of the internal cavity of the framework lattice changes depending on the type of organic link [4], which allows for the directed synthesis of highly selective sorbents (Fig. 3).

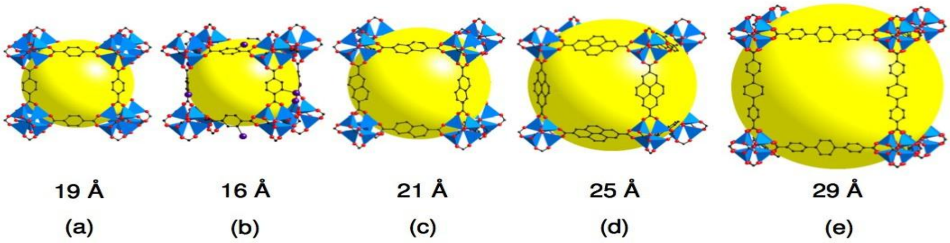
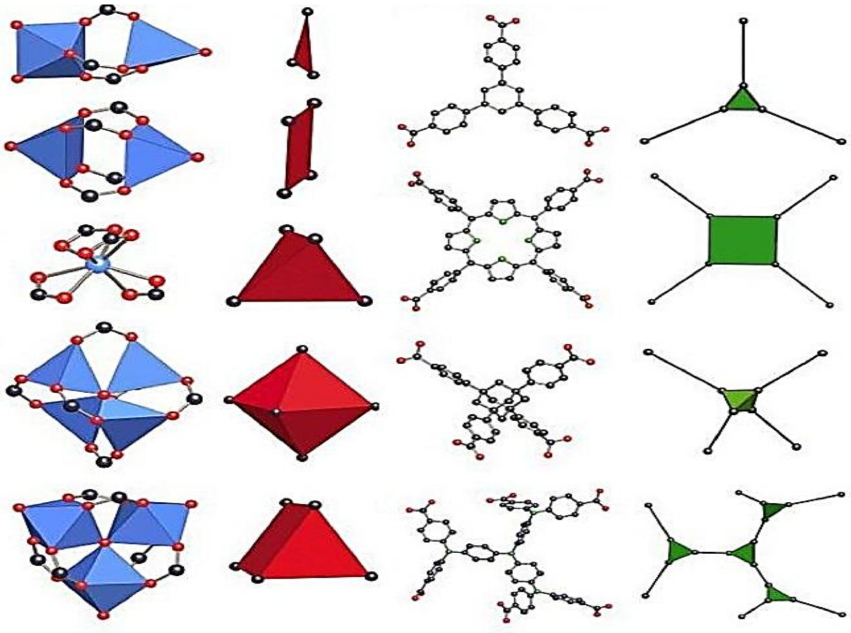


Figure 3. Dimensions of the MOF framework cavity depending on the type of binding molecules [4].

For a more detailed description of the structure of MOF, the concept of "secondary building unit" (SBU), which was initially used to describe the main fragments of zeolites, is also used [5]. Secondary structures to MOF are simple geometric shapes reflecting the structure of inorganic clusters or coordination spheres of metal ions, which are interconnected by organic links to a certain framework. Examples of secondary structures in carboxylate MOFs are shown in Figure 4.



a) b) c) d)

Figure 4. Secondary building units (SBU) in carboxylate MOFs[2] a) inorganic component b)SBUs c) organic component d)SBUs

Three-dimensional coordination polymers can be micro- and mesoporous materials. In particular, mesoporous metal-organic framework structures include a family of compounds obtained at the Lavoisier Institute in 2003 and named MIL (Materials of Institute Lavoisier, France). Porous organometallic coordination polymers MIL-100 and MIL-101 (Fig. 5) are characterized not only by the presence of large voids (up to 3.5 nm), but also by a high specific surface area (up to 2800 m^2/g) and are therefore widely studied for the purpose of using adsorbents and heterogeneous catalysts as carriers.

The most well-known MOFs with heteroaromatic ligands are porous metal-organic framework structures ZIF (zeolitic imidazolate framework) - zeolite-like imidazolate framework structures (see Fig. 6). These metal-organic framework structures are composed of metal ions and substituted imidazolate (Im) ligands. The topology of ZIF polymers corresponds to the topology of zeolite structures [8].

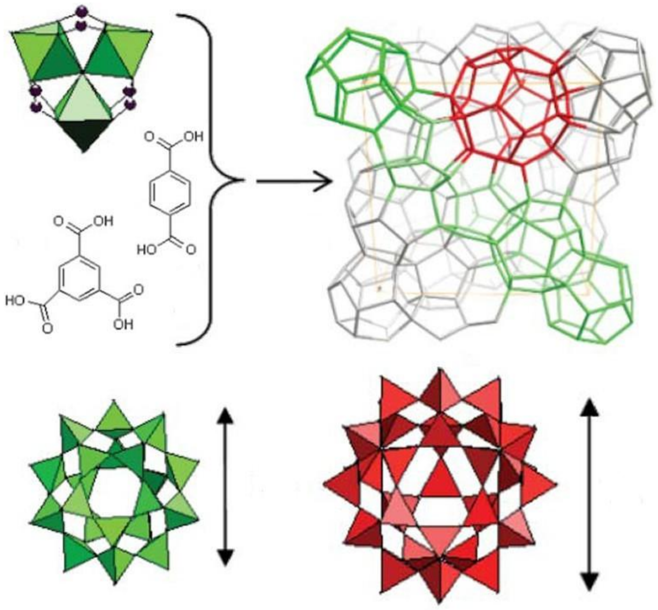


Figure 5. Structure of the framework of the MIL-100 and MIL-101 structures with a cubic lattice topology [7].

The structure of the ZIF-8 zeolite-like metal-organic framework has a high specific surface area - 1600 m^2/g. This three-dimensional tetrahedral framework structure has a topology similar to that of sodalite [7]. The angle (145°) formed by the bonding of methylimidazolate with metal is similar to the Si-O-Si angle between bonds in most zeolites (Fig. 6).

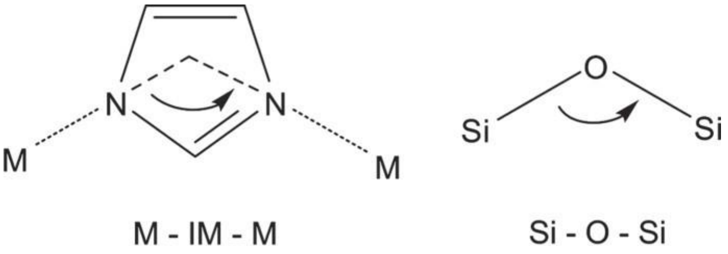


Figure 6. Correspondence of angles M - Im - M in ZIF and Si - O - Si in zeolites [7].

Unlike non-porous sodalite, ZIF-8 has "windows" with a diameter of 3.4 Å, which allows easy adsorption of small gas molecules, such as hydrogen and carbon monoxide, into the material, while the diameter of the gaps is 11.1 Å. For ZIF-8, high efficiency is noted in the separation of gas mixtures containing CO_2/CO at room temperature and low pressure.

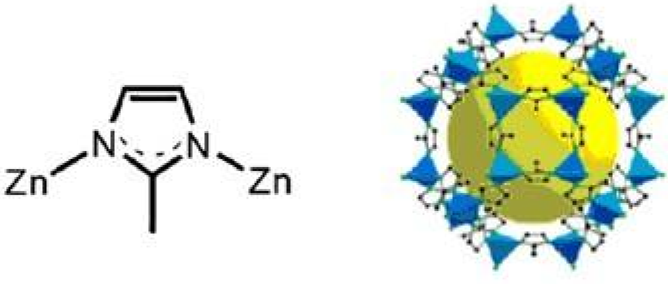


Figure 7. Structure of the ZIF-8 frame structure [9].

An important feature of MOFs is the relatively easy control of their chemical and spatial structure. This method of obtaining molecules with predetermined parameters or properties allows their application in various fields, in particular, for the sorption and selective separation of N_2, Ar, CO_2, CH_4, C_2H_2, and other gases [10].

In conclusion, such an approach to the analysis of the structure of the MOF gives an idea of the exact spatial structure of the resulting framework and allows the use of a large number of inorganic and organic secondary building units of various geometries. [6].

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