INTERRELATIONSHIP BETWEEN TOPOLOGY AND ADSORPTION PROPERTIES IN METAL-ORGANIC FRAMEWORKS

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Abstract

In this thesis, the relationship between the topology of metal-organic frameworks (MOFs), their spatial structure, and their adsorption properties was analyzed. The reticular chemistry approach and the topological descriptors adopted in the Reticular Chemistry Structure Resource (RCSR) system were used as the basis for representing the structural features of metal-organic frameworks. The nodes connectivity degree, specific surface area, pore or cavity sizes, and main functional adsorption properties of the pcu, sod, tbo, fcu, and mtn-type networks of MOFs were comparatively examined. The analysis showed that the framework topology determines not only the amount of porosity but also the geometric shape of the pores, molecular accessibility, selectivity, gas storage capacity, and the properties of the adsorption sites.

Keywords: metal-organic framework, MOF, topology, RCSR, reticular chemistry, porosity, adsorption, specific surface area, node connectivity, molecular sieving.

Introduction

Metal-organic frameworks hold an important position among modern porous materials. They are crystalline and porous structures formed by the interconnection of inorganic metal-containing nodes or secondary building units (SBUs) and multifunctional organic ligands. The main advantage of such materials is the ability to control their composition, geometric structure, and porosity to a certain extent.

As a result of the development of the reticular chemistry concept, it has become possible to obtain a vast number of MOF structures from various combinations of metal nodes and organic linkers. In addition to the chemical composition, the topology of the resulting three-dimensional network is of particular importance. The topology of the crystal structure can be represented as a simplified directed graph. In this representation, the SBUs and linkers are considered the nodes and edges of the graph, respectively.

The RCSR system allows for the representation of various crystal lattices using standardized symbols. For example, symbols such as pcu, sod, tbo, fcu, and others denote lattices with specific geometric bonding and coordination properties. MOFs can be based on the same topological network but with different chemical compositions. For this reason, topology is considered a structural parameter that is relatively independent of the material's chemical composition , yet strongly influences its pore geometry.

The adsorption properties of MOFs are generally related to the specific surface area, pore volume, pore diameter, the nature of the adsorption sites, and the size of the adsorbate molecules. However, a large specific surface area alone does not mean that the material will have high selectivity for a particular adsorbate. The shape of the pores, the entrance apertures, the accessibility of the metal centers, and the rigidity of the framework also determine the adsorption process.

From this perspective, the structural and adsorption properties of MOFs with different topologies were comparatively analyzed in this work.

Research Methods

The study was conducted based on a systematic comparison of the structural and adsorption data reported in the literature. Representative materials such as MOF-5 (pcu), ZIF-8 (sod), HKUST-1 (tbo), UiO-66 (fcu), and MIL-101(Cr) (mtn-type framework) were selected for the analysis.

For each material, key topological parameters, node degree, BET specific surface area, characteristic pore or cavity size, and dominant functional adsorption properties were examined.

In the topological analysis, the metal-containing SBUs and organic linkers were treated as the nodes and edges of a simplified graph, and the resulting periodic network was associated with the corresponding topological signature in the RCSR system.

Results and Discussion

The MOF-5 and IRMOF families are representatives of the pcu topology. In these structures, the metal-oxide clusters appear as six-coordinated nodes. Upon linking with organic dicarboxylate linkers, a regular and highly ordered three-dimensional network is formed.

For MOF-5, the article reports a BET surface area of approximately 3800 m^2/g and a characteristic pore size of about 11–15 Å. Such a structure provides favorable conditions for storing gases like H_2 and CH_4 due to its high porosity and large internal void space.

An important aspect of the pcu topology is that by varying the linker length, the pore size can be controlled while maintaining the basic topology. This is a significant advantage of the reticulated synthesis, as it allows for the preparation of materials with different porosity parameters based on the same topological framework.

ZIF-8 is considered the prototypical example of the sod topology. In it, metal centers form a four-connected tetrahedral network via imidazolate linkers. This connectivity is reminiscent of certain topological features of natural aluminosilicate zeolites.

For ZIF-8, the BET surface area is reported to be approximately 1300-1600 m^2/g, with an effective aperture of about 3.4 Å. The relatively small pore entrance gives rise to size- and shape-selective adsorption of adsorbate molecules. Therefore, an important functional property of the sod topology is molecular sieving of . At the same time, ZIF-8 is also distinguished by its chemical and thermal stability.

This indicates that the effect of topology on adsorption is not limited to the surface area alone. Although ZIF-8's BET surface area is not as high as that of MOF-5 or MIL-101(Cr), the presence of a small aperture allows it to discriminate certain molecules based on their size and shape.

HKUST-1 belongs to the tbo topology, which features nodes with varying degrees of connectivity. This topology is characterized by the formation of two distinct types of pores or voids. For HKUST-1, the BET surface area is approximately 1500–2100 m^2/g, and the pore sizes are around 9 and 13 Å.

The activation of HKUST-1 can lead to the formation of coordinatively unsaturated open metal centers. Such centers interact more strongly with polar or dipole-moment-bearing molecules such as CO_2 and H_2O. As a result, adsorption selectivity is determined not only by the surface area but also by the chemical nature of the adsorption centers.

UiO-66 is a prominent representative of the fcu topology, characterized by highly coordinated Zr-based clusters. According to the data in the article, the dominant node connectivity degree in UiO-66 is 12, the BET surface area is approximately 1000–1200 m^2/g, and the characteristic tetrahedral pore size is about 6 Å.

The main functional advantage of this structure lies in its very high chemical, thermal, and mechanical stability. Therefore, it is not enough to assess the functional performance of a MOF solely by its maximum porosity. In some practical conditions, the framework's stability and its ability to preserve the structure become primary requirements.

MIL-101(Cr) was considered as a macroporous framework. Its BET surface area is reported to be in the range of 4000–5900 m^2/g, and the size of the large pores in the framework is approximately 29–34 Å. Such large pores and voids create favorable conditions for large molecules to enter and adsorb onto the framework.

Conclusion

The results of the comparative analysis showed that the topology of metal-organic frameworks is one of the main structural factors that shape their adsorption properties. The pcu topology is characterized by large and regular pores and gas storage capability, the sod topology by molecular sieving and high stability, the tbo topology by open metal centers and selective adsorption, and the fcu topology by high structural stability. mtn-type frameworks, on the other hand, provide large pores and high porosity.

Thus, when designing an MOF material, it is important not only to select the chemical composition of the metal center or the organic linker, but also to anticipate the resulting network topology. The topological approach can serve as a systematic basis for the targeted control of an adsorbent's porous geometry, molecular selectivity, gas storage capacity, and structural stability.

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