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Computational structure characterization tools for the era of material informatics

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HIGHLIGHTS

- Current trends in computational structure characterization tools are reviewed.
- Focus on efficient ways of screening of novel porous materials.
- Examples for sensing, breath analysis, methane storage and carbon capture.
- Future needs and challenges in the field are discussed.

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ABSTRACT

Current advances in synthesis of new porous materials outpace our ability to test them in real adsorption applications. This situation is particularly evident in the area of metal-organics frameworks (MOFs), where hundreds of new MOFs are reported every year and the number of possible MOFs is virtually infinite. How to make sense out of this vast number of existing and possible structures?

In this article, we will review the application of computational structure characterization tools for systematic description and classification of porous materials and their adsorption properties. Using examples from recent research in our groups and others, we will discuss how the information obtained from computational characterization can be used in screening protocols to identify the most promising materials for a specific application before any costly and time consuming experimental effort is committed. We will finally touch upon the need for the tools to systematically organize the information generated in computational studies. These tools combined with the recent impressive advances in synthesis of porous materials may fundamentally change the way we approach material discovery, starting the era of material informatics.

1. Introduction

Adsorption in porous materials has been considered as an energy efficient alternative to absorption and distillation processes for industrial scale separations, including carbon dioxide removal from power plant streams and air separation. Other applications where adsorption is important include catalysis, gas storage, sensing and drug delivery, to name a few. Development of these applications critically depends on whether a suitable porous material exists with affinity, selectivity and other characteristics meeting the requirements of the application in question. In the recent years, progress in adsorption technologies has been stimulated by the unprecedented advances in the material science, where in addition to the conventional porous materials, such as activated carbons and zeolites, new families of porous structures have emerged, including molecularly imprinted polymers (MIPs), metal-organic and covalent-organic frameworks (MOFs, COFs), Zeolitic Imidazolate Frameworks (ZIFs) and polymers with intrinsic microporosity (PIMs).

Let us focus on just one new family of materials–metal-organic frameworks, or MOFs. Fig. 1 shows the number of papers published since 1999, which mention MOFs and a substantial proportion of these articles actually report newly discovered MOFs. The large number of already reported MOFs and essentially infinite number of possible MOFs stems from the principle of their synthesis based on a self assembly from building blocks, provided by metal complexes and organic linkers. Naturally, organic chemistry can provide an inexhaustible array of components for this approach.

It seems that this enormous variety of available and possible porous structures should substantially benefit the development of adsorption technologies, as for a every specific application it

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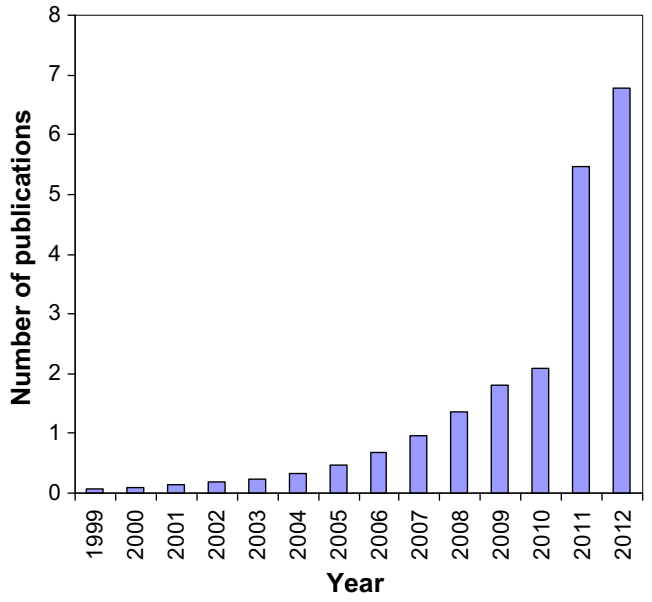

Fig. 1. Number of articles (in thousands) published between 1999 and 2012, with "metal-organic framework" used as the key word. Source: Thomson Reuters (ISI) Web of Knowledge.

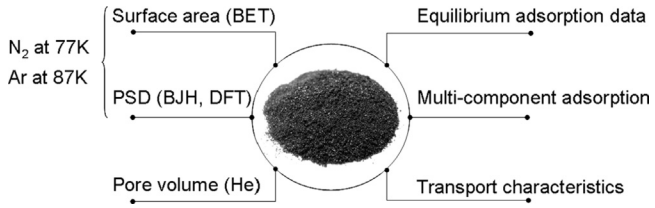

Fig. 2. Schematic description of structural characteristics and data required for adsorption application development, once a new porous material (shown as a black powder in the centre) is synthesized.

should be possible to find or design a range of materials with properties perfectly matching the requirements. This however is not the case and at the moment there is no single industrial application based on a MOF. There are several reasons for this.

On one hand, to be used on an industrial scale, MOFs must overcome several objective challenges associated with their stability, scalability of production and cost. On the other hand, the rate with which new MOFs are being discovered and reported clearly outpaces our ability to test them in any practical adsorption applications.

This is where computational structure characterization tools may become incredibly useful. To understand how they can help to streamline and accelerate the process between material discovery and the actual application, it is instructive to briefly review the typical steps involved in this process, as shown in Fig. 2. Once the structure of a new material is characterized *via* X-ray crystallography (if it is crystalline), the next steps involve structural characterization using physical adsorption of nitrogen or argon at cryogenic conditions, and helium porosimetry (or mercury porosimetry for macroporous structures). From these measurements the surface area, pore size distribution (PSD) and pore volume are obtained. In order to develop an actual adsorption application, in the next stage of the process, adsorption equilibrium data is acquired for single components and mixtures, as well as transport characteristics of the material. It is important to note here that experimental measurement of multi-component adsorption isotherms and transport diffusion coefficients remain extremely challenging and time consuming.

The idea of computational structural characterization tools is to replace as many of the experimental steps as possible with analogous computational procedures. Computational tools may provide a quick and efficient way to assess characteristics of porous materials, relate them to each other, provide reference values for various properties of the materials for future comparison with experiments, and in general, pre-screen large sets of candidate materials so that only a smaller group of most promising structures is indeed explored at the next experimental stage.

The idea of this contribution to the special issue of Chemical Engineering Science is to briefly explore recent developments in this area, including examples from own research. While working on this article, we became aware of a truly comprehensive review of the field byYang et al. (2013) and we can only strongly recommend it to the reader. Without trying to repeat the massive undertaking of the article by Yang et al., here we offer a more selective perspective on the topics of a specific interest to us and, hopefully, to the reader.

The article is organized as follows. We will first provide a short review of what structural characteristics of porous materials are, how they can be measured experimentally and how they can be calculated using computational tools. In the section on computational screening we will review recent examples of using these tools to optimize specific adsorption applications. Computational structure tools as a platform to explore new applications of MOFs is the subject of the next section. Finally, we will discuss recent developments in the advanced computational methods based on graphical processing units (GPU) aimed to speed up screening protocols.

We will conclude the article by offering our perspective on the current challenges and opportunities in this emerging field.

2. Structural characterization of porous materials: experiments and computer simulations

Physical adsorption of nitrogen at 77 K (or argon at 77 K and 87 K) is a standard experimental technique to obtain structural characteristics of a porous material, such as surface area, pore volume, and pore size distribution (Rouquerol et al., 1998). This is a two stage process, where in the first stage an adsorption isotherm is measured and in the second stage this isotherm is interpreted using a theory or a method, such as Langmuir or Brunauer–Emmett–Teller (BET) (Brunauer et al., 1938) methods for the surface area and the classical Barrett–Joyner–Halenda (BJH) method (Barrett et al., 1951) or more modern NLDFT (Ravikovitch et al., 2000) approach for the pore size distribution (PSD). These methods involve a number of assumptions and sound understanding of these assumptions (and hence the limitations of the methods) is a prerequisite for accurate results. For example, both Langmuir and BET methods of obtaining the surface area are based on a notion that nitrogen molecules form a layer of well defined capacity on the surface of the structure (multilayer formation is allowed in BET) and formation of this layer can be identified from the adsorption isotherm. Thus, knowing the size of a nitrogen molecule, the surface area of the structure can be defined. In both theories molecules do not interact with each other within the layer, and in BET molecules of one layer can serve as binding sites for the formation of the next layer. Even for the perfectly homogeneous surfaces, without any defects, this picture is oversimplified. To obtain PSD, BJH and NLDFT methods start by assuming the geometry of pores in the structure. Typically cylindrical pores, slit pores or spherical cavities are considered (in more advanced approaches some combinations of those geometries can be also tackled). Again, this is an oversimplified representation of the real materials, with complex disordered