

Functionalization chemistry of porous materials

Stefano Canossa and Stefan Wuttke*

Dr. Stefano Canossa

EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Antwerp, Belgium

Prof. Dr. Stefan Wuttke

BCMaterials, Basque Center for Materials, UPV/EHU Science Park, 48940 Leioa, Spain

Email: stefan.wuttke@bcmaterials.net

Prof. Dr. Stefan Wuttke

Ikerbasque, Basque Foundation for Science, 48013, Bilbao, Spain

Chemists are naturally more interested in what is there rather than what is not. We are spontaneously drawn to the chemical core of compounds and materials: the atoms, the ways in which they are connected and their interactions with electromagnetic radiation, other atoms/molecules or even biological systems. However, when it comes to porous materials we are less concerned about the atoms themselves rather the spaces between them (the “chemistry beyond matter”).

The concept of ‘pore’ is ubiquitous in a broad variety of scientific fields ranging from geology, biology, physics and materials science. Its definition is generally invariant with respect of the research topic, and usually identifies pores as openings that allow —and importantly regulate— the passage of substances between two distinct regions of a system, both of which contain non-solid phases. In simple terms, pores are gates, whose characteristics selectively allow some guests to pass through while rejecting others.

The definition of porosity appears less sharp and its origin, tied to the term “pore”, leaves room for ambiguities. The broad concept employed is borrowed from geology and defines porosity as the volume ratio between the voids and the bulk of a solid.^[1] According to this definition, any material featuring internal voids has a positive “porosity” value and therefore may be defined as “porous”. On the other hand, most of the scientific community studying porous materials^[2] adopts a more practical approach by associating both concepts of “pore” and “porous” to that of “effective permeability”. This was eloquently summarized by L. Barbour with the analogy: “(...) *the average door is porous to humans but perhaps not to an elephant. Thus, use of the word “pore” to describe the door in this context should consider the nature of the guest.*”^[3] Hence, the concept of porosity is clearly and tightly bound to the presence of 3-dimensional volumes (cavities) rather than 2-dimensional openings (gates, or pre-defined pores). The presence of pores and porosity are therefore not necessarily dependent, which justifies the existence of the so-called “porosity without pores”. Here a solid structure features internal voids which are inaccessible without a structural rearrangement of the entire crystal lattice.

Yet, the use of “pores” as a synonym for “cavities” is well rooted in scientific literature and, therefore, the terminology concerning porous materials needs some flexibility to favour the sharing of knowledge over that of a strict and unambiguous set of terms. Accordingly, we will embrace this synonymy in the following parts of this work.

The full potential of pore chemistry design can be reached only by adopting the broadest perspective on the essence of porous materials. The structural interplay of matter and empty space are both essential aspects to the resultant properties of porous materials and should be accounted for when considering strategies toward pore chemical modification. From this perspective, the pores act as a functionalisation platform where two kinds of modifiable parts can be identified: the material's constituents (matter) and the pore's void (empty space). Importantly it should be noted that the synthesis and functionalization of porous materials are often convoluted, especially when functionalization is carried out at the same time of backbone construction. To separate these two processes (backbone construction and functionalization) on the conceptual level, we define “functionalisation” as the practice of decorating the materials backbone with chemical groups capable of exercising functional behaviours. This definition holds regardless of whether a functionalised material is obtained by strategically selecting the reactants for its synthesis or by modifying its structure after the assembly of the backbone structure is completed.

Following this classification, we wish to give the following general pathway to design and control the internal functionalization of a porous material:

- (1) The intended specific application of the material should be identified, thus allowing to define the desired type, quantity, and positioning of the functional group(s) inside the pores. This is the first fundamental step of pore design, which defines all the following ones.
- (2) The appropriate functionalization approach is chosen from one of the following categories: *pre-synthesis functionalisation*, *inter-synthesis functionalisation*, and *post-synthesis functionalisation* (Figure 1).

In pre-synthesis functionalisation, the materials organic building blocks act as a chemical landscape allowing for attachment of desired functional groups. Commonly these functionalities remain intact during material synthesis and are reflected in the resulted properties. The primary advantage of pinning functional groups onto the backbone pre-synthetically is that it ensures every pore in the material is uniformly functionalised, providing ultimate synthetic control. Furthermore, complications residing from post-synthetic functionalization reactions' yield and kinetics are eliminated. The key challenge of this approach is the altered reactivity of the building blocks (*e.g.* solubility, size, etc.) that can inhibit the material formation or lead to the synthesis of additional undesired phases.

Post-synthesis functionalisation is until now the favoured approach, as evidenced by its widespread application. Here, the material is synthesized first and then subjected to functionalisation under controlled conditions. Frequently, an anchoring point in the material backbone is used as a reactive site for controlling the exact position of the introduced chemical group.

However, there may be cases where both approaches fail to successfully integrating framework-compatible functionalities in the pore environment. For instance, when a post-synthetic approach is necessary for the integration of species that, once attached, prevent the reactants to access the framework's interior, the post-synthetic functionalisation will unavoidably stop at an early stage

because the external pores will be readily blocked by the first few added functionalities. In such cases, an inter-synthetic functionalisation, being a stepwise reaction proceeding along with the framework growth, promotes the installation of desired functionalities in the pore volume.

(3) The functionalisation targets must be identified. These can be either the *pore backbone* or the *pore void* (Figure 1). In this context, we define pore void functionalisation as the process of inducing the inter- or post-synthetic formation of functional species, which remain enclosed in the cavities and cannot be removed without destroying the framework due to their size or structural role (ship-in-the-bottle strategy). These guests can be considered as a constituent part of the material and, as such, their structure is available for modification in appropriate conditions and can be used to add new properties targeted for different applications. As far as the pore backbone is concerned, the absence of building blocks that result in topological defects are a special kind of functionalisation target. Defect engineering is an important goal in material science as it offers a unique type of site selectivity advantage over other functionalization strategies. In fact, the exact position of framework terminations defines unequivocally where the modification reactions take place, provided their course proceeds to completeness. This makes the control over defect formation key to obtain materials where the density and distribution of functionalities is tailored with precision.

(4) Once the target sites for functionalisation are identified, three different chemical methods can be used to graft the desired functionalities onto the pore surface: *covalent bond formation*, *intermolecular interaction establishment*, and *mechanical docking* (Figure 1).

The key factor to selecting the appropriate functionalisation strategy is through careful assessment of the material's architecture. For example, the formation of covalent bonds often perturbs the structure and electronic properties of the nearby molecular arrangement. An alternative approach to avert such possibilities is to employ functionalisation methods which do not involve chemical modifications and instead use other effective binding, such as intermolecular interactions with specific chemical groups which compose the pores surface. This strategy allows for the reversible initialization of functional sites, with minor alteration to the pore scaffold. Here, it is key that the formed interaction is stable enough for the later intended use.

Mechanical docking occurs when species are constrained in specific locations of the material by their atomic structure and their migration is only allowed by its degradation. Here, it is possible to distinguish mechanical docking by size effect and by intramolecular connectivity. In the first case, the functional component cannot leave the pore due to its insufficiently large aperture. This is commonly encountered in the growth of metals or metal oxides nanoparticles templated by the cavities, which is a common and successful practice for all porous materials classes.^[4-8] Differently, mechanical docking by intramolecular connectivity is based on the synthesis of molecular loops or chains which remain locked with unterminated building blocks of the material. Therefore, the locked species maintain dynamic behaviour while their position is limited by the molecular architecture of the host material. Such 'robust dynamics' can precisely influence molecular function to a solid material, and hence merge organic and material chemistry.^[9]

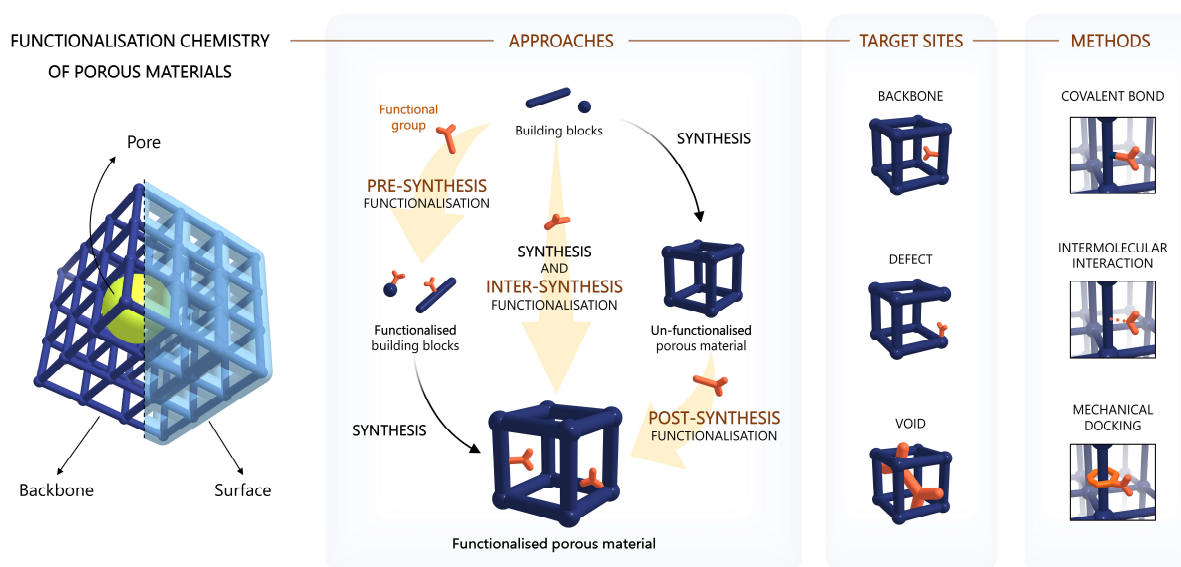


Figure 1. Main steps of the synthetic pathway for the functionalisation chemistry of porous materials.

The goal of this special issue is to critically review the functionalization chemistry of important porous materials in order to give the reader a fresh perspective that would stimulate them to build on the past and shape the future.

In the essay of Canossa and co-workers^[10] the importance of assessing architectural stability of porous materials is highlighted. The current protocols for the assessment of damage to framework materials are discussed, showcasing unexplored aspects of porous materials' wear and tear whose investigation currently lies at an early stage. For this reason, the term *connection completeness* is defined as the degree of architectural integrity of the material and analytical guidelines to its exploration are discussed.

In the essay contribution from the IPM Thomas J. Watson Research Center of Tulesvski and Falk,^[11] the challenge to assemble macroscopically carbon nanotubes at the industrial level is discussed in detail. The authors spotlight that synthesis and functionalization strategies of porous nanomaterials should be integrable into already existing processing technology. In this way, industry can much faster assess if the novel scientific finding can be transferred into a technology.

The progress report of Kuc, Heine and co-workers^[12] discusses the theoretical methods used to analyse the proximity effect in graphene, metal-organic framework, and covalent-organic framework materials. This effect results from van der Waals interactions and stacked aromatic compounds and influences material properties such as electrical conductivity.

Further, Bon, Kaskel and co-workers^[13] provide a review on how to characterise the dynamics inside porous frameworks with advanced *in situ* characterisation techniques. These *in situ* techniques allows for the accumulation of temporal information of dynamic phenomena inside a material at certain time points. The authors stress the point that the development of material characterisation techniques should be a major aspect of future material research.

Ji, Yaghi and co-workers^[14] discuss the metal-organic framework pore chemistry to guide the positioning of functional groups with precise control, owing to their molecular definitiveness, pore accessibility, structural robustness, and the diverse functionalisation chemistry. Depending on the interplay between functionalities, the authors define three functionalisation strategies: site isolation,

site coupling, and site cooperation. By highlighting the importance of the last two strategies, the authors aim to shift the attention of the community from the largely explored site isolation and encourage researchers to explore coupling and cooperative behaviours of functionalities, thereby fully taking advantage of the molecular definitiveness of metal-organic framework structures.

Ploetz, Wuttke and co-workers ^[15] provide a comprehensive overview of the functionalization chemistry of metal-organic framework, zeolitic imidazolate framework and covalent organic framework nanoparticles and describe how these materials can be used in a variety of applications. Reticular nanoparticles inherent bulk material properties, such as high surface area and chemical tunability, while also displaying new properties that dominate on the nanoscale. Given the potential of those bulk materials, the authors see a next generation of nanoparticles.

Zheng, Matyjaszewski and co-workers ^[16] provide a thorough review on porous polymeric and carbonaceous materials. A key aspect of this contribution is the task-specific preparation of those porous materials for certain applications. They also point out how to translate porous polymeric and carbonaceous materials from the lab bench to industrial applications. In its entirety, the authors see the future application in the environmental and energy storage fields.

Little and Cooper ^[17] discuss the design of porous organic molecular materials. The authors meticulously explore the definition of porosity in molecular solids by operating a distinction between intrinsic porosity of some classes of molecules and the extrinsic porosity of crystal lattices. Such basis underpins an extensive overview of how to use crystal engineering to tune functional host-guest properties of molecular solids.

Perovic, Oschatz and co-workers ^[18] present a review on tailoring the adsorption properties of porous carbon materials, highlighting the fundamental concepts of functionalizing their inner cavities to control host-guest interactions. Special attention is paid to the challenges of controlling chemical modifications involving the incorporation of heteroatoms and metallic species, and to the functionalisation strategies based on the concept “from molecules to materials”.

Huang, Cheng and co-workers ^[19] summarise the state of the art and perspectives in the chemistry of porous graphene and graphene oxide materials. The main strategies to achieve 2D or 3D porosity are discussed focusing on the structure-property relationships of this class of solid for various applications in energy storage, electrocatalysis, and molecular separation.

Lei, Zhu and co-workers ^[20] provide a comprehensive review on porous silica materials, with special emphasis on biomedical applications. Their primary focus is the preparation of mesoporous silica nanoparticles for drug delivery, mesostructured silica thin films acting as bioactive coatings or sensors, and biomimetic silicification/immobilisation of biomolecules.

Categorically, it can be concluded that the spirit of all contributions is to push the frontiers of knowledge and stimulate the minds of the next generation. Besides all the advantages of the functionalization chemistry of each considered porous material, emerging challenges are also discussed in order to stimulate research commitment that will lead to future steps towards improving society at large. With all these efforts the authors lay the foundation of new breakthroughs in this field and for this we are sincerely grateful. Finally, yet importantly, we would like to thank the whole editorial board of *Advanced Functional Materials*, especially Marc Zastrow, for their strong support.

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Stefano Canossa studied materials chemistry at the University of Parma (Italy), where he pursued his PhD research focusing on the crystallography of architectural defects in metal–organic frameworks under the guidance of Prof. Alessia Bacchi and Prof. Giovanni Predieri. After graduating in 2018, he worked as postdoc at the Delft University of Technology (The Netherlands) in the group of Prof. Monique A. Van der Veen. In 2019 he obtained his current individual postdoctoral grant from the Research Fund Flanders (FWO) to work at the EMAT centre (University of Antwerp) in the group of Prof. Joke Hadermann. His research focuses on the development of single-crystal electron total scattering analysis for the determination of correlated defects in framework nanomaterials.



Stefan Wuttke created the research group “wuttkegroup for science”, initially hosted at the Institute of Physical Chemistry at the University of Munich (LMU, Germany). Currently, he is an Ikerbasque Professor at the Basque Center for Materials, Applications and Nanostructures (BCMaterials, Spain). His research is focused on developing methodologies to write and read chemical information onto and from the backbone of hybrid framework materials. In addition, his research interests also include the acquisition of a fundamental understanding of the chemical and physical processes involved in their synthesis and functionalization.