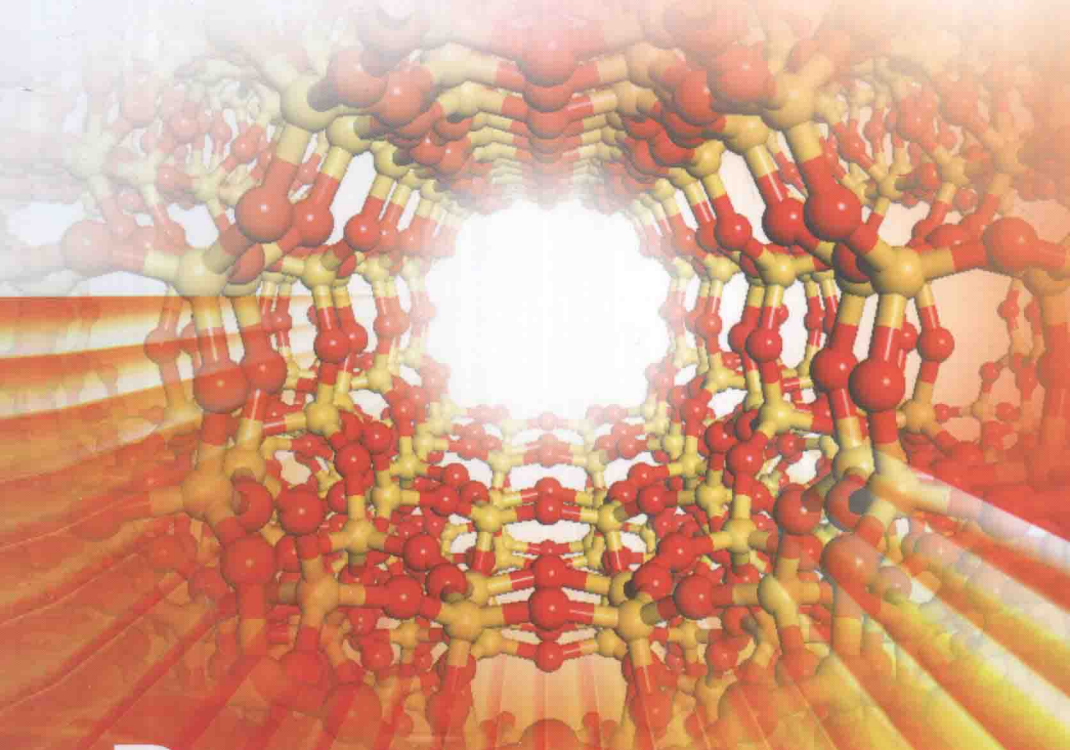
Inorganic Materials Series



Porous Materials

Editors
Duncan W. Bruce | Dermot O'Hare | Richard I. Walton

WILEY

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Series Titles

Functional Oxides
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Low-Dimensional Solids
Porous Materials
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Inorganic Materials Series Preface

Back in 1992, two of us (DWB and DO'H) edited the first edition of *Inorganic Materials* in response to the growing emphasis and interest in materials chemistry. The second edition, which contained updated chapters, appeared in 1996 and was reprinted in paperback. The aim had always been to provide the reader with chapters that while not necessarily comprehensive, nonetheless gave a first-rate and well-referenced introduction to the subject for the first-time reader. As such, the target audience was from first-year postgraduate student upwards. Authors were carefully selected who were experts in their field and actively researching their topic, so were able to provide an up-to-date review of key aspects of a particular subject, whilst providing some historical perspective. In these two editions, we believe our authors achieved this admirably.

In the intervening years, materials chemistry has grown hugely and now finds itself central to many of the major challenges that face global society. We felt, therefore, that there was a need for more extensive coverage of the area and so Richard Walton joined the team and, with Wiley, we set about a new and larger project. The *Inorganic Materials Series* is the result and our aim is to provide chapters with a similar pedagogical flavour but now with much wider subject coverage. As such, the work will be contained in several themed volumes. Many of the early volumes concentrate on materials derived from continuous inorganic solids, but later volumes will also emphasise molecular and soft matter systems as we aim for a much more comprehensive coverage of the area than was possible with *Inorganic Materials*.

We approached a completely new set of authors for the new project with the same philosophy in choosing actively researching experts, but also with the aim of providing an international perspective, so to reflect the diversity and interdisciplinarity of the now very broad area of inorganic materials chemistry. We are delighted with the calibre of authors who have agreed to write for us and we thank

them all for their efforts and cooperation. We believe they have done a splendid job and that their work will make these volumes a valuable reference and teaching resource.

DWB, York
DO'H, Oxford
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July 2010

Preface

Porosity in the solid-state is a topic of long-standing attention in materials science and the case of the zeolites exemplifies the importance of porous materials across many disciplines of science. Here, the study of naturally occurring silicate minerals led to the discovery of synthetic analogues in the laboratory that now have huge commercial value, ranging from large-scale industrial petroleum cracking catalysts to household applications in water-softening additives in detergents. This is an important example of how curiosity-driven, fundamental research in complex inorganic structures, and how they might be assembled in a controlled way, ultimately can lead to novel materials with societal benefit.

The field of porous materials has, however, undergone dramatic development in the past few decades, particularly with the increasingly routine use of advanced structural probes for studying the structure and dynamics of the solid state. Porosity in inorganic materials now extends from the nanoscale up to the macroscale and is a highly researched area, particularly since the idea of design in synthesis is being realised by control of solution chemistry in the crystallisation of complex extended structures. Properties are increasingly the goal in this field: novel solid hosts for confinement of matter on the nanoscale, highly specific shape selective catalysts for energy-efficient organic transformations, new media for pollutant removal, and gas storage materials for energy applications. The role of the synthetic chemist remains key to the discovery and classification of porous materials; the fact that novel porous materials are still reported at an increasing rate in the chemical literature demonstrates the vitality of the field.

The five chapters in this volume cover some of the key families of inorganic solids that are currently being studied for their porosity. The area of zeolites is still researched heavily since there remain long-standing questions in understanding crystallisation and the extent to which novel materials, with structure and chemical properties are tuned for particular applications, can be produced. The chapter on zeolite chemistry illustrates this and takes a novel angle, describing how the synthesis of porous materials can be inspired by nature. Various other important families are covered representing the scales of porosity from nanoporous through mesoporous, and also showing how various chemical classes of material can be rendered porous by elegant synthetic approaches.

We are very pleased that well-respected authors who are active in research in this important area agreed to prepared chapters for this volume and thank them for their excellent results. We hope that this collection will provide a useful and up-to-date introduction to an area of abiding interest in materials chemistry.

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Metal-Organic Framework Materials

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1.1 INTRODUCTION

In recent years there has been a rapid growth in the appreciation of molecular materials not just as arrangements of discrete molecular entities, but as infinite lattices capable of interesting cooperative effects. This development has arisen on many fronts and has seen the emergence of chemical and physical properties more commonly associated with non-molecular solids such as porosity, magnetism, and electrical conductivity. This chapter focuses on an area of molecular materials chemistry that has seen an extraordinarily rapid recent advance, namely, that of metal-organic frameworks (MOFs).[†] These materials consist of the linkage of metal ions or metal ion clusters through coordinative bridges to form

[†] Whilst certain qualifications on the use of the term 'metal-organic framework' have been put forward (*e.g.*, relating to formal bond valence and energy, ligand type, *etc.*),[3] the common usage of this term has spread well beyond these to become largely interchangeable with a number of more general terms such as 'coordination polymer', 'coordination framework', 'metallosupramolecular network' and 'hybrid material'. As such, this term is used here, with some reluctance, in its broadest general sense to encompass a very diverse range of material types in which metal atoms are linked by molecular or ionic ligands.

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frameworks that may be one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) in their connectivity.[1–14]

In the broadest sense, the use of coordination chemistry to produce framework materials has been with us since the discovery of Prussian Blue more than 300 years ago, with developments throughout the last century providing an array of framework lattices spanning a range of different ligand types.[15, 16] The rapid expansion of this early work into more structurally sophisticated families of materials can be traced to two developments. First, the exploitation of the strong directionality of coordination bonding has allowed a degree of materials design (so-called 'crystal engineering') in the synthesis of framework phases. Here, the use of molecular chemistry has allowed both the rational assembly of certain framework topologies – many not otherwise accessible in the solid state – and the control over framework composition through the incorporation of specific building units in synthesis or through post-synthetic modification. Secondly, the capability to construct materials in a largely predictive fashion has led to the emergence of a range of new properties for these materials. This most notably includes porosity, as seen in the ability to support extensive void micropore volume, to display high degrees of selectivity and reversibility in adsorption/desorption and guest-exchange, and to possess heterogeneous catalytic activity. A range of other interesting functionalities have also emerged, many in combination with reversible host–guest capabilities. A particularly attractive feature of the metal-organic approach to framework formation is the versatility of the molecular 'tool-box', which allows intricate control over both structure and function through the engineering of building units prior to and following their assembly. The adoption of this approach has been inspired in part by Nature's sophisticated use of molecular architectures to achieve specific function, spanning host–guest (*e.g.* ion pumping, enzyme catalysis, oxygen transport), mechanical (*e.g.* muscle action), and electronic (*e.g.* photochemical, electron transport) processes. Following rapid recent developments the immensely rich potential of MOFs as functional solids is now well recognised.

At the time of writing this field is experiencing an unprecedented rate of both activity and expansion, with several papers published per day and a doubling in activity occurring every *ca* 5 years. Faced with this enormous breadth of research, much of which is in its very early stages, the aim of this chapter is not to provide an exhaustive account of any one aspect of the chemistry of MOFs, rather, to provide a perspective of recent developments through the description of specific representative examples, including from areas yet to achieve maturity. Following a broad overview of the host–guest chemistry of these materials in Section 1.2, particular

focus is given to the incorporation of magnetic, electronic, optical, and mechanical properties in Section 1.3.

1.2 POROSITY

1.2.1 Framework Structures and Properties

1.2.1.1 Design Principles

1.2.1.1.1 Background

The investigation of host–guest chemistry in molecular lattices has a long history. Following early demonstrations of guest inclusion in various classes of molecular solids (*e.g.* the discovery of gas hydrates by Davy in 1810), major advances came in the mid twentieth century with the first structural rationalisations of host–guest properties against detailed crystallographic knowledge. Among early classes of molecular inclusion compounds to be investigated for their reversible guest-exchange properties were discrete systems such as the Werner clathrates and various organic clathrates (*e.g.* hydroquinone, urea, Dianin's compound, *etc.*), in which the host lattices are held together by intermolecular interactions such as hydrogen bonds, and a number of framework systems (*e.g.* Hofmann clathrates and the Prussian Blue family), in which the host lattices are constructed using coordination bonding.[15, 16] A notable outcome from this early work was that the host–guest chemistry of discrete systems is often highly variable due to the guest-induced rearrangement of host structure, and that the coordinatively linked systems – in particular those with higher framework dimensionalities – generally display superior host–guest properties with comparatively higher chemical and thermal stabilities on account of their higher lattice binding energies.

Whilst the excellent host–guest capabilities of coordinatively bonded frameworks have been appreciated for many decades, the extension of this strategy to a broad range of metals, metalloligands and organic ligands has been a relatively recent development. Concerted efforts in this area commenced in the 1990s following the delineation of broad design principles[1] and the demonstration of selective guest adsorption;[17] notably, these developments arose in parallel with the use of coordination bonds to form discrete metallosupramolecular host–guest systems.[18] A number of different families of coordinatively bridged material have since been developed, each exploiting the many attractive features conferred by the