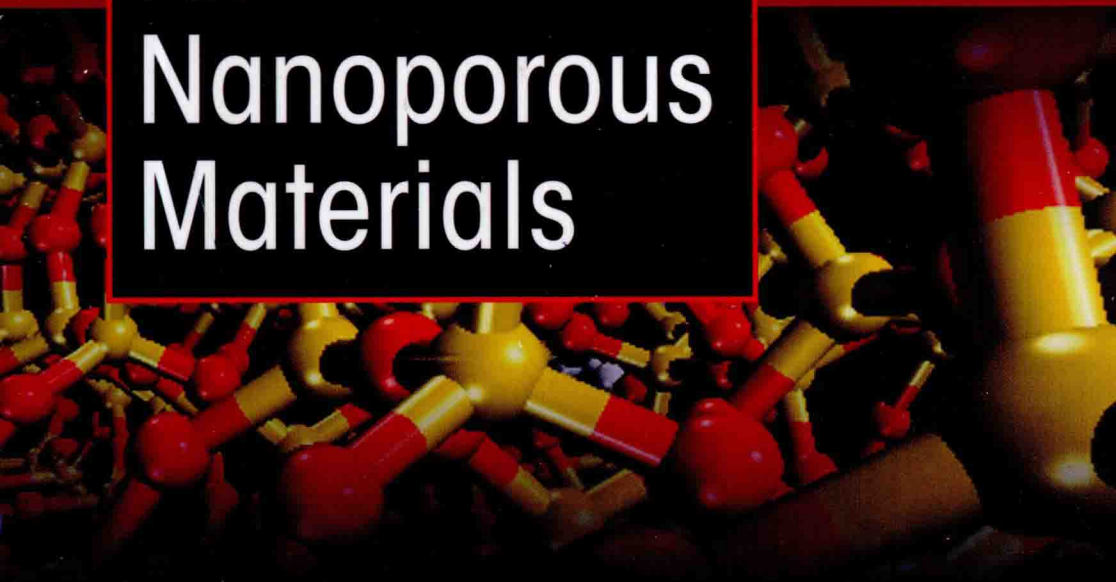
Structure Property Correlations for Nanoporous Materials



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Foreword

Nanomaterials are a major focus of nanoscience and technology. It is a growing field of study attracting tremendous interest, insight, and effort in research and development around the world for its multidomain applications. *Nanoporous* materials are nanostructured materials, which possess unique surface, structural, and bulk properties with applications in fields such as ion exchange, separation, catalysis, sensor applications, and molecular isolation and purification in biology. Nanoporous materials are of scientific and technological importance because of their immense capability to adsorb and interact with atoms, ions, and molecules on the large interior surfaces of the nanometer-sized pores. They also offer new opportunities in inclusion chemistry, guest–host syntheses, and molecular manipulations and reactions at a nanoscale for making nanoparticles, nanowires, and other quantum nanostructures.

Research on nanoporous materials can benefit from computer modeling/simulation studies not only to explain the experimental observations but to design new materials of interest. Materials with targeted properties can even be designed computationally. Modeling techniques can help in formulating the synthesis strategies and characterizing the materials from laboratory to pilot plant and further to plant production.

There is a need, in this context, for a book that introduces, reviews the literature, and discusses the correlation between the structure and property relationships of nanoporous materials and that can serve as a "bridge" between experiment and theory, simulation/modeling while addressing key issues in the area of nanoporous materials. This book is novel in its kind and its timely publication will be of interest to experimentalists in this area. Commercially available software is used throughout the book, which enhances its utility to the nonspecialist. The author has many years of research and experience in exploring, learning, and understanding the field of molecular modeling of nanoporous materials, especially those areas of interest in catalysis.

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Preface

Nanoporous materials consist of a regular organic or inorganic framework supporting a regular, porous structure. Due to the unique structure–property relation, nanoporous materials have huge potential for a wide range of applications.

Molecular modeling techniques are nonexperimental reasonings to explain or predict chemical phenomena, much of which has in fact fallen under the heading of computational chemistry; i.e., the application of computation to the solution of problems in chemistry. Chemical theorists have also used the power of statistical mechanics to provide a bridge between the microscopic phenomena of the quantum world and the macroscopic bulk properties.

To compare theoretical calculations with experimental, synthesizing a new material is always a challenge, starting from the choice of raw material, followed by several characterization techniques to determine the bulk and physical properties of the material. Moreover, the application of the material — for instance, as catalyst — demands molecular-level understanding to describe the mechanism, which is unknown most of the time and hence it is difficult to optimize the respective parameters. The optimization process is time consuming, requires expensive instruments, and still lacks molecular visualization for precise prediction. To solve this problem, computer simulation is an effective measure and is cost effective, convenient to study anytime, and has the potential to include complex, hazardous, real-world processes. Hence, I believe that computer simulation is an integral part of applied science, especially for materials.

This book aims to direct the experimentalist toward the capability of simulation as well as the level of accuracy on which one can depend on the technology. That belief then only will turn one's interest to really design the novel material of interest or explain the chemical phenomenon underneath by comparing the experiments with computer simulation.

To provide a comprehensive overview of the area of nanoporous materials, Chapter 1 begins with a definition of nanoporous materials followed by classifications, the importance of nanomaterial, current applications, challenges, and future prospects. The definitions in relation to porous materials and nanoporous materials are necessary to understand the concept of nanoporous materials in context to their applications. Following this introduction, the classification and scope of nanoporous materials are presented. The properties and their characterization and measurement methods are briefly described before major applications in various fields are reviewed. Finally, in this chapter, key scientific and engineering issues and future directions are identified as challenges and opportunities for researchers in this field.

In Chapter 2 the focus is on defining molecular modeling and showcasing different methodologies to solve the nanomaterial problem. The main focuses are on atomistic simulation techniques with Monte Carlo and molecular mechanics. Finally, the challenges and the future of these techniques within this domain are also discussed.

In Chapter 3 the focus is on introducing a density functional theory (DFT) technique to the readers. The methodology is introduced with a context of the basic wave

mechanics, followed by an explanation of density matrix. The chemical potential is then explained to address the issue with the modelling of chemical bonds. This is the main motivation of modeling to reproduce and explain the experimental scenarios. The challenges and the future of the DFT technology are described at the end of this chapter.

Chapter 4 aims to define and explain localized reactivity descriptors. The local softness and hardness paradigm along with philicity concepts has been explained to provide a basic idea of the concept, as well as to provide a background to discuss and rationale for the applications of these methodologies to understand the experimental postulates.

Structural complexity evolves during synthesis, and therefore one way of capturing such complexity within atomistic models is to "simulate synthesis," as explained in the Chapter 5. The discussion starts with the nucleation and growth of nanoporous material, which is where the synthesis process starts in an experimental workroom. This involves selection of raw materials, which includes changing the chemical composition and optimizing the bulk structure of the varied composition including the role of metal incorporation. Further demand is to look into the effect of pressure and temperature in the reaction process. This is performed to mimic the synthesis condition and to rationalize the synthesis process of nanoporous materials.

Experiments have their own limitations; thus, the combination of experiment and computer simulation is necessary to obtain a desired material with specific functionalities for proper applications. Chapter 6 covers the area of the structural characterization of the material mainly in terms of chemical composition, spectroscopic analysis, mechanical stability, and porosity to show the capability of simulation to justify and validate experimental observations. This also can provide a lot of space for experimentation where analysis is ambiguous.

The design of new nanoporous materials in terms of their specific applications like surface adsorption phenomena, sensors, or catalysts for various organic syntheses is the main theme of Chapter 7. Nanoporous materials are widely used as catalysts because of their large internal surface area and the consequent presence of controllable large voids. Microporous materials like zeolites are mainly used as heterogeneous redox catalysts in the petroleum industry, in various shape selective reactions, and in separation. In discussing the catalytic activity of the microporous material, it must be mentioned that the transition metal–substituted microporous materials (TMSM) with aluminosilicate or aluminophosphate framework are covering a large part of the catalysis. TMSM mainly take part in the various oxidative transformations in the presence of a mild oxidizing agent like hydrogen peroxide or oxygen. A number of applications in waste treatment processes, including removal of heavy metals and radioactive species, as well as ammonia, different phosphates, and toxic gases from water, soil, and air, are due to the unique structural and surface physico-chemical properties of microporous materials, such as excellent absorption and ion-exchange capacities. The details of these applications are described in Chapter 8, "Application of Nanoporous Materials." So, each of the functions demands a specific surface property such as pore architecture, pore size, surface area, and acidity or basicity of the matrix. Considering the surface properties, adsorption is generally used to characterize the surface structure. However, it is a complicated process and it is difficult to obtain a molecular-level scenario on an experimental basis. Thus, simulation can

play a significant role in simulating the actual situation occurring at the molecular level by comparing the binding energy or the attachment energy and by comparing the surface chemistry and producing a result to show the probability of physisorption and chemisorption.

Nanoporous materials combine with the advantages of porous materials. These tiny materials provide a huge surface area, controllable pore sizes, morphology, and capable of any surface-related applications. Due to their considerably small-size porous structure, material properties have increased compared to their bulk counterpart. Therefore, it is obvious that the revolutionary properties of nanoporous materials make them a strong contender for its wide range of applications. The main interest of Chapter 8 is in providing some promising applications of nanoporous materials, such as (a) photonic crystals, (b) bio-implants, (c) sensors, and (d) separation.

Now, the designed material, which is synthetically viable and technically applicable in terms of pore architecture, metal loading and other related parameters as established through experimental technique and computer simulation technology needs to be tested further to confirm the functionality. In Chapter 9 we focus on the catalytic activity of the nanoporous material. The discussion covers related topics of catalysis starting from shape-selective reactions within nanopores, chemical adsorption reactions, cracking, and the mechanistic aspect of a reaction using transition state theory, especially the activation barrier, the intrinsic reaction coordinate, and the effect of solvent on catalytic reactions. This chapter provides a detailed explanation of the methodology of simulation, so that one can follow these cases and approach their own problems for a solution.

I hope this book will convey the significance of the combination of traditional experimental work and molecular simulation to the researcher. I think this book will stimulate the interest of bench chemists in molecular modeling and remove the hurdle of understanding what simulation can provide and how one can successfully design a matrix for a specific application.

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Author

Abhijit Chatterjee was born in Chandananagore, a little town near Kolkata, India. He was a student of Kanailal Vidyamandir and received his Master's and Ph.D. from Burdwan University, West Bengal, India. After graduating from University with his Ph.D. in physico-analytical chemistry in 1992, he moved to the National Chemical Laboratory, Pune, India, and worked there until 1995 as a Research Associate in the Catalysis Division. He exposed himself to the simulation of catalytic material. He has traveled around the world and collaborated with many groups in catalysis before settling down in Japan as a researcher in the field of computational chemistry and established himself in this field with more than 100 papers in international journals of repute; he has presented invited talks at many international and national symposiums, and written chapters in books published by Elsevier, Taylor & Francis, and Wiley. He served as a member of the editorial board of the *International Journal of Molecular Science*. He is a member of many leading scientific societies (ACS, IOP, IZA, etc.). His research interest is focused on density functional theory and its application on different materials, especially related to catalysis (zeolite, clay, oxides). He also explored other materials of interest like composites, semiconductors, and metal clusters to rationalize the structure–property correlation and finally was involved in deriving reactivity index, Fukui function, and simpler algorithms to help experimentalists to design a novel material.

Contents

1 Basic Aspects of Nanoporous Materials

In recent years, nanomaterials have been a major focus of nanoscience and nanotechnology. It is a self-growing field of study attracting tremendous interest, insight, and effort in research and development around the world for its multidomain applications. Nanoporous materials are a type of nanostructured materials that possess unique surface, structural, and bulk properties. This underlines their important usage in various fields of research such as ion exchange, separation, catalysis, sensor applications, biological molecular isolation, and purification. Nanoporous materials are also of scientific and technological importance because of their great ability to adsorb and interact with atoms, ions, and molecules on their large interior surfaces and in the nanometer-sized pore space. They offer new opportunities in areas of inclusion chemistry, guest–host synthesis, molecular manipulations, and reactions in the nanoscale for making nanoparticles, nanowires, and other quantum nanostructures.

To provide a comprehensive overview of the area of nanoporous materials, this chapter will begin with a definition of nanoporous materials followed by their classifications, the importance of nanomaterials, current applications, and, lastly, challenges and future prospects. The basic concepts and definitions in relation to porous materials and nanoporous materials are necessary for understanding the concept of nanoporous materials as well as for the better understanding in context to their applications. Following this introduction, the classification and scope of nanoporous materials will be presented. The properties and their characterization and measurement methods will be briefly described before major applications in various fields are reviewed. Finally, key scientific and engineering issues and future directions are identified as challenges and opportunities for researchers in this field.

Porous inorganic solids have found great utility as catalysts and sorption media because of their large internal surface area and the presence of voids of controllable dimensions at the atomic, molecular, and nanometer scales. With increasing environmental concerns worldwide, nanoporous materials have become more important and useful for the separation of polluting substances as well as the recovery of useful ones. The prospective applications include their use as templates for the production of electrically conducting nanowires and for highly selective biosensors and biomembrane materials. Inorganic–organic or hybrid nanoporous crystalline materials have recently attracted much attention and increasing interest due to their potential in gas separation and hydrogen storage. This chapter will cover recent developments in the synthesis, characterization, and property evaluation of new nanoporous inorganic materials and some hybrid solids.

The idea of the book is to walk together with experimentalists and follow their way of approaching the nanoporous domain. The book therefore will proceed to

show the techniques available in the realm of simulation to approach this world of science. Chapters highlighting synthesis of nanoporous materials, their characterization, porosity measurement, and adsorption as a phenomenon will follow this, as well as some projected applications with a futuristic approach and finally the reaction mechanism. All of this will be done in comparison with experiments and a simulation recipe will be prescribed. There will be some emphasis on the silica and phosphate-based frameworks by using hydrothermal and microwave procedures with X-ray diffraction (XRD), spectroscopy (infrared [IR], nuclear magnetic resonance [NMR]), and electron microscopy characterization techniques in brief. Moreover, the functionalization of nanoporous materials by physical and/or chemical treatments; studies of their fundamental properties, such as catalytic effects or adsorption; and their applications will be described based on both theoretical studies and experimental studies in the following chapters.

1.1 DEFINITION

The journey of nanoscience starts with the famous lecture of Professor Feynman, "There's plenty of room at the bottom," in 1959 [1]. However, the real burst of nanoscience came after the 1990s, and now it has opened a wide door that does not leave any major research area outside. Nanomaterials are an integral part of nanoscience. The broad definition of nanomaterials is those materials, which possess a size that is smaller than one micron (μm) in at least one dimension. Actually, the definition does not restrict the material in question to any fixed minimum or maximum size but logically it must be between the micro- and atomic/molecular scale. According to the definition, it's a small world, and the prefix *nano* is a Greek word meaning dwarf or small. It should be mentioned that nanomaterials are not a simple miniaturization but are somewhere between the bulk and quantum scale. Now, the question is, why is the world running for the smallest material, the nanomaterials? The answer lies in their amazing and exclusive properties, which are completely different from bulk materials of the same composition. The uniqueness of their characteristic properties originates due to their smaller size and consequently the large surface area–to-volume ratio, high surface energy, and spatial confinement. Nanoporous materials are an important part of the nanomaterials, which contain unique porous surface structure, large porosity, and a pore size generally between 1 and 100 nm. These types of materials find wide applications in various fields ranging from sorption, ion exchange, catalysis, host–guest interaction, etc.

What makes nanoscale building blocks interesting is that by controlling the size in the range of 1–100 nm and the assembly of such constituents, one could alter and prescribe the properties of the assembled nanostructures. As Professor Roald Hoffmann, the chemistry Nobel Laureate put it, "Nanotechnology is the way of ingeniously controlling the building of small and large structures, with intricate properties; it is the way of the future, with incidentally, environmental benignness built in by design." [2] Nanostructured materials may possess nanoscale crystallites, long-range ordered or disordered structures, or pore space. Nanomaterials can be designed and tailor-made at the molecular level to have the desired functionalities

and properties. Manipulating matter at such a small scale with precise control of its properties is one of the hallmarks of nanotechnology.

Porous materials are like music: the gaps are as important as the filled-in bits. The presence of pores (holes) in a material can render all sorts of useful properties that the corresponding bulk material would not have. Generally, porous materials have porosity (volume ratio of pore space to the total volume of the material) between 0.2 and 0.95. Pores are classified into two types: open pores, which connect to the surface of the material, and closed pores, which are isolated from the outside. In functional applications such as adsorption, catalysis, and sensing, closed pores are not of any use. In separation, catalysis, filtration, or membranes, penetrating open pores is often required. Materials with closed pores are useful in sonic and thermal insulation or lightweight structural applications. Pores have various shapes and morphology such as cylindrical, spherical, and slit types. Pores can also take more complex shapes, such as hexagonal. Pores can be straight, curved, or have many turns and twists, thus having a high porosity. According to the International Union of Pure and Applied Chemistry (IUPAC), micropores are smaller than 2 nm in diameter, mesopores are in the range of 2 to 50 nm, and macropores have a pore diameter larger than 50 nm. However, this definition is somewhat in conflict with the definition of nanoscale objects. Nanoporous materials are a subset of porous materials, typically having large porosities (greater than 0.4) and pore diameters between 1 and 100 nm. In the field of chemical functional porous materials, it is better to use the term *nanoporous* consistently to refer to this class of porous materials having diameters between 1 and 100 nm. For most functional applications, pore sizes do not normally exceed 100 nm. Nanoporous materials actually encompass some microporous materials and all mesoporous materials. So, what are the unique properties of those materials? Nanoporous materials have a specifically high surface-to-volume ratio, with a high surface area and large porosity, of course, and very ordered, uniform pore structure. They have a very versatile and rich surface composition and surface properties that can be used for functional applications such as catalysis, chromatography, separation, and sensing. Many inorganic nanoporous materials are made of oxides. They are often nontoxic, inert, and chemically and thermally stable; in certain applications the thermal stability requirement is very stringent, so a highly thermally stable catalyst is necessary.

1.2 CLASSIFICATION

Porous materials consist of a network of interconnected pores of controllable dimension in the atomic, molecular, and nanometric scale. Porous materials are creating quite a stir among the material scientists because the size of the channel or the voids can be designed according to the potential applications. As mentioned before, porous materials can be grouped into three different categories depending on their pore diameter, such as (1) microporous where the pore size is less than 2 nm, (2) mesoporous with pore diameters in the range of 2–50 nm, and (3) macroporous, in which the pore size is larger than 50 nm. Nanoporous materials of pore sizes between 1 and 100 nm, generally categorized as bulk materials and membranes, can have open pores and closed pores. Bulk materials can be carbon, silica, metal oxide, organic metal composite, and organic silica composite where the membranes are mainly

developed with zeolite. In addition, mesoporous and inorganic/organic hybrid materials are secured in their place in the field of nanoporous materials.

To describe the fundamental properties of nanoporous materials it is necessary to have a microscopic understanding of the material. Molecular simulation along with the experimental tool has played a significant role, which will be discussed further. Material classification is based on the experimental numbers with the pore architecture, but it is an experimentalist's dream to walk through the channels to see where the active site is and how one can tune the active site, whether the structure contains multiple channels and other interesting features of the nanopore through visualization using simulation. Then, if one wants to probe more of the structure property-based correlations, one needs the help of methods to calculate them, which are based on what you want and to what level of accuracy.

1.3 KEY MATERIALS OF INTEREST

The term *nanoporous material* covers a vast area that deals with materials of pore size greater than 1 nm. This includes the conventional microporous crystalline aluminosilicates like zeolites, clay, periodic mesoporous materials, metal organic frameworks, porous polymers, etc. The main interest of this book will be zeolites and mesoporous materials, aluminum phosphate (AlPO), and metal organic frameworks.

Zeolites are a naturally occurring mineral. More than 150 types of zeolites have been synthesized and 40 types of zeolites are found in nature. Although natural zeolites occur in large quantities, they offer only a limited range of atomic structures and properties. The most common zeolites are silicalite-1, ZSM-5, and zeolite X, Y, A, and zeolite beta. Zeolites are generally crystalline aluminosilicate with a three-dimensional rigid and crystalline structure consisting of interconnected tunnels and cages. The general formula of zeolite is $M_{m/z} \times mAlO_2 \times nSiO_2 \times qH_2O$. In the crystalline structure of zeolite, the metal atoms (mainly Si and Al) are surrounded by four oxygen atoms to form an approximate tetrahedral structure. The metal atom as a cation sits at the center of the tetrahedron. This tetrahedral metal is called a *T-atom*. The framework structure of zeolite is typically anionic and the presence of the charge-compensating cation makes it neutral. When the cations are replaced with the proton zeolite can act as strong solid acid catalysts. Zeolites contain microscopically small channels, so sometimes they are referred to as a *molecular sieve*. Why are these zeolites of key interest to theoretical chemists in the last few decades? The answer is that zeolites are amazing materials because the physical and chemical properties and the crystal structures of zeolites can be varied easily by changing the chemical composition. Zeolites are extremely active catalysts but their small channel size restricts them to the smaller molecules. An example with the most used zeolite, ZSM-5, which is an MFI-type of zeolite, is shown in Figure 1.1. This zeolite, developed by Mobil Oil, is an aluminosilicate zeolite with high silica and low aluminum contents. Its structure is based on channels with intersecting tunnels and a regular pore structure. The maximum size of molecular or ionic species that can enter into the channel is dictated by the dimension of the channel. These channels are conventionally referred to according to their ring size; for example, an eight-membered ring represents a closed loop built with tetrahedrally coordinated 8 silicon or aluminum with oxygen. It is not necessary for the