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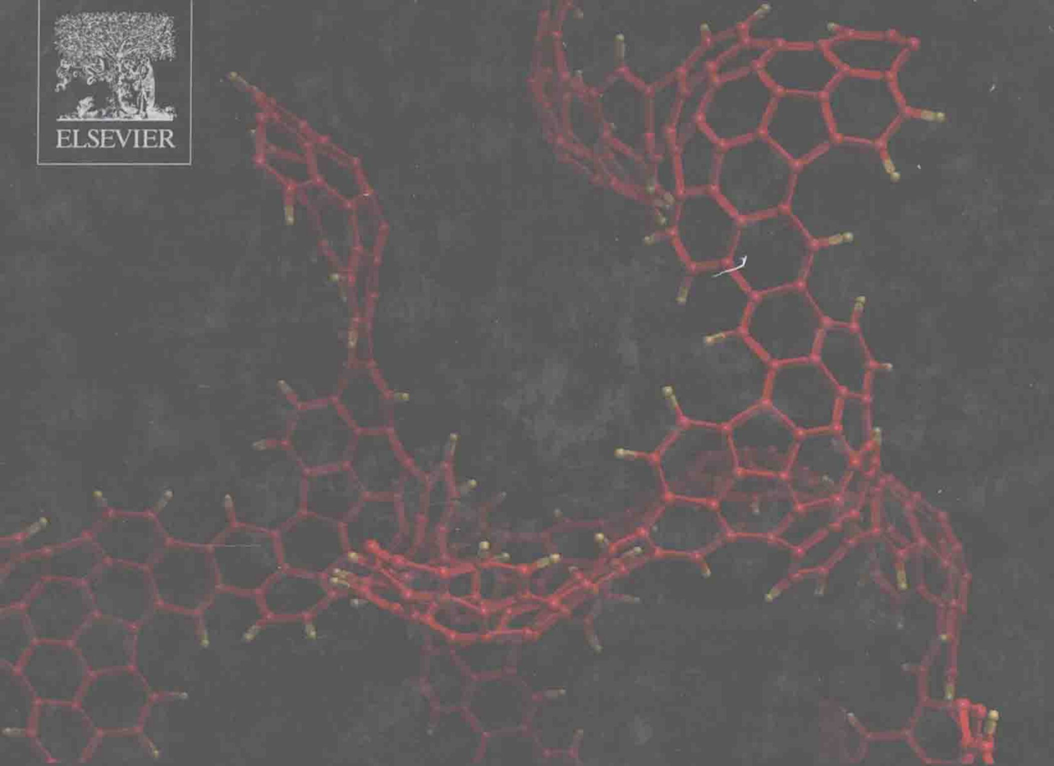

Novel Carbon Adsorbents

Edited by
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Preface

It is well known that the entire realm of carbon materials science and technology has evolved at an incredible pace over the last 25 years. The impetus for these revolutionary changes has emanated from a number of discoveries that have led to the award of two Nobel Prizes (one for Chemistry in 1996, the other for Physics in 2010), an unprecedented enhancement of the impact of publications in this field and the increasing use of carbon-based commodities by our society.

One of the carbon-related areas that has benefited most from these achievements is that of carbon adsorbents. Suffice it to say that most of the key results dealt with in this book have been produced in the 21st Century, which explains why I have used the term "novel" in the book title, a curious paradox considering that the use of wood charcoal as adsorbent is even mentioned in the Old Testament. Much more recently, when one might have thought that porous (i.e. activated) carbons had reached their zenith, the advent of carbon nanoforms has led to the addition of a number of novel nanostructured materials to the set of already available carbon adsorbents; and, perhaps more significantly, has fostered the development of new concepts and methodologies for producing materials with novel and controlled architectures and functions. The success achieved so far has been due, in part, to the existence of an experienced carbon surface scientific community that has been prepared to assimilate and assume the challenges brought about by all these changes. As a matter of fact, even before the nano-revolution, we were already accustomed to dealing with pores in chars and activated carbons, the majority of which were sub-nanometric in width; but we simply referred to them as micropores, even though "micro" is three orders of magnitude larger than "nano".

In a sense, this book is a follow-up to *Adsorption by Carbons*, another book that I edited together with the late E.J. Bottani and that was published in 2008, also by Elsevier. It consists of 21 chapters dealing with topics not treated in the previous book, most of which concern "newer" subjects. The book is divided into five basic parts: introduction, recent developments in theory, the use of new characterization methodologies, adsorption by novel carbon types, and emerging applications of carbon adsorbents. An introductory chapter that provides an overview of nanocarbons within the framework of adsorption is followed by two chapters on new developments in theory, both of which are very much concerned with carbon porosity. Then a chapter on advanced physical adsorption methods (that has deep roots in theoretical work) leads on to a section dealing with the use of adsorption for characterizing carbon surface features such as hydrophilicity or basicity. The largest section of the book in terms of number of chapters describes the adsorption behavior of novel carbon materials, such as carbon gels, phosphorus-containing carbons, carbide-derived carbons, zeolite-templated carbons, soft-templated carbons, carbon nanohorns and, last but not least, graphene. The final part of the book begins with a challenging discussion on the relative roles of porous texture and surface chemistry in the applications of adsorption by carbons and is followed by a series of chapters on the emerging uses of carbon adsorbents in the areas of catalysis, photochemistry, fuel cells, carbon dioxide capture and in the industrial (excluding environment-related uses) and biomedical sectors. In summary, this book contains a set of 21 authoritative chapters that provide, I hope, a consistent and integrated body of knowledge revolving around the field of novel carbon adsorbents.

As in the case of *Adsorption by Carbons*, the strength of the present book mainly emanates from the stature of the contributing authors (none of whom contributed to the previous book—therefore the team is also new). The book has an unquestionably international flavor, as it includes authors with affiliations to no fewer than 16 different countries (this figure would be larger if one took into account the number of nationalities or mother languages involved). If the previous *Adsorption by Carbons* book was slightly unbalanced in favor of countries from the New World, that imbalance has now been redressed with the majority of the chapters coming from European countries and a significant proportion from Asia/Oceania. I am particularly proud of having succeeded in getting together an outstanding group of carbon scientists who managed to find the time to prepare their contributions when time is one of our scarcest and most precious resources. To convince them, I had recourse to my personal friendships, contacts established during collaboration projects and colleagues both in Spain and abroad. Once won over to the cause, they showed a willingness, an enthusiasm and a professionalism that knew no bounds. Rather than cite the participants' authors names here, which would make this text exceedingly long, I prefer to thank them collectively for their efforts. My thanks go out to the staff of Elsevier, particularly Ms. Louisa Hutchins, Editorial Project Manager, for her constant willingness to help me and even, on occasions, for spurring me on when, owing to my official duties as Director of INCAR, I was forced to slow down my pace as editor.

I also wish to thank Prof. John W. Patrick for contributing the Foreword to this book. From his privileged watch-tower position, first at Chesterfield, then at Loughborough and now at Nottingham, Prof. Patrick has surveyed for many years the progress made in the field of carbon-based materials. Our scientific community is much indebted to him for his almost lifelong commitment as Editor of *Fuel* and for his hard work in different fields of coal and carbon science and technology (I had the pleasure of working with him in a joint research project several years ago). Due to its relevance to the topics discussed here, I would like to make explicit mention of *Porosity in Carbons,* a book which he edited in 1995, and which is a fine predecessor for this book. My warmest thanks also go to Sendai, the workplace of Prof. Hirotomo Nishihara, who provided me with a highly esthetic, yet precise picture of the nanostructure of a zeolite-templated carbon that is featured on the cover of this book. This diagram beautifully illustrates the complexity and intricacy of the graphene sheet network that constitutes this type of adsorbent. *Nishihara–sensei, arigatō gozaimasu!*

Juan M.D. Tascón

Foreword

Carbon as an adsorbent is hardly a novel concept since there is evidence that this remarkable element was used for that purpose as early as 1550 BC and the published literature bears testimony to the wide range of such applications since then. Indeed numerous books on this subject have been produced over the years. So the question can be asked as to what is the motivation for another book on carbon as an adsorbent and what is novel about this ubiquitous element.

The answer is that despite its long history as an adsorbent, this fascinating element carbon still continues to amaze and intrigue us with an enigmatic character which provides it with almost unbelievable variation in structural form and adaptability in use.

When I started on my scientific career, I was taught that carbon always tended toward the formation of six-membered rings which stacked in parallel layers in an ABAB or ABCABC sequence. Now we know that five-membered rings are not uncommon along with spherical and tubular forms as alternative stable structures and I now have to contend with buckyballs, nanotubes and even single layered graphene as remarkably different carbon forms with distinctive properties.

The development of the computer has facilitated the development of modern analytical equipment for improved characterization of surfaces and the measurement of adsorptive capacity of materials and this has facilitated the development of modeling, thereby making a significant contribution to the understanding of the mechanisms involved in the adsorption of both gases and liquids by the different carbon forms.

At the same time the demand for adsorbents has increased remarkably through enlightened considerations of such topics as health and safety, alongside the ever increasing environmental constraints imposed on industries ranging from production of chemicals, water and air purification, to solvent recovery and even gold recovery. This demand allied to the gradual development of our understanding of both the nature of the various forms of carbon materials and the mechanisms involved in the adsorption and desorption processes provide another inducement to the writing of this book.

The twenty one chapters contributed by well-known experts in their field, form a most useful and timely contribution to our knowledge and understanding of the novel carbon materials now available to us and their application as adsorbents in a variety of processes.

John W. Patrick

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Part I

Introduction

Chapter 1

Novel Nanocarbons for Adsorption

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Chapter Outline

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1.1. INTRODUCTION

Carbon is a fascinating element of the periodic table since it can establish bonds with almost any element, thus resulting in a wide spectrum of compounds and allotropic forms. Adsorption is a phenomenon that occurs on surfaces, and materials with larger surface area are strong candidates to adsorb high concentrations of different chemical species. For a long time, activated carbons (porous materials with large surface area) have been extensively used for water treatment and gas adsorption. The new generation of carbon structures built at the nanoscale (e.g. nanofibers, nanotubes, fullerenes, nanocones, graphene, graphene nanoribbons, nanodiamonds, etc.) with relatively large surface area, and exhibiting novel electronic and chemical properties, provides new horizons for achieving enhanced adsorption, which could result in new applications. For example, some of these carbon nanostructures could be used in wastewater treatments, routes for clean energy generation, hydrogen storage devices, sensors, catalytic supports, virus inhibitors, etc. In this chapter, we review a wide spectrum of novel carbon nanostructures and their potential in the adsorption of heavy metals, gases, polymers, and biomolecules. We emphasize the role of surface modification of these nano-systems via chemical doping, defect engineering and chemical functionalization, and discuss their effects in the adsorption properties of carbon nanomaterials.

1.2. GENERAL ASPECTS OF CARBON NANOSTRUCTURES

Nowadays there are numerous carbon nanomaterials, some of which could be curved in order to form fascinating morphologies with novel physico-chemical properties (see Fig. 1.1). Graphite is the best example of a very flexible layered material, which is able to form a wide variety of shapes, ranging from zero-dimensional, such as fullerenes [1,2], cones [3,4] and toroids [5], to 1-, 2-, and 3-dimensional. In particular, one-dimensional (1D) systems include single- and multiwalled nanotubes [6,7], nanoribbons, and nanohelices. Two-dimensional (2D) structures such as graphene, antidot graphene and super-graphene, and Haeckelites [8]. Three-dimensional (3D) systems consist of graphite and Schwarzite-like structures [9–12]. In addition, Fullerenes and cones exhibit positive Gaussian curvature due to the presence of pentagonal carbon rings, and there are other structures containing heptagonal or higher carbon-membered