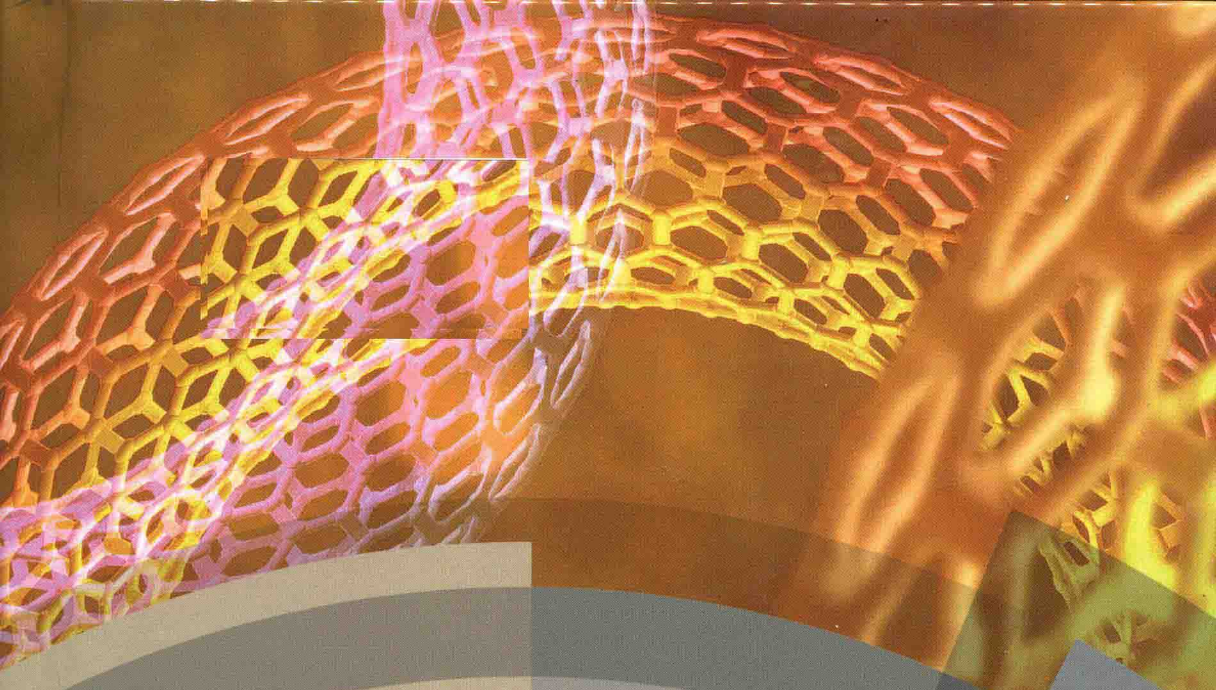

RSC Catalysis Series

Nanostructured Carbon Materials for Catalysis

Philippe Serp and Bruno Machado

ROYAL SOCIETY OF CHEMISTRY

Nanostructured Carbon Materials for Catalysis

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Foreword

Carbon plays a well-established and important role in catalysis for a wide range of applications, both as a support material and as catalyst in its own right. This role is growing for two independent but equally important reasons. Firstly, a number of emerging liquid-phase processes under demanding conditions and more specifically aqueous phase biomass conversion, call for a chemical stability of supports that surpasses that of metal oxide materials. Secondly, the almost explosive development of new carbon nanostructures over the last decades enables control of carbon materials at multiple length scales in very new ways. For a long period of time activated carbons, and carbon black to a lesser extent, have dominated catalysis applications. With the advanced control of nanostructured carbons in materials, *inter alia* carbon nanofibers, carbon nanotubes, carbon onions and most recently graphene, an unsurpassed control over carbon as catalyst or as support comes within reach. It seems, therefore, very timely that the current book authored by Bruno Machado and Philippe Serp appears. Both authors have contributed over the years in a very significant way to the utilization and scientific understanding of carbon nanomaterials in catalysis and can be considered as world-leading experts. What also makes this book special to me is its comprehensive nature. It starts from a description of the allotropes of carbon and ends with the engineering considerations of carbon utilization such as shaping, safety aspects and life cycle analysis. In between it discusses adsorption, surface chemistry, carbon as catalyst, emplacement of metals and grafting onto carbon supports, catalysis with supported metals for hydrogenation, and extending into oxidation catalysis, polymerization and photo-catalysis. Energy conversion and storage including carbon in electrodes and batteries is described as well. I consider

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this book a 'must have' and even a 'must read' for many that work in the area of (carbon in) catalysis.

Krijn de Jong
Professor of Inorganic Chemistry and Catalysis
Utrecht University

Preface

Different types of carbon materials, such as activated carbon, graphite, and carbon black, have been successfully used over the last century as catalysts or catalyst supports in the chemical industry or for energy or environmental applications. Even though significant research and development has been made during this period concerning the knowledge of carbon surface chemistry, carbon materials were often considered as "complex and poorly understood" by the catalysis community. Low mechanical and thermal stability, together with narrow microporosity and inconsistent quality of activated carbons are usually pointed out as main disadvantages, limiting their applications. Pure graphite and carbon black often suffer from irregular pore structure and insufficient anchoring sites for the active phase. Highly competitive carbon materials for catalysis should therefore combine a controlled porosity and surface chemistry, and good thermal and mechanical properties with an acceptable stability and price. If such a material did not previously exist, the arrival of nanotechnologies in the 1980s, with the discovery of fullerenes in 1985, and the identification of carbon nanotubes in 1991 has permitted a huge boost of carbon chemistry and physics. Last but not least, the production, isolation, identification and characterization of graphene in 2010 have significantly contributed to the fact that nowadays carbon materials have achieved an important place in the scientific community. Yearly, a huge number of scientific publications are published on nanostructured carbon materials, and in the last thirty years a significant part of them is devoted to their use in catalysis.

Though the use of carbon materials for catalysis is nowadays a well-recognized field of research (with dedicated congresses and books) the field of nanostructured carbon materials for catalysis has undergone explosive growth in recent years. We have witnessed the emergence of many novel approaches to synthesis and synthetic design, control of size, morphology,

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as well as novel applications of nanostructured catalytic carbon materials. Hence, we feel that there is a need to combine in a single platform the various properties of nanostructured carbon materials, particularly those related to catalysis such as surface chemistry and adsorption, the details of catalyst preparation, and how and where these novel materials are being used in catalysis. We believe that a fundamental understanding of the role of carbon surface properties should lead to a systematic procedure for the design of catalytic materials with improved performances. This is why we have introduced this book.

In the present book, we want to give the reader a comprehensive overview of what a nanostructured carbon is, and to rationalize the advantages of these catalytic materials regarding their activity, selectivity and stability. Thus, each chapter will provide a critical overview of a specific domain through relevant examples of the literature. In this sense, this book is the first to introduce the concepts and main achievements, while covering the main aspects of nanostructured carbon material for catalysis, both as a support and a metal-free catalyst. It is our hope that this book will not only prove suitable for self-study and teaching purposes, but will also inspire further research and discovery, thus setting the standard in the field of nanostructured carbon materials for catalysis for the years to come.

Philippe Serp
Bruno Machado
Toulouse

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CHAPTER 1

Carbon (Nano)materials for Catalysis

1.1 Introduction

Both organic and inorganic carbons play a key role in catalysis. Organic molecules form the huge and very complex discipline of organic chemistry, and they are, in most catalytic applications, the substrates and the products of the process under consideration. In homogeneous catalysis, carbon is often the main constituent of the organic ligands surrounding the metallic center. In enzymatic catalysis it constitutes the backbone of the active species. In heterogeneous catalysis, carbon materials are unique catalyst supports, allowing the anchoring of the active phase, and can also act as catalysts or catalyst poisons (carbon deposits) by themselves.

The physical and chemical properties of carbon materials, such as their tunable porosity and surface chemistry, make them suitable for application in many catalytic processes. Traditionally, carbon materials have been used as supports for catalysts in heterogeneous catalytic processes, although their use as catalysts on their own is becoming more and more common.[1] Although several kinds of carbon materials have been studied, activated carbon (AC) and carbon black (CB) are the most commonly used carbon supports. The typically large surface area and high porosity of activated carbon catalysts favor the dispersion of the active phase over the support and increase its resistance to sintering at high metal loadings. The pore size distribution can be adjusted to suit the requirements of several reactions. The surface chemistry of carbon catalysts influences their performance as catalysts and catalyst supports. Carbon materials are normally hydrophobic and they usually show a low affinity towards

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polar solvents, such as water, and a high affinity towards solvents such as acetone. Although their hydrophobic nature may affect the dispersion of the active phase over the carbon support, the surface chemistry of carbon materials can easily be modified, for example by oxidation, to increase their hydrophilicity and favor ionic exchange. Apart from an easily tailorable porous structure and surface chemistry, carbon materials present other advantages: (i) metals on the support can be easily reduced; (ii) the carbon structure is resistant to acids and bases; (iii) the structure is stable at high temperatures (even above 1023 K under inert atmosphere); (iv) porous carbon catalysts can be prepared in different physical forms, such as granules, cloth, fibers, pellets, *etc*.; (v) the active phase can be easily recovered; and (vi) the cost of conventional carbon supports is usually lower than that of other conventional supports, such as alumina and silica. Nevertheless, carbon supports also present some disadvantages: they can be easily gasified, which makes them difficult to use in high temperature hydrogenation and oxidation reactions, and their reproducibility can be poor, especially activated carbon-based catalysts, since different batches of the same material can contain varying ash amounts. In this introductory chapter, we will: (i) briefly introduce the main carbon and graphite (nano)materials relevant to catalysis, (ii) present the main application of carbon and graphite materials in catalysis, and (iii) highlight the possible perspectives of using nanocarbons in catalysis.

1.2 Carbon (Nano)materials

The capability of a chemical element to combine its atoms to form such polymorphs is not unique to carbon. Other elements in the fourth column of the periodic table (silicon, germanium, and tin) also have this characteristic. However carbon is unique in the number and the variety of its polymorphs. These allotropes are composed entirely of carbon but have different physical structures and, exclusively for carbon, have different names: graphite, diamond, lonsdaleite, and fullerene, among others. Additionally, carbon as a solid denotes all natural and synthetic substances consisting mainly of atoms of the element carbon, such as single crystals of diamond and graphite, as well as the full variety of carbon and graphite materials. A result of this diversity is that the carbon terminology can be confusing for the non-specialist. The terminology used so far is mainly based on technological tradition and on the standardized characterization methods derived from decades of industrial experience. As a consequence, for many years, carbon science was a very specialized field, considered by many to be too complicated. More recently, carbon science has gained high visibility with the discovery of fullerenes in 1985 and the first HR-TEM observations of carbon nanotubes (CNTs) in 1991. This visibility has been further heightened by the 1996 Nobel Prize in Chemistry awarded to R. F. Curl, H. Kroto and R. E. Smalley for their discovery of fullerenes and the 2010 Nobel Prize in Physics awarded to A. Geim and