

# CARBON MATERIALS FOR CATALYSIS

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*Edited by*

**Philippe Serp  
José Luís Figueiredo**



**WILEY**

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# Contributors

venu.arunajatesan, Evonik Degussa Corporation, 5150 Gilbertsville Highway, Calvert City, KY, 42029

e-mail: venu.arunajatesan@evonik.com

TERESA J. BANDOSZ, Department of Chemistry, Marshak Science Building J-1024, The City College of New York, The City University of New York, 160 Convent Avenue, New York, NY 10031

e-mail: tbandosz@ccny.cuny.edu

JOHANNES H. BITTER, Department of Inorganic Chemistry, Debye Institute, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

e-mail: j.h.bitter@uu.nl

HANNES-PETER BOEHM, Department of Chemistry and Biochemistry, University of Munich, Butenandtstrasse 5-13, 81377 Munich, Germany

e-mail: hpb@cup.uni-muenchen.de

BAOSHU CHEN, Degussa GmbH, Business Line Catalysts, Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang, Germany

e-mail: baoshu.chen@evonik.com

EDWIN CREZEE, Albemarle Catalysts, Nieuwendammerkade 1-3, P.O. Box 37650, 1030 BE Amsterdam, The Netherlands

e-mail: edwincrezee@yahoo.co.uk

KRIJN P. DE JONG, Department of Inorganic Chemistry, Debye Institute, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands

e-mail: k.p.dejong@uu.nl

KAREN M. DE LATHOUDER, Shell Nederland Raffinaderij B.V., Vondelingenweg 601, Postbus 3000, 3190 GA Hoogvliet, Rotterdam, The Netherlands

e-mail: karen.delathouder@shell.com

JOAQUIM LUÍS FARIA, Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

e-mail: jlfaria@fe.up.pt

JOSÉ LUÍS FIGUEIREDO, Laboratório de Catálise e Materiais, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

e-mail: jlfig@fe.up.pt

CRISTINA FREIRE, REQUIMTE/Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal  
e-mail: acfreire@fc.up.pt

FREEK KAPTEIJN, Catalysis Engineering, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands  
e-mail: f.kapteijn@tudelft.nl

JUN LI, Department of Chemistry, Kansas State University, 111 Willard Hall, Manhattan, KS 66506-3701  
e-mail: junli@ksu.edu

FRÉDÉRIC MAILLARD, Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces, UMR 5631 CNRS/INPG/UJF, 1130, rue de la Piscine, BP75, 38402 Saint Martin d'Hères, France  
e-mail: frederic.maillard@lepmi.inpg.fr

KONRAD MÖBUS, Evonik Degussa GmbH, Business Line Catalysts, Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang, Germany  
e-mail: konrad.moebus@evonik.com

CARLOS MORENO-CASTILLA, Inorganic Chemistry Department, Granada University, 18071 Granada, Spain  
e-mail: cmoreno@ugr.es

JACOB A. MOULIJN, Catalysis Engineering, DelftChemTech, Delft University of Technology, Julianalaan 136, 2628 BL, Delft, The Netherlands  
e-mail: J.A.Moulijn@tudelft.nl

DANIEL J. OSTGARD, Degussa GmbH, Business Line Catalysts, Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang, Germany  
e-mail: dan.ostgard@evonik.com

MANUEL FERNANDO R. PEREIRA, Laboratório de Catálise e Materiais, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal  
e-mail: fpereira@fe.up.pt

LJUBISA R. RADOVIC, Energy and Minerals Engineering, 205 Hosler Building, The Pennsylvania State University, University Park, PA 16802  
e-mail: lrr3@psu.edu

FRANCISCO RODRÍGUEZ-REINOSO, Universidad de Alicante, Departamento de Química Inorgánica, E-03080 Alicante, Spain  
e-mail: reinoso@ua.es

ELENA R. SAVINOVA, Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, UMR-7515, ECPM, Université Louis Pasteur, 67087 Strasbourg, France  
e-mail: elena.savinova@ecpm.u-strasbg.fr

ANTONIO SEPÚLVEDA-ESCRIBANO, Universidad de Alicante, Departamento de Química Inorgánica, E-03080 Alicante, Spain  
e-mail: asepul@ua.es

PHILIPPE SERP, Laboratoire de Chimie de Coordination, composante ENSI-ACET, UPR 8241 CNRS 118 Route de Narbonne, Toulouse University, 31077 Toulouse Cedex 4, France  
e-mail: Philippe.Serp@ensiacet.fr

ANA ROSA SILVA, REQUIMTE/Departamento de Química, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal *Present address*: Unilever R&D, Port Sunlight, UK  
e-mail: anarosa.silva@unilever.com

PAVEL A. SIMONOV, Boreskov Institute of Catalysis, Russian Academy of Sciences, Pr. Akademika Lavrentieva 5, 630090 Novosibirsk, Russia  
e-mail: spa@catalysis.nsk.su

THOMAS TACKE, Evonik Degussa GmbH, Science to Business Center Bio, Paul-Baumann-Strasse 1, 45764 Marl, Germany  
e-mail: thomas.tacke@evonik.com

WENDONG WANG, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, Anhui, China  
e-mail: wangwd@ustc.edu.cn

DORIT WOLF, Evonik Degussa GmbH, Business Line Catalysts, Rodenbacher Chaussee 4, 63457 Hanau-Wolfgang, Germany  
e-mail: dorit.wolf@evonik.com

ZHONGHUA (JOHN) ZHU, Division of Chemical Engineering, School of Engineering, University of Queensland, Brisbane 4072, Australia  
e-mail: z.zhu@uq.edu.au



# Preface

Carbon is a versatile and fascinating material that can be used in a number of technological processes, including high-tech processes. This is due largely to the ability of carbon atoms to bond with each other in various ways to form linear, planar, and tetrahedral bonding arrangements, thus producing materials with a large range of properties. Physicochemical characteristics such as electrical conductivity, surface area and porosity, and surface chemistry may be tuned for specific applications.

Carbon materials such as activated carbons, carbon blacks, graphite, and graphitic materials have been used for decades in heterogeneous catalysis, as either catalysts or catalyst supports. Activated carbon catalysts are used in the synthesis of phosgene from carbon monoxide and chlorine, in the synthesis of thionyl chloride from sulfur dioxide and chlorine, and in the oxidation of *N*-phosphonomethyliminodiacetic acid to produce a biodegradable herbicide, Glyphosate. Activated carbons impregnated with ZnO, CuO, or Fe<sub>2</sub>O<sub>3</sub> are designed specifically for the desulfurization of natural gas. The Merox process developed by Universal Oil Products to remove mercaptan sulfur from petroleum fractions involves a catalyst consisting of cobalt phthalocyaninedisulfonate impregnated onto a suitable high-surface-area activated carbon. Furthermore, because of their high thermal stability in reducing atmospheres and their ability to facilitate the preparation of well-dispersed metal particles on surfaces that do not exhibit acid–base properties, carbon materials are used to support precious metals for hydrogenation reactions in the fine-chemicals industry. The recovery and recycling of metals, particularly of noble metals, is simplified with carbons, as these supports can be burned off. These materials offer unparalleled flexibility in tailoring catalyst properties to specific needs.

Compared to the predominant applications of these carbon materials as adsorbents for drinking water, wastewater, and gas purification, as fillers in rubber production, or as refractory materials, however, their use in the catalyst market represents only a moderate share. The potential growth of the market for carbons in catalysis depends on (1) better understanding of the chemistry of carbon surfaces and fine tuning of the microstructure of these materials, which could then be exploited in the design of truly unique catalysts; and (2) improvements in quality control and production methods, to supply constant-quality materials (synthetic carbons). There are additional opportunities to increase the market value of carbon materials in the near future, due to the rapidly advancing development of fuel cells, the use of novel carbon materials, the increasing need for catalytic

materials in very selective reactions, and the identification of some high-volume applications.

Patents appear continuously to meet industrial needs, and the growth of scientific publications dealing with the use of carbon materials in catalysis is exponential. However, the last major review of this field was published over a decade ago (L.R. Radovic and F. Rodríguez-Reinoso, in P.A. Thrower, Ed., *Chemistry and Physics of Carbon*, Vol. 25, Marcel Dekker, New York, 1997, p. 243). In the meantime, new materials, such as carbon nanotubes, nanofibers, aerogels, and xerogels, have become widely available, and our knowledge of the surface chemistry of carbon materials has improved substantially. We are now able to modify in a controlled manner the nature and concentration of functional groups on the surface of carbon materials, which can serve as active sites in catalysis or as anchoring centers for active phases or their precursors. High-performance nanostructured catalysts can thus be prepared. Moreover, analytical tools have been developed for the identification and quantification of surface groups, paving the way for the proper interpretation of kinetic data and providing for useful correlations of catalytic activity. There is clearly a need to establish the state of the art in order to identify the required areas of research, to stimulate more systematic approaches, and to promote further technological developments in the field—and that is the purpose of this book.

The material is organized into 15 chapters written by recognized experts in their fields. It has been decided to cover in depth new and hot topics as well as those that have not yet been the subject of extensive reviews. In the first three chapters the properties of carbon materials relevant to catalysis are discussed, with a special emphasis given to the description of carbon surface features, in particular to surface functional groups and their characterization methods, and to the theoretical investigation of molecular interactions on carbon surfaces. This provides a fundamental background for an understanding of the material covered in subsequent chapters.

The next two chapters provide a comprehensive review of carbon-supported metal catalysts and their preparation methods. The most important applications are discussed, special attention being given to the most innovative.

Chapter 6 provides an extensive review of the uses of carbon as a catalyst, with particular emphasis being placed on cases in which active sites have been properly identified and activity correlations established. The special case of nitrogen-doped carbons and their catalytic activity in oxidation reactions is discussed in Chapter 7, and Chapter 8 covers the heterogenization of homogeneous catalysts by anchoring transition-metal complexes onto the surface of suitable carbon materials.

Two important classes of new carbon materials, carbon nanotubes/nanofibers and carbon aerogels/xerogels/cryogels are reviewed and discussed in the next two chapters. These materials exhibit interesting properties that can be exploited in many applications, particularly in catalysis.

Chapter 11 provides a short review of carbon-based monoliths, their preparation, and applications in various liquid-phase processes, including bioconversions.

Chapters 12 and 13 cover two of the most important novel catalytic applications of carbon materials, electrocatalysis and photocatalysis. In the first case, carbons are used mostly as supports for metal catalysts in fuel cells, while the synergistic effects of carbon-based composite semiconductor materials, such as C-TiO<sub>2</sub>, make them particularly effective in photocatalytic degradation reactions.

Chapter 14 addresses the special topic of sensors, in which advantage is taken of the unique properties of nanostructured carbon materials such as nanotubes and fullerenes. Finally, applications of carbon-supported precious metal catalysts are reviewed from an industrial perspective in Chapter 15.

Since this is a multiauthored book, significant differences in style from chapter to chapter are inevitable, but we have tried to avoid overlaps as much as possible. We thank all the authors for their efforts to meet the deadlines and to follow the format defined for the book. We would also like to acknowledge the assistance of Anita Lekhwani at Wiley, whose advice has been most helpful at the various stages of preparation of the manuscript. Finally, we hope that the book will be useful to fellow scientists and practitioners and will stimulate further research and discussion on the development of carbon materials for catalysis.

*Toulouse*

*Porto*

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PHILIPPE SERP

JOSÉ LUÍS FIGUEIREDO





# 1 Physicochemical Properties of Carbon Materials: A Brief Overview

LJUBISA R. RADOVIC

## 1.1 INTRODUCTION

To justify the title and the contents of this brief introductory review, it is appropriate to recall the words of Nernst, written more than a century ago (1893) in the Preface to the first edition of his *Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics* (<http://books.google.com>): “[T]he development of physical chemistry as a special branch of natural science means—and I would lay particular emphasis on this—not so much the shaping of a new science, but rather the co-operation of two sciences which hitherto have been, on the whole, quite independent of each other.”

Catalytic applications of carbon materials are as old as the discipline of physical chemistry, and probably even older. Over the past century or so, the level of fundamental understanding of these technological applications and this discipline has increased tremendously, of course. Yet, despite (or because?) of this progress, there is a pervasive problem in carbon science and technology: It is an eminently interdisciplinary field, and the danger that “the left hand doesn’t know what the right hand is doing” is considerable. In principle and increasingly in practice, as Nernst himself had anticipated, this problem has also plagued physical chemistry but it has been overcome; it took almost a century for Dirac’s prophecy to be realized, but it has been done. With the discovery of quantum mechanics, chemistry has been essentially reduced to physics. Dirac proclaimed that “the underlying physical laws necessary for the mathematical theory of a large part of physics and the whole of chemistry are thus completely known” [1]. So in the second century of existence of physical chemistry as a discipline, the key question is whether carbon chemists really understand what the carbon physicists are arguing, and vice versa. Here I explore some answers to this question, those that are considered

to be of greatest relevance to catalytic applications of carbon materials. Knowing that, despite the wonderful opportunities offered by electronic storage and retrieval of information, researchers today continue to struggle to keep up with the literature in their own (increasingly narrow?) field, it is anticipated that the path outlined by Dirac continues to be a difficult one. Yet the obvious rewards to those who succeed in integrating carbon physics and carbon chemistry should be a powerful enough incentive. Much of the evidence of progress in this endeavor, or lack thereof, has accumulated in the 30 volumes [2] of the book series *Chemistry and Physics of Carbon* inaugurated by Philip Walker almost half a century ago, when carbon science was in its infancy. It is true that “the study of carbon has grown to become a specialism” [3] but, as argued below, it is inappropriate to obscure it unduly [3] as not only “a combination of physics and chemistry” but also of “fluid dynamics and chemical engineering, with dashes of astrophysics and geology” [3]. From a historical perspective, the development of carbon science and technology provides several ironic and exemplary twists of fate for chemists and physicists. The most fascinating one is related to the discovery of C<sub>60</sub>, buckminsterfullerene. Its chemical identification [4] was brought about by the pursuit of an astrophysical issue (the nature of interstellar dust), whereas researchers in a physics department [5] were the first to achieve its chemical separation.

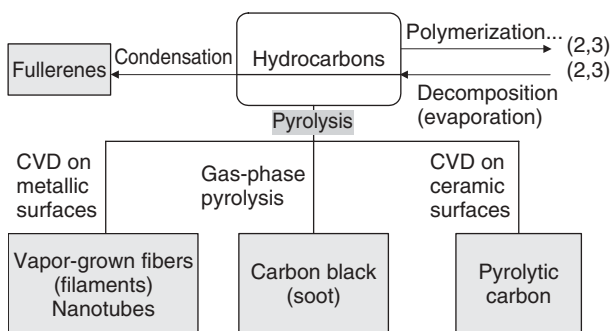
Catalytic behavior of carbon materials depends on their surface properties, but surface properties are to a large extent a consequence of bulk properties. Therefore, after a brief overview of the ways that carbon materials are formed, I discuss their bulk properties briefly before focusing on their physical and chemical surface properties and their chemical (re)activity.

## 1.2 FORMATION OF CARBONS

All carbon materials, including those used for catalytic applications, are formed in either the gas, liquid, or solid phase; and these conditions to a large extent dictate the variabilities possible in their physicochemical properties. The range of hydrocarbon feedstocks used as carbon precursors is also dictated by these conditions; and seemingly subtle changes often produce profound structural effects. These are discussed briefly below.

### 1.2.1 Gas Phase

Figure 1.1 summarizes the very wide range of carbon products that can be produced in gas-phase reactions under perhaps surprisingly similar conditions from a very wide variety of carbon-containing gases (e.g., CO, CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>6</sub>, natural gas, volatile products of coal or biomass pyrolysis). The relatively disordered (but not amorphous), nongraphitic and nongraphitizable carbon black or soot particles result because nucleation of the carbon precursors occurs during pyrolysis in the gas phase. The much more ordered (quasicrystalline)

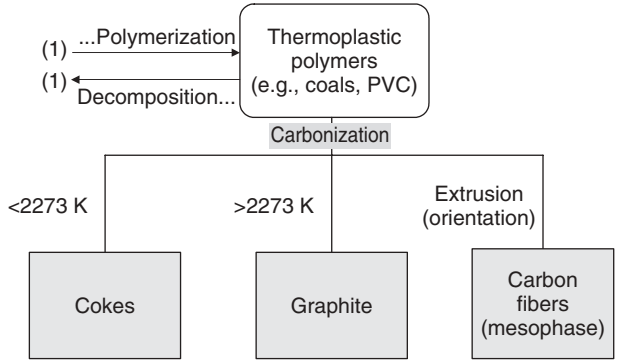


**Figure 1.1** Summary of the processes of carbon formation in the gas phase and the resulting carbon macrostructures. (Hydrocarbon polymerization or decomposition can lead to interconversion of gaseous, liquid, or solid carbon precursors; see also Figures 1.2 and 1.3.)

nongraphitic but graphitizable pyrolytic carbon is obtained by virtue of chemical vapor deposition (CVD) of carbon precursors on a relatively inert (e.g., ceramic) substrate; the structure of crystalline graphite (in pyrolytic graphite) is achieved upon simple heat treatment above about 2773 K. On a more reactive metallic surface (most notably, Fe, Co, or Ni), the deposition of carbon precursors typically results in carbon dissolution, intra- and/or suprametal diffusion, and precipitation in the form of nanotubes or filaments (fibers). The novel aspect of this process is the emergence of curvature of  $sp^2$  bonds in the growing graphene layers; its origin remains a debatable and arguably unresolved issue. Whether it is analogous to the curvature induced by formation and entrapment of pentagons and/or heptagons, phenomena responsible for the formation of fullerenes upon condensation of gas(eous fragments), or to some other effect, including the role of the crystallography or morphology of the metal substrate, remains to be verified.

### 1.2.2 Liquid Phase

Figure 1.2 summarizes the variety of carbon products obtained in liquid-phase reactions using thermoplastic polymers, either the natural (such as bituminous coals) or synthetic ones [such as poly(vinyl chloride),  $-\text{CH}_2\text{Cl}_2-n$ ]. At the most commonly utilized carbonization conditions, typically above 2273 K in a largely nonreactive medium, the degree of alignment and the mobility of emerging, growing, and coalescing carbon crystallites is considerable, but the consequent relative orientations of the resulting graphene layers are insufficient to achieve the perfect crystalline structure of graphite, and these materials are the nongraphitic but graphitizable cokes. However, their further exposure to higher temperature, typically in excess of 2773 K, results readily in the formation of (synthetic) graphite. If during the carbonization process the intermediate molten phase is

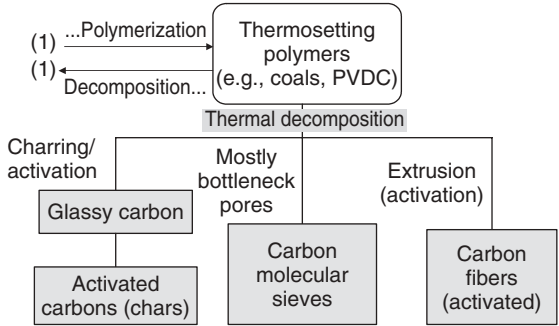


**Figure 1.2** Summary of the processes of carbon formation in the liquid phase and the resulting carbon macrostructures.

subjected to extrusion and orientation, highly graphitizable carbon fibers (e.g., from mesophase pitch) can be obtained.

### 1.2.3 Solid Phase

Figure 1.3 summarizes the carbon formation processes taking place in the solid phase, with thermosetting carbon precursors such as low-rank coals, preoxidized bituminous coals, and wood, or thermosetting polymers such as poly(vinylidene chloride) (PVDC),  $-\text{CHCl}_2-$ . (Note how very sensitive the carbonization process is to structural details of the carbon precursor: The absence of one hydrogen atom in the monomer precludes the formation of a molten phase during thermal decomposition of PVDC.) Because there is no plastic phase during the devolatilization process, there is extensive development of porosity in chars,



**Figure 1.3** Summary of the processes of carbon formation in the solid phase and the resulting carbon macrostructures.

and this can be tailored further by selective gasification to produce activated carbons or molecular sieves, from either carbonized granules or powders or fibers. If the heat-treatment temperature is high, the product remains nongraphitic and nongraphitizable, but it acquires a shiny appearance and its pores become very narrow and essentially impervious to most gases and liquids: It is glassy or glasslike (vitreous) [6] and possesses a low surface area, although its low density (e.g.,  $1.5 \text{ g/cm}^3$ ) reveals the presence of considerable closed porosity (even to helium at ambient temperature), which can be exposed and developed upon activation (selective gasification) at higher temperatures.

### 1.3 STRUCTURE AND PROPERTIES OF CARBONS

Both the bulk and the surface properties of carbon materials are dependent on their structure (i.e., on the spatial arrangement of carbon atoms). The structure is in turn dependent on the precursor used and the conditions of formation, as outlined in Section 1.2. Because of the prodigious variety of possible carbon atom arrangements within the seemingly restrictive constraint of  $\text{sp}^2$  hybridization characteristic of graphitelike carbons, it is useful to distinguish between the various levels of structure, and these are discussed in the following sections. The increasingly popular and often abused term *nanostructure* should be the easiest to define unambiguously, at a scale below 10 nm, although of course it is the most difficult one to verify experimentally. Conversely, the boundary between *macrostructure* and *microstructure* is much easier to ascertain experimentally, but it is less straightforward to define it precisely. The latter term is well recognized, especially for polycrystalline materials, although perhaps surprisingly it does not have an International Union of Pure and Applied Chemistry (IUPAC) definition (see [www.iupac.org/publications/compendium/index.html](http://www.iupac.org/publications/compendium/index.html)): for example, “the structure of a crystal on the scale on which deviations from perfect order become evident” [7] or “the structural features ... (e.g., grain and phase structure) that are subject to observation under a microscope” [8,9]. In practice, this sets the macro/micro boundary in a broad range of about 1 to 100  $\mu\text{m}$ .

In Table 1.1 we summarize the prodigious variety of bulk and surface properties of carbon materials, especially those of greatest relevance for catalytic behavior. Typical values or typical ranges are most often quoted rather than definite values, because these depend on too many factors to discuss here. Specific literature references are also not provided for this reason; not only handbooks [10,11] and the *Chemistry and Physics of Carbon* series [2] were consulted, but representative research or review papers as well as some commercial product brochures were examined.

#### 1.3.1 Macrostructure

The macrostructure level of carbon atom arrangement confers the most readily recognizable features on carbon materials, and it should not allow room for

Table 1.1 Typical Property Values of Principal Carbon Materials<sup>a</sup>

Property	Graphite	PC	CF	GLF	AC	CB	Cokes	Chars
True (He) density (g/cm <sup>3</sup> )	2.268	>2.0	<2.2	<2.0	<2.0	<2.0	<2.0	<2.0
Particle (Hg) density (g/cm <sup>3</sup> )	>2.0	>2.0	—	1.5	1.2–1.6	1.5–2.0	1.5–2.0	1.4–1.8
Packing (bulk) density (g/cm <sup>3</sup> )	>1.0	—	1.4–2.2	0.75	0.6–0.8	0.2–0.5	0.7–1.0	0.7–0.9
Spacing between two adjacent basal planes (nm) <sup>b</sup>	0.3354	0.34–0.36	0.34–0.36	>0.344	>0.344	0.35–0.36	0.34–0.36	>0.344
Crystallite height (nm)	>100	>10	>5	<10	<5	1.0–2.5	2.0–100	<5
Crystallite width (nm)	>100	>5	5.0–50	<10	<5	1.0–3.0	2.0–50	<5
Specific heat (kJ/kg/K)	0.8	—	—	—	—	—	—	—
Thermal conductivity (W/m/K)	—	—	—	5	—	0.02	—	10
Parallel to basal plane ( <i>ab</i> -direction)	400	190–390	8–1100	—	—	—	—	—
Perpendicular to basal plane ( <i>c</i> -direction)	<80	1.0–3.0	—	—	—	—	—	—
Electrical resistivity ( $\Omega \cdot \text{m} \times 10^6$ )	—	—	—	10–10 <sup>2</sup>	10 <sup>3</sup> –10 <sup>6</sup>	ca. 10 <sup>2</sup>	10–10 <sup>3</sup>	10 <sup>2</sup> –10 <sup>3</sup>
Parallel to basal plane ( <i>ab</i> -direction)	0.4	4.0–5.0	2.0–20	—	—	—	—	—
Perpendicular to basal plane ( <i>c</i> -direction)	>40	1000–3000	—	—	—	—	—	—
BET surface area (m <sup>2</sup> /g)	<10	<10	<10	<1	500–3000	20–2500	<500	<500

<sup>a</sup>PC, pyrolytic carbon; CF, carbon fibers; GLF, glasslike fibers; AC, activated carbon (including fibers or cloth); CB, carbon blacks.<sup>b</sup>Carbons with spacing greater than 0.344 nm are turbostratic.

Note: If no values are provided, the variability is considered too wide for a meaningful summary.