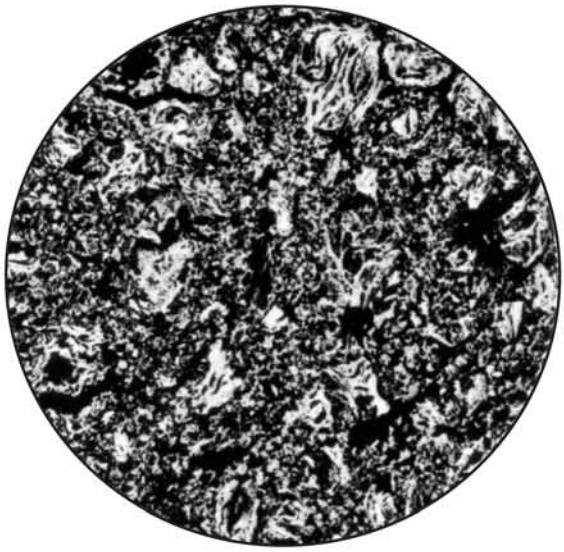

Chemistry and Physics of Carbon

Edited by LJUBISA R. RADOVIC

Volume 30

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Preface

This anniversary volume contains four chapters on a wide range of chemical and physical aspects of carbon science and technology. With it, as with its 29 predecessors, we want to illustrate the breadth and depth of knowledge required from carbon researchers for mastery of their subject. In today's age of emphasis on teamwork and networking, there is no question that carbon research is the ultimate example of both *multi*disciplinarity and *inter*disciplinarity.

No one knows more about the physics *and* chemistry of activated carbon *surfaces* than Prof. Angel Linares and his collaborators in Alicante. Following up on their important review of microporosity and adsorption phenomena in Vol. 21, here we can learn from the most authoritative source about important details and some general trends in a specific (and rather remarkable!) example of careful preparation and thorough characterization of activated carbons. No one knows more about the physics *and* chemistry of carbon *materials* than Prof. Michio Inagaki, and we are privileged to include in this volume another valuable contribution from his research group. Clean-up of oil spills is a fascinating, demanding and, alas, an increasingly important application of porous carbon materials. The authors inject an insight into the fundamentals of heavy oil sorption while attempting to resolve an eminently practical problem using carbons ranging from graphite to charcoal.

The remaining contributions are from relative 'newcomers' in carbon research, who have nevertheless taken head on the ambitious task of summarizing the state of the art of an old and a new issue in carbon (nano)science and (nano)engineering. Dr. Burg and Prof. Cagniant present their view, and an update, regarding the methodology of characterizing carbon surfaces, a topic that has been reviewed in Vol. 8 and more recently in Vols. 24, 25 and 27; they emphasize that a thorough and reliable knowledge of the essential details of these chameleonic surfaces requires the use of a battery of complementary techniques. Dr. Zhao and his collaborators discuss the fascinating (and still evolving!) field of molecular-level design of the porosity and pore size distribution of carbons using template-based synthesis; they illustrate the fact that opportunities for developing tailor-made carbon materials for wide-ranging applications – in adsorption, catalysis, electricity storage and medicine – are today more exciting than ever.

Our previous 29 volumes were published over the past four decades by Marcel Dekker. We hope that the next four decades with our new publisher, Taylor & Francis (CRC Press), will be an equally fruitful, pleasant and rewarding experience.

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*Preparation and Reactions, Porosity and Performance**

A. Linares-Solano, D. Lozano-Castelló, M. A. Lillo-Ródenas, and D. Cazorla-Amorós

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* This chapter is based on a plenary lecture presented at "Carbon2004," Brown University.

I. INTRODUCTION

Activated carbon (AC) is the collective name for a group of porous materials, consisting mostly of carbon, that exhibit appreciable apparent surface area and micropore volume (MPV) [1–4]. They are solids with a wide variety of pore size distributions (PSDs) and micropore size distributions (MPSDs), which can be prepared in different forms, such as powders, granules, pellets, fibers, cloths, and others. Owing to these features and their special chemical characteristics, they can be used for very different applications, for example, liquid- and gas-phase treatments and energy storage [1–7]. Considering the variety of fields in which AC is being used, it is extremely important to develop a suitable characterization for it. This will enable determination of the effect that its porous structure has on a given application, which will permit control and performance optimization, which in turn will facilitate the discovery of new applications. For this purpose, the three steps depicted in Figure 1.1 are needed. This figure emphasizes that characterization is one of the three essential steps that should not be omitted to optimize both the preparation of ACs and their applications.

In regard to the characterization of porous carbons, it should be pointed out, for a better understanding of the results presented in this chapter and of their importance, that all our ACs have been thoroughly characterized. Always, both N_2 at 77 K and CO_2 at 273 K adsorption isotherms have been determined for each sample studied. The combined use of both adsorptives improves their characterization considerably [8–13], allowing conclusions to be drawn that would not be possible without adsorption of CO_2 at 273 K. Nevertheless, for those readers interested in characterization of porous carbons, there is an extensive literature available, and the following general books, and their corresponding references, are recommended [14–17].

The development of ACs with tailored porosity is necessary to improve their performance in classical applications and to prepare better adsorbents to satisfy new and emerging applications [4–7,17,18]. The preparation of such ACs can be carried out by two different methods: the so-called physical and chemical activations [1,19–28]. The differences between them lie mainly in the procedure and the activating agents used.

Physical activation has traditionally included a controlled gasification of the carbonaceous material that has previously been carbonized, although occasionally the activation of the precursor can be done directly. Many different carbonaceous precursors have been employed for physical activation: lignocellulosic materials, coals, woods, and materials of polymeric origin. The samples are typically treated to 800–1100°C with an oxidant gas, mainly CO_2 or steam, so that carbon atoms are removed selectively. Although this process obviously involves a chemical reaction (and is not merely a physical process), it is known as *physical activation*.

Careful control of the carbon atom removal process by gasification in CO_2 or steam, usually termed *burn-off (BO) degree*, allows selection of the adsorption characteristics of an AC. Thus, highly activated carbons can be prepared

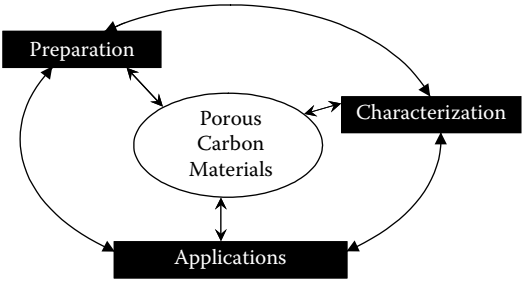

FIGURE 1.1 Relationship between the preparation, characterization, and applications of porous carbon materials that should always hold.

by physical activation, reaching high BO degrees. However, high BO degree is directly related not only to the development of the micropore volume, but also to the widening of porosity. Therefore, an AC with high adsorption capacity and narrow MPSD cannot be prepared by this process. This is one of the main disadvantages of physical activation: narrow MPSDs are needed for some applications (e.g., methane or hydrogen storage). The chemical activation process consists of contacting a carbonaceous precursor with a chemical activating agent, followed by a heat treatment stage, and finally by a washing step to remove the chemical agent and the inorganic reaction products [1,3,6]. In the literature, the use of several activating agents, such as phosphoric acid [29–32], zinc chloride [19,20,33–35], alkaline carbonates [36,37], KOH [23,38–43], and more recently NaOH [23,35,39,43,44], has been reported. In the case of chemical activation, we prefer not to use the term *BO degree*, as for physical activation; we prefer to talk about the *extent carbon reacted* (or *degree of activation*).

Chemical activation offers well-known advantages [3,19,21,42,43] over physical activation, which can be summarized as follows: (1) it uses lower temperatures and heat treatment times, (2) it usually consists of one stage, and (3) the carbon yields obtained are typically higher. On the other hand, chemical activation has some disadvantages [3,6,21,42,43], such as the need for a washing stage after heat treatment and the more corrosive behavior of the chemical agents used in comparison with CO_2 or steam. Traditionally, chemical activation has been carried out using one of two activating agents: phosphoric acid or zinc chloride.

In the case of chemical activation with phosphoric acid, lignocellulosic materials are preferred as precursors [6,30,45]. At low degrees of activation, the ACs do not have a highly developed area and they are essentially microporous, whereas at higher activation degrees, the surface area and the MPV increase, but there is also a remarkable increase in the mesopore volume and a widening of the MPSD [46,47]. Therefore, as with physical activation, in the case of activation with phosphoric acid both high adsorption capacity and narrow MPSD cannot be achieved. However, for ACs that need a well-developed mesoporosity, for example, for gasoline removal [5], phosphoric acid activation is a very suitable activation method [45].