

Chemistry and Physics of Carbon

Edited by LJUBISA R. RADOVIC

Volume 30



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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 *multidisciplinarity* and *interdisciplinarity*.

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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University Park, PA, and Concepción, Chile, September 2007

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1 Carbon Activation by Alkaline Hydroxides *Preparation and Reactions, Porosity and Performance**

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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

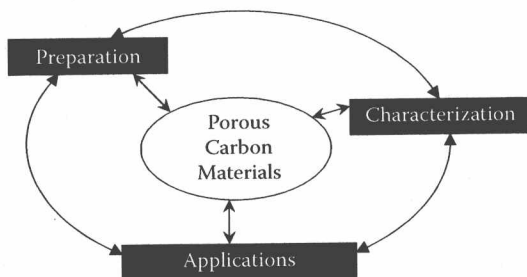


FIGURE 1.1 Relationship between the preparation, characterization, and applications of porous carbon materials that should always hold.

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 CO₂ 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].

The ACs prepared by chemical activation with ZnCl_2 are essentially microporous [19,20,33]. The loading of zinc has an important effect on porosity: samples activated at high loadings exhibit high porosity development and MPV, but also a more heterogeneous MPSD [33]. Although higher micropore volumes can be obtained by ZnCl_2 activation than by physical activation or by phosphoric acid activation, the increase in porosity development is also accompanied by a widening of the microporosity. The main disadvantage of this activating agent is that the emission of metallic zinc may cause serious environmental problems, which strongly limits its present use.

In summary, as is the case with physical activation, highly activated carbons with narrow MPSDs can hardly be prepared by chemical activation with either phosphoric acid or zinc chloride. Therefore, they can neither satisfy the demand for improving some AC applications nor for finding new ones, as high-pressure gas storage (e.g., CO_2 , H_2 , natural gas) requires both high MPV and narrow MPSD.

The purpose of developing ACs with tailored porosity in the whole range of microporosity has motivated continued research toward the use of other activating agents, such as alkaline hydroxides. After the pioneering patent of Wennerberg and O'Grady [48], the production of very-high-surface-area (superactive) ACs using alkaline hydroxide activation began on a commercial basis, first by Amoco and then by Kansai Coke and Chemical Company (Japan) [41,48]. In addition, a considerable number of studies have been carried out over the years that focus on chemical activation with hydroxides [20,21,23,35,38–45,48–97].

An example of the great attention that alkaline hydroxides have attracted recently can be seen in Figure 1.2, which divides the papers published in the journal *Carbon* in 2004 according to their AC preparation methods.

In this large number of papers, we can see that most of the variables affecting the activation process have been analyzed, especially the precursor, the hydroxide/carbon ratio, and the reaction temperature. From a cursory analysis of all these papers, it can be concluded that carbon activation by alkaline hydroxides is a promising process. However, very often a comparison between the results obtained by different authors is difficult and almost impossible to make, because of the different variables used (e.g., the activation process of a given lignocellulosic precursor is very different from that of its corresponding char). Therefore, general conclusions about this interesting activation process have not been compiled and are missing from the otherwise abundant literature.

During the last 15 years our group has been researching carbon activation by alkaline hydroxides, analyzing its different aspects. Thus, we have compared both NaOH and KOH with other chemical agents [23], we have analyzed several variables of this activation process [21,23,42,43,70–72,77,88,98], we have studied the reactions taking place [99–101], we have worked on their porosity characterization [12,13,70,102–106], and, finally, we have studied these ACs in several applications [71,107–114]. From all these studies, which cover most of the aspects of carbon activation by alkaline hydroxides, we have been able to identify additional advantages to those mentioned earlier: (1) the precursor ash content has no

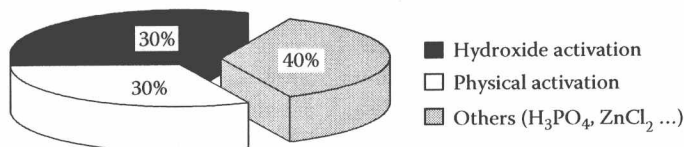


FIGURE 1.2 Distribution of the number of papers published in the year 2004 in the journal *Carbon* related to preparation of activated carbons by different methods.

effect on the activation, which is especially interesting in the case of coals; (2) the resulting ACs have low ash content (usually less than 1–2 wt% even with simple water washing); (3) the activation process is highly reproducible; (4) the control of experimental variables allows production of highly microporous ACs; and (5) precursors such as nanotubes that cannot be activated by physical activation can be activated with hydroxides [115].

Considering the increasing interest in the use of alkaline hydroxides as activating agents and the large number of published papers, the present review is timely because it provides an update on the most important aspects of this activation process. As our studies of carbon activation by alkaline hydroxides do not significantly differ from most of those available in the literature, the results obtained over the last 15 years will be used as the main source for review of this interesting process. The advantage of using our own results is that much better comparisons can be made, and the main objective of the chapter can be fulfilled more readily: to analyze and summarize the fundamentals of carbon activation by alkaline hydroxides (variables, reactions, types of porosity produced, and applications). The general concepts discussed are thought to be useful tools that will help the reader understand previously published results, even if they were obtained using different experimental conditions.

To achieve the general objective of this chapter, the following aspects of activation by sodium and potassium hydroxides will be analyzed:

1. Variables of the alkaline hydroxide activation method and suitability of the process
2. Singular characteristics of the AC prepared by alkaline hydroxide activation that can have both high MPV and narrow MPSD
3. Main reactions occurring during activation by hydroxides
4. Importance of controlling MPV and MPSD to improve performance applications of these ACs

To limit the length of the chapter, the discussion of these issues will be restricted to carbon materials (any type, independent of their origin, e.g., coals, chars, nanotubes). Hence, other carbonaceous materials (such as polyaromatic hydrocarbons, resins, polymers, lignocellulosic materials, pitches) that can also be activated when heated in the presence of hydroxides will not be considered.