Advances in Sol-Gel Derived Materials and Technologies
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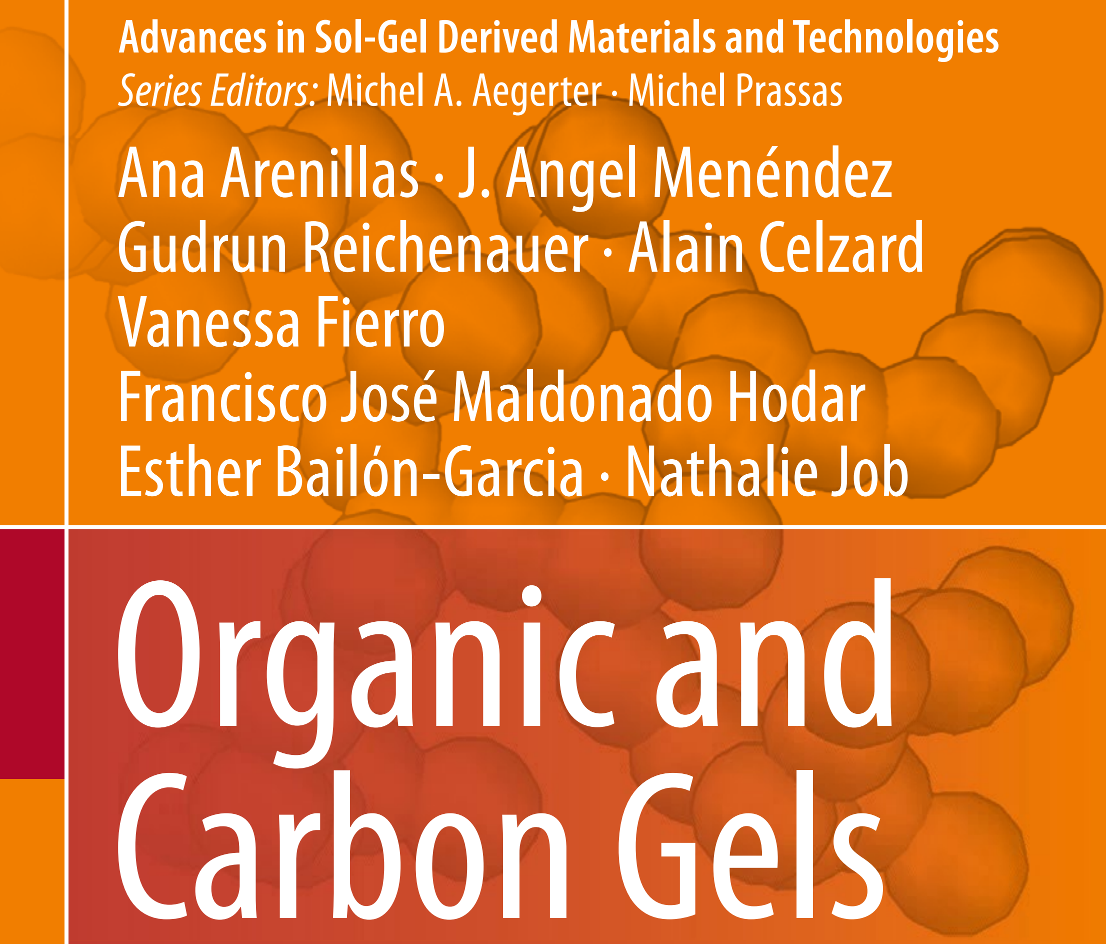

Organic and Carbon Gels

From Laboratory Synthesis to Applications

INTERNATIONAL SOL-GEL SOCIETY
ISGS
materials through chemistry

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Advances in Sol-Gel Derived Materials and Technologies

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Michel A. Aegerter
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The International Sol-Gel Society (ISGS)

Dear Readers,

The International Sol-Gel Society (ISGS) was established in 2003 as an international, interdisciplinary, not-for-profit organization whose primary purpose and objective is to promote the advancement of sol-gel science and technology. ISGS's aims are both to represent the particular needs and aspirations of the international sol-gel community and to support this sol-gel community. The society's mission is threefold:

- To coordinate the promotion of sol-gel science and technology in the scientific and industrial community
- To foster communication between researchers from different fields and geographical regions through the organization of conferences and the publication and circulation of technical papers
- To encourage education, training, and research in the field of sol-gel science and technology

To achieve these purposes, ISGS convenes the biannual International Sol-Gel Conference in many parts of the world. The 19th edition of this International Conference was held in Liège, Belgium, from 3 to 8 September 2017. These conferences play an important role in the education, federation, and dissemination of scientific knowledge to people working in related fields. To initiate young researchers and engineers into the sol-gel field, an introductory short course was planned and organized by the local organizers of the conference. The topic of the short course was "carbon gels," an important and emerging area in both scientific and industrial fields. This book is a summary of the lectures given in the course and thus enables readers to learn the fundamentals and applications of "carbon gels".

I wish you very pleasant and educative reading!

Masahide Takahashi
President of the International Sol-Gel Society
http://www.isgs.org

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Foreword

Sol-gel science and technology is now firmly established as a rich interdisciplinary domain, in which approaches for preparing materials that span the range from purely inorganic systems to hybrids with properties suitable for a breathtaking array of applications are now well established. Historically, sol-gel processing was shaped by a combination of physics and chemistry, taking advantage of "Chimie Douce" processes and complementary characterization tools, to prepare (mainly) metallic oxides at low temperatures. This pioneering work has been extended significantly during the past few decades, with organic moieties and biologically active species being incorporated within sol-gel-derived systems through control at the molecular level. These developments have led to an explosion in the availability of new hybrid materials with novel properties which are being exploited across a wide variety of application fields.

In parallel with developments in traditional sol-gel science and technology, purely organic (or carbon) gels have also been intensively developed to obtain versatile materials which are applied in many areas, including supported catalysis, separation science, and environmental remediation. When dried under appropriate conditions, such gels are chemically inert and stable and exhibit excellent thermal insulation characteristics. They can be transformed into highly porous and low-density aerogels, which exhibit good mechanical strength and high flexibility. Carbon gels are easily obtained from organic precursors (e.g., formed by resorcinol-formaldehyde) pyrolyzed under inert atmosphere. They also exhibit good electrochemical conductivity and are being used as capacitors and supercapacitors, as well as efficient solar energy collectors.

It is evident that there is now an opportunity to take advantage of the relative maturity and expertise within the carbon gel and the "classical" sol-gel communities to exploit synergies that might lead to the potential development of new hybrid materials. This book, which is entitled *Organic and Carbon Gels: From Laboratory Synthesis to Applications*, is intended to serve as a bridge between these two communities, to stimulate new ideas and collaborations leading to new classes of high-performance materials and new application domains that could not otherwise be envisaged. We hope that the dissemination of such knowledge will stimulate interest in contributing to the rich palette of opportunities that exist at the (largely unexplored) interface between these two cognate domains.

Michel Wong Chi Man
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Preface

Sol-Gel 2017, the 19th International Sol-Gel Conference, was organized from September 3rd to 8th in Liège, Belgium.

The great success of the Sol-Gel Conference series over the past 35 years attests that sol-gel science and technology is an extraordinarily multidisciplinary research area. However, while these Sol-Gel conferences have succeeded in connecting many actors of the sol-gel technology in the fields of inorganic chemistry and materials, the carbon gel community is usually not so well represented. In order to try to bridge the gap between the inorganic gels and the carbon gel research fields, it was decided to organize a 1-day workshop devoted to carbon gels as an introduction to the conference.

We are very pleased to present this book, which gathers chapters presenting carbon gels from the points of view of the five lecturers of the workshop, each being a renowned specialist in a specific field related to those materials.

On the one hand, carbon gels represent a promising class of materials in high added value applications using carbon materials. They present many assets, like the possibility to accurately tailor their structure, porosity, and surface composition as well as to easily dope them with numerous species. The ability to obtain them in custom shapes, such as powder, beads, monoliths, or impregnated scaffolds, opens the way toward numerous applications: catalysis, adsorption, electrochemical energy storage, etc. On the other hand, the feasibility of design synthesis and manufacturing processes from an economic and environmental perspective remains a crucial question.

The present book covers most of these aspects. Chapter 1 deals with the scale-up of the synthesis of classical carbon gels in order to transfer the technology from lab to industry. Chapter 2 presents variations of the synthesis procedure in order to move from fossil resources to renewable carbon precursors while preserving carbon gel's exceptional properties. In Chap. 3, the characterization of these materials is debated: indeed, applying characterization techniques to these materials is not always straightforward, and the reader will be made aware of the specific difficulties encountered with these materials. Finally, Chaps. 4 and 5 will provide an overview of the main applications of carbon gels in catalysis and electrochemistry.

Through the workshop and the present book, we hope to encourage new collaborations that bridge the gap between inorganic and organic sol-gel science. Let's bet that the present intense international research in the field will make it possible.

We wish you a rewarding lecture.

Nathalie Job, Vice-Chair

Benoît Heinrichs, Chair

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J. Angel Menéndez graduated from the University of Oviedo, Spain, where he received his M.Sc. in Chemistry and Ph.D. in Chemical Engineering in 1988 and 1994, respectively. He then worked as a research assistant at Penn State University, USA (1995–1996). In 1997, he joined INCAR-CSIC, Spain, where he currently works as a scientific researcher. His research activity is mainly focused on carbon materials and the use of microwave heating as applied to industrial processes. He leads various research projects in these fields. Díaz is author or coauthor of more than 200 scientific publications and 10 patents. He is founding editor of the *GEC Bulletin* and co-founder of SME Xerolutions Ltd. (http://www.xerolutions.com).

Gudrun Reichenauer obtained her Ph.D. in Physics at the University of Würzburg, Germany. She pursued her career as a research associate first at the Bavarian Center for Applied Energy Research (ZAE Bayern) and the Physics Department of the University of Würzburg (1993–1998) and then at Princeton University and Princeton Institute for the Science and Technology of Materials (NJ, USA, 1999–2000). Since 2000, she has led the Nanomaterials Group at ZAE Bayern. Her scientific interests lie in the identification of nanoeffects for use in energy-related fields, synthesis of well-scalable nanomaterials for applications in energy technology, and development of novel or adjusted methods for fast and artifact-free characterization of nanoporous materials.

Alain Celzard graduated with a degree in Chemical Physics in 1992 and received his Ph.D. in materials science in 1995 in Nancy, France. Since 2005, he has been a full-time professor at ENSTIB engineering school (Epinal). In 2010, he was appointed junior member of the Institut Universitaire de France. His scientific interests lie with disordered, porous, and related materials, ranging from composites and nanoporous adsorbents to macroporous solid foams through gels, with applications in catalysis, depollution, energy, and gas storage.

Vanessa Fierro graduated in Chemistry at the University of Zaragoza, Spain, and holds a doctorate degree in Sciences from the same university (1998). After working several years as a researcher in France (IFP Energies Nouvelles – Solaize and IRCE – Villeurbanne) and then in Spain (URV – Tarragona), she is now CNRS research director and head of the Bio-Sourced Materials research group at Jean Lamour Institute. Her present research deals with the preparation, characterization, and applications of porous solids. She is coauthor of more than 200 peer-reviewed papers.

Francisco José Maldonado Hodar obtained his Ph.D. in Chemistry with distinction from the University of Granada, Spain, in 1993, where he was a member of the group of research in Carbon Materials and received an Extraordinary Doctorate Award. In 2012, he returned to the university as a full professor in the Inorganic Chemistry Department. His primary research interest is in the areas of carbon materials and heterogeneous catalysis for the purpose of developing materials with fitted physicochemical properties to be used as adsorbents, molecular sieves, and heterogeneous catalysts in processes relating to environmental protection, clean energy, and fine chemistry. He is coauthor of more than 130 highly cited manuscripts (h=34), as well as book chapters and patents.

Esther Bailón-Garcia obtained her Ph.D. in Chemistry with distinction in the area of materials design for catalytic and photocatalytic applications from the University of Granada, Spain, in 2015. The quality of her work has been recognized through the awarding of the Young Researchers Award from the Spanish Carbon Group and the Extraordinary Doctorate Award from the University of Granada. After postdoctoral stays at the University of Trieste, Italy, and the Instituto Superior Técnico of Lisbon, Portugal, she earned a postdoctoral position (Juan de la Cierva fellow) at the University of Alicante, Spain, in the Department of Inorganic Chemistry, where she currently works on materials design for environmental and clean energy applications.

Nathalie Job received her Ph.D. in Chemical Engineering from the University of Liège, Belgium, in 2006. Her thesis work, dedicated to carbon gels for applications in heterogeneous catalysis, evolved toward carbon-supported electrocatalysts for fuel cells during her postdoctoral fellowship (F.R.S.-FNRS). Since 2014, she has held the position of associate professor in the Department of Chemical Engineering (NCE group) at the University of Liège. Her research now deals with electrochemical devices such as fuel cells, batteries, and supercapacitors from materials synthesis to the building of complete systems.

Chapter 1
Organic and Carbon Gels: From Laboratory to Industry?

Abstract Since the first report on organic gels based on the polycondensation of resorcinol with formaldehyde presented by Pekala in 1989, the number of publications, on both organic gels and carbon gels has experimented an enormous increase to the point where nowadays are published every year more than a hundred papers covering topics ranging from variations in the synthesis to the potential applications of this vast family of porous materials. This is due to the fact that, by controlling the synthesis conditions, it is possible to obtain materials with a suitable porosity for a specific application and even also with predetermined chemical properties, something that is practically impossible to achieve with any other porous materials. However, even after almost 30 years of continuous researching at laboratory scale, their industrial production and commercialization are still marginal compared with that of competitive materials. This chapter summarizes how the physicochemical properties of organic and carbon gels can be designed by controlling all the variables involved in the synthesis process. The chapter also addresses the most challenging problem of their mass production, i.e., scaling-up of production methods currently used in the labs.

Keywords Organic gel · Carbon gel · Gelation · Porous structure · Applications · Industrial production

1.1 Introduction

The continuous technological developments have led to an increase in efforts to find new materials with improved properties. Carbon materials have extraordinary and probably the most versatile properties due to the peculiar characteristics of the carbon element and the variety of carbon–carbon bonds [1]. However, carbon materials from natural sources have certain disadvantages such as the presence of impurities content, variability between batches, and the lack of control of their properties. Consequently attention has now shifted to synthetic carbon materials with a high purity, controllable chemistry, and the possibility they offer of being able to design

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their final properties. Nevertheless, the fact cannot be ignored that these synthetic carbon materials need to be obtained by means of as quick, as simple, and as a low cost process as possible, in order to reach the level of mass production and implementation. Of these synthetic carbon materials, polymers have attracted a lot of attention, and in particular carbon gels, which are highly porous materials, composed of primary particles that are interconnected to create a three-dimensional network structure.

1.1.1 What Are Organic and Carbon Gels?

On the basis of synthesis of inorganic silica gels, Pekala presented the first organic gel by applying sol-gel methodology in 1989 [2]. Stated in simple terms, the monomers, initially dissolved in a reaction media, initiate the polymerization reaction and a suspension of colloidal solid particles is formed (sol). These particles, also called clusters or nodules of polymeric material, tend to grow and interconnect to form an incipient polymeric network. As a consequence the liquid gradually densifies into a gel, until finally forming a polymeric and crosslinked solid structure. When the solvent, i.e., the reaction medium, is removed, the result is a solid organic polymer, called *organic gel*, formed by the sol-gel synthesis process. This material is not thermally stable, and a large amount of oxygen exists in its chemical composition. Therefore, it cannot be called a *carbon* material. Only after a heat treatment, where most of the heteroatoms are lost and the chemical composition of the material is based mainly on the carbon element, can it be called a *carbon gel*. Although both types of materials, organic and carbon gels, have very controlled chemistries and porosities, they exhibit very different chemical and physical properties. The organic gel has a large amount of carbon and oxygen in its composition and numerous oxygen surface functional groups. These materials are therefore characterized by a very low electrical and thermal conductivity, a highly hydrophilic character, and a low thermal stability. In contrast, carbon gels can display similar mesoporosity and have a high thermal stability. They are composed almost exclusively of highly condensed sp^2 carbon, which confers them a hydrophobic character and a much higher thermal and electrical conductivity than organic gels. From these descriptions of organic and carbon gels it follows that they are suited to different applications, as will be detailed below.

1.1.2 The Sometimes Misleading Nomenclature of the Gels

The chemical variables which control the polymerization reaction determine the final properties of the organic and carbon gels. However, the way the solvent is removed can also affect the porous properties due to surface tensions and may cause the polymeric structure to collapse. Traditionally, three types of drying method can

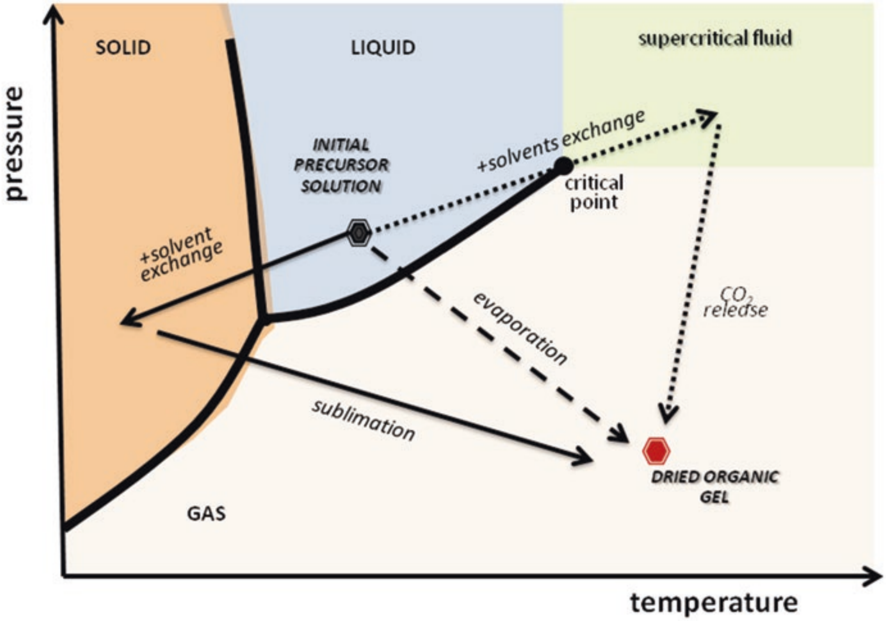

Fig. 1.1 The three most common pathways for removing the solvent

be found in the literature, supercritical drying, freeze-drying, and subcritical drying. The differences that distinguish them are the operating conditions (i.e., temperature and pressure) used to eliminate the solvent (see Fig. 1.1 for the use of water as the reaction medium).

The most common method to eliminate the solvent found in the scientific literature is supercritical drying [3]. CO_2 is exchanged for the solvent under supercritical conditions (i.e., high pressure and temperature), and then CO_2 is eliminated as a gas, thereby minimizing the surface tensions. When water is used as the solvent, the first solvent exchange must take place between the water and an organic solvent, due to the high solubility of CO_2 in water. In the case of cryogenic drying, the solvent is first frozen and then eliminated by sublimation; in this way the high liquid--vapor surface tension is also eliminated. If water is used as the reaction medium, it is also necessary to perform the solvent exchange before the freeze-drying, in order to avoid the formation of ice crystals inside the polymeric structure, which would lead to the uncontrolled formation of megalopores or voids. The third method for eliminating the solvent is by direct evaporation. In this case, there is a liquid--vapor interphase and therefore surface tensions occur with the subsequent collapse of the structure. However, we have demonstrated [4] that, under controlled operating conditions, the shrinkage of the gel structure can be minimized, and high porous materials with a controlled structure can be obtained. For this reason, subcritical drying is the most straightforward and consequently the most up-scalable alternative for producing gels on a large scale.

Traditionally, the organic and carbon gels obtained by different drying methods receive different names: aerogels, cryogels, and xerogels for the gels dried by supercritical, cryogenic, or evaporation procedures, respectively. However, according to IUPAC recommendations from 2007 for terms relating to the structure and processing of sols, gels, and networks [5], the term *aerogel* should be used to refer to any gel comprised of a microporous solid in which the dispersed phase is a gas, i.e., a porous gel, independently of the methodology used for its synthesis. *Xerogel* is defined as the network formed by the removal of all swelling agents from the gel, like the compact macromolecular structure of rubber. In their recommendations, there is no mention of the term *cryogel*. However, in the scientific literature, there is some confusion in the terminology when aerogel is used to refer to any dried gel with a porous structure [6] and to a gel dried under supercritical conditions, while xerogels are used to refer to gels dried by simple evaporation and also to a dense polymeric material with a low porosity [7].

Also misleading is the terminology regarding how the compound added to modify the pH of the precursor solution should be defined (see further Sect. 1.3). A lot of works in the literature refer this compound as *catalyst* [8], probably to reflect the notion that it is used to promote and accelerate the polymerization reaction. Strictly speaking however it is not a real catalyst, as it is not an independent compound in the reaction and it cannot be removed after the synthesis process. Other authors refer to these compounds as *boosters* [9], because of their augmentative effect on the kinetics of the polymerization reaction. However, many studies show that the modification of the pH of the reaction medium influences not only the speed of the reaction, but also the mechanism of the polymerization reactions (i.e., see Sect. 1.1.3 for mechanisms) [10]. Furthermore, these compounds cannot be recovered after the synthesis process and are incorporated into the polymeric structure. For this reason, many scientific works indicate that the nature of these compounds modifies the porous structure when they are incorporated, independently of the pH of the initial precursor solution [11–13]. Therefore, the proper way to refer to these compounds would be as *additives* that modify the polymerization reaction.

1.1.3 Advantages and Disadvantages of the Organic and Carbon Gels Compared with Other Porous Materials

Organic and carbon gels are synthetic materials with very controlled chemical composition and pore structures. The ability to design and tailor a material with a high degree of purity and with a pore-size distribution suited to a certain application confers to these materials a clear advantage versus active carbons and other porous carbon materials. The synthesis process is, however, sometimes complex, especially under supercritical or cryogenic conditions. Only in the case of controlled evaporation that requires mild operating conditions, does the scalability of synthesizing organic and carbon gels seem more feasible than that offered by synthetic materials based on templating techniques [14] or other multistep processes involving very expensive raw materials (i.e., MOFs) [15].

From the chemical point of view, organic and carbon gels are mainly composed of carbon, oxygen, and hydrogen, but they can incorporate any targeted heteroatom considered necessary for an additional application. The advantage afforded by these gels is that the heteroatom can be incorporated either after the synthesis process (i.e., incorporated onto the surface of the gel structure) like any other carbon material, but also during the synthesis process by adding the heteroatom to the reaction medium, which causes the heteroatom to be incorporated directly into the gel structure itself.

However, the main advantage of the gels is that their pore-size distribution may be designed by modifying the chemical variables involved during the synthesis process. They have a polymeric structure in which the monomers tend to react and form interconnected clusters or nodules of a certain size. The mesopores (i.e., pores between 2 and 50 nm) and macropores (i.e., pores wider than 50 nm) are formed by the space between the nodules of the polymer, whereas the microporosity (i.e., pores with a size of <2 nm) are located inside the nodules. The micropores that are formed by the release of volatiles and are therefore present mainly in carbon gels have a structure which is very similar to that of active carbons in their tortuosity and the shape of the open pores. In order to establish the size or width of these micropores, some models in the bibliography assume that they have a cylindrical or slit shape [16]. In any case, they are irregular and have a certain tortuosity that makes it difficult to gain access to all of the microporosity. However, in the meso and macroporosity of the organic and carbon gels, the porous network is regular and very open miming the spaces between aggregated spheres. This porous network is characteristic of the carbon gels, because other carbon materials show the same tortuosity in their meso/macroporosity as in their microporosity. This characteristic confers a hierarchical porous structure on these organic and carbon gels, with a very open porous structure easily accessible even to the narrowest pores. Moreover, this peculiarity of organic and carbon gels gives a positive curvature to the porosity that may

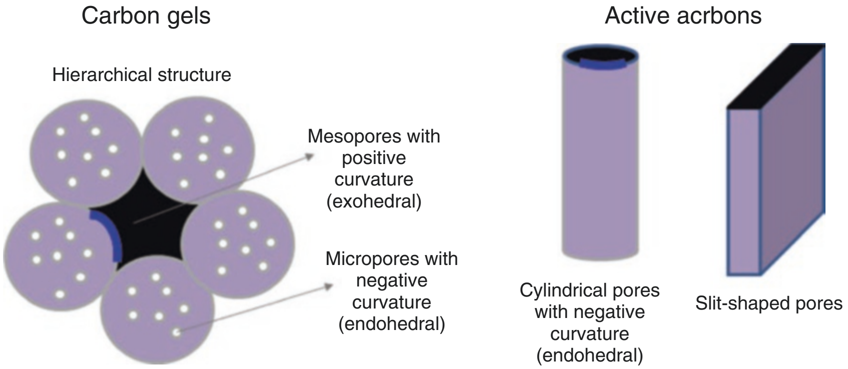

Fig. 1.2 Differences between the porosities of carbon gels and active carbons

favor the surface interaction with other molecules in the medium in certain electrochemical applications such as those of electrode–electrolyte [17, 18]. Figure 1.2 schematizes this peculiarity of the porous structure of these gels.

1.2 The Synthesis Process of the Organic Gels

The synthesis of organic gels starts with the preparation of the precursor solution which consists in mixing a hydroxylated benzene, an aldehyde, the solvent, and eventually a fourth compound in order to modify the pH of the initial mixture [19]. A number of precursors can be used for the synthesis of the organic gel: phenol [20, 21], cresol [22, 23], cellulose [24], or tannins [25, 26] have been used as the hydroxylated benzene, although resorcinol is the most commonly used for the synthesis of organic gels [2, 19, 27–29]. Formaldehyde is the most widely employed as aldehyde [30], but the use of furfural [31] or hexamethyletetramine [32] has also been reported in the bibliography. The used solvent or reaction medium is also important in the synthesis of carbon gels. Several solvents can be used including water [33, 34], acetone [35], methanol [36], or ethanol [37]. Each one produces a different surface tension and they interact with the reactants in different ways, giving rise to a different final pore structure. Water is the least expensive solvent and the most preferred for synthesizing organic gels. The last component of the mixture is the additive to modify the pH of the precursor mixture. The nature of this compound influences the sol-gel reaction depending on the different polarization of the reactants. The reactant may be an acid such as perchloric acid [38], nitric acid [39], citric acid [40], or acetic acid [41]; or a base such as alkali carbonates [42] or hydroxides [43]. Basic compounds are the most frequently used. Therefore, of all the possible reagents, the most commonly employed for synthesizing carbon gels are resorcinol and formaldehyde, with water as a solvent. Hence, from now on, the influence of other synthesis variables will be analyzed referring to this precursor mixture.

Once the reagents involved in the sol-gel process have been mixed, the precursor solution is subjected to a heating process in order to initiate the sol-gel reaction. The temperature must always be lower than 100 °C. During this process polymeric particles are formed and the fluidity of the precursor solutions decreases (see Fig. 1.3). These particles or clusters tend to aggregate and crosslink with each other to form a three-dimensional porous network in a liquid medium. Usually the solvent used in the precursor solution covers the polymeric structure and fills all the pores. Therefore, in order to obtain a dry organic gel, with all the porosity accessible, the solvent must first be eliminated by a drying process. As mentioned in Sect. 1.1.2, several options are available for eliminating the solvent and the process of elimination may have a decisive influence on the porous structure of the final organic gel. This chapter focuses mainly on the controlled evaporation, as this seems to be the most suitable process for scaling up for the purpose of mass organic gel production.

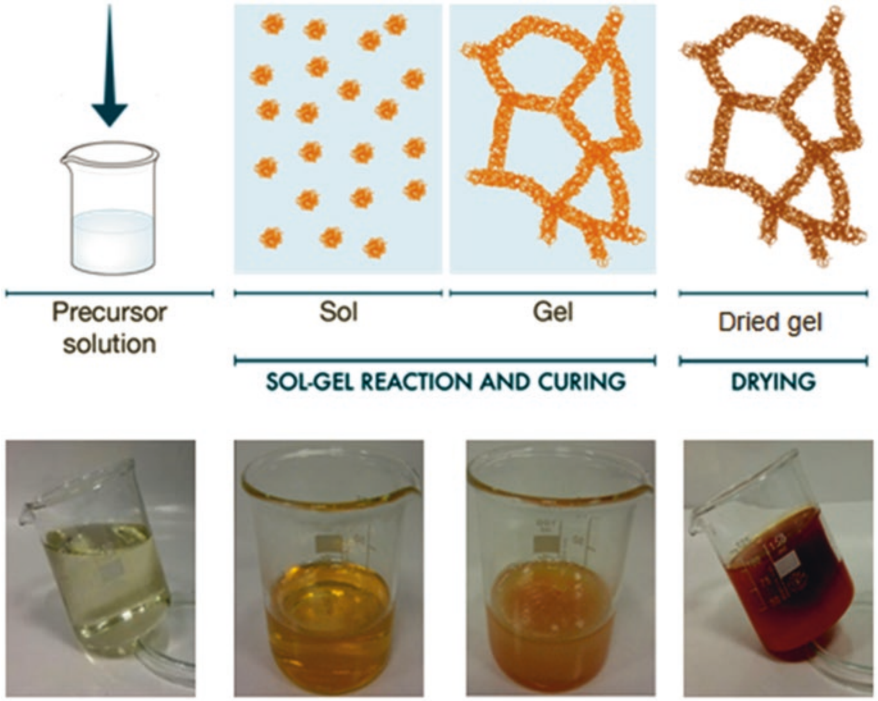

Fig. 1.3 Stages in the synthesis process of the organic gels

1.2.1 Acidic and Basic Routes: The Two Main Mechanisms

When the most common monomers, i.e., resorcinol and formaldehyde, are mixed in water as a solvent, the initial pH of the precursor solution is around 3–4. This mixture can react and lead to the formation of an organic gel, without the addition of any other compound. The reaction occurs slowly and the nodules formed are relatively large (in the order of hundreds of nm), being the size of the pores defined by the space among the nodules. This reaction can be accelerated and the size of nodules modified by varying the pH of the precursor solutions. As already mentioned, an acid or a basic compound can be added to modify and accelerate the reaction mechanism. However, the pH of the media must always be between 1 and 7 to ensure that a meso/macroporosity is obtained. Otherwise the result is a non-sol-gel process that gives rise to a phenolic resin with an uncontrolled porosity. Consequently, there are two possible routes for the organic gel synthesis: an acidic or a basic route, depending on whether an acid or a base is added, respectively, although the pH of the media will never be higher than 7. This may also lead to a misunderstanding in the nomenclature (i.e., acidic or basic synthesis), in the same way as other points mentioned in Sect. 1.1.2 (i.e., the use of the term *catalyst* or the type of gels as a function of the drying process employed).