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Covalent Bonds on Activated Carbon

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This microreview presents a concise overview of the different synthetic approaches that have been applied to activated carbons over the years, with particular attention paid to the most recent contributions to achieving stable covalent linkage on their surfaces. The method of choice for covalent immobilization of molecules on carbon surfaces has been the creation of functional groups such as carboxylic acid, acyl halide, lactone and hydroxy groups on a surface through chemical reactions. The molecules or fragments of choice to be introduced are then tethered or covalently anchored to the reactive surface.

Introduction

Carbon materials today play major roles in nanosciences (fullerenes, nanotubes), the electronic industry (diamond), metallurgy (graphitic carbon), electrochemistry, catalysis, adsorption, etc. The majority of these applications have arisen thanks to the existence of superficial layers of chemically bonded elements. Surface functional groups thus govern self-organization, chemical stability and the reactivity in adsorptive and catalytic processes.[1,2]

“Activated carbon” is the generic term used to describe a family of carbonaceous adsorbents with highly crystalline forms and extensively developed internal pore structures. A wide variety of activated-carbon products, exhibiting markedly different characteristics depending upon the raw material and activation technique used in their production, is available. Currently, activated carbon is manufactured from suitable precursors in two ways: chemical activation and physical activation. Wood, coal, lignite, coconut shell and peat are the most important raw materials for the production of activated carbons, although other materials such as fruit pits, synthetic polymers or petroleum processing residues can also be used.[3] The final products show different properties (e.g., pore structure and surface area), depending on the nature of the precursor, the nature of the activating agent and the conditions of the activation process. These properties largely define the application of the active carbon.

One of the most important applications of carbon-based materials is catalysis: they can act as catalysts by themselves or as supports. This latter application is based on the relative chemical inertness of carbon and on the ease of tailor-

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M^a^ Dolores López de la Torre was born on 11th February, 1968 in Jaén (Spain). She obtained her Ph.D at the University of Jaén in 1997 and was a Post Doc at the University of Aveiro (Portugal) in 2001. During this time she was working on reaction on fullerene derivatives with flavones, under the supervision of Professors A. C. Tomé, A. M. Silva and J. A. S. Cavaleiro. The experience obtained during this time means that she is now able to develop new work on carbonaceous materials through the collaboration that she has established with the Inorganic Chemistry research groups at the University of Jaén and at the University of Granada and with Dr M. Melguizo of the Department of Organic Chemistry at the University of Jaén.

Manuel Melguizo Guijarro, was born in 1963 in Jaén (Spain). He obtained his degree in Chemistry in 1986 and his Ph.D. degree in 1990 at the University of Granada (Spain) with Professor A. Sánchez in the field of synthesis of nucleoside analogues. He was an associate postdoctoral fellow at the University of Granada and an invited research fellow (1994) at the University of Konstanz (Germany) with Professor W. Pfleiderer. Since 1996 he has been a permanent lecturer at the University of Jaén (Spain). His research has been devoted to the synthesis and characterization of nitrogen heterocycles, polyamines and, more recently, surface functionalization and analysis of carbonaceous materials.

ing the porous texture of its activated form. Activated-carbon surfaces are known to include heteroatoms such as O, N or S in the form of functional groups either remaining from the raw material or introduced during the activation (by chemical or electrochemical[4] processes) step, which are responsible for acid-basic character. These functions can be removed by thermal treatment[5] or modified by appropriate reagents. Oxygenated functions, for example, can be introduced by oxidation and quantified by the so-called Boehm titration method.[5,6] Apart from the introduction of oxygenated functions, with the emergence of nanoscopic forms of carbon, a variety of functional groups have recently been investigated.[7] Rapid development of carbon surface chemistry is hindered, however, by several major drawbacks: lack of reactivity, hydrophobicity, difficulties in spectroscopic characterization and so forth.

These functional groups located on the surface can be used as building blocks through which to attach metal complexes or organic fragments to the support and their variety allows the use of various immobilization procedures. In this context the introduction of new fragments is a research area of particular interest because it is possible to obtain materials with higher degrees of selectivity, especially in the area of catalysis where their development has been greater. These materials are known as carbon-supported or carbon hybrids.

Carbonaceous materials are ideal supports in catalysis because they are widely available, robust and resistant to pressure, temperature and moisture, and they also usually present very high specific surface areas.[8] It is possible to obtain supports with high surface areas over which to disperse the active phase and with the required pore-size distribution to facilitate the diffusion of reactants and products to and from the active phase.[1f] Although many types of carbon materials have been used to prepare carbon-supported catalysts, high-surface-area activated carbon is one of the materials of choice for most carbon-supported catalysts.[9]

The main problems associated with heterogenisation on solid supports are the leaching of metal complexes under the reaction conditions and reductions in catalytic activity relative to the homogeneous process. Because of this, robust anchorages are required for supported complexes or other kind of molecules if their function is to be preserved from leaching processes. A new strategy – the development of a system with the compound anchored to the support by a covalent bond – has thus been developed.[10]

Here we aim to compile the findings in this important research area,[11] with particular attention to the most recent contributions to the field. This review is organized firstly with an account of the main procedures for functionalization of activated carbon surfaces, or "primary functionalization", and secondly with a comprehensive description of the main routes for the formation of supported activated carbons, also called activated-carbon hybrids, with attention to the uses to which these materials have been put.

We hope that this organization will allow readers to gain an overall perspective of this subject and to find potential applications of this chemistry beyond this area. We apologize for the inevitable omissions.

2. Functionalization of an Activated Carbon

The surface construction of a supported activated carbon by chemical means starts with the introduction of "primary functions" for further introduction of other molecules or systems. The yields of such "secondary" introduction are highly dependent on the concentrations and distributions of the primary functions, so the selection of the primary functions for introduction onto the carbon materials is a very important process (Scheme 1).

"Secondary functionalization" can be carried out by two procedures:

a) In the first one, the target hybrid activated carbon is obtained in a one-pot process. The fragment of interest is then introduced directly on the surface of the functionalized activated carbon.

b) In the second one, the fragment of interest is introduced successively in two or more steps. In this approach, an organic molecule (used as spacer) is anchored on the surface of the activated carbon and other fragments are then grafted onto the spacer to afford the target carbon-supported functions.

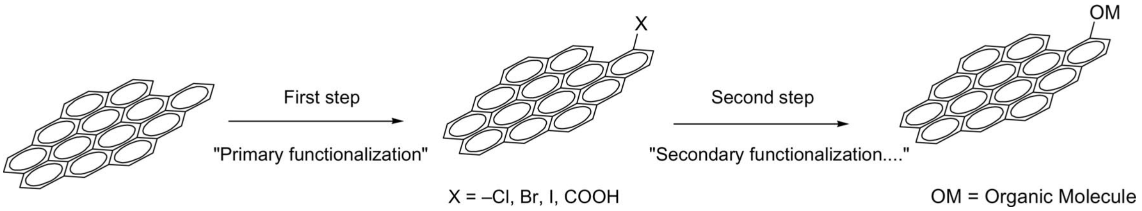
This study is divided into:

2.1. Procedures for the "primary functionalization" of an activated carbon.

2.2. Synthesis of the carbon-supported functions or activated-carbon hybrids.

2.1. Procedures for the "Primary Functionalization" of an Activated Carbon

The functionalization of carbon materials[1b,12] through the introduction of heteroatoms on the surface is a rela-



Scheme 1. Steps used during the functionalization of the activated carbon.

tively common process. Of these procedures, the introduction of oxygen functionality is the most developed. In most cases, oxygen functionalities are introduced either by oxidative aqueous solution treatments – HNO_3, H_2O_2, $(NH_4)_2S_2O_8$, NaClO, etc. – or in the gas phase with O_2, CO_2 or steam.[13] These treatments will drastically increase the concentrations of oxygen surface groups capable of anchoring organic molecules or organic complexes, but in most cases they also cause modification of the textural characteristics of the original activated carbon, which can be a drawback in carbon materials with narrow microporosity or well-defined porosity. For this reason, other methods of introducing chemical groups that allow the original texture to be maintained have been developed. These other treatments involve the introduction of surface heteroatoms through the use of cold plasmas.

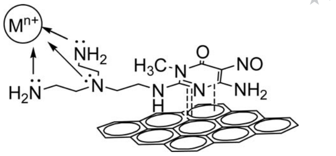
Cold plasmas are frequently used for the introduction of heteroatoms onto polymer surfaces.[14] Among them, oxygen plasmas or air plasmas are the most common, although other gases such as ammonia have been employed to introduce nitrogen functionalities. In addition, inert gas plasmas, especially helium, have been used for cleaning surfaces and subsequent weak fixation of atmospheric oxygen. Oxygen and carbon dioxide plasmas have been used for the introduction of oxygen functionalities onto several active carbons.[13] From these studies, it can be concluded that the treatments are very effective with regard to the amount of chemical surface groups introduced. A wide variety of oxygen groups is introduced, carboxylic acid groups being the most abundant.

2.2. Synthesis of Supported Activated Carbon or Activated-Carbon Hybrids

Once the primary functions have been introduced, they can act as intermediates for attachment of other fragments of organic molecules, leading to activated-carbon hybrids or supported activated carbon.

López Garzón, Gutiérrez and co-workers have proposed the attachment of appropriate molecular receptors on the graphitic surface of activated carbon for use in metal ion recovery from waste waters. These receptors consist of organic compounds containing a pyrimidine heteroaromatic residue and a designed Lewis base function, connected by a polymethylene residue (Scheme 2). The Lewis base function acts as an active site for complexation of metal centres, whereas the interaction of the pyrimidine moiety with the graphitic surface results in irreversible adsoption of the ligand onto the activated carbon. This material can be reused for long periods without leaching of the pyrimidine derivative.

Martínez Román and co-workers[15,16] have carried out the syntheses of several rhodium and palladium complexes and have studied their catalytic behaviour, specifically in the hydroformylation and hydrogenation reactions. The surface of the activated carbon is frequently prepared by chemical treatment (aqueous solutions of HNO_3, HF, HCl or, in the gas phase, O_2, CO_2).



Scheme 2. Anchoring of pyrimidine derivatives on a an activated-carbon surface (López Garzón, Gutiérrez et al.).

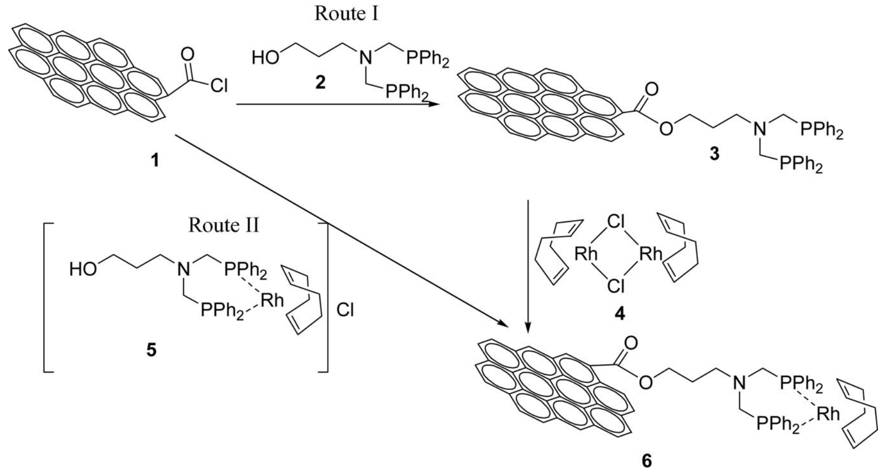
For hydroformylation reactions the development of the supported functionalization includes several steps beginning with oxidation and chlorination of the original carbon to provide **1** (Scheme 3). From this, two strategies have been applied to obtain the activated-carbon-surface-anchored rhodium(I) diphosphane complex **6**. One (Scheme 3, route I) consists of attachment of ligand (**2**) and subsequent supported complex formation by treatment with the Rh^I complex **4**. The second (Scheme 3, route II) involves the direct linking of the appropriate Rh^I complex to the COCl function in **1**, thus providing the same carbon-supported complex **6**. The two synthetic routes produce supported activated carbons that are active, selective and stable enough for use in consecutive catalytic runs in the hydroformylation of oct-1-ene. The catalyst prepared by route II showed outstanding behaviour, being fully active and with almost constant selectivity for the linear aldehyde over four consecutive catalytic runs (Scheme 3).

For hydrogenation reactions (hydrogenation of cyclohexene and hept-1-yne), other hybrid material complexes such as $[Rh(\mu\text{-}C1)(C_8H_{12})]_2$-AC, $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$-AC, $[RhCl(NH_2\ (CH_2)_{12}CH_3)_3]$-AC, $[PdCl_2(NH_2(CH_2)_{12}CH_3)_2]$-AC[16a–16d] and $[Rh(C_8H_{12})NH_2CH_2CH_2\ NH(CH_2)_3\ Si(OCH_3)_3]BF_4$-AC have been synthesized.[17c,17d]

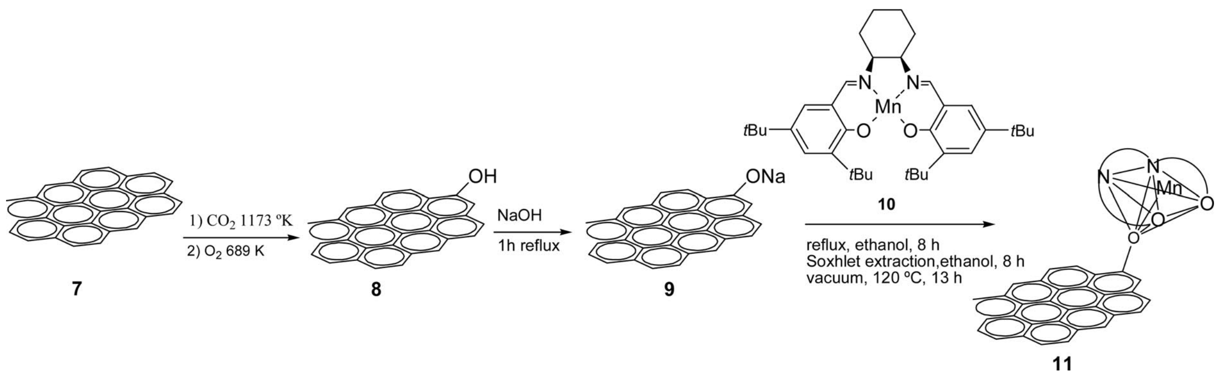
The procedure used by these researchers to produce surface oxidation was considered to affect the location of the metal complex on the support surface, with the catalyst prepared with the air-oxidized support being the most active and stable one. The metal complex was not deactivated in consecutive reaction cycles, but in most cases some leaching took place.

Freire, de Castro, Figueiredo, and co-workers have carried out the immobilization of various Schiff bases such as Cu^{II} acetylacetonate, bis[*o*-[*N*-(3-aminopropyl)formimidoyl]phenolato-*O*,*N*,*N*′]nickel(II), and bis[3-methoxy-*o*-[*N*-(3-aminopropyl)formimidoyl]phenolato-*O*,*N*,*N*′]nickel(II) and Mn^{III} salen complexes for use as catalysts.[17] In one example, Jacobsen's catalyst (**10**, Scheme 4) was immobilized onto four activated carbons with different average pore sizes. The preparation of the carbon support was achieved by CO_2 gasification followed by molecular oxygen oxidation. The influence of the textural properties of the activated carbon in the immobilization process and in the catalytic performance of the Mn^{III} heterogeneous catalysts was investigated in detail.

Three different catalytic systems involving the hybrid activated carbon **11** were studied: styrene epoxidation with *m*-chloroperoxybenzoic acid and 6-CN-2,2-diMeChromene epoxidation with either NaOCl or iodosylbenzene (PhIO)



Scheme 3. Synthetic routes to anchoring an Rh complex on an activated-carbon surface (Martínez Román et al.).



Scheme 4. Anchoring procedure for Jacobsen's catalyst on modified activated carbons (Freire et al.).

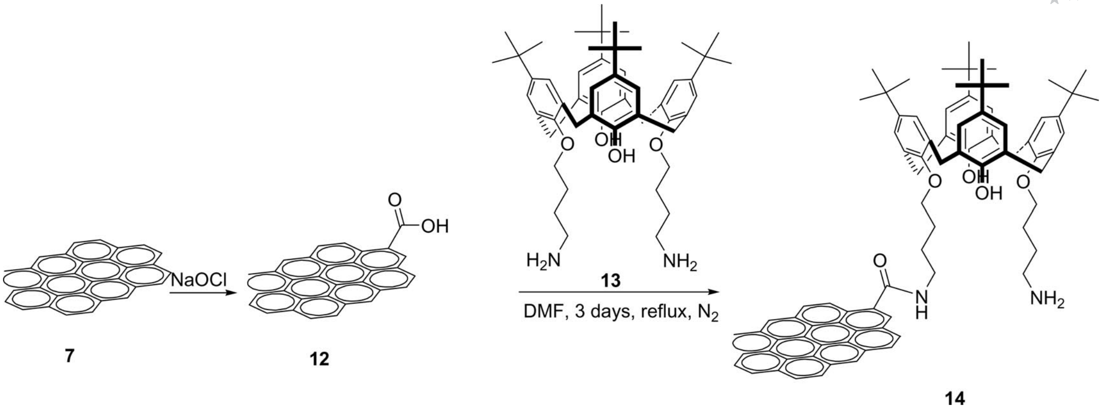
as oxidants. The catalysts tested were active and enantioselective in the three systems. Selectivity towards the desired epoxide only decreased in the case of the material with smaller pores, remaining identical to that seen in the homogeneous phase in all the other materials. The enantiomeric excess values for alkene epoxidation increased with the pore size of the heterogeneous catalysts, and in the styrene epoxidation reaction were even higher than their homogeneous counterparts.

Other organic compounds, each containing two different functionalities, were anchored to functionalized activated carbons in order to assess their use either as potential coupling agents for metal complexes or as models for grafting metal complexes with the same functionalities by Freire, de Castro, Figueiredo and co-workers.[18] The selected compounds were cyanuric chloride, 5-chloro-1-phenyl-1*H*-tetrazole and 1,2-phenylenediamine. The supports were activated carbons derived from coconut shell charcoal, which were oxidised, either with oxygen (5% in a mixture of nitrogen and air) or with concentrated nitric acid, to increase the amount of surface functional groups in a selective manner. Additional treatment with $LiAlH_4$ was carried out before attachment of chlorine-containing molecules, whereas the anchoring of 1,2-phenylenediamine was preceded by treatment with thionyl chloride to enable the formation of amide bonds with the amine.

The calix[4]arene amine derivative **13** (Scheme 5) was anchored on activated carbon previously oxidized with NaOCl through an amide function by Bonnamour and co-workers.[19] The anchored calixarene, unlike calixarene deposited by impregnation, could not be removed from the surface of carbon by washing with chloroform at room temperature. This first attempt to anchor a calixarene on activated carbon paved the way for anchoring of different kinds of calixarenes on this support. The efficiencies and selectivities of the extraction properties of these new materials towards metal ions are currently under investigation.

A little research into the use of modified activated-carbon supports (or activated carbon hybrids) to heterogenise homogeneous catalysts for liquid-phase processes has been done. For this purpose the catalyst is grafted onto a modified activated-carbon support. Two examples are presented in Scheme 6 and Scheme 7, below.

In this context, and with the aim of optimising procedures to prepare activated carbon-based heterogeneous catalysts, C. Freire, B. de Castro, J. L. Figueiredo, and co-

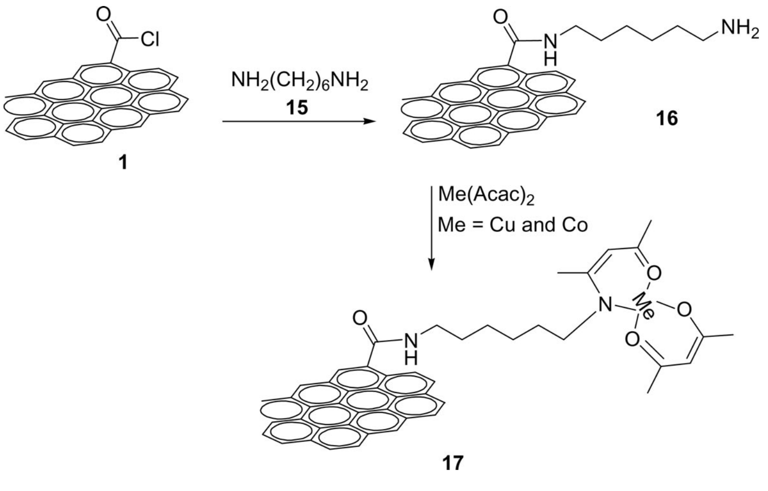


Scheme 5. Synthetic procedure to obtain calix[4]arene covalently bonded to the activated-carbon surface (Bonnamur et al.).

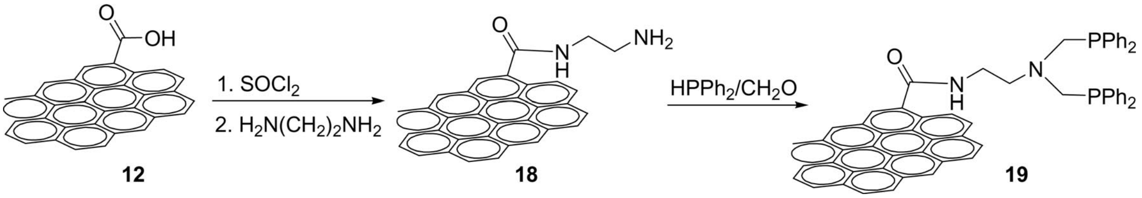
workers have developed several strategies for the immobilization on activated-carbon supports of Schiff base transition metal complexes[20] that were catalytically active in oxidation/reduction reactions. We are referring to *N*,*N*′-ethylene-bis(4-hydroxysalicyliminate)Ni^{II}, for which they used cyanuric chloride as linking agent, and a copper(II) acetylacetonate that was anchored onto a triamine-functionalized activated carbon.

The copper and cobalt acetylacetonate complexes **17** (Scheme 6) were chemically grafted onto a functionalized activated carbon by Valente, Botelho do Rego et al. These catalysts were active and highly selective for 2-pinane hydroperoxide in the oxidation of pinane at room temperature and atmospheric pressure.[21] The modification of the activated carbon surface was achieved by oxidation with nitric acid, providing carboxylic acid groups. The conversion of the carboxylic acid into the acyl chloride was then carried out by heating with thionyl chloride, leading to **1**. Hexamethylenediamine (**15**) was chemically bonded to the carbon to provide surface groups containing aliphatic carbon chains bearing terminal primary amines (Scheme 6). Acetylacetonate complexes were attached at the primary amines through Schiff condensation reactions. The obtained materials **17** were used in liquid-phase oxidations and proved to be very stable toward leaching.

An activated-carbon support was functionalized by Hermans and co-workers in order to introduce chelating phosphane groups on its surface.[22] This was done in several steps, each studied in detail and optimized in turn. The first step consisted of increasing the number of oxygenated surface groups by oxidative treatment with HNO_3, whereas the second involved the coupling of an amine with the surface carboxylic groups by formation of an amide bond, leading to **18** (Scheme 7). Various coupling agents were studied, with $SOCl_2$ being found to be the most efficient. Fluorinated and brominated amines were used as model amines (easier surface quantification by XPS thanks to the presence of heteroatoms such as F or Br), before treatment with ethylenediamine. The pendant arm of the diamine could then be further transformed to provide the desired bidentate phosphane **19** in the last step. The success of the procedure was confirmed and verification of the surface chemical reactions was achieved. Two coordination compounds, $Pd(dba)_2$ and $Ru_3(CO)_{12}$, were then incorporated on the



Scheme 6. Synthetic procedure for obtaining acetylacetonate complexes covalently bonded to an activated-carbon surface (Botelho do Rego et al.).

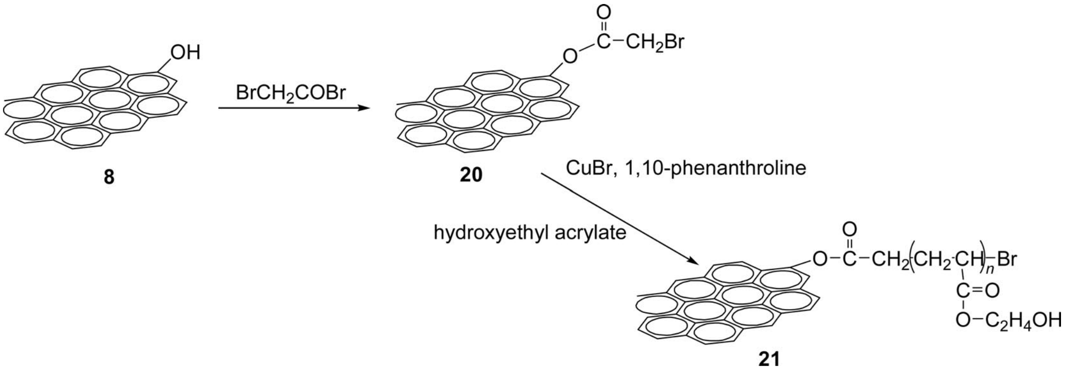


Scheme 7. Procedure for obtaining chelating phosphane on an activated carbon (Hermans et al.).

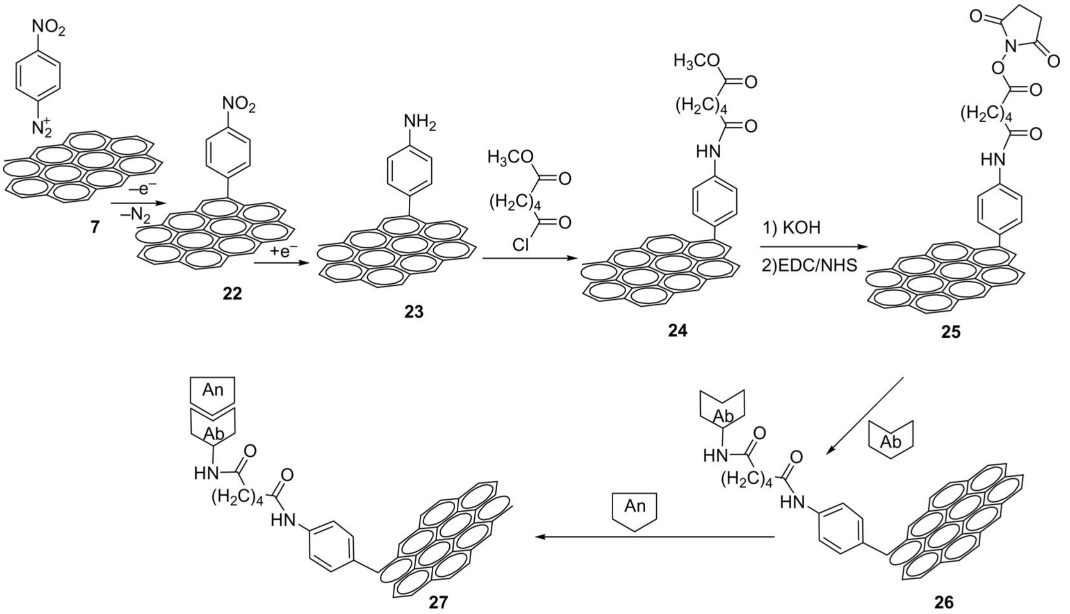
starting carbon support and on the functionalized one. It was found that the presence of chelating phosphane groups at the surface of the functionalized support allowed both the yield of incorporation and the metallic dispersion at the surface to increased.

The chosen complexes were a Pd^0 species [Pd(dba)$_2$] and a ruthenium cluster [Ru$_3$(CO)$_{12}$]. The former was selected in view of the wide applicability of Pd in catalysis, the latter as a model polynuclear precursor, in the knowledge that transition metal clusters are ideal precursors for the preparation of catalytically active supported nanoparticles.

Other fragments have been grafted on hybrids activated carbon for use either as adsorbents (Scheme 8) or as supports for sensitive biomolecules, such as antibodies (Scheme 9, below). The hyperbranched aliphatic polyester-grafted compound **21** (Scheme 8) was successfully prepared by Liu Peng et al.[23] The surface functional groups of activated-carbon particles were first homogenized to hydroxy groups (compound **8**) through oxidation with nitric acid and subsequent reduction with LiAlH$_4$. Secondly, the surface hydroxy groups were treated with bromoacetyl bromide to introduce bromoacetyl groups, leading to **20**. In the



Scheme 8. Preparation procedure for a hyperbranched aliphatic polyester (Liu Peng et al.).



Scheme 9. Step-by-step method for the immobilization of antibodies and antigen–antibody recognition (Dauphas et al.).

third step, the bromoacetyl activated carbon **20** was used in powder form as a macro-initiator for the surface-initiated atom transfer radical polymerization of hydroxyethyl acrylate in the presence of 1,10-phenanthroline and $Cu^{I}Br$ as catalyst in a water system.

A special procedure for the covalent attachment of sensitive biomolecules such as antibodies (Abs) to active carbon surfaces has been described by Dauphas et al.[24] An activated-carbon surface (**7**) was derivatized by electrochemical reduction of 4-nitrobenzenediazonium salts (Scheme 9). The nitro group of **22** was then electrochemically reduced to afford the amine **23**. This was then allowed to react with methyl 5-(chlorocarbonyl)pentanoate to give **24**. After deprotection by saponification, the resulting carboxylic acid was activated by treatment with 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) and *N*-hydroxysuccinimide (NHS) to give **25**. Anti-human transferrin antibodies (Abs) were then covalently immobilized by reaction with the *N*-hydroxysuccinimide-activated carbon surfaces to give species **26** in the last step of the modification procedure, under native conditions and at physiological pH to minimize their denaturation. The proposed method, based on an electrochemically assisted grafting process and on the use of a monoprotected homobifunctional linker, allowed the production of a stable and compact layer of anchored antibodies. Moreover, a better degree of coverage of the surface was achieved than in a classical procedure involving a homobifunctional linker.

3. Conclusions and Outlook

We have focused our attention on organic reactions that have been carried out on activated-carbon surfaces to which covalent bonds have been formed.

From our point of view, it is the chemistry that has developed around the production of the supported activated carbon that is of particular interest, because although the reactions are quite simple, as we have seen here, the usefulness of the materials obtained is quite large. The critical issue that has prevented the application of a more diverse group of synthetic transformations for activated-carbon functionalization is probably the characterization of the transformed materials (usually achieved by spectroscopic techniques in conventional organic synthesis). However, the difficulties in the application of spectroscopic techniques caused by the large radiation adsoptivities and conductivities associated with activated carbon makes those synthetic transformations that can be examined by “chemical” methods such as acid–base or redox titrations more valuable. The main catalytic advantage of these materials is high selectivity, as well as the fact that they can be used for several runs, which additionally represents an environmental advantage. Furthermore, the synthetic work involved in the multiple steps of isolation and purification of the final product/s obtained is considerably simplified because these materials are solids. Finally, other fields of exploration have been opened with the synthesis of these materials for use variously in antigen-antibody recognition, as adsorbents for wastewater treatment etc.

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[1] a) J. L. Figueiredo, M. F. R. Pereira, *Catal. Today* **2010**, *150*, 2–7; b) J. Lahaye, *Fuel* **1998**, *77*, 543–547; c) F. Rodríguez-Reinoso, *Carbon* **1998**, *36*, 159–175; d) T. J. Bandosz, C. O. Ania, in: *Surface chemistry of activated carbons and its characterization* (Ed.: Teresa J. Bandosz), chapter 4, Interface Science and Technology, Elsevier, **2006**, vol. 7, pp. 159–229.

[2] a) Y. Akinori, T. Atsushi, K. Masashi, Y. Masaaki, *Surface modification method of carbonaceous material, and carbonaceous material or activated carbon fiber*, JP2009149460(A), 9 July **2007**; b) S. Chang Ho, L. Young Taeg, L. Hee Jin, K. Dong Kyun, *Process for surface modification of activated carbon*, KR100669490(B1), 9 January **2007**; c) L. Hwa Yeong, K. Seong Gyu, *Surface modification method of activated carbon for wastewater treatment*, KR20030080485(A), 17 October **2003**; d) J. D. McNamara, *Removal of mercury from liquid hydrocarbons*, EP0433677(A1), 26 June **1991**; e) N. Shigeki, *Pretreatment of compound semiconductor substrate*, JP8325100(A), 10 December **1996**.

[3] a) E. Auer, A. Freund, J. Pietsch, T. Tacke, *Appl. Catal. A* **1998**, *173*, 259–271; b) J. L. Figueiredo, M. F. R. Pereira, M. M. A. Freitas, J. J. M. Órfão, *Carbon* **1999**, *37*, 1379–1389; c) A. Ahmadpour, D. D. Do, *Carbon* **1996**, *34*, 471–479; d) C. Moreno-Castilla, J. Rivera-Utrilla, *MRS Bull.* **2001**, *26*, 890–894.

[4] S. Dauphas, A. Corlu, C. Guguen Guillouzo, S. Ababou Girard, O. Lavastre, F. Geneste, *New J. Chem.* **2008**, *32*, 1228–1234, and references cited therein.

[5] A. Polania, E. Papirer, J. B. Donnet, G. Dagois, *Carbon* **1993**, *31*, 473.

[6] H. P. Boehm, *Carbon* **1994**, *32*, 759.

[7] S. Banerjee, T. Hemraj-Benny, S. S. Wong, *Adv. Mater.* **2005**, *17*, 17.

[8] R. C. Bansal, J.-B. Donnet, F. Stoeckli, *Active Carbon*, Marcel Dekker, New York, **1998**.

[9] J. A. C. Alves, C. Freire, B. de Castro, J. L. Figueiredo, *Colloids Surf. A* **2001**, *189*, 75–84.

[10] J. A. Díaz Auñón, M. C. Román Martínez, P. L’Argentiére, C. Salinas Martínez de Lecea, Stud. Surf. Sci. Catal. **2000**, 130 (International Congress on Catalysis, **2000**, Pt. C) 2075.

[11] *Carbon Materials for Catalysis* (Eds.: P. Serp, J. L. Figueiredo), Wiley, **2009**.

[12] a) M. A. Lillo Ródenas, M. D. Lozano Castello, D. Cazorla Amoros, A. Linares Solano, *Procedimiento para la obtención de carbones activados mediante mezcla física de precursores carbonosos con hidróxido sódico, hidróxido potásico o sus mezclas*, ES2176121(A1), 16 October **2002**; b) F. Rodriguez Reinoso, M. Molina Sabio, C. Almansa Carrascosa, *Procedimiento para la obtención de monolitos de carbon activado, monolitos obtenidos y su empleo*, ES2165784(A1), 16 March **2002**.

[13] a) M. Domingo-García, F. J. López-Garzón, M. Pérez-Mendoza, *J. Colloid Interface Sci.* **2000**, *222*, 233–240; b) M. Pérez-Mendoza, M. Domingo-García, F. J. López-Garzón, *Carbon* **1999**, *37*, 1463–1474; c) K. Kinoshita, *Carbon: Electrochemical and Physicochemical Properties*, Wiley, **1988**, p. 14; d) O. P. Mahajan, P. L. Walker Jr., *Analytical Methods for Coal and Coal Products* (Ed.: C. Karr), Academic Press, **1978**, vol. 2; e) D. L. Bierdman, A. J. Miles, F. J. Vastola Jr., P. L. Walker, *Carbon* **1976**, *14*, 35–38.

[14] a) R. Mix, K. Hoffmann, H.-J. Buschmann, J. F. Friedrich, U. Resch-Genger, *Vak. Forsch. Prax.* **2007**, *19*, 31–37; b) R. Mix, K. Hoffmann, U. Resch-Genger, R. Decker, J. F. Friedrich (Ed.: K. L. Mittal), *Polymer Surface Modification: Relevance to Adhesion* (Proceedings of the 5th International Symposium on Polymer Surface Modification: Relevance to Adhesion), Toronto, ON, Canada, 20–22 June **2005**; c) J. F. Friedrich, R. Mix, G. Kuhn, *Surf. Coat. Technol.* **2003**, *174–175*, 811–815; d) M. C. Almazán-Almazán, J. I. Paredes, M. Pérez-Mendoza, M. Domingo-García, F. J. López-Garzón, A. Martínez-Alonso,

J. M. D. Tascón, *J. Colloid Interface Sci.* **2006**, *293*, 353–363; e) M. C. Almazán-Almazán, J. I. Paredes, M. Pérez-Mendoza, M. Domingo-García, F. J. López-Garzón, A. Martínez-Alonso, J. M. D. Tascón, *J. Colloid Interface Sci.* **2005**, *287*, 57–66.

[15] a) J. A. Diaz Auñón, M. C. Román Martínez, C. Salinas-Martinez de Lecea, H. Alper, *Stud. Surf. Sci. Catal.* **2002**, *143*, 295–304; b) J. A. Díaz Auñón, M. C. Román Martíınez, C. Salinas Martíınez de Lecea, P. C. L'Argentière, E. A. Cagnola, D. A. Liprandi, M. E. Quiroga, *J. Mol. Catal. A* **2000**, *153*, 243–256; c) J. A. Díaz Auñón, J. García Martínez, M. C. Román Martínez, C. Salinas Martínez de Lecea, *Catal. Lett.* **2001**, *76*, 41–43; d) P. C. L'Argentière, M. E. Quiroga, D. A. Liprandi, E. A. Cagnola, M. C. Román Martínez, J. A. Díaz-Auñón, C. Salinas Martínez de Lecea, *Catal. Lett.* **2003**, *87*, 97–101; e) I. Such Basáñez, M. C. Román-Martínez, C. Salinas Martínez de Lecea, *Carbon* **2004**, *42*, 1357–1361.

[16] a) M. C. Román-Martínez, J. A. Díaz Auñón, C. Salinas Martínez de Lecea, H. Alper, *J. Mol. Catal. A* **2004**, *213*, 177–182; b) L. Lemus Yegres, I. Such-Basáñez, C. Salinas-Martínez de Lecea, P. Serp, M. C. Román Martínez, *Carbon* **2006**, *44*, 605–608; c) L. J. Lemus-Yegres, I. Such Basáñez, M. C. Román-Martínez, C. Salinas-Martínez de Lecea, *Appl. Catal.* **2007**, *331*, 26–33; d) L. J. Lemus-Yegres, M. C. Román-Martínez, I. Such Basáñez, C. Salinas-Martínez de Lecea, *Microporous Mesoporous Mater.* **2008**, *109*, 305–316.

[17] a) A. R. Silva, J. Vital, J. L. Figueiredo, C. Freire, B. de Castro, *New J. Chem.* **2003**, *27*, 1511–1517; b) A. R. Silva, M. M. A. Freitas, C. Freire, B. de Castro, J. L. Figueiredo, *Langmuir* **2002**, *18*, 8017–8024; c) A. R. Silva, M. Martins, M. M. A. Freitas, J. L. Figueiredo, C. Freire, B. de Castro, *Eur. J. Inorg. Chem.* **2004**, 2027–2035; d) A. R. Silva, J. L. Figueiredo, C. Freire, B. de Castro, *Microporous. Mesoporous Mater.* **2004**, *68*, 83–89; e) F. Maia, R. Silva, B. Jarrais, A. R. Silva, C. Freire, M. F. R. Pereira, J. L. Figueiredo, *J. Colloid Interface Sci.* **2008**, *328*, 314–323.

[18] a) J. A. C. Alves, C. Freire, B. de Castro, J. L. Figueiredo, *Colloids Surf. A* **2001**, *189*, 75–84.

[19] N. Toumi, I. Bonnamour, J. P. Joly, G. Finqueneisel, L. Retailleau, R. Kalfat, R. Lamartine, *Mater. Sci. Eng.* **2006**, *26*, 490–494.

[20] a) A. R. Silva, C. Freire, B. Castro, M. M. A. Freitas, J. L. Figueiredo, *Microporous Mesoporous Mater.* **2001**, *46*, 211–221; b) A. R. Silva, J. L. Figueiredo, C. Freire, B. de Castro, *Catal. Today* **2005**, *102–103*, 154–159.

[21] A. Valente, A. M. Botelho do Rego, M. J. Reis, I. F. Silva, A. M. Ramosa, J. Vital, *Appl. Catal. A* **2001**, *207*, 221–228.

[22] a) C. Willocq, S. Hermans, M. Devillers, *J. Phys. Chem. C* **2008**, *112*, 5533–5541.

[23] a) N. Tsubokawa, M. Koshiba, *J. Macromol. Sci. Pure Appl. Chem.* **1997**, *34*, 2509–2524; b) P. Liu, T. Wang, *Surf. Rev. Lett.* **2007**, *14*, 269–275; c) P. Liu, L. Zhang, *Surf. Rev. Lett.* **2007**, *14*, 1025–1032.

[24] S. Dauphas, A. Corlu, C. Guguen Guillouzo, S. Ababou Girard, O. Lavastrea, F. Geneste, *New J. Chem.* **2008**, *32*, 1228–1234.

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