The scientific impact of Francisco Rodríguez-Reinoso in carbon research and beyond

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ABSTRACT

This review article is dedicated to the memory of Francisco (Paco) Rodríguez-Reinoso (Granada 1941 - Alicante 2020). Paco dedicated more than 56 years of his life to research on carbon materials, covering from their synthesis and characterization, to their evaluation using a range of processes such as gas adsorption/separation, heterogeneous catalysis, and drug delivery, among others. His extensive research was mainly performed in the Advanced Materials Laboratory (LMA) located at the University of Alicante, Spain. This research has been reflected in more than 400 research articles in high quality international journals. This review article summarizes some of Paco's main achievements in carbon-related research emphasizing his main contributions and perspectives in the field.

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1. Introduction

Francisco Rodríguez-Reinoso, also known as Paco, initiated his research career in 1964 at the University of Granada (Spain). His PhD Thesis focused on the synthesis of carbon materials from olive stones, under the supervision of Prof. Juan de Dios López-González, who was a pioneer in Spain in the preparation and characterization of active carbons (later called activated carbons), and their subsequent application in adsorption processes. After PhD, Paco began two post-doctoral research periods at Bristol (UK), under the supervision of Prof. Douglas Everett, and at The Pennsylvania State University (USA), under the supervision of Prof. Phillip Walker, Jr. During these post-doctoral periods, Paco managed to improve his knowledge in the preparation and characterization of novel microporous carbons from polymeric precursors (Saran) and the evaluation of the reactivity of highly-oriented pyrolytic graphite. In 1971, Paco returned to Granada where he continued his research on activated carbon materials and non-porous graphite to be used either as adsorbents or as supports for heterogeneous catalysts. Paco's presence in Granada was extremely important to expand the international recognition of his research group and to increase the visibility of Spain in the carbon field. Then, in 1981, he moved to a newly created university, the University of Alicante (Spain), where

he started a new research group, the Advanced Materials Laboratory (LMA). From 1981 to 2020, a large number of students had the opportunity to learn from Paco about the synthesis, characterization and application of novel carbon materials, emphasizing adsorption, catalysis, structural materials and, at the end of his career, in nanomedicine. This review summarizes some of Paco's main achievements and his research team in the different fields investigated by the LMA group.

2. Synthesis of carbon materials

One of Paco's first studies was published in 1980, and it was devoted to the synthesis of active carbons from almond shells using physical activation with CO_2 or air [1]. These initial studies indicated the better performance of CO_2 as activating agent to achieve a highly developed porous material. Furthermore, these studies anticipated the possibility to directly apply the physical activation step to the raw material, instead of the conventional activation procedure after the carbonization under inert atmospheres, or the combination of two stages in the activation process, for instance, a treatment at "low temperature" with air followed by the activation with CO_2 [2,3]. One of Paco's main achievements was the preparation of a wide set of activated carbons from different precursors (almond shells, olive stones, peach stones, etc.), but with a perfectly controlled burn-off process. These samples included series C & D, prepared with CO_2 as activating agent, using almond shell and olive

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stones, respectively, series B, using air as activating agent and olive stones, and series H, using steam for the activation of olive stones [4–8]. These samples were an excellent platform for the understanding of the activation process under different reaction conditions. This information became extremely useful for the subsequent design of an activated carbon material with a perfectly defined micro- and mesoporous structure upon request. A few years later, Paco and coworkers introduced a novel approach for the preparation of granular activated carbons from lignocellulosic precursors through the use of different chemicals. Under these reaction conditions, activation could be carried out at lower temperatures than with physical activation, with the associated benefits in terms of cost and yield, while preserving a highly developed porous structure. These studies were initiated in 1991 using $ZnCl_2$ as activating agent, H_3PO_4 being introduced a few years later [9,10]. The work showed that the chemical activation process follows a completely different mechanism based on dehydration and de-polymerization reactions, the developed porosity being slightly wider (including a larger mesopore volume) than the one developed using physical activation, but at a higher yield [11]. The differences between physical and chemical activation processes were extensively revised in 2012 for granular activated carbons [12]. While physical activation allows tailoring the pore size distribution more accurately, although with a low packing density (large empty space) of the final material, chemical activation minimizes the packing density issues, and allows the synthesis of carbon materials with higher mechanical resistance and with a wider pore size distribution (with an elevated proportion of mesopores). Despite the excellent results achieved so far with physical and chemical activation, activated carbon materials obtained using these two methodologies were mainly microporous in nature, with a small proportion of mesoporosity. Taking into account the importance of well-developed mesocavities in the adsorption of large molecules (e.g., in biochemical applications), in 2009 Paco and his research group developed a new methodology based on the physical activation with CO_2, but using $CaCl_2$ as a catalyst [13]. Fig. 1 shows that under these experimental conditions a large volume of mesopores could be developed in the synthesized carbon materials, while preserving a similar microporous structure.

The nature of these mesocavities was further investigated by the combination of N_2 and Ar adsorption at cryogenic temperatures, together with *n*-nonane pre-adsorption [14]. The combination of these techniques was very useful to identify cavitation effects due to the presence of mesoporous cavities ($\approx 20-30$ nm), connected with the external surface through narrow mesoporous necks ($\approx 3-4$ nm).

Another important aspect extensively covered by Paco and his research group was the evaluation of the surface chemistry in carbon materials and the effect of these functionalities in the subsequent adsorption processes. These studies were mainly focused in oxygen surface groups incorporated through post-synthesis treatments, either in gas phase (air oxidation) or liquid phase (oxidation with HNO_3 or H_2O_2) [15]. A proper characterization of these functionalities using temperature-programmed decomposition, suggested that low-temperature CO_2-evolving groups where preferentially developed in liquid phase oxidation, while high-temperature CO_2-evolving groups prevailed after oxidation with air. Further studies confirmed that the nature and amount of these oxygen groups exhibit an important effect in the adsorption of polar molecules (e.g., SO_2, H_2O), whereas porosity is the main factor controlling the adsorption of non-polar molecules (e.g., N_2) [16].

3. Characterization of the porosity in carbon materials

One of the topics where Paco put most effort was the development of a proper methodology for an accurate characterization of the porous structure in carbon materials. Although nitrogen adsorption at cryogenic temperatures was the most widely accepted methodology at that time, and even now, for the characterization of the micro and mesoporous structure in carbons, in the nineties Paco and his group observed that at these low temperatures nitrogen could undergo important diffusional limitations, especially in chars and some low-burn off activated carbons [17]. To avoid these kinetic limitations, CO_2 adsorption at a higher temperature, i.e., 273 K, was proposed to complement nitrogen in the characterization of microporous carbon materials. While nitrogen adsorption at 77 K reaches up to $p/p_0 \approx 1$ at atmospheric pressure and provides information about the microporous and mesoporous structure, CO_2 adsorption at 273 K is limited to a final relative pressure of 0.03, thus providing exclusively information about the narrow microporosity, i.e. pores below 0.7 nm. A few years later, further investigations with carbon materials with narrow constrictions, such as carbon molecular sieves (e.g. Takeda materials - Fig. 2) suggested that even at this relatively "higher temperature" (273 K), CO_2 adsorption can also exhibit kinetic limitations to reach these narrow pores, with the subsequent uncertainty in the characterization results [18].

In samples with a narrow porous network, CO_2 will exhibit kinetic limitations to reach the inner cavities, as shown in Fig. 2. To confirm the presence of these kinetic restrictions, two different approaches can be performed when working with automatic equipments to ensure that adsorption isotherms are obtained under true equilibrium conditions: either to increase the equilibrium time (increase the time in between two consecutive pressure readings in the software to check equilibrium, for instance, from 30 s to 300 s), or to increase the temperature of the adsorption measurement (e.g. from 273 K to 298 K; Fig. 2). Although adsorption is an exothermic process and the amount adsorbed must decrease after an increase in the adsorption temperature, this is not the case when kinetic restrictions are present. In this case, a slightly higher temperature will promote the diffusion process, and indirectly, the adsorption capacity (Fig. 2). By using these two approaches, the operator must ensure that the isotherms are measured under true equilibrium conditions. A subsequent collaborative work with Thommes and coworkers extended these
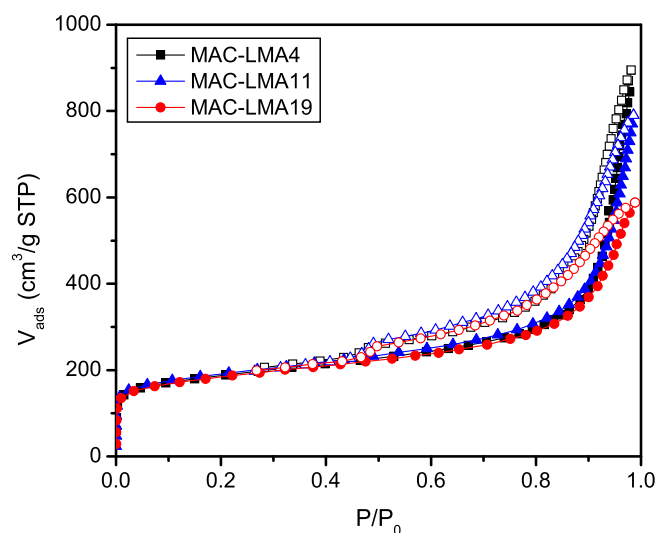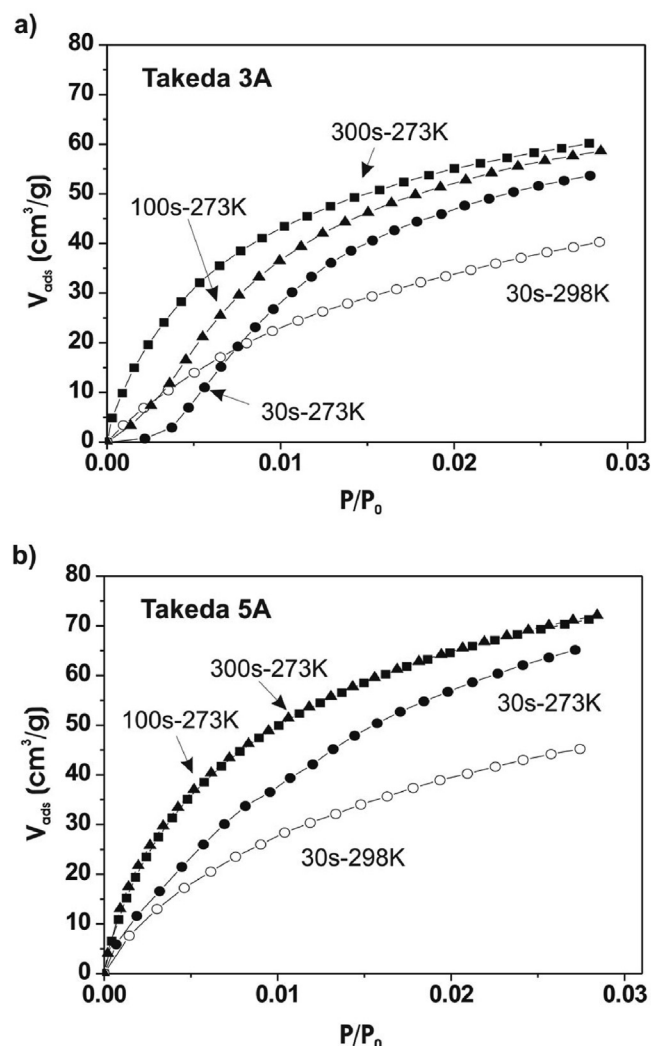

Fig. 1. Nitrogen adsorption/desorption isotherms of mesoporous activated carbons [13]. Reprinted with permission from Elsevier. (A colour version of this figure can be viewed online.)

Fig. 2. CO_2 adsorption isotherms at different equilibration times (30, 100, and 300 s) for (a) Takeda 3A and (b) Takeda 5A, at 273 and 298 K [18]. Reproduced with permission from American Chemical Society.

from the weight increase after *n*-nonane pre-adsorption or from the subtraction of the N_2 adsorption isotherms performed before and after *n*-nonane pre-adsorption. The potential and limitations of this approach was confirmed in a comparative study for a wide range of carbon materials with different burn-off degrees [22,23].

In summary, Paco and coworkers proposed CO_2 adsorption at 273 K and *n*-nonane pre-adsorption (followed by N_2 adsorption at 77 K) for characterizing the narrow microporosity of activated carbons, while N_2 and Ar adsorption at 77 K and 87 K, respectively, was used for the characterization of the whole microporosity and mesoporosity.

Following some preliminary studies by Denoyel [24] and Stoeckli [25] about immersion calorimetry, Paco et al. also introduced this technique as a complement to gas adsorption, and more specifically, for the estimation of the surface area accessible and the pore size distribution [26,27]. Using a non-porous carbon material as a reference (V3G), these studies allowed a complete description of the experimental pore size distribution in the narrow micropore range (ca. 0.3—0.7 nm), and the surface area accessible to the selected probe molecules (e.g., benzene, dichloromethane, among others). Immersion calorimetry was also very useful for characterizing the surface chemistry of carbon materials through the evaluation of the specific adsorbate-adsorbent interactions by combining polar and non-polar probe molecules [28]. Immersion enthalpy of non-polar molecules was not altered by the surface chemistry, being sensitive only to the available porosity. However, for polar liquids such as H_2O the immersion enthalpy is highly affected by the presence of oxygen functional groups, preferentially those with a high thermal stability.

4. Application of carbon materials in adsorption processes

Although Paco's research group has been an international reference in adsorption science, the initial adsorption studies performed in the eighties and nineties were mainly devoted to study the porous structure in carbon materials. As described in the previous section, these studies involved preferentially N_2 adsorption at cryogenic temperatures and, later, CO_2 adsorption at 273 K [2,17]. The main goal of these adsorption processes was to get a clear picture about the porous structure of these carbon networks (evaluation of the microporous and mesoporous structure). These studies were complemented by liquid-phase adsorption processes using organic molecules such as phenols and dyes, including methylene blue [1,3,29]. Adsorption of hydrocarbon molecules with a different size and shape (e.g., benzene, *n*-butane, iso-butane, cyclohexane, etc.) was also introduced in the evaluation of carbon materials to obtain the real pore size distribution [4]. These tests were very useful to identify molecular sieving properties in carbon materials with a low burn-off degree. These molecular sieving properties were further exploited years later for the separation of industrially relevant gas mixtures such as O_2/N_2 and CO_2/CH_4 [30,31]. The evaluation of the adsorption performance of carbon materials towards probe molecules with different polarity (e.g., N_2, SO_2, H_2O, and CH_3OH) was also introduced in 1992 to complement the characterization of the porous materials, and more specifically, to evaluate their surface chemistry [16]. These studies confirmed that the adsorption of polar molecules is highly influenced by the amount and nature of the oxygen surface groups.

The incorporation of high-pressure adsorption equipment in Paco's research group allowed to extend these adsorption measurements to more relevant processes, for instance high-pressure methane storage and CO_2 capture. The first study dates back to 2003, when phosphoric acid-based carbons were conformed into discs and applied in the adsorption of methane at 3.4 MPa [32]. These studies constitute a stepping stone in the adsorption of gases

studies with "problematic" samples to the usage of argon adsorption instead of nitrogen, both at cryogenic temperatures [19]. These studies demonstrated that a spherical molecule such as Ar exhibits certain advantages when compared to N_2 during the characterization of carbon materials. These include the presence of a weaker effective adsorption potential, i.e., the absence of specific interactions of argon with the adsorbent surface, the absence of a dipole or quadruple moment, and the well-defined dimensions of the probe molecule (spherical instead of linear, and monoatomic instead of diatomic). Consequently, argon adsorption at 87 K was proposed as a useful tool for a reliable and detailed characterization of the microporosity in activated carbons.

Paco and his research team also pioneered in the application of *n*-nonane pre-adsorption for the specific evaluation of the microporosity in activated carbon materials. This approach is based on the preferential blocking of the narrow microporosity by *n*-nonane, so that only wide micropores, mesopores, macropores, and external surface are available for adsorption [20,21]. These measurements were very useful to estimate the narrow micropore volume in different activated carbons and the pore size distribution, either

at high-pressure, and introduced an important concept not widely explored at that time, the necessity to achieve a complex balance between a widely developed porous structure and a high density (both concepts are reversed), to achieve a high adsorption capacity, not only gravimetrically but also volumetrically. Using H_3PO_4 as activating agent, high-density monoliths were obtained without the need of a binder and with a total CH_4 storage capacity as high as 150 v/v. Similar results were obtained for methane storage in activated carbon synthesized from olive stones and using $ZnCl_2$ as activating agent [33]. These numbers were highly improved after the incorporation of KOH as activating agent. Under these conditions, activated carbons with a highly developed narrow microporous structure were obtained (micropore volume above 1 cm^3/g). These KOH-based carbon materials were able to adsorb up to 160 v/v of CH_4 at 10 MPa (0.24 g/g) and around 1600 mg/g of CO_2 at 4.5 MPa [34–37]. Interestingly, these samples were able to outperform the behavior of selected MOFs in volumetric basis and at high pressures (see Fig. 3) due to the excellent adsorption performance, higher density and structural stability of the carbon materials.

However, the breakthrough in this topic was introduced in 2015 through a fruitful collaboration between the University of Alicante - Spain, with Paco's group, and Shinshu University - Japan, with Prof. Kaneko's group. Although the concept was already known in the literature, these two groups managed to highly improve the adsorption capacity in carbon materials under wet conditions through the nucleation and growth of confined gas hydrates [38]. This nature-inspired approach allowed Paco's group to increase the methane uptake up to three times (up to 0.6–0.7 g/g at 10 MPa and 275 K) when compared to the dry material. The presence of these confined gas hydrates was confirmed via inelastic neutron scattering (INS) and synchrotron X-ray powder diffraction. These studies were extended to other guest molecules such as CO_2. Under proper pressure and temperature conditions, CO_2 was also able to nucleate in carbon cavities to produce gas hydrates with an improved adsorption capacity compared to the dry system [39]. Compared to CH_4, studies with CO_2 hydrates were performed at lower pressures (pressure range for nucleation: 1.5–2.0 MPa for CO_2 and 3.0–4.0 MPa for CH_4; see Fig. 4).

In general, the successful development of these confined gas hydrates under mild pressure and temperature conditions and with fast kinetics (compared to the bulk system), constituted a significant advance in the field of adsorption at high-pressure.

5. Application of carbon materials as a support in heterogeneous catalysis

In addition to adsorption-based processes, Paco soon recognized the potential of carbon materials as catalytic supports, especially in reactions under conditions where carbon inertness was preserved. For activated carbons, he always remarked three properties that make them highly suitable for many catalytic applications: i) high surface area and porosity, allowing good dispersion of the active phase, ii) a rich surface chemistry, which can be tailored by the introduction of heteroatoms (e.g. oxygen functionalities) that can modify its acid-base character, its hydrophilicity and can improve the preparation process of the catalyst, and iii) chemical inertness (under a non-oxidizing atmosphere), which favors the interaction among supported active phases and promoters [40].

His earliest studies dealt with the use of an activated carbon prepared by pyrolysis and activation of a polymer (Saran), as support of Ru or Fe nanoparticles that were tested in the CO hydrogenation reaction. Paco and coworkers studied the behavior of Fe and Ru [41], the effect of the metal precursor for Fe-based catalysts [42], the effect of oxygen surface functional groups and nitrogen-doping [43], and the reduction temperature of the catalysts prior to the activity measurements [44]. The effect of both the textural properties and surface chemistry of the activated carbon supports and metal precursors were determined in Fe-based catalysts for the CO hydrogenation reaction [45]. Carbons with different activation degrees were used as supports, and Fe-based catalysts were prepared by impregnation using aqueous solutions of $Fe(NO_3)_3$ and acetone solutions of $Fe(CO)_5$. It was demonstrated that the porosity and surface properties of the carbon support had a clear effect on the Fe dispersion and catalytic activity when the metal precursor is $Fe(NO_3)_3$, whereas the effect is minimum when $Fe(CO)_5$ was used as the metal precursor. It was concluded that the observed differences were mainly due to the non-polar solvent (acetone) used for $Fe(CO)_5$ impregnation, that made it more accessible than water to the inner porosity of the carbon supports.

The last study carried out on the CO hydrogenation reaction exploited the chemical inertness of the carbon support to favor the interactions between the active phase (iron, in this case) and promoters (Cr or Mo). For Cr, a dilution effect was observed by which the irreversible chemisorption of CO and the catalytic activity decreased as the Cr amount increased, as less Fe atoms were available on the catalyst surface, and no effect was observed on selectivity [46]. However, a very important effect was obtained
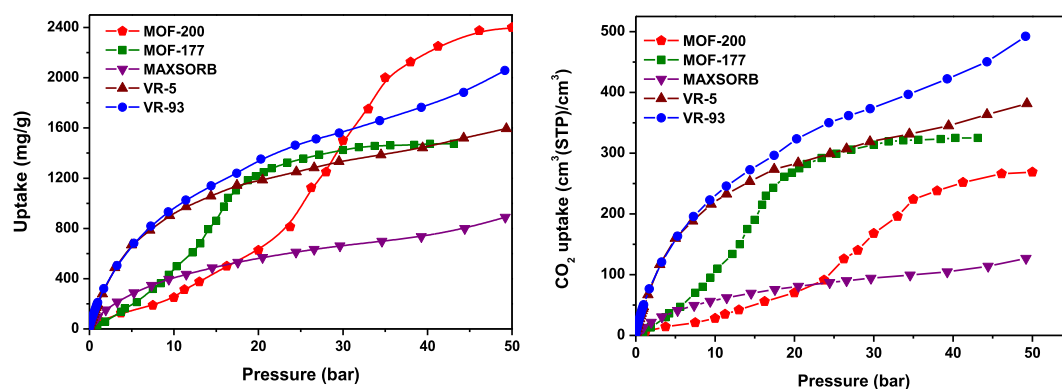

Fig. 3. CO_2 adsorption isotherms in a gravimetric basis (mg/g) and volumetric basis (cm^3/cm^3) for the VR carbon molecular sieve samples at 298 K and up to 50 bar. MOF materials (MOF-177 and MOF-200) with exceptional adsorption properties and commercial activated carbon MAXSORB are included for the sake of comparison [34]. Reprinted with permission from Royal Society of Chemistry. (A colour version of this figure can be viewed online.)
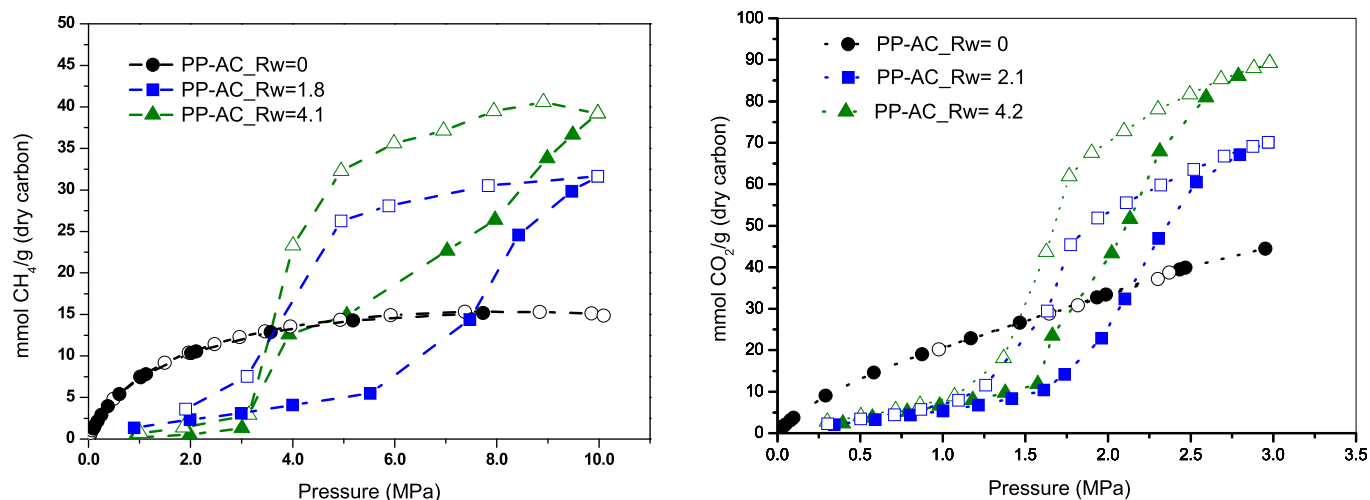
Fig. 4. High-pressure gas adsorption (filled symbols) and desorption (empty symbols) isotherms, (left) CH_4 and (right) CO_2, at 273 K for sample PP-AC dry and after a pre-humidification step with H_2O at low (Rw = 1.8–2.1 g/g) and high (Rw = 4.1–4.2 g/g) humidity [39]. Reprinted with permission from Wiley-VCH. (A colour version of this figure can be viewed online.)

upon the addition of Mo. The catalytic activity of the FeMo/C catalyst was higher than that of the monometallic sample, Fe/C, and strongly depended on the reduction temperature. Furthermore, the selectivity was also affected as the bimetallic catalyst produced a higher methane yield at the expense of larger hydrocarbons production [47].

The relative inertness of the carbon support that, unlike other materials such as Al_2O_3, CeO_2 or TiO_2, avoids any strong interaction with the actives phases and/or promoters, was used by Paco and coworkers to prepare and study carbon-supported bimetallic Pt/Sn catalysts, sometimes promoted by CeO_2, that were used in several reactions of industrial interest [48–50]. In these systems, the interactions between Pt and Sn species, and the ceria promoter, were favored by the inertness of the carbon support.

In this way, in a first study on Pt–Sn catalysts supported on a furnace carbon black which had been heat-treated at 2273 K under He, it was observed that the amount of surface Pt atoms decreased as the relative amount of Sn in the catalysts increased. Furthermore, XPS studies detected the presence of metallic Pt and both metallic and oxidized tin species in the reduced catalysts (623 K, flowing H_2). It is noteworthy that the tin precursor is not reduced to the metallic state under these conditions when supported on alumina or titania. Catalysts were tested in the selective hydrogenation of crotonaldehyde (2-butenal) to crotyl alcohol (2-butenol) in the vapor phase. Despite the decrease in the amount of surface Pt atoms, the presence of Sn produced an increase of catalytic activity, and even selectivity towards the hydrogenation of the carbonyl bonds to yield crotyl alcohol. This was assigned to the promoter effect of tin oxide species that promoted the hydrogenation of the carbonyl bonds, together with the formation of Pt–Sn alloy species that are less active than Pt alone to hydrogenate the olefinic bonds [48].

The high surface area of activated carbons, together with the inertness of their surface, was used in other studies to prepare highly dispersed cerium oxide that could act as a promoter of active Pt in different reactions. In this context, the promoter effect of this oxide was enhanced because it was in the form of small crystallites that offered a large surface area able to interact with Pt nanoparticles. When complex Pt–Sn/CeO_2/C catalysts were used in the nonoxidative dehydrogenation of iso-butane, the best activity was observed when Sn/Pt = 0.5. Furthermore, the deactivation behavior was significant due to the presence of ceria, and the deactivated

catalysts could be recovered with an oxidation treatment at a mild temperature (537 K) [49]. This bimetallic Pt–Sn system promoted by cerium oxide was also used in the liquid phase hydrogenation of citral in order to obtain unsaturated alcohols (geraniol + nerol) [50]. The idea was to combine the promoter effect of ceria for the preferential hydrogenation of the carbonyl bond, and that of SnO_x and Pt–Sn alloys described above. Again, the high surface area provided by the activated carbon support was key to obtain very small ceria crystallites that offered a relatively large surface to interact with Pt–Sn alloy nanoparticles. In this way, it was observed that citral conversion decreased upon tin addition; however, the selectivity towards the unsaturated alcohols improved. Furthermore, the temperature at which the catalysts were reduced prior to the reaction tests was a very important parameter. Reduction at 773 K strongly increased the selectivity with respect to the reduction at 473 K, and this was attributed to the large amount of metallic Sn able to form Pt–Sn alloys and to the partial reduction of cerium oxide [50].

One of Paco's interests in the carbon and catalysis fields was the influence of carbon surface characteristics in the dispersion and catalytic properties of carbon-supported Pt catalysts. As noted above, the large surface area and developed porosity of carbon supports facilitate the dispersion of active phases, but the surface chemistry also plays a key role by governing the interactions with the metal precursor during catalyst preparation.

A very first study was devoted to determine the effect of inorganic constituents of activated carbons in the characteristics of the final Pt/AC catalysts. In this context, two commercial activated carbons were successively treated with concentrated HCl and HF solutions to remove inorganic species. When these materials were used as supports for Pt, and compared to those prepared with the parent un-treated activated carbons, it was concluded that inorganic matter acts as a geometric promoter for Pt nanoparticles, hindering their deactivation by sintering at 773 K [51].

In a comprehensive work, Paco and coworkers studied the effect of different parameters during the preparation of activated carbon-supported Pt catalysts: carbon precursor (olive stones or almond shells), Pt precursors ($H_2PtCl_6 \cdot 6H_2O$ or $[Pt(NH_3)_4]Cl_2$), impregnation techniques (incipient wetness or soaking), solvents (water or benzene-ethanol mixture), and reduction conditions. The catalysts were characterized by a complete set of techniques and their catalytic behavior was evaluated in the isomerization and

hydrogenolysis of *n*-butane [52,53]. Several conclusions were obtained from this study. First, the role of the support's surface area was clearly evidenced, as it was demonstrated that the presence of pores with sizes ranging from 9 to 11 nm was critical for obtaining a homogeneous Pt dispersion. Whereas the preparation conditions had no effect of Pt dispersion when H_2PtCl_6 was used as a metal precursor; the reduction treatment under H_2 had a detrimental effect on the Pt dispersion when $[Pt(NH_3)_4]Cl_2$ was used. In this case, it was shown that it is necessary to decompose the metal precursor under He at 673 K prior to the reduction treatment under H_2 in order to obtain a suitable Pt dispersion. It was argued that the formation of an unstable platinum hydride was avoided. Regarding the catalytic behavior of the reaction between H_2 and *n*-butane, the main reaction was hydrogenolysis with the preferential splitting of the terminal C—C bonds. In addition, selectivity for hydrogenolysis *vs.* isomerization increased as the mean Pt particle size decreased, thus confirming the structure-sensitive character of this reaction, opposite to isomerization.

With less surface area than activated carbons, graphitized carbon blacks constitute a an attractive carbon-based support for Pt nanoparticles, with applications in catalytic and electrocatalytic reactions. The interactions between the carbon black surface and the Pt precursor (H_2PtCl_6) upon catalysts preparation by impregnation in aqueous solution, was studied with three pre-graphitized carbon blacks with the same porous texture but different amounts of oxygen surface groups. The parent carbon black was heat-treated in He at 2073 K; then a part of it was oxidized with an aqueous solution of H_2O_2 12 N to introduce oxygen surface functionalities. Finally, another support was prepared by treating the oxidized carbon black with He at 773 K to remove less stable oxygen surface groups. A very important finding was that the carbon surface of pristine graphitized carbon blacks oxidized upon the impregnation with the Pt precursor, whereas Pt(IV) was reduced to Pt(II) and even metallic Pt, as it was concluded from XPS measurements. In addition, the surface oxidation of the carbon black support made its surface more hydrophilic, thus favoring the wettability and the interaction with the aqueous solution of the Pt precursor. Interestingly, it was observed that the surface oxygen groups acted as anchoring centers for Pt species; in principle, this could favor the final metal dispersion, but the decomposition of the less stable groups during the reduction treatment with H_2 at 623 K to achieve the Pt metallic phase favored the mobility of the Pt species and thus, the formation of large metal particles [54]. In this way, a complex relationship between the chemical properties of the support's surface and the Pt dispersion in the final catalyst was observed. The effect of the surface oxygen groups was more important when $[Pt(NH_3)_4]Cl_2$ in aqueous solution at pH around 9, was used as Pt precursor. In this case, the more acidic oxygen functionalities, negatively charged at the solution pH, interacted with the cationic metal precursor favoring their anchoring to the carbon surface [55]. Thus, these studies provided the guidelines to tailor the interaction between the carbon surface and the Pt precursor, which are of paramount importance to define the metal dispersion and the surface chemistry of the support in the catalyst design. In fact, the modifications of the carbon surface chemistry at different stages in the preparation of the catalysts (impregnation, reduction), were clearly evidenced in these studies. It was also demonstrated that the carbon surface chemistry of the final catalysts could be determinant in the catalytic behavior of some reactions. This is the case of the selective hydrogenation of crotonaldehyde to obtain crotyl alcohol. It was shown that, for both activated carbons and carbon blacks as Pt supports, the activity and selectivity in this reaction was improved when they were oxidized prior to the impregnation with the metal precursor. Interestingly, both parameters increased when the reduction temperature was

increased. Taking into account that the reduction treatment removed surface oxygen groups, the less stable ones, it was concluded that the promoting effect was not due to the presence of these functionalities, but to their removal upon reduction. It was demonstrated that the removal of the oxygen surface groups upon the reduction treatment created surface sites which were able to retain hydrogen, and it was proposed that these hydrogen species could promote the hydrogenation of the carbonyl bonds in crotonaldehyde by a polarization effect through interaction with the oxygen atom, weakening the double bonds and favoring its hydrogenation by hydrogen atoms dissociated on the surface of the Pt nanoparticles [56,57].

6. New carbon materials: graphite, carbon composites and SiC

One field in which Paco was involved in collaboration with industry, especially the Spanish company Repsol and Professor H. Marsh, is the preparation of new carbon materials derived from petroleum residues. This research includes a large number of precursor materials such as cokes, petroleum pitches, self-sintering mesophase, graphite, metal-infiltrated graphites, graphite/ceramic composite materials, silicon carbide, etc. [58–79].

The research began with basic pyrolysis studies of petroleum residues of different reactivity that are used for coke production, and it was found that the viscosity and the evolution of gases during mesophase formation were crucial for the orientation of the domains and improvement of the optical texture [58]. Kinetic studies of the pyrolysis of petroleum residues for mesophase formation were also carried out, using techniques such as optical microscopy and sequential extraction to follow the evolution of pyrolysis [59–61]. In this context, it was found that the evolution of material soluble in heptane (HS), toluene (TS) and methylpyrrolidone, NMP, (NMPS) and insoluble in NMP (NMPI), followed a mechanism of consecutive reactions: HS↔TS↔NMPS↔NMPI (Fig. 5), with calculated activation energies of 240 ± 20 kJ mol-1 [61].

Based on these basic pyrolysis studies, the optimal pyrolysis conditions for the development of mesophase, maximizing the percentage of spheres were also studied in order to synthesize materials similar to mesocarbon microbeads, produced from petroleum residues. It was found that by using a high pressure treatment (1 MPa), in which the nucleation of the spheres took place, followed by depressurization at high temperature, in which the viscosity rises and the spheres grow, it was possible to maximize the formation of mesophase in the form of spheres [62].

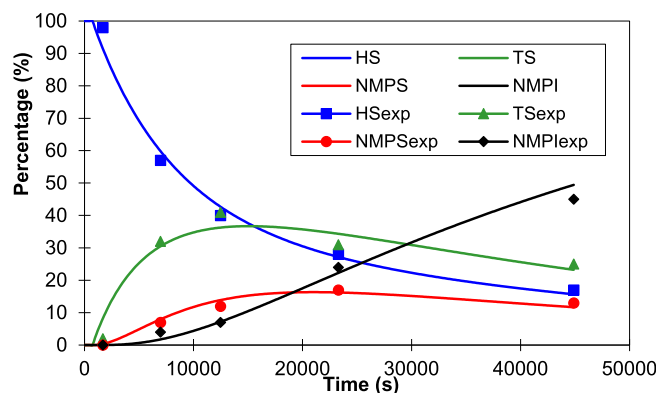With this knowledge, different studies were conducted to obtain

Fig. 5. Experimental and calculated data applying the consecutive reaction method for a Decanted Oil (DO), at 440C and 1.0 MPa [61]. Reprinted with permission from Elsevier. (A colour version of this figure can be viewed online.)

self-sintering mesophase powders for the preparation of high-performance graphites with robust mechanical properties. To optimize the self-sintering properties of carbon materials, it was necessary to adjust the thermo-fusibility of the carbons and three alternative methods were studied: extraction with solvents [63,64], devolatilization treatments (thermal curing) [65], and oxidative stabilization [66].

In the case of extraction with solvents, the selection of the solvent and extraction temperature [64], as well as the washing conditions [67], are of utmost importance. The monitoring of the thermo-fusibility of the prepared carbons was successfully followed by TMA in the penetration mode, Fig. 6.

The material's density and mechanical properties depended on the ability to sinter the carbon materials and, therefore, on their thermo-fusibility. It was found that the synthesized materials exhibited better properties, such as density or bending strength, when the materials were prepared with mesophase pitches with lower mesophase content, and when using solvents with lower extraction power such as toluene or decaline, whereasother properties such as the electrical conductivity, required a good sintering of the carbon particles but also a higher mesophasecontent. Therefore, the material's performance improved when using solvents with lower extraction power but higher mesophase contents [64].

For materials obtained by thermal curing [65], the performance of devolatilization treatments at low temperature (623—673 K), adjusted the sintering properties of mesophase pitches and semicokes to give similar properties to those materials obtained by solvent extraction, Fig. 7, thus avoiding the use of solvents; more friendly for the environment. Therefore, heat-treated compacts (2773K) exhibited high densities, >1.9 g cm^{-3}, with excellent mechanical properties (BS > 90 MPa).

The study of the co-pyrolysis of petroleum residues with dopants such as B, Sior Ti, allowed the dispersion of dopants at the nanoscale level. Thus, the co-pyrolysis with pyridine borane, phenyl silane or titanates were studied to understand the changes in the mesophase structure and composition of the resulting pitches and semicokes [68—70]. One example is the preparation of graphite nano-TiC composites using Ti-doped semicokes and semicokes containing nano-TiC particles. In these materials, the incorporation of 4 at.% of Ti to the nanoTiC—graphite composites yield excellent mechanical properties and improved thermal conductivity, from 40 to 180 W/m K [71], Fig. 8.

In the 80s, Paco also opened a new line of research based on SiC, and a fruitful relationship with the aluminum industry (INESPAL-ALCAN). The idea was to develop SiC to be used in metal matrix composite materials, especially in the form of whiskers [72,73], developing a very high control of whisker shapes (see Fig. 9) on the one hand and, and on the other hand, increasing the quality and performance in the production of traditional SiC through a more exhaustive control of the carbon material used [74]. Traditionally, the only property required by the SiC producers for coke was a maximum S content and a minimum content in fixed carbon. It was revealed that the main factor that governs the reaction is actually the optical texture index (OTI).

Within this SiC production, the next step was the manufacturing of SiC parts, especially, the development of SiC-based and Si-free composite materials [75,76], as a priors step to the preparation of Reaction Bonded Silicon Carbide (RBSC) materials by reactive infiltration. The production of SiC using carbon preforms by reactive infiltration was studied in detail [77]. First, the preparation of pieces using four types of Mediterranean wood as carbon precursors was studied. Carbon biotemplates were pyrolyzed up to 1673K and infiltrated in two different directions. A linear correlation between bending strength and the density of as-prepared SiC samples for different types of softwood and hardwood was found. Moreover, the fabrication of SiC from carbon bio-templates heat-treated up to 2773K was also studied, and an improvement of up to 56% in the flexural strength was reached by densification of carbon preforms at such high temperature.

The preparation of SiC using sawdust by reactive infiltration was also studied [78]. Components showed a maximum in bending strength when the material was processed from carbon preforms exhibiting around 40% of open porosity, which seems to be the optimum value for carbon preforms treated at 1673 K and 2773 K. However, the heat treatment of the carbon preforms at 2773 K resulted in SiC components with a finer and more homogeneous microstructure improving their bending strength up to 22%.

Additionally, the preparation of SiC pieces by reactive infiltration using coke as carbon precursor was also studied. The effect of the porosity of the sample and microstructure of mesophase was analysed [79]. SiC pieces made from the optimum carbon preforms (made up by combining the most graphitic carbon and 40% of open porosity), reached bending strength values of around 260 MPa. It must be pointed out that an improvement in the mechanical properties of SiC pieces up to 66% was achieved due to the structural modification caused by the graphitization of the carbon preforms.

Paco, through a series of European projects and in collaboration with Professor Louis Cereceda (University of Alicante), worked on
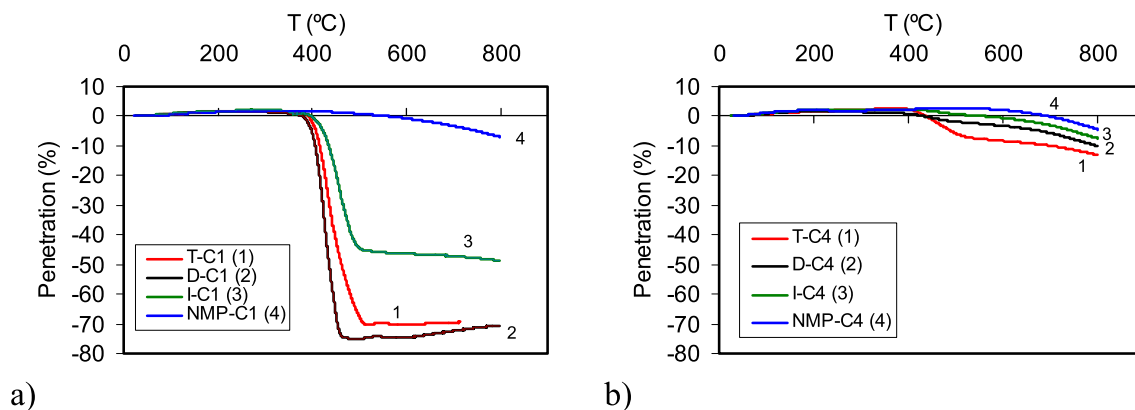
Fig. 6. Penetration vs. temperature for binderless polyaromatic mesophase obtained by extraction with toluene (T), decahydronaphtalene (D), industrial solvent (I) and NMP of: a) low mesophase content semicoke (C1) and b) high mesophase content semicoke (C4) [64]. Reprinted with permission from Elsevier. (A colour version of this figure can be viewed online.)
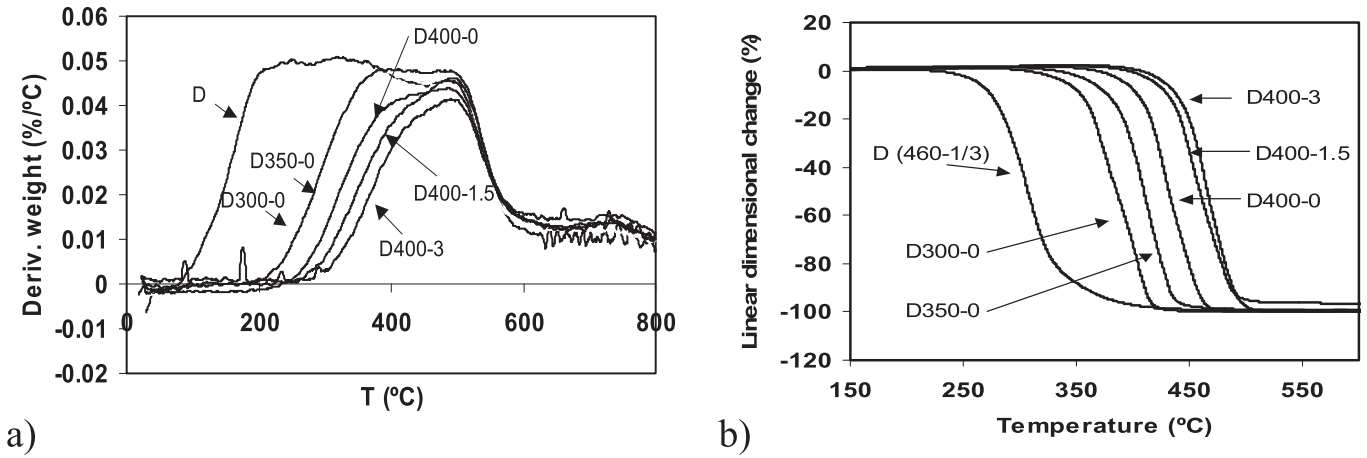
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Fig. 7. a) TGA derivative curves and b) TMA penetration mode for the original semicoke (D) and the post-treated powders [65]. Reprinted with permission from Elsevier.
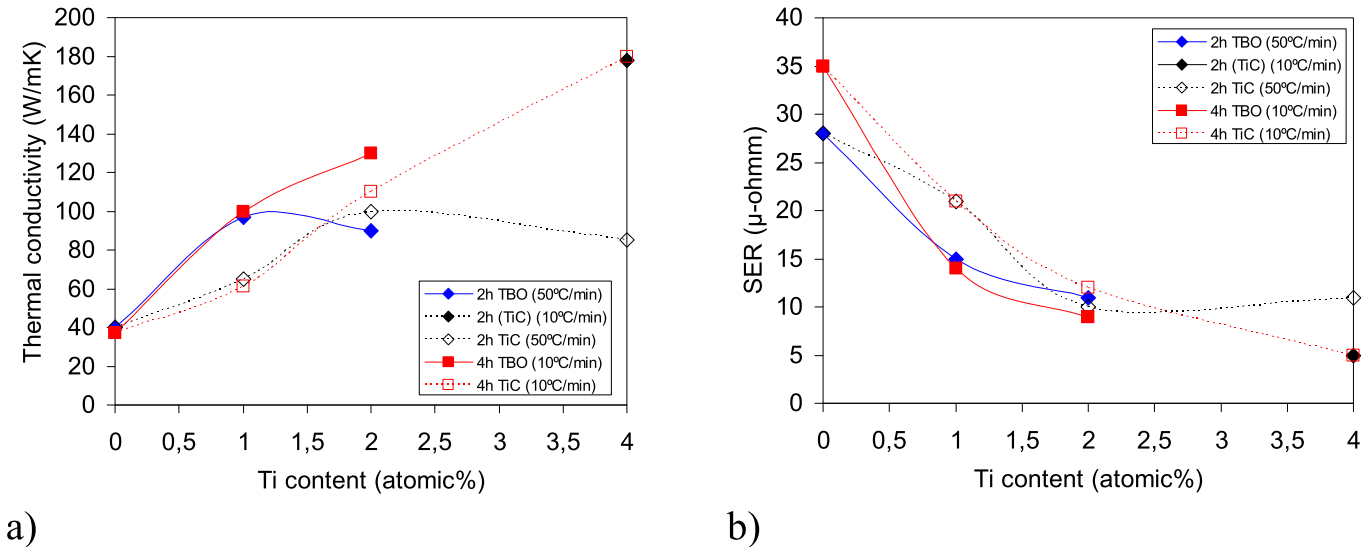

Fig. 8. Evolution of thermal conductivity (a) and electrical resistivity (b), at room temperature, with titanium content (atomic) [71]. Reprinted with permission from Elsevier. (A colour version of this figure can be viewed online.)

the synthesis of interpenetrated composite materials (Graphite-Al alloys, see Fig. 10) using the gas-assisted pressure infiltration technique (Gas Pressure Infiltration, GPI). The objective was to increase the fracture toughness of graphite structural materials. More specifically for its possible application as pistons in Otto-Engines. The main problem was that Al does not wet the carbon (remember the porosimetry of Hg), but reacts with it:

$$C + Al \rightarrow Al_4C_3; \ Al_4C_3 + H_2O \rightarrow AlOOH + CH_4$$
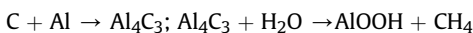
which leads to a deterioration of the interface and a drastic reduction in properties. First, all the variables related to the infiltration process (threshold pressure, permeability, drainage curves, contact angle), were studied [80–82], which allowed the development of a product with excellent properties that met the requirements of the end consumer [83,84]. New technologies were also developed such as infiltration with two liquid metals simultaneously [85], and improved wetting through the use of fluorinated salts [Morgan Award, Carbon congress Aberden 2006], which

allowed for a better knowledge and optimization of the process of infiltration [86].

7. Novel applications of carbon materials

One of the last achievements of Paco in the carbon field was the evaluation of carbon nanostructures as reinforcement agents for ocular therapeutics. This research was initiated in 2013 in close collaboration with Prof. Jorge L. Alió from the ophthalmological hospital VISSUM Corporation (Spain). The main goal of this investigation was to improve the mechanical properties of the cornea through the incorporation of single-walled carbon nanotubes (SWCNTs) and graphene. This approach is extremely important to treat degenerative diseases, such as keratoconus, associated with a progressive weakening and deformation of the cornea [87]. The selection of these nanostructures was based on their excellent mechanical characteristics, transparency, biocompatibility and reduced dimensions, needed to exhibit a proper diffusional performance through the collagen fibrils. In the first step of the project,
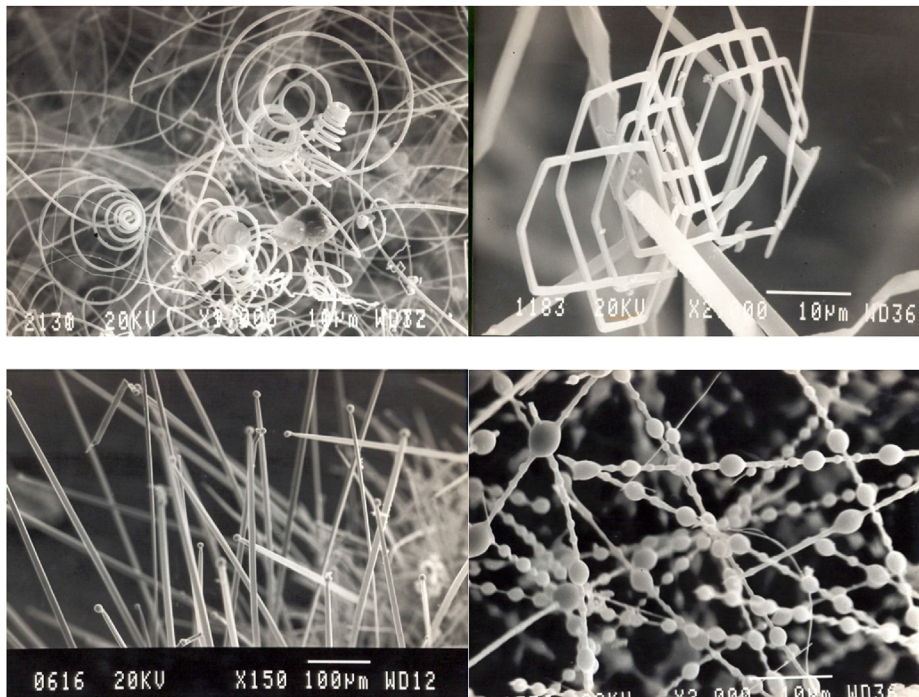
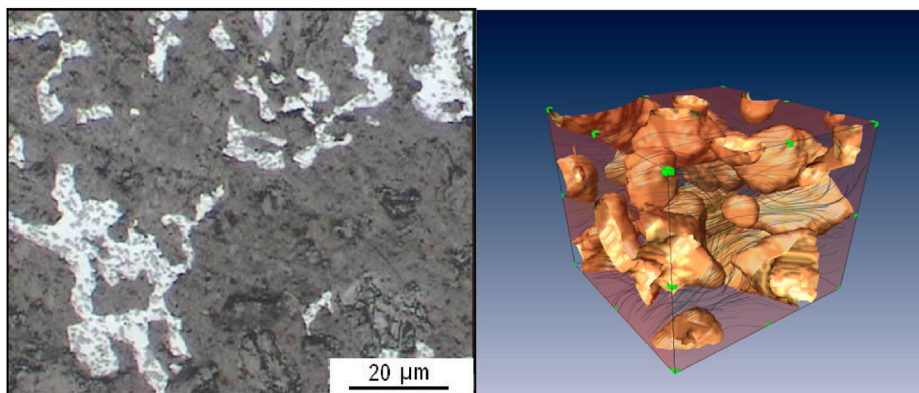**Fig. 9.** Whiskers of different silicon carbides produced at the LMA group.

Fig. 10. Micrograph of a Graphite/Al12Si composite material, simulation of flow line in the infiltration process based in the X-Ray-Tomography of the carbon precursor.

carbon nanostructures were incorporated into the cornea in a specific pocket created in the inner section of the corneal stroma (Fig. 11).

Following this approach, the mechanical properties of the cornea could be slightly improved [88]. However, the main limitation was the low dispersion of the nanostructures within the cornea, and their associated aggregation. That was a critical aspect since the presence of aggregated nanostructures in the cornea can alter/modify the visual field. To this end, in a second approach carbon nanostructures were incorporated using topical administration, after a proper removal of the epithelium [89]. Under these conditions, carbon nanostructures were homogeneously distributed within the first layers of the cornea. Furthermore, the mechanical properties were largely improved, and the obtained results in tangent elastic modulus were comparable to the actual cross-linking technology applied in patients. These results indicate that carbon nanostructures have a huge potential to be applied in ocular tissue reinforcement.

8. Paco's legacy to carbon science

It is clear that the contributions of Paco to the carbon field has been tremendous. He was the pioneer in Spain in this field with the initial studies at the University of Granada during his PhD working on the synthesis and characterization of activated carbons from olive stones. During this period there were no commercial equipments and he had to design the oven for the activation of the olive stones, as well as the adsorption equipment (volumetric systems), as shown below (Fig. 12).

This knowledge has been reflected in the well-known "Granada School", and some years later in the "Alicante School", with a number of excellent scientists grown up under Paco's umbrella that have been able to continue his legacy in the field of carbon materials worldwide.
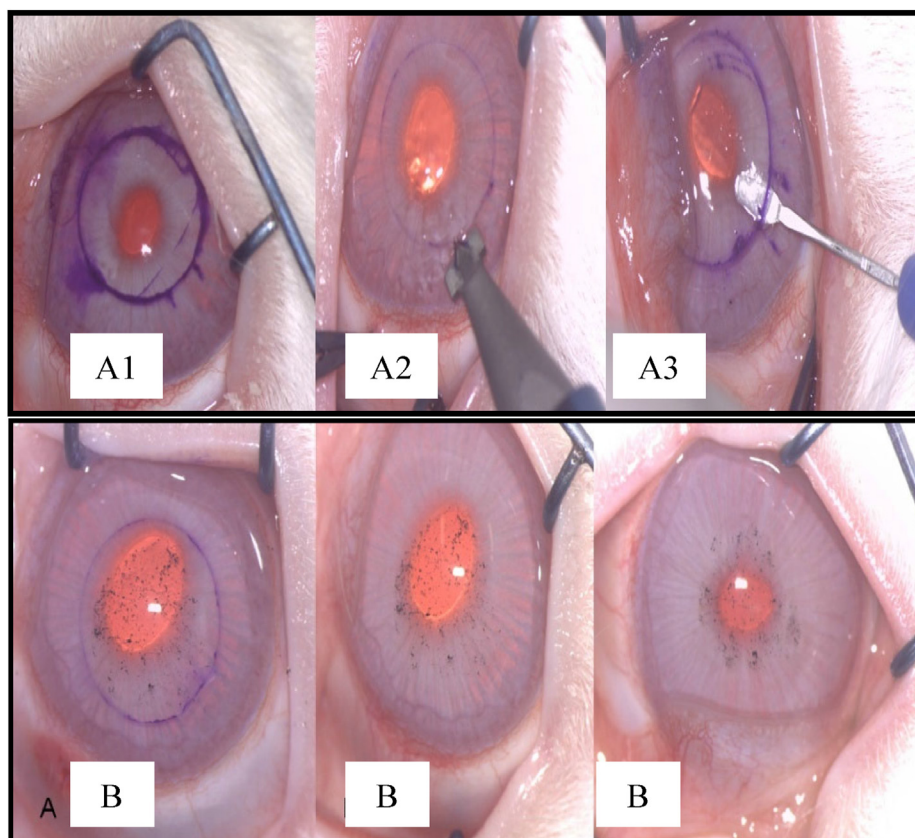
Fig. 11. (a) Rabbit eye at the moment of the surgical procedure showing the different steps for the creation of the pocket in the corneal stroma, and (b) Appearance of the dispersion composed of carbon nanotubes (CNTs) mixed with saline solution which concentration is 1 mg/ml. (A colour version of this figure can be viewed online.)
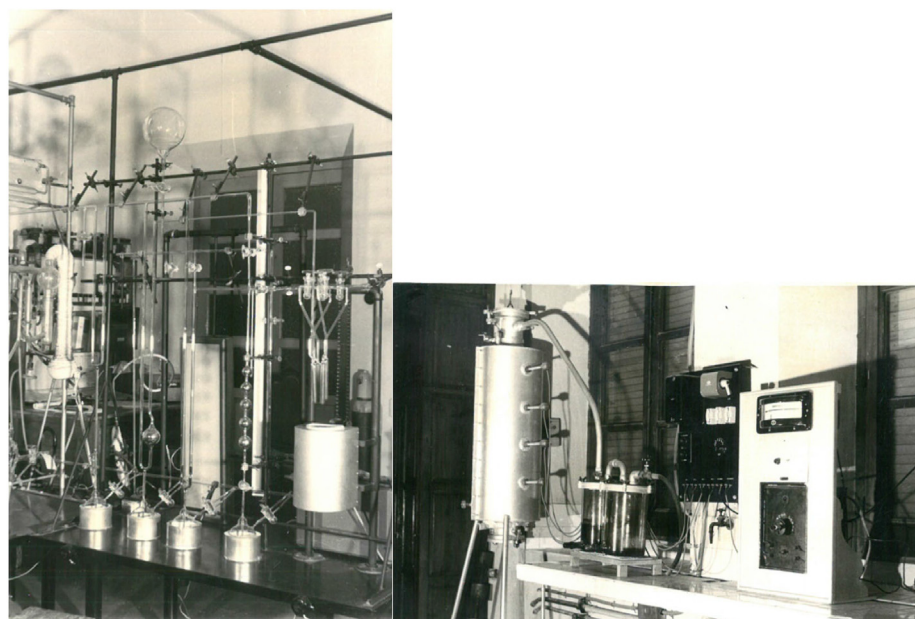

Fig. 12. Glass-made gas adsorption equipment (left) and activation oven (right) designed by Paco during his PhD.

In addition to be one of the first scientists in Spain working on carbon materials, Paco will be always remembered as a reference in the characterization of carbon materials using gas adsorption. The introduction of CO_2 adsorption at 273 K in the eighties as a complement to N_2 adsorption at 77 K was a stepping stone in the characterization of the porosity in samples with narrow constrictions, where nitrogen diffusion could exhibit kinetic restrictions. Paco and coworkers also devoted huge efforts to incorporate

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immersion calorimetry using liquids of different nature (polarity, molecular size and shape, etc.), as a powerful tool to complement gas adsorption during the characterization of textural properties and surface chemistry of materials. The incorporation of reference non-porous carbon materials (e.g., carbon black) in these calorimetric studies was fundamental to obtain information not only about the pore size distribution in activated carbon, but also to estimate the surface area accessible for a given molecule. All these efforts in the characterization of the porosity and surface chemistry of porous materials were crucial to improve the international recognition of Paco as a worldwide leader in the field of adsorption. To spread this knowledge Paco, together with Prof. Kenneth S.W. Sing, Prof. Jean Rouquerol, and Prof. Klaus Unger decided in 1987 to initiate a series of conferences (COPS conferences) devoted to stimulate the scientific debate about novel characterization tools (including modeling) for the evaluation of porous solids. These COPS conferences initiated by Paco and his colleagues in 1987 have been running every three years up to now. One of the last achievements of Paco and his group in the field of adsorption has been the adsorption of methane under wet conditions in the cavities of carbon materials. By taking advantage of the confinement effects in these cavities, the LMA group was able to significantly improve the storage capacity of methane via the formation of confined gas hydrates.

Besides adsorption, Paco was also a pioneer in the use of carbon as a support for metallic nanoparticles or as a catalyst by itself in a number of catalytic reactions (e.g., hydrogenation, oxidation, etc.). There has also been a significant contribution of Paco and his team in the design of novel materials with improved properties, such as graphites, composites, carbides, etc. Finally, it is important to highlight his contribution to the field of nanomedicine with drug delivery platforms and carbon materials as reinforcement agents. Overall, we can say that Paco was an exceptional scientist, very intuitive, hard worker, very strict in all his research, always giving priority to ethics and scientific rigour and, above all, an excellent person and an extraordinary mentor for all his students. We will miss Paco but his legacy will never be forgotten by the scientific carbon community.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

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