Research Article

Catalytic Chemical Vapor Deposition Synthesis of Carbon Aerogels of High-Surface Area and Porosity

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In this work carbon aerogels were synthesized by catalytic chemical vapor deposition method (CCVD). Ferrocene were employed as a source both of catalytic material (Fe) and of carbon. Gaseous hydrogen and argon were used as reductant and carrier gas, respectively. The products of reaction were collected over alumina. The morphology and textural properties of the soot produced in the reaction chamber were investigated using Scanning Electron Microscopy, High-Resolution Transmission Electron Microscopy, X-ray photoelectron spectroscopy, and N₂ physisorption (BET and BHJ methods). After the evaluation of the porous structure of the synthesized products, $780 \pm 20 \text{ m}^2/\text{g}$ of S_{BET} and $0.55 \pm 0.02 \text{ cm}^3/\text{g}$ of V_{BJH} were found. The presence of iron carbide and the partial oxidation of carbon nanostructures were revealed by XPS.

1. Introduction

The fabrication of carbon nanostructures with characteristic morphologies will determine further applications such as field emitters, gas storage (H₂ for fuel cells), sensors, and biosensors, and so forth [1]. The high capacity of adsorption, chemical inertia, and the easy regenerability that have the carbon nanostructures make them potential useful adsorbents [2].

Carbon aerogels are nanostructured porous materials consisting in a network of carbonaceous particles of uniform nanosized dimensions, with superficial areas that commonly are found between 400 and 1100 m²/g and an electric conductivity of approximately 1000 A/cm. They are highly demanded in scientific technology: the most important applications of these carbonaceous structures are as electrodes and supercapacitors, where they serve as support for metal nanoparticles [3, 4].

Carbon aerogels are usually synthesized by high-temperature pyrolysis of organic aerogels, which in turn are prepared by polymerization of two monomers (e.g.,

resorcinol-formaldehyde) using sol-gel methods and processing the resulting material under supercritical conditions [5, 6]. This type of synthesis involves several steps under very diverse conditions. Thus, a simpler preparation way would be an important advance in the synthesis of this kind of materials. Chemical Vapor Deposition (CVD) from hydrocarbon gaseous compounds or carbon monoxide is a relatively simple synthesis method that has been employed for the growth of carbon nanostructures [7]. When using metallic nanoparticles as catalytic sites for the growth of such carbon nanomaterials, it has been described as Catalytic CVD (CCVD) [8]. In particular, it has been proposed as a method for growing carbon nanotubes and filaments within the porous structure of conventionally prepared carbon aerogels [9, 10].

In this context, the objective of this work is to apply the technique of CCVD, employing a single organometallic compound, ferrocene [Fe(C₅H₅)₂], as source of both the catalyst and of carbon and a continuous flow reaction system with two separated heating zones.

FIGURE 1: CVD reactor scheme employed the synthesis of the carbon aerogels.

2. Experimental Setup

In order to synthesize the aerogels, ferrocene was used as a simultaneous source of catalytic material (Fe) and filler material (C). Gaseous hydrogen was employed as reductant, while argon was an inert carrier gas. The reaction products were collected onto either alumina or silica substrates.

A reaction chamber similar to that described previously [11] was employed. The ferrocene was sublimated in a preheating chamber, which temperature was set at 150°C and was transported to the cracking reactor by a flow of H₂ and Ar. In total, 150 mg of ferrocene was evaporated, in two consecutive steps of 100 mg and 50 mg, with 10 min in between. The pyrolysis temperature in the cracking furnace was 900°C, and the total gas flow was 10 mL/min with a composition of 1 : 1 v/v of Ar : H₂.

In order to eliminate Fe from the products, concentrated HCl and sonication were used. The resulting materials were characterized using Scanning Electronic Microscopy (SEM) with a JEOL scanning microscope, model JSM-6390, 30 KV; High Resolution Transmission Electronic Microscopy (HRTEM) with a JEOL transmission microscopy, model JEM-2100, 200 KV; X-ray Photoelectron Spectroscopy (XPS) with a Thermo Scientific VG-Escalab 220i-XL; N₂ physisorption with a Micrometrics Surface Analyzer, model ASAP 2000, using the BET and BJH methods for the textural analysis. In Figure 1 a schematic drawing of the CVD homemade reactor and experimental conditions is presented.

3. Results and Discussion

In Figure 2(a), three SEM micrographies of the synthesized carbon aerogel at different magnifications are shown, in which a network of carbon nanotubes and nanospheres can be observed. At the lower magnification, nanotubes foam clusters deposited on a SiO₂ substrate can be observed, while in the 5000x and 10000x micrographies the network of carbon nanotubes coated with nanospheres of carbon nanoparticles is clearly appreciated. The composition of these structures was determined by means of a chemical analysis by EDX in the same microscope, finding only C, Fe and O in weight percentages of 72.10; 26.84; 1.06%, respectively (see Figure 2(b)). The presence of oxygen could be attributed to surface oxidation of Fe nanoparticles due to exposition to the atmosphere when samples are removed

from the CVD reactor. Carbon aerogel grew evenly across the surface of SiO₂.

In Figure 3, four HRTEM micrographies of the synthesized carbon aerogel are shown in which it can be seen a network of carbonaceous structures, such as nanotubes and nanospheres (see micrographs (a) and (b)). In the micrographs (c) and (d), consecutive increases of (b) are shown, where it can be seen on average 40 nm diameter carbon nanospheres.

XPS tests revealed the presence of iron carbide and partial oxidation of carbon nanostructures. XPS spectra of carbon aerogels in the C 1s and Fe 2p regions are presented in Figures 4(a) and 4(b), respectively. In the first one, we see three peaks with binding energies (BEs) of 286, 284, and 280 eV, corresponding to the *sp*³ C–C bonds of tetrahedral structures, C–C *sp*² of graphitic structures, and Fe₃C, respectively [12–14]. The peak of iron carbide is displaced to a lower BE as compared to other reports (283 eV [13, 15]), this large shift of about 3 eV can be attributed to interactions with the magnetic field of nanoparticles of Fe or inefficient electrical connection that may exist between Fe and C atoms [14, 16]. A fourth peak that appears around 278 eV in the C 1s region, which is denoted by the symbol ψ , can be attributed to the fullerene carbon filaments [17].

In the Fe 2p region there are three peaks with BEs of 712, 720, and 726 eV. The 712 and 726 signals correspond to the 2p_{3/2} and 2p_{1/2} Fe³⁺ species, respectively, while the intermediate signal is due to a satellite of the same species [18].

In Figure 5, the N₂ adsorption isotherm at 77 K of the synthesized carbon aerogel can be observed. It is of type IV in the IUPAC/Brunauer-Emmett-Teller classifications, typical of mesoporous materials [19]. Given the very low increase of physisorbed volume below P/P_0 0.05, it can be deduced that the microporous volume is negligible in this sample. In the high-pressure region it appears a H₃ hysteresis loop at a relative pressure higher than 0.8. This indicates the existence of extraparticle large mesopores which could be formed between interconnected carbon nanoparticles [20]. After evaluating the pore structure of synthesized products by BET and BJH procedures, it is found a BET surface area, S_{BET} , of 780 ± 20 m²/g and BJH pore volume, V_{BJH} , of 0.55 ± 0.02 cm³/g. The measured surface area is quite large for a non-microporous material.

Ferrocene has been frequently employed as a precursor of iron catalysts for the CVD synthesis of carbon nanotubes

FIGURE 2: (a) SEM microographies of carbon aerogels on SiO₂, at 95x, 5000x, and 10000x. (b) EDX spectrum of carbon aerogels. K_α characteristics peaks are observed for C, O, and Fe.

FIGURE 3: HRTEM microographies of carbon aerogels. The displayed scale bars are (a, b, c) 200 nm and (d) 50 nm.

FIGURE 4: XPS spectra of carbon aerogels: (a) C 1s region, and (b) Fe 2p region.

FIGURE 5: N_2 adsorption isotherm type IV (77 K) of Carbon Aerogels.

[21, 22], normally used as carbon source organic gases or vapors (hydrocarbons, alcohols, etc.). It has been much less employed for carbon nanotube preparation as the sole source of catalyst and carbon [23]. In the present work it is proposed a simple CCVD methodology for the synthesis of carbon aerogels uses ferrocene as source of both Fe catalyst and of carbon filler material. The proposed method is simpler than the usually employed synthesis through organic aerogels, which involves several steps under conditions varying in an ample range. A key procedure in the methodology reported is the division in two consecutive steps of the evaporation of the ferrocene, with a short time in between the two evaporation steps. This way, a two-phase system is generated, with imperfections in carbon nanotubes, which couple with nanocapsules of carbon nanotubes produced in the second step, finally leading to the carbon aerogels.

4. Conclusions

Using the CCVD method and ferrocene as the starting material, carbon aerogels with surface areas and pore volumes of $780 \pm 20 \text{ m}^2/\text{g}$ (S_{BET}) and of $0.55 \pm 0.02 \text{ cm}^3/\text{g}$ (V_{BJH}),

respectively, are obtained. The large surface area is not due to microspores but to mesopores formed by the aggregation of carbon nanostructures. These porous properties are promising features for applications in the physisorption of gases, for example, in the storage of molecular hydrogen for fuel cell applications. The XPS tests revealed the presence of iron carbide and the partial oxidation of carbon nanostructures.

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