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Effect of the reaction time on the microstructure and porous texture of carbon materials obtained by chlorination of $Ti(C_5H_5)Cl_2$

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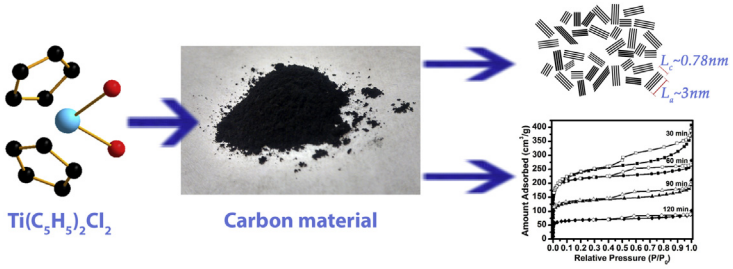
HIGHLIGHTS

- Micro-mesoporous carbon materials were obtained by chlorination of $Ti(C_5H_5)_2Cl_2$ at 900 °C.
- The effect of chlorination exposure time on the microstructure and textural properties was studied.
- Microstructural analysis by XRD and Raman showed that carbon samples are mainly disordered.
- N_2 adsorption/desorption isotherms showed isotherms type 1 with hysteresis H4.
- Micropore size increases at longer chlorination time; in contrast, pore volume decreases.

GRAPHICAL ABSTRACT



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ABSTRACT

Carbon materials have been obtained by the chlorination reaction of $Ti(C_5H_5)Cl_2$ at 900 °C, varying the reaction time at 30, 60, 90 and 120 min. The average microstructure, studied by X ray powder diffraction, suggest that these materials consist mainly of disordered carbon with low graphitization degree (from 13.5 to 16.5%). These results are in agreement with the Raman data since the D band (at ≈ 1350 cm^{-1}) indicates that disordered carbon networks have appeared. The calculated in-plane correlation length increases from 4.04 to 4.70 nm as the chlorination time increases from 30 to 120 min. The textural analyses reveal adsorption isotherms type 1 with hysteresis H4, microporous areas as high as 855 m^2/g and pore volume of 0.55 cm^3/g. Additionally, an important contribution of mesoporosity, around 3.6 nm, was also detected.

1. Introduction

The last few decades have shown important interest in the development of novel carbon nanomaterials with specific characteristics such as high surface area, defined shape and controlled pore size distribution [1,2]. This significant attention is strongly related to their nanostructure and also due to a wide range of applications, going from gas adsorption, molecular sieves, catalytic support, electrodes in batteries and supercapacitors, systems of air and water purification or even medical devices [3].

There are many ways to produce carbon materials. The classical procedures require extremely severe synthetic conditions; for

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instance, high temperature is required to produce ordered graphitic materials due to the very low mobility of carbon atoms in its covalent layers [4]. Diamond and related structures are produced either at high pressures or using plasma [5] that is also the main way for fullerenes and nanotubes manufacture [6], nevertheless recent works make possible the formation of these structures by gas-injected arc-in-water method using low pressures but high temperatures [7], additionally hierarchical assembly and aqueous phase exfoliation methods are also available [8,9]. However, recent progress in materials science have delivered nanostructured carbons from several high refractory precursors like metal carbides with a simple extraction of their metals by different methods such as, leaching in supercritical water, high-temperature treatment in halogens, vacuum decomposition and others [4]. These techniques can be used to produce carbon coatings, bulk and powder carbon [7,4]. Moreover, in the last couple of years, novel techniques to extract functionalized nanoporous hybrid carbon from metal-organic frameworks have been developed [11,12]. And even thought, direct carbonization of metal-organic frameworks is found to be a straightforward route for the preparation of nanoporous carbons possessing an extremely high surface area [12,13]; as one of the newest techniques the expected functionalities are very limited and may require further investigation.

In contrast, chlorination reaction to produce carbon from metal carbides as precursors, known as carbide-derived carbon (CDC), has been well accepted in the scientific community since it allows the synthesis of almost every carbon allotropic form and microstructure without using extremely high temperatures, pressure or vacuum [4]. The vastly differences in microstructure of carbon materials obtained from this method are achieved by tuning the synthesis conditions; as an example, TiC is used for obtaining disordered graphitic planes and even onion like structures just varying the reaction temperature [14]. On the other hand, SiC is used to obtain carbon onions and diamond-like carbon [9,14,15]. Disordered and barrel-like carbons were obtained from Al4C3 [16] while ordered/disordered carbon was obtained from VC [17], WC [18], B4C [19] and recently also from TiC as a result of the introduction of hydrogen in the chlorine flow [20]. However, most of these studies describe the differences in the CDCs microstructure in close correlation with the reaction temperature variation. Only a few studies report that the reaction time also affects the microstructure of the CDC. One of them explains the effect of chlorination time on the CDC microstructure starting from SiC whiskers. Authors described that the kinetics of the chlorination reaction was found to be linear, indicating that transformation of SiC into CDC was controlled by the interface reaction time [21].

Even though metal carbides have been the principal source to produce carbon materials, via chlorination [1], organometallic compounds offer an alternative approach to obtain carbon nanostructures applying the chlorination scheme since their chemical composition provides the carbon source and the metal catalyst [22]. The chlorination of organometallics can be used to obtain several carbon nanostructures, for instance, carbon nanotubes, bags, lobes, and branches, just adjusting the synthesis conditions i.e. temperature and reaction time [23].

Several studies of carbons derived from organometallic compounds via halogenation focus on ferrocene [24]. However, bis(-cyclopentadienyl)tungsten dichloride [18], bis(cyclopentadienyl) titanium dichloride [25], chromocene [26,27], chromobenzene [28], and cobaltocene [29], as carbon precursors, have been also reported. These works analyzed the effect of chlorination temperature on the final carbon structure by Transmission Electron Microscopy and other associated techniques. Only on carbons derived from ferrocene the role of the reaction time was also analyzed [24].

$Ti(C_5H_5)Cl_2$ is a bis(cyclopentadienyl) derivate, which change the regular composition of the basic cyclopentadienyl, $M(C_5H_5)_2$, to the $M(C_5H_5)_2Cl_2$ one. In addition, $Ti(C_5H_5)Cl_2$ does not adopt the typical "sandwich" structure, like ferrocene, due to the four ligands around the metal center. Election of $Ti(C_5H_5)Cl_2$ as carbon precursor lies in its relative low cost, easy accessibility, high stability in presence of air and high reactivity in presence of chlorine gas, at relative low temperatures.

The present work describes the influence of the chlorination time on the microstructure and porous texture of carbon materials obtained by chlorination of $Ti(C_5H_5)Cl_2$, as carbon precursor, at 30, 60, 90 and 120 min. Besides, the microstructural changes and textural parameters measured by Raman spectroscopy, X-ray powder diffraction (XRD) and nitrogen adsorption/desorption at 77 K. The complex porous structure of this type of carbonaceous materials was assessed by phenomenological and empirical methods applied to the textural data.

2. Experimental

2.1. Synthesis

Carbon samples were obtained by the chlorination reaction of bis(cyclopentadienyl)titanium(IV) dichloride. 0.35 g of the precursor from Sigma–Aldrich, (purity of 97%), melting point of 289 °C, P-1 space group with triclinic structure and lattice parameters a = 0.7882 nm, b = 1.9478 nm, c = 1.2156 nm, α = 90.46°, β = 102.58°, γ = 143.49° [25], were placed in a quartz vessel while heating in a tube furnace. Previously, the reactor was purged with pure N_2 gas at 30 cm^3/min during 30 min. Then, additionally to the N_2 flow, a continuous flow of chlorine gas at 50 cm^3/min flooded the chamber and the temperature raised up to 900 °C with a heating rate of 50 °C/min. Once the temperature reached 900 °C, the reaction was kept for 30, 60, 90 or 120 min, respectively. After each, the furnace was turned off and the chlorine gas flow was closed remaining only the N_2 flow during cooling time in order to remove the excess of chlorine and metal halides. Such volatiles were neutralized with NaOH saturated solution at the reactor exit. The main reaction between the precursor and the chlorine could occur as follows:

$$Ti(C_5H_5)_2Cl_2 + 6Cl_2 \xrightarrow{\Delta} 10C + TiCl_4 + 10HCl \quad (1)$$

During the reaction, a light yellow gas appeared indicating the formation of the $TiCl_4$ halide, as main phase, rather than the $TiCl_3$ which is a red-violet gas. Presence of the $TiCl_4$ phase could be attributed to its lower boiling point (140 °C) compared to the 960 °C of the $TiCl_3$. A possible explanation for the formation and elimination of the metal halide has been recently proposed [26]. Here, a model describes the equilibrium between both phases ($TiCl_4$ and $TiCl_3$) in presence of Cl_2, according to the reaction squeme: $2TiCl_{3(s,g)} + Cl_{2(g)} \leftrightarrow 2TiCl_{4(g)}$. So, at this stage the formed halide is partially eliminated, by its own diffusion rate, but is also trapped among the carbon fragments particles, yielding (after its elimination) the porous texture. The complete elimination of the metal halide, takes place slowly, due to an increment of the chlorination temperature up to 900 °C and by exposing the samples at different reaction times. In addition, the flow of nitrogen during the cooling of the reactor promotes the total elimination of the trapped halide.

2.2. Characterization techniques

2.2.1. Microstructure

The X-ray powder diffraction (XRD) analyses were done using a Bruker D8 Advance X-ray diffractometer, wavelength of 0.15406 nm from 10° to 80° in 2θ. It is well known that the Scherrer equations