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THERMOGRAVIMETRIC STUDIES ON THE ACTIVATION OF NANOMETRIC CARBON FIBERS

*F. Suárez-García**, *J. Nauroy, A. Martínez-Alonso and J. M. D. Tascón*

Instituto Nacional del Carbón, CSIC, Apartado 73, 33080 Oviedo, Spain

Nanometric vapor grown carbon fibers (VGCF) constitute an attractive, novel precursor for nanostructured fibrous carbon adsorbents, but their highly ordered structure is a possible drawback to activation. The objective of this work was to evaluate VGCF reactivity toward different agents for physical or chemical activation. TG results showed that CO_2 gasification of VGCF begins at about 823 K and becomes more pronounced above 1123 K. Catalyzed gasification was studied using VGCF impregnated with either 1 or 20 mass% K_2CO_3 or KOH, which was gasified with CO_2 in the same thermobalance. Both compounds, especially KOH, exhibited strong catalytic effects on VGCF gasification. The VGCF were also impregnated with K_2CO_3 and KOH in amounts typical for chemical activation. In this case, reaction begun at about 943 K, and reactivity was maximal at 1123 K. VGCF reactivity with KOH was higher than with K_2CO_3, the effects of both compounds becoming stronger as their concentrations increased.

Keywords: *nanoporous carbons, TG, vapor grown carbon fibers (VGCF)*

Introduction

There is nowadays an increased interest in the thermal characteristics of materials with a nanometer scale [1]. This work concerns the use of thermogravimetry to evaluate the reactivity of a nanostructured material, namely nanometric vapor grown carbon fibers (VGCF). This material is obtained by pyrolytic decomposition of hydrocarbons at temperatures of the order of 1373 K in presence of catalysts (usually iron or iron-containing) in form of ultrafine metallic particles [2–7]. The catalyst can be either deposited on a substrate (seeded catalyst method), or directly injected into the gas (floating catalyst method). Fiber growth takes place in two steps. First, carbon filaments or nanofibers are formed by carbon dissolution and diffusion on the exposed catalyst surface; the fibers grow in length and this step ends when the catalyst particle becomes fully covered with carbon. In the second step the fibers grow in width by pyrolytic deposition of carbon [2, 4, 7–9]. Due to the difference between these two regimes, the internal filament in the VGCF is highly ordered (graphitic) whereas the outer pyrolytic layers exhibit a lower degree of structural order [8, 9]. Fiber thickening by pyrolytic carbon deposition occurs very rapidly when using the floating catalyst method; however, in the case of seeded catalyst, this type of growth must be favored by increasing the residence time. Nevertheless, considered as a whole, these fibers are much more graphitic than other more conventional types of carbon fibers.

The small diameter of VGCF makes them an attractive precursor for nanostructured fibrous porous carbons utilizable in adsorption, gas storage, etc. Moreover, the ordered structure and high electrical and thermal conductivities of VGCF offer potential advantages for certain applications of the resulting carbon porous materials, e.g., when used as electrodes. Conversely, the graphitic structure of VGCF can constitute a serious drawback for their activation, particularly physical activation, in comparison with highly isotropic carbon fibers [10–12]. Therefore, the objective of this work was to explore the possibility of using VGCF as precursor for porous carbon adsorbents. To this end, thermogravimetry (TG) has been used to study the interaction between nanometric VGCF and different activating agents, used either in physical activation (oxidizing gases) and/or in chemical activation (potassium compounds).

Experimental

The VGCF used in this work were of type Pyrograph III, grade PR-24-PS (Pyrograph products, Inc., Cedarville, OH, USA). Previous characterization by STM [9] evidenced the occurrence of skin-core structure in this material, which was not unexpected as it was prepared by the floating catalyst method. The VGCF had a density of 1.95 g cm^{-3}, a diameter comprised between 50 and 150 nm, and a length of 30–100 μm. Their proximate analysis was carried out following ISO standards,

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* Author for correspondence: fabian@incar.csic.es

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

by determining the mass losses at 373 K/air (moisture), 1173 K/inert atmosphere (volatile matter), and 1088 K/air (ash). Elemental analysis was carried out in a LECO CHNS-932 microanalyzer provided with a LECO VTF-900 accessory for oxygen.

TG studies were performed in a CI Electronics microbalance, using ca. 20 mg sample and a gas (Ar or CO_2) flow of 50 STP cm^3 min^{-1}. The VGCF samples were used either fresh or impregnated with different amounts of K_2CO_3 or KOH. Impregnations with potassium compounds were done by mixing 2 g of VGCF with 200 mL of solutions of different concentrations of either KOH or K_2CO_3. Then the slurry was boiled while stirring until reaching complete evaporation of excess water. Finally, the resulting solids were dried for 12 h at 383 K in a vacuum furnace. The impregnation ratio, calculated as X_i=[(g chemical agent/g VGCF)·100], was varied between 1 and 400%.

Results and discussion

Proximate analysis of the studied VGCF gave 0.2 mass% moisture, 2.1 mass% ash (attributable to the metallic catalyst used in their preparation) and 0.75 mass% volatile matter (dry basis). Elemental analysis (dry basis) gave 95.6 mass% C, 0.16 mass% H, 0.76 mass% N, 0.53 mass% S and 0.73 mass% O. This agrees with expectations for a material rich in carbon and poor in functional groups.

Figure 1 shows TG curves obtained during heating at 10 K min^{-1} of fresh VGCF from room temperature to 1273 K under inert (Ar) or slightly oxidizing (CO_2) gas flow. Mass loss begins at ca. 823 K in either atmosphere. As expected from proximate and elemental analysis results, heating of VGCF in inert atmosphere results in a small mass loss (4.1 mass% at 1273 K under Ar, Fig. 1). This can be associated with elimination of heteroatoms as well as volatilization and/or decomposition of amorphous pyrolytic carbon (soot) that unavoidably accompanies VGCF and is formed in parallel with them [5, 9]. In the TG curve obtained in CO_2, mass loss becomes pronounced above 1123 K, attributable to carbon gasification. As indicated in the Introduction, the objective of this work is to gain some insight on the possibility of using VGCF as precursor for porous carbons. Based on Fig. 1, a suitable temperature for physical activation with carbon dioxide would be ca. 1123 K.

The rate of gasification with CO_2 will depend, among other factors, on the structural order of the carbon material [13]. In general, an increase in the degree of structural order lends a decrease in reactivity [13, 14]. The studied VGCF are highly ordered [7, 9], therefore their reactivity for gasification is low. An alternative to make the process more feasible from a practical point of view is catalytic gasification; in this context, it is well known that carbon gasification is catalyzed by alkali and alkaline-earth metal compounds [15–19].

Figure 2 compares the TG curves corresponding to gasification with CO_2 of VGCF, fresh or impregnated with different amounts of KOH or K_2CO_3 at 1123 K (temperature at which an increase in mass loss rate was observed for VGCF in presence of CO_2, Fig. 1). These experiments were aimed at simulating a typical physical activation process, thus the samples were heated at 10 K min^{-1} to 1123 K in inert atmosphere (argon flow of 50 STP cm^3 min^{-1}), kept for 10 min under the same Ar flow until the temperature was stabilized and then the gas was changed to CO_2 (flow of 50 STP cm^3 min^{-1}). As can be seen in Fig. 2, the mass loss rate increases in presence of potassium compounds. The gasification rates calculated from the slope of the linear, intermediate part of the isothermal curves were $8.3\cdot10^{-5}$ (non-impregnated VGCF), $1.6\cdot10^{-4}$ (1 mass% K_2CO_3), $2.4\cdot10^{-4}$ (1 mass% KOH), $8.0\cdot10^{-4}$ (10 mass% KOH), and $9.5\cdot10^{-4}$ g min^{-1} (20 mass% K_2CO_3). Therefore, both

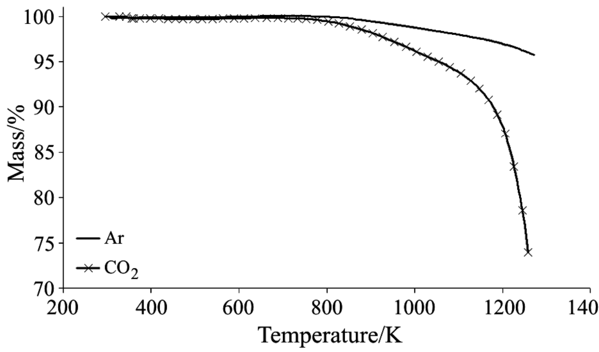

Fig. 1 TG curves of VGCF under two different atmospheres: inert (argon) and oxidative (CO_2). Gas flows of 50 STP cm^3 min^{-1}. Heating rate of 10 K min^{-1}

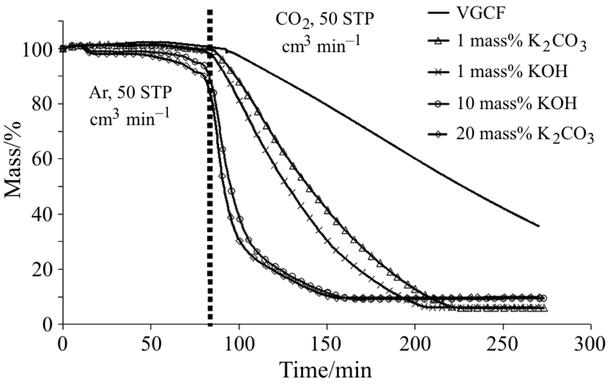

Fig. 2 TG curves corresponding to gasification with CO_2 of VGCF fresh or impregnated with different amounts of KOH or K_2CO_3 at 1123 K

potassium compounds catalyze the gasification of VGCF with CO_2, the effect of KOH being stronger.

An alternative method to prepare carbon porous adsorbents is chemical activation, which consists in heating the precursor in inert atmosphere in presence of an added chemical compound. The most common chemical activating agents are different chlorides (e.g., $ZnCl_2$), acids (e.g., H_3PO_4) and carbonates or hydroxides of alkali metals. The chlorides and acids are dehydrating agents well suited to activate precursors giving rise to abundant volatile evolution, such as lignocellulosic feedstocks [20–24]. On the other hand, alkali hydroxides and carbonates can be used to activate high-rank coals (anthracites), chars or even activated carbons [25–27]. As indicated previously, the studied VGCF have a low volatile matter yield (0.75 mass%) and they are highly ordered materials; therefore, KOH and K_2CO_3 are the most suitable chemical activation agents for this type of precursor.

Figure 3a and b shows the TG curves obtained during heating in inert atmosphere (Ar flow of 50 STP cm^3 min^{-1}) of VGCF samples impregnated with KOH (Fig. 3a) or K_2CO_3 (Fig. 3b) in amounts of the order of those typically used in chemical activation of other precursors with these additives (impregnation ratios from 1 to 400%). With both reagents, a single mass loss step is observed, the magnitude of which increases with increasing impregnation ratio.

In Fig. 4a and b are given the derivative thermogravimetric (DTG) curves calculated from the TG curves in Fig. 3a and b. For both activating agents, and for all the impregnation ratios used, the mass loss step begins at ca. 923 K. As the impregnation ratio increases the mass loss increases and there is a progressive displacement of the characteristic temperatures for the end of mass loss and for maximum mass loss rate.

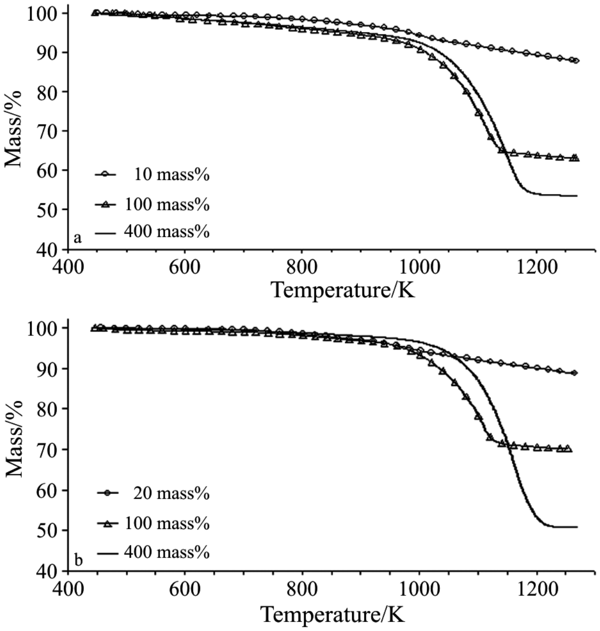

Fig. 3 TG curves of VGCF impregnated with different amounts of a – KOH or b – K_2CO_3 in inert atmosphere (Ar flow of 50 STP cm^3 min^{-1})

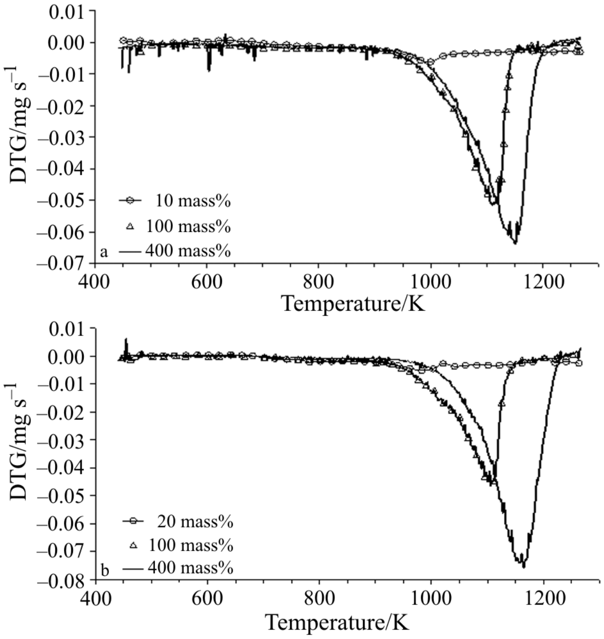

Fig. 4 DTG curves calculated from the TG curves in Fig. 3 (a and b)

Taking into account that the melting and boiling points of KOH are, respectively, 679 and 1600 K [28] and that K_2CO_3 melts at 1171 K and decomposes before boiling [28], the mass loss observed is attributable to a reaction between the VGCF and the corresponding reagent. Results from Figs 3 and 4 indicate that the temperature for chemical activation of VGCF with KOH and K_2CO_3 should be comprised between 923 and 1223 K as it is in this interval where the reactions between VGCF and the two activating agents take place.

In summary, TG/DTG studies have allowed us to identify reactions between VGCF and physical and chemical activating agents and to select suitable conditions for physical or chemical activation. The occurrence of such reactions involving mass loss does not imply necessarily that porosity development has taken place, since the process could merely involve external carbon burning. However, recent results from our team [29] have demonstrated that both physical and chemical activations produce significant surface area and pore volume development, the best results being obtained by chemical activation with KOH. These results will be the subject of subsequent publications.

Conclusions

Thermogravimetric studies have allowed us to evaluate the reactivity of nanometric VGCF toward different activating agents, and to select suitable operation conditions for the preparation of carbon adsorbents from these fibers by either physical activation with CO_2, physical activation catalyzed by potassium salts, or chemical activation.

Gasification of VGCF with CO_2 becomes significant above 1123 K, which is the temperature to be selected for their physical activation.

The use of small amounts of potassium compounds catalyzes VGCF gasification with CO_2 at 1123 K. Of the two compounds used (KOH and K_2CO_3) the former has a stronger catalytic effect. Therefore, from the point of view of energy saving, it seems interesting to carry out physical activation with CO_2 of VGCF pre-impregnated with small amounts of KOH or K_2CO_3.

Both KOH and K_2CO_3 react with the VGCF above 923 K. Consequently, the chemical activation with these compounds has to be carried out at temperatures higher than 923 K.

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