

SYNTHESIS OF GRAPHITIZED MICROPOROUS CARBONS PREPARED BY HEAT TREATMENT OF ORDERED POROUS CARBON MATERIALS

Cathie Vix-Guterl¹, S. Saadallah¹, Michel Trinquecoste², Mohammad Reda^{1,3}, Julien Parmentier³, Joël Patarin³ and Pierre Delhaes²

¹*Institut de Chimie des Surfaces et Interfaces (ICSI), CNRS, Mulhouse (France)*

²*Centre de Recherche Paul Pascal et Laboratoire de Physicochimie Moléculaire, CNRS et Université Bordeaux (France),*

³*Laboratoire de Matériaux Minéraux (LMM), CNRS, ENSCMu, UHA (Mulhouse)*

Corresponding author e-mail address: C.Vix@uha.fr

Introduction

Ordered porous carbon materials can be synthesized by a templating process [1]. These new materials are interesting for several potential applications mainly related with their specific chemical reactivity (as catalyst supports or selective adsorbants) or microporous electrodes for energy storage [2]. The proposed templating process can be summarized in two steps: (i) the carbon precursor is infiltrated in the porosity of the pristine inorganic material (the template) and further carbonized if necessary, (ii) the carbon is recovered after removal of the template by an acid treatment. The resulting carbon materials present the particularity to display an ordered interconnected porosity, a high specific surface area, a high total pore volume associated with a possible bimodal micro-mesoporosity [1,3,4,5]. The structure and the texture of these carbons can be controlled and modulated by the choice of the silica template and the type of carbon precursor and consequently the processing way as already explained in previous works [4,5,6]. Generally, the carbon corresponds to the template replica since the pores and the walls of the template become the walls and the pores of the carbon, respectively. However, modifications may occur during the synthesis like the formation of an additional microporosity or a symmetry change [5,7]. They depend on the nature of the template, of the carbon precursor and consequently on the selected deposition or impregnation way. The ordered porous carbon materials have been obtained at a carbonization temperatures lower than 1000°C. At these temperatures, the structural organization of the pregraphitic carbons at the atomic scale is poor and a further heat temperature treatment (HTT) can furnish a more developed graphitic type organization [8,9]. Starting from these general statements, the following questions then arise: (a) Is it possible to synthesize a carbon material with an ordered porous structure and graphitized carbon walls?, (b) How does the carbon organization is related to the type of carbon precursor and the pristine template used ?. To try to answer to these questions three type of ordered porous carbon materials were heat treated at 2500°C in inert atmosphere. These materials are synthesized using an organized mesoporous silica (type SBA-15) and three different carbon precursors (propylene, sucrose and pitch). These precursors belong to classical types of carbon materials, either soft-type (graphitizing carbons) or hard-type (non-graphitizing carbons) [8]. Therefore, the

structural evolution of the three types of synthesized carbon materials should be different during the heat treatment. The thermal evolution of the carbon materials is followed by using different techniques as explained in the experimental part.

Experimental

The carbon precursors (propylene, sucrose and mesophasic pitch) are introduced in the template porosity by chemical vapor infiltration at 750°C or liquid impregnation, respectively. After liquid impregnation, the carbon samples are further stabilized above 900°C. The synthesis procedure is detailed elsewhere [1,4,5]. The materials synthesized are named CX (X= Pr, S or P and is relating to propylene, sucrose or pitch, respectively). The obtained carbon materials were then heat-treated at 2500°C during 1.5 hour in nitrogen atmosphere in a graphite furnace. After heat treatment, the carbon materials are noted CXT. The characteristics of the carbon materials before and after heat treatment like the intrinsic density, the structural and textural ordering, the porosity are determined by using XRD, gas adsorption techniques, transmission electronic microscopy but also Raman spectroscopy which is now recognized as a well adapted tool for the characterization of graphitic carbon materials [10]. The determination of the structural characteristics of ordered porous carbons by Raman spectroscopy is detailed elsewhere [11,12].

Results and Discussion

We have shown in previous work [5] that the organisation of the porous structure is preserved at temperatures as high as 1500°C. Only a slight decrease of the unit cell parameter (3%) and of the total surface area (15%) is observed after a heat treatment at 1500°C; the microporosity decrease in particular for the sucrose-based carbon is also confirmed [5,13]. On the contrary, the heat treatment at 2500°C leads to important structural and textural changes as shown by the results reported in Table 1. In this table, the characteristics of the carbon materials CPr, CS and CP determined before and after heat treatment at 2500°C are summarized. La corresponds to the in-plane crystallite size. This value determined by Raman spectroscopy is a good graphitization witness [14].

Materials	<i>a</i> (nm)	<i>TSA</i> (m²/g)	<i>Density</i>	<i>Weight loss</i> <i>During HTT</i> %wt.	<i>La</i> (nm)
CPr	10.5	713	2.09	-	2.2
CPrT	/	220	1.47	18	4.6
CS	9.4	1470	2.35	-	2.3
CST	/	284	1.41	28	14.5
CP	10.3	923	2.03	-	2.7
CPT	/	150	1.58	28	4.4

As expected, the carbon with the highest initial oxygen content shows the highest weight loss during the heat treatment due to the departure of small oxygenated groups and other hydrocarbon molecules. As seen in Table 1, a significant decrease of the total surface area is measured. TEM observations show the existence of local well-organized porous areas but the long-range ordering is lost (as confirmed also by X-Ray diffraction). The total surface areas measured are higher than the corresponding geometrical surface ($0.5 \text{ m}^2/\text{g}$) of the carbon materials; this geometrical surface is roughly calculated assuming the powders as spherical particles of a mean size equal to $0.5 \mu\text{m}$ (indicated by TEM observations). This suggests that mesoporosity is still present after treatment as also indicated by the isotherms (Figure 1). As seen in figure 1, a strong decrease of the microporosity is observed. The predominant effect is the conversion of open micropores to closed ones. This is confirmed by the resulting helium density which is located around 1.40 after heat treatments, such value is typical for a glasslike carbon obtained for a non-graphitized carbon [15]. The disappearance of these open microporosities is related with the textural change occurring under HTT (collapse of the initial microstructure). From Raman results (L_a values), it turns out that the graphitization process is sensitive to the different types of carbon precursors (sucrose, propylene, pitch). The most curious results concerns the “ex-sucrose” carbon materials which are well graphitized as confirmed by the large in-plane correlation length L_a . This result is very surprising since sucrose is known to give a hard-type carbon; it should be remembered however that after grinding or other mechanical treatments which release the mechanical constraints, an heterogeneous graphitable carbon can be found [16]. Finally a new type of carbon materials which display the particularity to have a graphitized nano size porosity have been obtained.

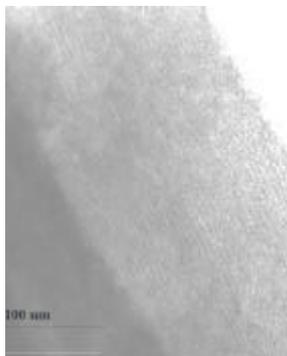


Figure 1: TEM image of sample CP15 heat-treated at 2500°C

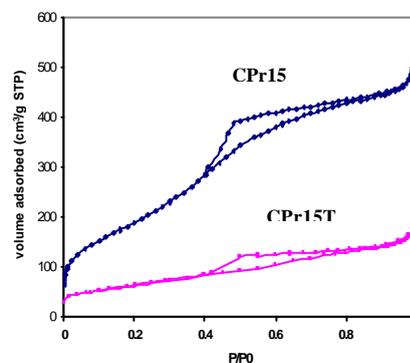


Figure 2: Nitrogen adsorption/desorption isotherms for materials CPr15 and CPr15T

Conclusion

The carbon precursors used in this work belong to two classes of carbon materials: soft-type or graphitizing carbons (propylene and pitch) and hard-type or non-graphitizing carbons (sucrose). In other words, the carbons prepared from the sucrose should be less well-organised as the carbons issued from propylene or pitch after a high temperature heat treatment. Since the carbon materials studied here are formed in a confined surface represented by the pores of the silica template, their synthesis conditions are different from those used for classical bulk carbons and the reversed result is found for the three different precursors. The graphitization process itself modifies the porosity distribution with the formation of closed micropores, due to a large textural change when the template effect is lost under high temperature treatment. This new fact opens the way to control both the pore sizes and the nature of their walls which is crucial to select an adsorption phenomena.

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