RAMAN SPECTROSCOPY: AN USEFUL TOOL FOR THE CHARACTERIZATION OF ORDERED POROUS CARBON MATERIALS

C. Vix-Guterl[1], M. Couzi[2], S. Saadallah[1], M. Reda[1,3], J. Parmentier[3], J. Patarin[3] and P. Delhaes[2]

[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 synthesized by a templating process are actively studied due to the numerous potential applications offer by this type of carbon materials. They present the particularity to display an interconnected porosity, a high specific surface area, a high total pore volume associated with a micro-mesoporosity. The structure and the texture of the carbons at a nanometric scale can be controlled by the choice of the silica template and the type of carbon precursors (and consequently the impregnation route) as already explained [1,2,3]. Besides the conventional characterization methods (XRD, nitrogen adsorption and TEM), there is a need to perform other techniques giving valuable information about the degree of structural organization, the surface and the porosity distribution of the carbon replica. For this purpose, measurements by SAXS [4] and more recently by Raman spectroscopy were undertaken. The results obtained by this spectroscopic method are presented in this paper. Micro-Raman spectroscopy, exhibiting a high spatial resolution, is now recognized as a well adapted tool for the characterization of graphitic carbon materials [5]. It combines a surface selectivity due to the strong electromagnetic wave absorption, with an exceptional sensitivity to the degree of structural order (at the atomic scale). In addition to the G band typical for graphite crystal at 1580 cm^{-1}, carbon materials present, in their first order Raman spectrum, other active modes with in particular a second band (D band) around 1350 cm^{-1} as well as another weak band at 1620 cm^{-1} (D' band). Both D and D' bands are assigned to defects within the carbon structure (edges, distorded graphene layers..). The D to G bands intensity ratios (named Raman ratio) are thus established parameters to quantify the degree of disorder in other carbon materials [6, 7]. Hence, the evolution of the Raman peaks and in particular the intensity ratio I(D)/I(G) was determined for the different kinds of ordered porous carbons and for the same materials after a graphitation process at 2500°C. Consequently, it was possible from the present results to determine the influence of the carbon precursor on the structural characteristics of the final carbon. To the best of our knowledge, it is the first time that such methods are used to characterize the ordered porous carbons.

Experimental

Ordered porous carbon materials have been synthesized by a templating procedure starting from an organized porous silica material [1,2,3]. Two silica templates (MCM-48 and SBA-15) and different carbon precursors (propylene, sucrose and mesophasic pitch) were selected leading to carbon materials with different structural and textural properties [2]. The materials are named CXY (X=48 or 15 for MCM-48 or SBA-15 templates; Y= 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. They were analyzed by Raman spectroscopy. The Raman spectra were collected in back-scattering geometry, using a LABRAM spectrometer from JOBIN-IVON coupled with a CDD detector from whose the intensity ratio R was determined. As proposed by Tuinstra and Koenig [8], a relationship can be established between the intensity ratio of the D and G bands and the inverse of the in-plane coherence length La. La is the cristallite size by using the following relation: $R(\lambda) = I(D)/I(G) = C(\lambda)/La$ with $C(\lambda) = 8.28nm$ for a wavelength of 632.8 nm. This relation is valid for La> 2 nm (7).

Results and Discussion

The Raman spectra of all the carbon materials have been examined at 614.5 nm. As an example, the spectrum of a graphitized carbon using sucrose and SBA-15 as carbon precursor and silica template, respectively is shown in figure 1. As expected, the four well resolved bands, namely D (1350 cm^{-1}), G (1580 cm^{-1}), D'(1620 cm^{-1}) and G' (2700 cm^{-1}) can be observed. The G' band is the most important feature of the second order spectrum (2500-3000 cm^{-1}).This band is very sensitive to structural variations in highly organized carbons.
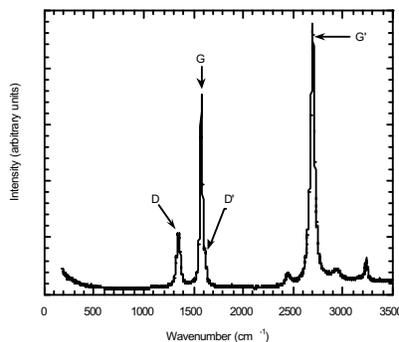

Figure 1. Raman spectra of material C15S after
heat treatment temperature (HTT) at 2500°C

As mentioned above, a relevant approach to characterize the different carbon materials is to follow the integrated intensity ratio of the D band to the G band (this ratio varies inversely with the in-plane crystallite size La). As an example, the values of R of the

synthesized carbon materials are reported in Table 1 as well as the total surface area (TSA) of the corresponding carbon materials.

Materials	TSA (m²/g)	Raman ratio (R)	La (nm)
C15Pr	713	1.8	4.6
C15S	1470	>2	<6.4
C15P	923	2.2	3.8
C15Pr HTT	220	1.0	8.3
C15S HTT	284	0.35	55
C15P HTT	100	1.1	10.9
C48Pr	850	n.d.	n.d.
C48Pr HTT	35	0.9	9.2
C48S	2017	n.d.	n.d.
C48S HTT	33	0.5	17

n.d.: not determined

Table 1 : Raman intensity ratio and total surface area of some porous carbon materials

After a heat treatment (HTT) at 2500°C, during 90 min. a significant decrease of the total surface area is observed. TEM observations point out the existence of local well-organized porous areas but the long-range ordering is lost (as confirmed also by X-Ray diffraction). However, the TSA value of the carbon after heat treatment is higher when SBA-15 is used as template. The most peculiar Raman result is related with the La values after graphitation at 2500°C which are much higher for the carbon material prepared with sucrose than for the other two types of carbons and this whatever the type of template. This result is very surprising since carbon issued from precursor like sucrose should not be graphitable at the opposite of the other ones. Hence, it turns out that in a confined medium the thin film of carbon (which corresponds to the 'carbon' wall in the final material) can be reorganized in a rather crystalline form with larger graphene planes as already observed for other types of carbons [9]. The values of R are close for carbon materials issued from the propylene and pitch. Moreover, it can also be observed in this table that the values of R are similar for materials C48Y and C15Y. Hence, the structural organization of the final carbon seems not to be really influenced by the characteristics of the silica template.

Conclusions

The characterization of ordered porous carbon materials by Raman spectroscopy provides important complementary informations of the structural organization of the carbon. By this technique, it appears that the film graphitation process is different from the usual bulk one and fundamental for the understanding of surface properties of the carbon materials involving wettability and adsorption phenomena. It appears therefore that the knowledge of structural tortuosity and associated gas permeability together with the surface characteristics of these carbon materials is of prime importance for their further potential applications.

Acknowledgment

References

[1] R. Ryoo, S.H. Joo, M. Kruk and M. Jaroniec, Adv. Mater. 2001;13: 677

[2] C. Vix-Guterl, S. Boulard, J. Parmentier, J. Werckmann, J. Patarin, Chem.Lett. 2002; 10:1062

[3] C. Vix-Guterl, S. Saadallah, L. Vidal, M. Reda, J. Parmentier, J. Patarin J.Mat.Chem. 2003;13: 2535

[4] F. Ehrburger-Dolle, I. Morfin, E. Geissler, F. Bley, F. Livet, C. Vix-Guterl, S. Saadallah, J. Parmentier, M. Reda, J. Patarin, M. Illiescu, J. Werckmann, Langmuir 2003;19:4303

[5] P.C. Eklund, J.M.Holden and R.A. Jishi, Carbon 1995; 33:959

[6] S. Cui, R. Canet, A. Derre, M. Couzi and P. Delhaes, Carbon, 2003, 41, 797

[7] C.Ferrari and J.Robertson, Phys.Rev.B 2000;61:14095

[8] F. Truinsta and J.L. Koenig, J. Chem. Phys. 1970; 50:1126

[9] M. Inagaki, In « New Carbons », Editor Elsevier 2000: 79.