

ELABORATION AND CHEMICAL ACTIVATION OF CARBON NANOFIBERS OVER ALUMINA AND GRAPHITE SUPPORTS

Xavier Py - PROMES CNRS UPR8521-UPVD, rambla de la Thermodynamique Tecnosud 66100 Perpignan France

Roger Gadiou, Joseph Dentzer, Cathie Vix-Guterl - ICSI CNRS UPR9069, 15 rue Jean Starcky BP2488 68057 Mulhouse France

Jean-Noël Rouzaud - Laboratoire de Géologie de l'École Normale Supérieure, CNRS UMR 8538, 24 rue Lhomond 75231 Paris cedex 5 France

Roland Pellenq - CRMCN CNRS UPR7251, Campus de Luminy case 913 13288 Marseille cedex 9 France

Abstract

Among the new carbonaceous nano-sized materials, nanofibers (NF) have been proved to be one of the most promising new precursors for the elaboration of microporous adsorbent. Nevertheless, only few information has been already published on their activation by chemical reactants and on the effect of the catalyst support over this activation. In the present communication, chemical vapor deposition (CVD) herringbone-type carbon NF have been elaborated over alumina and over various graphite supports: graphite tissue (GT), expanded natural graphite (ENG) and graphite foils (GF), and they have been activated with KOH. The obtained raw and activated NF have been characterized by nitrogen sorption isotherm measurements (77K), mercury porosimetry, XRD, SEM and TEM.

Before activation, all NF present type II isotherms while after KOH activation, graphite supported NF present type I isotherms typical of current carbonaceous adsorbent. Over alumina and ENG, microporous volume W_0 up to $0.32 \text{ cm}^3 \text{ g}^{-1}$ and BET surface area up to $870 \text{ m}^2 \text{ g}^{-1}$ were observed while over GF W_0 up to $0.56 \text{ cm}^3 \text{ g}^{-1}$ and BET surface area up to $1535 \text{ m}^2 \text{ g}^{-1}$ were obtained. Those results linked to high resolution TEM observations lead to a better identification of the adsorption sites in carbonaceous adsorbents. Moreover, numerical simulations have been proceeded to study the NF growth at the surface of a nano - aggregate and the stability and cohesion of the NF.

Introduction

For years, nanofibers and other carbonaceous nano-materials have focussed extended research. Nevertheless, the possibility to use them as adsorbent precursor has been rarely studied. Among filamentous nano-materials, herringbone type nanofibers have already demonstrated their ability to lead to adsorbents by physical [1] or chemical [2,3] activations. Nevertheless, the obtained adsorptive properties were rather poor and intensive chemical activations were needed to get performances in the medium range.

According to the fact that all those studies were based on the same catalyst support: alumina, its effect upon the adsorptive properties is not known. Moreover, considering the great interest in thermal control of adsorption/desorption phenomena [4], conductive supports such as graphite would be preferable. Then, in the present study, previous results obtained by activation of nanofibers grown by CVD over alumina supported catalyst were extended to different graphite supports for comparison.

Experiments

Catalyst supports

In the present study, various catalyst supports have been experimented: the conventional alumina powder, graphite KF1500 tissue (GT), graphite foil (GF) and expanded natural graphite (ENG). The three graphite supports were selected for their particular interest in thermal solar applications or gas separation/purification. The catalyst was the Cu-Ni (30% / 70% wt) system which was already selected and experimented with success over alumina. It was deposited over graphite supports using different protocols:

- 1- by impregnation: the catalysts NiNO_3 and $\text{Cu}(\text{NO}_3)_2$ are first dissolved in alcohol, the graphite support is soaked in the solution and the solvent is withdrawn by heating at 80°C .
- 2- by dispersion: the catalyst in the form of powder is mixed to the graphite support, the mixture is placed in a mould and pressed to obtain a consolidated material (this protocol is specifically adapted to the ENG support).
- 3- by dispersion/impregnation: this protocol is the succession of protocol 2 and 1. It allows getting high amount of deposited catalyst (thanks to protocol 2) and forming the efficient Cu-Ni structure and crystal configuration (thanks to the crystallisation of protocol 1).

Nanofibers elaboration

The raw nanofibers over the different supports have been synthesized by a common CVD technique. The Cu-Ni (3/7wt) catalyst was first deposited at the surface of the selected support and the mixture placed in a ceramic basket at the centre of a tubular electric oven. The chemical vapor deposition was then proceeded using an ethylene and hydrogen (80% / 20% vol) mixture at 580°C.

Nanofibers activation

In a previous study [3], the most current chemical species used for activation of conventional activated carbons have been tested on alumina supported nanofibers: KOH, NaOH, ZnCl₂ and H₃PO₄. Among those reactants, KOH used by the so-called coating method was found to be the most relevant. Then, KOH was the sole activating agent used in the present study more particularly devoted to the applicability of the graphite catalyst supports. All chemical activations have been achieved in a tubular furnace under nitrogen flow with a heating rate of 5°C/min and 3 hours at the activation temperature of 900°C. After activation, the obtained materials were rinsed with distilled water until neutrality was reached and dried at 120°C for 24h.

Characterizations

The microporous texture of the nanofibers has been characterized by mean of the nitrogen isotherms at 77K. These isotherms were analyzed by the Dubinin-Radushkevish (DR) method to obtain the micropore volume W_0 and the mean micropore size L_0 . The nanofibers have been observed by both SEM and HRTEM microscopy and the corresponding results analysed using laboratory-made image analysis methods [5].

Modeling

The growing of nanofibers as well as the hydrogen adsorption were studied by grand canonical Monte Carlo (GCMC) simulations. The stability of the nanofibers was studied using the so-called simulation method molecular dynamic in the statistical canonic ensemble.

Results and discussions

Nanofibers growing

Among the different supported catalysts, only the graphite foils and the ENG were found to be efficient. The KF1500 tissue led to too weak materials. Moreover, impregnation method led to rather low deposited catalyst amounts (5.4%wt and 7.8%wt for ENG and GF) while dispersion led to higher amounts (20%wt) but in a rather uncontrolled crystal shape and no adhesion to the support. The mixed dispersion/impregnation method led to high and effective catalyst deposition (23%wt). The corresponding composite materials obtained by growing nanofibers over the supports contained various amounts of nanofibers: 71%wt over GT, 83%wt over GF, 57-79%wt over ENG depending upon the catalyst deposition method.

Adsorptive properties

The adsorptive properties have been studied in terms of raw isotherms as well as in terms of current adsorptive parameters (mean pore size L_0 , specific microporous volume W_0). In the Figure 1 are gathered the nitrogen isotherms at 77K of the raw and KOH (reactant/carbon ratio 4/1 in weight) activated nanofibers initially grown over alumina or graphite supports. All alumina supported materials (raw and activated) and raw graphite supported ones present type II isotherms characteristic of rather non porous solids. Nevertheless, the raw nanofibers supported on graphite present adsorptive capacities twice higher than those of alumina supported ones.

In comparison, activated graphite supported materials present type I isotherms characteristic of microporous materials and currently observed in the case of conventional activated carbons.

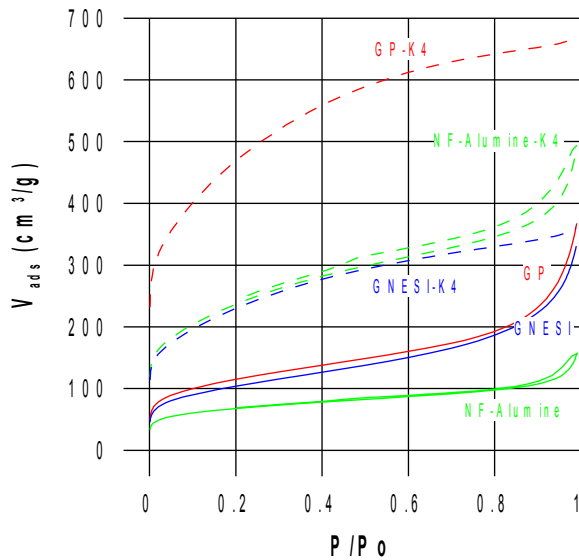


Figure 1 : nitrogen isotherms (77K) of raw and activated nanofibers: GP: graphite foil supported, GNESI: expanded graphite supported, samples K4 are activated with KOH (ratio carbon/reactant 4/1)

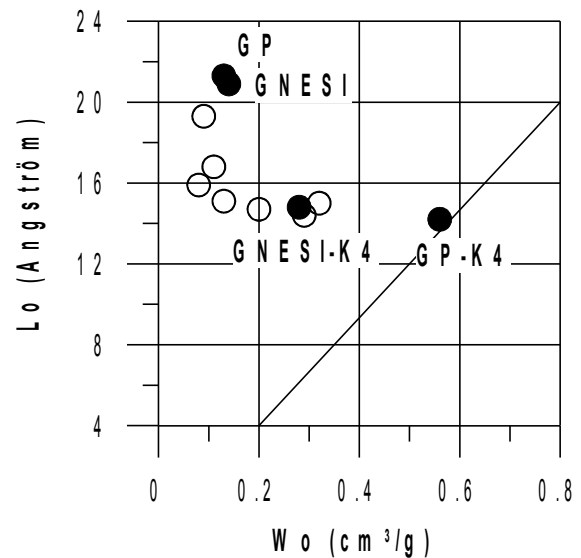


Figure 2 : textural diagram of raw and activated materials (activation with KOH, ratio carbon/reactant 4/1). Open symbols: over alumina, black symbols: over graphite. the line correspond to the correlation observed for conventional activated carbons.

The corresponding textural parameters calculated by mean of the DR method are gathered the textural diagram (L_0 versus W_0) of Figure 2 on which conventional activated carbons form a linear curve [6]. As already shown in case of the alumina support [3], at increasing activation level the nanofibers follow a very original behaviour induced by the increasing importance (statistically) of the small pores formed by the activation before the initial large pores present in the raw nanofibers. The graphite supported materials follow the same tendency, indicating that the nature of the microporosity should be the same independently to the nature of the support. Nevertheless, only the activated nanofibers supported on graphite foils (GP-K4) meet the linear curve of the conventional activated carbons. Such adsorptive properties ($W_0 = 0.56 \text{ cm}^3 \text{ g}^{-1}$ and $S_{BET} = 1535 \text{ m}^2 \text{ g}^{-1}$) on activated nanofibers have never been observed before and are in the range of conventional commercial adsorbents.

High Resolution Transmission Electron Microscopy (HRTEM)

The nanostructure of the nanofibers at the nanometric scale has been studied by HRTEM. The profile of the graphene layers are directly visualized in the form of black fringes. From such photography, thanks to a laboratory made analysis method [5], the following structural parameters can be quantified: L the mean length of the graphene layers, N the mean number of stacked layers, d the mean distance between to adjacent layers and the percentage of layers which can no more be considered as stacked, i.e. when the spacing between two adjacent fringes is larger than 0.6 nm and/or when the angle between them is larger than 15° .

Both the raw and activated nanofibers have been observed. The raw ones generally present herring-bone nanostructures (Figure 3a) with long and well stacked parallel layers. The corresponding structural parameters are gathered in Table 1. In comparison, the activated nanofibers present at their edges very disturbed nanostructures in the form of cages which have been already observed in more conventional super-activated activated carbons. Then, the effective porosity with respect to adsorption could be identified as those cages which form small mesopores whereas some so-called slit like pores could be found between two adjacent graphene layers characterized by large d (0.4 – 0.5 nm, see the Table 1).

The structural parameters of the activated NFs are gathered in Table 1 for various activating agents. According to those statistical values, the chemical activation leads to an increase in the mean interlayer distance d (from 0.345 nm to 0.48 nm for the raw and KOH(5/1) nanofibers respectively), a simultaneous decrease in the mean length of graphene layer L (from 2.1 to 0.5 nm respectively), a decrease in the mean number of stacked layers N (from 5.4 to 2.2 respectively) and an increase in number of non stacked layers (from 8 to 70%). Then, the observed interlayer distance d presents no similarity with the mean pore size L_0 and consequently discredits the slit-like pore approach currently considered in adsorption. In comparison, the very important increase in non stacked layers seems well correlated to the simultaneous increase in adsorption capacity. More details on the HRTEM observations are given in a companion paper in this Carbon 2007 Conference [7].

	<i>activation method</i>				
	<i>Raw NFs</i>	<i>NaOH 4/1</i>	<i>H₃PO₄ 4/1</i>	<i>KOH 4/1</i>	<i>KOH 5/1</i>
d (nm)	0.35-0.38	0.36-0.37	0.37-0.39	0.39-0.42	0.39-0.48
L (nm)	1.3 – 2.1	0.9 – 1.4	0.7 – 1.2	0.7 – 0.8	0.5 – 0.8
N	4.6 – 5.4	3.4 – 5.3	3.6 – 4.4	2.3 – 3.0	2.2 – 2.6
non stacked layers %	8 – 13	10 – 13	14 - 26	33 – 54	42 – 70

Table 1: structural parameters for raw and activated nanofibers.

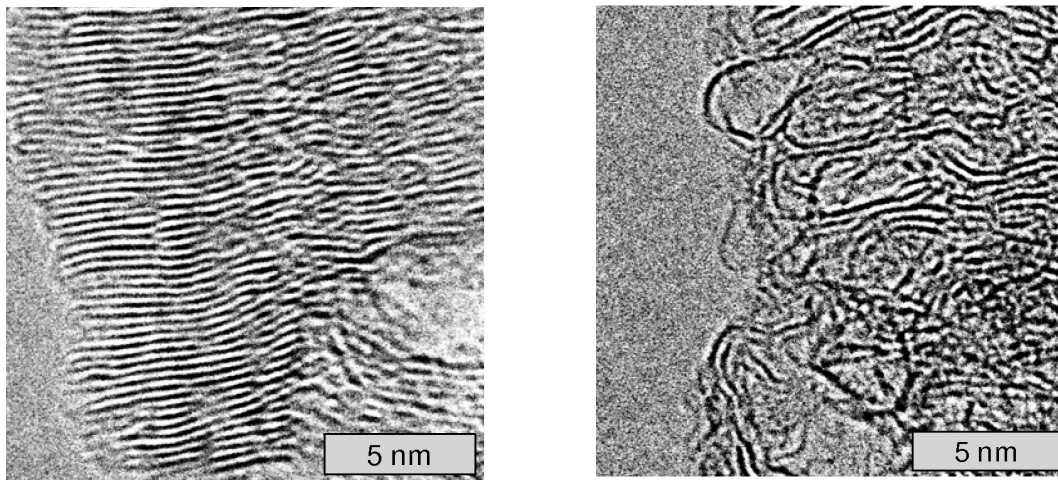


Figure 3: HRTEM microscopy on raw nanofibers GP (left) and highly activated nanofibers GP-K4 (right).

Modeling

Various modelings have been achieved concerning the growing of nanofibers on different catalyst geometries, as well as the stability and reactivity of different nanofibers morphology and size. As illustrated in Figure 4, a system of stacked graphene layers presenting initially unsaturated edges forms interlayers chemical bonds which could be experimentally visualized at the edge of nanofibers (see Figure 3 left).

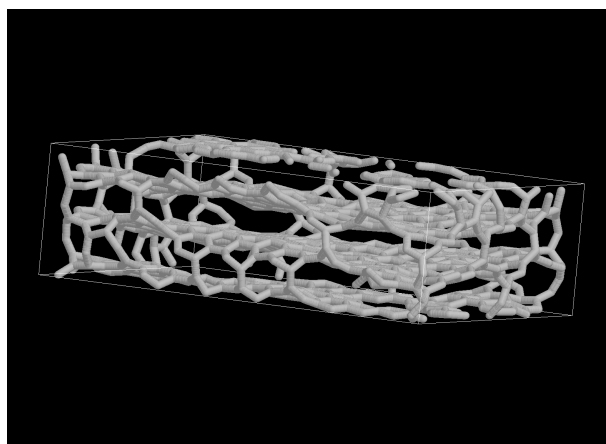


Figure 4 : chemical bonds formed between adjacent layers initially formed of unsaturated edges.

Such interlayer chemical bonds as well as hydrogen saturated edge sites are probably withdrawn during the activation procedure leading to a destabilisation of the original structure.

Then, initially saturated herringbone type nanofibers (Figure 5) have been numerically activated (by the withdrawal of peripheral hydrogens) and allowed to develop a more stable configuration. The corresponding stabilized form illustrated in Figure 6 is very similar to the cages observed experimentally in Figure 3 right.

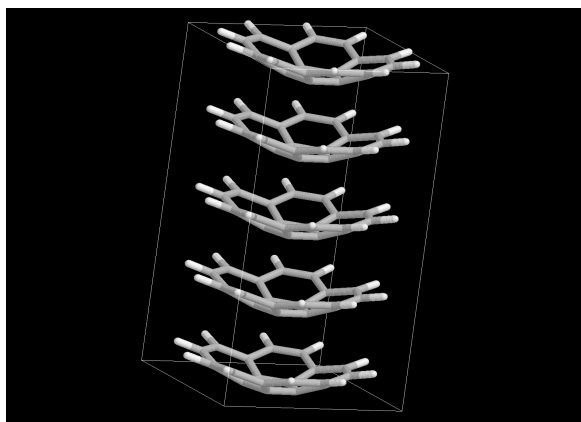


Figure 5 : herringbone type nanofiber with saturated edges.

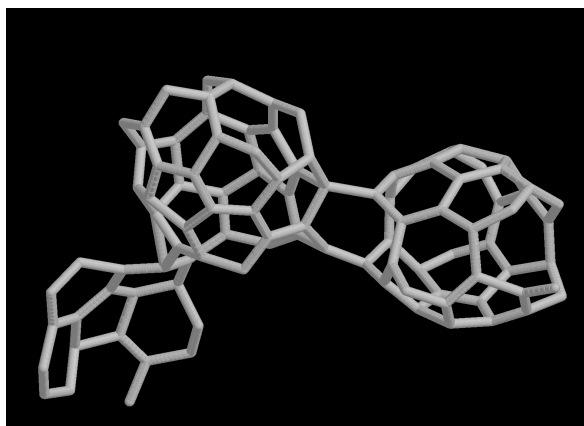


Figure 6 : rearranged herringbone type nanofiber initially unsaturated at its edges.

This model will be used further to study the adsorption of various gases on the different spatial configurations. This will probably help for a better understanding of the adsorption phenomena on carbonaceous matters.

Conclusions

The Cu/Ni catalyst deposition over graphite supports has been achieved using different protocols. Among them, the impregnation was found to be efficient, but the corresponding amount of deposited catalyst enhanced by mean of an initial dispersion. With respect to the nanofibers elaboration and activation, the graphite foil (GF) support has to be preferred.

If compared to the material supported over alumina, the nanofibers supported over graphite foil lead after activation to intensified adsorptive properties. All the other activated nanofibers present type II nitrogen (77K) isotherms and rather poor microporous storage capacities, while graphite foil based KOH activated nanofibers present adsorptive properties in the range of conventional adsorbents.

The observations of the obtained materials by HRTEM microscopy linked to image analysis and adsorptive properties discredit the so-called slit-like pore approach for highly activated carbon materials. On the contrary, these results support the assumption of cage-like structures which could define large micropores and small mesopores. The numerical results obtained by Monte Carlo approach confirm the formation of those adsorptive cages during the activation.

References

- [1] Blackman, J. M.; Patrick, J. W.; Arenillas, A.; Shi, W. & Snape, C. E. Activation of carbon nanofibres for hydrogen storage Carbon, 2006, 44, 1376-1385
- [2] Yoon, S.; Lim, S.; Song, Y.; Ota, Y.; Qiao, W.; Tanaka, A. & Mochida, I. KOH activation of carbon nanofibers Carbon, 2004, 42, 1723-1729
- [3] Luxembourg, D.; Py, X.; Didion, A.; Gadiou, R.; Vix-Guterl, C. & Flamant, G. Chemical activations of herringbone-type nanofibers Micro. Meso. Mat., 2007, 98, 123-131
- [4] D. Menard, X. Py, N. Mazet. Carbon 41 (2003) 1715-1727.
- [5] Rouzaud, J.-N, & Clinard, C. Quantitative high-resolution transmission electron microscopy: a promising tool for carbon materials characterization Fuel Proc. Tech., 2002, 77-78, 229-35
- [6] Stoeckli, F.; Daguerre, E. & Guillot, A. The development of micropore volume and widths during physical activation of various precursors Carbon, 1999, 37, 2075-2077
- [7] Rouzaud, J.-N, Pellenq, R. J.-M., Py X. , Gadiou, R. Vix-Guterl, C. HRTEM study of activated carbon nanofibres, Carbon 2007, Seattle (USA)