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## Ni CVD Catalyst for the Selective Preparation of small-diameter herringbone-type Graphite Nanofibers and their use in catalysis

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Graphite nanofibers (GNF) constitute an interesting carbon material for catalytic applications. Indeed, in addition to their large mesoporosity, the peculiar orientation of the graphene layers may influence the metal-support interaction [1] and thus, results in specific catalytic activity. As far as the production of GNF is concerned, most of the catalytic CVD processes used afford ill-defined materials. Indeed, GNF diameters distribution is usually large (20-100nm) [2-4] and the resulting specific surface area is often in the range 50-100m<sup>2</sup>/g [5,6]. These two points can reduce the field of their applications as catalyst support in heterogeneous catalysis. In this work, we report the selective growth of small diameter herringbone-type GNF by C-CVD on catalysts produced by fluidized bed organometallic CVD. First results dealing with the catalytic performances of PtRu/GNF systems for the selective hydrogenation of cinnamaldehyde will be also presented.

The monometallic Ni/Al<sub>2</sub>O<sub>3</sub> OMCVD catalysts for GNF growth have been prepared from nickelocene, [Ni(Cp)<sub>2</sub>]\*. We have demonstrated that the introduction of a partial pressure of H<sub>2</sub> during the OMCVD catalyst preparation allows to produce pure Ni<sup>0</sup> deposits. The GNF have been prepared by catalytic CVD from ethylene at 650°C. We will discuss the influence of some parameters on the quality of the material and on the catalytic performances of the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. We will also present a characterization of the catalyst, the composite material and the purified GNF. These nanofibers are all of the herringbone-type [fig 1a] and present a narrow distribution of diameters around 10-15nm, with a specific surface area of 170m<sup>2</sup>/g. Finally, we have used the GNF as support for PtRu bimetallic catalysts preparation. Preliminary results concerning the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol with this bimetallic systems will be presented.

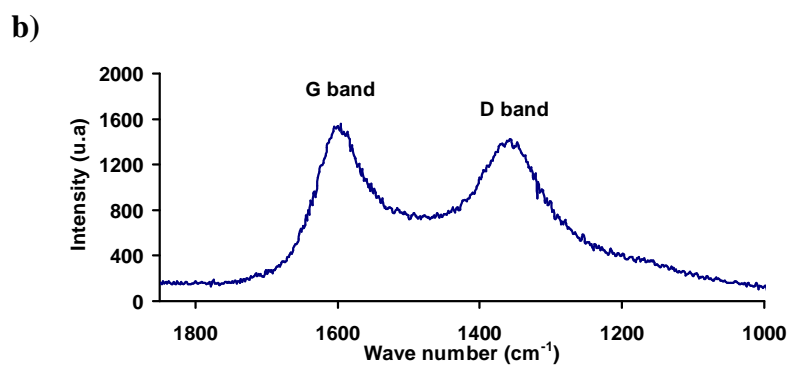
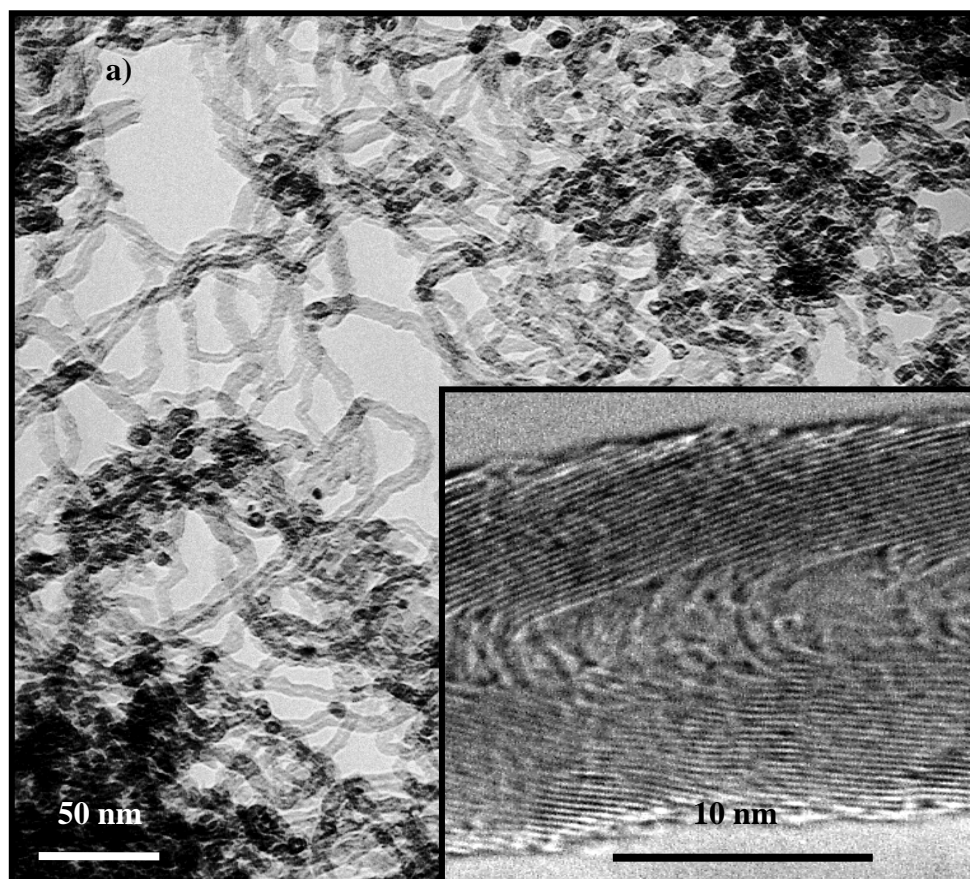
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System	Productivity <sup>a</sup> (g <sub>GNF</sub> /g <sub>Catalyst</sub> )	Catalytic activity (g <sub>GNF</sub> /g <sub>Ni</sub> /h)	Selectivity <sup>b</sup>	I <sub>D</sub> /I <sub>G</sub> <sup>c</sup>
Ni 4.4%	0.33	7.52	++++	Not measured
Ni 8.3%	1.00	12.08	++++	Not measured
Ni 12.5%	1.22	9.76	++++	0.91

a ) from TGA; b ) from TEM observation; c ) from Raman spectroscopy

**Table 1: Nickel Catalysts performances for the synthesis of nanofibers**



**Fig. 1: a) TEM and HRTEM micrographs of the composite material obtained after deposition of carbon b) Raman spectrum of purified nanofibers**