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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 50-100m²/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/Al₂O₃ OMCVD catalysts for GNF growth have been prepared from nickelocene, [Ni(Cp)₂]*. We have demonstrated that the introduction of a partial pressure of H₂ during the OMCVD catalyst preparation allows to produce pure Ni⁰ 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/Al₂O₃ 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 170m²/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 ^a (g _{GNF} /g _{Catalyst})	Catalytic activity (g _{GNF} /g _{Ni} /h)	Selectivity ^b	I _D /I _G ^c
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

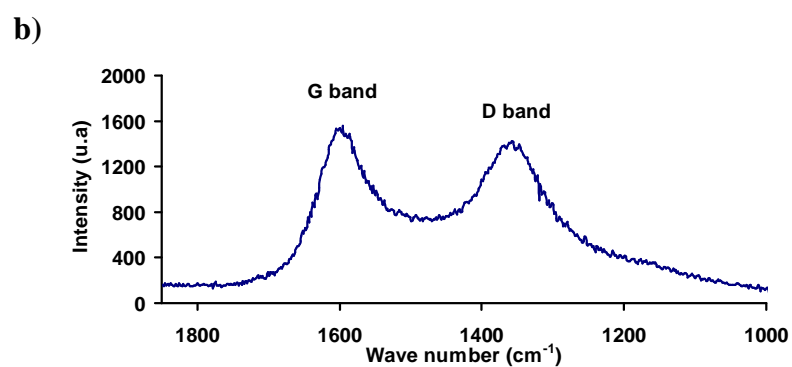
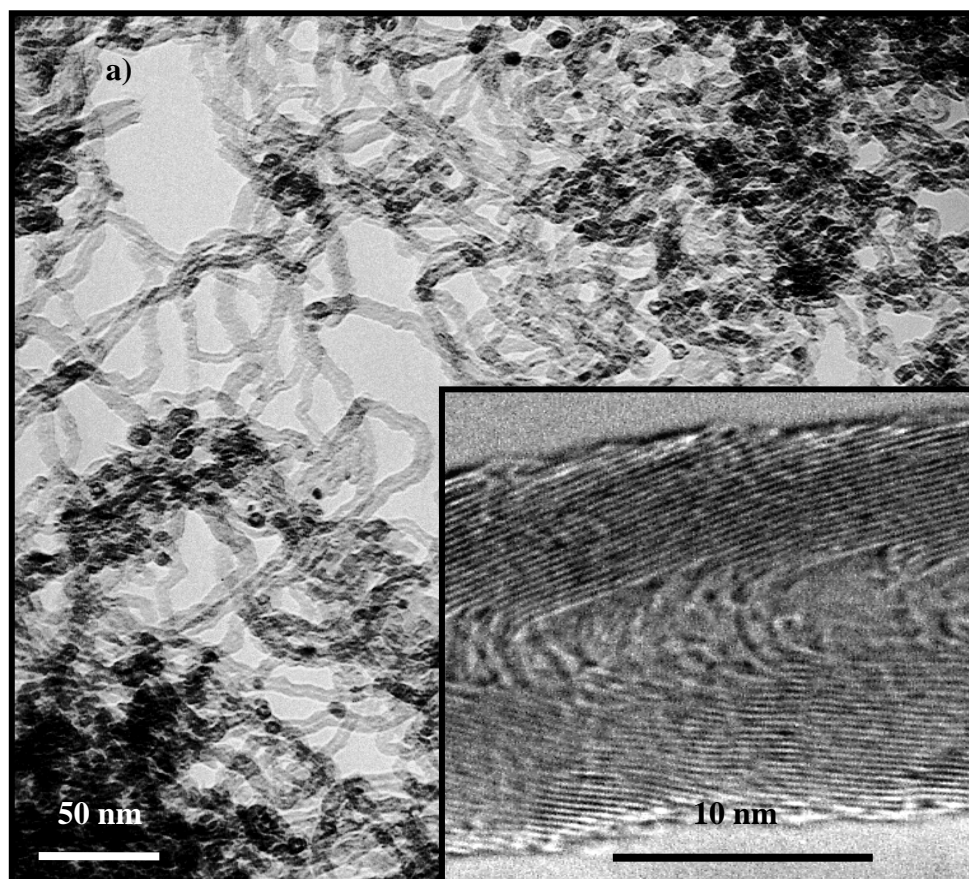


Fig. 1: a) TEM and HRTEM micrographs of the composite material obtained after deposition of carbon b) Raman spectrum of purified nanofibers