



**HAL**  
open science

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

Régis Philippe, Yolande Kihn, Brigitte Caussat, Dominique Plee, Philippe Kalck, Philippe Serp

► **To cite this version:**

Régis Philippe, Yolande Kihn, Brigitte Caussat, Dominique Plee, Philippe Kalck, et al.. Ni CVD Catalyst for the Selective Preparation of small-diameter herringbone-type Graphite Nanofibers and their use in catalysis. II International Symposium on Carbon for Catalysis - CARBOCAT-II, Jul 2006, Saint Petersburg, Russia. pp.0. hal-04105814

**HAL Id: hal-04105814**

**<https://hal.science/hal-04105814v1>**

Submitted on 25 May 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

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

R.Philippe<sup>1,3,4</sup>, Y. Kihn<sup>2</sup>, B. Caussat<sup>3</sup>, D. Plee<sup>4</sup>, P. Kalck<sup>1</sup> and P. Serp<sup>1</sup>

<sup>1</sup>Laboratoire de Catalyse, Chimie Fine et Polymères, Ecole Nationale Supérieure d'Ingénieurs en Arts Chimiques Et Technologiques, 118 Route de Narbonne, 31077 Toulouse Cedex 4, France. <sup>2</sup>CEMES-CNRS n°8001, 2 rue Jeanne Marvig 31055 Toulouse, France. <sup>3</sup>Laboratoire de génie Chimique, Ecole Nationale Supérieure d'Ingénieurs en Arts Chimiques et Technologiques, 5 rue Paulin Talabot, BP 1301, 31106 Toulouse cedex 01, France. <sup>4</sup>Arkema, Groupement de Recherches de Lacq, BP 34, 64170 Lacq, France.

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.

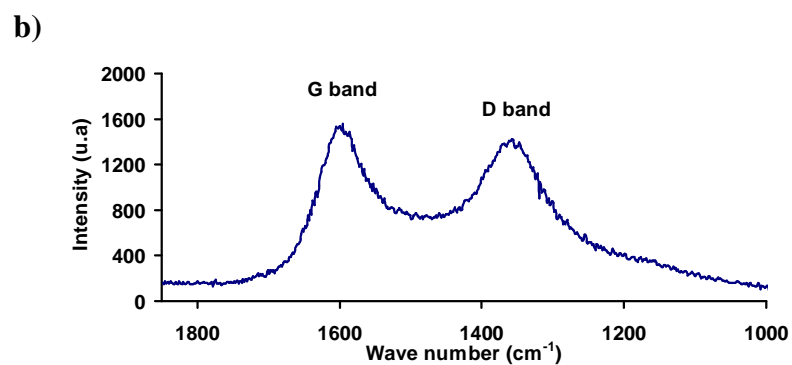
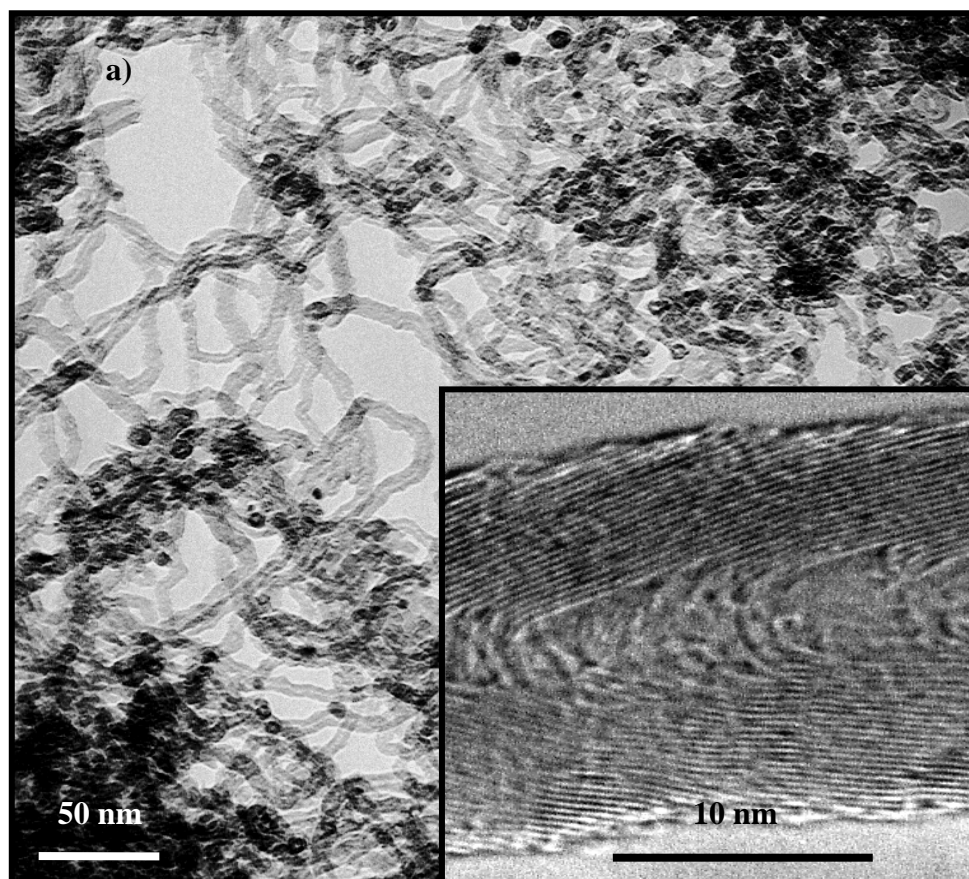
### References

1. C. Park, R. T. K. Baker, J. Phys. Chem. B 103 (1999) 2453
2. M.A. Ermakova, D.Y. Ermakov, A.L. Chuvilin, G.G Kuvshinov, J. Catal. 201 (2001) 183
3. M.A. Ermakova, D.Y. Ermakov, Catalysis Today 77 (2002) 225
4. J. Li, G. Lu, K. Li, W. Wang, J. Mol. Catal. A: Chem 221 (2004) 105
5. C. Amorim, G. Yuan, P.M. Patterson, M.A. Keane, J. Catal. 234 (2005) 268
6. G. Mestl, N. I. Maksimova, N. Keller, V. V. Roddatis, R. Schlögl, Angew. Chem. Int. Ed. 40 (2001) 2066

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**