

# Carbon nanofiber supported palladium catalyst for liquid-phase reactions. An active and selective catalyst for hydrogenation of C=C bonds

C. Pham-Huu,<sup>a</sup> N. Keller,<sup>a</sup> L. J. Charbonniere,<sup>b</sup> R. Ziessel<sup>b</sup> and M. J. Ledoux<sup>\*a</sup>

<sup>a</sup> Laboratoire de Chimie des Matériaux Catalytiques, ECPM-ULP, UMR 7504 CNRS, 25, rue Becquerel, 67087 Strasbourg Cedex 02, France. E-mail: ledoux@cournot.u-strasbg.fr

<sup>b</sup> Laboratoire de Chimie, d'Electronique et de Photonique Moléculaire, ECPM-ULP, UPRES-A 7008 CNRS, 25, rue Becquerel, 67087 Strasbourg Cedex 02, France

Received (in Oxford, UK) 30th June 2000, Accepted 21st August 2000

First published as an Advance Article on the web 18th September 2000

**Carbon nanofibers with a mean diameter of about 50 nm were successfully used as support for a palladium catalyst in the liquid phase selective hydrogenation of the C=C bond in an  $\alpha,\beta$ -unsaturated molecule: a less critical problem of mass-transfer limitation led to the obtention of a highly active and chemo-selective catalyst compared to a commercial high surface area activated charcoal supported palladium catalyst.**

Since their discovery at the beginning of the last decade,<sup>1</sup> carbon nanotubes and nanofibers seemed to be promising candidates for use as catalyst supports for heterogeneous catalytic reactions.<sup>2–4</sup> Such materials were expected to be efficient in liquid phase media due to their high external surfaces which can allow a significant decrease in critical mass transfer limitations,<sup>5,6</sup> also leading to an increase in the rate and the selectivity of the reactions.<sup>7–10</sup>

The aim of the present communication is to report the preparation of a highly dispersed palladium catalyst supported on carbon nanofibers, which is active and chemo-selective in the liquid phase hydrogenation of the C=C bond of cinnamaldehyde, at atmospheric pressure. The reaction rate and the product distribution are compared with those obtained on a commercially available activated charcoal supported palladium catalyst under the same reaction conditions.

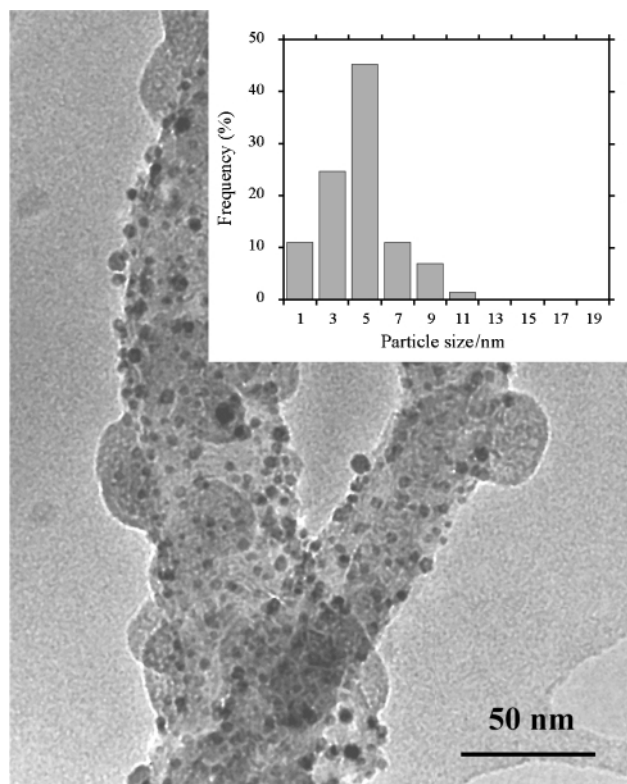
The carbon nanofibers (CNF) were synthesized by a gas phase catalytic decomposition of a mixture of ethane and hydrogen over a high surface area alumina supported nickel catalyst at 650 °C. This nickel catalyst was prepared by incipient wetness impregnation of an alumina support with an aqueous solution of nickel nitrate containing 20 vol% of glycerol as viscous agent. After synthesis and sonication the carbon nanofibers were subsequently purified by acid treatment at 80 °C for 2 h in order to dissolve any residual nickel catalyst that they might have contained. The carbon nanofibers had a mean diameter of around 50 nm and lengths up to several micrometers and they were built with graphene planes in a herringbone pattern, sometimes connected in the middle of the fiber, forming a closed angle of about 75°. The distance between the planes was found to be  $0.34 \pm 0.01$  nm.

The palladium deposition (5 wt%) onto the support was achieved by incipient wetness impregnation with an aqueous solution of palladium nitrate. The solid was dried overnight at 110 °C and subsequently reduced under flowing hydrogen at 350 °C for 2 h. Transmission Electron Microscopy (TEM) images evidenced the high and homogeneous dispersion of spheroidal palladium metal particles, with a narrow particle size distribution centered at around 3–5 nm diameter (Fig. 1). This homogeneous dispersion was attributed to a relatively strong metal-support interaction between the metal salt precursor and the graphite edges of the carbon nanofibers, increasing the resistance to the growth of the palladium particle. A similar observation has also been reported by Baker and co-workers<sup>2–4</sup> for graphite nanofibers supported on a nickel catalyst. However the distribution profile of the metal particles was relatively

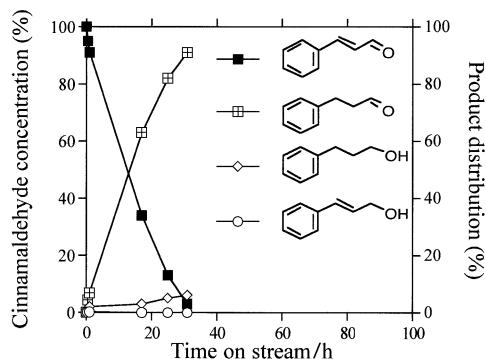
broad, ranging in size from 1.5 to 43.5 nm, with an average size of the metal particles of *ca.* 7–10 nm.

The hydrogenation of cinnamaldehyde was carried out at atmospheric pressure and low temperature, *i.e.* < 100 °C, with bubbling hydrogen. For the test, 10 ml of cinnamaldehyde (Athos, > 99.95 vol%) were dissolved in 40 ml of dioxane (RP, > 99.95 vol%). The catalyst (loading  $1.05 \times 10^{-3}$  g Pd) was added to the liquid under vigorous stirring (400 rpm) and subsequently, the reaction temperature was increased from rt to 80 °C, under continuous hydrogen bubbling through the liquid phase. The cinnamaldehyde concentration and the product distribution were followed by gas chromatography analysis (PONA capillary column equipped with a FID detector) of microsamples periodically withdrawn, and diluted with dioxane.

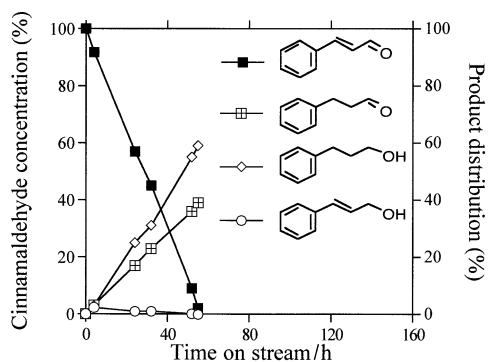
The catalytic results obtained over the Pd supported on carbon nanofibers and the commercial catalyst (Aldrich), are reported in Figs. 2 and 3. The superiority in terms of reaction rate of the nanofiber based catalyst was clear when the slopes of disappearance of CALD were compared. This performance was quite surprising as the literature reports that a relatively low surface area ( $45 \text{ m}^2 \text{ g}^{-1}$  instead of  $900 \text{ m}^2 \text{ g}^{-1}$  for the



**Fig. 1** A Transmission Electron Microscopy image of the carbon nanofibers supported palladium catalyst and the particle distribution.



**Fig. 2** Cinnamaldehyde conversion and product distribution as a function of time on stream obtained at 80 °C over the carbon nanofibers supported palladium catalyst. Cinnamaldehyde = CALD, cinnamyl alcohol = CALH, hydrocinnamaldehyde = HCALD and 3-phenylpropanol = PP.



**Fig. 3** Cinnamaldehyde conversion and product distribution as a function of time on stream obtained at 80 °C over the commercial activated charcoal supported palladium catalyst.

commercial catalyst) creates a major drawback for such an application.<sup>4,11–13</sup> Such behaviour is comparable to the results reported by Baker *et al.* over graphite nanofiber and alumina supported nickel catalysts.<sup>4</sup> This high catalytic activity was attributed to the high external surface area (high surface-to-volume ratio) of the carbon nanofibers compared to the charcoal grains (grains size *ca.* 50–100  $\mu\text{m}$ ) which improves the mass transfer during the reaction. In addition, the presence of a large amount of micropores (>60% of the total surface area) in the commercial catalyst can be at the origin of diffusion phenomena, slowing down the apparent rate of the reaction. The total absence of microporosity in the nanofibers avoided such a drawback.

It is worth noting that only hydrocinnamaldehyde (HCALD) was detected and only trace amounts of C=O hydrogenated products (CALH or PP) were found over the carbon nanofiber catalyst, thus demonstrating a high selectivity for the C=C bond hydrogenation (98%), while a mixture of dihydrocinnamaldehyde (HCALD), cinnamyl alcohol (CALH) and 3-phenylpropanol (PP) was observed on the commercial catalyst (Fig. 3) and for related catalysts.<sup>14–17</sup> This could be explained both by the presence of microporosity and by some residual acidity on the activated charcoal surface which could favour the hydrogenation of the C=O bond in a consecutive reaction pathway.<sup>4,14</sup>

In conclusion, carbon nanofibers (mean diameter at *ca.* 50 nm) can be efficiently used as a catalyst support, for liquid phase reactions. The high external surface area of the catalyst inhibits the mass transfer limitation of the reactant to the active sites and leads to the obtention of an active and chemo-selective catalyst. Such performances can open routes for the design of new catalysts for liquid phase heterogeneous catalysis, and particularly for enantioselective allylic substitutions or ketone reductions.

## Notes and references

- 1 S. Iijima, *Nature*, 1991, **354**, 56.
- 2 A. Chambers, T. Nemes, N. M. Rodriguez and R. T. K. Baker, *J. Phys. Chem. B*, 1998, **102**, 2251.
- 3 C. Park and R. T. K. Baker, *J. Phys. Chem. B*, 1998, **102**, 5168.
- 4 F. Salman, C. Park and R. T. K. Baker, *Catal. Today*, 1999, **53**, 385.
- 5 J. M. Planeix, N. Coustel, B. Coq, V. Brotons and P. M. Ajayan, *J. Am. Chem. Soc.*, 1994, **116**, 7935.
- 6 J. W. Geus, A. J. van Dillen and M. S. Hoogenraad, *Mat. Res. Soc. Symp. Proc.*, 1995, **368**, 87.
- 7 P. N. Rylander, *Catalytic Hydrogenation in Organic Syntheses*, Academic Press, New York, 1979, pp. 1.
- 8 J. M. Smith, *Chemical Engineering Kinetics*, 3rd Edn., McGraw-Hill, New York, 1981, pp. 450.
- 9 R. J. Madon and M. Boudart, *Ind. Eng. Chem. Fundam.*, 1982, **21**, 438.
- 10 S. Sato, R. Takahashi, T. Sodesawa, F. Nozaki, X.-Z. Jin, S. Suzuki and T. Nakayama, *J. Catal.*, 2000, **191**, 261.
- 11 N. M. Rodriguez, *J. Mater. Res.*, 1993, **8**, 3233.
- 12 N. M. Rodriguez, A. Chambers and R. T. K. Baker, *Langmuir*, 1995, **11**, 3862.
- 13 M.-S. Kim, N. M. Rodriguez and R. T. K. Baker, *Mat. Res. Soc. Symp. Proc.*, 1995, **368**, 99.
- 14 L. Zhang, J. M. Winterbottom, A. P. Boyes and S. Raymahasang, *J. Chem. Technol. Biotechnol.*, 1998, **72**, 264.
- 15 B. Liu, L. Lu, T. Cai and K. Iwatani, *Appl. Catal. A: General*, 1999, **180**, 105.
- 16 K.-C. Tin, N.-B. Wong, R.-X. Li, Y.-Z. Li, J.-Y. Hu and X.-J. Li, *J. Mol. Catal. A: Chemical*, 1999, **137**, 121.
- 17 Y. Zhang, S. Liao, Y. Xu and D. Yu, *Appl. Catal. A: General*, 2000, **192**, 274.