

# Carbon nanofiber supported Ni catalyst: Effects of nanostructure of supports and catalyst preparation

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## Abstract

Carbon nanofibers (CNFs) have been used as templates for manipulating the properties of Ni catalyst particles. Both incipient wetness impregnation and deposition–precipitation have been used to prepare the catalysts. Relatively well-dispersed Ni nanoparticles have been prepared on oxidised CNFs by incipient wetness impregnation. The diameter of the CNFs has been shown to have a significant effect in determining the Ni crystal size. In addition, CNFs are suitable templates to induce microstrain to metal particles. Such microstrain has significant effects on the activity of Ni crystals during ethane hydrogenolysis. This provides new opportunities to manipulate the crystal size and activity of the metal by selecting proper carbon nanofibers as support. TPO has been demonstrated as a powerful tool to study the CNF supported catalyst and to provide information on Ni loading and relative activity of NiO for CNF oxidation.

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## 1. Introduction

Carbon nanofibers (CNFs) have many interesting properties, resulting in a wide range of applications such as catalyst supports, selective adsorption/absorption agents, energy storage (including hydrogen and power battery), composite materials, nano-electric and nano-mechanical devices, as well as field emission devices [1,2].

CNFs have been considered as promising alternative support materials because of their special properties. CNFs present high mechanical strength, chemical inertness, and they can be used both in acidic and basic solutions. It is relatively easy to use combustion for recovery of the precious metal after deactivation of the catalysts. Furthermore, the structure and porosity can be tuned by synthesis conditions, CNFs are chemically pure, and the surface properties can be controlled by surface oxidation [3]. A variety of metal catalysts have been prepared on CNF supports and tested in hydrogenation reactions [4–10].

The present work deals with an investigation of the preparation and characterisation of CNF supported Ni catalyst. Incipient wetness and deposition–precipitation procedures are compared and the influence of the pre-oxidation of the fibers is also reported. Special attention has been given to develop temperature-programmed oxidation as a simple tool for a fast evaluation of Ni catalyst supported on CNF. The TPO results are related with the turnover frequency (TOF) for the hydrogenolysis of ethane. A detailed TEM analysis of the deposited Ni particles has been performed. TEM examination provides not only direct information of particle size, but also the size distribution over a certain range.

## 2. Experimental

Three types of CNF support materials have been prepared in our laboratory: platelet (PI), carbon filament (CF) and herring-bone (HB) [7]. CNF supported nickel catalysts (12.5 wt.% Ni) were prepared by both incipient wetness impregnation (IW) and deposition–precipitation (DP) of

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nickel nitrate ( $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) onto the three types of nanofibers. The CNFs were previously treated for 3 days in a 1 M HCl solution in order to remove impurities. A fraction of HB supports were oxidised by boiling in a  $\text{HNO}_3$  (65%) solution for 10 min for studying effects of the surface modification of CNFs.

Temperature programmed oxidation (TPO) measurements of the supports and prepared Ni/CNF catalysts were carried out under air-flow ( $80 \text{ ml min}^{-1}$ ) in a Thermogravimetric Analyser (Perkin-Elmer). The temperature was increased from room temperature to 1253 K at a heating rate of  $10 \text{ K min}^{-1}$ . The TEM investigation was performed on a JEOL 2010F transmission electron microscope. The TEM samples were prepared by dispersing nanofibers in ethanol by ultrasonication and then depositing a few drops onto a copper grid. XRD spectra were recorded on a Siemens diffractometer (D500) using monochromatic radiation. Analysis of the experimental spectra for the crystal size determination was performed in two steps. Firstly, the experimental XRD peaks were simulated by means of the software *Profile* [11], where several models can be selected to fit the experimental data. Secondly, the program *Win-crysize* [12] was used to estimate the crystallite size and microstrain. Hydrogen chemisorption measurements were performed on a Micromeritics ASAP 2010C V2.01 apparatus. The  $\text{H}_2$  adsorption isotherms were measured at 308 K. Ethane hydrogenolysis has been used as a probe reaction in the present work to test the catalytic activities of Ni nanoparticles. The reaction was carried out in a vertical flow reactor system connected to a mass spectrometer. Details about CNFs synthesis, catalyst preparation and further characterisation have been reported earlier [7].

### 3. Results and discussion

TPO experiments have been found to be an efficient tool to evaluate the CNF-supported catalyst and to provide information on Ni loading and relative activity of NiO for CNF oxidation. The Ni loading measured by TPO on most of the catalysts are close to the nominal value 12.5 wt.%. The Ni loading has been calculated as a function of the difference between the remaining weight of the catalyst and the support after complete oxidation of the carbon. Fig. 1(a) shows a typical TPO profile of CNF support and supported NiO prepared by both IW and DP. Selected properties of the different catalysts are listed in Table 1. The results clearly indicate that both the CNF structure and the preparation method have pronounced effects on the catalysts properties. Better control of the metal loading is reached by IW preparation, where the nickel loading established by thermogravimetric analysis are closer to the nominal value than for the catalyst prepared by DP. The dispersion measured by chemisorption ranges from 1% to 2.5% depending on the nanostructure of CNFs and the catalyst preparation. The Ni dispersion for DP was in general equal

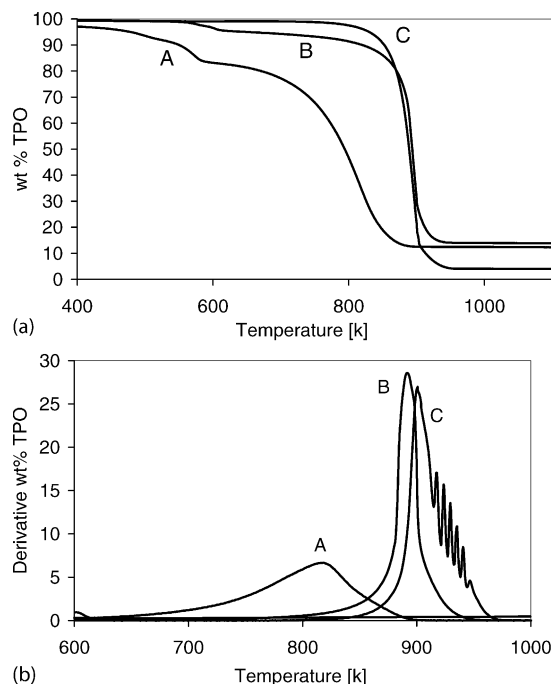


Fig. 1. (a) TPO and (b) TPO derivative profiles: (A) CF IW, (B) CF DP and (C) CF support. Heating rate:  $10 \text{ K min}^{-1}$ , air-flow:  $80 \text{ ml min}^{-1}$ .

Table 1

Properties of Ni catalyst supported on CNF and their activation energy for ethane hydrogenolysis

Catalyst	Ni loading (wt.%)	Dispersion <sup>a</sup> (%)	Strain ( $\times 10^2$ )	$E_a$ (kJ/mol)
Carbon filament IW	10.81	1.61	2.38	102.2
Carbon filament DP	8.67	2.13	3.26	105.0
Platelet DP	12.53	0.77	2.57	112.3
Herring-bone IW	11.19	1.53	0.51	101.5
Herring-bone ox. IW	11.50	2.39	0.19	103.2
Herring-bone ox. DP	8.17	2.39	3.31	76.2

<sup>a</sup> From  $\text{H}_2$ -chemisorption.

to or higher than that for the corresponding IW catalyst. However, the XRD measurements indicate that the DP method yields larger Ni particles than IW, which is in good agreement with the TEM observation as reported previously [7]. It should be noted that these DP results are in contrast to the observation reported by Bitter et al. [13]. DP obtained highly dispersed and highly loaded Ni nanocrystals on CNF in their investigation. This may be due to a difference in the oxidation conditions, since Bitter et al. [13] used a much stronger oxidant and a longer reflux time. The concentration of surface functional groups seems to be an important factor for the deposition-precipitation method.

As mentioned above, TPO experiments provide information about the relative activity of the catalysts. The derivatives of the TPO profiles for the CF support and the catalysts prepared by incipient wetness and deposition-precipitation are plotted in Fig. 1(b). The CF support has an

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