

# Synthesis of highly loaded highly dispersed nickel on carbon nanofibers by homogeneous deposition–precipitation

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Highly loaded (45 wt%) Ni on graphitic carbon nanofiber (diameter 50 nm) catalysts were prepared by means of homogeneous deposition–precipitation (HDP) from an aqueous solution. The obtained Ni metal particles were small (9 nm). This shows clearly that HDP can be used for the preparation of catalysts based on inert supports, like carbon nanofibers, which cannot form surface co-precipitates between the catalyst support and the metal precursor. The latter is known to be a crucial step in the preparation of metal-on-oxidic support catalysts. The oxygen-containing groups on the surface of the carbon nanofiber act as nucleation and anchoring sites in the deposition of highly dispersed Ni.

**KEY WORDS:** carbon nanofibers; HDP; nickel; high dispersion; high loading.

## 1. Introduction

Nickel-based catalysts are widely used in processes like hydrogenations [1], hydrodesulfurization [2] and steam reforming of hydrocarbons [3]. In general, these catalysts consist of small Ni clusters (nm range) dispersed on oxidic carriers like SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>.

Nowadays, new support materials for metal-based catalysts with properties potentially surpassing those of conventional supports are available. Carbon nanofibers (CNF) comprise such a material. It is suitable for both gas- and liquid-phase applications [4–6]. The material is pure, mechanically strong and chemically inert. Moreover, metals can be easily recovered from a spent catalyst by burning off the support. The inertness of CNF is an advantage in many metal-catalyzed reactions because side reactions on the support are suppressed; however, it makes the deposition of metal precursors difficult owing to the lack of anchoring sites. This can be addressed by an oxidative pretreatment that results in oxygen-containing surface groups thus forming anchoring sites, while the hydrophilicity is increased [7,8]. By using oxidized CNF, it appeared possible to deposit metal precursors on the surface via impregnation or ion exchange at low loadings with high dispersions and narrow size distributions [4–6,9,10]. Up to now, homogeneous deposition–precipitation (HDP), which has been developed for preparing highly loaded, highly dispersed metal/oxide catalysts [11–18], has not been used for the deposition of metal precursors on CNF. Most likely, this is due to the supposed absence of a

strong interaction between the support and metal precursor, which is thought to be indispensable for HDP [11–18]. For metal-on-oxide catalysts, this interaction is believed to be the formation of a surface co-precipitate between the support and the metal precursor. After careful reduction of the co-precipitate, a well-dispersed supported metal catalyst is obtained [11–18].

In this paper, we will show, however, that it is possible to prepare highly loaded (~50 wt% Ni), highly dispersed Ni/CNF via HDP.

## 2. Experimental

Fishbone carbon nanofibers were grown from a CO/H<sub>2</sub> mixture using a nickel-on-silica growth catalyst as described elsewhere [4–6,19,20]. After fiber growth, the CNF together with the remaining Ni/SiO<sub>2</sub> catalyst were collected.

The silica was removed by refluxing the collected product in a potassium hydroxide solution (1 M). Subsequently, the material was filtered, washed and dried. The thus obtained product (CNF with Ni) was divided into two portions. One portion was refluxed in concentrated hydrochloric acid in order to remove exposed Ni. After washing and drying, ‘as-synthesized’ carbon nanofibers (CNF-as) were obtained. From the second portion, oxidized CNF (CNF-ox) were prepared by refluxing the potassium hydroxide pretreated CNF with a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (1:1) [7,8]. This treatment removes the exposed nickel and induces oxygen-containing surface groups on the CNF. Some physicochemical properties of the CNF and Ni-loaded CNF are compiled in table 1.

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Table 1  
Some properties of reduced Ni/CNF materials as a function of the preparation history

Synthesis <sup>a</sup>	Treatment	Ni loading (wt%)	Ni-particle size <sup>b</sup> (nm)	Ni-particle size distribution	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )
–	–	–	–	–	169
–	Ox	–	–	–	179
IW	Ox	10	9–11	Narrow	n.d.
HDP	Ox	10	5–7	Narrow	165
IW	Ox	30	8–60	Broad	167
HDP	Ox	45	8–10	Narrow	156

<sup>a</sup>IW = Incipient wetness impregnation; HDP = homogeneous deposition–precipitation; n.d. = not determined.

<sup>b</sup>Determined on the basis of transmission electron microscopy.

The Ni precursor was deposited on the oxidized CNF by both incipient wetness impregnation (IW) and homogeneous deposition–precipitation (HDP). We prepared with both techniques materials containing 10 wt% of Ni. In addition, 30 wt% Ni/CNF-ox was prepared by IW, while 50 wt% Ni/CNF-ox was prepared via HDP.

For IW, 1-g CNF was evacuated at room temperature and the carbon nanofiber supports were once impregnated with an aqueous solution of nickel nitrate ( $[\text{Ni}^{2+}] = 0.2 \text{ g mL}^{-1}$ ) resulting in a 10 wt% metal loading. The impregnated carbon nanofibers were dried overnight at 120 °C and subsequently reduced in a 20% hydrogen-in-argon flow at 500 °C for 1 h. After cooling in Ar to room temperature and subsequent exposure to air, the Ni/CNFs were stored for further use. For the 30 wt% sample, successive impregnations were performed with a solution of 0.2-g Ni<sup>2+</sup>/mL prepared from nickel nitrate. In between each impregnation, the material was dried at 120 °C.

For HDP, 0.8 g of nickel nitrate hexahydrate was dissolved in 200-mL deionized water and 1.5 g of the oxidized CNF was added. When needed, the solution was brought to pH 2 with a few drops of HNO<sub>3</sub>. While stirring, the suspension was brought to 90 °C and kept at that temperature during the precipitation. An aqueous solution (10 mL) containing 0.6-g urea was added at the final temperature. After deposition for 18 h and cooling to room temperature, the loaded carbon nanofibers were thoroughly washed, dried at 120 °C and subsequently reduced in a 20% hydrogen-in-argon flow at 500 °C for 1 h at 1 bar. After cooling to room temperature and subsequent exposure to air, the Ni/CNFs were stored for further use. In this way, 10 wt% nickel-on-carbon nanofiber samples were prepared. The nickel loading of these systems were established by thermogravimetric analysis (TGA). The same procedure but with a higher concentration of Ni in the solution was applied with the aim of preparing 50 wt% nickel on carbon nanofibers.

The reduced CNF-supported nickel catalysts were examined in a Philips Tecnai-20 FEG TEM operated at 200 kV. Samples were prepared by suspending the fibers in ethanol under ultrasonic vibration. Some drops of the

thus produced suspension were brought onto a holey carbon film on a copper grid.

### 3. Results and discussion

In figure 1(a), a TEM micrograph of a reduced 10 wt% Ni/CNF prepared by HDP is shown. Figure 1(b) shows a TEM micrograph of the same sample at a higher magnification. Clearly, the sample contains well-dispersed Ni particles (6 nm) with a narrow size distribution on the surface of the CNF (table 1). Also,

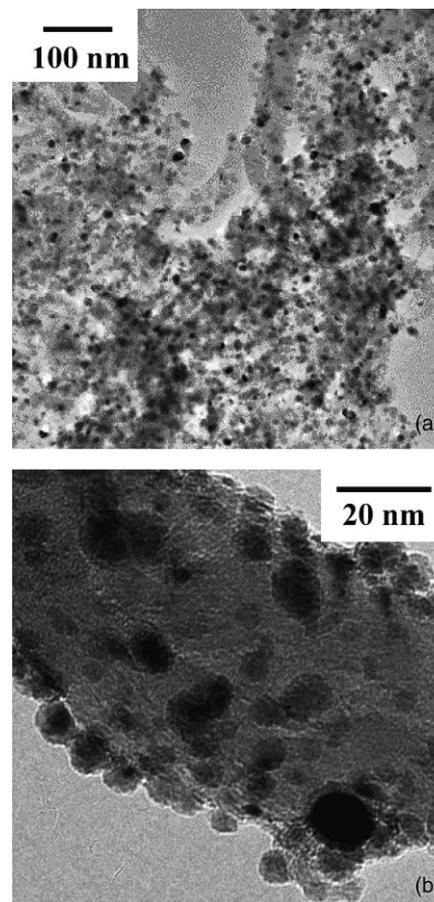


Figure 1. TEM micrograph of reduced 10 wt% Ni/CNF prepared via HDP: (a) low magnification and (b) high magnification.

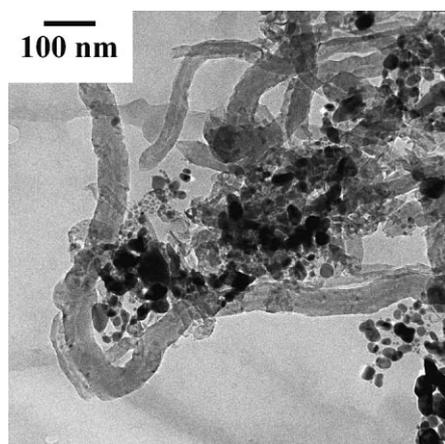


Figure 2. TEM of reduced 10 wt% Ni/CNF-as prepared by HDP.

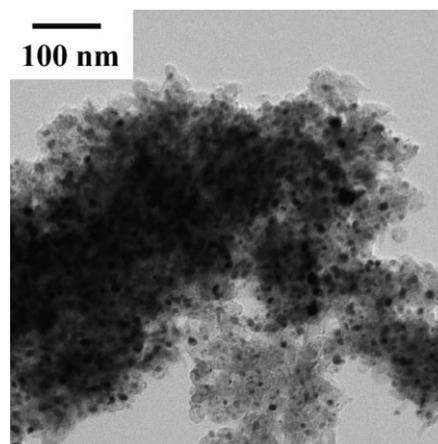


Figure 4. TEM of reduced 45 wt% Ni/CNF-ox prepared via incipient wetness.

the 10 wt% Ni/CNF sample prepared by impregnation shows well-dispersed Ni particles. A TEM analysis revealed that the average Ni particle in this case was 10 nm (table 1) also with a narrow size distribution.

Thus, both techniques lead to well-dispersed Ni at 10 wt% loading (table 1). This is tentatively explained by the similar processes occurring during preparation independent of the intended deposition method. When it is assumed that the Ni precursor is deposited by sorption on the surface of the oxidized CNF, one can calculate that a maximum loading of 10 wt% can be obtained. It must be assumed that two oxygen-containing groups per  $\text{nm}^2$  exist [21]; the Ni precursor is present as  $\text{Ni}_4$  clusters in solution [22] and sorbs as such in a 1 to 1 ratio on the oxygen-containing groups. Please note that the oxygen-containing groups are indispensable since the use of as-synthesized CNF resulted in the formation of Ni aggregates not attached to the support with a size ranging between 10 and 60 nm, independent of the synthesis technique (a representative TEM micrograph is shown in figure 2).

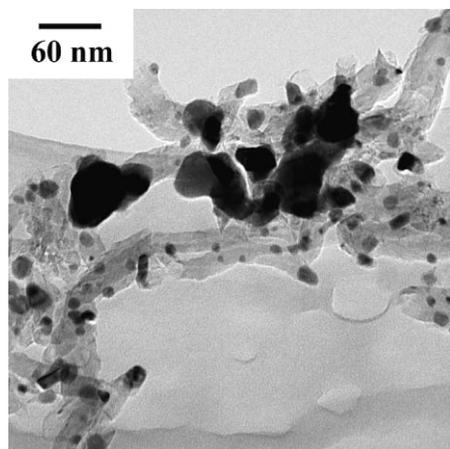


Figure 3. TEM of reduced 30 wt% Ni/CNF-ox prepared via incipient wetness impregnation.

In order to demonstrate the potential of the HDP technique on CNF, we prepared 30 wt% Ni/CNF-ox via IW and 50 wt% Ni/CNF-ox via HDP. The impregnated sample of 8–60 nm (figure 3), while the sample prepared by HDP contained well-dispersed Ni (9 nm) with a narrow size distribution (table 1 and figure 4). The HDP sample contained only 45 wt% of Ni instead of the aimed 50 wt%. The discrepancy between the intended weight loading (50 wt%) and the actual loading (45 wt%) can be explained by the formation of soluble Ni-amine [11,12] species during the deposition.

We have shown above that HDP is eminently suitable for the preparation of Ni/CNF catalysts even though the interaction between support and metal precursor is low, as can be demonstrated by means of temperature-programmed reduction (TPR). In figure 5, the TPR data of the catalysts' precursor i.e., after deposition of the Ni compound onto the support by HDP, are shown for Ni/SiO<sub>2</sub> and for Ni/CNF, both containing about 50 wt% Ni. Clearly, Ni/SiO<sub>2</sub> is reduced at a much

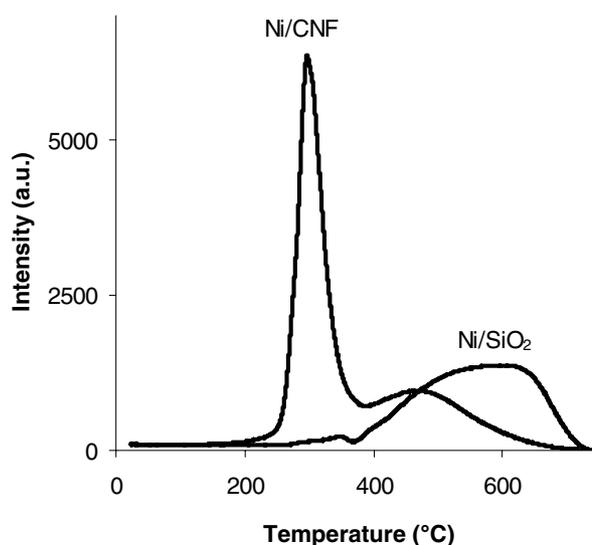


Figure 5. TPR results of 50 wt% Ni/SiO<sub>2</sub> and 45 wt% Ni/CNF.

higher temperature (maximum at 600 °C) compared to the Ni/CNF precursor system (300 °C). The reduction peak at 500 °C in Ni/CNF is most likely due to some gasification of the CNF by hydrogen. The high reduction temperature needed for Ni/SiO<sub>2</sub> is caused by the presence of difficult-to-reduce nickel hydrosilicates, which is the form in which nickel is deposited during synthesis [11–18]. Nevertheless, reduction of this material at 750 °C results in small Ni particles (7 nm) with a homogeneous size distribution.

Because Ni<sup>2+</sup> in Ni/CNF is reduced at a lower temperature (figure 5), it is evident that it is present in a different form in this system compared to the Ni/SiO<sub>2</sub> system. Since it is now not possible to form a chemical compound between support and metal precursor, like the Ni-hydrosilicate in Ni/SiO<sub>2</sub>, we believe that, in the Ni/CNF system, Ni-hydroxides nucleated on and anchored to the oxygen-containing groups of the CNF support are present after deposition. Clearly, reduction of nickel hydroxide proceeds easily (figure 5).

The weaker interaction between CNF and Ni is also reflected in the evolution of the Ni particle size as a function of the reduction temperature. Reduction of Ni/CNF at 500 °C resulted in Ni particles of 9 nm (table 1), while reduction of Ni/SiO<sub>2</sub> at 750 °C resulted in Ni particles of 7 nm. This clearly indicates a somewhat higher thermostability of the Ni/SiO<sub>2</sub> catalyst.

#### 4. Conclusion

In conclusion, homogeneous deposition–precipitation from aqueous solutions can be used to obtain highly dispersed, highly loaded Ni-on-CNF catalysts. To this end, the CNFs need to be oxidized in order to obtain oxygen-containing groups on the surface on which the Ni precursor can nucleate and anchor. In this way, a 45 wt% Ni catalyst with particles of 9 nm with a narrow particle size distribution was obtained.

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