

# On the importance of carboxylic groups on carbon nanofiber surfaces for the deposition of nickel using homogeneous deposition precipitation

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## Introduction

Homogeneous Deposition Precipitation is an excellent method for preparing metal on oxide catalysts when a high metal loading with a high and uniform metal dispersion is required [1]. A typical synthesis mixture consists of an aqueous slurry of the metal-precursor, catalyst support and urea. By increasing the temperature the pH of the reaction mixture rises slowly and homogeneously due to the decomposition of the urea. As a result of the strong interaction between the catalyst support and the precipitating metal-precursor the metal deposits, on the support, as a mixed oxide between support and metal precursor [2]. After careful reduction small metal particles on the support are obtained.

In the current contribution we will show that also carbon nanofiber (CNF) based catalysts can be prepared using HDP even though a mixed support-metal precursor phase, as described above, cannot be formed. By using HDP 10-45wt% Ni/CNF with uniform 9 nm Ni particles could be prepared. To that end oxidized CNF i.e., CNF with oxygen containing groups on the surface are indispensable. On these CNF different types of oxygen containing groups are present ranging from acidic to neutral to basic. When the acidic groups are removed either by a heat treatment in N<sub>2</sub> [3] or by chemical reduction using LiAlH<sub>4</sub> [4] it was found that after deposition a large fraction of the Ni(OH)<sub>2</sub> was not attached to the CNF surface. This indicates that the interaction between the acidic i.e., carboxylic groups and the metal precursor is strong and a key to the success of the technique.

## Experimental

CNF were prepared from CO/H<sub>2</sub> over a Ni/SiO<sub>2</sub> catalyst as described elsewhere [3,5]. Oxygen-containing groups were introduced on the CNF surface (CNF-ox) by treatment of CNF with boiling HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> [3,5].

For HDP 0.8 gram of nickel nitrate hexahydrate was dissolved in 200 ml de-ionized water and 1.5 grams CNF was added. The solution was brought to pH 2 with diluted HNO<sub>3</sub>. While stirring, the suspension was brought at 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 hours and cooling to room temperature the loaded carbon nanofibers (20wt% Ni) were thoroughly washed and dried at 120°C.

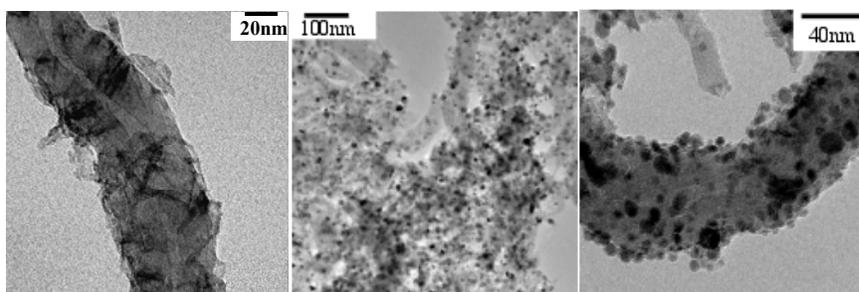
Please note that in this way also 45wt% Ni/CNF can be prepared [6]

One CNF-ox sample was heated to 873K in N<sub>2</sub> for 0.5h (CNF-ox-dT) before the deposition. This treatment resulted in the removal of the acidic oxygen groups [3]. A second sample was treated in LiAlH<sub>4</sub> (in dry THF at 298K with the exclusion of air) in order to reduce the oxygen containing groups to hydroxyl groups (CNF-ox-LiAlH<sub>4</sub>; [4] before the deposition.

## Results and Discussion

In Figure 1 representative TEM micrographs of Ni/CNF-ox prepared by HDP in different stages of synthesis are shown. The left micrograph shows the Ni(OH)<sub>2</sub> platelets which

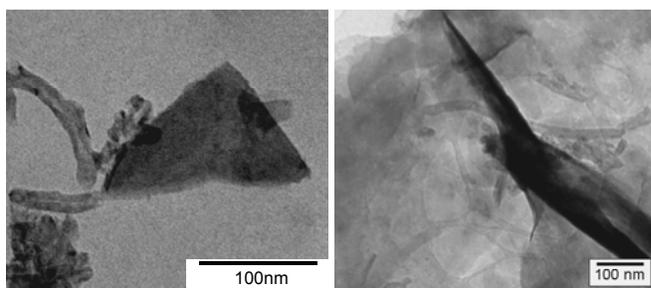
**Figure 1:** TEM micrographs of Ni/CNF prepared via HDP. Left: Ni(OH)<sub>2</sub> attached to CNF-ox after deposition; Middle: Ni/CNF after reduction at 773K; Right: enlargement of the middle micrograph



are formed during the deposition of the Ni precursor. Clearly the Ni(OH)<sub>2</sub> platelets are attached to the surface of the CNF-ox. After reduction (middle and right micrographs in Figure 1) a

catalyst is obtained with well-dispersed Ni (9 nm) with a narrow-size distribution. Clearly HDP is eminently suitable for the preparation of Ni/CNF-ox catalysts. Obviously the formation of a mixed phase between support and metal precursor as in the case of metal/metal oxide materials [2] is not possible when CNF-ox is used as a support. Apparently the presence of oxygen-groups on the CNF-ox surface brings about a sufficient interaction between support and Ni precursor, finally resulting in well-dispersed Ni particles.

**Figure 2:** TEM micrographs of Ni(OH)<sub>2</sub> platelets formed during HDP on CNF-ox-dT (left) and CNF-ox-LiAlH<sub>4</sub> (right). Please note that in the right panel the light gray areas are also Ni(OH)<sub>2</sub>. In both cases the Ni(OH)<sub>2</sub> is not attached to the CNF



In order to gain insight in the nature of the oxygen groups responsible for the interaction between metal precursor and CNF-ox support the deposition of the Ni-precursor was performed on heat-treated CNF-ox (CNF-ox-dT). From these CNF the acidic oxygen groups are removed leaving only the neutral and basic groups behind [3]. In addition CNF with only hydroxyl groups i.e., CNF-ox treated with LiAlH<sub>4</sub> [4] were used (CNF-ox-LiAlH<sub>4</sub>).

The resulting materials, before reduction, are shown in Figure 2. In both materials a large fraction of the Ni(OH)<sub>2</sub> platelets were not attached to the CNF surface while the contrary was observed when CNF-ox was used (Figure 1). Since the latter sample is the

only one containing carboxylic oxygen groups it is concluded that these groups are a prerequisite to obtain high-dispersed high loaded Ni/CNF catalysts.

## Conclusions

Highly loaded, highly dispersed Ni on carbon nanofiber (CNF) catalysts can be prepared via homogeneous deposition precipitation. The presence of acidic oxygen groups on the CNF surface is essential for obtaining these catalysts. The interaction between the Ni precursors and the acidic oxygen groups is of sufficient strength in order to form a large number of nuclei during deposition resulting in a highly dispersed, highly loaded Ni/CNF catalyst.

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