

# Novel supported catalytic materials based on multiwalls carbon nanotubes

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## ABSTRACT

In this work is presented a method that allows proper control of the nanoscale curvature of the external surface in multiwall carbon nanotubes (MWCNT), and shown its effect on the properties of Ni/MWCNT catalyst. After removal of residual nickel by treatment with HNO<sub>3</sub> the external surface of parent CNT's was decorated with 15-17 nm nanoparticles of CaCO<sub>3</sub> (25 wt.%) by carbonization of deposited Ca-nitrate. The followed partial catalytic air-combustion of CNT's at conversions 30-50% modified the morphology of their walls. After removal of CaCO<sub>3</sub> catalyst by treatment of the CNT's surface with HNO<sub>3</sub> the modified nanotubes were decorated with metallic nickel by sonochemical deposition. The partial combustion of carbon constituting the CNT walls catalyzed by CaCO<sub>3</sub> nanoparticles converts their structure from parallel grapheme layers to aggregates formed by grapheme onions with diameter of 5-12 nm. The nickel nanoparticles were located exclusively at the onions tops due to increasing the energetic barrier for metal adatoms (clusters) surface diffusion. It decreased the Ni crystal size from 8 to 2 nm at similar loadings of 50-60 wt.% and increased the catalytic activity in hydrogenation of chloroacetophenone more than twice.

**Keywords:** advanced materials, carbon nanotubes, nickel nanoparticles, nanostructured catalyzer.

## 1 INTRODUCTION

Since their discovery in 1991, many applications have been suggested for carbon nanotubes (CNT) including supports for metal nanoparticles (NP) that display catalytic activity in many catalytic reactions. Nickel catalysts are widely used for catalytic hydrogenations in production of fine chemicals and in food industry for manufacture of saturated oils and fats. Due to proper controlled pore size, moderate to high surface area, great thermal and chemical stability in acidic and basic environments many attempts were done to use CNT and especially multiwall CNT (MWCNT) as cheaper and more convenient in handling, as supports for nickel nanocrystals for various applications. They demonstrated wide opportunities to decorate the outer surface of MWCNT with nickel NP [1,2] and/or to fill their internal channels having diameter of >30 nm with nickel

nanocrystals [3]. For catalytic applications it is vital to reach maximal exposed surface area of nickel located at the external surface of MWCNT in order to avoid diffusion limitations inside the long nanotube channels. For spherical NP with cubic symmetry and theoretical density of  $\rho = 8.907 \text{ g/cm}^3$  usually stabilized in MWCNT matrices the metal surface area ( $S.A.=6000/\rho*d$ ) varies from 13 to 170 m<sup>2</sup>/g Ni when the nickel crystal size (d) decreases from 50 to 4 nm. In order to achieve the high metallic surface area per gram of catalyst is important to combine the small crystal size with maximal metal loading.

Different groups used in their studies MWCNT with surface areas varied in wide range from 10-15 to more than hundred m<sup>2</sup>/g. The % reduction of nickel precursors was not reported in available publications. This makes difficult the selection of most efficient deposition strategy for decoration of MWCNT with nickel NP. The highest nickel dispersion was obtained at relatively low (<10 wt.%) loadings by deposition of reducible precursors on acid-activated MWCNT. Preparation of highly loaded (>20 wt.% Ni) materials with small (<10 nm) nickel NP is still a challenge that requires development of special fabrication strategies. For better control of nickel crystals growth at the surface of MWCNT the nanotubes are activated by treatment with oxidizing acids (HNO<sub>3</sub> and/or H<sub>2</sub>SO<sub>4</sub>). Activation creates surface carboxylic groups anchoring nickel cations from solutions.

The theoretical calculations showed that the strain-relief of the solids' surfaces allows controlling the multiwall carbon nanotubes' external surface curvature which is critical for successful decorating of MWCNT with nanoparticles of desired size and stability. It was established that partial combustion of carbon constituting the walls of MWCNT catalyzed by decorating CaCO<sub>3</sub> nanoparticles converts the multiwalls structure from parallel grapheme layers to aggregates formed by grapheme onions with diameter of 5-12 nm. The areas with positive curvature of grapheme layers at the external surface of air-etched MWCNT played a role of docking stations for nickel nanoparticles inserted by sonochemical deposition after removal of CaCO<sub>3</sub>.

In the present study we investigated the efficiency of the new catalyst – nickel nanoparticles on the acid-activated MWCNT with high surface area of 216 m<sup>2</sup>/g. It was demonstrated that sonochemical deposition using Ni(CO)<sub>4</sub> carbonyl as precursor of nickel nanoparticles that was never

used before for this purpose allows to prepare Ni/MWCNT composite materials decorated with nickel NP of <10 nm at metal loadings 25-50 wt.%.

## 2 EXPERIMENTAL

### 2.1 Materials preparation

The MWCNT's with diameter ranging from 50 to 100 nm were synthesized by direct injection of benzene-alcohol solution of nickel acetylacetonate into high-temperature reactor (1000°C) followed by insertion of benzene vapor as a carbon source [4]. The residual Ni was removed by extraction with 65% HNO<sub>3</sub> at room temperature followed by washing with THF and drying in air at 80°C. After that the surface of MWCNT's was carboxylated by treatment with H<sub>2</sub>SO<sub>4</sub>/HNO<sub>3</sub> (3:1 by volume) under sonication (Sonic VC-750) in a water bath for 3 h at 40°C followed dilution with 1:5 by volume of distilled water. The obtained material was washed by water up to neutral pH value, filtered and dried at 80°C in air. The external surface of carboxylated MWCNT's was decorated with metallic nickel by direct deposition of metallic nickel from carbonyl precursor in decaline under sonication. Namely, the sonication (150 mg CNT in 100 ml of metal precursor solution) was conducted in a sonication flask by employing a high-intensity Ti-horn (20 kHz, 100 W/cm<sup>2</sup>) sonicator (VCX 750, Sonics&Materials) under Ar at temperature of 5-10°C for period of 3 h. The metal loading was controlled varying the concentration of metal precursor at the sonochemical deposition step in range of 0.02M to 0.05 M. After sonication decalin was removed by decantation and the material was washed two times with pentane. These procedures were made in a glove box (<5 ppm O<sub>2</sub>). Resulting black powder was dried for 1h at room temperature in an antechamber under vacuum and kept inside the glove box.

### 2.2 Materials characterizations

The prepared materials were characterized by TPR, XRD, EDAX, N<sub>2</sub>-adsorption, and HRTEM methods. The metal containing materials were protected from direct contact with air by transferring from glove box or H<sub>2</sub>-reduction tube to measurements chambers under inert atmosphere (HRTEM) or wetting with decaline or isopropanol (XRD, catalytic tests).

The nickel content in Ni/MWCNT-supported catalysts was calculated based on metal/carbon atomic ratios measured by energy-dispersive X-ray analysis spectroscopy (EDAX) after passivation in 0.1%O<sub>2</sub>-He flow at room temperature and by ICP method.

Surface areas, pore volumes, and pore size distributions of prepared materials were calculated by conventional BET and BJH methods from N<sub>2</sub> adsorption-desorption isotherms measured at 77 K and. The samples passivated in 0.1%O<sub>2</sub>-He flow at room temperature were outgassed under vacuum at 523 K.

### 2.3 Materials performance

The activity and selectivity of Ni/MWCNT catalysts was tested in hydrogenation of chloroacetophenone (ClAcPh). The reaction was conducted in a stainless steel batch reactor of 20 ml volume with the internal Teflon coating equipped with a magnetic mixer. The reduced or vacuum-dried (direct nickel deposition) catalysts were loaded in the glow box to the reactor filled with liquid reaction mixture that protected it from contacting with air at the following testing steps. The testing conditions: P<sub>H<sub>2</sub></sub> = 30 atm., T = 100°C, catalyst loading 0.2 g, reaction mixture – 0.3 g ClAcPh in 12 cm<sup>3</sup> i-propanol, reaction time τ =5-12 h needed for keeping the ClAcPh conversion in range of 10-30%. The selectivities to chlorophenylethanol (ClPhEtOH), and acetophenone were calculated based on the concentrations of these compounds found in the products mixture by GC analysis.

## 3 RESULTS AND DISCUSSION

### 3.1 Deposition of nickel

The starting MWCNT material was obtained in form of bundles of carbon nanotubes aggregated in microspherical particles of 2-3 micron size (Figure 1a). Higher magnification demonstrated the size (external diameter in range 30-100 nm) and packing mode of individual nanotubes inside the microspherical particles (Figure 1b). The nanotubes contained narrow empty channels with diameter of 3-4 nm while the voids between MWCNT's formed wider mesopores inside the microspherical aggregates. The nanotubes walls consisted of parallel grapheme layers forming graphite domains slightly disoriented relative to each other (Figure 1c). This structure of CNT walls was confirmed by XRD patterns recorded after removal of residual nickel.

Sonochemical deposition of nickel at loadings of 25 (S1) and 50 wt.% (S2) shown in Table 1. This is evident for complete decomposition of carbonate precursor that did not leave in precursors solution being embedded in the solid MWCNT support during sonication. The absence of reflections in XRD diffractograms (Figure 2) corresponding to any phases besides metallic nickel and similarity of the nickel contents obtained by chemical and phase analysis showed that all the amount of Ni(CO)<sub>4</sub> precursor was converted under sonication to the metallic nickel phase. The average crystal size of nickel estimated by XRD was 4 and 8 nm in samples S1 and S1, respectively. The TEM micrographs presented in Figure 3a,b show that nickel nanoparticles in these materials are uniformly distributed at the external surface of MWCNT's as individual crystals or their aggregates. HRTEM images of material S1 demonstrate that the nickel nanoparticles display narrow size distribution, so that the size of individual nanoparticles corresponds to that calculated from the width of XRD reflections (Figure 3c,d). The nanocrystals are partially embedded in the graphite body of multilayered CNT walls. This should stabilize them against sintering and partially

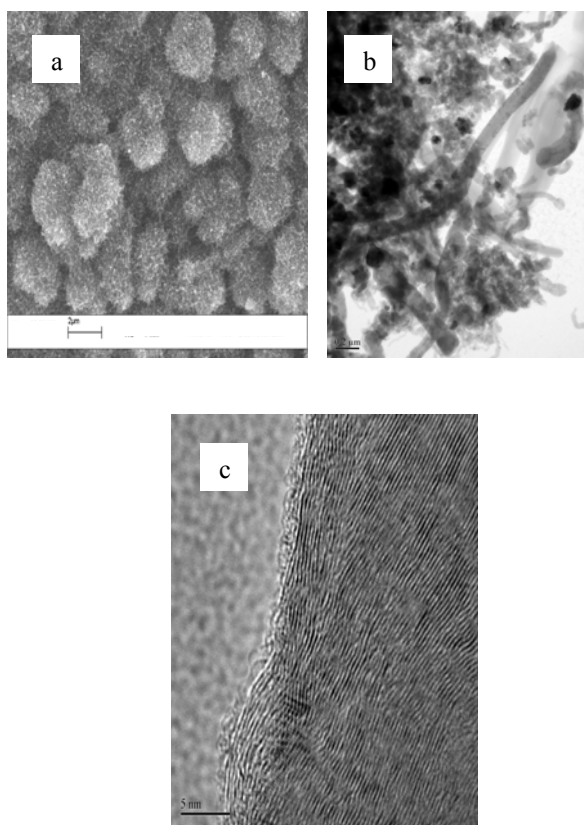


Figure 1. Micrographs of parent MWCNT's prepared by direct injection method:  
 a) microspherical bundles of MWCNT's (SEM);  
 b) residual Ni<sup>0</sup> and NiO nanoparticles inside the MWCNT's bundles (TEM);  
 c) graphene layers constituting the multiwall CNT's structure (HRTEM).

decrease the exposed surface area of metallic nickel relative to that calculated based on the nickel crystal size.

### 3.2 Catalytic performance of Ni/MWCNT materials

The effect of MWCNT's decorating strategy with nickel nanocrystals on the catalytic performance of Ni/CNT catalyst was evaluated by testing the activity and selectivity of prepared catalytic materials containing metallic nickel phase in hydrogenation of Cl-acetophenone (ClAcPh). Selective hydrogenation is the method of choice for reducing ketones and especially aromatic ketones as acetophenones on a large scale [5]. The advantage of Ni catalysts is their high selectivity in hydrogenation of carbonyl groups with negligible saturation of aromatic ring. Selecting the Cl-substituted acetophenone as a substrate for catalysts testing allowed estimating in parallel the hydrodechlorination function of prepared catalytic materials.

The main products of ClAcPh conversion with all tested Ni/MWCNT catalysts were p-chlorophenylethanol and

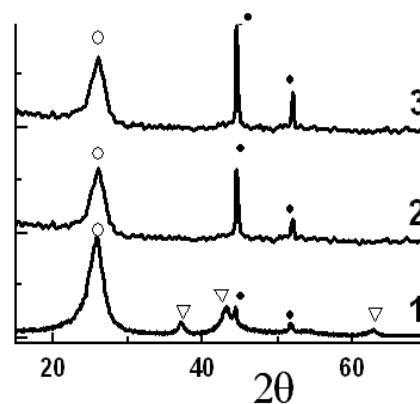


Figure 2. XRD patterns of Ni/MWCNT materials:  
 1) – parent CNT  
 2) – parent CNT after H<sub>2</sub> reduction at 550°C, S1  
 3) – material S2 after H<sub>2</sub> reduction  
 • - Ni cub., ○ - C graphite, ▽ - NiO

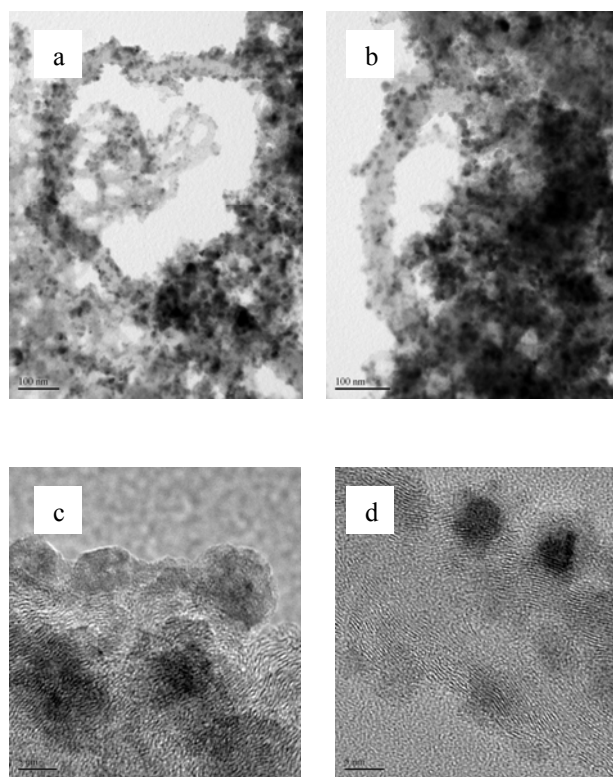


Figure 3. TEM micrographs of materials obtained by sonochemical decoration of MWCNT: general view – S1 (a); S2 (b); Ni<sup>0</sup> nanocrystals partially embedded in body of graphite walls at the external MWCNT surface (S1) (c,d)

acetophenone – products of selective hydrogenation of carbonyl group and hydrodechlorination of starting

Table 1. Characteristics of Ni/MWCNT materials

	Total surface area, m <sup>2</sup> /g	Nickel content, wt. %		Nickel crystal size, nm
		Chemical analysis (total Ni)	Phase analysis (Ni <sup>0</sup> )	
S1	163	24.6	26	4
S2	138	51.3	50	8

Table 2. Testing of Ni/MWCNT catalysts in hydrogenation of p-chloroacetophenone (ClAcPh). Testing conditions: batch reactor; T = 100°C, P<sub>H<sub>2</sub></sub> = 30 atm., t = 3-20 h; catalysts loading 0.1-0.5 g

Catalyst	ClAcPh hydrogenation rate,		ClAcPh hydrogenation selectivity, %	
	[mmol / g cat. hour] x 10 <sup>3</sup>	[mmol / g. Ni hour] x 10 <sup>3</sup>	ClPhEtOH	Acetophenone
S1	228	912	67.2	15.6
S2	234	468	69.2	21.0

substrate, respectively (Table 2). The high selectivity to corresponding alcohol in this case was achieved without implementation of basic additives [6] or addition of second metallic component [7] for depressing of undesirable side reactions. In contrast to Pd catalyst supported on carbon nanotubes yielding complete hydrodechlorination of halogeno-benzene compounds at mild conditions [8] Ni/MWCNT prepared in present study displayed high, up to ~ 70% selectivity to hydrogenation of carbonyl group. The total rate of ClAcPh conversion normalized per gram of catalyst as well as specific reaction rate per gram of active nickel component measured with materials S1 and S2 were by 2-18 times higher compared with conventional Ni – based precursors. The measured total rate of ClAcPh conversion and selectivity was nearly prop samples S1,S2 presented in Table 2.

## 4 CONCLUSIONS

Decoration of MWCNT's with nickel nanocrystals by direct sonochemical deposition of metallic phase as a result of in situ decomposition of carbonyl precursor significantly increases the dispersion and uniformity of size distribution of metallic phase at high loadings: average crystal size 4-8 nm at 25-50 wt.% nickel content. This enhanced the catalytic activity of Ni/MWCNT material in selective hydrogenation of chloroacetophenone by factors of 2-18

compared with that prepared by traditional decoration methods.

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