

# Functionalization Effect of Multi-Walled Carbon Nanotubes Used as Supports for Cu-Based Catalysts <sup>†</sup>

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**Abstract:** In this study, commercial Multi-Walled Carbon Nanotubes (MWCNTs) were subjected to two treatments: oxidation in a liquid phase using concentrated nitric acid and oxidation in a gas phase using air flow. Cu-based catalysts were prepared by ultrasound-assisted impregnation of each support in order to obtain a metal composition of 1 wt%, followed by drying and calcination under an inert atmosphere. Commercial MWCNTs without treatment were used as references. The crystalline structure of the samples was characterized by X-ray diffraction (XRD), while their textural properties were analyzed by N<sub>2</sub> physisorption (BET). The distinctive physicochemical properties achieved in the MWCNT supports could be related to the nature of the functionalization treatment that was used, with consequent effects on the features of the Cu catalysts.

**Keywords:** multi-walled carbon nanotubes (MWCNTs); surface functionalization; catalyst support; copper catalysts; physicochemical properties



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## 1. Introduction

Carbonaceous supports are widely used in heterogeneous catalysis, especially for liquid phase reactions, due to their tunable physicochemical properties, high specific surface areas, stability and easy recovery after reaction [1–4]. In particular, carbon nanotubes have a high external surface area, where metal particles can be deposited on and be easily accessible for reactants, thus improving the efficiency of the catalysts [4–9]. The nature and concentration of the functional groups on the surface of these carbon materials is of particular interest, since they can act as anchoring sites and reducing agents for the active phases and also serve as active sites for specific catalytic reactions, transforming an ‘inert support’ into an ‘active support’ [1,2,10,11]. Oxygenated functional groups (OFGs) are the most important in this context, as they can be spontaneously formed by exposure to the atmosphere, or their concentration can be increased by oxidative treatments, such as acid impregnation and thermal treatments under different atmospheres [1,9,10,12,13]. The present work proposes to study the effect of functionalization on the physicochemical properties of commercial MWCNTs, used as supports, and their interaction with copper particles in the final catalysts, which is of paramount importance in structure-sensitive reactions such as glycerol hydrogenolysis.

## 2. Materials and Methods

### 2.1. MWCNT Functionalization

Two functionalization methods were used on the pristine MWCNT supports (Nanocyl 3100). In the first method, 0.95 g of support was submitted to oxidative treatment in 0.05 L of 1 M HNO<sub>3</sub> (65% v/v) aqueous solution at 70 °C for 1 h. Subsequently, the support was

filtered, washed and dried in an oven at 70 °C for 24 h. The second treatment involved a gas phase procedure, in which 1 g of support was introduced in a fixed-bed stainless-steel tubular reactor and heated at 300 °C (10 °C min<sup>-1</sup>) for 3 h under an air flow of 300 mL min<sup>-1</sup>. Supports were labeled accordingly: MWCNT (pristine), MWCNT-N (nitric acid treatment) and MWCNT-A (air treatment).

## 2.2. Catalysts Synthesis

The copper precursor was deposited on the supports using the ultrasound-assisted impregnation method. Then, 1 g of each support was placed in a beaker along with an aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O and sonicated for 5 min. Subsequently, it was dried in a muffle furnace for 24 h at 70 °C and calcined under Ar for 2 h at 450 °C. Three catalysts with 1 wt% Cu loading were obtained: Cu/MWCNT, Cu/MWCNT-N and Cu/MWCNT-A.

## 2.3. Characterization

X-ray diffraction (XRD) was performed using a Rigaku Ultima IV diffractometer, operated at 20 mA and 30 kV with a Cu K $\alpha$  ( $\lambda = 0.15405$  nm) radiation lamp. The samples were scanned at a rate of 3° per minute in the range of  $10^\circ \leq 2\theta \leq 80^\circ$ . Diffractograms were compared with the JCPDS-ICDD references. N<sub>2</sub> physisorption (BET method) was carried out in a Micromeritics Gemini V device to determine the specific surface area ( $S_{\text{BET}}$ ) of each sample.

## 3. Results and Discussion

Supports and catalysts were characterized by different techniques to study the structural and textural properties achieved. The XRD spectra (Figure 1) of the supports showed the typical crystalline structure of amorphous carbonaceous materials, with two wide diffraction lines at 26° and 43°, which were attributed to graphitic carbon (PDF 01-075-2078), as reported by other authors [1–3,10]. No evident modifications were observed after the oxidative treatments. In the case of the catalysts, distinctive copper species were observed when functionalization was applied. Cu-MWCNT showed a predominance of diffraction lines, corresponding to Cu<sub>2</sub>O (PDF 03-065-3288), while Cu/MWCNT-N and Cu-MWCNT-A displayed diffraction lines that were attributed to Cu<sup>0</sup> (PDF 00-004-0836). Moreover, the higher intensities of these lines in Cu-MWCNT-A could be associated with the presence of larger Cu crystals. It has been reported [3] that reduced copper species could be formed due to the presence of oxygenated functional groups (OFGs) close to Cu particles. This behavior is in line with the expected increase in OFGs after the oxidative treatments and calcination under inert atmosphere in order to preserve the physicochemical properties that we achieved [3,10]. Comparing both oxidative strategies, air treatment could be preferred due to its simplicity. In addition, Cu<sup>0</sup> species can be obtained, avoiding a forward reduction step, which is commonly performed when a reduced metal phase is needed, as in the case of glycerol hydrogenolysis [14,15].

Regarding the specific surface area (Table 1), the pristine support showed an  $S_{\text{BET}}$  value of 243 m<sup>2</sup> g<sup>-1</sup>, which was slightly reduced after both oxidative treatments. These drops could be related to the formation of OFGs in the proximity of pores, blocking the N<sub>2</sub> molecules' access, and some surface erosion due to acid and air oxidation [2,10]. In the case of the catalysts, the expected reduction in  $S_{\text{BET}}$  values was observed, attributed to pore occlusion due to metal particles loading and/or thermal treatments being applied during synthesis [1,2]. However, the obtained values were considered high enough to achieve a good dispersion of copper species and therefore a good catalytic performance under glycerol hydrogenolysis.

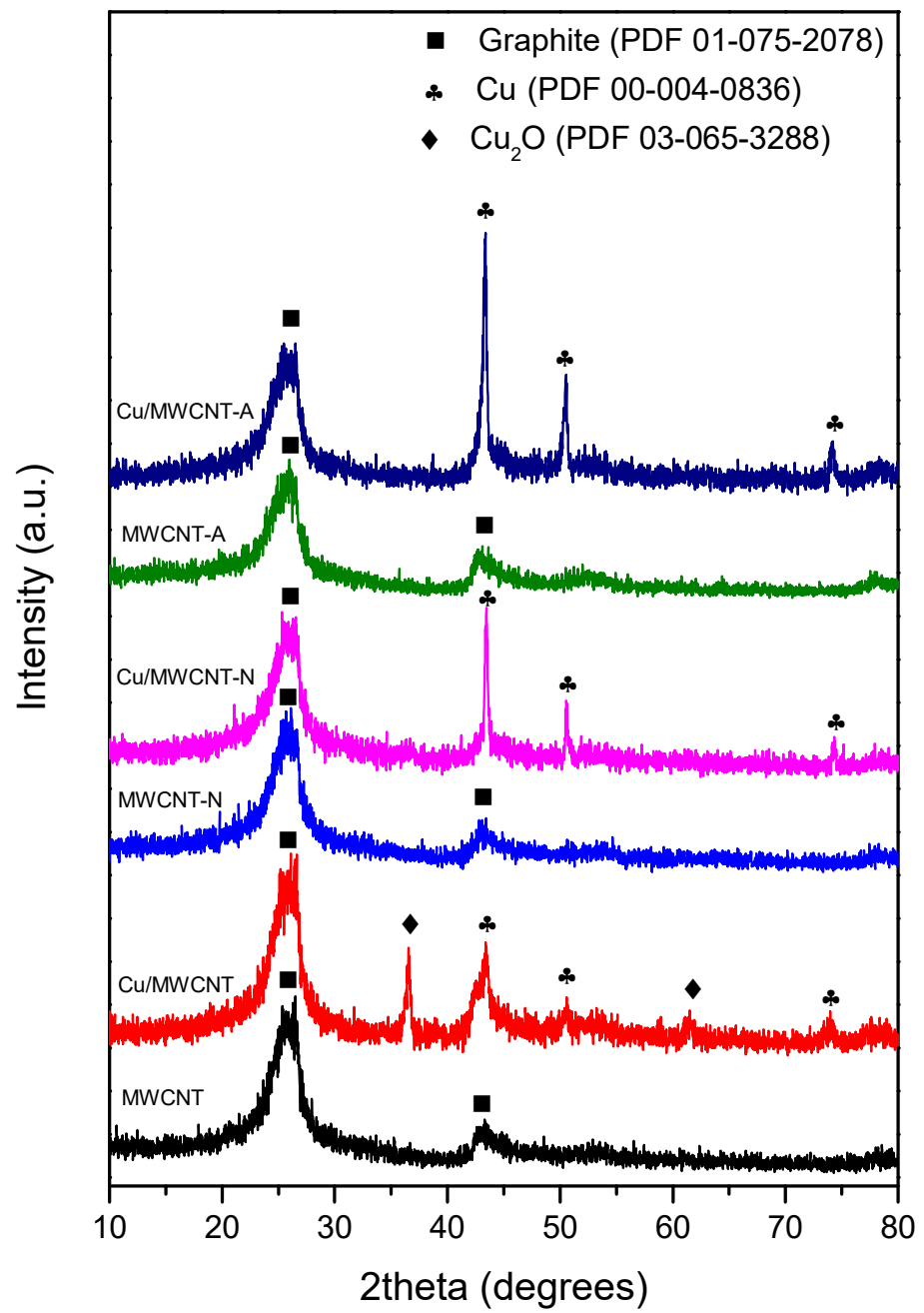


Figure 1. XRD spectra of supports and catalysts.

Table 1. Specific surface areas of samples.

Sample	$S_{BET}$ ( $m^2 g^{-1}$ )
MWCNT	243
Cu/MWCNT	215
MWCNT-N	237
Cu/MWCNT-N	219
MWCNT-A	220
Cu/MWCNT-A	213

#### 4. Conclusions

Functionalization treatments are capable of enhancing the physicochemical features of supports and catalysts. The formation of surface functional groups could serve as active sites for the anchoring of metal particles, also promoting their reduced oxidation state and/or the adsorption of reactants. The catalysts presented herein are being thoroughly characterized in order to confirm the functional groups that are present and the physicochemical properties achieved. The stability and performance of their catalytic features will be finally tested under mild conditions of liquid-phase glycerol hydrogenolysis.

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