



Short communication

Sequential catalytic growth of sulfur-doped carbon nanotubes and their use as catalyst support



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ABSTRACT

A sequential process has been developed to produce sulfur-doped carbon nanotubes (7% w/w sulfur) on iron supported catalysts. In this procedure it is necessary to first activate the iron catalyst to initiate the growth of all-carbon CNTs from ethylene, prior to growth sulfur doped CNTs from thiophene. The resulting sulfur-doped carbon nanotubes constitute an excellent support for the anchoring of very small (1.8 nm) palladium nanoparticles. This Pd based catalyst is very active for ethanol aerobic oxidation to acetic acid.

1. Introduction

It is known that the performances of carbon nanotubes (CNTs) can be improved by modifying the electronic properties of their sp^2 carbons, and a large number of developments have been carried out in this direction in recent years. This improvement is in particular obtained by insertion of heteroatoms, such as boron, nitrogen, phosphorous or sulfur, within the CNT structure, leading to substitutional doping [1]. These doped CNTs are proposed for various applications such as in the fields of catalysis, optoelectronics, solar panels, or even energy storage [2]. Many studies have attempted to produce B-, N-, or S-containing CNTs with the same methods to produce pristine CNTs. The morphology of the obtained materials differs notoriously from pure CNTs, which are tubular structures with hollow cores. For example, N-doping creates hollow sections separated by one to few graphitic layers (bamboo-like structures), and it was reported that S-doping produces branched morphologies [3]. Another approach to produce these doped-CNTs starts from pristine CNTs and involves costly post-synthesis treatment. The works describing the direct synthesis of S-CNTs are scarce compared to those concerning nitrogen doping. Denis et al. have shown by DFT calculation that it is possible to dope CNTs with sulfur [4]. The larger size of S atoms compared to the C ones and the longer C–S bond compared to the C–C bond should distort the structure, but they conclude that CVD could be an effective method to synthesize such structures. Zhou et al. describe a single step synthesis to obtain S-CNTs from dimethyl sulfide on a Co/MgO catalyst at 1273 K [5]. However, the material synthesized appear to be assemblages of CNTs covered

with sulfur-containing sheaths, and not CNTs containing sulfur atoms within their structure. High temperatures were also used to prepare branched CNTs (Y-junction CNTs) from thiophene and nickel catalysts; however these structures contain only very small amounts of sulfur (< 1% at.) [3]. Additionally, it was shown that these structures exhibited a stacked-cone morphologies similar to the one obtained in carbon nanofibers. Small amounts of sulfur (0.7% w/w) were also obtained by decomposing carbon disulphide at 1173 K on iron catalysts [6]. Finally, it is interesting to note that the CNT synthesis by CVD in the presence of sulfur precursors does not necessarily lead to the synthesis of sulfur doped structures. Indeed, Lee et al. have shown that the presence of sulfur (they use in particular thiophene) during the synthesis by CVD at 1443 K makes it possible to decrease the catalyst sintering and to increase the purity of the CNTs produced [7]. The CNTs prepared have very regular walls and the sulfur is concentrated on the surface of the catalyst particles and not in CNT walls. It thus appears that the direct synthesis of S-CNTs containing significant amount of sulfur is still challenging.

We describe herein a simple sequential procedure to selectively produce at moderate temperature S-CNTs containing sound amounts (7% w/w) of sulfur in their structure, and their use as catalyst support for palladium deposition. The Pd/S-CNT catalyst have been used for ethanol aerobic oxidation to acetic acid, and compared to palladium catalysts deposited on undoped CNT, oxidized CNTs and nitrogen doped CNTs.

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2. Experimental

2.1. Materials

2.1.1. Nanotube synthesis

The multi-walled carbon nanotubes (CNT), nitrogen doped multi-walled carbon nanotubes (N-CNT), and sulfur doped multi-walled carbon nanotubes (S-CNT) were synthesized by a catalytic chemical vapor deposition process into a fluidized bed reactor using ethylene (C_2H_4) as a carbon source [8], acetonitrile (C_2H_3N) as a carbon and nitrogen source [9], and thiophene (C_4H_4S) as a carbon and sulfur source. The oxidized CNTs were obtained by nitric acid oxidation of the CNTs [10]. For S-CNT growth, the catalyst (Fe/Al_2O_3 or $AlFeCoO_4$) were reduced in a fluidized bed reactor under a nitrogen ($225\text{ mL min}^{-1} N_2$) and hydrogen ($150\text{ mL min}^{-1} H_2$) flow at 1023 K. After this reduction step the nitrogen and hydrogen flow was followed to ethylene for 3 min and then thiophene for 27 min to produce S-CNT. The S-CNT were recovered and then purified by aqueous solution (50 vol% H_2SO_4) under reflux at 413 K for 3 h. The product was then filtered and washed. The resulting solid was finally dried overnight at 353 K.

2.1.2. Palladium catalyst synthesis

A wet impregnation method was used to prepare the palladium catalysts supported on carbon nanotubes. The desired amount of palladium (II) nitrate dihydrate [$Pd(NO_3)_2 \cdot 2H_2O$] was added to an acetone solution (100 mL) containing 1 g of carbon nanomaterial, as to introduce 2 wt% of metal phase. The solution was then sonicated at room temperature for 1 h followed by magnetic stirring at room temperature overnight. The solid was then filtered and washed with acetone. The resulting solid was then dried overnight in an oven at 393 K. Finally, the catalyst was reduced in a horizontal tube oven under a nitrogen and hydrogen flow (20 vol% H_2) at 573 K for 2 h.

2.1.3. Oxidation of ethanol

The oxidation experiments were conducted in a 65 mL stainless steel autoclave reactor equipped with magnetic stirring and heated in a silicone oil bath. The reactor was charged with 10 mL of 5wt% aqueous ethanol and 0.1 g of catalyst. The reactor was then closed and heated to the desired reaction temperature (373–473 K) and then pressurized with technical air (80 vol% N_2 and 20 vol% O_2) at a required pressure (10–50 bar) the reaction was allowed to stir for a required reaction time (3–25 h). The stirring rate was kept constant at 400 rpm for all experiments. When the reaction was finished, the reactor was cooled with an ice-water mixture at a temperature below 278 K, to ensure that the volatile products such as acetaldehyde remain in solution before analysis [6]. The analyses were performed in a Clarus 500 gas chromatograph, equipped with a split/splitless injector, a capillary column (Stabilwax®-DA Fused Silica 30 m, 0.25 mm i.d.) and a flame ionization detector (FID). At the end of each experiment, the catalyst was separated from the liquid reaction mixture by filtration and the liquid reaction mixture was analyzed by Coulometry to determine the water amount from ethanol oxidation reaction using a Titrator TitroLine KF trace.

2.2. Methods

TEM micrographs were taken with a JEOL JEM 1011 microscope operating at 100 kV. The high resolution analyses were conducted using a JEOL JEM2100F microscope equipped with a Field Emission Gun (FEG) operating at 200 kV with a point resolution of 2.3 Å and a JEOL JEM-ARM200F Cold FEG microscope operating at 200 kV with a point resolution of > 1.9 Å. The approximation of the particle mean size was made through a manual analysis of enlarged micrographs by measuring at least 250 particles on a given grid. The Brunauer–Emmett–Teller (BET) analyses by N_2 adsorption isotherms at 77 K (QuantaChrome

instrument) were performed to give the specific surface area and pore volume and pore size distribution. XRD diffractograms were obtained at room temperature with a Panalytical X'PERT PRO diffractometer, employing Cu K α radiation ($\lambda = 1.54\text{ \AA}$) and a parabolic MPD-mirror for Cu radiation. The diffractograms were acquired in 2θ range from 5° to 90°, using a continuous scan mode with an acquisition step size of 0.0170° and a counting time of 299.72 s. Raman spectra were obtained in a micro Raman Spectrometer HR 800 Jobin Yvon Horiba using a laser of 633 nm wavelength as an excitation source. The thermograms were acquired in a temperature range from 303 to 1273 K at 10 K min^{-1} under air atmosphere using a TG/DTA Shimadzu. The elemental results were obtained using a CHN Perkin-Elmer elemental analyzer. The palladium percentage were measured using an iCAP 6300 ICP Spectrometer. The X-ray photoelectron spectroscopy was performed on XPS K-alpha ThermoScientific apparatus, which operated with a non chromatized Mg K source (1253.6 eV).

3. Results and discussion

Sulfur is known to be a source of poisoning for metal catalysts. A complex mechanism of poisoning has been proposed, which comprises site-blocking, and a change of the number of active sites driven by temperature [11]. It is also known that sulfur plays an important role to promote or inhibit the CNT growth [12]. At low concentration, optimized CNT yields can be obtained; whereas high concentration of sulfur inhibit the growth of CNTs [12,13]. The positive role of sulfur has been explained through the formation of a layer on the surface of the catalyst particles that plays a role in encouraging nanotube growth by surface diffusion [14]. Interesting comparison can be made with the Fischer-Tropsch synthesis on iron catalysts. In this reaction, sulfur is also considered as a severe poison [15], even if addition of low amounts of this heteroelement can, in some specific cases, improve the performances [16–18]. In that case, monolayer surface sulfides are formed on the iron catalysts at H_2S concentrations below 2 ppm, while bulk sulfides are formed at higher sulfur concentrations [19]. In the Fischer-Tropsch synthesis [20], as for CNT growth [21], both metallic iron and iron carbides are suspected to be the active phases. Interestingly, it has been shown that, for the Fischer-Tropsch reaction, iron carbides are more resistant to poisoning by sulfur than metallic iron [18]. Since iron carbide(s) should be present during CNT growth we investigate the possibility to grow S-CNTs from a sequential process; in which the iron catalyst will be activated *via* the initial growth of all-carbon CNTs. During this phase, iron carbide should be at the surface of the catalyst particles; so that if the thiophene is introduced these particles should be less prone to deactivation. We have recently shown that it was possible to grow hybrid CNT@N-CNT structures containing undoped and N-doped sections on the same tube by using a sequential approach [9]. We have followed a similar approach to initiate the growth of S-CNTs. Indeed, the direct approach, *i. e.* direct decomposition of thiophene on 5% Fe/Al_2O_3 (C1) or $AlCoFeO_4$ (C2) catalysts did not lead to S-CNT, but to a poorly defined material (see SI.1) with a low yield ($0.45\text{ g}_C \cdot \text{g}_{CataC1}^{-1}$, and $2.2\text{ g}_C \cdot \text{g}_{CataC2}^{-1}$), and with a low surface area ($47\text{ m}^2\text{ g}^{-1}$) and a high sulfur content (12.7%). In the first sequence (the activation step), an ethylene/ Ar/H_2 mixture is introduced for a short duration (1 to 3 min) to initiate the CNT growth. Then, for the second sequence, the ethylene/ Ar/H_2 mixture is switched-off and replaced by a thiophene/ Ar/H_2 mixture. At 1023 K, this procedure allows the production of S-CNTs with yields of $0.23\text{ g}_C \cdot \text{g}_{CataC1}^{-1}$ for C1 and of $3.6\text{ g}_C \cdot \text{g}_{CataC1}^{-1}$ for C2. The lower yields obtained compared to the synthesis of undoped CNTs ($1.2\text{ g}_C \cdot \text{g}_{Cata}^{-1}$ (C1) and $9.8\text{ g}_C \cdot \text{g}_{Cata}^{-1}$ (C2), respectively) should be correlated to the fact that sulfur, as nitrogen [22], decreases the CNT growth rate.

After a purification step in boiling H_2SO_4 in order to remove the catalyst, the S-CNTs were characterized. TEM micrographs of S-CNT produced from C1 are shown in Fig. 1.

The S-CNT mean diameter is 15 nm. The S-CNT prepared from C2

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