Oxidative dehydrogenation of 9,10-dihydroanthracene using multi-walled carbon nanotubes

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Abstract

Multi-walled carbon nanotubes (MWCNTs) have been used in the oxidative dehydrogenation of 9,10-dihydroanthracene in an organic solvent (toluene) using molecular oxygen as the oxidant, and in the absence of trace amounts of metals. The process is very selective and almost no anthraquinone is formed. Thermal treatment of the MWCNTs at 2600 °C favors deoxygenation of the support and markedly improves the catalytic activity. MWCNTs are better catalysts than either charcoal or exfoliated carbon.

Keywords: Carbon nanotubes; Oxidative dehydrogenation; Anthracene; Metal free; Thermal treatment

1. Introduction

Carbon nanotubes (CNT) have been the subject of much research since their discovery as a by-product in arc-discharge materials in 1991 [1]. A large number of studies have been devoted to the synthesis and uses of these new materials in the field of nanotechnology and numerous potential applications in several advanced domains have been demonstrated [2-4]. Many recent publications have been focussed on the use of CNTs in supported catalysts [5-7]. Advantageous properties of CNTs here include their high specific surface area, and good electrical and thermal conductivity, as well as inertness towards acidic or basic reagents. In some specific cases, multi-walled carbon nanotubes (MWCNTs) have been used as supports for metallic palladium nanoparticles and as microwave absorbers [8], thereby leading to unusual chemical transformations such as regio-selective double alkynylation of substrates [8].

The present work concerns the use of MWCNTs as a catalyst for the oxidative dehydrogenation (ODH) of dihydroanthracene under mild reaction conditions and in the absence of surface loaded metals. This unusual catalytic activity is extremely interesting as it allows the avoidance of metal-based active phases which normally need to be recovered or disposed of at the end of the life of the catalyst. It also enables the use of molecular oxygen as the oxidant, which is attractive both for cost reasons and for the absence of toxic wastes. ODH reactions of 9,10-dihydroanthracene have already been described in the literature [9] but none has involved the use of MWCNTs. Known procedures include the use of an oxidant in large excess [10], and/or of catalysts such as precious metals [11], strong bases [12] or Pd/charcoal [10,11]. Activated carbon has also been used as a catalyst but it has been suggested that its activity may be the result of the presence of traces of metals such as iron [13]. Herein, we describe an

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investigation of the efficacy of MWCNTs as catalysts for the dehydrogenation of 9,10-dihydroanthracene, including an assessment of the influence of surface treatment on the catalyst activity.

2. Experimental

2.1. Catalyst preparation

The multi-walled carbon nanotubes (MWCNTs) were synthesized by a catalytic route (CVD) using ethane and dihydrogen as precursors and were purified by acid and base washing as described elsewhere [14]. The yield amounted to about 2000 wt. % with respect to the loading of the starting iron catalyst, which represents one of the highest yields cited in the literature. The very pure and homogeneous carbon nanotubes produced had a mean diameter of *ca.* 40 nm and a length of up to several hundred nanometers. The as-synthesized carbon nanotubes had both ends closed. The nanotubes were highly entangled and significant structural defects were observable on the outer wall surface. These defects were mainly due to the low synthesis temperature (640°C). The as-synthesized MWCNTs were subsequently treated in flowing argon (20 cm^3/min) at 2600°C for 2 h. Exfoliated graphite was provided by Carbone Lorraine (France) and activated charcoal by Calgon Carbon Corporation, Pittsburgh, USA, sample reference 9422-3793.

2.2 Catalytic measurements

The ODH of 9,10-dihydroanthracene (100 mg 0.555 mmol) was carried out over different carbon-based materials (100 mg) in toluene (10 mL) under a molecular oxygen atmosphere (1 atm) at 110°C in a 50 mL round bottom flask equipped with a condenser equipped and a gas outlet. Regularly, sample of the reaction mixture (after decantation of the mixture) was analyzed after evaporation of the solvent by NMR spectroscopy. At the end of the reaction excess methanol was added to the mixture insuring complete desorption of the chemicals from the nano-tubes surface. On each case the products were isolated by column chromatography and the final products characterized by ^{1}H NMR spectroscopy in deuteriated chloroform. All reactions were performed under an atmosphere of oxygen using standard Schlenk tube techniques. All chemicals were used as received from commercial sources without further purification unless otherwise stated. Toluene was used as received and chromatographic purifications were performed using 40-63 μm silica gel. TLC was performed on silica gel plates coated with fluorescent indicator.
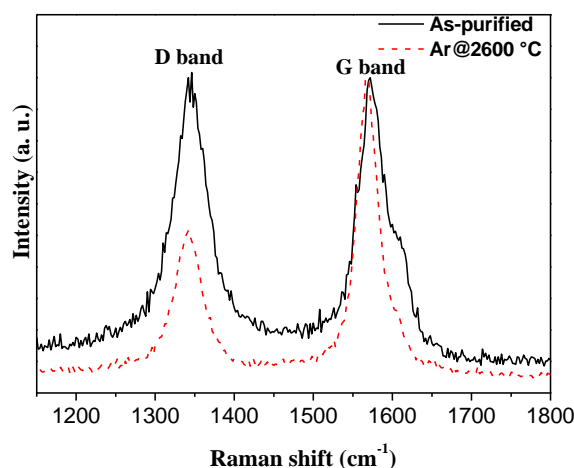

Fig. 1: Raman spectra of the MWCNTs after synthesis at 640°C and after heat treatment in flowing Ar at 2600°C.

2.3 NMR characterization

^{1}H NMR (300.1 MHz) and ^{13}C NMR (75.5 MHz) spectra were recorded at r.t. on a Bruker Advance 300 MHz spectrometer, using perdeuteriated solvents as internal standards. FT-IR spectra were recorded as KBr pellets. UV-Vis absorption spectra were recorded on a Perkin-Elmer Lamda Uvikon 933 spectrometer in CH$_2$Cl$_2$. Fast atom bombardement (FAB, positive mode) mass spectra were recorded with ZAB-HF-VB analytical apparatus with *m*-nitrobenzyl alcohol (*m*-NBA) as matrix.

3. Results and discussion

The as-prepared MWCNTs were heated under an inert atmosphere at 2600 °C for a short period of time. The degree of graphitization was analyzed by means of Raman spectroscopy (Figure 1) based on the use of the G band (graphite E$_{2g}$ vibration) at 1580 cm^{-1} as a measure of the abundance of sp^2-hybridised carbon atoms and the D band at 1350 cm^{-1} as a measure of the abundance of disordered carbon atoms [15]. An increase in the band intensity ratio I$_D$/I$_G$ after the heat treatment indicated a decrease in disordered carbon and this was consistent with TEM observations (Figure 2) showing a more ordered structure. SEM observations (not shown) indicated that the general morphology of the tubes was not modified after the heat treatment.

The specific surface area of the as-synthesized carbon nanotubes, measured by N$_2$ adsorption at 77 K, was 160 m^{2}g^{-1}, which is typical of values reported in the literature [16]. Consistent with the removal of surface defects, heat treatment resulted in a small decrease of the surface area to 130 m^{2}g^{-1}. The heat treatment also significantly diminished oxygen functionality on the outer

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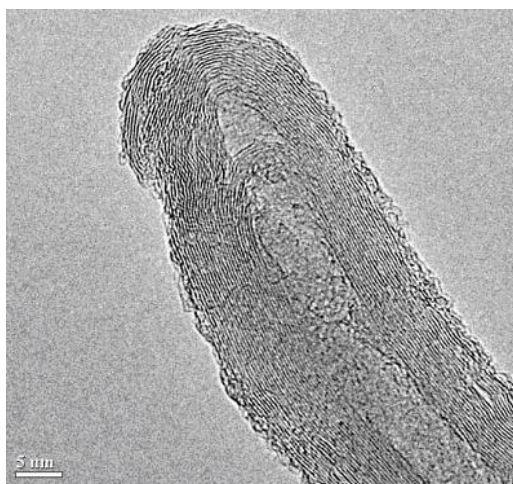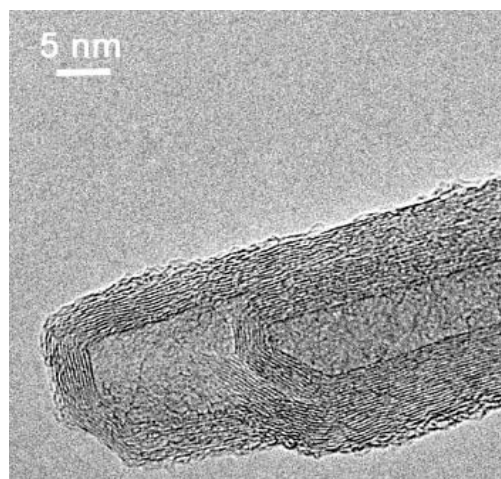
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Figure 2A

Figure 2B

Fig. 2: TEM images of MWCNTs before (2A) and after (2B) a thermal treatment at 2600°C
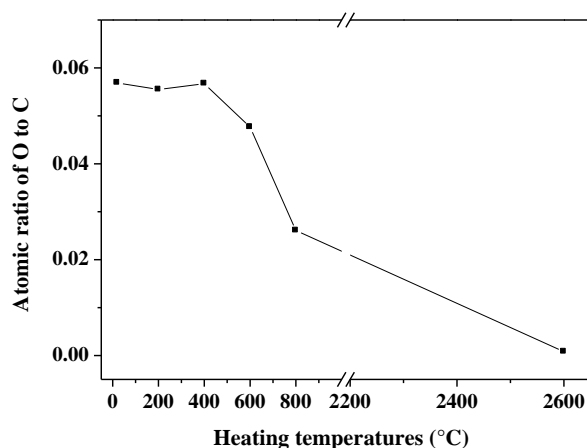
Fig. 3: Evolution of oxygen concentration at the MWCNTs surfaces as a function of temperature.

Fig. 4: Catalytic activity of various carbon based support for the synthesis of anthracene.

surface, as shown by XPS measurement of the surface O:C ratio (Fig ure 3). The oxygen concentration sharply decreased at 800 °C and oxygen was no longer detectable after heat treatment at 2600 °C, consistent with observations by Peng *et al.* [17].

The ODH results are gathered in Table 1, and clearly show the chemical selectivity of the reaction no matter what catalyst was used: anthracene (A) along with only traces (<1 %) of anthraquinone (Q) were formed.

The spectacular improvement of the ODH activity after thermal treatment of the catalyst (Figure 4), is likely attributable to the extremely low concentration of oxygenated functions on the surface as indeed shown in Figure 3. The presence of oxygenated groups on the carbon nanotubes surface could modify the strength of the adsorption of 9,10-dihydroanthracene on the surface and reduce the overall conversion rate [18]. The adsorption of aromatic
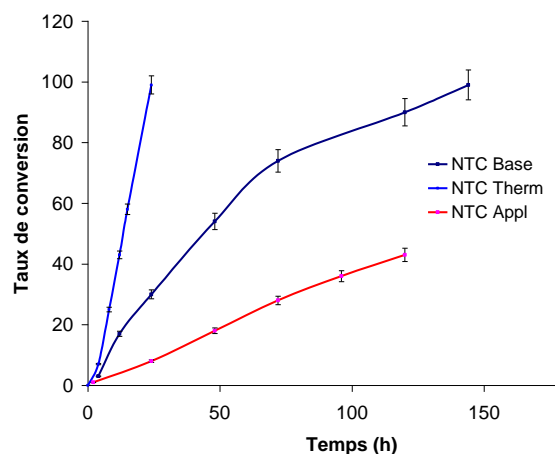
molecules is favoured by the delocalization and the hybridization of π-electrons between the nanotubes and the adsorbed molecules. The better catalytic activity may also reflect the better co-adsorption of oxygen, which would speed up the bimolecular surface reaction [19].

In comparing different catalyst systems, it is clear that adsorption selectivity is important and that solvent and product adsorption should be minimal. In the case of activated charcoal, the weak catalytic activity found is probably due to the marked ability of the support to adsorb the solvent and anthracene. The adsorption characteristics of the different supports was checked by UV-vis absorption at 000 nm on a model system based on water containing trace amounts of benzene (X mg/mL, Figure 5). As was expected, the rate of benzene absorption with activated charcoal is very fast and almost complete depletion of the ben-benzene in the solution is found after 1h. In contrast, with

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Table 1: Catalysis results for 9,10-dihydroanthracene ODH. determined by ^{1}H NMR: MWCNT$_{prist}$ as-synthesized MWCNTs without post-treatment, MWCNT$_{therm}$ after heat-treatment at 2600°C. (*) Measured by ICP-MS. (**) Reaction carried out in the absence of molecular oxygen, C$_{ex}$ = exfoliated graphite. (***) from Calgon Carbon Corporation Pittsburgh, USA.
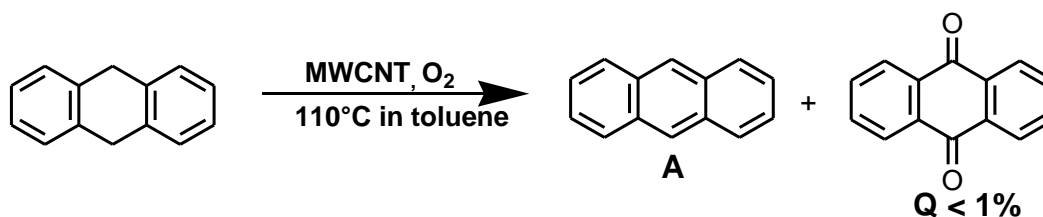
Carbon phase	Reaction times (hours)	Yield of A (mol %)	Specific surface (m^2/g)	Fe* (ppm)
MWCNT$_{prist}$	4	3	160	0.4
	72	74		
	144	99		
MWCNT$_{Therm}$	4	7	130	< 0.1
	24	99		
MWCNT$_{Therm}$**	64	< 1	130	-
Activated charcoal***	4	4	800	30
	24	36		
C$_{Ex}$	168	5	30	< 0.1
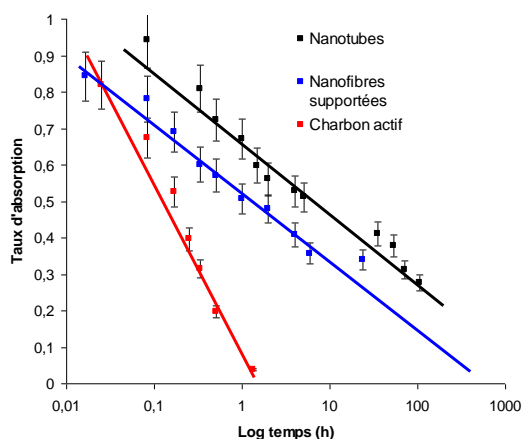
Fig. 5: Adsorption of benzene present in water as a function of contact time.

Fig. 6: Time dependence of the catalytic activity of MWCNTs Therm in the formation of anthracene

MWCNTs the adsorption process is slower by at least two orders of magnitude and complete adsorption of benzene was not attained even after 100 h contact (Figure 5). In the case of activated charcoal, the very efficient adsorption of benzene and by extension anthracene is probably the cause of the ineffective conversion of 9,10-dihydroanthracene to anthracene. The high adsorptivity of charcoal may be due to its known microporosity, which is not present with MWCNTs. Careful monitoring of the early stages of the reaction catalysed by MWCNTs revealed the occurrence of an induction period of a few hours which may be a reflection of the low affinity of the nanotubes for the
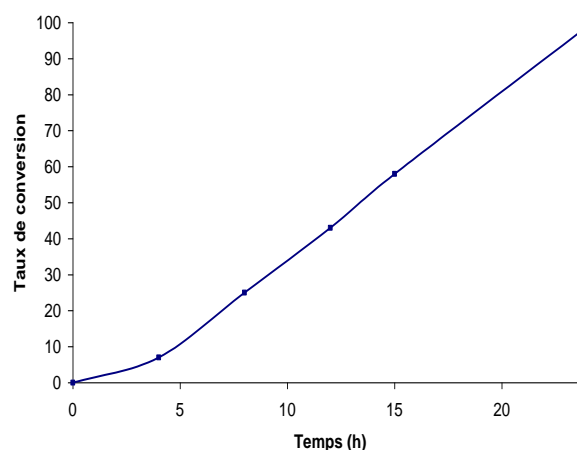
dihydroanthracene reactant and the consequent slow adsorption (Figure 6).

In the as-grown MWCNT$_{prist}$ support, the carbon surface was functionalised with numerous polar, oxygen-containing groups (–COOH and –OH), groups unfavourable to the chemisorption of 9,10-dihydroanthracene, which is hydrophobic. Additionally, the curvature shape of the nanotubes could play a role favourising the Van der Walls interaction of the roof shape 9,10-dihydroanthracene and consequently the catalytic reaction. Similar effects have been evoked in the literature in the case of adsorption of Krypton [23] or methane [24] on curved surfaces due to
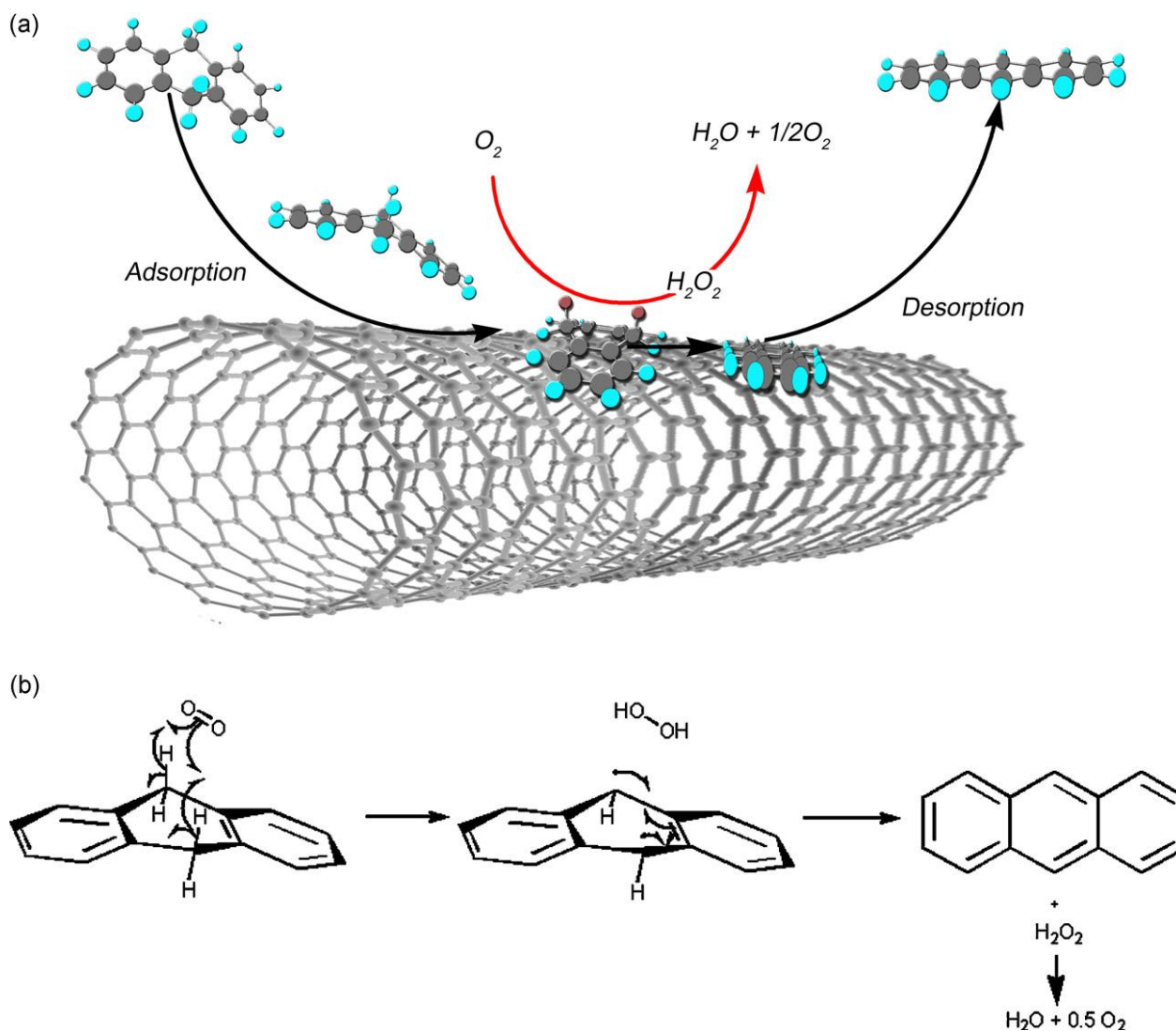
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(a)

(b)

Fig. 7: (a) Top: hypothetical mechanism concerning oxidative dehydrogenation of dihydroanthracene on the surface of multi-walled carbon nanotubes. (b) Bottom: chemical drawings of electron and atom balance during the chemical transformation.

energetically favourable interactions. For the exfoliated graphite used under similar reaction conditions, the catalytic activity is negligible. Here the surface interactions with the reactants, 9,10-dihydroanthracene and molecular oxygen, are certainlyweak due to the absence of marked curvature.

From a mechanistic view point it is envisaged that the roof shaped dihydroanthracene substrate is adsorbed on the nanotube surface. During this process the folded conformation will be distorted due to strong adsorption forces and the two hydrogen atoms pointing to the outside of the surface are likely susceptible to interact with molecular oxygen to give hydrogen peroxide and anthracene as the outcome (Fig. 7a). Under the used conditions (toluene at 110 ◦C) hydrogen peroxide is decomposed to oxygen and water. The flat anthracene target is then partially desorbed and the catalytic cycle is perpetuated by interactions with the starting substrate. At the end of the catalytic run, all anthracene is desorbed by treatment with a polar solvent. During the catalytic cycle, oxygen is reduced to water (pos-

sibly via the formation of H_2O_2), and dihydroanthracene oxidized to anthracene. Likewise isolated radicals are certainly not formed owing the absence of diquinone formation during the overall process (Fig. 7b).

These results highlight the unique properties of MWCNTs as dehydrogenation catalysts working under mild conditions (atmospheric pressure, 110 ◦C). It may be noted that they appear to be of similar efficacy in catalysing the ODH conversion of ethylbenzene into styrene [10] or n-butane into 2-butene [11]. It is worth noting also that less than 0.4ppm of Fe is present in solution after the first catalytic run. This is considerably less than the iron present in commercially available carbon supports [16]. The deliberate addition of $Fe(ClO_4)_2 \cdot 6H_2O$ to the catalytic medium had little effect on the rate of conversion of 9,10-dihydroanthracene into anthracene but a significantly greater yield of anthraquinone (0.4%) was obtained.

To conclude, we have demonstrated that carbon nanotubes can be effectively used as a catalyst for oxidative dehydrogenation under mild conditions with molecular

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oxygen as the hydrogen acceptor. The ODH activity was significantly enhanced by thermal treatment of the as-synthesized carbon nanotubes. The treatment at 2600°C decreases the specific surface area and removes oxygenated groups from the surface. The heat treated MWCNTs are not only more active than their untreated precursors but also are more active than exfoliated graphite. Adsorption of the reactants (9,10-dihydroanthracene and oxygen) is certainly a key factor in the catalytic reaction and the activity of the MWCNTs appears to be a result of the relatively weak adsorption of both reactants and products incomparison to the situation with a conventional catalyst such as activated charcoal.

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