

Properties and catalytic applications of carbon nanotubes

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ABSTRACT

The production of nanomaterials has been developing rapidly as an attractive option for a variety of applications such as electronic devices for storage and energy conversion, chemical and biological sensors, as well as catalysts and catalyst supports. Among these materials, carbon nanotubes have attracted increasing scientific and technological interest due to their fascinating properties. Since its discovery in 1991, many studies have been addressed to their synthesis, purification and characterization as well as their applications. In catalysis, these materials exhibit a great potential for application due to their excellent chemical and textural properties, which include mainly small size, mesoporosity and high specific surface area, as well as their electronic properties, high adsorption capacity and the presence of functional groups on the surface. These properties make them promising candidates for application both as a support and as active phase in a great variety of reactions such as ethylbenzene dehydrogenation, Fischer-Tropsch synthesis, hydrogenation of alkenes, oxidation of methanol, methane decomposition and removal of organic compounds in wastewater, among others. By considering the importance of these materials for catalysis, this review aims to describe critically and concisely, some of the fascinating properties of carbon nanotubes and their relationship with catalysts. In addition, some key catalytic applications will be reported in order to

highlight the importance of these materials in catalysis field, referencing recent work by authors with experience in the area.

KEYWORDS: catalyst, single-walled carbon nanotubes, multi-walled carbon nanotubes, nanotechnology, nanocatalyst

1. INTRODUCTION

Nanoscience and nanotechnology are concerned with phenomena related to structures in a scale ranging from 1 to 100 nm. Because of such small size, nanomaterials have unique physical, chemical and biological properties which are typically different from those of a molecule or a comparable bulk material. These properties can be controlled by changes in their size at nanoscale and have attracted increasing scientific and technological interest in recent years, being the subject of a large number of papers and patents [1, 2].

Among the nanomaterials, carbon nanotubes emerge as a fascinating material with unique properties that make them attractive for a variety of applications, such as optoelectronics devices, catalysts, catalyst supports, ceramics, energy storage, displays, gas storage, bio-medicine materials and others [3, 4]. These properties include high chemical and thermal stability, high elasticity, high tensile strength and high specific surface area [5]. In addition, theoretical studies have shown that carbon nanotubes can behave as metallic or semiconducting materials depending on their size and chirality, which make them a unique candidate for potential applications as

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nanoscale electronic devices and quantum wires [6-8]. Also, they are considered as the strongest man-made material, with a Young's modulus estimated as high as 130 GPa [9, 10]. Because of these extraordinary properties, the studies related to carbon nanotubes have grown rapidly since the first work of Iijima in 1991, as shown in Figure 1.

2. Structure and characteristics of carbon nanotubes

The discovery of carbon nanotubes, an allotropic form of carbon, was attributed to Sumio Iijima, in 1991, who obtained multi-wall carbon nanotubes (MWCNs) in fullerene soot made by the arc-discharged method [5]. These nanotubes showed at least two layers and diameters ranged from 3 to

30 nm. In 1993, a new class of nanotubes has been discovered, with only a single wall (single-wall carbon nanotubes, SWCNTs) [11].

Carbon nanotubes are tubular structures of nanometer diameter and several microns in length. These structures are unusual due to their very small diameters (e.g. 0.4 nm with ten atoms around the circumference) and thickness of the tubes which can have only one atom [12]. A single-wall carbon nanotube, which typically has diameter of about 0.5-2 nm, is formed by a graphene sheet (a polyaromatic layer made of a hexagonal display of sp^2 hybridized carbon atoms) rolled-over into a cylinder of nanometric dimensions and hollow internal cavity, as illustrated in Figure 2. The driving force for the formation of

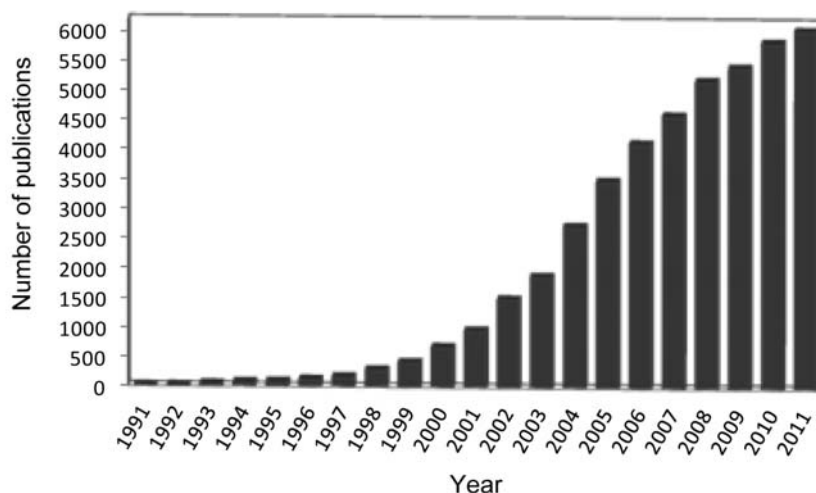


Figure 1. Number of publications related to carbon nanotubes from 1991 to 2011 (Search performed in the Scopus database using the keyword “carbon nanotubes”).

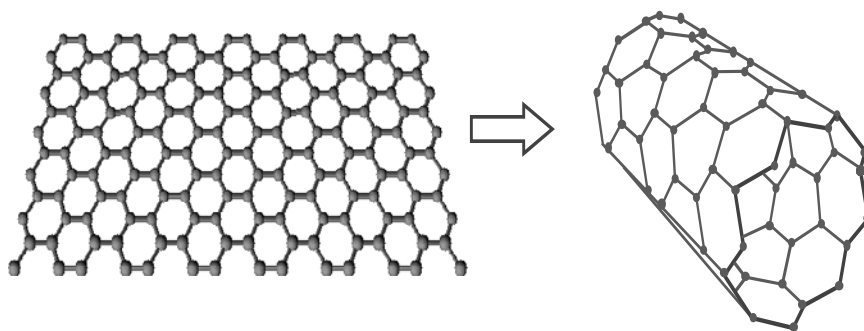


Figure 2. Illustration of a carbon nanotube made from a graphene sheet.

these nanostructures has been attributed to the thermodynamically unstable sheet of graphene, due to the finite number of carbon atoms, which lead to a high density of dangling bond atoms. Therefore, at small sizes, this unstable structure closes onto itself and removes all the dangling bonds, becoming a stable one [13, 14]. On the other hand, a multi-wall carbon nanotube, which typically has diameter of 2-50 nm, consists of concentric cylinders (Figure 3) with interlayer spacing of 3.4 Å and a diameter of around 10-20 nm. These concentric nanotubes are held together by van der Waals bonding. Both types of nanotubes can grow up to hundreds of microns or even centimeters [14-16].

The structure of single-wall carbon nanotubes is described by the chirality of the tube, that is, how the hexagons of carbon atoms are oriented to the tube axis. The chirality of the nanotube is defined by the chiral vector (C_h) that determines the direction in which the graphene sheet is rolled up, as shown in Equation 1, where n and m are integers and a_1 and a_2 are the unit cell vectors. Each pair (n, m) describes one of three possible types of carbon nanotubes: (i) when $n = m$ ($\theta = 30^\circ$) the nanotube is called *armchair*; (ii) when $m = 0$ ($\theta = 0^\circ$) it is called *zig-zag* and (iii) when $n \neq m$ ($0^\circ < \theta < 30^\circ$) it is called *chiral nanotube*, as shown in Figure 4 [17, 18]. The value of (n, m) determines the chirality of the nanotube and

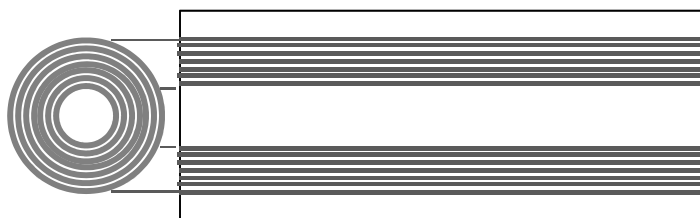


Figure 3. Illustration of a multi-wall carbon nanotube (MWNT).

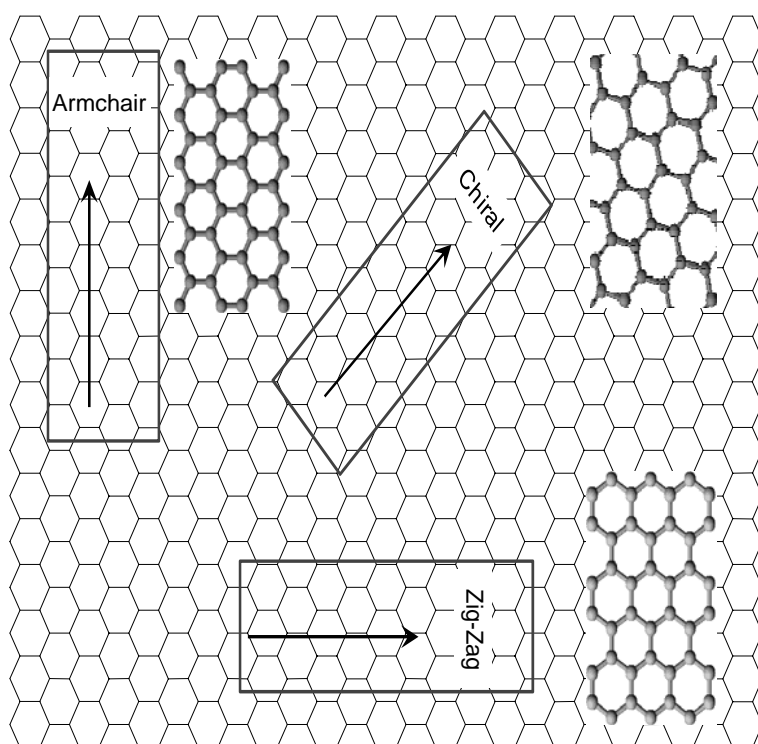


Figure 4. Scheme showing a graphene sheet and the definition of the chiral vector to form the different types of single-wall carbon nanotubes.

affects the optical, mechanical and electronic properties.

$$C_h = na_1 + ma_2 \quad (1)$$

3. Properties of carbon nanotubes

The combination of size, structure and topology of carbon nanotubes is responsible for the wide range of remarkable properties of these materials, as compared to other forms of carbon. The basic constitution of nanotube lattice, made by C-C strong covalent bond in graphite planes, as well as by the perfect alignment of the lattice along the tube axis and the closed topology, gives carbon nanotubes properties similar to the graphite ones, such as high conductivity, excellent strength and stiffness, chemical specificity and inertness, besides some unusual properties such as the electronic structure and elasticity. Also, carbon nanotubes show high specific surface areas which can be useful in mechanical and chemical applications [13].

3.1. Electronic properties of carbon nanotubes

The nanometer dimensions of carbon nanotubes as well as their unique electronic structures, coming from the two-dimensional graphene sheet rolled-up, give highly unusual electronic properties to these one-dimensional materials. This structure strongly contrasts with the two-dimensional graphene sheet which is a zero-gap semiconductor [19]. In the case of single-wall carbon nanotubes, several experiments have proved that individual SWNT can be regarded as pure quantum wires (1D-system), where the electrons are confined along the tube axis [13, 20]. Their electronic properties are strongly affected by the diameter and chirality of nanotubes [5, 19, 21, 22]. This occurs because the way in which the graphene sheet is rolled up directly affects the position of both valence and conduction band, generating metallic or semi-conducting behavior. Therefore, SWNTs may be either metallic or semiconducting, depending on their diameter and chirality, which are obtained from a pair of integers (m , n), as shown in Equation 1. They have been classified as follows: if $(n-m)$ is a multiple of 3, the nanotube is semiconductor with a very low, nearly zero energy gap; if $(n-m)$ is not a multiple of 3, the

nanotube is semiconductor with higher energy gap; if $n = m$ (*armchair*), the nanotubes are metallic. Therefore, all nanotubes *armchair* are metallic and all others are semiconductors [4]. However, the electronic properties of carbon nanotubes can be strongly affected by defects such as pentagons, heptagons, vacancies or dopants. The introduction of such defects into the carbon network has been used for tailoring the intrinsic properties of carbon nanotubes, creating new potential nanodevices and for proposing new potential applications for nanotubes in nano-electronics [12].

In the case of multi-wall carbon nanotubes, it has been proposed [23] that they behave like a carbon fiber: at high temperature the electrical conductivity may be described by semi-classical models used for graphite while at low temperature they show 2D-quantum transport features. For these materials, it is more difficult to predict the electronic properties, because the rolling up of the different graphene sheets may vary generating different kinds of nanotubes (*armchair*, *zigzag* or *chiral*) [13, 20]. In addition, the high complexity of the structure makes the presence of defects easier [20]. Despite the influence of the several layers in the band structure [24], it is believed that only the outer layer is responsible for electric transport in the nanotube [25]. Also, systematic four-probe measurements on several individual MWNT have shown that they can behave as metallic, semiconducting and semimetallic materials [26]. This finding and several other experiments [27, 28] indicate that the MWNTs also have unique conduction properties.

3.2. Mechanical properties of carbon nanotubes

Due to the strong carbon-carbon chemical bond in graphene sheet, carbon nanotubes are expected to have exceptional mechanical properties, with potential for applications in the reinforcement of composite materials. Indeed, the covalent bond, probably the strongest bond known in nature, makes carbon nanotubes one of the strongest and stiffest materials ever known [13, 15, 29].

The mechanical properties of carbon nanotubes can be conveniently described by their unique Young's modulus, elastic constants, Poisson ratio, response to deformation in the elastic regime,

tensile and compressive strains, strength at failure, toughness and buckling when bent [30]. The Young's modulus of isolated SWNTs does not depend on diameter or chirality and has a value of around 1 TPa, as found by calculations [31]. On the other hand, the tensile strength of carbon nanotubes is expected to be dependent on the concentration of different types of defects, experimental elastic parameters and synthesis techniques. A carbon nanotube has a tensile strength about a hundred times higher than steel and can tolerate large strains before mechanical failure [32], despite the very high Young's modulus. This was shown by several experiments by atomic force microscopy [33], which indicates that carbon nanotubes can bend into loops without breaking, proving their flexibility, toughness and capacity for reversible deformation. Moreover, SWNTs with small diameter were found to be elongated by around 30% before breaking [34] and values of around 55 GPa for the breaking strength have been reported [35].

The elasticity of carbon nanotubes is associated to the in-plane flexibility of the graphene sheet and the ability for carbon atoms to rehybridize with the degree of sp^2 - sp^3 rehybridization depending on the strain [13]. In addition, it is accepted that the single-wall nanotubes accommodate large strains by forming dislocations with a Stone-Wales 5/7/7/5 pair at the core of the dislocation which, however, trigger the fracture of nanotubes. For accommodating large strains on compression, MWNTs show reversible buckling [36]. As found by tensile strength experiments, MWNTs break at the outermost layer, with the inner layers being pulled out and smaller values for the tensile strength were found [35].

The mechanical properties of carbon nanotubes are sensitive to structural details [37]. The multi-wall nanotubes are invariably produced with a high frequency of structural defects, which can change their electronic properties and mechanical resistance, among other properties. Nevertheless, unique properties such as stiffness and flexibility are preserved, generating considerable interest for these solids [9].

3.3. Thermal properties of carbon nanotubes

Considering that carbon nanotubes should reflect the in-plane properties of graphite, their thermal

conductivity is expected to be extremely high. The in-plane thermal conductivity of graphite is around 3000 W/m K, which is second only to certain forms of doped diamond [13]. In fact, it has been demonstrated [12] that the thermal properties of carbon nanotubes, such as specific heat, thermal conductivity and thermopower, are quite special.

The thermal properties of carbon nanotubes display a wide range of behaviors, which are related to a two-dimensional graphene layer and to their unique structure and small size [30]. The specific heat and thermal conductivity of carbon nanotubes are determined primarily by the phonons, mainly at low temperatures [29, 38]. At high temperatures, the specific heat of individual nanotubes is expected to be similar to that of two-dimensional graphene but the effects of phonon quantization should be apparent at lower temperatures for single nanotubes of small diameter (<2 nm); in this case, a linear dependence of the specific heat with temperature is expected. The excitation of specific low-frequency optical phonon modes should be observable as anomalies in the temperature dependence of the specific heat. However, to study these effects, a single nanotube should be used, which are technically difficult. [12]. Therefore, the thermal properties have not been as extensively studied as the electronic and mechanical properties, in part because the experimental techniques are still under development [12, 30, 39].

3.4. Specific surface area and adsorption properties of carbon nanotubes

The specific surface areas of single-wall carbon nanotubes determined by BET techniques were found to range from 400 to 900 $m^2 g^{-1}$ while for multi-wall carbon nanotubes the values range between 200 and 400 $m^2 g^{-1}$, which are often lower than those for SWNTs [20, 40, 41]. The porous nature of both single-wall and multi-wall carbon nanotubes was demonstrated by several experiments [40-42], being single-wall carbon nanotubes typically microporous, with micropore volume ranging from 0.15 to 0.3 $ml g^{-1}$ [40] while multi-wall carbon nanotubes are mesoporous [41]. Both carbon nanotubes show Type II adsorption isotherms but with very different low pressure region, the uptake amount by SWNTs being much

higher than that by MWNTs due to micropores [40, 41].

For single-wall nanotube bundle, adsorption can occur inside the tubes (pore) or in the interstitial channels between the tubes or even on the external surface of the bundle or on the grooves at the contact between adjacent tubes on the outside of the bundle, as shown in Figure 5. The groove sites of SWNT are supposed to be the preferred low coverage adsorption sites due to their higher binding energies. On the other hand, in the case of multi-wall nanotubes, the adsorption sites are located in the aggregated pores, inside the tube or on the external walls [20]. For these materials, pores can be divided into inner hollow cavities of small diameter (3-6 nm) and aggregated pores (20-40 nm) formed by the interaction of isolated MWNT, being the latter more important for adsorption [20]. Multi-wall carbon nanotubes usually do not exist as bundles except for aligned nanotubes [43] and the aggregated pores, generated by the aggregation of MWNTs, play a more important role in adsorption [42].

Several adsorption studies carried out on carbon nanotubes [20, 44] have shown that they have special adsorption properties when compared to graphite or to activated carbon. This finding was related to their peculiar morphology, presence of defects, opening and closing of the tubes and presence of impurities such as catalyst particles.

In line with these properties, carbon nanotubes were found to show exceptional ability and high

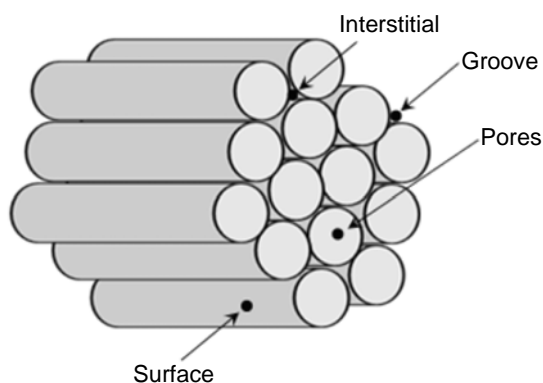


Figure 5. Illustration of the adsorption sites for single-wall carbon nanotubes.

adsorption efficiency for removing metals and organic compounds from wastewater, showing great potential for remediation and environmental protection. A lot of studies have shown that carbon nanotubes are more effective adsorbents for organic chemicals in solid phase extraction and water treatment than other forms of carbon [45-49]. Other studies have demonstrated that carbon nanotubes could efficiently remove trace concentrations of toxic air pollutant contaminants from wastewater, such as 1,2-dichlorobenzene [50, 51] toluene and methyl ethyl ketone [52]. Li *et al.* [53], for instance, have demonstrated that carbon nanotubes are efficient for removing fluoride, showing an adsorption capacity higher than charcoal. Similarly, Long *et al.* [54] have found that carbon nanotubes are more efficient for the removal of dioxin (a highly toxic and stable pollutant) than charcoal. In addition, Li *et al.* [55] have reported the use of carbon nanotubes for removing lead from water. The adsorption was influenced by pH and also by the presence of functional groups on the surface of the nanotubes, which can be controlled by chemical and thermal treatments.

Besides these applications, the single-walled carbon nanotubes have shown hydrogen storage capacity at room temperature [56] and high efficiency as sensors for detecting carbon monoxide and dioxide [57], as well as nitrous oxide and ammonia [8].

3.5. Chemical reactivity of carbon nanotubes

Since carbon nanotubes reflect the in-plane properties of graphite, the chemical reactivity of these materials is similar to a graphene sheet but enhanced as a direct result of the curvature of the nanotube surface. Therefore, the reactivity is related to the pi-orbital mismatch caused by an increased curvature and then is different for the sidewall and for the end caps of a nanotube; also, a smaller nanotube diameter is more reactive [58].

In fact, oxidation studies have demonstrated that the ends of nanotubes are more reactive than the cylindrical parts and thus can be opened after oxidation [59, 60]. These pentagonal defects at the ends and the extra dimensional curvature as well as the strain caused by these defects are responsible for this enhanced tip reactivity [13].

The surface of nanotubes is supposed to be inherently more reactive as compared to graphite due to the presence of many topological defects, such as bond rotational defects or pairs of 5-7 rings, defects which would not create any visible change in the overall topology or curvature [13].

4. Catalytic applications of carbon nanotubes

It is well-known that carbon-based materials are efficient catalysts and catalyst support for several reactions. As far as the environmental protection is concerned, the active carbon-based catalysts have proven to be efficient for removing several contaminants from wastewater, such as nitrate [61], chlorophenols [62] and phenols [63, 64] as well as for removing pollutants in gas phase like carbon dioxide and nitrogen oxides [65, 66]. Other applications include ethylbenzene dehydrogenation [67-69] methanol carbonylation to produce acetic acid [70], alcohols dehydration, olefins isomerization [71] and crotonaldehyde hydrogenation [72].

The large use of carbon-based materials for catalytic applications is mainly due to their high versatility in textural properties and surface chemistry and their chemical stability under many conditions as well as easy recovery of active metallic phase. Active carbon, for instance, typically show high hardness, high thermal resistance, high resistance against corrosion, high electrical conductivity, presence of functional groups on the surface, ability to adsorb ions, high specific surface area, resistance to acid/basic media and possibility of controlling the porosity [20, 73]. These materials can also be used to prepare hybrid catalysts, where the support has intrinsic catalytic activity, increasing their catalytic properties and porosity [74].

Other forms of carbon such as graphite nanofibers and carbon nanotubes have also been considered as promising materials for supports and catalysts. Regarding carbon nanofibers, they have proven to be efficient supports in catalysts for ethene hydrogenation [75], cinnamaldehyde hydrogenation [76], hydrogenation of light alkanes [77] and liquid phase hydrogenation reactions [78].

However, carbon nanotubes differ from usual carbon-based materials, exhibiting exceptional

properties such as unique electronic and mechanical properties, thermal stability, high chemical stability, large specific surface areas [13], uniform pore diameter, high length to diameter ratio, ability of very high hydrogen uptake [79] and surface with hydrophobic or hydrophilic character which can be controlled by chemical treatment [80]. These properties give a great potential of carbon nanotubes for application as promising supports for advanced catalytic systems.

Because of their unique electronic properties, carbon nanotubes show important differences as compared to activated carbon, mainly related to the interaction of transition metal atoms with the support. Theoretical calculations have shown that the anchoring sites are different on carbon nanotubes and on graphite and, for instance, nickel species show different stabilities on each support. This was assigned to differences in curvatures of the two supports and can allow the tailoring of the bonding site on the surface where the active phase will be deposited by varying the curvature of nanotubes [81].

Another important property of carbon nanotubes, regarding catalytic applications, concerns with thermal stability under reaction conditions. It has been noted that carbon nanotubes are more stable to oxidation than activated carbon but more reactive than graphite. However, the presence of residual metal in nanotubes can catalyze carbon gasification decreasing their stability. Also, the concentration of surface defects decreases the stability of nanotubes: the single-wall nanotubes which have lesser defects are more stable than the multi-wall ones [82].

In addition, the small size of carbon nanotube, as well as the high specific surface areas of mesoporous nature of the multi-wall nanotubes, is expected to significantly contribute to the catalytic performance, since most catalytic heterogeneous reactions are governed by mass and heat transfer phenomena [83]. This structure differs from that of active carbons which are typically microporous. By reducing the dimensionality of the catalyst and making easier the access of the reactants to the active sites, it is expected that faster transfers can be achieved during reaction [84].

In line with the advantageous properties of carbon nanotubes, a lot of work has been done concerning catalysts based on these materials. Most of the papers have focused on multi-wall nanotubes, since their high external surface and mesoporosity are expected to significantly decrease the mass-transfer limitations when compared to active carbons. Less work has been dedicated to single-wall nanotubes, due to their microporosity and to the difficulty for obtaining enough amounts of pure material to perform the catalytic studies.

4.1. The use of carbon nanotubes as catalytic supports

Several reactions were studied using metal particles supported on carbon nanotubes, as shown in Table 1. Giordano *et al.* [85], for instance, have evaluated the performance of 1% (w/w) Rh/MWNT in liquid phase hydrogenation of trans-cinnamaldehyde and the hydroformylation of hex-1-ene and have found that the mesoporous nature of the multi-wall carbon nanotube has improved the transfer processes. The same effect was noted by Vu *et al.* [86] by comparing the performances of platinum and/or ruthenium supported on both single and multi-wall carbon nanotubes and on active carbons, in hydrogenation of cinnamaldehyde to cinnamyl alcohol. They have found that the highest activities were shown by the catalysts based on mesoporous MWNT that decreased the mass transfer limitations in contrast with the other supports. A bimetallic catalyst, activated at high temperature, has shown a remarkable selectivity (93%) for high conversion levels (80%), due to electron transfer from the support to the metal and to the increased electrical conductivity of the support due to heating.

The selective hydrogenation of cinnamaldehyde has also been studied over platinum-based bimetallic catalysts supported on multi-wall carbon nanotube prepared by a microwave-assisted polyol reduction method [87]. It was found that the surface properties of carbon nanotubes, the solvent and the promoters largely affect the catalytic performance. The removal of oxygen-containing groups from the surface of carbon nanotubes increased both activity and selectivity, because of the suppression of side reactions catalyzed by acid

and because of the enhanced electron transfer from carbon nanotube to platinum nanoparticles. The iron and cobalt-modified platinum catalyst showed the best performance after removing the oxygen-containing groups from carbon nanotubes surfaces.

On the other hand, Lordi *et al.* [88] have demonstrated the potential of single-wall nanotubes for preparing platinum-based catalysts for hydrogenation of prenal to prenol, which is the first report about metal-loaded SWNT material. They have shown a simple and effective purification method for SWNT involving oxidation with concentrated nitric acid followed by centrifugation, washing and ultrasonication to disperse and mix the suspensions. The oxidation step was found to be critical for the catalyst performance, by creating surface oxides, mostly carboxylic acid functions, which act as anchors for platinum particles on nanotubes surface. Platinum particles are supposed to be chemically anchored to the surfaces of SWNTs through -COO-Pt bonds and do not anchor to the surface of oxidized SWNTs.

The catalytic propene hydroformylation was also studied using catalysts based on carbon nanotubes. Zhang *et al.* [89] have compared two kinds of Rh-phosphine complex catalysts supported on multi-wall carbon nanotubes grown by catalytic decomposition of methane or carbon monoxide. It was noted that the carbon nanotubes-based catalysts have shown not only high activity for propene conversion but also high regioselectivity to butylaldehyde.

By studying catalysts for the selective dehydrogenation of cyclohexanol to cyclohexanone, multi-wall carbon nanotubes-supported cobalt were produced by acetylene catalytic decomposition and oxidized by nitric acid [90]. A strong effect of the oxidizing pre-treatment of the support surface on the catalytic performances was found. The cobalt nanoparticles deposited on the oxidized nanotubes showed smaller size and higher dispersion, resulting in significantly better catalytic performance in the reaction.

The use of multi-wall carbon nanotubes as catalytic supports for ammonia synthesis was also investigated, by evaluating ruthenium-based

Table 1. Some examples of the use of carbon nanotubes as catalytic supports.

Catalyst	Reaction	Temperature (°C)	Remarks	Ref.
Rh/MWNT	Hydrogenation of trans-cinnamaldehyde and hydroformylation of hex-1-ene in the liquid phase	100°C	Mesoporous nature of MWNT ameliorates transfer processes.	[85]
Pt, Ru e Pt-Ru/ MWNT(SWNT)	Hydrogenation of cinnamaldehyde to cinnamyl alcohol	100°C	MWNT led to the highest active catalysts, decreasing mass transfer limitations	[86]
Pt-Fe(Co)/MWNT	Selective hydrogenation of cinnamaldehyde	35°C	The removal of oxygen-containing groups from the surface of carbon nanotubes increased both activity and selectivity	[87]
Pt/SWNT	Hydrogenation of prenal to prenal	110°C	Oxidation provides sites for anchoring platinum particles on MWNT	[88]
Rh-phosphine/MWNT	Propene hydroformylation	120°C	High activity of propene conversion but also high regioselectivity to butylaldehyde	[89]
Co/MWNT	Selective hydrogenation of cyclohexanol to cyclohexanone	250°C	MWNT oxidation by nitric acid improves catalytic performance	[90]
Ru/MWNT	Ammonia synthesis	420°C	MWNT improves metal dispersion and activity	[91]
Ni/MWNT	n-Heptane Cracking	450°C	MWNT increases metal dispersion and activity	[92]
Co/SWTC	Fischer–Tropsch synthesis	220°C	SWNT increases cobalt reduction and then activity and selectivity	[93]
Fe-Cu/MWNT	Fischer–Tropsch synthesis	70°C	The preparation method affects the different crystallite size distributions and then the catalytic performance	[94]

catalysts. Various alkali-promoters and carbon-based supports (graphite, fullerenes and active carbon) were compared and the effect of ruthenium and potassium amounts, the treatment of MWNT and the reaction temperature on the catalyst activity were investigated. It was found that potassium-promoted ruthenium catalysts supported on MWNT were four or five times more active than the graphite-based catalyst. This difference was assigned to the higher specific surface area of nanotubes, leading to an improvement of dispersion and to the electronic properties of carbon nanotube which increase the electron transfer from potassium to ruthenium [91].

Multi-wall carbon nanotubes were also used for preparing nickel-based catalysts for n-heptane cracking, providing high metal dispersion. The optimal nickel loading of about 5.2 mmol/g generates a catalyst with remarkable activity. These results indicated that the catalysts were promising for cracking of heavy hydrocarbons [92].

The activity of single-wall nanotube-supported cobalt catalysts has been studied in Fischer-Tropsch reaction. It was found that carbon nanotubes improve the activity by 22%, as compared to the conventional Co/alumina catalysts and increased the selectivity to C5+. The olefin/paraffin ratio on the Co/SWNT-MgO catalyst was about 7.7 times higher than the conventional cobalt catalysts. These improvements were related to an increase of cobalt reduction due to carbon nanotube [93]. The activity of multi-wall nanotube-supported iron doped with copper was also investigated in Fischer-Tropsch reaction [94]. The active phase was deposited on the support by three different techniques (incipient wetness, deposition/precipitation using potassium carbonate and deposition/precipitation using urea) leading to different metal particle sizes. The incipient wetness method and the deposition/precipitation technique using urea yielded highly dispersed iron species on carbon nanotubes while the use of potassium carbonate leads to larger iron oxide crystallites. However, after reduction all catalysts showed similar metal surface areas. Even through, the catalytic activity differed significantly as a function of the

preparation method, the catalyst prepared by incipient wetness being the most active one. This finding was assigned to the different crystallite size distributions, which would result in different amounts of the several catalyst phases under reaction conditions. On the other hand, the selectivity of the catalysts has not been changed due to the different preparation methods.

The use of carbon nanotubes as catalytic supports was also investigated for environmental applications, as shown in Table 2. Both platinum and ruthenium supported on multi-wall nanotubes were evaluated for the removal of aniline from wastewater by catalytic wet air oxidation, the most promising technology for the treatment of wastewater containing organic compounds [64, 95, 96]. For platinum-based catalysts, different supports (MWNT, carbon xerogels and active carbon) were compared. It was noted that the catalysts were active for the removal of the pollutant, the activity and carbon dioxide selectivity showing a dependency on the kind of the support and on concentration of oxygen containing functional groups on the catalyst surface. However, the catalyst based on MWNT was the least active and selective one [95]. A different result was obtained for ruthenium-based catalysts, for which multi-wall carbon nanotubes have led to an improvement of activity and selectivity. In this case, different ruthenium precursors were used as well as different methods of metal impregnation (excess solution and incipient wetness impregnation) and several methods of treatments for changing the functional groups on carbon nanotubes surface. It was found that the impregnation technique did not affect the catalysts performance while the surface chemistry influences the catalyst properties, sodium carbonate being the most suitable to oxidize the surface [96].

Other environmental application of multi-wall nanotubes was reported by Zuo *et al.* [97]. They have proposed a highly efficient oxidation catalyst, based on magnetic nanoparticles, for the removal of phenols from wastewater. It was demonstrated that the iron nanoparticles were readily adsorbed on the surface of multi-wall nanotubes, forming a nanocomplex that resembles natural horseradish peroxidase. Compared to this

Table 2. Some examples of the use of carbon nanotubes as supports for environmental catalysts.

Catalyst	Reaction	Temperature (°C)	Remarks	Ref.
Pt/MWNT	Removal of aniline from wastewater	200°C	MWNT decreases activity and selectivity as compared to active carbon and carbon xerogels	[95]
Ru/MWNT	Removal of aniline from wastewater	200°C	MWNT improves activity and selectivity as compared to active carbon	[96]
Fe/MWNT	Removal of phenol from wastewater	60°C	Iron on MWNT forms a nanocomplex similar to natural horseradish peroxidase	[97]
Rh/MWNT	Decomposition of nitric oxide	300-700°C	Carbon nanotubes are more efficient in keeping rhodium in metallic state	[98]
Au/SWNT	Selective oxidation of 1-phenylethanol to acetophenone	120°C	Electronic transfer from gold nanoparticles to the support improve the activity	[99]
Rh/CNT	Conversion of carbon monoxide and hydrogen to ethanol	350°C	Remarkable increase in the activity of rhodium particles inside nanotubes	[100]
Pt/MWNT	Electrochemical reaction in direct methanol cell	90°C	High electrocatalytic activity due to unique structure and electric properties of MWNT	[101]
Pt-Ru/MWNT (SWNT)	Electrochemical reaction in direct methanol cell	90°C	Carbon fiber-containing nanocomposites showed the highest performance	[102]
Pt-Ru filled MWNT fuel cell anode	Electrochemical reaction in direct methanol cell	--	Increased current density is due to high specific surface area and electrocatalytic activity of nanoclusters inside CNT	[103]
Pt-WO ₃ (Ru)/CNT, Pt/CNT	Electrochemical reaction in direct methanol cell	--	The high electrochemical activity of CNT based on materials is due to the higher electroactive surface area.	[104, 105]
Pt/CNT	Electrochemical reaction in a proton exchange membrane fuel cell	Room temperature	The metal deposition was sensitive to aging time of sensitizing solution and pH of the plating solution	[106]
Pd/MWNT	Electrochemical reaction direct ethanol fuel cells	70°C	Catalyst prepared by a redox method showed high electrochemical activity	[107]
Ru/CNT	Ammonia decomposition	400-600°C	More active than those based magnesia titania and active carbon	[86]

enzyme, the nanocomplex is chemically stable and can be produced in large scale, showing high efficiency, low cost, easy operation, high stability and reusability.

The use of carbon nanotubes as supports for the reduction of nitric oxide by hydrogen was also studied by using 1% (w/w) Rh/MWNT [98]. It was found 100% of conversion was achieved at 600°C over pure carbon nanotubes; after rhodium was loaded, 100% of conversion was achieved at 450°C. After reduction with hydrogen at or above 300°C, the catalyst led to 100% of conversion at 300°C. Compared to alumina, carbon nanotubes are more efficient in keeping rhodium in metallic state.

Another important application of carbon nanotube concerning environmental protection is the production of catalysts for green chemical reactions. Shanahan *et al.*, for instance [99], have prepared single-wall carbon nanotube-supported gold nanoparticles and have evaluated in solvent-free liquid-phase selective aerobic oxidation of 1-phenylethanol to acetophenone. Crystalline gold particles were obtained with a narrow particle-size distribution centered around 7 nm. It was found that gold nanoparticles adhered to the SWCNT surface, with an electronic transfer from these particles to the support. The 5% Au/SWCNT composite has led to a conversion of 95%.

Carbon nanotubes can also act as nanoreactors generating confinement effects as shown by Pan *et al.* [100]. They have noted a remarkable increase in the activity of rhodium particles confined inside nanotubes for the conversion of carbon monoxide and hydrogen to ethanol. The rate of ethanol production inside nanotubes exceeds that on the outside of nanotubes by more than an order of magnitude, a fact that is related to synergetic confinement which has not been observed before in catalysis involving carbon nanotubes.

On the other hand, carbon nanotubes can be used efficiently as catalytic supports for fuel cell electrodes replacing the classic carbon blacks. Li *et al.* [101], for instance, have studied a 10% (w/w) Pt/MWNT cathode in a direct methanol single cell, which has shown better performance than a catalyst based on a commercial Vulcan

carbon; in addition, pure MWNT did not show any electrocatalytic activity. The high electrocatalytic activity obtained may be assigned to the unique structure and electric properties of carbon nanotubes, that can increase the electrode conductivity, as well as to the specific interaction between platinum and carbon nanotube.

In addition, Steigerwalt *et al.* [102] have compared the effect of different supports (MWNT, SWNT and nanofibers) on the performance of platinum-ruthenium anode catalysts for direct methanol fuel cells, by using a molecular hetero-bimetallic precursor as metal source. The carbon fiber-containing nanocomposites with some ruthenium metal phase separation have shown to give the highest DMFC performance.

Platinum-ruthenium anode catalysts for direct methanol fuel cells were also prepared by a template method using multi-wall carbon nanotube (200 nm diameter), platinum (7 nm) and platinum-ruthenium (1.6 nm) filled MWNT fuel cell anode [103]. The current density of methanol oxidation at carbon/Pt nanocluster membrane electrodes is around twenty times higher than at bulk platinum electrodes. This increased current density is related to both the high specific surface area and the electrocatalytic activity of nanoclusters dispersed inside the carbon nanotubes. As the catalyst nanoclusters are only inside the carbon nanotubes, each carbon nanotubule is a separate reactor which could increase catalytic selectivity.

Rajesh *et al.* [104, 105] also have used a template method to prepare tubular carbon structures-alumina composites containing platinum, platinum-ruthenium or platinum-tungsten oxide for using as electrodes in methanol oxidation. The highest electrochemical activity was shown by Pt-WO₃/CNT followed by Pt-Ru/CNT and Pt/CNT. When compared to electrodes prepared from commercial carbons (Vulcan or E-TEK carbon) the most active catalyst was Pt-WO₃/CNT followed by Pt-Ru/E-TEK-Vulcan, Pt/CNT, Pt/E-TEK-Vulcan and bulk platinum, in this order. The highest electrochemical activity of carbon nanotube-based catalysts has been related to the highest electroactive surface area.

The importance of functionalizing carbon nanotubes for fuel cells applications was demonstrated by

Liu *et al.* [106]. Multi-wall carbon nanotubes were treated with nitric acid or a mixture of sulfuric acid and potassium dichromate and platinum was deposited on these supports, by electroless plating facilitated by a two-step sensitization-activation pretreatment. The deposition was sensitive to the aging time of the sensitizing solution and the pH of the plating solution. The Pt/CNT electrodes showed high electrocatalytic activity for oxygen reduction as tested by a single stack proton exchange membrane fuel cell.

A novel catalyst for alcohol electrooxidation was proposed by Chen *et al.* [107], based on palladium nanoparticles-carboxylic functional carbon nanotubes (Pd-MWNT), prepared by a facile spontaneous redox method. The catalyst has shown high electrochemical activity for alcohol electrooxidation on a glassy carbon electrode in an alkaline medium. The material is promising for direct ethanol fuel cells and ethanol sensors.

Carbon nanotubes were also considered for preparing catalysts for producing high pure hydrogen by ammonia decomposition for proton exchange membrane fuel cell. They were compared with other supports such as alumina, magnesia, titania and active carbon for ruthenium-based catalyst. Carbon nanotube produced the most active catalyst, probably due to the highest ruthenium dispersion, as well as to the high graphitization and high purity of carbon nanotubes. By modifying this catalyst with potassium hydroxide, the activity increased sharply, a fact which was related to the role of potassium hydroxide in making nitrogen desorption and hence ammonia decomposition easier.

4.2. The use of carbon nanotubes as heterogeneous catalysts

Besides their use as catalytic supports, carbon nanotubes have shown intrinsic activity for some reactions such as methane decomposition and oxidative dehydrogenation of ethylbenzene [108-111].

Direct decomposition of methane is an attractive method to produce high pure hydrogen from natural gas, without any carbon oxides. This process is particularly important for generating high pure hydrogen for fuel cells [112]. The use

of carbon-based catalyst offers several advantages [108], encouraging the use of carbon nanotubes. In line with these ideas, catalysts based on multi-wall nanotubes were prepared and compared with other forms of carbon. It has been noted that disordered forms of carbon were more active than the ordered ones and that the activity is structure and surface area dependant [108].

On the other hand, ethylbenzene dehydrogenation is the most important commercial route to obtain styrene, a high value intermediate for chemical industry [113]. Carbon-based materials have been pointed out as efficient catalysts for oxidative ethylbenzene dehydrogenation, an attractive alternative route to produce styrene [114]. Specially, carbon nanotubes have been recently investigated and have shown promising performances. It was found, for instance, that multi-wall carbon nanotubes, with different oxygen surface groups, were active in the reaction, showing performances close to those of active carbon and graphite. However, carbon nanotubes showed the advantage of being more stable under oxidative conditions. Also, pre-oxidized MWNT were more active in the beginning of reaction, highlighting the importance of oxygenated surface groups [109].

In another work [110], different sp^2 -hybridized carbon structures (multi-wall carbon nanotubes, onion-like carbon, carbon black and graphite) evidenced the activity of sp^2 carbon as catalyst for the selective oxidative dehydrogenation of ethylbenzene to styrene. The importance of microstructure of the sp^2 -bound carbon material to achieve high and stable efficiencies has been noted. The well-defined and oxygen free surface of onion-like carbon was considered as a valuable model to derive criteria for designing efficient carbon catalysts and to propose a reaction model. This catalyst showed the highest styrene yield (62%) at the highest stable ethylbenzene conversion as compared to carbon nanotubes (54%) and graphite (44%), in correlation with a decreasing basal plane-edge/kink site ratio, while carbon black was completely combusted on stream. The perfectness of the nanocarbons provided enough stability towards oxidation and was essential for gas phase oxygen activation.

The effect of graphitization on the performance of carbon nanotubes for oxidative dehydrogenation

of ethylbenzene to styrene was studied by Delgado *et al.* [111]. It was demonstrated that the concentration of oxygenated functional groups on the catalyst surface is responsible for the catalytic performance of carbon nanotubes. The elimination of functional groups by heating caused a decrease in catalytic performance in the beginning of reaction, while the microstructure did not change significantly. During reaction, the functional groups are regenerated, leading to a significant improvement in activity.

CONCLUDING REMARKS

Carbon nanotubes have demonstrated to have an enormous potential for catalytic applications, as a consequence of their extraordinary properties, mainly their unique electronic properties, which provide new specific interactions between the support and the active phase and the mesoporosity which improves the mass and heat transport during catalytic reactions. In addition, their surface chemistry can be changed by simple chemical treatments and, more importantly, these properties can be tailored for preparing catalysts with desired properties for different reactions. However, these properties are strongly affected by the presence of impurities and the choice of purification methods also depends on the subsequent application of nanotubes, since the presence of certain kinds of impurity can limit the potential applicability. Although a lot of methods of preparation and purification have been proposed, there is still a lack of efficient and economic routes to allow low cost production of carbon nanotubes. Moreover, it is still very difficult to obtain homogeneity in all the characteristics of these materials. In spite of these limitations, the use of carbon nanotubes for catalytic applications is attractive and the encouraging results have increasingly stimulated the catalytic studies for different purposes.

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