

# Carbon Nanotubes as Supports for Palladium and Bimetallic Catalysts for Use in Hydrogenation Reactions

doi:10.1595/147106711X577274

<http://www.platinummetalsreview.com/>

By R. S. Oosthuizen<sup>†</sup> and V. O. Nyamori<sup>\*</sup>

School of Chemistry, University of KwaZulu-Natal,  
Westville Campus, Private Bag X54001, Durban 4000,  
South Africa

Email: <sup>†</sup>robb@ukzn.ac.za; <sup>\*</sup>nyamori@ukzn.ac.za

*Carbon nanotubes (CNTs) possess unique properties which make them competitive with conventional catalyst supports. This short review collates findings from many research groups on the benefits of palladium/carbon nanotubes in hydrogenation reactions. The effects of modified CNTs and bimetallic platinum group metal (pgm) catalyst/CNT systems for hydrogenation reactions are also discussed.*

## Introduction

The need to optimise industrially important processes and new technologies, and to create a sustainable society and environment, drives the search for better energy sources and better materials. Coupled with this is the need for economic development and competitiveness in the global market. Worldwide trends are towards greener chemistry, greener energy and a decrease in our reliance on fossil fuels. Catalysis plays an important role in this and two recent papers have discussed how it has shaped, and will continue to shape, society (1, 2). Progressive research into novel catalytic systems is a part of this endeavour.

Palladium is one of the most versatile metal catalysts used in industry. Two of the main reasons for its importance are its ability to catalyse the formation of carbon–carbon bonds and the insensitivity of many Pd catalysts to water or oxygen. Pd is particularly efficient as a catalyst in hydrogenation reactions. Metal catalysts reach a much greater potential when supported. This is because metal catalyst particles can be dispersed to a greater degree, and therefore are exposed to a larger number of substrate molecules. Up to 75% of hydrogenation reactions are currently carried out over Pd/C catalysts.

A variety of carbon supports for precious metal catalysts have, for several decades, been used in heterogeneous catalysis (3). Emerging carbonaceous supports, such as the newly discovered carbon allotropes and shaped carbon nanomaterials (SCNMs), including CNTs (4), see **Figure 1(a)**, carbon microspheres (5),

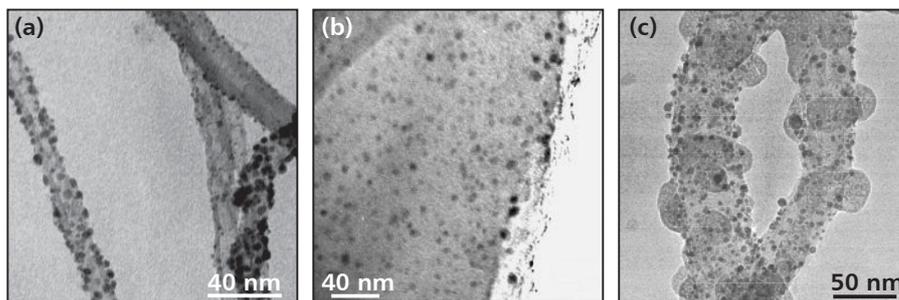


Fig. 1. TEM image of: (a) Pd/MWCNTs used for heterogeneous hydrogenation of *trans*-stilbene (76); (b) Pd/microspheres before a hydrogenation reaction (5); (c) Pd/CNFs used for the heterogeneous hydrogenation of cinnamaldehyde (6) (Reproduced by permission of The Royal Society of Chemistry and Elsevier)

see **Figure 1(b)**, and carbon nanofibres (CNFs) (6), see **Figure 1(c)**, are gaining more interest. The remarkable properties of CNTs, such as being relatively light in weight and strong in nature, make them worthwhile to investigate as supports for Pd metal catalysts. Although the existence of filamentous carbon nanomaterials (7) has been known for decades, it is only since the report in 1991 by Iijima (8) that many researchers have devoted much time and effort in developing new strategies for the synthesis of SCNMs.

Trends in technological and scientific progress in catalysis lean towards the production of more efficient catalysts, smaller particle sizes and more finely dispersed particles to optimise yields and decrease reaction times. For this reason, nanosized catalytic particles have received much attention and they are known to display higher catalytic activity (9). Hybrid metal-CNT systems have been shown by theoretical calculations to have altered properties compared to unmodified CNTs (10). The results of hydrogenation reactions on various supports suggest that the interaction between the metal catalyst and the support greatly influences the catalytic activity in a hydrogenation reaction (11–13). Hence, this review addresses the issue of catalyst support use with the aim of broadly answering the following questions:

- How do CNTs compare with other traditional carbonaceous supports for catalysts and in what cases are CNTs superior as Pd supports in hydrogenation reactions?
- How do chemically modified CNTs influence the activity of Pd nanoparticles (NPs), especially in hydrogenation reactions?
- What effect does a secondary metal have on the catalytic activity of the Pd/CNT system?

Lastly, we look at a few literature examples involving the use of Pd/CNT hybrids in hydrogenation reactions.

This article covers a wide range of literature on Pd/CNT systems. The examples chosen for this review mainly involve some current studies of Pd/CNT systems for hydrogenation reactions. Specifically, examples based on cinnamaldehyde (**Figure 2(a)**), which has useful applications such as a flavouring, fungicide, antimicrobial agent or anticancer agent among others, are provided. The reduction of this organic compound is interesting because it has more than one functional group that can be reduced. The useful products that are obtained include cinnamyl alcohol (**Figure 2(b)**), 3-phenylpropionaldehyde (**Figure 2(c)**) and 3-phenylpropan-1-ol (**Figure 2(d)**), among others, depending on chemoselectivity. Hence, this compound, as an example, could form the basis for the comparison of conversions and the effect or influence of the support on Pd chemoselectivity.

### Synthesis of Carbon Nanotubes

CNTs and other SCNMs can be made by a variety of procedures and these include numerous variations of arc discharge (14, 15), laser ablation (16, 17) and chemical vapour deposition (CVD) processes (18–21). In the arc discharge and laser ablation methods, the catalysts required for synthesis are generally made from metals or metal salts. Both of these methods produce relatively pure CNTs but are currently not easy to scale up to industrial levels of production. The CVD processes, by contrast, allow for easy scale-up.

There are two main approaches to the CVD synthesis of CNTs. The first method entails passing a gas phase carbon source over a supported catalyst. The catalyst used can be derived from any metal source including an organometallic complex (22). In the second method, both the catalyst and the carbon source are in the gas phase and the CNTs are formed in the

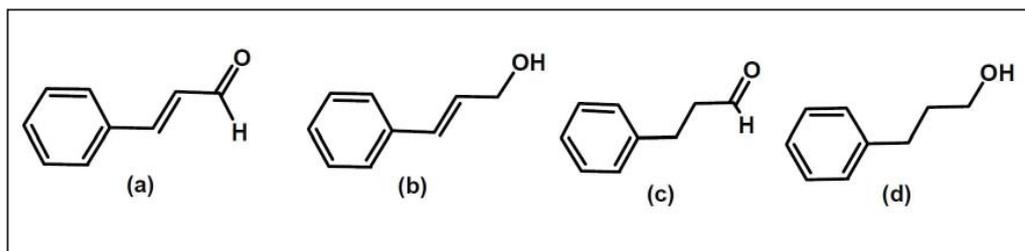


Fig. 2. Structure of: (a) cinnamaldehyde; (b) cinnamyl alcohol; (c) 3-phenylpropionaldehyde (hydrocinnamaldehyde); (d) 3-phenylpropan-1-ol

gas phase. This latter process is called the 'floating catalyst' method and typically requires volatile organometallic complexes.

Many studies have attempted to rationalise the mechanism of catalytic synthesis of CNTs. There is now a consensus as to the mechanism involved in the synthesis of CNTs over supported catalysts (23–27). In this process, small catalyst (metal) particles are deposited on a support and the carbon from the gas phase deposits onto, or dissolves in, the catalyst particle. For metals like iron and cobalt, growth of the CNT then arises from the precipitation of the carbon out of the metal. If the catalyst–support interaction is strong then the carbon tubes grow away from the support surface ('base-growth' mechanism), but if the catalyst–support interaction is weak, then the metal particle is displaced from the surface by the carbon ('tip-growth' mechanism) (27). The mechanism has been further simplified by Moissala *et al.*, who proposed that the metal catalyst particles act as nuclei for the growth of CNTs in the gas phase (28).

Another type of CVD approach to CNT synthesis involves the reactions taking place in a closed container (for example, an autoclave or a sealed quartz tube) at elevated temperatures. Typically, in this method, organometallic complexes (at times containing an external carbon source) are used as starting materials (29–39).

### Catalytic Applications of Carbon Nanotubes

CNTs exhibit extraordinary properties which are required for several potential applications (40). Among these applications, the use of CNTs as catalyst supports seems to be one of the most promising fields, with large economic implications. CNTs can be used as synthesised ('pristine') or can be modified, functionalised, doped or used as a part of a composite. Many applications involve hybrids or composites of CNTs with precious metal NPs. It is predicted that such composites will find uses in modern materials as

well as industrial hydrogenation catalysts for liquid (41–43) and gas (44) phase processes.

### The Advantages of Carbon Nanotubes as Catalyst Supports

A host of supports for Pd catalysts are available, from metal oxide supports such as alumina, silica and zeolites, to the traditional carbonaceous supports such as activated charcoal or activated carbon (AC), carbon blacks, graphites and the emerging carbon nanomaterials (3).

Oxide supports are often mechanically and thermally unstable. In the case of alumina, at high temperatures the ions of the catalytically active phase can interact with the support in such a manner as to lower the catalyst availability and catalytic activity (45). In transition aluminas, conversion to  $\alpha$ -alumina at temperatures near 1100°C can occur, resulting in a lowered surface area (46). Heat dispersion in certain oxide supports, such as alumina, is not always uniform, due to the insulating nature of this material. Thus, under oxidising conditions, so called 'hot-spots' can form, resulting in alteration of both the support and catalyst metal (47).

There are a variety of AC products that differ in certain key properties such as porosity, pore size and particle size distribution, surface area, resistance to attrition and content of ash, depending on the process of manufacture. AC is commonly used in liquid phase processes and remains the popular choice of support for hydrogenation reactions. This is due to its ease of separation from the reaction mixture, resistance towards aggressive media such as high pH, and the relative ease of metal recovery after use. Carbon black, which is produced from acetylene under high temperatures, is more suitable for use as a support than conventional carbon black made from other petroleum fractions. However, carbon black in general has a relatively low ash content (3).

In order to overcome some of the disadvantages of the common commercial supports, there is a need to

research and develop new nanodimensional supports such as CNTs or CNFs. These nanostructured carbon-based materials display good physical and chemical properties which are ideal for catalyst supports. The two main types of CNT considered here are the single-walled carbon nanotube (SWCNT) and the multiwalled carbon nanotube (MWCNT) (Figure 3).

### Electronic Properties

The arrangement of carbon atoms determines the surface and electronic properties of CNTs. According to theoretical predictions, the geometry of the ring structures imparts either a metallic or semi-metallic nature to CNTs (48, 49). This naturally has an effect on the properties of metals loaded onto the support. Duca *et al.* studied the combined properties of graphite versus SWCNTs with Pd<sub>9</sub> clusters by means of computational methods (50). Their findings showed that Pd<sub>9</sub> clusters may have a stronger interaction with a CNT than with traditional flat graphite sheet bilayers due to the curvature of the nanotube which has an effect on metallic properties.

### Mechanical Strength

The high mechanical strength of CNTs makes them not only favourable in composites (47, 48), but also in

mechanically taxing catalytic environments such as vigorously stirred liquid phase reactions. On more conventional supports, high levels of friction may lead to attrition, effectively altering the surface area of the exposed metal catalyst (47). Moreover, the relatively lower mechanical stability of common commercial carbon-based supports initiates the formation of fine particulates during operation. The existence of a large amount of micropores can reduce the full accessibility of the reactant particles to the active site.

The high strength of CNTs results from the covalent sp<sup>2</sup> bonds, which form a honeycomb lattice between the individual carbon atoms. In 2000, a MWCNT was tested and found to have a tensile strength of 63 GPa (51). A SWCNT has been shown to be the strongest material synthesised to date with a Young's modulus of ca. 1 TPa (52).

### Reactivity and Stability

Carbon supports are often unreactive and stable in many acidic and basic media, and consequently find use in a wide range of industrial applications (3, 53) while many other supports are rendered useless after reaction. However, traditional carbon-based supports have limitations not only when it comes to mechanical stability but also in terms of resistance to oxidising atmospheres at high temperatures (47). Oxidation and hydrogenation processes can result in gasification when the temperature is above 500°C and approximately 700°C, respectively (5). The order of ease of oxidation is: amorphous carbon > MWCNTs > SWCNTs. SWCNTs are generally more structured and have fewer surface defects than MWCNTs, and hence are more stable under most conditions (4).

AC is more easily oxidised than CNTs (4), and CNTs are more easily oxidised than graphite. Chiang *et al.* showed by thermogravimetric analysis (TGA) that acid oxidised MWCNTs were more thermally stable than AC fibres or C<sub>60</sub> fullerene (54). However, impurities in carbonaceous supports, such as metal residues from CVD processes, as well as defects in the structure, may not only limit the temperature at which hydrogenation takes place, but may also poison the active metal catalyst, such as Pd, and lower the temperature at which carbon oxidises (4). CNTs have good thermal conductivity and therefore reactions catalysed by metal/carbon systems need to be carefully controlled, especially if they are exothermic. Temperature can affect the performance of the catalyst on the carbon support and more research is needed to explore this aspect.

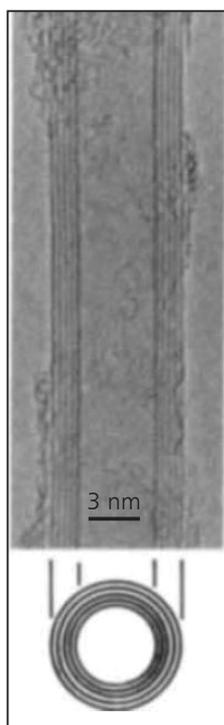


Fig. 3 Micrograph of a MWCNT, with cross-section showing five carbon layers (8) (Reproduced by permission of Nature Publishing Group)

The effect of microwave irradiation on MWCNTs has been studied by Olivier *et al.* (55). The authors prepared 10 wt% Pd on MWCNTs with metal particles found only on the outer walls. Microwave irradiation was used to drive the hydrogenation of cinnamate esters with ammonium formate as a reductant. Chemoselective C=C bond hydrogenation occurred for all substrates and the catalyst could be recycled more than five times without loss of activity. The same reaction carried out under the same conditions with Pd/AC generated a variety of other products due to microwave degradation of chemical species, demonstrating that Pd/AC is less regio- and stereoselective than 10 wt% Pd on MWCNTs.

Liang *et al.* investigated the hydrogenation of carbon dioxide catalysed by supported palladium/zinc oxide catalysts (56). Pd/ZnO on MWCNTs proved more favourable than Pd/ZnO on either alumina or AC, with the MWCNTs providing a promoting effect. Also, herringbone-type MWCNTs had a greater promoting activity than parallel-type MWCNTs in these studies. The high conversion and selective formation of methanol from CO<sub>2</sub> by the MWCNT-supported catalysts was due to their favourable ability to reversibly adsorb a greater amount of hydrogen, thus increasing the rate of surface hydrogenation reactions.

#### Surface Area and Selectivity

SWCNTs, which are inherently microporous, are considered by some to be very suitable supports for metal

catalysts. One reason for this is the high surface-to-volume ratio of SWCNTs compared to other supports. They also have high surface areas, 1587 m<sup>2</sup> g<sup>-1</sup> (57) (see **Table I**) after purification and tube end opening. The SWCNT structure is such that every atom is exposed to not one but two surfaces – both the inner and outer surfaces of the nanotube. **Table I** shows the approximate surface areas of various carbon supports. In the case of AC, the micropores are large in quantity and their size may actually slow the progress of substrate molecules into the pores (47). The ACs can have macro-, meso- and micropores, which can decrease the reproducibility of metal loading. Surface areas can range from 800–1200 m<sup>2</sup> g<sup>-1</sup> (3). However, the loading of Pd on the SWCNTs has been found to be lower than that obtained on MAXSORB® AC for hydrogen sorption studies (58). The authors of that study suggest that this is due to the larger pore volumes and surface area of the AC, and thus the correspondingly larger number of sites on which nucleation can occur. However, smaller Pd crystallites were formed on SWCNTs than on AC.

It has been shown that Pd's activity for the hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes is high, but its selectivity remains challenging and many times it has been boosted by the addition of promoters (59). A much researched model compound of this class of aldehydes is cinnamaldehyde. Pd's selectivity for cinnamyl alcohol is low when compared to Pt or ruthenium, however, using CNTs as supports seems to

**Table I**  
**Comparison of the Surface Areas of Carbon-Based Supports**

| Support                     |              | Typical surface area, m <sup>2</sup> g <sup>-1</sup> | Reference         |       |
|-----------------------------|--------------|--|-------------------|-------|
| Activated carbon            |              | 800–1200   | (3)               |       |
| Carbon black                | Conventional | 100–1500   | (3)               |       |
|                             | Graphitised  | 60–300   | (3)               |       |
| Graphite                    |              | 10–50  | (3)               |       |
| Shaped carbon nanomaterials | CNTs         | SWCNTs   | 1587 <sup>a</sup> | (57)  |
|                             |              | MWCNTs   | 400 <sup>b</sup>  | (62)  |
|                             | Other        | Carbon nano- and microspheres                        | 10                | (117) |

<sup>a</sup> After (i) debundling with DMF/EDA; (ii) acid treatment; (iii) wet oxidation

<sup>b</sup> After basic treatment

provide advances in overcoming this challenge. Corma *et al.* compared Pd/SWCNTs with Pd/AC prepared by the same method (60). They showed that Pd/AC had higher activity for the hydrogenation of cinnamaldehyde to 3-phenylpropionaldehyde than Pd/SWCNTs. However, there was a wider range of particle sizes for Pd/AC than for Pd/SWCNTs. This was thought to be due to the larger variety of functional groups on AC. This may cause Pd<sup>2+</sup> ions not to be uniformly deposited in the beginning stages of deposition, resulting in bigger agglomerates over time, and hence a larger range of sizes.

MWCNTs are inherently mesoporous structures. The pore sizes of MWCNTs allow for diffusion, reaction and desorption of chemical species and thus are good supports for catalysts (61). They also possess high surface areas, reaching up to approximately 400 m<sup>2</sup> g<sup>-1</sup> after basic treatments (62). These supports sometimes give better activity than microporous supports such as AC. Janowska *et al.* showed that selectivity for the C=C bond hydrogenation product of cinnamaldehyde can exceed 80% when performed over Pd/CNTs (63). The explanation given was the lack of micropores as well as the high surface area of the CNTs. Lack of micropores affects the time spent by reactants and products on the support surface as well as affecting the manner in which desorption occurs. Also, Pd crystallites and CNTs may interact to alter the adsorption and selectivity properties.

In other research, Pd NPs inside MWCNTs and on AC both achieved complete conversion of cinnamaldehyde, although the completion times for the former were slightly faster (64). In this work it was shown that at a higher hydrogen flow rate, the rate of hydrogenation increased, but more so for the AC support than for the MWCNTs. The MWCNT-supported catalyst hydrogenated predominantly the C=C bond, rather than the C=O bond, with only about 10% of the totally hydrogenated product forming. The AC-supported catalyst showed an equal selectivity for both products. Neither catalyst showed any selectivity for cinnamyl alcohol. It was concluded that the MWCNT-supported catalyst was superior in terms of selectivity for hydrocinnamaldehyde and that the MWCNTs had a higher surface area (some micropores on the traditional support being inaccessible to some substrates), resulting in a higher catalytic activity.

Zhang *et al.* used MWCNTs with different Pd loadings for benzene hydrogenation (43). They then compared the results with those from Pd/zeolite (SiO<sub>2</sub>: Al<sub>2</sub>O<sub>3</sub> = 5.1) and Pd/AC prepared under the same

conditions. They showed that benzene conversion to cyclohexane approximates 100% at the highest loading (12.0 wt%) Pd/MWCNT. An intermediate loading (8.0 wt%) yielded nearly double the conversion of benzene compared to that achieved using the AC- or zeolite-supported catalysts. This was despite the fact that the specific surface area of the MWCNTs was lower than those of the zeolite and AC as determined after acid treatment. It was also shown that diluted Pd salt solutions yielded smaller Pd particles inside tubes and more concentrated solutions yielded larger particles, which would influence catalytic rates.

In a study on the partial hydrogenation of phenylacetylene, CNT, AC and carbon black were used as supports for Pd (65). Although all active phases achieved over 95% conversion to styrene, the selectivity was highest for the Pd/CNT catalyst, with five runs maintaining the activity and selectivity. The AC support showed agglomeration of the Pd NPs.

Pd/CNFs (5 wt% Pd) and Pd/AC were used in the liquid phase hydrogenation of the C=C bond in cinnamaldehyde by Pham-Huu *et al.* (6). Both the surface area:volume ratio and thus catalytic activity were higher for the CNF-supported catalyst. This was assumed to be due to the large number of micropores on AC leading to diffusion problems which affect the catalytic rate. This cannot occur in CNFs because they have no micropores. Pd/CNFs produced almost exclusively (98%) hydrocinnamaldehyde and negligible amounts of cinnamyl alcohol and 3-phenylpropanol, showing that the selectivity of the catalyst for C=C hydrogenation under these conditions was good. The AC catalyst produced a mixture of all products. However, the nature of the carbon support was shown to have negligible effect on the hydrogenation of a variety of polar aromatic compounds in a recent article by Anderson *et al.* (66). They showed that the nature of the solvent is a bigger factor in selectivity.

Graphite has a comparatively low surface area (10 to 50 m<sup>2</sup> g<sup>-1</sup>), although grinding processes can increase it up to approximately 300 m<sup>2</sup> g<sup>-1</sup> (3). The capacity for adsorption of volatile organic compounds onto MWCNTs and CNFs is lower than for high surface area graphite (67).

### Recovery and Recycling of Precious Metals

The high price of precious metals makes the recovery and reuse of such catalysts economically important. Carbon supports make recovery more economical compared to metal oxide supports as they can be burnt off the metal catalyst and the catalyst recovered

from a small volume of ash. The solid waste is minimal. The metal can then be dissolved and recovered from acidic solutions.

Oxidation of AC over long periods of time can decrease its usefulness as a support (3). The inertness of CNTs, on the other hand, enables them to resist oxidation over long periods of time and allows them to be recycled many times. CNT-metal hybrids can be dispersed to a fairly uniform degree by stirring in organic solvents. After use, the hybrid CNT-NPs can be recovered by gravitational sedimentation. Hence, as a support, CNTs are economical and stable when it comes to the processes of recovery and reuse of catalysts.

### Loading Techniques and Considerations

A fair amount of research has gone into mechanisms suitable for attaching Pd NPs to the walls of SWCNTs and MWCNTs (68). Common loading techniques for Pd include impregnation (42, 43, 64), deposition precipitation (69), electroless deposition (70, 71) and electrochemical deposition (72, 73). Less commonly used methods include CVD (74) and microemulsion techniques (75). Supercritical CO<sub>2</sub> has been used instead of conventional solvents to effect a greener approach to Pd loading techniques (76). However, the Pd NP size, crystal structure and distribution cannot be accurately manipulated by many of these processes.

Considerations for choosing a loading technique include the desired level of Pd loading, required particle size and/or size distribution ranges, and the macroscopic distribution of particles on the support. The higher the Pd loading, in general, the greater the rate of product formation, since more Pd catalyst particles are exposed to substrate molecules. Most methods yield heterogeneously dispersed particle sizes, although controlling the size of metal particles is still being investigated. Typically, the smaller the particle size, the larger the surface area of Pd metal and the higher the catalytic activity. Pore structure and accessibility of the substrate to the metal in the pores also influences the macroscopic distribution. The most common types of supported catalyst structure are eggshell, uniform distributions or intermediates of the two (3). Typically, uniform distribution of small metal NPs is ideal for hydrogenations. However, uniformly impregnated catalysts are more likely to lose part of the Pd metal loading through leaching (3). This can be minimised by improving the availability of hydrogen in the liquid reaction medium and by

either using less catalyst for the reaction or decreasing the Pd metal loading.

Pristine CNTs are considered to be relatively inert, allowing for only low levels of Pd deposition (4) at defect sites such as Stone-Wales defects, dangling bonds at open tips and vacancies (77). The CNTs do not contain many functional groups on their surfaces and thus need to be activated to create anchoring sites for better Pd metal deposition. Many of these techniques are similar to the pretreatment of other carbon supports and are primarily used to remove metallic impurities, such as iron derived from the CNT synthesis, and generate surface groups in the process. Functionalisation can be done through ball milling (78) or by chemical or electrochemical means. Chemical means often incorporate the use of highly oxidising conditions such as sulfuric or nitric acid (79–81) or molecular oxygen (79). Sometimes sonication is used in conjunction with a chemical means (82). Plasmas can also be employed (79, 83, 84). Covalent functional groups such as alcohols (–OH), carbonyl groups (–C=O) and carboxylic acids (–COOH) form.

In general, more oxygen groups aid higher dispersion of Pd, although some authors maintain that oxygen-containing groups are not sites onto which the metals anchor, but rather that they merely increase wetting. Enhanced wetting allows for better dispersion in aqueous deposition solutions. Unger *et al.* achieved very low loadings of Pd (1 wt%) on pre-oxidised CNTs (85). They suggest that covalent bonding does not occur between the oxide groups and the metal, and that Pd therefore cannot attach in large quantities. However, Guo *et al.* suggested that more Pd particles form at positions where –COOH groups would preferably form, for example at the end of SWCNTs (86).

Most reports discuss Pd NPs decorated on the exterior of CNT surfaces. However, some state that certain Pd metal catalysts loaded on the inside of nanotubes exhibit a higher catalytic activity than the same amount on more conventional supports (43, 87). **Figure 4** shows a transmission electron microscopy (TEM) image of such a system. The supposition is that the partial pressure of the substrates inside the tubes is increased, altering the rate of catalysis. Factors affecting the placing of Pd particles inside tubes include the hydrophobicity of tubes, the inner diameter, the concentration of the Pd in the precursor solution and the surface tension of the Pd deposition solution. Pd particles found near the tips of tubes were probably deposited there due to the fast rate of evaporation of water out of the tubes. The strong interaction

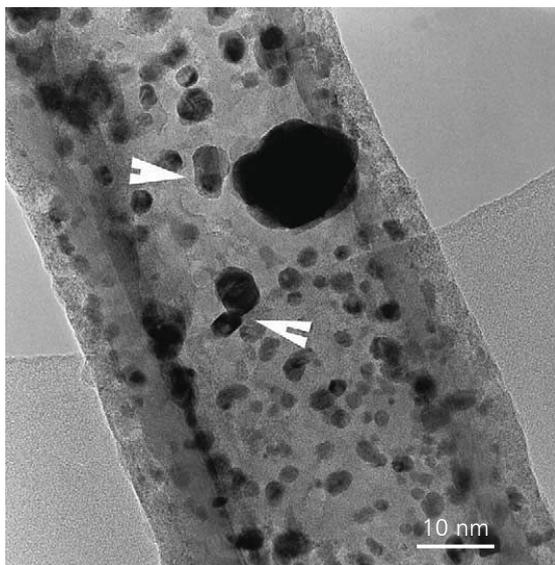


Fig. 4. TEM image of Pd NPs located primarily on the inside of MWCNTs with the arrowheads indicating the presence of some highly faceted Pd particles (87) (Reproduced by permission of Elsevier)

between Pd particles and the tube could give rise to the faceted nature of the catalyst particles (87). It has been suggested that this interaction may affect dispersion (43). Tessonnier *et al.* suggest that the morphology of the inner wall may alter the electronic nature of the adsorbed metal and thus modify the adsorption of the substrate and selectivity for the product (64). They stated that the nature of the precursor solution seemed to have a negligible effect on dispersion.

Factors influencing the properties of the nanometallic particles include size, shape and crystalline geometry (88). Computational calculations indicated that CNT-supported Pd<sub>9</sub> clusters would have a higher activity than the unsupported cluster for H<sub>2</sub> bond breaking in hydrogenation reactions, (89). Franklin *et al.* reported the first controlled decoration of SWCNTs with Pd particles of a consistent morphology (90), and Ansóñ *et al.* found that the mass ratios of the Pd: support (SWCNTs or MAXSORB® AC) directly determined the percentage of Pd loaded (58). These latter authors suggested, from their results, that a threshold for Pd saturation is reached when the mass ratio of support: Pd is 1:4. Also, the crystallite size was larger at higher Pd loadings. These authors demonstrated that the quantity of Pd loaded onto the SWCNTs was not altered in runs that used oxidative pretreatments, although their Pd wt% loading values decreased slightly after a nitric acid treatment in the case of

Pd(PPh<sub>3</sub>)<sub>4</sub> as the Pd source. Different precursor Pd compounds were also found to influence the loading on CNTs and AC in the same studies.

### Modified CNTs as Supports

Besides modification with oxide groups, other means of functionalisation can produce further benefits. Functionalisation can be covalent (91) or non-covalent (92). CNTs have the ability to attach a wide range of chemical species at active sites, such as their sidewalls, tubular tips or defect areas. Exohedral and endohedral functionalisation can also provide an opportunity to create unique catalyst supports for Pd.

Agglomeration of NPs reduces the surface area of catalytically active metal particles. Some loading techniques, such as modification of the support with a surfactant or an ionic liquid (IL) before metal deposition, can be employed to control the formation of larger nanoclusters on the surface of CNTs. Surface moieties are thought to aid stabilisation of the crystallites during sintering (3). Chun *et al.* functionalised MWCNTs with an imidazolium bromide followed by Pd (93). They effectively formed an IL catalytic system rendering the functionalised MWCNTs soluble in water, and thereby successfully prevented CNT agglomeration and aided dispersion in the aqueous phase ready for Pd deposition. Following this, hydrogenation of *trans*-stilbene was performed with turnover frequency (TOF) values up to 2820 mol h<sup>-1</sup>, which is considered to be high. Varying the anion was shown to influence the catalytic activity in this hydrogenation reaction. Pd/IL-*f*-MWCNTs (where *f* indicates functionalised; IL is [1-butyl-3-methylimidazolium] [hexafluoroantimonate]) remained active after 10 cycles and were then used in olefin hydrogenations. Only after 50 runs did the activity significantly decrease.

Sodium dodecyl sulfate (SDS) (94) and sodium bis(2-hexylethyl)sulfosuccinate (AOT) (75) also aid in the homogenous distribution of Pd particles on the support by acting as surfactants. Agglomeration of Pd particles is prevented. Figures 5(a) and 5(b) show Pd/CNTs prepared with and without AOT, respectively (75). The fairly even distribution of NPs in Figure 5(a) is apparent, whereas Figure 5(b) shows significant agglomeration. SDS (95) and sodium *n*-tetradecyl sulfate (SC<sub>14</sub>S) (96) also induce reduction of the Pd precursor. Karousis *et al.* used Pd/MWCNTs with SDS to hydrogenate a variety of olefins (97). Four olefins were successfully hydrogenated. The Pd/MWCNTs were then compared to Pd/AC for the hydrogenation of methyl-9-octadecenoate and 2-methyl-2-pentenal.

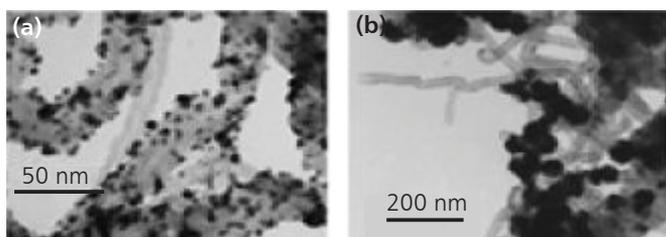


Fig. 5. TEM image of Pd/MWCNTs prepared: (a) with a surfactant, showing fairly uniform distribution of Pd NPs; and (b) without a surfactant, resulting in agglomeration of Pd NPs (75) (Reproduced by permission of the American Chemical Society)

The molar ratio of Pd:substrate was kept constant. TOF values for Pd/MWCNTs for both compounds were 3 to 5 times higher than for Pd/AC. Large amounts of the Pd precursor also cause agglomeration. Thus it is important to control the amounts of both the precursor and the SDS added to the reaction mixture for optimal dispersion (94).

In another paper, Pd was loaded onto SDS-stabilised MWCNTs and SWCNTs and then used in successful hydrogenations of the same four olefins as well as 3-phenyl-2-propenal (98), although a detailed comparison of the two supports was not given. The Pd/MWCNTs were then compared with Pd/AC for the hydrogenation of methyl-9-octadecanoate and 2-methyl-2-pentenal. TOF values for Pd/MWCNTs approximated 3 to 5 times higher than for the conventional catalyst. Even after 7 cycles of the Pd/MWCNTs there was little to no leaching of Pd off the support.

Doping of CNTs has been fairly extensively researched for N- and B-dopants (99–101) resulting in modified properties. Many properties such as electronic properties (102) and even the strength with which other species adsorb (103) are affected by doping. Most CNT doping studies have been carried out for MWCNTs, with a few on SWCNTs for applications such as field emission devices. Generally, CNTs are inert, but the incorporation of heteroatoms into their structure can give rise to a more chemically active material. Disadvantages include the fact that often N-doped counterparts are less thermally stable and more prone to oxidation (104). The nitrogen incorporation can greatly alter the morphology of the CNTs (104, 105), although in some cases no morphology change was observed (101).

Graphitisation was found to be enhanced in B-doped MWCNTs (106). An and Turner studied the binding between transition metals and CNTs by making use of density functional theory (DFT) calculations for individual metal atoms on N- or B-doped SWCNTs at chosen sites (103). These initial studies showed, among other things, that a range of commercially important transition metals, including Pd, undergo higher chem-

isorption with doped SWCNTs as opposed to pristine SWCNTs. B-doped CNTs gave the most enhanced binding. Amadou *et al.* carried out experiments in which the dispersion of Pd was found not to be significantly different on doped or undoped tubes (42). However, it was interesting to note that no Pd NPs were found inside the N-doped tubes. This was thought to be due to compartmentalisation as shown in Figure 6. The Pd/N-doped CNTs were compared with Pd/CNTs and Pd/AC for the liquid phase hydrogenation of cinnamaldehyde. Pd/AC, with the highest specific surface area, displayed the highest activity. Pd/N-doped CNTs had an activity nearly equal to that of Pd/AC, but almost double that of the undoped Pd/CNTs. This indicated a significant influence of the N incorporation on the activity of the catalyst for C=C bond hydrogenation. In terms of selectivity, the doped support was best for hydrocinnamaldehyde production while the Pd/AC catalyst was the least selective.

### Bimetallic Catalysts – Effect of Secondary Metal

Research has shown that bimetallic catalysts can influence the catalytic activity of a system (107) and sometimes have higher catalytic performance in certain reactions than a single metal catalyst (108). The additional metal(s) can improve the size and

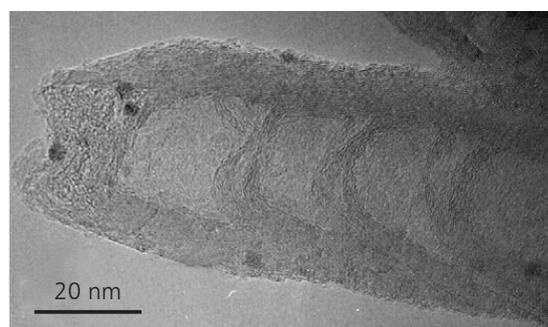


Fig. 6. TEM showing the 'bamboo' cross-structures in a Pd loaded N-doped MWNT without Pd NPs incorporated inside the cavities (42) (Reproduced by permission of Elsevier)

morphology of active particles as well as the catalyst selectivity (108).

The activity of palladium-platinum is superior to that of other commercial bimetallic catalysts in the hydrogenation of aromatic compounds, a pre-step in the desulfurisation of fuels. Noble metals are susceptible to poisoning by sulfur. Use of acidic supports or bimetallic Pd-Pt catalysts has proven to enhance the resistance to poisoning by sulfur (109). Pawelec *et al.* studied Pd-Pt/MWCNTs in the hydrogenation of toluene and naphthalene in the presence of dibenzothiophene in the gas phase to monitor, simultaneously, the hydrodesulfurisation of the sulfur-containing compound (110). A Pd-Pt/zirconium phosphate-silica zeolite and a Pd-Pt/amorphous SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (ASA) catalyst were also prepared for comparison although different loading techniques were used. The results suggested that all catalysts were more active for toluene hydrogenation than for the polyaromatic compound. Pd-Pt/MWCNTs had the lowest loading and BET specific areas but the highest activity for toluene hydrogenation. However, Pd-Pt/ASA was the best catalyst for naphthalene hydrogenation and the hydrodesulfurisation of dibenzothiophene. The combined effect of the Pd-Pt alloy may be a factor, coupled with the location of these NPs on the MWCNTs, since a marked lack of steric hindrance for the substrate would be found on the outer surfaces of MWCNTs as compared to the other catalysts. However, the bimetallic effect is still not yet well understood.

Qiu *et al.* observed that the conversion and selectivity towards cinnamyl alcohol was highest for a Pd-Ru bimetallic catalyst on CNTs than for either of the two monometallic catalysts under identical conditions (111). This finding was attributed either to Ru's promoting effect on Pd or to a combined enhanced effect from Pd and Ru together.

Arene hydrogenation is important in industry, for example, for diesel fuels with low aromatic contents. Heterogeneous catalysis with metals at high temperatures is the traditional method for arene hydrogenation. Yoon *et al.* hydrogenated benzene at room temperature under 1–20 atm over palladium-rhodium/CNTs (112). A high activity for benzene reduction, with no solvent, was found. Commercially available Pd/C and Rh/C cannot do this under these conditions yet. Pd/CNT had very low or no activity at room temperature, whereas the Pd-Rh/CNT had a catalytic activity much higher than either of the monometallic systems. A conversion of 98% of benzene to cyclohexane occurred after 24 h at room temperature and

10 atm. Pd/CNT needed 24 h at 50°C and 10 atm to achieve a near 50% conversion of benzene to the saturated product. Pd-Rh/CNT was shown to be recyclable multiple times.

Functionalised MWCNTs in a water-in-hexane micro-emulsion with a surfactant were loaded with Pd, Rh or Pd-Rh (75). Arene hydrogenation tests revealed that Pd-Rh/CNTs (see **Figure 7**) were more active than the monometallic systems for anthracene hydrogenation. However, the detailed morphology of this bimetallic catalyst system was not studied or confirmed.

It has also been shown that the molar ratio of the two metals in a bimetallic oxide catalyst, such as Pd/ZnO, has influence on the catalytic activity of CO<sub>2</sub> hydrogenation (56).

### Hydrogenation on Palladium/CNT Catalysts

Palladium on CNT supports is effective as a catalyst for the reduction of a variety of functional groups. Below are specific examples for carbon-carbon multi-bond and nitrogen-containing group hydrogenations.

### Alkene and Alkyne Hydrogenation

Pd/CNTs grown and supported on carbon microfibres were used as catalysts in the gas phase hydrogenation of cyclooctene (74). Initial studies showed the system to be active for the reduction of this alkene.

The first report of the use of Pd/CNT to hydrogenate C≡C discussed the successful hydrogenation of toluene, phenylacetylene and 1-heptyne with 5% Pd on CNTs (113). The results showed that only 0.02 mol% Pd/CNT was needed to convert all the starting materials to products, indicating that this catalytic system had a high activity towards C≡C hydrogenation. This catalytic activity was higher than that found in earlier work by the same authors for the hydrogenation of toluene over Pd complexes supported on fullerenes (114). The ratio of the two reaction products was found to be determined largely by the temperature and length of time of hydrogenation. The lower the hydrogenation time, or the higher the temperature (within the range 22–60°C), the greater the conversion to a

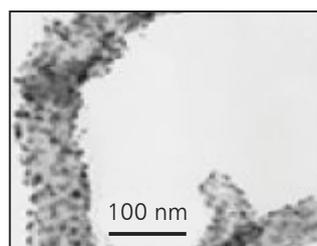


Fig. 7. TEM image of Pd-Rh/MWCNTs (75) (Reproduced by permission of the American Chemical Society)

saturated product. Further reactions with the Pd/CNT catalyst showed the same catalytic performance. All three acetylenic hydrocarbons underwent complete conversion to a mixture of ethylenic and saturated compounds. Reapplication of the catalyst at 60°C for 7 h yielded 100% selectivity for the saturated product.

Jung *et al.* studied Pt on CNFs and CNTs for cinnamaldehyde hydrogenation and Pd on CNFs for 1-octyne hydrogenation (115), amongst other supports. They used a colloidal microwave process to load metals onto supports. This method makes pretreatment unnecessary and yields a high dispersion of the catalyst. Unloaded supports (CNFs, CNTs, AC and Al<sub>2</sub>O<sub>3</sub>) were tested for cinnamaldehyde catalysis but no activity was found. Pd is possibly the most selective catalyst for the semi-hydrogenation of alkynes. Previous studies had shown the hydrogenation of cinnamaldehyde over Pt/CNTs to be poorer than over Pt/CNFs, thus only CNFs were used in the 1-octyne studies. Conversion of 1-octyne by Pd on two types of CNFs yielded the semi-hydrogenated product 1-octene, which had a slow conversion to the saturated product.

#### Conversion of Nitro to Amino Group via Hydrogenation

Pd/AC is a common catalyst for the selective hydrogenation of nitrobenzene and derivatives thereof. In one study, nitrobenzene was hydrogenated in the liquid phase by using Pd deposited on the inside of MWCNTs (87). This reaction was compared with a Pd/AC system. The activity of the Pd/MWCNT catalyst hybrid was superior to that of the Pd/AC catalyst system, even though the surface area of the AC was higher than that of the MWCNTs. The observed results were explained in terms of the lack of micropores in the MWCNTs. It was also suggested that convection in the liquid phase in the MWCNTs increased the rate of substrate collision with H<sub>2</sub> molecules and thereby increased the activity.

Jiang *et al.* hydrogenated the nitro group of *o*-chloronitrobenzene to provide an amine derivative using Pd supported on three different supports: CNTs,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> (116). Both the activity and selectivity for the formation of the amine product were favoured by the CNT-based catalyst. These results may be influenced by the geometric and electronic effects of CNTs on the catalytic process as well as the textures and properties of the CNTs.

#### Hydrogenation of Nitric Oxide

Wang *et al.* used pre-hydrogenated Pd/CNTs to reduce NO (44). The reducing action of the hydrogenated

Pd/CNT showed that such systems can take up hydrogen effectively in significant amounts. This may also be of interest to the hydrogen storage industry. CNTs without a metal additive were hydrogenated to a far lesser extent. Subsequent addition of NO caused reduction of this gas in only the Pd/hydrogenated CNTs.

Many examples of Pd/CNTs and bimetallic pgm/CNTs as hydrogenation catalysts are found in the literature. **Table II** summarises some of this research.

#### Conclusions

This survey of the literature has shown that the catalytic activity of nanosized Pd metal particles in hydrogenation reactions is greatly influenced by the support on which this metal is loaded. CNTs may be highly advantageous as supports compared with the more traditional carbonaceous supports. CNTs do not display many of the disadvantages that the more common commercial supports possess. In particular, CNTs have very high mechanical strength and thus are preferable over other supports in mechanically taxing stirred batch reactions. In terms of surface area, SWCNTs, in particular, have very high surface areas and are inherently microporous. Their high surface areas also allow for more reproducible loading compared to some of the currently used ACs. CNTs lower the rate of metal NP agglomeration, due to the strong metal-support interaction arising from the unique curvature of the CNTs, thereby enhancing the lifespan of the catalyst and ensuring its high level of activity. The chemical stability of CNTs makes them less easily oxidised than ACs, and they are economical and stable when it comes to the recovery and reuse of catalysts.

In many cases the chemoselectivity of Pd/CNTs in hydrogenation reactions has been shown to be superior to Pd/AC systems. One study showed that surfactant-modified Pd/MWCNTs gave higher TOF values for hydrogenation than the equivalent Pd/AC hybrids. Almost double the activity and a superior selectivity for a specific product was found for Pd/N-CNTs compared to undoped Pd/CNTs and a Pd/AC catalyst, respectively, in a study on hydrogenation reactions.

Studies of bimetallic Pd systems on CNTs revealed that selectivity and conversion for the hydrogenation of selected bonds, as well as activity towards hydrogenation of certain substrates, is enhanced by the presence of a secondary metal.

In summary, evidence exists for the superior activity and selectivity of Pd/CNTs in a range of hydrogenation reactions. There is also evidence for improved catalytic performance in certain cases by the use of

Table II

## Examples of Palladium and Platinum Group Metal Bimetallic Catalysts Supported on Carbon Nanotubes Used in Hydrogenation Reactions

| Metal-catalyst system |                                       | Substrate for hydrogenation  | References   |
|-----------------------|---------------------------------------|--|--------------|
| Monometallic catalyst | Pd/CNTs                               | Cinnamaldehyde   | (60)         |
|                       | Pd/MWCNTs <sup>b</sup>                | NO   | (44)         |
|                       |                                       | Benzene  | (43)         |
|                       |                                       | Cinnamaldehyde   | (47, 63, 64) |
|                       |                                       | <i>trans</i> -Stilbene   | (76)         |
|                       |                                       | Cyclooctene  | (74)         |
|                       |                                       | Nitrobenzene   | (87)         |
|                       |                                       | Phenylacetylene  | (65)         |
|                       |                                       | Cinnamate esters   | (55)         |
|                       |                                       | Toluene, phenylacetylene, 1-heptyne  | (113)        |
|                       |                                       | <i>o</i> -Chloronitrobenzene   | (116)        |
|                       |                                       | Cinnamaldehyde   | (6)          |
|                       |                                       | 1-Octyne   | (115)        |
| Bimetallic catalyst   | Pd/ZnO- <i>h</i> -MWCNTs <sup>d</sup> | Benzoic acid, benzaldehyde, acetophenone, benzamide, phenylacetic acid, cinnamic acid, 4-hydroxybenzoic acid | (66)         |
|                       | Pd/ZnO- <i>p</i> -MWCNTs <sup>e</sup> |  |              |
|                       | Pd-Ru/CNTs                            |  |              |
|                       | Pd-Pt/MWCNTs                          |  |              |
|                       | Pd-Rh/MWCNTs                          |  |              |
|                       |                                       | CO <sub>2</sub>  | (56)         |
|                       |                                       | CO <sub>2</sub>  | (56)         |
|                       |                                       | Cinnamaldehyde   | (111)        |
|                       |                                       | Toluene/naphthalene/dibenzothiophene   | (110)        |
|                       |                                       | Benzene  | (112)        |

(Continued)

As-synthesised CNTs

Table II (Continued)

| Metal-catalyst system                    | Substrate for hydrogenation   | References   |
|--|---|--------------|
| Modified CNTs with monometallic catalyst | Methyl-9-octadecanoate, 2-methyl-3-buten-2-ol, 3,7-dimethyl-2,6-octadien-1-ol, 2-methyl-2-pentenal<br>Methyl-9-octadecanoate, 2-methyl-3-buten-2-ol, 3,7-dimethyl-2,6-octadien-1-ol, 2-methyl-2-pentenal, 3-phenyl-2-propenal | (97)<br>(98) |
|  | Methyl-9-octadecanoate, 2-methyl-3-buten-2-ol, 3,7-dimethyl-2,6-octadien-1-ol, 2-methyl-2-pentenal, 3-phenyl-2-propenal   | (98)         |
|  | <i>trans</i> -Stilbene  | (93)         |
|  | Anthracene  | (75)         |
| Bimetallic-surfactant composite          | Anthracene  | (75)         |
| Doped                                    | Cinnamaldehyde  | (42)         |

Modified CNTs

<sup>a</sup> SWCNTs = single-walled carbon nanotubes<sup>b</sup> MWCNTs = multiwalled carbon nanotubes<sup>c</sup> CNFs = carbon nanofibres<sup>d</sup> h = herringbone-type<sup>e</sup> p = parallel-type<sup>f</sup> SDS = sodium dodecyl sulfate

modified or bimetallic Pd/CNT systems. Such findings will, hopefully, spur on research in this field. However, ACs are still widely chosen as hydrogenation supports due to their ease of preparation and low cost. The challenge remains of improving the cost-effectiveness of CNT synthesis to make them an economically viable alternative to ACs as Pd supports for hydrogenation reactions.

### Acknowledgements

We extend a grateful acknowledgement and thanks to the National Research Foundation (NRF) Nanotechnology Flagship Programme 'Nano-architecture in the Beneficiation of Platinum Group Metals' through the grant holder, Dr Leslie Petrik (University of the Western Cape) for funding. We are also grateful to Professor Neil Coville (University of the Witwatersrand) for his advice in the construction of this review and Professor Bice Martincigh (University of KwaZulu-Natal) for assisting in proof reading and comments during the manuscript development.

### References

- 1 C. Adams, *Top. Catal.*, 2009, **52**, (8), 924
- 2 G. Centi and S. Perathoner, *Catal. Today*, 2008, **138**, (1–2), 69
- 3 E. Auer, A. Freund, J. Pietsch and T. Tacke, *Appl. Catal. A: Gen.*, 1998, **173**, (2), 259
- 4 P. Serp, M. Corrias and P. Kalck, *Appl. Catal. A: Gen.*, 2003, **253**, (2), 337
- 5 K. C. Mondal, L. M. Cele, M. J. Witcomb and N. J. Coville, *Catal. Commun.*, 2008, **9**, (4), 494
- 6 C. Pham-Huu, N. Keller, L. J. Charbonniere, R. Ziessel and M. J. Ledoux, *Chem. Commun.*, 2000, (19), 1871
- 7 I. Martin-Gullon, J. Vera, J. A. Conesa, J. L. González and C. Merino, *Carbon*, 2006, **44**, (8), 1572
- 8 S. Iijima, *Nature*, 1991, **354**, (6348), 56
- 9 R. Schlögl and S. B. Abd Hamid, *Angew. Chem. Int. Ed.*, 2004, **43**, (13), 1628
- 10 E. Durgun, S. Dag, S. Ciraci and O. Gülseren, *J. Phys. Chem. B*, 2004, **108**, (2), 575
- 11 A. Yu Stakeev and L. M. Kustov, *Appl. Catal. A: Gen.*, 1999, **188**, (1–2), 3
- 12 A. Chambers, T. Nemes, N. M. Rodriguez and R. T. K. Baker, *J. Phys. Chem. B*, 1998, **102**, (12), 2251
- 13 C. Park and R. T. K. Baker, *J. Phys. Chem. B*, 1998, **102**, (26), 5168
- 14 T. W. Ebbesen and P. M. Ajayan, *Nature*, 1992, **358**, (6383), 220
- 15 H. Huang, H. Kajiura, S. Tsutsui, Y. Hirano, M. Miyakoshi, A. Yamada and M. Ata, *Chem. Phys. Lett.*, 2001, **343**, (1–2), 7
- 16 A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tománek, J. E. Fischer and R. E. Smalley, *Science*, 1996, **273**, (5274), 483
- 17 J. Liu, A. G. Rinzler, H. Dai, J. H. Hafner, R. K. Bradley, P. J. Boul, A. Lu, T. Iverson, K. Shelimov, C. B. Huffman, F. Rodriguez-Macias, Y.-S. Shon, T. R. Lee, D. T. Colbert and R. E. Smalley, *Science*, 1998, **280**, (5367), 1253
- 18 M. José-Yacamán, M. Miki-Yoshida, L. Rendón and J. G. Santiesteban, *Appl. Phys. Lett.*, 1993, **62**, (6), 657
- 19 A.-C. Dupuis, *Prog. Mater. Sci.*, 2005, **50**, (8), 929
- 20 S. Amelinckx, X. B. Zhang, D. Bernaerts, X. F. Zhang, V. Ivanov and J. B. Nagy, *Science*, 1994, **265**, (5172), 635
- 21 J.-B. Park, G.-S. Choi, Y.-S. Cho, S.-Y. Hong, D. Kim, S.-Y. Choi, J.-H. Lee and K.-I. Cho, *J. Cryst. Growth*, 2002, **244**, (2), 211
- 22 V. O. Nyamori, S. D. Mhlanga and N. J. Coville, *J. Organomet. Chem.*, 2008, **693**, (13), 2205
- 23 R. Saito, G. Dresselhaus and M. S. Dresselhaus, "Physical Properties of Carbon Nanotubes", Imperial College Press, London, UK, 1998
- 24 G. Cao, "Nanostructures and Nanomaterials: Synthesis, Properties and Applications", Imperial College Press, London, UK, 2004
- 25 M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund, "Science of Fullerenes and Carbon Nanotubes", Academic Press, San Diego, California, USA, 1996
- 26 "Carbon Nanotubes: Properties and Applications", ed. M. J. O'Connell, CRC Press, Boca Raton, Florida, USA, 2006
- 27 M. Endo, T. Hayashi, Y. A. Kim, M. Terrones and M. S. Dresselhaus, *Phil. Trans. R. Soc. Lond. A*, 2004, **362**, (1823), 2223
- 28 A. Moisala, A. G. Nasibulin and E. I. Kauppinen, *J. Phys.: Condens. Matter*, 2003, **15**, (42), S3011
- 29 V. O. Nyamori and N. J. Coville, *Organometallics*, 2007, **26**, (16), 4083
- 30 D. Jain, A. Winkelm and R. Wilhelm, *Small*, 2006, **2**, (6), 752
- 31 J. Liu, M. Shao, Q. Xie, L. Kong, W. Yu and Y. Qian, *Carbon*, 2003, **41**, (11), 2101
- 32 M. Laskoski, W. Steffen, J. G. M. Morton, M. D. Smith and U. H. F. Bunz, *J. Am. Chem. Soc.*, 2002, **124**, (46), 13814
- 33 B. El Hamaoui, L. Zhi, J. Wu, U. Kolb and K. Müllen, *Adv. Mater.*, 2005, **17**, (24), 2957
- 34 L. Zhi, T. Gorelik, R. Friedlein, J. Wu, U. Kolb, W. R. Salaneck and K. Müllen, *Small*, 2005, **1**, (8–9), 798
- 35 J. Wu, B. El Hamaoui, J. Li, L. Zhi, U. Kolb and K. Müllen, *Small*, 2005, **1**, (2), 210
- 36 S. Liu, X. Tang, Y. Mastai, I. Felner and A. Gedanken, *J. Mater. Chem.*, 2000, **10**, (11), 2502
- 37 C. Wu, X. Zhu, L. Ye, C. OuYang, S. Hu, L. Lei and Y. Xie, *Inorg. Chem.*, 2006, **45**, (21), 8543

- 38 P. I. Dosa, C. Erben, V. S. Iyer, K. P. C. Vollhardt and I. M. Wasser, *J. Am. Chem. Soc.*, 1999, **121**, (44), 10430
- 39 V. S. Iyer, K. P. C. Vollhardt and R. Wilhelm, *Angew. Chem. Int. Ed.*, 2003, **42**, (36), 4379
- 40 "Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications", eds. A. Jorio, G. Dresselhaus and M. S. Dresselhaus, Springer, Berlin, Heidelberg, Germany, 2008
- 41 B. F. Machado, H. T. Gomes, P. Serp, P. Kalck and J. L. Faria, *ChemCatChem*, 2010, **2**, (2), 190
- 42 J. Amadou, K. Chizari, M. Houllé, I. Janowska, O. Ersen, D. Bégin and C. Pham-Huu, *Catal. Today*, 2008, **138**, (1–2), 62
- 43 A. M. Zhang, J. L. Dong, Q. H. Xu, H. K. Rhee and X. L. Li, *Catal. Today*, 2004, **93–95**, 347
- 44 S. J. Wang, W. X. Zhu, D. W. Liao, C. F. Ng and C. T. Au, *Catal. Today*, 2004, **93–95**, 711
- 45 "Catalyst Supports and Supported Catalysts: Theoretical and Applied Concepts", ed. A. B. Stiles, Butterworth-Heinemann, Stoneham, Massachusetts, USA, 1987
- 46 M. Inoue, H. Otsu, H. Kominami and T. Inui, *Ind. Eng. Chem. Res.*, 1996, **35**, (1), 295
- 47 J.-M. Nhut, R. Vieira, L. Pesant, J.-P. Tessonier, N. Keller, G. Ehret, C. Pham-Huu and M. J. Ledoux, *Catal. Today*, 2002, (1), **76**, 11
- 48 "Understanding Carbon Nanotubes: From Basics to Applications", Lecture Notes in Physics, Vol. 677, eds. A. Loiseau, P. Launois, P. Petit, S. Roche, and J.-P. Salvetat, Springer-Verlag, Berlin, Heidelberg, 2006
- 49 J. W. Mintmire, B. I. Dunlap and C. T. White, *Phys. Rev. Lett.*, 1992, **68**, (5), 631
- 50 D. Duca, F. Ferrante and G. La Manna, *J. Phys. Chem. C*, 2007, **111**, (14), 5402
- 51 M.-F. Yu, O. Lourie, M. J. Dyer, K. Moloni, T. F. Kelly and R. S. Ruoff, *Science*, 2000, **287**, (5453), 637
- 52 J.-P. Salvetat, G. A. D. Briggs, J.-M. Bonard, R. R. Bacsa, A. J. Kulik, T. Stöckli, N. A. Burnham and L. Forró, *Phys. Rev. Lett.*, 1999, **82**, (5), 944
- 53 M. L. Toebe, J. A. van Dillen and K. P. de Jong, *J. Mol. Catal. A: Chem.*, 2001, **173**, (1–2), 75
- 54 Y.-C. Chiang, C.-C. Lee and C.-Y. Lee, *Toxicol. Environ. Chem.*, 2009, **91**, (8), 1413
- 55 J.-H. Olivier, F. Camerel, R. Ziessel, P. Retailleau, J. Amadou and C. Pham-Huu, *New J. Chem.*, 2008, **32**, (6), 920
- 56 X.-L. Liang, X. Dong, G.-D. Lin and H.-B. Zhang, *Appl. Catal. B: Environ.*, 2009, **88**, (3–4), 315
- 57 M. Cinke, J. Li, B. Chen, A. Cassell, L. Delzeit, J. Han and M. Meyyappan, *Chem. Phys. Lett.*, 2002, **365**, (1–2), 69
- 58 A. Anson, E. Lafuente, E. Urriolabeitia, R. Navarro, A. M. Benito, W. K. Maser and M. T. Martínez, *J. Alloys Compd.*, 2007, **436**, (1–2), 294
- 59 V. Ponc, *Appl. Catal. A: Gen.*, 1997, **149**, (1), 27
- 60 A. Corma, H. Garcia and A. Leyva, *J. Mol. Catal. A: Chem.*, 2005, **230**, (1–2), 97
- 61 Q.-H. Yang, P.-X. Hou, S. Bai, M.-Z. Wang and H.-M. Cheng, *Chem. Phys. Lett.*, 2001, **345**, (1–2), 18
- 62 S. Musso, S. Porro, M. Vinante, L. Vanzetti, R. Ploeger, M. Giorcelli, B. Possetti, F. Trotta, C. Pederzoli and A. Tagliaferro, *Diamond Relat. Mater.*, 2007, **16**, (4–7), 1183
- 63 I. Janowska, G. Winé, M.-J. Ledoux and C. Pham-Huu, *J. Mol. Catal. A: Chem.*, 2007, **267**, (1–2), 92
- 64 J.-P. Tessonier, L. Pesant, G. Ehret, M. J. Ledoux and C. Pham-Huu, *Appl. Catal. A: Gen.*, 2005, **288**, (1–2), 203
- 65 S. Domínguez-Domínguez, Á. Berenguer-Murcia, B. K. Pradhan, Á. Linares-Solano and D. Cazorla-Amorós, *J. Phys. Chem. C*, 2008, **112**, (10), 3827
- 66 J. A. Anderson, A. Athawale, F. E. Imrie, F.-M. McKenna, A. McCue, D. Molyneux, K. Power, M. Shand and R. P. K. Wells, *J. Catal.*, 2010, **270**, (1), 9
- 67 E. Díaz, S. Ordóñez and A. Vega, *J. Colloid Interface Sci.*, 2007, **305**, (1), 7
- 68 "Carbon Materials for Catalysis", eds. P. Serp and J. L. Figueiredo, John Wiley and Sons, Hoboken, New Jersey, USA, 2009
- 69 E. van Steen and F. F. Prinsloo, *Catal. Today*, 2002, **71**, (3–4), 327
- 70 L.-M. Ang, T. S. A. Hor, G.-Q. Xu, C.-h. Tung, S. Zhao and J. L. S. Wang, *Chem. Mater.*, 1999, **11**, (8), 2115
- 71 L. Qu and L. Dai, *J. Am. Chem. Soc.*, 2005, **127**, (31), 10806
- 72 T. M. Day, P. R. Unwin and J. V. Macpherson, *Nano Lett.*, 2007, **7**, (1), 51
- 73 B. M. Quinn, C. Dekker and S. G. Lemay, *J. Am. Chem. Soc.*, 2005, **127**, (17), 6146
- 74 W. Xia, O. F.-K. Schlüter, C. Liang, M. W. E. van den Berg, M. Guraya and M. Muhler, *Catal. Today*, 2005, **102–103**, 34
- 75 B. Yoon and C. M. Wai, *J. Am. Chem. Soc.*, 2005, **127**, (49), 17174
- 76 X. R. Ye, Y. Lin and C. M. Wai, *Chem. Commun.*, 2003, (5), 642
- 77 J.-C. Charlier, *Acc. Chem. Res.*, 2002, **35**, (12), 1063
- 78 K. Niesz, A. Siska, I. Vesselényi, K. Hernadi, D. Méhn, G. Galbács, Z. Kónya and I. Kiricsi, *Catal. Today*, 2002, **76**, (1), 3
- 79 H. Ago, T. Kugler, F. Cacialli, W. R. Salaneck, M. S. P. Shaffer, A. H. Windle and R. H. Friend, *J. Phys. Chem. B*, 1999, **103**, (38), 8116
- 80 M. S. P. Shaffer, X. Fan and A. H. Windle, *Carbon*, 1998, **36**, (11), 1603
- 81 S. Porro, S. Musso, M. Vinante, L. Vanzetti, M. Anderle, F. Trotta and A. Tagliaferro, *Physica E*, 2007, **37**, (1–2), 58
- 82 Y. Xing, L. Li, C. C. Chusuei and R. V. Hull, *Langmuir*, 2005, **21**, (9), 4185
- 83 J. Chen, Z. H. Zhu, Q. Ma, L. Li, V. Rudolph and G. Q. Lu, *Catal. Today*, 2009, **148**, (1–2), 97

- 84 J. Yang, X. Wang, X. Wang, R. Jia and J. Huang, *J. Phys. Chem. Solids*, 2010, **71**, (4), 448
- 85 E. Unger, G. S. Duesberg, M. Liebau, A. P. Graham, R. Seidel, F. Kreupl and W. Hoenlein, *Appl. Phys. A: Mater. Sci. Process.*, 2003, **77**, (6), 735
- 86 D.-J. Guo and H.-L. Li, *J. Colloid Interface Sci.*, 2005, **286**, (1), 274
- 87 J.-M. Nhut, L. Pesant, J.-P. Tessonier, G. Winé, J. Guille, C. Pham-Huu and M.-J. Ledoux, *Appl. Catal. A: Gen.*, 2003, **254**, (2), 345
- 88 B. Wiley, Y. Sun, B. Mayers and Y. Xia, *Chem. Eur. J.*, 2005, **11**, (2), 454
- 89 V. D'Anna, D. Duca, F. Ferrante and G. La Manna, *Phys. Chem. Chem. Phys.*, 2009, **11**, (20), 4077
- 90 A. D. Franklin, J. T. Smith, T. Sands, T. S. Fisher, K.-S. Choi and D. B. Janes, *J. Phys. Chem. C*, 2007, **111**, (37), 13756
- 91 C. A. Dyke and J. M. Tour, *J. Phys. Chem. A*, 2004, **108**, (51), 11151
- 92 R. J. Chen, Y. Zhang, D. Wang and H. Dai, *J. Am. Chem. Soc.*, 2001, **123**, (16), 3838
- 93 Y. S. Chun, J. Y. Shin, C. E. Song and S.-g. Lee, *Chem. Commun.*, 2008, (8), 942
- 94 X. Chen, Y. Hou, H. Wang, Y. Cao and J. He, *J. Phys. Chem. C*, 2008, **112**, (22), 8172
- 95 C.-L. Lee, C.-C. Wan and Y.-Y. Wang, *Adv. Funct. Mater.*, 2001, **11**, (5), 344
- 96 C.-L. Lee, Y.-C. Huang, L.-C. Kuo and Y.-W. Lin, *Carbon*, 2007, **45**, (1), 203
- 97 N. Karousis, G.-E. Tsotsou, N. Ragoussis and N. Tagmatarchis, *Diamond Relat. Mater.*, 2008, **17**, (7–10), 1582
- 98 N. Karousis, G.-E. Tsotsou, F. Evangelista, P. Rudolf, N. Ragoussis and N. Tagmatarchis, *J. Phys. Chem. C*, 2008, **112**, (35), 13463
- 99 Y. Zhang, H. Gu, K. Suenaga and S. Iijima, *Chem. Phys. Lett.*, 1997, **279**, (5–6), 264
- 100 D. Golberg, Y. Bando, W. Han, K. Kurashima and T. Sato, *Chem. Phys. Lett.*, 1999, **308**, (3–4), 337
- 101 S. Maldonado, S. Morin and K. J. Stevenson, *Carbon*, 2006, **44**, (8), 1429
- 102 D.-P. Kim, C. L. Lin, T. Mihalisin, P. Heiney and M. M. Labes, *Chem. Mater.*, 1991, **3**, (4), 686
- 103 W. An and C. H. Turner, *J. Phys. Chem. C*, 2009, **113**, (17), 7069
- 104 C. J. Lee, S. C. Lyu, H.-W. Kim, J. H. Lee and K. I. Cho, *Chem. Phys. Lett.*, 2002, **359**, (1–2), 115
- 105 E. N. Nxumalo, V. O. Nyamori and N. J. Coville, *J. Organomet. Chem.*, 2008, **693**, (17), 2942
- 106 W. Han, Y. Bando, K. Kurashima and T. Sato, *Chem. Phys. Lett.*, 1999, **299**, (5), 368
- 107 J. R. Croy, S. Mostafa, L. Hickman, H. Heinrich and B. R. Cuenya, *Appl. Catal. A: Gen.*, 2008, **350**, (2), 207
- 108 M. H. Jordão, V. Simões and D. Cardoso, *Appl. Catal. A: Gen.*, 2007, **319**, 1
- 109 T. Fujikawa, K. Idei, T. Ebihara, H. Mizuguchi and K. Usui, *Appl. Catal. A: Gen.*, 2000, **192**, (2), 253
- 110 B. Pawelec, V. La Parola, R. M. Navarro, S. Murcia-Mascarós and J. L. G. Fierro, *Carbon*, 2006, **44**, (1), 84
- 111 J. Qiu, H. Zhang, X. Wang, H. Han, C. Liang and C. Li, *React. Kinet. Catal. Lett.*, 2006, **88**, (2), 269
- 112 B. Yoon, H.-B. Pan and C. M. Wai, *J. Phys. Chem. C*, 2009, **113**, (4), 1520
- 113 E. V. Starodubtseva, M. G. Vinogradov, O. V. Turova, N. A. Bumagin, E. G. Rakov and V. I. Sokolov, *Catal. Commun.*, 2009, **10**, (10), 1441
- 114 E. V. Starodubtseva, V. I. Sokolov, V. V. Bashilov, Y. N. Novikov, E. V. Martynova, M. G. Vinogradov and O. V. Turova, *Mendeleev Commun.*, 2008, **18**, (4), 209
- 115 A. Jung, A. Jess, T. Schubert and W. Schütz, *Appl. Catal. A: Gen.*, 2009, **362**, (1–2), 95
- 116 L. Jiang, H. Gu, X. Xu and X. Yan, *J. Mol. Catal. A: Chem.*, 2009, **310**, (1–2), 144
- 117 S. D. Mhlanga, K. C. Mondal, N. Naidoo, N. Kunjuzwa, M. J. Witcomb and N. J. Coville, *S. Afr. J. Sci.*, 2009, **105**, (7/8), 304

### The Authors



Rachel Oosthuizen obtained her BSc (Hons) in Chemistry from the University of Natal, Durban, in 2002. After a brief period teaching at high school she studied towards and received a Post Graduate Certificate in Education from the University of South Africa. Currently she is an MSc student in the School of Chemistry, University of KwaZulu-Natal, working under the supervision of Dr Vincent O. Nyamori. Her study involves the influence of ferrocenyl and ferrocenoyl derivatives as catalysts, under varying reaction parameters, on carbon nanotube synthesis and application of CNTs as supports for heterogeneous catalysis. She also works for the Centre for Science Access at the University of KwaZulu-Natal.



Vincent Nyamori received his BSc degree from Egerton University, Kenya, and his BSc (Hons), MSc and PhD degrees from the Nelson Mandela Metropolitan University, South Africa. In June 2006 he joined the University of the Witwatersrand as a Postdoctoral Fellow with Professor N. J. Coville as his host. After post-doctoral work, he joined the University of KwaZulu-Natal in April 2008. He is a member of the South Africa Chemical Institute, South African Nanotechnology Initiative and is currently working on India-Brazil-South Africa Nanotechnology collaborative projects. He is also involved with the Nanotechnology Flagship Programme 'Nano-Architecture in the Beneficiation of Platinum Group Metals' through the National Research Foundation (NRF) programme with Dr L. Petrik as the Project Coordinator.