Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Catalysis 221 (2004) 77–84
JOURNAL OF CATALYSIS
www.elsevier.com/locate/jcat

Vanadyl salen complexes covalently anchored to single-wall carbon nanotubes as heterogeneous catalysts for the cyanosilylation of aldehydes

Carlos Baleizão,[a,b] Bárbara Gigante,[a] Hermenegildo Garcia,[b,*] and Avelino Corma [b]

[a] *INETI–Departamento de Tecnologia das Industrias Químicas, Estrada do Paço do Lumiar, 22, 1649-038 Lisbon, Portugal*
[b] *Instituto de Tecnología Química/CSIC, Av. de los Naranjos, s/n, 46022 Valencia, Spain*

Received 25 April 2003; revised 20 August 2003; accepted 26 August 2003

Abstract

Single-wall carbon nanotubes (SWNT) have a special structure and morphology consisting of long tubes (μm scale) of less than 2 nm in diameter. We have taken advantage of this geometric feature of SWNT to use them as supports for the preparation of a heterogeneous catalyst. Styryl functionalized vanadyl Schiff base has been covalently anchored on mercapto-modified SWNT through a radical chain mechanism. SWNT is more suitable as support for the complex than high-surface-area activated carbon because the latter exhibits some adventitious activity. The vanadyl-modified SWNT solid was used to effect the catalytic cyanosilylation of aldehydes with trimethysilylcyanide. The system is truly heterogeneous (no leaching observed) and reusable (no decrease in activity) in five consecutive runs. The asymmetric version was also performed using a chiral vanadyl complex obtaining 66% of enantiomeric excess.

Keywords: Heterogeneous catalysis; Single-wall carbon nanotubes; Cyanohydrins; Vanadyl salen complex; Activated carbon

1. Introduction

High-surface-area carbons have been the supports of choice for many noble metals and Lewis acids to convert a homogeneous into a heterogeneous process [1]. A special type of carbon that is attracting much current interest is carbon nanotubes [2] and in particular single-walled carbon nanotubes (SWNT) [3]. Besides chemical composition (SWNTs are considered a new allotropic form of elemental carbon, while active carbons contain H as well as significant percentages of O, N, and S depending on the source [1]), the major difference between carbon nanotubes and active carbons is the well-defined structure of the former that contains exclusively fibers or bundles of fibers of several micrometers in length. The structure of SWNT can be considered as arising from the rolling up of a graphene sheet with some degree of helicity defined by two integer numbers (n and m), a common case being when $n \neq 0$ and $m = 0$ (zig-zag nanotube). In contrast, active carbons have an ill-defined structure formed by a random distribution of polycyclic aromatic lamelles connected by bridges of $–CH_2–$, –O–, –S–, –NH–, etc. In particular, the sample of SWNT used in the present work is formed exclusively by nanotubes of 1.4 nm in diameter and bundles of them with lengths of 5 μm, having a specific surface area of 300 $m^2\,g^{-1}$. While this area is far from the maximum specific area achievable in activated carbons, the special structured topology of the SWNT surface introducing a characteristic periodicity and regularity may play a positive role when these materials are used as supports in heterogeneous catalysis. Moreover, the covalent functionalization of these SWNTs either at the open tips of the tube or on the walls through well-defined reactions [4] has become a powerful tool that can serve to prepare solid catalysts in which the active sites are covalently anchored to the carbon scaffold. Typical supports for covalent grafting on their surface are silicas, inorganic oxides, and organic polymers. In the case of active carbons, their ill-defined structure has precluded covalent grafting and the relevant catalytic species on activated carbons is simply adsorbed by van der Waals interactions. In the present paper we describe the preparation of a solid catalyst having a vanadyl salen (VOsalen) complex covalently attached to the SWNT that is active for the cyanosilylation of aldehydes at a substrate to catalyst ratio as low as 1000:3. As far as we know, our report constitutes the

* Corresponding author.
E-mail address: hgarcia@qim.upv.es (H. Garcia).

0021-9517/$ – see front matter
doi:10.1016/j.jcat.2003.08.016

first example of SWNT as support for metal salen complexes in heterogeneous catalysis.

2. Experimental

Starting reagents (ethylenediamine, *trans-R,R*-(−)-1,2-cyclohexanediamine, 3-*tert*-butyl-salicylaldehyde, 5-*tert*-butyl-salicylaldehyde, 3,5-di-*tert*-butyl-salicylaldehyde, bromine, 2-aminoethanethiol, triethylamine, thionyl chloride), vanadyl acac, azoisobutyronitrile (AIBN), TMSCN, aldehydes, and anhydrous solvents were purchased from Aldrich. The reagent-grade solvents were obtained from Scharlau and used without further purification. 5-Bromo-3-alkylsalicylaldehyde [5], 4-hydroxy-5-alkyl-4′-vinylbiphenyl-3-carbaldehyde obtained by the Suzuki cross-coupling reaction [6], the asymmetrical salen ligands [7], and the vanadyl salen complex [8] were prepared according to the procedures reported in the literature. The SWNT sample was of the HiPCO type obtained by high-pressure (30 atm) disproportionation of CO on iron catalysts at 1200 °C and was purified before use. Active carbon was provided by Norit and has a specific surface area of 1400 $m^2\,g^{-1}$. Combustion chemical analyses were carried out using a Fisons EA 1108-CHNS-O analyzer. FT-IR spectra of ligands, complexes, and SWNT were recorded in KBr disks at room temperature in a Nicolet 710 FT spectrophotometer. Near-infrared spectra of opaque powders were recorded in a Varian Cary 5G UV-Vis-NIR spectrophotometer adapted with a praying mantis attachment and using $BaSO_4$ as standard. FT Raman spectra were obtained using Bio-Rad Model II FT Raman, Nd:YAG laser as the excitation source, and a liquid-nitrogen-cooled detector. The power of the laser at the sample was 100 mW and the spectral resolution was 4 cm^{-1}. ^{1}H NMR spectra were recorded in a 300-MHz Varian Geminis Plus using $CDCl_3$ as solvent and TMS as internal standard. The data are reported in δ scale (ppm) and the coupling constants in Hz. Analysis of the salen ligand mixtures was carried out by GC using a Hewlett-Packard HP5890 with a TRB-5 (30 m × 0.25 mm) column and operating with an injector temperature of 280 °C and a detector temperature of 300 °C (FID). Optical purity of the ligands was determined by chiral GC in a Fisons 8035 using a Chiraldex γ-TA (30 m × 0.25 mm) column and operating with an injector temperature of 230 °C and a detector temperature of 230 °C (FID). FAB MS spectra for the vanadyl salen complexes were recorded using a VG-AutoSpec.

2.1. Purification of SWNTs

SWNTs (200 mg) were suspended in a 3 M HNO_3 solution (20 mL) and maintained at reflux temperature for 24 h. After this treatment, the product was vacuum-filtered using a Teflon membrane with a pore size of 0.2 µm. The resulting solid was then thoroughly washed with deionized water and THF and dried in vacuum.

2.2. Chlorination of SWNT

The purified SWNT (100 mg) previously dried under vacuum was suspended in a solution of $SOCl_2$ (25 mL) and DMF (1 mL). The suspension was stirred at 65 °C for 24 h. The solid was then separated by filtration and washed with anhydrous THF, and dried in vacuum.

2.3. Functionalization of COCl@SWNT

To a solution of 2-aminoethanethiol hydrochloride (586 mg, 5 mmol), triethylamine (1.4 mL, 10 mmol) in dry CH_2Cl_2 (5 mL), COCl@SWNT (100 mg) was added. The suspension was allowed to stir under N_2 atmosphere at 45 °C for 48 h. The solid was then separated by filtration, washed with water and THF, and dried in vacuum.

2.4. Preparation procedure and spectroscopic data of synthetic intermediates

2.4.1. 5-Bromo-3-methylsalicylaldehyde

A solution of Br_2 (3.94 g, 25 mmol) in CH_2Cl_2 (45 mL) was slowly added to 3-methylsalicylaldehyde (2 g, 14.7 mmol) in dry CH_2Cl_2 (45 mL). After stirring at 0 °C for 1 h, a saturated aqueous solution of $Na_2S_2O_5$ was added. After separation, water was added to the organic phase. After the organic phases were dried over $MgSO_4$, 5-bromo-3-methylsalicylaldehyde (3.16 g, 97%) was obtained as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 11.18 (s, 1H; OH), 9.77 (s, 1H; C*H*O), 7.50 (d, $J = 2.2$ Hz, 1H; 1 arom. H), 7.48 (d, $J = 2.2$ Hz, 1H; 1 arom. H), 2.25 (s, 3H; CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 195.98, 159.40, 140.53, 133.42, 130.04, 121.39, 111.24, 15.33; IR (KBr): ν (cm^{-1}) = 2883, 1654, 1608, 1452, 1415, 1378, 1303, 1272, 1236, 1199, 1024, 968, 865, 705; MS (FAB): 215; elemental analysis calcd (%) for $C_8H_7O_2Br$ (215.05): C 44.68, H 3.29; found: C 44.40, H 2.95.

2.4.2. 4-Hydroxy-5-methyl-4′-vinylbiphenyl-3-carbaldehyde

A solution of 5-bromo-3-methylsalicylaldehyde (2.5 g, 11.6 mmol), 4-vinylphenyl boronic acid (2.23 g, 15.1 mmol), $[Pd(PPh_3)_4]$ (389 mg, 3% mol), and Na_2CO_3 (2 M, 15 mL, 30.2 mmol) in THF (56 mL) was heated at reflux temperature under Ar for 3 h. After separation of the phases, the aqueous layer was extracted with Et_2O (70 mL). After the combined organic phases were dried over $MgSO_4$, the solvent was evaporated, hexane (20 mL) was added to the residue, and the Pd salts were precipitated and filtered over Celite. Flash column chromatography (hexane/AcOEt 9.5/0.5) afforded 4-hydroxy-5-methyl-4′-vinylbiphenyl-3-carbaldehyde (1.93 g, 70%) as a yellow solid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 11.30 (s, 1H; OH), 9.97 (s, 1H; C*H*O), 7.64–7.46 (m, 6 H; 6 arom. H), 6.75 (dd, $J = 17.6$, 10.9 Hz, 1H; C*H*CH_2), 5.79 (dd, $J = 17.6$, 0.7 Hz, 1H; 1 vinyl. H), 5.28 (d, $J = 10.9$, 0.7 Hz, 1H; 1 vinyl. H), 2.34

(s, 3H; CH_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm) = 195.25, 157.90, 137.36, 135.02, 134.86, 134.69, 130.71, 127.73, 126.04, 125.86, 125.23, 125.08, 118.56, 113.81, 112.49, 13.7; IR (KBr): ν (cm^{-1}) = 2982, 2919, 2840, 1668, 1593, 1508, 1469, 1412, 1379, 1271, 1192, 1021, 994, 914, 841, 710; MS (FAB): 238; elemental analysis calcd (%) for $C_{16}H_{14}O_2$ (238.30): C 80.63, H 5.93; found: C 80.23, H 6.32.

2.4.3. Mixture of salen ligands containing asymmetric N-(3-methylsalicylidene)-N′-(4-vinylphenyl-3-methylsalicylideneethylenediimine

A solution of 4-hydroxy-5-methyl-4′-vinylbiphenyl-3-carbaldehyde (0.47 g, 1 mmol), 3-methylsalicylaldehyde (0.41 g, 3 mmol), and ethylenediamine (0.12 g, 2 mmol) in EtOH (10 mL) was heated under reflux for 1 h. After that time, the solvent was removed and CH_2Cl_2 was added. The organic solution was dried over $MgSO_4$ and evaporation of the solvent rendered a statistical mixture (98% in overall yield with respect to the diamine) of the 3,3′-dimethyl salen ligands. GC analysis of the mixture established that the proportion of the *para* unsubstituted, 5-(4-vinylphenyl), and 5,5′-bis(4-vinylphenyl) was 9, 6, 1, respectively. The GC-MS showed the corresponding mass of each ligand at 294, 396, and 498 amu. ^1H NMR spectrum was recorded for the mixture, assigning the signals of the title compound from the spectrum. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 13.49 (s, 2H; 2 OH), 8.44 (s, 2H; 2 imine H), 7.49–7.42 (m, 9 H; arom. H), 6.73 (dd, $J = 17.6$, 10.9 Hz, 1H; 1 CHCH_2), 5.76 (d, $J = 17.6$, 0.7 Hz, 1H; CHCH_2), 5.24 (d, $J = 10.9$, 0.7 Hz, 1 H; CHCH_2), 3.97 (s, 4H; 2 NCH_2), 2.31 (s, 6H; 2 CH_3).

2.4.4. Mixture of ligands containing asymmetric N-(3,5-di-tert-butylsalicylidene)-N′-(4-vinylphenyl-3-tert-butylsalicylidene)-1,2-cyclohexadiimine

A solution of 4-hydroxy-5-*tert*-butyl-4′-vinylbiphenyl-3-carbaldehyde (0.47 g, 1 mmol), 3,5-di-*tert*-butylsalicylaldehyde (0.41 g, 3 mmol), and *trans-R,R*-(−)-1,2-cyclohexadiamine (0.22 g, 2 mmol) in EtOH (10 mL) was heated under reflux for 1 h. After that time, the solvent was removed and CH_2Cl_2 was added. The organic solution was dried over $MgSO_4$ and evaporation of the solvent rendered a statistical mixture (94% in overall yield with respect to the diamine) of the 3,5,3′-tri-*tert*-butylsalchen ligands. GC analysis of the mixture established that the proportion of the 5,5′-di-*tert*-butyl, 5-*tert*-butyl-5′-(4-vinylphenyl), and 5,5′-bis(4-vinylphenyl) was again 9, 6, 1, respectively. The GC-MS showed the corresponding mass of each ligand at 544, 590, and 636 amu. ^1H NMR spectrum was recorded for the mixture, assigning the signals of the title compound from the spectrum. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 13.49 (s, 2H; 2 OH), 8.35 (s, 2H; 2 imine H), 7.49–7.42 (m, 9 H; arom. H), 6.73 (dd, $J = 17.6$, 10.9 Hz, 1H; 1 CHCH_2), 5.75 (d, $J = 17.6$, 0.7 Hz, 1H; CHCH_2), 5.24 (d, $J = 10.9$, 0.7 Hz, 1 H; CHCH_2), 3.97 (s, 4H; 2 NCH), 2.04–1.47 (m, 8H; 8 cyclohexyl H), 1.39 (s, 27H, 9 CH_3).

2.4.5. Mixture of VOsalen complexes

VOacac (0.348 g, 1 mmol) was added to a solution containing an equivalent amount of ligand mixture (either derived from ethylenediimine or from 1,2-cyclohexadiimine) in MeOH (15 mL). The solution was stirred overnight at room temperature. After removal of the solvent, and flash column chromatography, a mixture of vanadyl salen complexes was obtained. Vanadyl *N*-(3-methylsalicylidene)-*N*′-(4-vinylphenyl-3-methylsalicylidene)ethylenediimine was obtained as a green solid. ^1H NMR was recorded and the signals corresponding to the asymmetric complex were assigned from the mixture. ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 9.96 (s, 2H; 2 imine H), 7.54–7.47 (m, 9 H; arom. H), 6.76 (dd, $J = 17.4$, 10.8 Hz, 1 H; 1 CHCH_2), 5.81 (d, $J = 17.4$ Hz, 1H; CHCH_2), 5.29 (d, $J = 10.8$ Hz, 1H; CHCH_2), 3.90 (s, 4H; 2 NCH_2), 2.30 (s, 6H; 2 CH_3). MS (FAB): 461. Vanadyl *N*-(3,5-di-*tert*-butylsalicylidene)-*N*′-(4-vinylphenyl-3-*tert*-butylsalicylidene)-1,2-cyclohexadiimine: ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) = 8.35 (s, 2H; 2 imine H), 7.46–7.19 (m, 9 H; arom. H), 6.73 (dd, $J = 17.7$, 10.8 Hz, 1H; 1 CHCH_2), 5.75 (d, $J = 17.7$ Hz, 1H; CHCH_2), 5.24 (d, $J = 10.8$ Hz, 1H; CHCH_2), 3.9 (s, 2H; 2 NCH), 2.30 (s, 6H, 2CH_3) 2.04–1.47 (m, 8H; 8 cyclohexyl, H), 1.39 (s, 27H, 9 CH_3); MS (FAB): 653 amu.

2.5. Anchoring the asymmetric VOsalen complex to the SH@SWNT

To a solution of styryl VOsalen (100 mg) and AIBN (50 mg) in degassed $CHCl_3$ (8 mL), SH@SWNT was added (50 mg) and the suspension was stirred for 20 h under N_2 atmosphere at 70 °C. The solid was then separated by filtration and exhaustively washed with THF and CH_2Cl_2 and dried in vacuum. The loading of VOsalen complex in the SWNT determined by elemental (N) analysis was 82 μmol g^{-1}. The chiral version of the catalyst (VOsalen*) was synthesized using the same procedure with a mixture of chiral complexes. The loading determined by elemental (N) analysis was 62 μmol g^{-1}. The V content for the two vanadyl salen complexes on SWNT was below the detection limit of quantitative absorption spectroscopy.

2.6. Preparation of VOsalen@activecarbon

This catalyst was prepared following exactly the same procedure and proportions as those described above for VOsalen@SWNT, without the purification step, but substituting SWNT by active carbon. This solid was chlorinated with $SOCl_2$, functionalized with 2-aminoethanothiol, and reacted with styryl VOsalen in the presence of radical initiator.

2.7. General procedure for the addition of cyanide to aldehydes

For control reactions with the homogeneous catalysts, the experimental procedure described by Belokon el al.

was followed [13]. Thus, a Schlenk tube was charged with the homogeneous catalyst (0.2 mmol%) and 1.9 ml of dry chloroform. The aldehyde (1.64 mmol) and nitrobenzene (1.64 mmol, internal standard) were also added. The mixture was stirred for 5 min and then TMSCN was added (1.1 eq, 1.8 mmol). The resulting mixture was stirred at room temperature under a nitrogen atmosphere and the course of the reaction followed by GC (TRB-5, 30 m, 0.25 mm). For the VOsalen@SWNT catalysts a similar procedure was followed: 15 mg of heterogeneous catalyst (0.3% mol) was suspended in dry chloroform (0.5 mL) followed by the addition of the aldehyde (0.41 mmol) and the nitrobenzene as internal standard (0.41 mmol). The suspension was stirred for 5 min and then TMSCN (1.23 mmol) was added. The heterogeneous reaction mixture was stirred at room temperature and the course of the reaction followed by analyzing the organic phase with GC (with the same column as before). The physical and analytical data of the trimethylsilyl ethers of corresponding cyanohydrins were consistent with those reported in the literature [9]. When the chiral VOsalen*@SWNT was used as catalyst, the reaction was carried out at 0 °C with 20 mg (0.3 mol%) of catalyst. The enantiomeric excess (ee) was determined using a GC with a chiral column (ChiralDex Γ-TA chiral column, 30 m, 0.25 mm).

2.8. Reuse tests

The reusability of the catalyst was tested by filtering the catalyst from the crude of reaction, washing with fresh solvent, and using in a next run under the same reaction conditions described above.

2.9. Leaching tests

The percentage of activity due to the complex or vanadium species leached from the solid and present in the solution was determined by performing the reactions under the reaction conditions described above until the conversion was about 40%. At this conversion, half the volume was filtered and the resulting clear solution let to react. The percentage of leaching was estimated by comparing the time-conversion plot of the twin reactions with and without catalyst.

3. Results and discussion

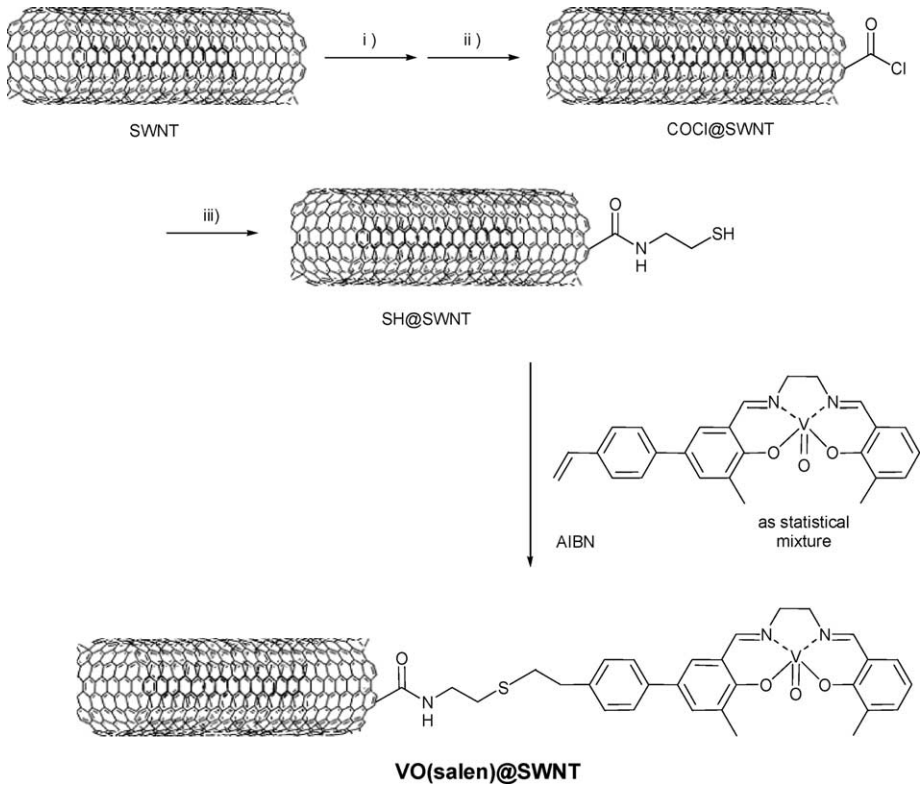
Given the current interest in SWNT, it occurred to us that this carbon would be a suitable support for covalently anchoring a metallosalen complex. The key feature of our strategy for obtaining these solid vanadyl salen catalysts is the preparation of a VOsalen complex having a peripheral C=C double bond on the ligand that will serve to connect covalently the complex to modified SWNT. The SWNT has been previously functionalized at the tips with terminal thiol groups. Preparation of this SWNT containing thiol groups is depicted in Scheme 1.

After purification of the commercial sample of SWNT by nitric acid treatment at 100 °C to remove metal impurities, the purified sample contains carboxylic groups at the tips and defects of the nanotubes formed through the acid oxidation [10]. The preferential location of the carboxylic groups at the tips has been previously inferred from electron microscopy studies that show that upon acid purification the formation of carboxylic groups is accompanied by the cutting and shortening of the tubes. Fig. 1 is an electron micrograph showing the morphology and blundle agglomeration of the SWNT sample used in this work. The diameter of the individual nanotubes was estimated as 14 Å as determined by measuring in Raman spectroscopy the wavenumber of the breathing vibration band characteristic of single-walled nanotubes. Fig. 2 shows the corresponding Raman spectrum.

These carboxylic groups were reacted with thionyl chloride in DMF and subsequently were transformed into amides by treatment with 2-aminoethanethiol in the presence of a tertiary amine to trap the evolved hydrochloric acid [11]. The presence of thiol groups anchored on the nanotubes was demonstrated by combustion chemical analysis of sulfur as well as by the observation in the IR spectrum the characteristic SH-stretching band at 2679 cm^{-1}.

On the other hand, the VOsalen complex was in turn prepared by complexation with vanadyl acetylacetonate (acac) of a statistical mixture of three ligands, which contained an asymmetric salen compound having a styryl unit at the *para* position of the salen complex. The mixture of the salen ligands was obtained by reacting a diamine with a mixture of two salicylic aldehydes in proportion 1 to 3 and was analyzed by GC. This strategy for preparing in a single pot asymmetric salen ligands has been used in related precedents in which metal salen complexes have been anchored to inorganic oxides [12] and polymers [13]. The styryl-alkylsalicylic aldehydes were synthesized by Suzuki cross-coupling of 4-vinylphenyl boronic acid with the corresponding 4-bromosalicylaldehyde. The sequence of reactions followed to obtain the VOsalen complex is indicated in the Scheme 2.

All the synthetic intermediates were characterized by analytical and spectroscopic techniques. Of special relevance are the data corresponding to the mixture of salen complexes. Thus, in UV–visible spectroscopy the corresponding metal–ligand charge transfer band appearing at λ_{max} of 380 cm^{-1} is observed. In IR spectroscopy, the most salient feature is the phenolate stretching band recorded in all metal salen complexes appearing at 1540 cm^{-1}. In ^1H NMR the vinyl group present in the mixture of complexes is clearly seen as three peaks of an ABM system between 5.2 and 6.8 ppm, as well as the aromatic imine proton at 8.4 ppm. The final covalent linkage between SH@SWNT and the mixture of complexes was carried out through a radical chain mechanism initiated by AIBN. In this process those complexes that do not contain terminal vinyl groups cannot obviously be anchored and they remain in the solution and washed out in the reaction work up.



Scheme 1. Modification of the SWNT: (i) 3 M HNO_3, reflux, 24 h; (ii) $SOCl_2$, DMF, 60 °C, 24 h; (iii) 2-aminoethanethiol hydrochloride, Et_3N, CH_2Cl_2, 45 °C, 48 h.

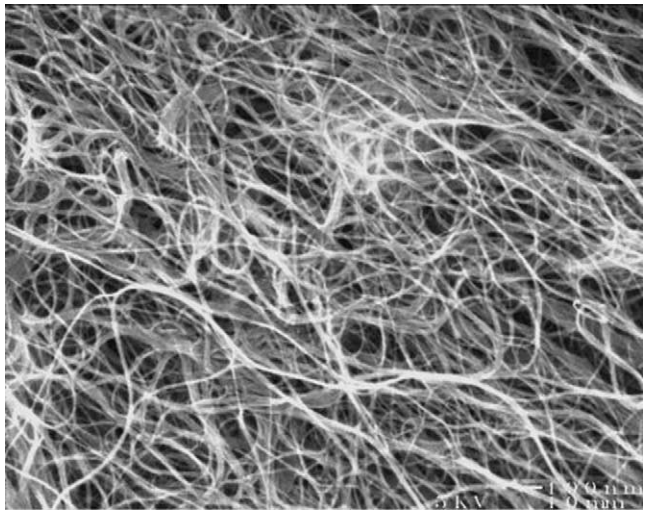


Fig. 1. Scanning electron micrograph showing the morphology of the bundle agglomeration of SWNT sample used in this work.

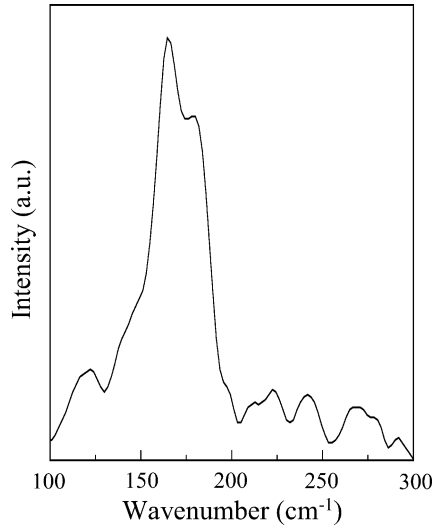
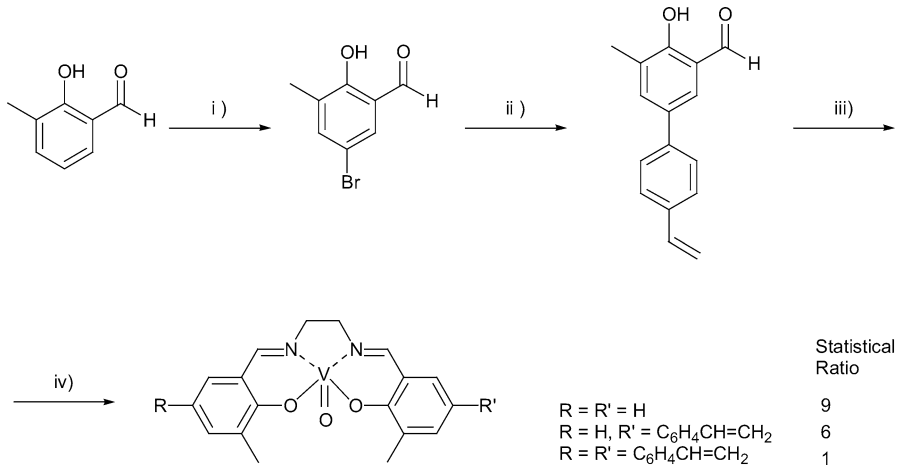


Fig. 2. Expansion of the FT-Raman spectrum of VOsalen@SWNT showing the breathing band characteristic of single-walled carbon nanotubes from which the diameter is obtained.

Scheme 1 illustrates the synthetic step and the structure of the resulting VOsalen complex anchored to the SWNT. According to Fig. 1 in which bundles of SWNTs rather than isolated tubes are seen, drawing in Scheme 1 a single nanotube represents a simplification of the functionalization process.

The solid obtained was analyzed by combustion analysis of sulfur and nitrogen. Before anchoring of the complex, the 1-to-1 atomic ratio between sulfur and nitrogen agrees with the presence of 2-thiolethaneamide. After anchoring of the complexes, the increase in the relative percentage of nitrogen is compatible with a portion of the terminal thiol groups being reacted with the styryl function. The VOsalen content of the SWNT was calculated based on this analytical data of N, since the vanadium content was below the detection limit



Scheme 2. Preparation of mixtures of the asymmetric salen complexes: (i) Br_2, CH_2Cl_2, 0 °C, 1 h; (ii) 4-vinylphenyl boronic acid, $[Pd(PPh_3)_4]$, 2 M Na_2CO_3, THF, 70 °C, 3 h; (iii) 3-methylsalicylic aldehyde, ethanediamine, EtOH, relux, 1 h; (iv) VOacac, MeOH, RT, overnight. The composition of the mixtures was determined by GC or ^{1}H NMR.

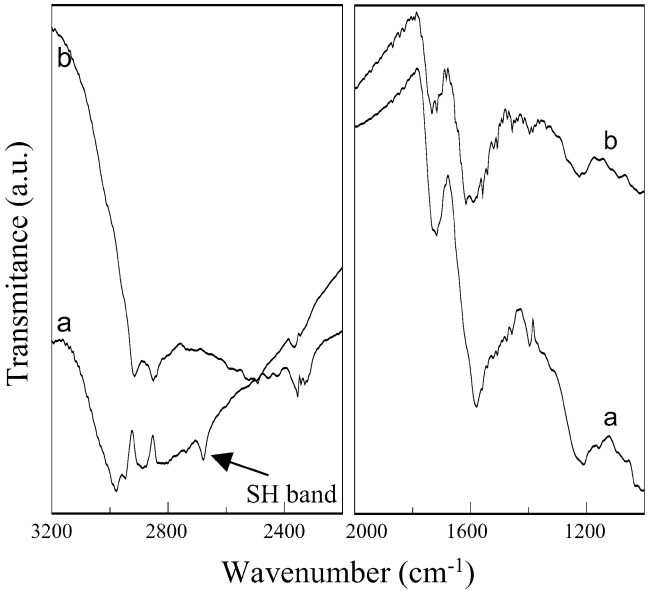


Fig. 3. Infrared of SH@SWNT (a) and VO(salen)@SWNT (b).

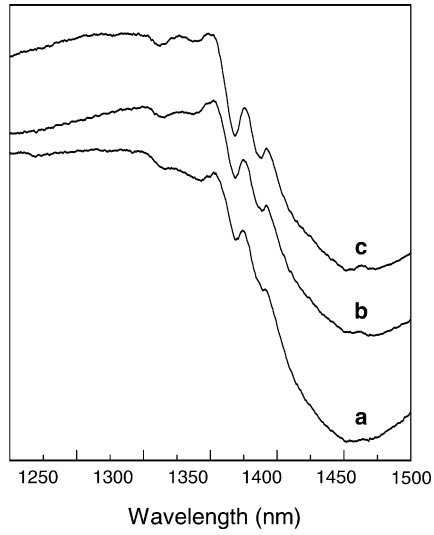


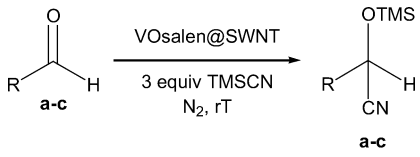
Fig. 4. Near-infrared spectra of purified SWNT (a), SH@SWNT (b), and VO(salen)@SWNT (c).

of atomic absorption spectroscopy. The loading of complex was 82 µmol g^{-1}.

The most informative spectroscopic data to support the covalent anchoring of the VOsalen complex on the modified SWNT were obtained from the comparison of the set of IR corresponding to the purified SWNT, SH@SWNT, and VOsalen@SWNT (Fig. 3). Thus, AIBN treatment leads to the disappearance of the SH-stretching band, while the amide vibrations are still present at 1726 cm^{-1}. The near-IR region of the purified SWNT was preserved upon functionalization in SH@SWNT and VOsalen@SWNT, thus showing that the single-walled structure of the nanotubes has been preserved unaltered during the treatment (Fig. 4). In addition, a control experiment in which a mechanical mixture of SWNT and 100 µmol g^{-1} of commercial vanadyl *N*, *N′*-bis(2,4-di-*tert*-butylsalicylidene)-1,2-cyclohexadiimine (no covalent linkage between the complex and SWNT) was submitted to the extraction procedure with $CHCl_3$ revealed that essentially all the complex can be recovered by our workup procedure.

The solid was used as heterogeneous catalyst for the cyanosilylation of aldehydes (Scheme 3 and Table 1) [9]. One of the major advantages of anchoring the VOsalen complex on the SWNT as support is the ease in which the catalyst can be suspended on the solvent due to the bundled agglomerates of SWNT that aggregate slowly. Upon initial stirring of the suspension, the black solid remains suspended without setting down for long period of time.

The VOsalen@SWNT solid shows a high activity for this reaction using benzaldehyde as substrate and working at a low substrate to catalyst ratio (below 1000:3). The reaction occurs with almost complete selectivity toward the silylated cyanohydrin. For comparison the reaction was carried out under the same conditions but using the tetrabutyl



	R
a	C_6H_5
b	*p*-F-C_6H_4
c	n-C5H11

Scheme 3. Cyanosilylation of aldehydes.

Table 1
Results of the cyanosilylation of aldehydes in the presence of vanadyl catalysts[a]

Aldehyde	Catalyst	Reuse	Conversion (%)
Benzaldehyde	Tetra-*tert*-butylvanadyl salen in homogenous phase (2 h)	–	98
Benzaldehyde	SH@SWNT	–	5
Benzaldehyde	VOsalen@SWNT	0	93
Benzaldehyde	VOsalen@SWNT	1	96
Benzaldehyde	VOsalen@SWNT	2	94
Benzaldehyde	VOsalen@SWNT	3	97
Benzaldehyde	VOsalen@SWNT	4	95
Benzaldehyde	SH@activecarbon	–	25
Benzaldehyde	VOsalen@activecarbon	–	83
4-Fluorobenzaldehyde	VOsalen@SWNT	–	96
Hexanal	VOsalen@SWNT	–	97
Benzaldehyde	VOsalen*@SWNT (72 h, 0 °C)	–	67; ee 66%

[a] Reactions were carried out at room temperature under N_2 atmosphere for 12 h: aldehyde (0.41 mmol), TMSCN (3 eq), VOsalen@catalyst (0.3 mol%), nitrobenzene (0.41 mmol), and $CHCl_3$ (0.5 mL).

VOsalen dissolved in chloroform as a homogeneous catalyst. The results are also included in Table 1. From this comparison it can be concluded that attaching the complex to the SH@SWNT does not produce a significant decrease in the intrinsic activity of the catalyst. A control experiment in which SH@SWNT was tested as catalyst demonstrates that this solid is inactive to promote the cyanosilylation reaction.

In order to provide a valid comparison between SWNT and active carbons as supports, we repeated the preparation procedure followed for VOsalen@SWNT, but using a high-surface-area active carbon. We also tested as a blank the activity of SH@activecarbon. The results are included in Table 1. As can be seen, SH@activecarbon has a significant catalytic activity. This residual activity can arise from the presence of adventitious acid sites and plays a negative role since it is expected the support to be inert (particularly for enantioselective catalysis on chiral complexes). On the other hand, the conversion achieved with VOsalen@activecarbon was significantly lower than that of VOsalen@SWNT despite the about fivefold larger surface area of the active carbon. These comparative results indicate the superior properties of SWNT with respect to active carbons as support and can be explained by the chemical composition and periodicity and regularity of SWNT with respect to active carbons.

Leaching experiments were undertaken to demonstrate that the catalysis with VOsalen@SWNT is truly heterogeneous and that no catalytically active vanadium species are dissolved in the solution. For these experiments, the reactions were allowed to occur until 40% of conversion and at this point the solid was filtered out and the clear solution allowed to react up to the final reaction time. These experiments show that after filtration of the solid, the reaction completely stops. This observation rules out the presence of active vanadium species in the solution.

Reusability of the VOsalen@SWNT was confirmed by performing a series of consecutive experiments in which the used catalyst was filtered, washed with fresh solvent, and employed without any further treatment in another run. The results shown in Table 1 clearly prove that no loss of activity occurs, giving a minimum productivity of 317 mol of product per mole of complex. Besides benzaldehyde, two other aldehydes were also tested and the VOsalen@SWNT was found to be equally active.

Given the excellent results in activity achieved with the achiral VOsalen@SWNT, we expanded the results to the asymmetric version of the cyanosilylation using a chiral VOsalen derived from (1*R*,2*R*)-(−)-cyclohexanediamine and a 3,5-di-*tert*-butyl-2-hydroxybenzaldehyde, obtained following the same route as indicated in Scheme 2. The VOsalen*@SWNT solid and the involved synthetic intermediates were also characterized analytically and spectroscopically, exhibiting spectroscopic properties analogous to those recorded for the intermediates of the VOsalen@SWNT series. Molecular modeling at the MNDO semiempirical level predicts a size for the chiral salicylidenecyclohexadiimine vanadyl complex of about 13 Å and, therefore, it is very unlikely that this complex could be incorporated inside the carbon nanotubes (14 Å). A view of the model based on molecular mechanics for the stretched conformation of the VOsalen complex anchored to the tips of the nanotube is provided in Chart A. As expected in view of the reports in solution for analogous chiral vanadyl salen complexes [9], VOsalen*@SWNT is also a highly efficient heterogeneous catalyst. The result obtained for the enantioselective cyanosilylation is also contained in Table 1. Since SH@activecarbon already shows an undesirable activity leading to racemic cyanohydrins, the anchoring of VOsalen* on active carbon was not pursued, SWNT being a superior inert support than active carbon.

Although the enantiomeric excess obtained with VOsalen*@SWNT is significantly lower than those reported for related homogeneous VOsalen complexes in solution (around 90%) [9], they are encouraging and higher than those obtained for other supported metal salen complexes on inorganic oxides in which much lower ee's have been reported [14]. For instance, olefin epoxidation using Mn(III) salen complex supported on MCM-41 [14a] gives ee's between 35 and 51% and when the same complex is sup-

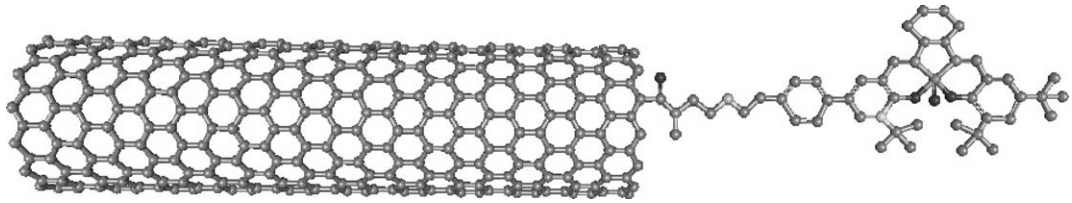


Chart A. VOsalen*@SWNT.

ported on silica gel [14b] the ee's obtained varied between 30 and 58% and chiral vanadyl salen anchored on the MCM-41 walls promotes the cyanohydrin formation with 30% ee [14c]. Probably, further functionalization of the SWNT to avoid trace OH groups or longer tethers linking the walls and the complex that minimize the influence of the support surface morphology could contribute to increase the asymmetric induction ability of these solid catalysts.

4. Conclusion

In conclusion, analogous to how activated carbons have been used as suitable supports in heterogeneous catalysis, we have shown here that SWNTs are also very convenient supports for the covalent anchoring of metal complexes. Compared to activated carbons, SWNTs have the advantage of having a well-defined structure and the possibility of introducing covalent functionalization through reliable synthetic methods. The special structural characteristics of SWNTs, particularly the morphology of the tubes, their reliability of functionalization, and the ease in which they can be suspended, constitute advantageous features for SWNT with respect to active carbons. In this way a VOsalen complex anchored on SWNT is a highly active, truly heterogeneous, and reusable catalyst for the cyanosilylation of aldehydes. The asymmetric version of this SWNT-supported catalysts seems also to be promising at this stage and may lead to a whole family of new supported catalyst.

Acknowledgments

Financial support to C. Baleizão from Fundação para a Ciência e Tecnologia, Portugal (PRAXIS XXI/BD/21375/99) is gratefully acknowledged. Part of this work was financed by the Spanish DGES (MAT2000-1768-CO2-01).

References

[1] (a) N.E. Leadbeater, M. Marco, Chem. Rev. 102 (2002) 3217–3274;
(b) C.A. McNamara, M.J. Dixon, M. Bradley, Chem. Rev. 102 (2002) 3275–3300.
[2] (a) P.M. Ajayan, Chem. Rev. 99 (1999) 1787–1799;
(b) R. Andrews, D. Jacques, D. Qian, T. Rantell, Acc. Chem. Res. 35 (2002) 1008–1017.
[3] (a) H. Dai, Acc. Chem. Res. 35 (2002) 1035–1044;
(b) C.N.R. Rao, B.C. Satishkumar, A. Govindaraj, M. Nath, Chem. Phys. Chem. 2 (2001) 78–105.
[4] (a) J.L. Bahr, J. Yang, D.V. Kosynkin, M.J. Bronikowski, R.E. Smalley, J.M. Tour, J. Am. Chem. Soc. 123 (2001) 6536–6542;
(b) V. Georgakilas, K. Kordatos, M. Prato, D.M. Guldi, M. Holzinger, A. Hirsch, J. Am. Chem. Soc. 124 (2002) 760–761;
(c) H. Peng, P. Reverdy, V.N. Khabashesku, J.L. Margrave, Chem. Commun. (2003) 362–363;
(d) D.E. Hill, Y. Lin, A.M. Rao, L.F. Allard, Y.P. Sun, Macromolecules 35 (2002) 9466–9471.
[5] M.A. Esteves, N. Narender, B. Gigante, M.J. Marcelo-Curto, F. Alvarez, Syn. Commun. 29 (1999) 275–280.
[6] H. Sellner, J.K. Karjalainen, D. Seebach, Chem. Eur. J. 7 (2001) 2873–2887.
[7] (a) D.A. Allen, E.N. Jacobsen, J. Am. Chem. Soc. 121 (1999) 4147–4154;
(b) T.S. Reger, K.D. Janda, J. Am. Chem. Soc. 122 (2000) 6929–6934.
[8] J.A. Bonadies, C.J. Carrano, J. Am. Chem. Soc. 108 (1986) 4088–4095.
[9] (a) Y.N. Belekon, M. North, T. Parsons, Org. Lett. 2 (2000) 1617–1619;
(b) Y.N. Belekon, B. Green, N.S. Ikonnikov, M. North, T. Parsons, V.I. Tararov, Tetrahedron 57 (2001) 771–779.
[10] (a) S. Banerjee, S.S. Wong, Nano Lett. 2 (2002) 49–53;
(b) A. Hirsch, Angew. Chem. Int. Ed. 41 (2002) 1853–1859;
(c) Y.P. Sun, W. Huang, Y. Lin, K. Fu, A. Kitaygorodskiy, L.A. Riddle, Y.J. Yu, D.L. Carrol, Chem. Mater. 13 (2001) 2864–2869.
[11] M.L. Bushey, A. Hwang, P.W. Stephens, C. Nuckolls, Angew. Chem. Int. Ed. 41 (2002) 2828–2831.
[12] (a) C.E. Song, M. Lemaire, Chem. Rev. 102 (2002) 3495–3524;
(b) D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615–3640.
[13] (a) D.A. Allen, E.N. Jacobsen, J. Am. Chem. Soc. 121 (1999) 4147;
(b) L.E. Martínez, J.L. Leighton, D.H. Carsten, E.N. Jacobsen, J. Am. Chem. Soc. 117 (1995) 5897;
(c) Q.H. Fan, Y.M. Li, A.S.C. Chan, Chem. Rev. 102 (2002) 3385–3466.
[14] (a) D.W. Park, S.D. Choi, S.J. Shoi, C.Y. Lee, G.J. Kim, Catal. Lett. 78 (2002) 145–151;
(b) D. Pini, A. Mandoli, S. Orlandi, P. Salvadori, Tetrahedron Asymmetry 10 (1999) 3883–3886;
(c) C. Baleizão, B. Gigante, D. Das, M. Alvaro, H. Garcia, A. Corma, Chem. Commun. (2003) 1860–1861.