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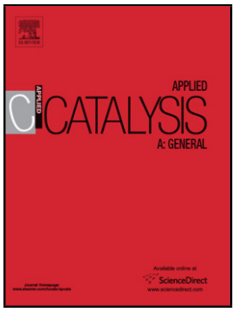

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# Grafting of Copper (II) Schiff Base Complex on Functionalized Multi-Wall Carbon Nanotubes: Synthesis, Characterization and Catalytic Aziridination of Olefins

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*Highlights*

*► Multi-Wall carbon Nanotubes were functionalized by copper(II) Schiff base complex. ► Functionalized Multi-wall carbon nanotubes catalyze the aziridination of alkenes. ► MWNTs covalently anchored copper(II) complex obtained via chemical modification.*

Graphical abstract

Abstract

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In this study, hydroxyl functionalized copper(II) Schiff-base; [Cu((OH)$_2$-salophen)], [(OH)$_2$-salophen] = (*N*,*N´*-bis(4-hydroxysalicylidene)phenylene-1,2-diamine); has been covalently anchored on modified multi-wall carbon nanotubes (MWNTs); [Cu((OH)$_2$-salophen)]@MWNTs. The new modified MWNTs have been characterized by transmission electron microscopy, X-ray diffraction, thermogravimetric analysis, ultraviolet–visible spectroscopy, diffuse reflectance, fourier transform infrared spectroscopy and elemental analysis. The results suggest that the symmetrical Schiff-base is a bivalent anion with tetradentate $N_2O_2$ donors derived from the phenolic oxygen and azomethine nitrogen. MWNTs covalently anchored copper (II) complex catalyze the aziridination of alkenes employing [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (PhI=NTs) as the nitrogen source.

Keywords: Copper(II); Schiff-base; Nanocatalyst; Nanotubes; Aziridination; Transmission electron microscopy.

## 1. Introduction

The aziridination of alkenes is a reaction of great importance since aziridines are used as intermediates in organic synthesis for pharmaceuticals and agrochemicals [1]. The synthesis of aziridines has therefore been a subject of considerable research interest over the last few years. A single atom transfer to olefins is the shortest route to three-membered cyclic compounds. Catalytic addition of a carbene moiety to an imine results in the formation of an aziridine, but the yields are often low [2]. The transfer of a nitrogen atom onto an olefin offers an attractive synthesis of aziridines.

Evans et al. reported that [Cu(acac)$_2$] (acac = acetylacetonate) is a very efficient homogeneous catalyst for the aziridination of alkenes using [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane] (PhI=NTs) as nitrogen source [3]. Copper(II) Schiff base complexes have also been used as homogeneous catalysts in the aziridination of olefins [4]. Currently, transition metal complexes with Schiff base ligands, of salen type, have been the object of intense research due to their high activity, chemoselectivity and enantioselectivity in a large range of catalytic

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processes [5]. Evans et al. reported copper(I) and copper(II) salts as the most effective and extensively used homogeneous catalysts for aziridination of olefins using PhI=NTs as the nitrene donor. Taylor and co-workers and Ando et al. have reported copper-catalyzed aziridination of alkenes using chloramine-T as the source of the nitrene. [6–9]. Hutchings et al. have used, however, for the first time, heterogeneous copper-exchanged zeolite Y (CuHY) catalyst, using PhI=NTs as a nitrene donor for aziridination reactions [10, 11]. Later, a polymer-supported Ru-porphyrin catalyst, a silica-supported polypyrazolylborate copper complex, Copper (II) acetylacetonate anchored onto a triamine functionalised activated carbon, [Cu(acac)$_2$trien]@AC, and a polymer-supported Mn(II) complex were also used for the aziridination of olefins by several other workers [12–16]. However, these catalysts have some limitations such as tedious catalyst preparation, low yields of aziridines and long reaction times.

Since homogeneous catalysts cannot be separated from the reaction media and, subsequently, cannot be recycled, the last decade has witnessed a growing interest in the heterogenisation of homogeneous transition metal complexes using several types of supports [17–22]. Initially the complexes were just ion exchanged or adsorbed on the porous supports and, consequently, they could be susceptible to leaching [17–22]. More recently, several grafting and tethering procedures have been developed to covalently attach transition metal complexes to organic polymers [18], silica, zeolites and other micro and mesoporous inorganic materials [23].

The use of carbon nanotubes (CNTs) and other carbon materials as support for homogeneous catalysts is an untapped area, despite of their broad use as catalysts and as supports for metals in its reduced state [24–30]. Conversely, CNTs present several advantages when compared to inorganic supports; they are thermally stable, resistant to chemical attack in acid and basic media [24–30]. In this context, and with the aim of optimizing procedures to prepare CNTs-based heterogeneous catalysts, we have developed several strategies for the immobilization of Schiff base transition metal complexes on CNTs [24–30]. From our different methodologies,

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the direct complex anchoring was applied to the preparation of transition metal Schiff base salen-based CNTs. The resulting materials have showed to act as efficient and reusable heterogeneous catalysts in the oxidation.

During the last decade, studies on the isolation, characterization and catalytic activity of transition metal complexes covalently grafted on various CNTs received considerable attention because of their specific catalytic applications when compared to homogeneous complexes [24–30]. The heterogenization process provides a rigid framework to the metal complex outside the CNTs due to spatial restrictions, and covalent bonding. It also facilitates the reactions to occur under mild experimental conditions. Anchoring of metal complexes on CNTs alters the redox properties. Due to these features, the transition metal complexes grafted on various CNTs resemble, to a certain extent, to the enzymes where the catalytic active centers might be a transition metal ion and the protein sheath provides the stability and steric constraints. Inorganic complexes supported in such constrained environments can therefore be termed as zeozymes [24-30]. In the present work, we have reported the catalytic activity in the aziridination of alkenes using PhI = NTs as nitrogen source at room temperature, of [Cu($(OH)_2$-salophen)] [$(OH)_2$-salophen] = (*N*,*N´*-bis(4-hydroxysalicylidene)phenylene-1,2-diamine) anchored on a chemically oxidized multi-wall carbon nanotubes (MWNTs).

## 2. Experimental

### *2.1. Materials and physical measurements*

MWNTs of purity > 95% and length 1–10 μm, outer diameter: 5-20 nm, inner diameter: 2-6 nm, number of walls 3–15 were purchased from Plasma Chem GmbH (Berlin, Germany). All reagents and solvents used in the modification of the CNTs and in the anchoring of the copper(II) complex were purified by distillation. The nitrene donor PhI=NTs was synthesized using reported procedures [31]. Phenylene-1,2-diamine, 4-hydroxysalicylaldehyde, copper(II) acetate tetrahydrate and cyclohexene ($C_6H_{10} \geq 99.0\%$) were purchased from Merck Chemical Company. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV. The electronic

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spectra of the neat complexes were taken on a Shimadzu ultraviolet–visible (UV-Vis) scanning spectrometer (Model 2101 PC). The stability of the complex covalently attached to the MWNTs was checked after the reaction by UV-Vis and the possible leaching of the complex was investigated by UV-Vis in the reaction solution after filtration of the heterogeneous catalyst. The amounts of copper complex grafted in MWNT matrix were determined by the elemental analysis and by subtracting the amount of copper complex left in the solutions from the amount taken for the synthesis after the synthesis of the catalysts as determined by UV-Vis spectroscopy. Atomic absorption spectrometer (AAS) was recorded on a Perkin-Elmer 4100–1319 Spectrophotometer using a flame approach, after acid hydrogen fluoride (HF) dissolution of known amounts of the nanotubes. Diffuse reflectance spectra (DRS) were registered on a Shimadzu UV/3101 PC spectrophotometer the range 1500–200 nm, using MgO as reference. The elemental analysis (carbon, hydrogen and nitrogen) of the materials was obtained from Carlo ERBA Model EA 1108 analyzer. The metal content was measured using inductively coupled plasma (ICP; Labtam 8440 plasmalab) after leaching the metal ions with concentrated nitric acid and very dilute aqueous KOH solution to specific volumes. The products were identified by gas chromatography (GC) with a CHROMPACK CP 9001 gas chromatograph, and compared with retention times of authentic samples. The gas chromatography–mass spectrometry (GC–MS) system consisted of a GC HP 6890 series instrument and a MS HP 5973 MSD instrument. Thermogravimetric-differential thermal analysis (TG-DTA) was carried out using a thermal gravimetric analysis instrument (Shimadzu TGA-50H) with a flow rate of 20.0 ml min$^{-1}$ and a heating rate of 10 ˚C min$^{-1}$. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on Shimadzu Varian 4300 spectrophotometer in KBr pellets. Hydrogen nuclear magnetic resonance spectroscopy ($^{1}$H-NMR) spectra was recorded with a Bruker DRX-400 spectrometer at 400 MHz and reported as parts per million (ppm) downfield from tetramethylsilane as internal standard. X-ray

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diffraction analysis (XRD) patterns were recorded by a Rigaku D-max C III, X-ray diffractometer using Ni-filtered Cu Kα radiation.

### 2.2. *Preparation of N,N-bis(4-hydroxysalicylidene)phenylene-1,2-diamine;* $H_2[(OH)_2$*-salophen]*

The stoichiometric amount of 4-hydroxysalicylaldehyde (2.44 g)) dissolved in ethanol (25 ml) was added drop by drop to phenylene-1,2-diamine solution (1.08 g in 25 ml ethanol). The contents were refluxed for 4 h and a bright yellow precipitate of $H_2[(OH)_2$-salophen] was obtained. The yellow precipitate was separated by filtration, washed and dried in vacuum. It was then re-crystallized from ethanol to yield $H_2[(OH)_2$-salophen]. Elemental and spectroscopic analysis of neat and MWNTs covalently anchored complex confirmed the molecular composition of ligand. Anal. Calculated for Schiff-base ligand: C, 68.96; H, 4.63; N, 8.04; C/N, 8.58%. Found: C, 68.80; H, 4.51; N, 8.17; C/N, 8.42%. IR (KBr, ν cm$^{-1}$): 2970 (O-H); 2917 (C-H); 1618); 1531 (C=C); 1085 (C-O); 1638 cm$^{-1}$ (C=N). Elemental and spectroscopic analysis of [Cu($(OH)_2$-salophen)] and [Cu($(OH)_2$-salophen)]@MWNTs confirmed the molecular composition of ligand. $^1$H-NMR (DMSO-$d_6$, ppm) δ 13.4 (s, 2H, O· ·H· ·N); 10.3 (s, 2H, O-H); 8.73 (s, 2H, CH=N); 7.3-7.4 (m, 3H, aldehyde); 6.3-6.4 (m, 4H, diamine).

### 2.3. *Preparation of [Cu(*$(OH)_2$*-salophen)]*

The Schiff-base ligand (3.30 g, 0.0095 mol) was dissolved in 100 ml of refluxing ethanol and a stream of nitrogen was purged for 4 h to eliminate the oxygen. A solution containing 0.0095 mol of copper(II) acetate tetrahydrate in water was added dropwise to the deoxygenated ligand solution. The resulting mixture was agitated and refluxed under nitrogen with 5 ml of ethanol followed by 5 ml of water. The mixture was then cooled and filtered under reduced pressure. The collected solid was washed with diethyl ether and dried in air to give red crystalline [Cu($(OH)_2$-salophen)] which was purified by recrystallization from chloroform (Yield: 77%). Anal. Calculated for [Cu($(OH)_2$-salophen)]: C, 58.61; H, 3.44; N, 6.83; C/N, 8.58; Cu, 15.50; Cu/N, 2.27%. Found: C, 58.49; H, 3.32; N, 6.95; C/N, 8.42; Cu, 15.39; Cu/N, 2.21%; IR (KBr, cm$^{-1}$) $\nu_{C=N}$ 1619.

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### *2.4. MWNTs purification*

The raw product was first immersed in an aqueous solution of HF to remove $SiO_2$, then filtered and washed with distilled water, and refluxed in diluted $HNO_3$ for 4 h to remove the metals and amorphous carbon. The resulting solid was then thoroughly washed with deionized water and tetrahydrofuran (THF) and dried in vacuum.

### *2.5. Anchoring the copper(II) complex to the MWNTs; [Cu((OH)$_2$-salophen)]@MWNTs*

The purified MWNTs (100 mg) previously dried under vacuum were suspended in a solution of $SOCl_2$ (25 ml) and dimethylformamide (DMF) (1 ml). The suspension was stirred at 65 ˚C for 24 h. The solid; ClCO@MWNTs; was then separated by filtration and washed with anhydrous THF, and dried in vacuum. ClCO@MWNTs was added (50 mg) to a solution of [Cu((OH)$_2$-salophen)] (100 mg) in degassed $CHCl_3$ (8 ml), 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 (Fig. 1). The loading of [Cu((OH)$_2$-salophen)] complex in the MWNTs determined by elemental (N) analysis was 82 μ mol $g^{-1}$. Anal. Calculated for [Cu((OH)$_2$-salophen)]@MWNTs: Cu/N, 2.23%; IR (KBr, $cm^{-1}$) $\nu_{C=N}$ 1623. Elemental and spectroscopic analysis of [Cu((OH)$_2$-salophen)] and [Cu((OH)$_2$-salophen)]@MWNTs confirmed the molecular composition of ligand.

### *2.6. General procedure for aziridination of styrene*

[Cu((OH)$_2$-salophen)]@MWNTs] (5.6 mol%), styrene (0.56 ml, 5 mmol) and PhI=NTs (0.372 g, 1 mmol) were added to acetonitrile (3 ml) and the reaction mixture was stirred at room temperature. The reaction was monitored by disappearance of the PhI=NTs from the reaction mixture. After completion of the reaction, the catalyst was filtered and the filtrate was concentrated and purified by column chromatography (hexane/ethyl acetate, 95/5, v/v) to afford pure product as white solid. $^1H$ NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, 2H, J=8.3 Hz, Ar-H), 7.28 (m, 7H, Ar-H), 3.79 (dd, 1H, J*cis*=7.2 Hz, $J_{trans}$=4.5 Hz, CHPh), 3.00 (d, 1H, J=7.8 Hz, *cis*-CH-

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aziridine) 2.43 (s, 3H, Ar-Me), 2.40 (d, 1H, J=4.4 Hz, *trans*-CHaziridine). Reutilization of the immobilized copper-Schiff base catalyst was tested using the procedure for the aziridination in which the catalyst was filtered after the experiment and reused for the next experiment. The percentage conversions for three consecutive experiments reusing the same catalyst sample are as follow: 93.1, 92.0 and 90.6%. This experiment shows that the catalyst is reusable, but the catalytic activity is reduced after three catalytic cycles.

## 3. Results and Discussion

### *3.1. Synthesis and characterization*

Immobilization of copper(II) Schiff base on the MWNTs was performed in three steps (i) oxidation of the MWNTs with nitric acid; (ii) reaction with $SOCl_2$ and then (iii) anchoring of the complex on the modified CNTs. These materials have been extensively characterized by us and thus only the results of their characterisation that are relevant to the catalytic experiments will be discussed. The data have been summarized in the Tables and Figures. Elemental analysis indicates that the complex is formed by coordination of 1 mol of the Cu(II) and 1 mol Schiff base ligand. In this study, the metal chelates were insoluble in water but soluble in most organic solvents. Electrical conductivity measurements of the Cu(II) complex give $\Lambda_M$ values of 29 $\Omega^{-1}$ $cm^{-1}$ $mol^{-1}$ and it confirms that they are non-electrolytes. The copper contents of the MWNT catalysts were estimated by dissolving the known amounts of the heterogeneous catalyst in concentrated $HNO_3$ and from these solutions, copper contents were estimated by AAS. The chemical composition confirmed the purity and stoichiometry of the neat and MWNTs-grafted complex. The chemical analysis of the samples revealed the presence of the organic matter with a Cu/N ratio roughly similar to that of the neat complex. The loading of the complex was 83 μ mol $g^{-1}$. Furthermore, a control experiment in which a mechanical mixture of MWNTs and 100 μmol $g^{-1}$ of commercial [(bis(salicylidene)phenylene-1,2-diimino)copper(II)]; [Cu((OH)$_2$-salophen)]; (no covalent linkage between the complex and MWNTs) was submitted to the extraction procedure with $CHCl_3$ revealed that all the complexes can essentially be recovered by our workup procedure.

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The electronic spectra of the Schiff base and complex have been summarized in the experimental section. The spectra of the ligand exhibit three main peaks: at about 268, 330 and 370 nm. The first and the second peaks are attributed to benzene $\pi\rightarrow\pi^*$ and imino $\pi\rightarrow\pi^*$ transitions, respectively. These bands were not significantly affected by chelating. The third band in the spectra of the ligand (370 nm) is assigned to $n\rightarrow\pi^*$ transition. This band is shifted to a longer wave length (18 nm) along with increasing in its intensity. This shift may be attributed to the donation of the lone pairs of the nitrogen atoms of the Schiff base to the metal ion (N→M) [22–32]. The spectra of copper(II) complex show two bands in the visible region at about 565 and 426 nm and they are assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. The observed magnetic moment value of this complex is 1.84 B.M. These electronic bands and paramagnetism value suggest also a square-planar geometry around the Cu(II) ion [33]. The electronic spectra of the complex [Cu($(OH)_2$-salophen)] and [Cu($(OH)_2$-salophen)]@MWNTs have been measured (Fig. 2). These two bands appeared at *ca*. 562 and 423 nm for [Cu($(OH)_2$-salophen)]@MWNTs (Fig. 2). The shifting of d↔d band to the higher energy region clearly demonstrates that the in-plane ligand field around the metal ion becomes stronger upon immobilization of the complex on MWNT matrix. The results are attributed to the electronic properties of the substituent group and are supported by similar observations with copper(II) Schiff-base complexes [34].

TGA analysis was carried out on the acylated MWNTs to investigate the content of [Cu($(OH)_2$-salophen)] grafted onto the MWNT-COOH surface. Fig. 3 shows the TGA curves of ([Cu($(OH)_2$-salophen)]@MWNTs, MWNT-COOH and [Cu($(OH)_2$-salophen)] samples. It is clear that a small weight loss of 3.28% appears in Fig. 3, which is ascribed to the decomposition of the carboxyl groups in the MWNT-COOH. On the other hand, Fig. 3 is the TGA curve for the as-prepared MWNT Schiff base complexes, [Cu($(OH)_2$-salophen)]@MWNTs, presenting several weight loss at the temperature range of 125–700 ˚C. According to the Fig. 3 decomposition [Cu($(OH)_2$-salophen)] starts above 280 ˚C. The significant weight loss of at 280–700 ˚C is due to the surface

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grown salophen groups. Another weight loss at below 200 ˚C corresponds to the loss of humidity. No further weight loss can be observed over 750 ˚C.

The X-ray diffraction patterns of MWNTs contained copper(II) complex which are similar to MWNTs. This indicates that the crystallinity and morphology of MWNTs have been preserved during grafted. Modified MWNTs still had the same cylinder wall structure as raw MWNTs and inter-planner spacing of all samples remained the same [35].

The Schiff base ligand exhibits a broad band in the 2455–2756 $cm^{-1}$ due to extensive hydrogen bonding between phenolic hydrogen and nitrogen of azomethine group. Absence of this band in the spectra of covalently anchored complex indicates the destruction of the hydrogen bond followed by the coordination of phenolic oxygen after deprotonation. The sharp band appearing at 1638 $cm^{-1}$ due to ν(C=N) (azomethine), shifts to lower wave number and appears at 1619 $cm^{-1}$. This indicates the involvement of azomethine nitrogen in coordination. Neat complex [Cu(OH)$_2$-salophen)] exhibits a sharp band at 1619 $cm^{-1}$ due to ν(C=N) stretch, while on covalently anchored copper(II) complex location of bands due to ν(C=N) structure shifts to higher wave number and appears at 1623 $cm^{-1}$. The intensity of the peaks on covalently anchored complex is, though, weak due to their low concentration on MWNTs, the spectra of covalently anchored as well as their neat complex show essentially similar bands. FT-IR spectra can display that the [Cu((OH)$_2$-salophen)] complex was chemically attached to the functionalized MWNT-COCl. Fig. 4 presents the IR spectra of Schiff base, [Cu((OH)$_2$-salophen)], MWNT, MWNT-COOH, MWNT-COCl and [Cu((OH)$_2$-salophen)]@MWNTs. A weak peak at 1740 $cm^{-1}$ is attributable to a carbonyl (C=O) stretching mode of carboxylic acid groups in pristine MWNT-COOH, and a peak at 3400 $cm^{-1}$ is ascribed to –OH stretching vibration, indicating that –COOH groups are present at the ends of the MWNTs, which help in the functionalization of the MWNT-COOH. The sharp peak at A: 1519 $cm^{-1}$ in the IR spectrum (Fig. 4) is from the stretch mode of the aromatic carbon–carbon bond in raw MWNTs. After the reaction of the shortened MWNTs with $SOCl_2$, the IR spectrum (Fig. 4)

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showed well defined bands at about 1724, 1221, 615 $cm^{-1}$ which are clearly related to the formation of the group –COCl on the ends and side-wall of MWNTs. The near-IR region of the purified MWNTs was preserved upon functionalization in ClCO@MWNTs and [Cu($(OH)_2$-salophen)]@MWNTs, showing that the multi-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 MWNTs and 100 μmol $g^{-1}$ of commercial [(bis(salicylidene)phenylene-1,2-diimine)copper(II)]; [Cu($(OH)_2$-salophen)]; (no covalent linkage between the complex and MWNTs) was submitted to the extraction procedure with $CHCl_3$ revealed that all the complexes can be recovered essentially by our workup procedure.

The TEM images of raw MWNTs and [Cu($(OH)_2$-salophen)]@MWNTs have been shown in Fig. 5. It can be seen from the Fig. 5 that the tips of the raw MWNTs were closed, which is a feature of unmodified MWNTs. After acid-oxidation, however, the end tips of many MWNTs were opened, indicating the breaking of the C–C bond along the graphene layers of the co-axial tubes and thus allowing for the generation of functional groups at the open ends. Fig. 5 shows the surface morphology of the Schiff base complex-functionalized MWNTs. The layered structure of the MWNTs remained largely intact, which indicates that there was no real damage to the MWNTs during the functionalization process. It is also observed from these figures that MWNTs retained their external average diameter of 10–15 nm even after their oxidation and functionalization.

### *3.2. Catalytic activity*

Transition metal Schiff base complex binding on modified MWNTs enhanced chemical and thermal stability in much common solvent. The homogeneous suspension of MWNTs-Schiff base complex in ethanol without any surfactant can be formed by stirring and remains very stable for at least 3 months at room temperature (no breakdown was detected even after high-speed centrifugation or high temperature treatment), while pristine MWNTs are easy to breakdown after high-speed centrifugation or high temperature treatment. The enhanced chemical and thermal stability of MWNTs-Schiff-base complexes might result from covalent interaction

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between MWNTs and Schiff-base complex. Since Schiff-base complexes were covalently bonded to MWNTs, the strong and super-stable covalent bond interaction between the Schiff-base complexes and MWNTs were responsible for the thermal stability of MWNTs-Schiff-base complexes materials.

Comparing between “neat complex” and covalently anchored copper(II) Schiff base complex on MWNTs; [Cu((OH)$_2$-salophen)]@MWNTs; as catalyst evidence that “neat complex” gave lower conversion of styrene than its corresponding supported catalyst. For homogeneously catalyses reactions, the termination of catalytic cycle may occur because of two factors, due to the formation of Cu–O–Cu species, which has poor catalytic activity, or due to the oxidative degradation of metal complexes (Table 1). This was confirmed by taking the IR spectra of the solid after catalytic reaction. The IR spectra of these solids are very different from that of the IR spectra of the parent compound. To improve the stability of the metal complex under the reaction conditions we have heterogenised the complexes by preventing the catalytic species from dimerizing or aggregation, and to tune the selectivity of the reaction using the walls of the MWNTs of the solid through steric effects. The Schiff base copper(II) complex; [Cu((OH)$_2$-salophen)]; exhibited good activity in the aziridination of styrene (Table 1). Blank reactions performed over MWNTs under identical conditions show only negligible conversion indicating that MWNTs is inactive for aziridination. Furthermore, PhI=NTs alone is unable to aziridination the substrates in the absence of any catalyst.

The heterogeneity of the [Cu((OH)$_2$-salophen)]@MWNTs was evaluated by following studies. The [Cu((OH)$_2$-salen)]-MWNTs was removed after the reaction by centrifugation, fresh aliquots of reactants were added to the centrifuged solvent and the reaction was monitored. The formation of the desired product was not observed indicating no leaching of the catalyst. Furthermore, the recovered heterogeneous catalysts were reused for three cycles with consistent activity in each of the aziridination and cyclopropanation reactions. The results have been presented in Table 1. The catalyst displayed good recyclability. A small decrease in activity is attributed to blocking of some of the active sites of the catalyst by residual organics. The ICP-AES analysis

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of the centrifuge after the fourth cycle shows 0.01% leaching of copper. The copper content was found to be almost same in the fresh and used catalyst after the 3rd cycle as shown by ICP-AES analysis. These studies demonstrate that the copper bounded to MWNTs during the reaction is active and the reaction proceeds on the heterogeneous surface

We have carried out aziridination of styrene using different nitrene donors such as chloramine-T, bromamine-T and PhI = NTs and the leaching of the copper for these nitrene donors were determined using an AAS. The results have been summarized in Table 1. The results confirmed that PhI=NTs is the preferred nitrene donor for our catalytic system.

A variety of alkenes were examined for this [Cu((OH)$_2$-salophen)]@MWNTs catalyzed aziridination using PhI=NTs. Under the standardized conditions ($CH_3CN$, 5.6 mol% of grafted catalyst, 1 equiv. of PhI=NTs, 5 equiv. of olefin, 25 °C), good yields of aziridines were obtained with both aromatic and aliphatic olefins. The results have been summarized in Table 2. PhI=NTs, like its oxygen analogue PhI=O, is insoluble in a variety of solvents, including $CH_3CN$, dissolution of this reagent in the reaction indicates the completion of the reaction. It is clear from Table 2 that the catalyst gives the best results with phenyl substituted alkenes and moderate to good yields with simple olefins like *trans*-2-octene and 1-octene (Table 2). All aliphatic olefins afforded good yields of aziridines without allylic insertion. The reaction of PhI=NTs with norbornene (Table 2) occurs from the less hindered *exo* face of the bicyclic nucleus to provide the *exo* adduct in high yield and sterically hindered olefins like *trans*-stilbene (Table 2) afforded the corresponding aziridines in good yields.

The present covalently anchored catalyst is more active than its homogeneous analogue, homogeneous or a heterogeneous copper catalyst [12-16]. It is noteworthy that in earlier studies in the homogeneously catalyzed reaction, the yield of aziridine decreased to 37% when the molar ratio of styrene: PhI=NTs was 1:1, due to the competing breakdown of the PhI=NTs reagent to yield toluene-*p*-sulfonamide, whereas with our catalyst the

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yield is 94.9% [36-39]. This is a particularly important observation because this procedure can be applied to the aziridination of expensive alkenes.

## 4. Conclusion

The MWNTs covalently bonded by copper(II) Schiff-base complex were successfully obtained through the methods of chemical modification. The “neat” and MWNT covalently anchored copper(II) Schiff-base complex exhibit efficient catalytic activity in the aziridination of alkenes using PhI=NTs as the nitrene source. The solid supported Schiff base copper catalyst; [Cu($(OH)_2$-salophen)]@MWNTs; exhibits enhanced conversion and selectivity in the aziridination reaction. These supported systems offer structural integrity by having a uniform distribution of the metal complex on the surface structure of the support. The MWNT framework keeps the guest complexes dispersed and prevents their dimerization leading to the retention of catalytic activity. This complex is stable and do not leach during the catalytic reaction as it has been confirmed by testing the filtrate for the corresponding metal ion and thus this suggests their heterogeneous nature. Comparable IR spectral patterns of fresh and used covalently anchored catalyst suggest that these can be used further for catalytic study.

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**Figures captions**:

Fig. 1. Illustration grafting of copper (II) schiff base complex on functionalized MWNTs.

Fig. 2. UV-Vis spectra of the (a) raw MWNTs, (b) [Cu((OH)$_2$-salophen)] and (c) [Cu((OH)$_2$-salophen)]@MWNTs.

Fig. 3. TGA curve of the (a) MWNT-COOH, (b) [Cu((OH)$_2$-salophen)] and (c) [Cu((OH)$_2$-salophen)]@MWNTs.

Fig. 4. FT-IR spectrum of (a) MWNT-COOH, (b) MWNT-COCl, (c) [Cu((OH)$_2$-salophen)]@MWNT and (d) [Cu((OH)$_2$-salophen)].

Fig. 5. TEM Images of (a) pristine MWNTs and (b) [Cu((OH)$_2$-salophen)]@MWNT.

Table 1. [Cu((OH)$_2$-salophen)]@MWNTs-catalyzed aziridination of styrene (Reaction conditions: solvent, $CH_3CN$; 5.6 mol% of grafted catalyst, temperature, 25 °C)

| Catalyst | Time (h) | Alkene : PhI=NTs molar ratio | Yield (%) |
|---|---|---|---|
| [Cu((OH)$_2$-salophen)] | 1 | 5:1 | 58.3 |
| [Cu((OH)$_2$-salophen)]@MWNTs | 1 | 5:1 | 94.9 |
| [Cu((OH)$_2$-salophen)]@MWNTs$^a$ | 1 | 5:1 | 93.1 |
| [Cu((OH)$_2$-salophen)]@MWNTs$^b$ | 1 | 5:1 | 92.0 |
| [Cu((OH)$_2$-salophen)]@MWNTs$^c$ | 1 | 5:1 | 90.6 |
| [Cu((OH)$_2$-salophen)]@MWNTs | 1 | 4:1 | 90.3 |
| [Cu((OH)$_2$-salophen)]@MWNTs | 1 | 3:1 | 88.5 |
| [Cu((OH)$_2$-salophen)]@MWNTs | 1 | 2:1 | 85.4 |
| [Cu((OH)$_2$-salophen)]@MWNTs | 1 | 1:1 | 83.2 |

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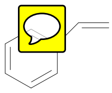
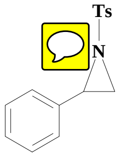
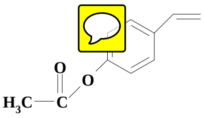
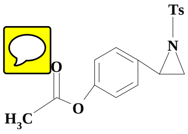
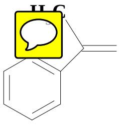
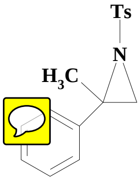
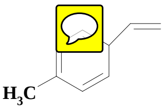
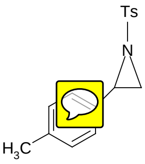
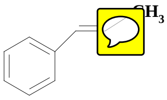
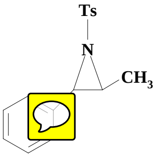
| | | | |
|---|---|---|---|
| [Cu((OH)$_2$-salophen)]@MWNTs[d] | 6 | 5:1 | 40.3 |
| [Cu((OH)$_2$-salophen)]@MWNTs[e] | 6 | 5:1 | 51.4 |
| MC-Cu(acac)$_2$ | 1 | 5:1 | 92.0 |
| Cu(II)HY[g] | 5 | 5:1 | 81.0 |
| Cu(II)HY + bis(oxazoline)[h] | 3 | 5:1 | 78.0 |
| Polymer anchored Mn-complex[i] | 1 | 5:1 | 42.0 |
| Polymer anchored Fe-complex[i] | 1 | 5:1 | 57.0 |

[a] First reuse.
[b] Second reuse.
[c] Third reuse.
[d] chloramine-T as nitrene donor.
[e] bromamine-T as nitrene donor.
[f] Microencapsulated copper(II) acetylacetonate = [MC-Cu(acac)$_2$] [37]
[g] copper-exchanged zeolite Y (CuHY) as catalysts [38].
[h] Copper-exchanged zeolite Y (CuHY) modified with a bis(oxazoline) as catalyst [38].
[i] Catalytic aziridination of olefins with Mn and Fe polymer catalysts [39].

Table 2. Different alkenes were examined for the [Cu((OH)$_2$-salophen)]@MWNTs catalyzed aziridination using PhI=NTs.

| Alkene | Product | Time (h) | Yield (%) |
|---|---|---|---|
|  |  | 1 | 94.5 |
|  |  | 4 | 77.3 |
|  |  | 1 | 84 |
|  |  | 1 | 87 |
|  |  | 3 | 82 |

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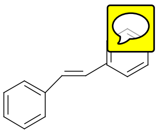
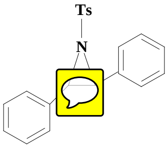
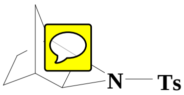
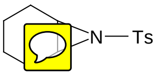
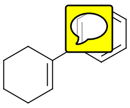
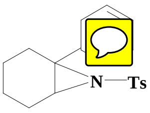
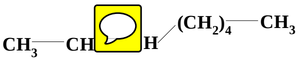
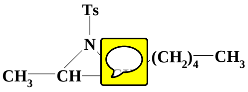
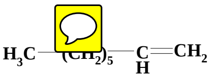
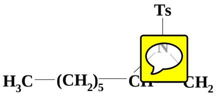
|  |  | 2 | 81 |
|  |  | 2 | 90 |
|  |  | 3 | 51 |
|  |  | 3 | 68 |
|  |  | 5 | 35 |
|  |  | 8 | 30 |

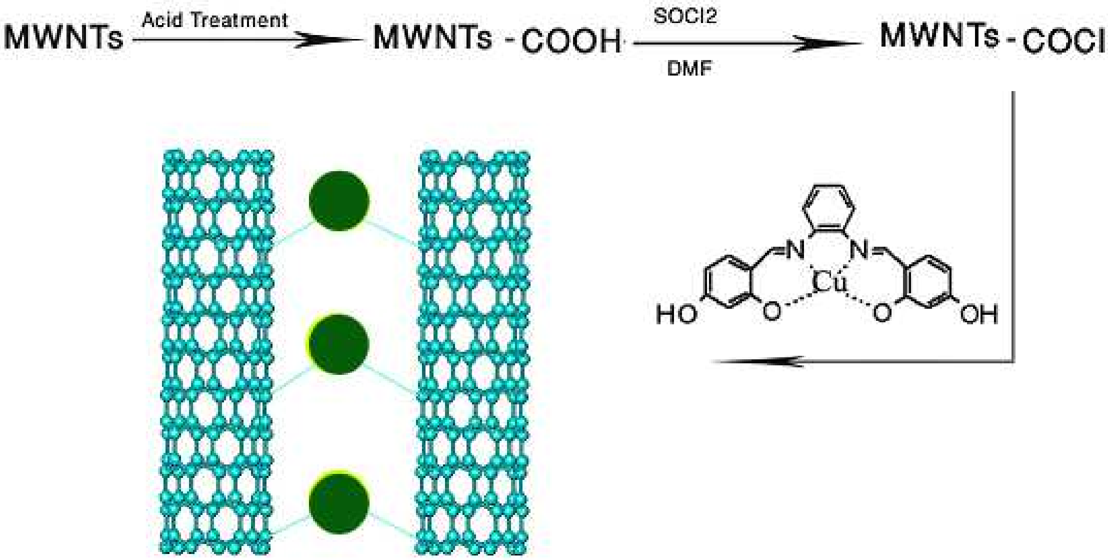


Fig. 1. Illustration grafting of copper (II) schiff base complex on functionalized MWNTs

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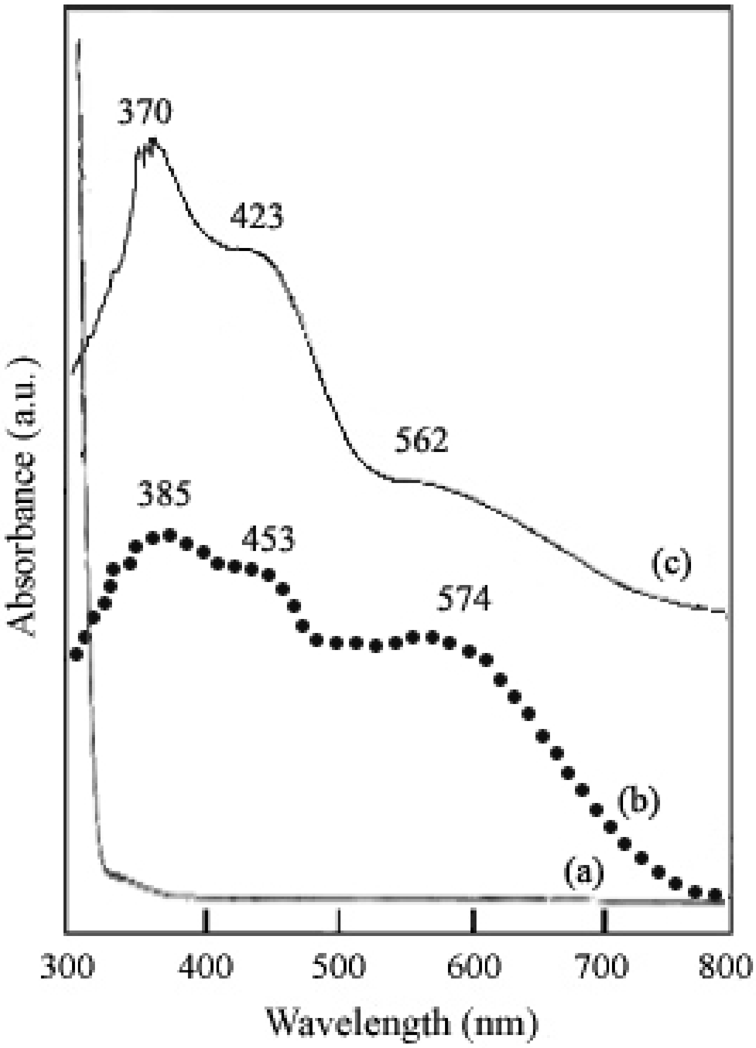

Fig. 2. UV-Vis spectra of the (a) raw MWNTs, (b) [Cu((OH)$_2$-salophen)] and (c) [Cu((OH)$_2$-salophen)]@MWNTs.

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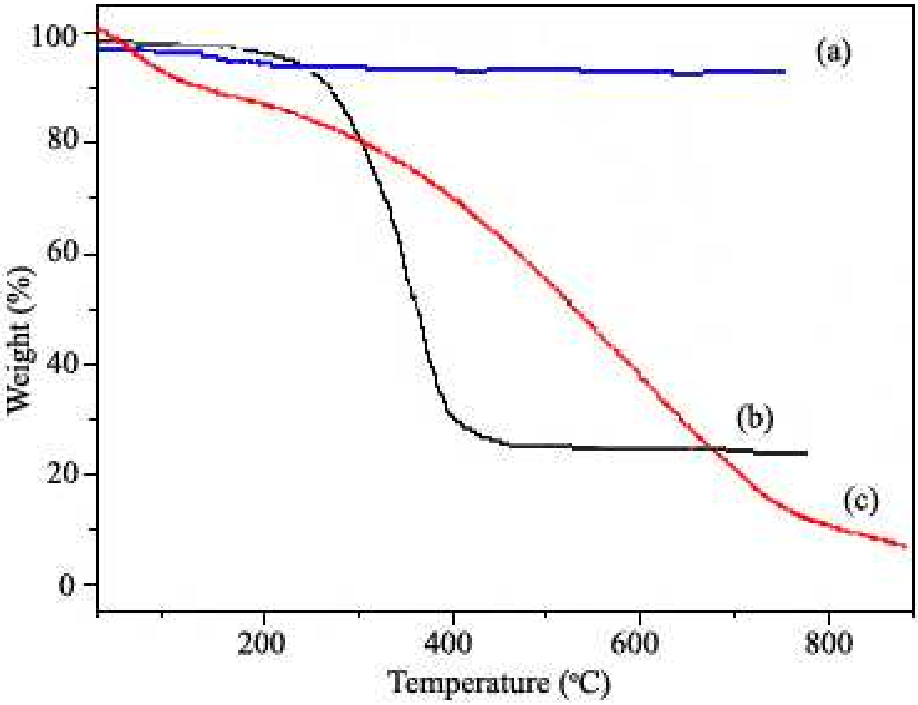

Fig. 3. TGA curve of the (a) MWNT-COOH, (b) [Cu((OH)$_2$-salophen)] and (c) [Cu((OH)$_2$-salophen)]@MWNTs.

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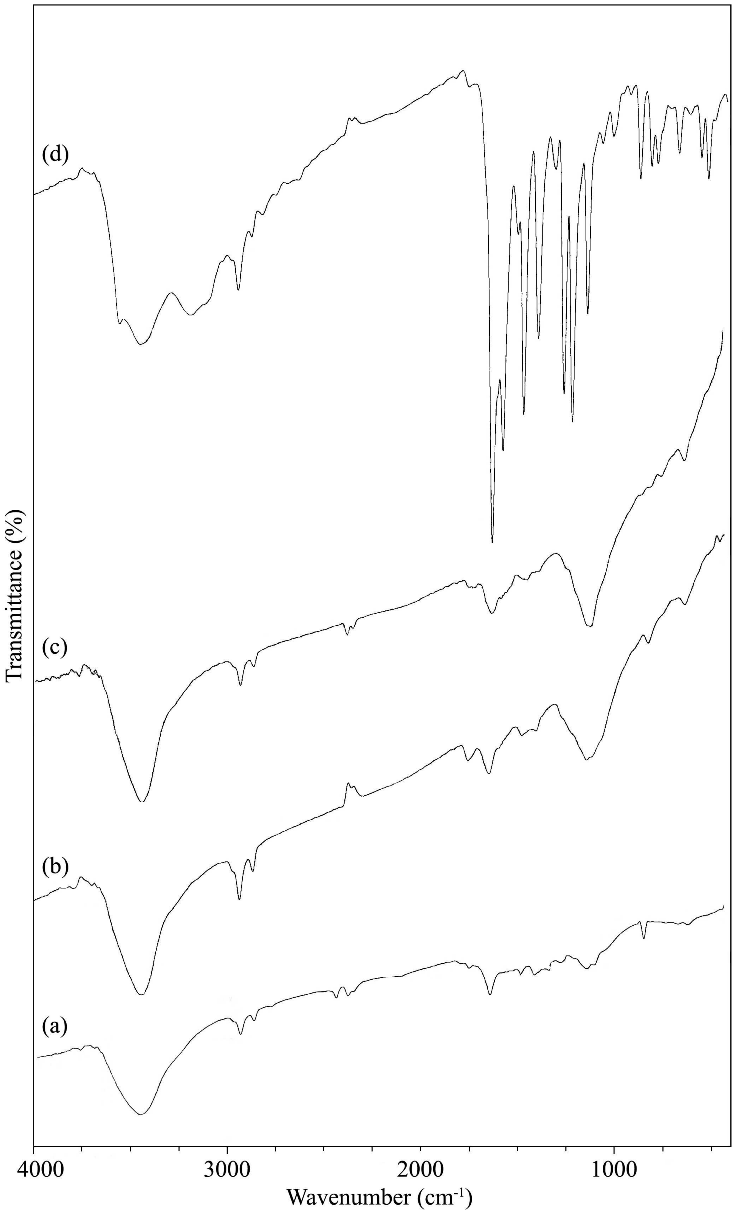

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