

New hybrid nanomaterial derived from immobilization of a molybdenum complex on the surface of multi-walled carbon nanotubes

M. Masteri-Farahani^{*}, and S. Abednatanzi

Department of Chemistry, Faculty of Sciences, Kharazmi University, Tehran, Islamic Republic of Iran

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Abstract

In this work, we report a new well dispersed molybdenum complex attached through the mediation of aminopropylsilyl groups on the surface of multi-walled carbon nanotubes (MWCNTs). The prepared hybrid nanomaterial was characterized with different physicochemical methods such as Fourier transform infrared and atomic absorption spectroscopies, transmission electron microscopy, energy-dispersive X-ray and nitrogen adsorption-desorption analyses. Nitrogen adsorption-desorption analysis revealed that the textural characteristics of the support were preserved during the grafting experiments despite sequential reduction in surface area. Elemental analysis showed the presence of 0.1 mmol molybdenum per gram of the catalyst. The prepared hybrid nanomaterial showed good performance and stability in the catalytic epoxidation of olefins under mild reaction conditions.

Keywords: Carbon nanotube; Hybrid nanomaterial; Molybdenum; Epoxidation.

Introduction

The field of organic-inorganic hybrid materials is expanding because of their important role in the development of advanced functional materials [1-8]. In this regard, design and construction of organic-inorganic hybrid nanomaterials with tunable physical properties have attracted extensive research interest in materials chemistry. Organic-inorganic hybrid materials can be grossly divided into two major classes: Class I in which only weak bonds exist and class II in which the building blocks are connected by covalent bonds.

Hybrid materials of multi-walled carbon nanotubes

(MWCNTs) take advantage of the properties of the MWCNTs support, as well as of the immobilized surface groups [5,9]. The advantages of MWCNTs such as their high aspect ratio (>1000), excellent mechanical, electrical, and optical properties support MWCNTs as an ideal building block in hybrid materials. On the other hand, hybridization results in materials with higher specific surface areas that allow the use of less material, reducing cost and toxicity.

In recent years, various methods for functionalizing the surface of multi-walled carbon nanotubes with different groups have been investigated as the surface modification permits tailoring of the surface properties

^{*} Corresponding author: Tel: +98 263 4551023; Fax: +98 263 4551023; Email: mfarahany@yahoo.com

for numerous potential applications including catalysis [10-14], enzyme immobilization [15], environmental pollution management [16], chemical sensing [17,18], and electrochemistry [19].

In general, MWCNTs can be functionalized by (a) covalent attachment of chemical groups through bonding to the π -conjugated skeleton of the MWCNTs or (b) noncovalent adsorption of various functional molecules. The most common way for covalent functionalization involves the incorporation of carbonyl and carboxyl groups via an oxidation treatment with a mixture of $\text{HNO}_3/\text{H}_2\text{SO}_4$. Carboxyl groups may then be reacted with thionyl chloride to give reactive acyl groups which can be used for next attachment of different organic groups and desired species.

Soluble transition metal complexes catalyze various important chemical reactions including C-C bond formation, oxidation reactions, etc [20-22]. However, separation of these homogeneous catalysts from reaction mixture poses a considerable challenge. Immobilization of these complexes to a solid support which is easy to separate and retains the activity of the catalyst would have numerous benefits in terms of process design and environmental factors. Ideas like this have resulted in the great interest in the area of hybrid materials in recent years [4,6].

Although great efforts have been made to immobilize molybdenum complexes on the surface of various supports such as functionalized polymers [23,24], zeolites [25,26], mesoporous molecular sieves [27-31] and silica coated magnetite nanoparticles [32,33], there are little reports in the literature regarding immobilization of molybdenum complexes on the surface of multi walled carbon nanotubes (MWCNTs) [11,34].

Our current interest in the preparation of hybrid materials with potential applications in catalysis of organic reactions [30-33,35] led us to investigate the safe preparation and characterization of MWCNTs hybrid nanomaterial containing molybdenum complex which belongs to the type II of organic-inorganic hybrid materials. Previous works on the functionalization of MWCNTs have the disadvantage of utilizing SOCl_2 which is a toxic and hazardous reagent. However, our proposed method does not involve the requirement of using such hazardous and toxic reagent and thus is environmentally friendly. The prepared hybrid nanomaterial acts as an active and selective heterogeneous catalyst for the epoxidation of olefins and easily recovered at the end of reaction.

Materials and Methods

MWCNTs were obtained from Plasma Chem GmbH (Berlin, Germany). All other chemicals were purchased from Merck chemical company and used without further purification. $\text{MoO}_2(\text{acac})_2$ (acac = acetylacetonate) was prepared according to literature method [36].

Elemental analyses were performed by a scanning electron microscope with EDX detector INCA Penta FETx3 and *VARIAN VISTA-MPX ICP-AES atomic absorption spectrometer*. Fourier transform infrared spectra were recorded using Perkin-Elmer Spectrum RXI FT-IR spectrometer, using pellets of the materials diluted with KBr. The transmission electron micrographs of the nanomaterials were recorded using a Philips EM 208 S instrument with an accelerating voltage of 100 kV. *Nitrogen sorption studies were performed at liquid nitrogen temperature (-196°C) using Quantachrome Nova 2200, Version 7.11 Analyzer. Before the adsorption experiments the samples were outgassed under vacuum at 120°C.* All calculations were performed using the program of Quantachrome Nova 2200e surface area analyzer.

Preparation of molybdenum complex-MWCNTs hybrid nanomaterial, Mo-AmpMWCNTs

The tethering approach for functionalization of MWCNTs and proposed structure of the Mo-AmpMWCNTs hybrid nanomaterial is schematically shown in Figure 1.

In order to generate reactive functional groups, the MWCNTs were refluxed with a 5 mol.dm^{-3} nitric acid solution for 24 h, washed with deionized water until pH 6-7 and then dried in vacuum oven at 110°C overnight. The resulting material was further treated with sodium borohydride in methanol to reduce the carbonyl groups and increase the OH surface groups. Aminopropylsilyl modified MWCNTs (AmpMWCNTs) were prepared by the reaction of 2 mmol γ -aminopropyltriethoxy silane with OH surface groups of the resulted MWCNTs in dry toluene for 24 h. Finally, a methanolic solution of $\text{MoO}_2(\text{acac})_2$ and AmpMWCNTs was refluxed for 24 h to give Mo-AmpMWCNTs catalyst through Schiff base condensation of acetylacetonate carbonyl groups with amine groups of AmpMWCNTs. The solution was filtered and the precipitate was Soxhlet extracted with dichloromethane to remove any residues, and then dried in vacuum oven at 110°C overnight.

Catalytic epoxidation of olefins in the presence of Mo-AmpMWCNTs hybrid nanomaterial

Epoxidation of olefins was carried out in a 25 ml round bottomed flask equipped with a condenser and a

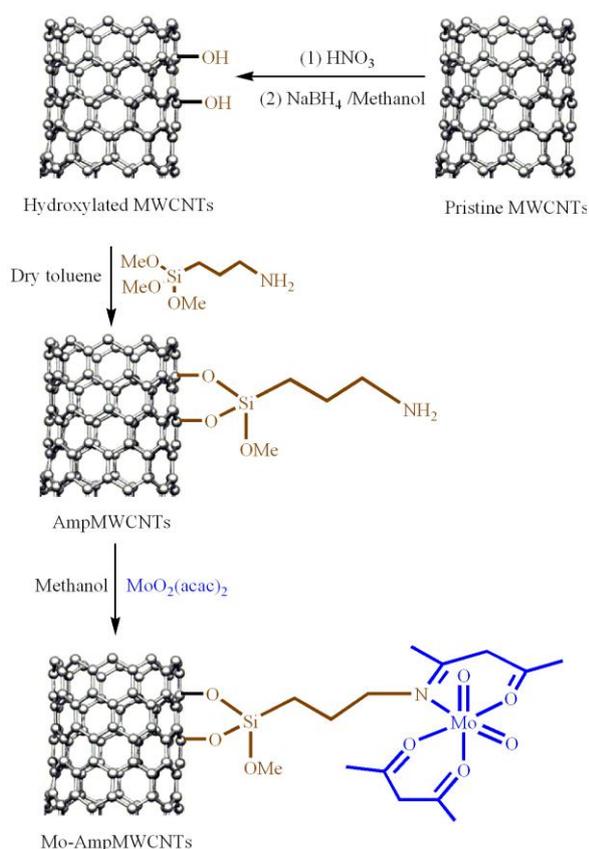


Figure 1. The sequence of events in the preparation of Mo-AmpMWCNTs hybrid nanomaterial.

magnetic stirrer. In a typical procedure, to a mixture of

catalyst (100 mg) and olefin (8 mmol) in chloroform (10 ml) was added oxidant (TBHP, 80% in di-tertiary butyl peroxide, 14.4 mmol) under nitrogen atmosphere and the mixture was refluxed for appropriate time. Samples were withdrawn periodically and after dilution with chloroform and cooling were analyzed using a gas chromatograph (HP, Agilent 6890N) equipped with a capillary column (HP-5) and a FID detector. Products were quantified using isooctane (1 g, 8.75 mmol) as internal standard.

Results and Discussion

Characterization of the Mo-AmpMWCNTs hybrid nanomaterial

In order to confirm the modification of the surface of MWCNTs, the FT-IR spectra of the pristine MWCNTs, AmpMWCNTs, and Mo-AmpMWCNTs materials were obtained and have been shown in Figure 2. The FT-IR spectrum of AmpMWCNTs (Figure 2b) showed the characteristic band of the propyl groups ($\nu_{\text{C-H}}$) at 2924 cm^{-1} as well as a broad band about 1000-1100 cm^{-1} assigned to Si-O stretching vibrations which were not present in pristine MWCNTs. The presence of these bands suggested that during the anchoring of aminopropyltrimethoxy silane (APTS), a condensation reaction occurred between the OH surface groups of the oxidized MWCNTs and methoxy groups of APTS to form the stable covalent Si-O-C linkage, leading to the attachment of aminopropyl groups on the surface of MWCNTs. On the other hand, the observation of two adjacent bands at 900 and 950 cm^{-1} in the FT-IR

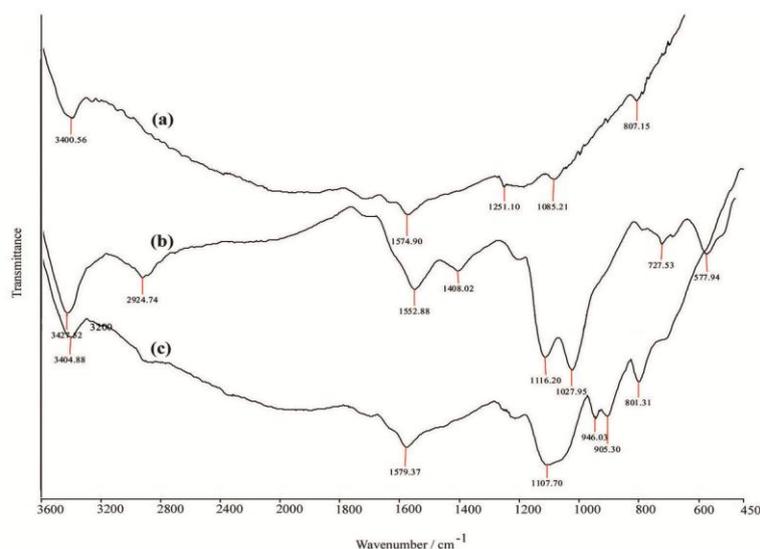


Figure 2. FT-IR spectra of (a) pristine MWCNTs, (b) AmpMWCNTs, and (c) Mo-AmpMWCNTs hybrid nanomaterial.

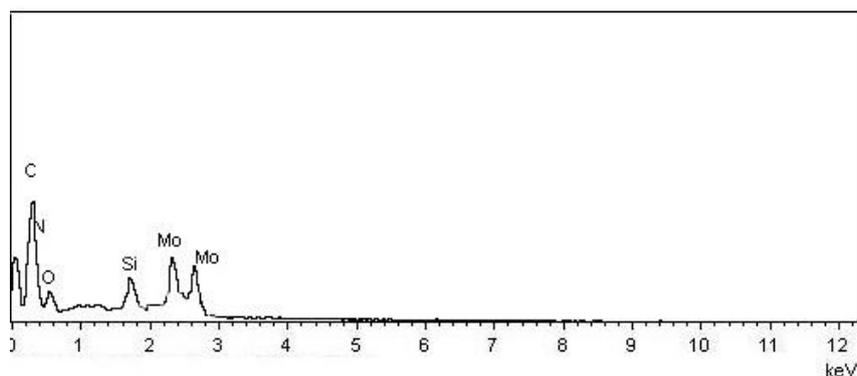


Figure 3. EDX spectrum of the prepared Mo-AmpMWCNTs hybrid nanomaterial.

spectrum of Mo-AmpMWCNTs (Figure 2c) proved the existence of cis-MoO₂ groups [37] and successful tethering of the molybdenum complex to the surface of MWCNTs.

The surface chemical composition of the prepared hybrid nanomaterial was determined by energy

dispersive X-ray (EDX) analysis (Figure 3) which revealed the existence of 0.1 mmol.g⁻¹ molybdenum in the Mo-AmpMWCNTs.

The textural properties of the MWCNTs and Mo-AmpMWCNTs were examined by means of nitrogen sorption analysis. The adsorption-desorption isotherms of N₂ at -196°C for both nanomaterials (Figure 4) are of type II and show hysteresis loops which indicate the presence of mesoporosity in these nanomaterials. The observed porosity may be due to aggregated pores formed by interaction of isolated MWCNTs. An important feature of MWCNTs is their aggregation due to van der Waals forces into stable bundles in which the axes of individual MWCNTs are parallel to one another. Both MWCNTs and Mo-AmpMWCNTs nanomaterials show no microporosity, as calculated by t-method. Pore

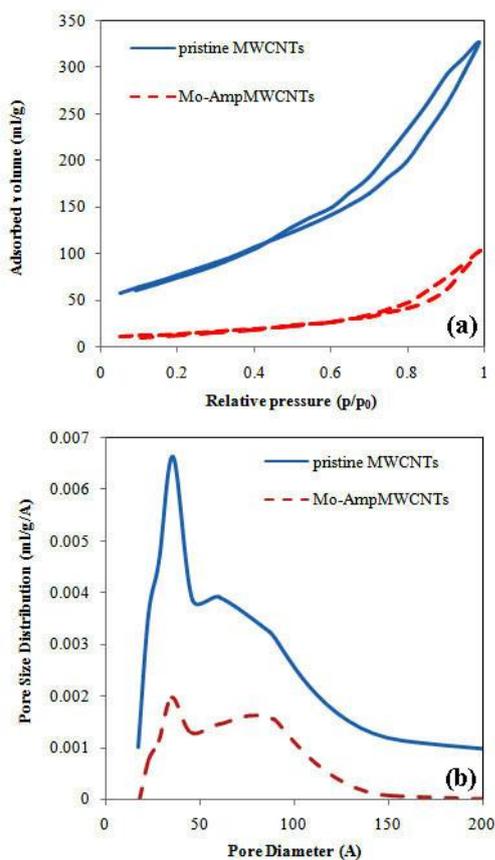


Figure 4. Nitrogen sorption isotherms of (a) pristine MWCNTs and (b) Mo-AmpMWCNTs hybrid nanomaterial.

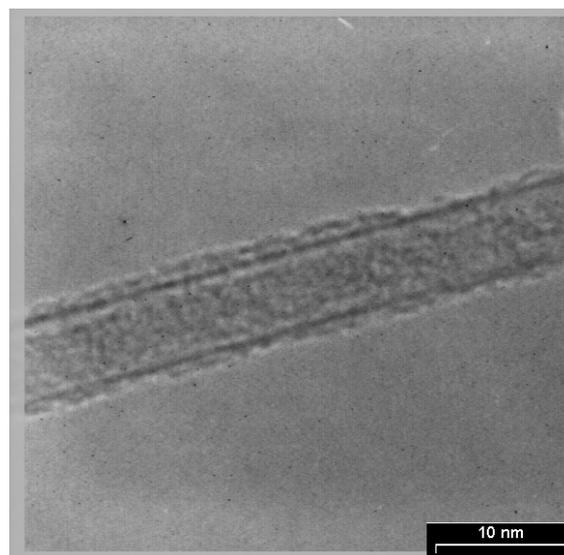


Figure 5. TEM image of the Mo-AmpMWCNTs hybrid nanomaterial.

Table 1. Texture parameters of samples taken from nitrogen sorption studies

Sample	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	V_{T} ^a ($\text{ml} \cdot \text{g}^{-1}$)	Pore diameter ^b (nm)
Pristine MWCNTs	283	0.50	3.6
Mo-AmpMWCNTs	53	0.16	3.5

^a Total pore volume at $p/p_0 = 0.98$.

^b Calculated based on the desorption isotherm branch using the BJH method.

Table 2. Results of catalytic epoxidation of some olefins with TBHP in presence of Mo-AmpMWCNTs hybrid nanomaterial.

Entry	olefin	Time (h)	Conversion (%)	Selectivity ^a (%)
1	3-Methyl-2-butene-1-ol	8	99	>99
2 ^b	3-Methyl-2-butene-1-ol(1 st)	8	97	>99
3 ^b	3-Methyl-2-butene-1-ol(2 nd)	8	98	>99
4 ^c	3-Methyl-2-butene-1-ol	8	11	51
5	Trans-2-hexene-1-ol	8	78	>99
6	1-Octene-3-ol	8	61	>99
7	Cyclooctene	8	92	>99
8	Cyclohexene	8	89	98
9	1-Hexene	8	52	>99

Reaction conditions: catalyst (100 mg), olefin (8 mmol), TBHP (1.6 ml, 14.4 mmol), refluxing chloroform (10 ml).

^a Selectivity toward the formation of corresponding epoxide.

^b Catalytic test with first and second recovered catalyst.

^c Reaction was carried out without catalyst.

size distributions of MWCNTs and Mo-AmpMWCNTs are obtained from the desorption branch of the isotherms using the Barrett, Joyner and Halenda (BJH) method [38] and are shown in Figure 4. Both materials show similar bimodal pore size distributions with maxima indicating the presence of mesopores.

On the basis of the nitrogen sorption studies of the Mo-AmpMWCNTs hybrid nanomaterial we can reveal the location of the molybdenum complex on the surface of MWCNTs. As can be seen in Figure 4, there is no significant difference in the adsorption type of N_2 in the Mo-AmpMWCNTs with respect to the original MWCNTs support and the final nanomaterial shows similar textural properties with the support. It means that the molybdenum complex is introduced to the external surface of MWCNTs rather than inside the channels. If the complex is located inside the channels, the pore blockage results in significant difference between sorption isotherms of both nanomaterials.

The texture parameters of MWCNTs and Mo-AmpMWCNTs are collected in Table 1. Determination of total surface area is commonly based on the BET theory of multilayer adsorption with the relative pressure (p/p_0) in range of 0.05–0.30. In comparison with pristine MWCNTs, the Mo-AmpMWCNTs shows a decrease of specific surface area due to incorporation of molybdenum complex on the external surface of MWCNTs.

The total pore volume is directly calculated from the volume of nitrogen held at the highest relative pressure ($p/p_0 = 0.98$), using $0.8081 \text{ g} \cdot \text{cm}^{-3}$ for the density of N_2 in its normal liquid state. As can be seen, the total pore

volume is decreased with immobilization of molybdenum complex on the surface of MWCNTs.

Figure 5 shows a typical TEM image of Mo-AmpMWCNTs in which a nanotube can be observed. This image reveals that the walls of the nanotubes are constructed by layers of graphite-like platelets and the inner and outer diameters of the nanotube is 4 and 7 nm, respectively.

Catalytic epoxidation of olefins in the presence of Mo-AmpMWCNTs hybrid nanomaterial

The catalytic activity of the Mo-AmpMWCNTs hybrid nanomaterial was then evaluated in the epoxidation of some olefins and allyl alcohols with TBHP and the results are shown in Table 2. We have included the results of epoxidation in the absence of the catalyst in order to clear up the catalytic effect of the prepared Mo-AmpMWCNTs. It is evident that the Mo-AmpMWCNTs acts as an active and selective catalyst in the epoxidation of olefins using tert-butylhydroperoxide. It is worth noting that the Mo-AmpMWCNTs nanomaterial has comparable catalytic activity to our previous heterogeneous catalysts anchored onto the large surface area MCM-41, using similar functionalization method [30]. So, it can be concluded that increasing the hydrophobic nature of the support increases the activity and selectivity toward the formation of epoxides. Furthermore, diffusion limitations can be avoided, as all of the molybdenum active sites are located on the external surface area of MWCNTs.

The recyclability of Mo-AmpMWCNTs in the

catalytic epoxidation was then examined using 3-methyl-2-butene-1-ol as the substrate. After each run, the catalyst was collected by centrifugation and after washing with dichloromethane, the recovered catalyst was used directly for the next run. The recovered Mo-AmpMWCNTs maintained similar activity after 2 cycles. Elemental analysis indicated no decrease of molybdenum content of the catalyst. Altogether, these results suggest that Mo-AmpMWCNTs is quite stable under the reaction conditions.

In summary, we have developed safely prepared covalently attached cis-dioxomolybdenum complex on the surface of MWCNTs as a new hybrid nanomaterial.

Chemical oxidation of MWCNTs followed by reduction with NaBH_4 resulted in hydroxylated MWCNTs. Next modifications with aminopropyltriethoxy silane and $\text{MoO}_2(\text{acac})_2$ produced Mo-AmpMWCNTs hybrid nanomaterial. Physicochemical characterization of the product confirmed the formation of covalent bonds and successful tethering of molybdenum complex to the surface of MWCNTs. The prepared hybrid nanomaterial was found to be efficient as a heterogeneous catalyst in the selective epoxidation of olefins with TBHP as oxidant.

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