



Molybdenum hexacarbonyl supported on functionalized multi-wall carbon nanotubes: Efficient and highly reusable catalysts for epoxidation of alkenes with *tert*-butyl hydroperoxide

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ARTICLE INFO

Article history:

Received 21 February 2010

Received in revised form

24 April 2010

Accepted 6 May 2010

Available online 26 May 2010

Keywords:

Multi-wall carbon nanotubes

Molybdenum hexacarbonyl

Heterogeneous catalyst

Epoxidation

tert-Butylhydroperoxide

ABSTRACT

In the present work, highly efficient epoxidation of alkenes catalyzed by Mo(CO)₆ supported on amines modified multi-wall carbon nanotubes, MWCNTs, is reported. The prepared catalysts were characterized by elemental analysis, scanning electron microscopy, FT-IR and diffuse reflectance UV–Vis spectroscopic methods. These new heterogenized catalysts, [Mo(CO)₆@amines-MWCNT], were used as highly efficient catalysts for epoxidation of alkenes with *tert*-BuOOH. These robust catalysts could be reused several times without loss of their catalytic activities.

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1. Introduction

Epoxidation of alkenes is of academic and industrial interest, because epoxides are one of the most widely used intermediates in organic synthesis. Epoxides undergo ring-opening reactions with a variety of reagents to produce mono- or bi-functional organic products [1–3].

Molybdenum complexes have been known as versatile and useful catalysts for the epoxidation of alkenes by organic hydroperoxides. The most important example of industrial application of molybdenum base catalysts is liquid-phase epoxidation of propylene with alkyl hydroperoxides catalyzed by homogeneous Mo(VI) compounds which is known as Halcon process. A number of soluble molybdenum complexes with different ligands have been synthesized and employed as homogeneous catalysts for epoxidation of various alkenes [4–8].

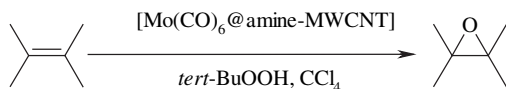
The homogeneous catalysts of transition metals are often more difficult to prepare and expensive to purchase. On the other hand, some industrial problems such as deposition on reactor wall, difficulty in recovery and separation of the catalyst from reaction products are associated with homogeneous catalysts. One way to overcome these disadvantages is immobilization of homogeneous catalysts on solid supports.

Different approaches have been used for immobilization of molybdenum complexes on various supports to obtain heterogeneous catalysts. Sherrington and coworkers have reported efficient epoxidation of alkenes with *tert*-butyl hydroperoxide catalyzed by reusable Mo(VI) supported on imidazole containing polymers [9–12]. Other organic polymers including modified polystyrenes [13–17], polyaniline [18], ion-exchange resins [19], ethylene–propylene rubber and modified poly(ethylene oxide) [20] have been used as support for immobilization of molybdenum compounds. On the other hands, several approaches have been reported for supporting of molybdenum catalysts on silica [21–25], modified MCM-41 [26–34], zeolites [35] and layered double hydroxides [36].

Recently, molybdenum complexes have been used for epoxidation of alkenes and oxidation of alcohols with hydrogen peroxide [37,38].

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Scheme 1.

Carbon nanotubes (CNTs) have attracted much attention in the synthesis, characterization, and other applications because of their unique structural, mechanical, thermal, optical and electrical properties [39–41].

Since CNTs are insoluble in the most solvents, these materials can be used as catalysts support. For example, Pt nanoparticles supported on CNTs have been used for methanol oxidation [42], palladium nanoparticles supported on CNTs for semihydrogenation of phenylacetylene [43], chiral vanadyl salen complex supported on single-wall CNTs for enantioselective cyanosilylation of aldehydes [44,45] and manganese(III) porphyrin supported on MWCNTs for epoxidation of alkenes with NaIO_4 [46].

In this paper, the preparation, characterization and investigation of catalytic activity of Mo(CO)_6 supported on amines modified multi-wall carbon nanotubes in the epoxidation of alkenes with tert-BuOOH is reported (Scheme 1).

2. Experimental

All materials were commercial reagent grade and obtained from Merck and Fluka. All alkenes were passed through a column containing active alumina to remove peroxide impurities. A 400 W Hg lamp was used for activation of metal carbonyl. FT-IR spectra were obtained as potassium bromide pellets in the range

Table 1

The specification of MWCNT-COOH used in this study.

MWCNT-COOH				
Outside diameter	Inside diameter	Length	COOH content	Specific surface area
20–30 nm	5–10 nm	30 μm	1.5%	>110 m^2/g

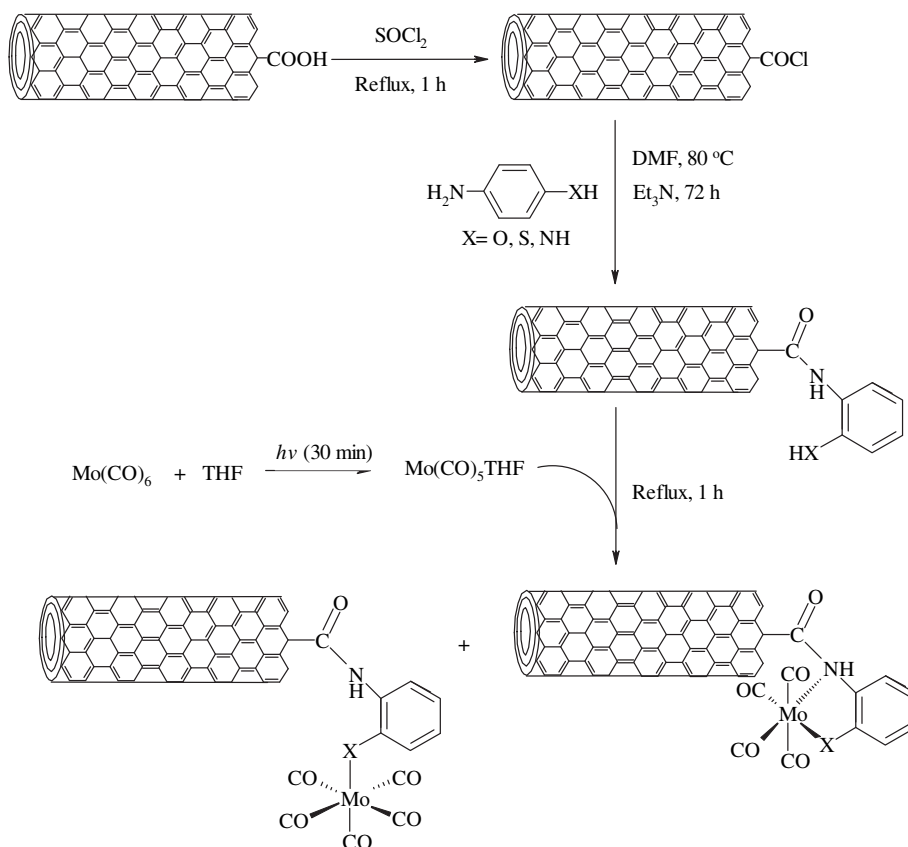
500–4000 cm^{-1} with a Bomen–Hartmann instrument. Scanning electron micrographs of the catalyst were taken on SEM Philips XL 30. ^1H NMR spectra were recorded on a Bruker-Arance AQS 400 MHz. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column peaked with silicon DC-200 or Carbowax 20 m and *n*-decane was used as internal standard. The ICP analyzes were performed on an ICP Spectrociros CCD instrument. MWCNTs (multi-wall carbon nanotubes containing –COOH groups, purity 96%) were purchased from Shenzhen NTP Factory (China).

2.1. Preparation of multi-wall carbon nanotubes supported molybdenum hexacarbonyl

2.1.1. Modification of MWCNT-COCl with amines

The carboxylic acid groups (MWCNT-COOH) in MWCNTs were converted to acid chloride (MWCNT-COCl) according to the reported procedure [46].

To a suspension of MWCNT-COCl (5 g) in DMF (50 mL), were added 1,2-diaminobenzene (DAB), 2-aminophenol (AP) or 2-aminothiophenol (ATP) (2.5 g) and triethylamine (5 mL). The mixtures were vigorously stirred at 80 °C for 72 h. After cooling the mixtures,



Scheme 2.

Table 2
Characteristics of the prepared catalysts.

Catalyst	N content (mmol/g)	Mo content (mmol/g)	C=O band (cm ⁻¹)	UV–Vis peak (nm)
[Mo(CO) ₆]	–	–	2004	230, 286
[Mo(CO) ₆ @DAB-MWCNT]	2.98	0.35	1965	231, 283
[Mo(CO) ₆ @AP-MWCNT]	1.63	0.25	2000	232, 284
[Mo(CO) ₆ @ATP-MWCNT]	1.43	0.29	1996	228, 286

the black solids were collected by filtration, washed thoroughly with CH₃CN and dried in vacuum for several hours.

2.2. Preparation of the catalysts

Mo(CO)₆ (2 g, 0.01 mmol) was dissolved in THF (60 mL) and stirred under UV irradiation for 15 min. Then, amine modified MWCNTs (2 g) was added to this solution and refluxed for 1 h. At the end of the reaction, the solution was filtered, washed thoroughly with THF and dried in vacuum.

2.3. General procedure for epoxidation of alkenes with TBHP catalyzed by prepared catalysts

In a 25 mL round bottom flask equipped with a magnetic stirrer bar, a mixture of alkene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg) and CCl₄ (6 ml) was prepared and refluxed under stirring. The reaction progress was monitored by GLC. At the end of the reaction, the reaction mixture was diluted with Et₂O (20 ml) and filtered. The catalyst was thoroughly washed with Et₂O and the combined washing and filtrates were purified on a silica gel plate to obtain the pure product.

2.4. Reusability of the catalyst

The reusability of the catalysts was studied in the repeated epoxidation reaction of cyclooctene. The reactions were carried out as described above. At the end of each reaction, the catalysts were filtered, washed thoroughly with Et₂O, dried and reused.

3. Results and discussions

3.1. Preparation and characterization of the catalysts, [Mn(CO)₆@DAB-MWCNT], [Mn(CO)₆@AP-MWCNT] and [Mn(CO)₆@ATP-MWCNT]

The specifications of multi-wall carbon nanotubes containing carboxylic acid groups, MWCNT-COOH, which was used as support, are listed in Table 1. Scheme 2 shows the preparation route of the [Mn(CO)₆@DAB-MWCNT], [Mn(CO)₆@AP-MWCNT] and [Mn(CO)₆@ATP-MWCNT]. In this scheme, the most probable modes for coordination of Mo(CO)₆ to amines modified MWCNTs are shown. First, in order to increase the reactivity of MWCNT-COOH, the carboxylic acid groups were converted to acyl chloride. Then, 1,2-diaminobenzene (DAB), 2-aminophenol (AP) or 2-aminothiophenol (ATP) was reacted with MWCNT-COCl to obtain the amine modified MWCNTs (DAB-MWCNT, AP-MWCNT and ATP-MWCNT). The [Mn(CO)₆@DAB-MWCNT], [Mn(CO)₆@AP-MWCNT] and [Mn(CO)₆@ATP-MWCNT] catalysts were prepared by the reaction of DAB-MWCNT, AP-MWCNT or ATP-MWCNT with a solution of Mo(CO)₅THF (this compound was prepared by activation of Mo(CO)₆ in THF under UV irradiation) [47]. These catalysts were characterized by elemental analysis, scanning electron microscopy, FT-IR and diffuse reflectance UV–Vis spectroscopic methods.

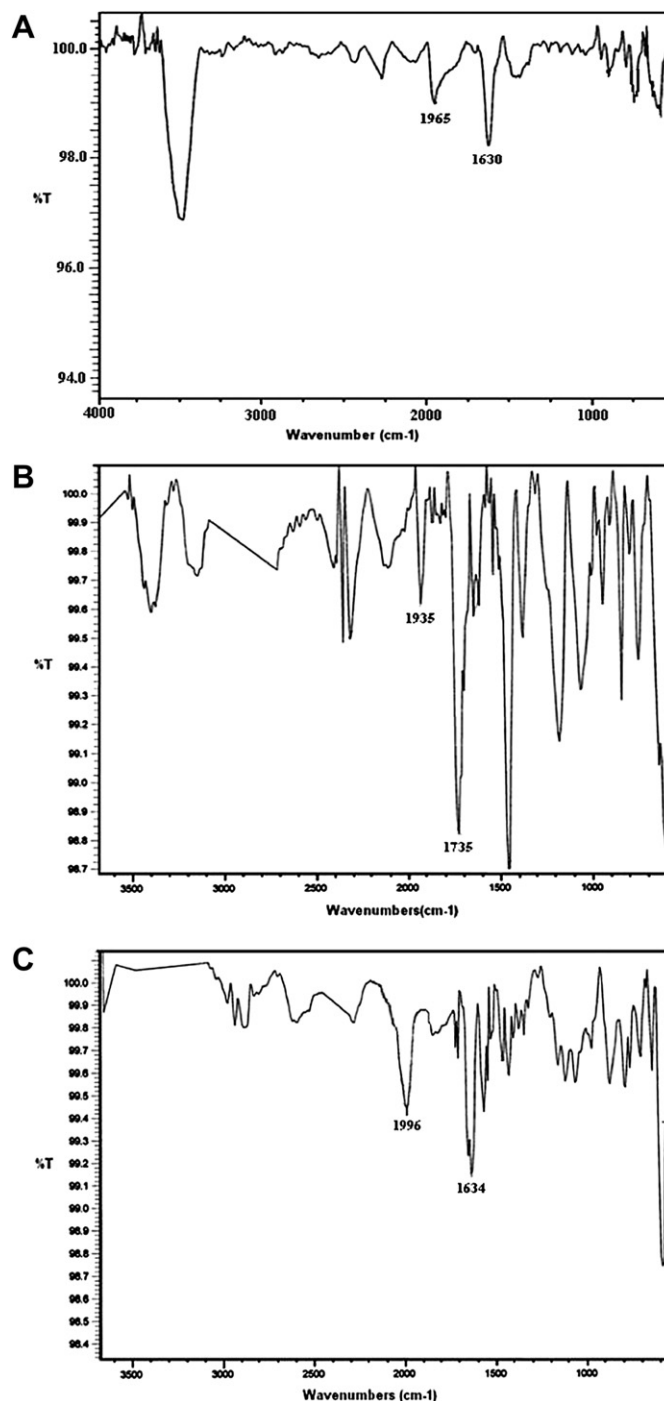


Fig. 1. FT-IR spectrum of: (A) [Mo(CO)₆@DAB-MWCNT]; (B) [Mo(CO)₆@AP-MWCNT] and (C) [Mo(CO)₆@ATP-MWCNT].

The nitrogen content of the supports was determined by CHN analysis which showed values of 4.16, 2.28 and 2.01% for DAB-MWCNT, AP-MWCNT and ATP-MWCNT, respectively. Based on these values, the nitrogen content of the supports were obtained about 2.87, 1.63 and 1.44 mmol per gram of the DAB-MWCNT, AP-MWCNT and ATP-MWCNT, respectively. The Mo content of the catalysts was also measured by ICP, which showed values of about 0.35, 0.25 and 0.29 mmol/g for [Mo(CO)₆@DAB-MWCNT], [Mo(CO)₆@AP-MWCNT] and [Mo(CO)₆@ATP-MWCNT], respectively (Table 2).

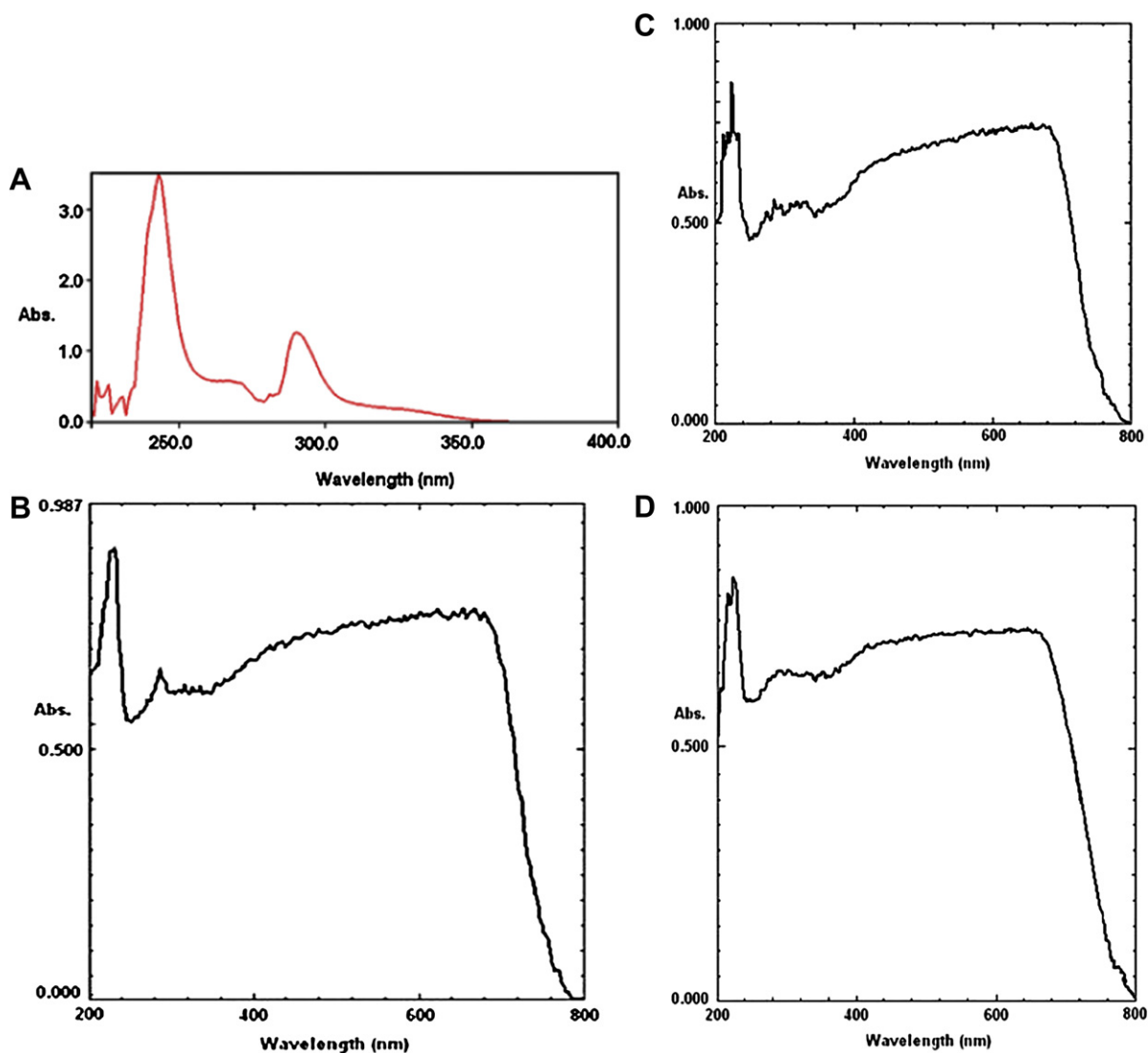


Fig. 2. The UV–Vis spectrum of: (A) $[\text{Mo}(\text{CO})_6]$; (B) $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$; (C) $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$; (D) $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$ and (E) MWCNTs.

The most informative spectroscopic data, which confirmed the anchoring of the $\text{Mo}(\text{CO})_6$ on the functionalized MWCNTs, were obtained by FT-IR spectra of $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$, $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$ and $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$ (Fig. 1 and Table 2). The C=O stretching band of $\text{Mo}(\text{CO})_6$ is appeared at 2004 cm^{-1} . This band was appeared in the supported catalysts at 1964 , 2000 and 1996 cm^{-1} for $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$, $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$ and $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$, respectively (Fig. 1A–C and Table 2). These observations clearly confirmed the attachment of $\text{Mo}(\text{CO})_6$ to amine modified MWCNTs. On the other hand, UV–Vis spectroscopy, in the diffuse reflectance mode, was employed for characterization of the supported catalysts. $\text{Mo}(\text{CO})_6$ showed absorption peaks at 230 and 280 nm which were attributed to $\text{Mo} \rightarrow \text{CO}$ charge transfer bands (Fig. 2A). These peaks were appeared at 231 and 283 nm for $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$, 232 and 284 nm for $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$, 228 and 286 nm for $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$ (Fig. 2B–D), while MWCNTs showed no absorption peak in this region (Fig. 2E). These observations indicated that molybdenum hexacarbonyl has been supported on MWCNTs. The SEM images of the $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$, $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$ and $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$ showed that the nanotubes are aggregated and have retained their nanotube nature (Fig. 3).

3.2. Catalytic experiments

The prepared catalysts were used for epoxidation of olefins with *tert*-BuOOH at room temperature. First, the reaction parameters such as catalysts amount and kind of solvent were optimized in the epoxidation of cyclooctene.

3.2.1. The effect of catalysts amount in the epoxidation of cyclooctene

In order to optimize the catalysts amount, different quantities of each catalyst were used in the epoxidation of cyclooctene (1 mmol) with *tert*-BuOOH (2 mmol). The best results were obtained with 100 mg of each catalyst (Table 3).

3.2.2. The effect of solvent on the epoxidation of cyclooctene catalyzed by $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$, $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$ and $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$

In order to choose the reaction media, different solvents were checked in the epoxidation of cyclooctene with *tert*-BuOOH. Among the different solvents such as acetonitrile, acetone, chloroform, carbon tetrachloride and 1,2-dichloroethane, CCl_4 was chosen as the reaction medium, because the higher catalytic activity was observed in this solvent (Table 4). It seems that non-coordinating

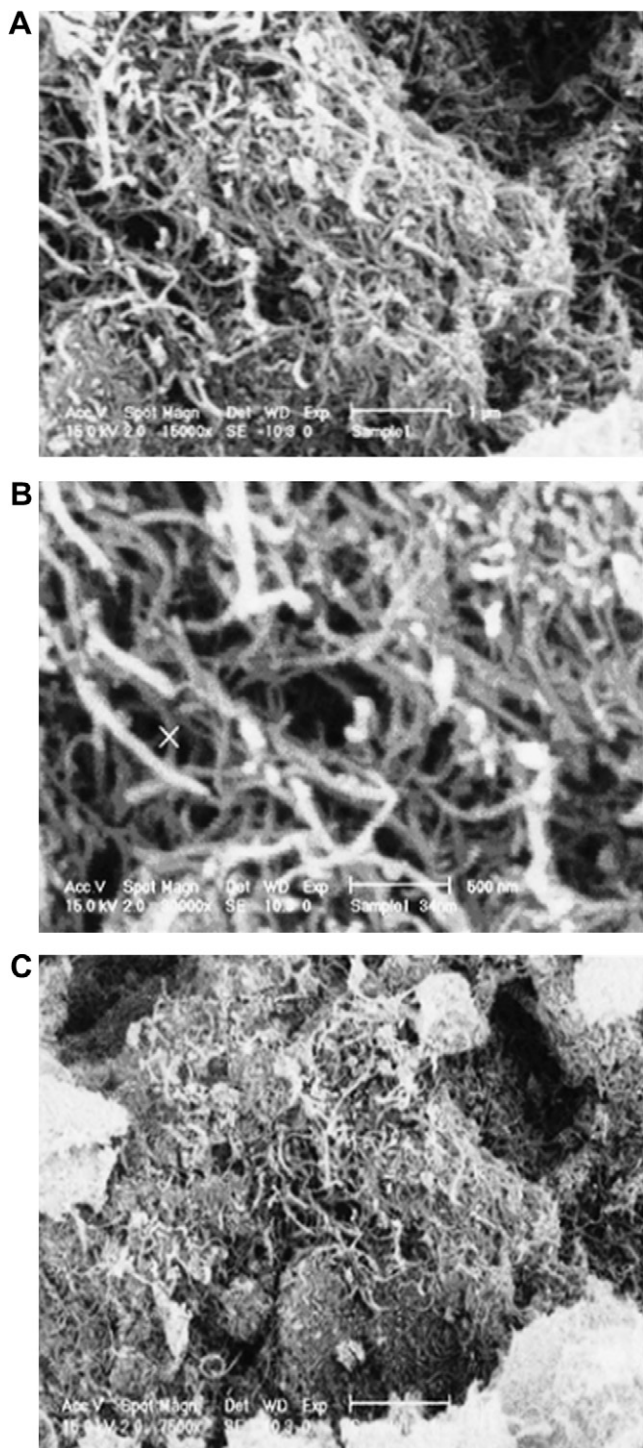


Fig. 3. The SEM image of: (A) $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$; (B) $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$ and $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$.

solvents such as chlorinated ones are the best solvents for oxidation reactions catalyzed by molybdenum-based catalysts.

3.3. Epoxidation of alkenes with *tert*-BuOOH catalyzed by $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$, $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$ and $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$

The supported catalysts were used for epoxidation of olefins with *tert*-BuOOH under optimized conditions. During the reaction,

Table 3

Optimization of the catalysts amount in the epoxidation of cyclooctene with TBHP.^a

Catalyst amount (mg)	Epoxide yield (%) ^b		
	$[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$	$[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$	$[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$
	Time (20 min)	Time (35 min)	Time (30 min)
0	5	5	5
25	20	22	24
50	34	45	41
100	97	100	98
100	35 (45 min) ^c	31 (35 min) ^c	27 (40 min) ^c
150	97	100	98

^a Reaction conditions: cyclooctene (1 mmol), TBHP (2 mmol), catalyst, CCl_4 (6 ml).

^b GC yield based on the starting alkene.

^c The reactions were carried out with cyclooctene (10 mmol), TBHP (2 mmol) and catalyst (neat reaction).

the catalysts are suspended in the solvent. This is due to the bundled agglomerates of MWCNT that aggregate slowly and let the catalysts to suspend without setting down for a long period of time. The $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$, $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$ and $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$ were found as efficient catalysts for epoxidation of alkenes with *tert*-BuOOH (Tables 5–7). In three catalytic systems, the cyclohexene was oxidized in high yield and selectivity to cyclohexene oxide and no by-product was observed. In the case of linear alkenes such as 1-octene and 1-dodecene, the corresponding epoxides were obtained in high yields with 100% selectivity. In the case of stilbenes, *trans*-stilbene was epoxidized in a stereospecific manner with complete retention of configuration (88–99% yields), while oxidation of *cis*-stilbene was associated with some loss of stereochemistry and a mixture of *cis*- and *trans*-epoxides was obtained.

Previously, we have reported the supporting of $[\text{Mn}(\text{CO})_6]$ on the polystyrene via amine spacers [14–17]. The polystyrene, which was used as support, had a size in the micron range. Comparison of the catalytic activity of these MWCNTs supported $[\text{Mn}(\text{CO})_6]$ and polystyrene supported $[\text{Mn}(\text{CO})_6]$ catalysts showed that $[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$, $[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$ and $[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$ are more efficient than polystyrene bound $[\text{Mn}(\text{CO})_6]$ (by comparison of their TOFs). This can be related to the nanoparticle nature of the MWCNTs and isolation of active sites which in turns increases the catalytic activities.

3.4. Catalyst reuse and stability

While, the homogeneous $[\text{Mo}(\text{CO})_6]$ cannot recovered even one time, the MWCNT supported catalysts can be filtered and reused several times without significant loss of their activities. The

Table 4



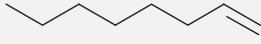
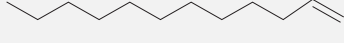
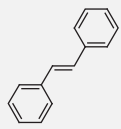
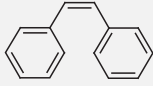
The effect of solvent on the epoxidation of cyclooctene with *tert*-BuOOH catalyzed by $[\text{Mo}(\text{CO})_6]$ supported on modified MWCNTs.^a

Row	Solvent	Epoxide yield (%) ^b		
		$[\text{Mo}(\text{CO})_6@DAB\text{-MWCNT}]$	$[\text{Mo}(\text{CO})_6@AP\text{-MWCNT}]$	$[\text{Mo}(\text{CO})_6@ATP\text{-MWCNT}]$
		Time (20 min)	Time (35 min)	Time (30 min)
1	CCl_4	97	100	98
2	CHCl_3	53	47	50
3	$\text{ClCH}_2\text{CH}_2\text{Cl}$	18	20	21
4	CH_3CN	5	5	5
5	CH_3COCH_3	8	6	10



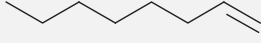
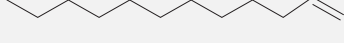
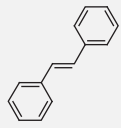

^a Reaction conditions: cyclooctene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg), solvent (6 ml).

^b GC Yield based on the starting alkene.

Table 5
Epoxidation of alkenes with *tert*-BuOOH catalyzed by [Mo(CO)₆@DAB-MWCNT].^a



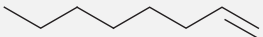
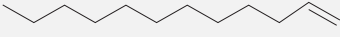
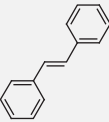
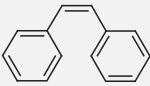
Row	Alkene	Epoxide yield (%) ^b	Epoxide selectivity (%)	Time (min)	TOF (h ⁻¹)
1		97	100	20	83.98
2		95	100	40	41.13
3		88	100	95	15.88
4		87	100	105	14.20
5 ^c		88 ^d	100	160	9.42
6 ^c		93 ^e	100	160	9.95

^a Reaction conditions: alkene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg, 0.035 mmol), CCl₄ (6 ml).^b GLC yield based on the starting alkene.^c Both ¹H NMR and GLC data approved the reported yields.^d Only *trans*-epoxide was produced.^e 90% *cis*-Epoxide and 3% *trans*-epoxide were produced.**Table 6**
Epoxidation of alkenes with *tert*-BuOOH catalyzed by [Mo(CO)₆@AP-MWCNT].^a

Row	Alkene	Epoxide yield (%) ^b	Epoxide selectivity (%)	Time (min)	TOF (h ⁻¹)
1		100	100	35	68.57
2		93	100	50	44.64
3		86	100	140	14.74
4		85	100	165	12.36
5 ^c		95 ^d	100	160	14.25
6 ^c		100 ^e	100	160	15.00

^a Reaction conditions: alkene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg, 0.025 mmol), CCl₄ (6 ml).^b GLC yield based on the starting alkene.^c Both ¹H NMR and GLC data approved the reported yields.^d Only *trans*-epoxide was produced.^e 95% *cis*-Epoxide and 5% *trans*-epoxide were produced.

Table 7
Epoxidation of alkenes with *tert*-BuOOH catalyzed by $[\text{Mo}(\text{CO})_6\text{@ATP-MWCNT}]$.^a

Row	Alkene	Epoxide yield (%) ^b	Epoxide selectivity (%)	Time (min)	TOF (h^{-1})
1		98	100	30	67.58
2		96	100	60	33.10
3		80	100	110	15.05
4		70	100	150	9.66
5 ^c		99 ^d	100	120	17.07
6 ^c		100 ^e	100	120	17.24

^a Reaction conditions: alkene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg, 0.029 mmol), CCl_4 (6 ml).

^b GLC yield based on the starting alkene.

^c Both ¹HNMR and GLC data approved the reported yields.

^d Only *trans*-epoxide was produced.

^e 95% *cis*-Epoxide and 5% *trans*-epoxide were produced.

reusability of $[\text{Mo}(\text{CO})_6\text{@DAB-MWCNT}]$, $[\text{Mo}(\text{CO})_6\text{@AP-MWCNT}]$ and $[\text{Mo}(\text{CO})_6\text{@ATP-MWCNT}]$ was investigated in the multiple sequential epoxidation of cyclooctene with *tert*-BuOOH. At the end of each reaction, the catalysts were separated by simple filtration, washed with methanol and dried carefully before using it in the next run. After using the catalysts for twenty consecutive times, the

epoxide yields were 90, 93 and 91% for $[\text{Mo}(\text{CO})_6\text{@DAB-MWCNT}]$, $[\text{Mo}(\text{CO})_6\text{@AP-MWCNT}]$ and $[\text{Mo}(\text{CO})_6\text{@ATP-MWCNT}]$, respectively (Table 8). In tenth first runs, the catalysts were as active as initial catalysts, but in the next runs, the reaction times were completed in longer times. The filtrates were collected for determination of Mo leaching. The results showed that after two first runs, no

Table 8
The results of catalysts recovery and the amounts of Mo leached in the epoxidation of cyclooctene with *tert*-BuOOH.^a

Run	$[\text{Mo}(\text{CO})_6\text{@DAB-MWCNT}]$			$[\text{Mo}(\text{CO})_6\text{@AP-MWCNT}]$			$[\text{Mo}(\text{CO})_6\text{@ATP-MWCNT}]$		
	Time (min)	Yield (%) ^b	Mo leached (%) ^c	Time (min)	Yield (%) ^b	Mo leached (%) ^c	Time (min)	Yield (%) ^b	Mo leached (%) ^c
1	20	97	1	35	100	2	30	98	4
2	20	97	0.6	35	100	1.6	25	98	2.5
3	15	97	–	35	100	–	25	98	–
4	15	97	–	35	100	–	25	98	–
5	15	97	–	35	100	–	25	98	–
6	15	97	–	35	100	–	25	98	–
7	20	97	–	35	100	–	25	98	–
8	20	96	–	35	100	–	25	98	–
9	20	96	–	35	100	–	25	98	–
10	20	96	–	35	100	–	25	98	–
11	25	96	–	40	100	–	25	97	–
12	25	96	–	40	100	–	30	97	–
13	25	95	–	40	100	–	30	94	–
14	30	95	–	50	100	–	30	94	–
15	30	95	–	50	100	–	35	93	–
16	35	95	–	50	100	–	35	93	–
17	35	92	–	50	96	–	40	93	–
18	45	92	–	90	96	–	45	93	–
19	45	90	–	95	96	–	45	92	–
20	85	90	–	135	93	–	95	91	–

^a Reaction conditions: Cyclooctene (1 mmol), *tert*-BuOOH (2 mmol), catalyst (100 mg), CCl_4 (6 ml).

^b GLC yield based on the starting alkene.

^c Determined by ICP.

molybdenum was detected in the filtrates by ICP. The Mo leaching of these catalysts has the following order $[\text{Mo}(\text{CO})_6@\text{ATP-MWCNT}] > [\text{Mo}(\text{CO})_6@\text{AP-MWCNT}] > [\text{Mo}(\text{CO})_6@\text{DAB-MWCNT}]$. The higher Mo leaching in the case of $[\text{Mo}(\text{CO})_6@\text{DAB-MWCNT}]$ can be attributed to the oxidation of arm and the appearance of a band at 1060 cm^{-1} ($\text{S}=\text{O}$ stretching band) in the FT-IR of the recovered catalyst confirmed this explanation.

Also, the catalytic behavior of the separated liquids was tested by addition of fresh cyclooctene and *tert*-BuOOH to the filtrates after each run. Execution of the oxidation reactions under the same reaction conditions, as with catalyst, showed that the obtained results were the same as blank experiments.

4. Conclusion

In conclusion, molybdenum hexacarbonyl supported on amines modified MWCNTs are highly efficient catalysts for epoxidation of alkenes with *tert*-BuOOH in CCl_4 . Due to the particle size of MWCNTs and dispersion of Mo species, the catalytic activity of these heterogeneous catalyst are higher than our previously reported catalysts. Finally, these catalysts are robust and recoverable in the epoxidation of alkenes with *tert*-BuOOH.

Acknowledgement

We acknowledge the support of this work by Center of Excellence of Chemistry of University of Isfahan (CECU).

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