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Multi-wall carbon nanotube supported tungsten hexacarbonyl: an efficient and reusable catalyst for epoxidation of alkenes with hydrogen peroxide

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Multi-wall carbon nanotube supported tungsten hexacarbonyl: an efficient and reusable catalyst for epoxidation of alkenes with hydrogen peroxide

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Highly efficient epoxidation of alkenes with H₂O₂ catalyzed by tungsten hexacarbonyl supported on multi-wall carbon nanotubes (MWCNTs) modified with 1,2-diaminobenzene is reported. The prepared catalyst, [W(CO)₆@DAB-MWCNT], was characterized by elemental analysis, scanning electron microscopy, FT-IR, and diffuse reflectance UV-Vis spectroscopic methods. The prepared catalyst was applied as an efficient catalyst for green epoxidation of alkenes with hydrogen peroxide in CH₃CN. This heterogeneous metal carbonyl catalyst showed high stability and reusability in epoxidation without loss of its catalytic activity.

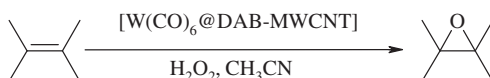
Keywords: Multi-wall carbon nanotubes; Tungsten hexacarbonyl; Heterogeneous catalyst; Epoxidation; Hydrogen peroxide

1. Introduction

Epoxides play an important role in industry as intermediates for production of fine chemicals and pharmaceuticals [1]. Application of green oxidations has received great interest from economical and environmental points of view. Environmentally friendly oxygen donors such as molecular oxygen and hydrogen peroxide have attracted attention. In particular, hydrogen peroxide has been widely used as oxidant due to its high oxygen content and formation of water as by-product [2, 3]. Catalysts such as iron and manganese porphyrins [4, 5], phthalocyanines [6], iron amide complexes [7–9], TAML [10], selenoxides [11], polyoxometalates [12–15], titanium silicalite [16, 17], tungsten, molybdenum, and vanadium complexes [18], Sn–zeolite beta [19, 20], and MTO [21–28] are known to activate hydrogen peroxide.

Transition metal complexes are effective catalysts for a variety of organic reactions, especially epoxidation of alkenes [29]. But the major problem associated with these homogeneous catalysts is recovery of catalyst from the reaction medium. There have

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Scheme 1. Epoxidation of alkenes with H_2O_2 catalyzed by $[\text{W}(\text{CO})_6@\text{DAB-MWCNT}]$.

been intense efforts for recovering and reusing homogeneous catalysts [30]. An efficient and practical way for commercial applications of these catalysts is their immobilization on solid supports [31–51].

Supported catalysts based on tungsten species have found many applications in heterogeneous catalysis, widely used in several important industrial reactions, such as hydrotreatments, hydrocracking of heavy fractions from oil, dehydration of alcohols, metathesis, and isomerization of olefins [52]. The supports carrying tungsten species are Al_2O_3 and TiO_2 [53–56], SiO_2 [57, 58], MgO [59], activated carbon [60], polymers [51, 61–63], and MgF_2 [64]. These catalysts have been used for efficient oxidation reactions.

Carbon nanotubes (CNTs) have attracted attention in synthesis, characterization, and other applications because of their unique structural, mechanical, thermal, optical, and electronic properties [65, 66]. Due to their high surface area, chemical stability, and insolubility in most solvents, CNTs can be used as catalyst supports. For example, Pt nanoparticles supported on CNTs have been used for methanol oxidation [67], palladium nanoparticles supported on CNTs for semihydrogenation of phenylacetylene [68], chiral vanadyl salen complex supported on single-wall CNTs for enantioselective cyanosilylation of aldehydes [69, 70], manganese(III) porphyrin and manganese(III) salophen supported on multi-wall CNTs (MWCNTs) for epoxidation of alkenes with NaIO_4 [71, 72], and molybdenum hexacarbonyl supported on MWCNTs for alkene epoxidation with *tert*-BuOOH [73–75].

In this article, preparation, characterization, and investigation of catalytic activity of $\text{W}(\text{CO})_6$ supported on functionalized MWCNTs is reported (scheme 1). The catalyst, $[\text{W}(\text{CO})_6@\text{DAB-MWCNT}]$, was characterized by elemental analysis, scanning electron microscopy (SEM), FT-IR, and diffuse reflectance UV-Vis spectroscopic methods. This heterogeneous catalyst was applied as an efficient catalyst for green epoxidation of alkenes with H_2O_2 in CH_3CN . The stability and reusability of this catalyst were also investigated in the epoxidation.

2. Experimental

All materials (SOCl_2 , Et_3N , DMF, 1,2-diaminobenzene, CH_3CN , $\text{W}(\text{CO})_6$, THF, H_2O_2 , and Et_2O) were of commercial reagent grade, purchased from Merck and Fluka chemical companies. All alkenes (cyclooctene, cyclohexene, styrene, α -methylstyrene, 1-octene, 1-dodecene, *cis*-stilbene, and *trans*-stilbene) 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 from 500 to 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-Avance AQS 400 MHz. Gas chromatography (GC) experiments

were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20M. The ICP analyses were performed on an ICP-Spectrociros CCD instrument. The products were identified by comparison of their retention times with known samples and also with their ^1H NMR spectra. MWCNTs containing carboxylic acid groups (MWCNTs with diameters between 20 and 30 nm) were purchased from Shenzhen NTP Factory.

2.1. Chlorination of MWCNT-COOH

In a 100 mL round-bottom flask equipped with a condenser and a magnetic stir bar, MWCNT-COOH (5 g) and SOCl_2 (30 mL) were mixed and refluxed under N_2 for 1 h. Then, the reaction mixture was cooled and SOCl_2 evaporated. The resulting precipitate is chlorinated MWCNTs, MWCNT-COCl [72].

2.2. Modification of MWCNT-COCl with 1,2-diaminobenzene

1,2-Diaminobenzene (DAB) (2 g) and triethylamine (5 mL) were added to a suspension of MWCNT-COCl (5 g) in DMF (50 mL). The mixture was vigorously stirred at 80°C for 48 h. After cooling the mixture, black solids were collected by filtration, washed thoroughly with CH_3CN , and dried in vacuum for 5 h to reach the modified support, DAB-MWCNT [74].

2.3. Preparation of the catalyst, $[\text{W}(\text{CO})_6@\text{DAB-MWCNT}]$

$\text{W}(\text{CO})_6$ (1.5 g, 4.26 mmol) was dissolved in THF (60 mL) and stirred under UV irradiation for 15 min [76]. Then, DAB-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 to remove unreacted $\text{W}(\text{CO})_6$ and dried in vacuum at room temperature to remove THF [74].

2.4. General procedure for epoxidation of alkenes with H_2O_2 catalyzed by $[\text{W}(\text{CO})_6@\text{DAB-MWCNT}]$

In a 25 mL round bottom flask equipped with a magnetic stir bar, a mixture of alkene (1 mmol), H_2O_2 (0.5 mL), catalyst (200 mg, 0.006 mmol), and CH_3CN (5 mL) was prepared and refluxed with stirring. The reaction progress was monitored by GC. At the end of the reaction, the mixture was diluted with Et_2O (20 mL) and filtered. The catalyst was thoroughly washed with Et_2O and the combined washing and filtrates were purified on a silica gel plate to obtain the pure product.

2.5. Reusability of the catalyst

The reusability of the catalyst was studied in the repeated epoxidation of cyclooctene. The reactions were carried out as described above. At the end of each reaction, the catalyst was filtered, washed thoroughly with Et_2O , dried, and reused.

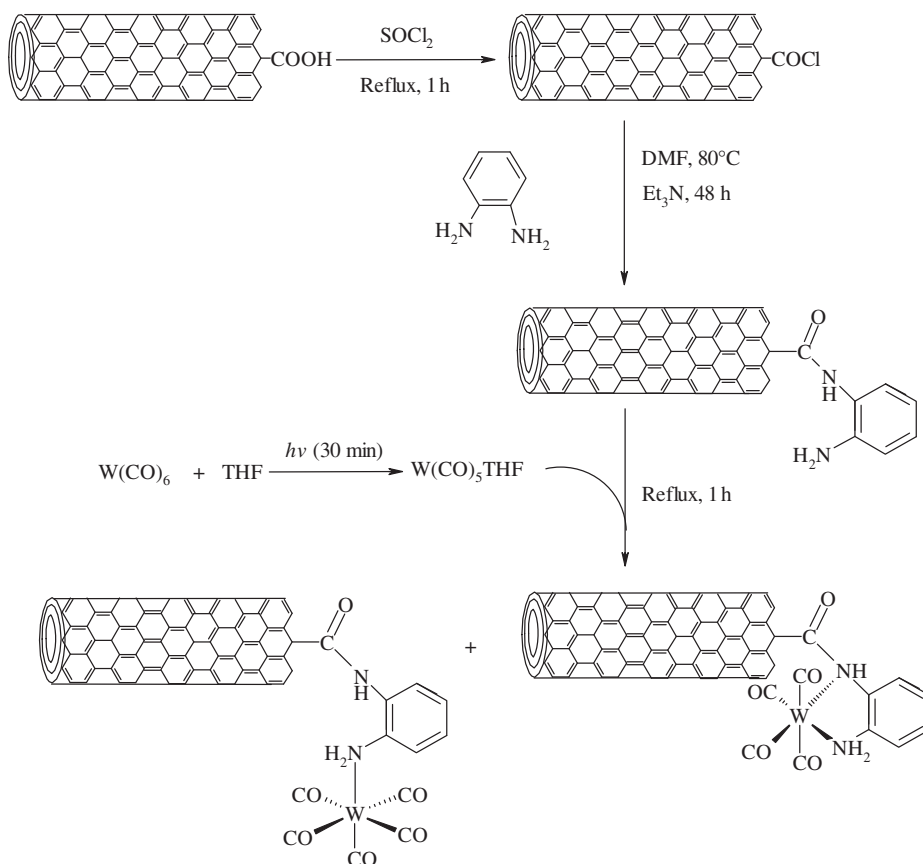
3. Results and discussion

3.1. Preparation and characterization of $[W(CO)_6@DAB-MWCNT]$

The specifications of MWCNT-COOH used in this study are presented in table 1. The preparation route for attachment of $W(CO)_6$ to MWCNTs modified with 1,2-diaminobenzene, DAB-MWCNT, is shown in scheme 2. First, MWCNT-COOH was chlorinated to activate the MWCNTs. Then, DAB-MWCNT was prepared by covalent attachment of 1,2-diaminobenzene to MWCNT-COCl *via* an amide linkage.

Table 1. The specifications of MWCNT-COOH used in this study.

Outside diameter	Inside diameter	Length	COOH content	Specific surface area
20–30 nm	5–10 nm	30 μ m	1.5%	> 110 m ² g ⁻¹



Scheme 2. The preparation route for $[W(CO)_6@DAB-MWCNT]$.

Such functionalization allows preparation of a ligand which can coordinate to a metal center. Then, $W(CO)_5THF$ (prepared by activation of $W(CO)_6$ in THF under UV irradiation) was reacted with DAB-MWCNT to produce $[W(CO)_6@DAB-MWCNT]$. The tungsten species coordinated to amine groups. The DAB-MWCNT can act as unidentate or bidentate ligand. Both proposed structures could be catalysts, active in epoxidation. The prepared catalyst, $[W(CO)_6@DAB-MWCNT]$, was characterized by elemental analysis, SEM, FT-IR, and diffuse reflectance UV-Vis spectroscopic methods. The nitrogen content of DAB-MWCNT was determined by CHN analysis which showed a value of 2.94%. Based on these values, the nitrogen content of the support was about 2.1 mmol g^{-1} of the DAB-MWCNT. The nitrogen content of the catalyst was about 2.84% (2.02 mmol g^{-1}). The W content of the catalyst was also measured by ICP, which showed a value of about 0.03 mmol g^{-1} of $[W(CO)_6@DAB-MWCNT]$.

FT-IR spectra of MWCNTs, DAB-MWCNT, and $[W(CO)_6@DAB-MWCNT]$ are shown in figure 1. The $C=O$ stretching band of the carboxylic acid is at 1640 cm^{-1} (figure 1a). Upon attachment of DAB to MWCNTs, the $C=O$ stretch of amide appeared at 1632 cm^{-1} (figure 1b). In the FT-IR spectrum of $[W(CO)_6@DAB-MWCNT]$, bands at 1948 and 1801 cm^{-1} were assigned to the terminal carbonyl groups (figure 1c). These observations prove coordination of $W(CO)_6$ species to DAB-MWCNT. Further evidence for the attachment of $W(CO)_6$ to DAB-MWCNT was provided by UV-Vis spectroscopy in the diffuse reflectance mode. $W(CO)_6$ showed two strong absorptions at 246 and 290 nm which were attributed to $W\rightarrow CO$ charge transfer bands (figure 2a). These peaks were also observed in the diffuse reflectance UV-Vis of $[W(CO)_6@DAB-MWCNT]$ (figure 2b), while MWCNTs showed no absorption peak in this region (figure 2c). These observations indicated that tungsten hexacarbonyl is supported on MWCNTs. The SEM images of the $[W(CO)_6@DAB-MWCNT]$ showed that the nanotubes are aggregated and retain their nanotube nature (figure 3).

3.2. Epoxidation of alkenes with H_2O_2 catalyzed by $[W(CO)_6@DAB-MWCNT]$

First, the catalytic activity of $[W(CO)_6@DAB-MWCNT]$ was studied in epoxidation of cyclooctene with hydrogen peroxide. Different amounts of $[W(CO)_6@DAB-MWCNT]$ were used to optimize the catalyst amount. The best results were obtained in the presence of 200 mg (0.006 mmol) of catalyst (table 2). In order to optimize the reaction media, different solvents such as acetone, tetrahydrofuran, 1,2-dichloroethane, acetonitrile, carbon tetrachloride, chloroform, and dichloromethane were checked in the epoxidation of cyclooctene with H_2O_2 under reflux (for obtaining the highest product yield). The results (table 3) showed that the highest epoxide yield was observed in CH_3CN . The exact role of the solvent is not completely clear. But the higher catalytic activity of the catalyst in acetonitrile can be attributed to the polarity of the solvent and better solubility of all substrates in it. CH_3CN can facilitate formation of metal oxo complex which is responsible for oxidation of alkenes. During the reaction, $[W(CO)_6@DAB-MWCNT]$ is suspended in the solvent. This is due to the bundled agglomerates of MWNT that aggregate slowly (this is due to the presence of functional groups and also the weak $\pi-\pi$ interactions) and make the catalyst suspend in the reaction mixture for a long period of time; other heterogeneous catalysts were aggregated more rapidly in comparison with CNTs. Control experiments in the absence

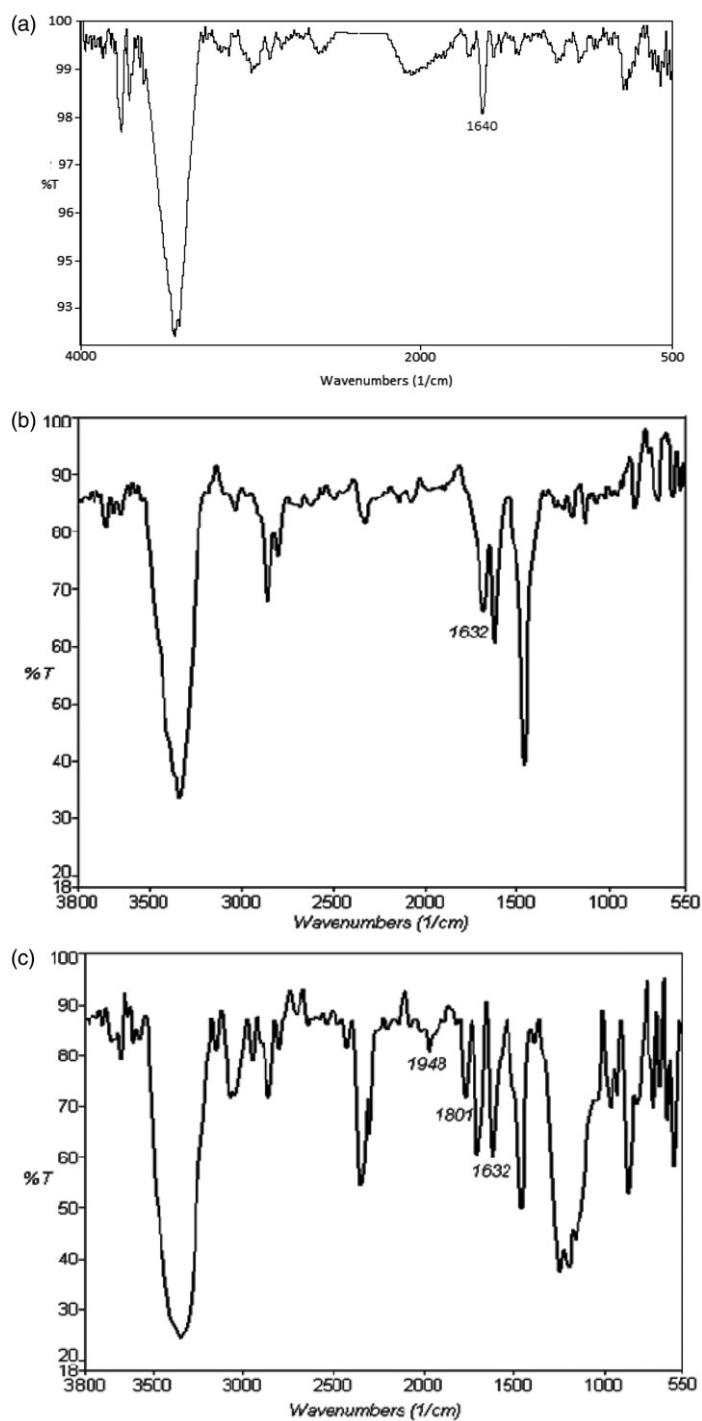


Figure 1. FT-IR spectrum of (a) MWCNTs, (b) DAB-MWCNT, and (c) [W(CO)₆@DAB-MWCNT].

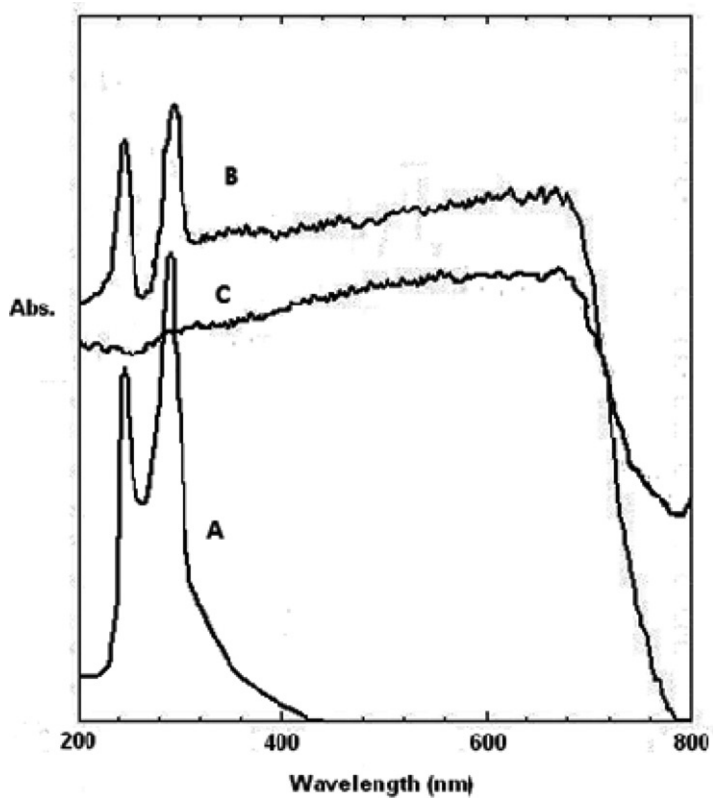


Figure 2. UV-Vis spectrum of (a) homogeneous $W(CO)_6$, (b) $[W(CO)_6@DAB-MWCNT]$, and (c) MWCNT.

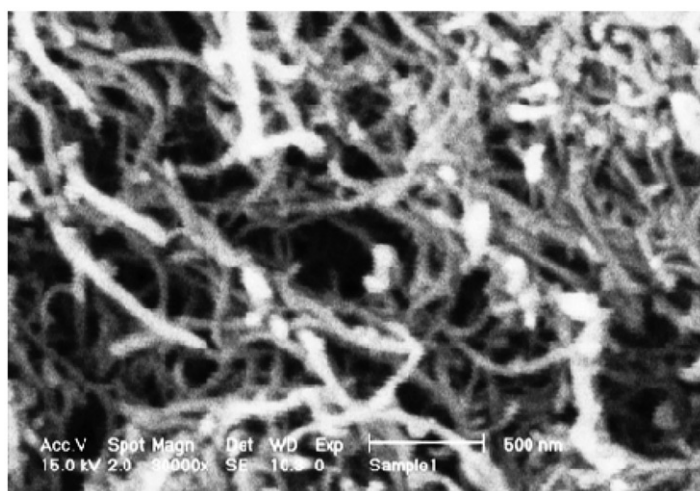


Figure 3. SEM image of $[W(CO)_6@DAB-MWCNT]$.

Table 2. Optimization of catalyst amount in the epoxidation of cyclooctene with H₂O₂.^a

Entry	Time (h)	Catalyst amounts (mmol, mg)	Yield (%) ^b
1	2	No catalyst	10
2	2	50 mg (0.0015 mmol)	78
3	2	100 mg (0.003 mmol)	90
4	2	150 mg (0.0045 mmol)	93
5	2	200 mg (0.006 mmol)	98
6	2	250 mg (0.0075 mmol)	98
7	2	DAB-MWCNT (200 mg)	12
8	2	W(CO) ₆ (0.006 mmol)	67

^aReaction conditions: cyclooctene (1 mmol), H₂O₂ (0.5 mL), catalyst, CH₃CN (5 mL).^bGC yield based on the starting cyclooctene.Table 3. Epoxidation of *cis*-cyclooctene with H₂O₂ catalyzed by [W(CO)₆@DAB-MWCNT] under reflux in different solvents.^a

Solvent	Epoxide yield after 2 h (%) ^b	<i>T</i> (°C)
(CH ₃) ₂ CO	9	53
THF	17	61
CH ₃ CN	98	77
ClCH ₂ CH ₂ Cl	29	78
CHCl ₃	22	57
CCl ₄	18	72
CH ₂ Cl ₂	14	38



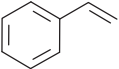
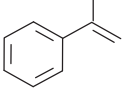


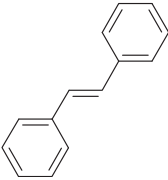
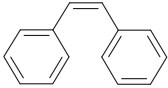
^aReaction conditions: cyclooctene (1 mmol), H₂O₂ (0.5 mL), catalyst (200 mg, 0.006 mmol), solvent (5 mL).^bGC yield based on the starting cyclooctene.

of catalyst or using MWCNT-DAB as catalyst were also performed (table 2); the amount of epoxide was about 10–12%. When the same reaction was carried out using W(CO)₆ (0.006 mmol, which is equal to the amount of W(CO)₆ in 200 mg of MWCNTs) as catalyst, the epoxide yield was 67%. The reaction conditions were also optimized for epoxidation of 1-octene and the same results were observed.

Under the optimized conditions, [W(CO)₆@DAB-MWCNT]/H₂O₂ catalytic system was used for epoxidation of a wide range of alkenes in refluxing acetonitrile (table 4). Both cyclic and linear alkenes were efficiently converted to their corresponding epoxides with H₂O₂ in the presence of catalytic amounts of [W(CO)₆@DAB-MWCNT]. Cyclooctene, cyclohexene (as cyclic alkenes), 1-octene, and 1-dodecene (as linear alkenes) were efficiently converted to their corresponding epoxides by [W(CO)₆@DAB-MWCNT]. In the case of styrene and α -methyl styrene, benzaldehyde and acetophenone were produced as by-products, respectively. In the case of *trans*-stilbene, the reaction was stereospecific and only *trans*-epoxide was produced while for *cis*-stilbene some loss of stereochemistry was observed and afforded 80% *cis*- and 10% *trans*-stilbene epoxides (table 4). During the oxidation reactions, no acetamide due to oxidation of acetonitrile was observed.

The results obtained with [W(CO)₆@DAB-MWCNT]/H₂O₂ are compared with some previously reported epoxidation catalysts in table 5. These comparisons show that the present catalytic system is more efficient than the others. Comparison of the catalytic

Table 4. Epoxidation of alkenes with H₂O₂ catalyzed [W(CO)₆@DAB-MWCNT] in refluxing CH₃CN.^a

Entry	Alkene	Conversion (%) ^b		Epoxide (%) ^b	Time (h)
1		98	98		2
2		100	100		2
3		76 ^c	73		5
4		84 ^d	60		3
5		100	100		3
6		26	26		5
7		84 ^e	84 (<i>trans</i> -epoxide)		10
8		90 ^e	80 (<i>cis</i> -epoxide) 10 (<i>trans</i> -epoxide)		10

^aReaction conditions: alkene (1 mmol), H₂O₂ (0.5 mL), catalyst (200 mg, 0.006 mmol), CH₃CN (5 mL).

^bGC yield based on starting alkene.

^cThe by-product was benzaldehyde.

^dThe by-product was acetophenone.

^eBoth ¹H NMR and GC data approved the reported yields.

Table 5. Comparison of the results obtained for epoxidation of cyclooctene catalyzed by [W(CO)₆@DAB-MWCNT] with some of those reported in the literature.

Entry	Catalyst	Support	Oxidant	Conditions (°C)/solvent	TOF (h ⁻¹)	Ref.
1	Tungsten hexacarbonyl	MWCNT	H ₂ O ₂	Reflux/CH ₃ CN	81.7	This work
2	Tungsten hexacarbonyl	Polystyrene	H ₂ O ₂	Reflux/CH ₃ CN	18.8	[51]
3	Molybdenum hexacarbonyl	Polystyrene	TBHP	Reflux/CCl ₄	31.3	[50]
4	Molybdenum hexacarbonyl	MWCNT	TBHP	Reflux/CCl ₄	78.4	[74]
5	[Mn(salophen)Cl]	MWCNT	NaIO ₄	RT/CH ₃ CN–H ₂ O ₂	8.0	[72]
6	Mn(TNH ₂ PP)Cl	MWCNT	NaIO ₄	RT/CH ₃ CN–H ₂ O ₂	9.5	[71]

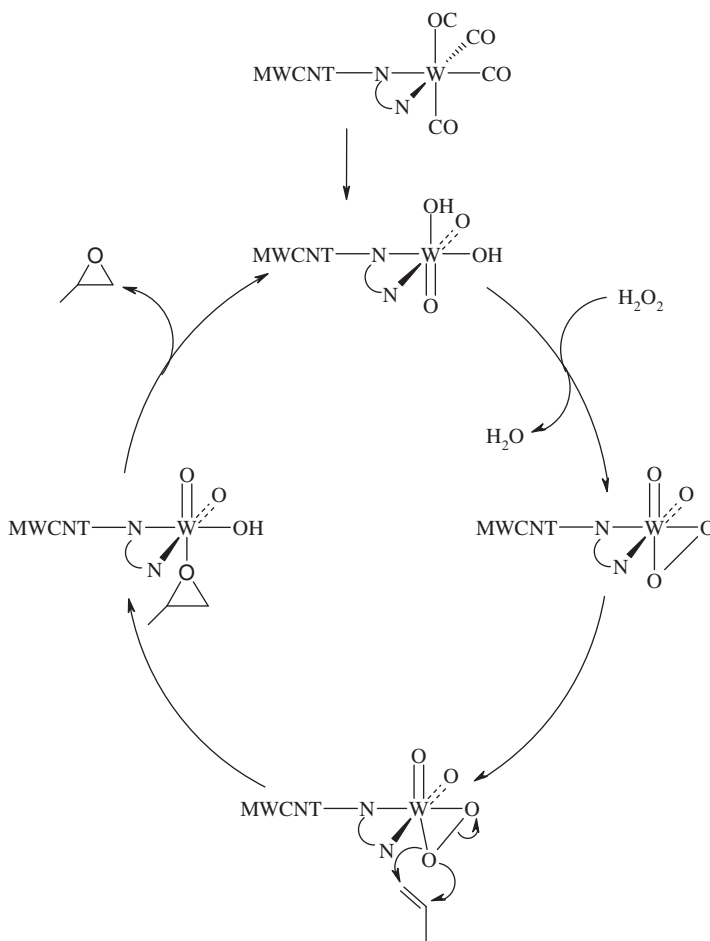
Table 6. Reusability of $[\text{W}(\text{CO})_6@\text{DAB-MWCNT}]$ in the epoxidation of cyclooctene with H_2O_2 under reflux.^a

Run	Time (h)	Yield (%) ^b	W leached (%) ^c
1	2	98	1.1
2	2	98	0.5
3	2	98	0
4	2	98	0
5	2	98	0
6	2	98	0

^aReaction conditions: cyclooctene (1 mmol), H_2O_2 (0.5 mL), $[\text{W}(\text{CO})_6@\text{DAB-MWCNT}]$ (200 mg, 0.006 mmol), CH_3CN (5 mL).

^bGC yield based on starting alkene.

^cDetermined by ICP.



Scheme 3. Proposed mechanism for epoxidation of alkenes with H_2O_2 catalyzed by $[\text{W}(\text{CO})_6@\text{DAB-MWCNT}]$.

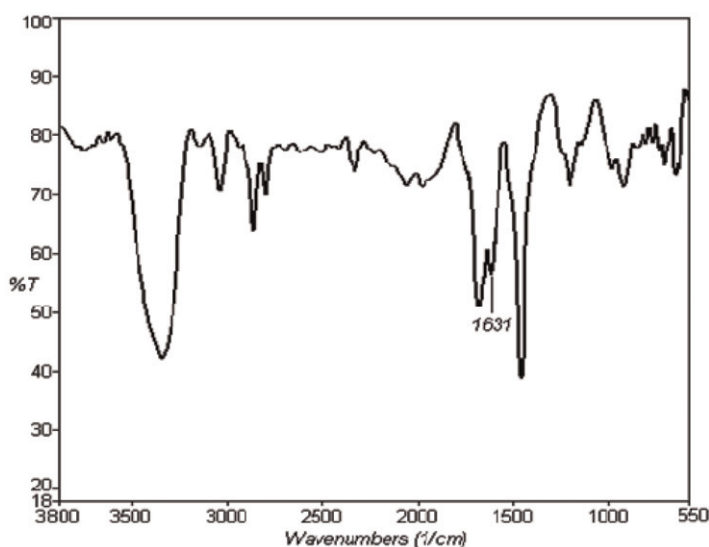


Figure 4. FT-IR spectrum of recovered $[W(CO)_6@DAB-MWCNT]$.

activity of tungsten hexacarbonyl supported on polystyrene [51] and MWCNTs shows the effect of support in which the TOF increases from 18.8 for polystyrene to 81.7 for MWCNTs. This can be attributed to the higher surface area of MWCNTs compared to polystyrene.

3.3. Catalyst reuse and stability

The reusability of $[W(CO)_6@DAB-MWCNT]$ was monitored in multiple sequential epoxidations of cyclooctene with H_2O_2 (table 6). At the end of each reaction, the catalyst was filtered and reused in the next run. The catalyst was reused (six consecutive times were checked) without loss of its initial activity. The amount of tungsten, which was detected in the filtrates in first two runs, was low and after 3rd run no tungsten was detected in the filtrates. These results demonstrate the strong attachment of W to the MWCNT. The catalytic behavior of the separated liquid was also tested by addition of fresh cyclooctene and H_2O_2 to the filtrates after each run. Execution of the oxidation reaction under the same reaction conditions, as with catalyst, showed that the obtained results were the same as the results of blank experiments.

The recovered catalyst was studied by FT-IR spectroscopy. No band corresponding to terminal C=O was observed in the FT-IR spectrum of the recovered catalyst. This is in accord with the mechanism previously reported [77]. In this mechanism, CO ligands are eliminated and the W=O species are produced (scheme 3, figure 4). Therefore, $W(CO)_6$ can be considered as a catalyst precursor.

4. Conclusion

Tungsten hexacarbonyl supported on MWCNTs modified with 1,2-diaminobenzene was used as an efficient catalyst in epoxidation of alkenes with H_2O_2 . This supported

catalyst, $[\text{W}(\text{CO})_6@\text{DAB-MWCNT}]$, was reactive in the epoxidation of a wide range of alkenes such as linear and cyclic ones. The catalyst was reusable and recycled six times without loss of catalytic activity.

Acknowledgments

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