Immobilization of MoO₂(acac)₂ on Multiwall Carbon Nano Tube and Epoxidation of Alkenes

Nafar, Mahdieh; Grivani, Gholamhossein*⁺
School of Chemistry, Damghan University, Damghan, I.R. IRAN

ABSTRACT: *The acidic group (-CO₂H) of MultiWall Carbon Nanotube (MWCNT) converted to acyl chloride group (-COCl) producing of MVCNT@COCl. Then the reaction of MVCNT@COCl and MoO₂(acac)₂ resulted in direct immobilization of the MoO₂(acac)₂ and the formation of MVCNT@CO(acac)MoO₂(acac) catalyst. In addition, the MVCNT@COCl was esterified by NaOC₂H₅ and formed the esteric MVCNT@COC₂H₅ reagent. In a subsequent reaction of MVCNT@COC₂H₅ by ethylene diamine, the MVCNT@CONHCH₂CH₂NH₂ was produced. It was reacted with MoO₂(acac)₂ and immobilized the MoO₂(acac)₂ via imine bond formation and produced the MVCNT@CONHCH₂CH₂N(acac)MoO₂(acac) catalyst. The functionalized MVCNT reagents were characterized by FT-IR spectra and elemental analysis. The molybdenum loading on MVCNT was determined by ICP analysis. The catalytic activity of the two molybdenum immobilized catalysts (MVCNT@COMoO₂(acac)₂ and MVCNT@CONHCH₂CH₂N(acac)MoO₂(acac)) was investigated in the epoxidation of cyclooctene and different reaction parameters such as solvent, oxidant, amount of catalyst and oxidant were optimized and the epoxidation of different alkenes was investigated in these optimized conditions. The obtained results showed that the supported catalysts of MVCNT@CO(acac)MoO₂(acac)₂ and MVCNT@CONHCH₂CH₂N(acac)MoO₂(acac) were highly active and selective in the epoxidation of a wide range of alkenes. The reusability of the supported catalysts was also studied. The results showed that they had good reusability in the epoxidation of alkenes.*

KEYWORDS: *Carbon nano tube; Immobilization; Mo; Epoxidation; Alkene.*

INTRODUCTION

Epoxides are very important intermediates for the synthesis of a wide variety of fine chemicals and find a range of applications in the pharmaceutical industry as drug intermediates, preparation of epoxy resins, polymers and paints. They are normally prepared by oxidizing C=C double bonds in the presence of different oxygen donors such as NaIO4, NaOCl, PhIO, ROOH, and H_2O_2 over a homogeneous or heterogeneous catalysts. Many highly active transition metal complexes of Co, Ti, Mn, Mo, and V were used as homogeneous catalyst in epoxidation of alkenes [1]. However, these homogeneous catalysts are often more difficult to handle and expensive to prepare or purchase. Some industrial problems such as corrosion, deposition on reactor wall and difficulty in recovery and separation of the catalyst from reaction

products are associated with these homogeneous catalysts. Immobilization of the homogeneous catalysts over the organic or inorganic supports is one of the most important strategies to overcome these problems, retaining the advantageous of transition metal complex catalysts [2-4]. In recent years, there has been an enormous groth in the use of supported transition-metal complex catalysts and the area is a current subject of intense research activity [5-11]. Different approaches have been used for immobilization of active metal complexes on various supports. During the last decade Carbon Nano Tubes (CNTs) have attracted mch attention in the synthesis, characterization, and applications due to their unique structural, mechanical, thermal, optical and electronical properties [12-14]. The easy functionalization and nonsolubility of CNTs in the most solvent have candidate theme as useful support for immobilization of many active metal complexes. In this research we describe the immobilization of the $MoO_2(acac)_2$ onto the MCNTs and catalytic study of the prepared catalysts in epoxidation of the alkenes.

EXPERIMENTAL SECTION

All materials were commercial reagent grade and obtained from Merck. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4,000 cm^{-1} with a Perkin Elmer instrument. All GC yields based on starting materials were obtained by using Teif Gostar Faraz Co with silicon-DC 200 column.

Preparation of MWCNT@COCl

MWCNT (3 g) was added in a 100 mL round bottom flask equipped with a magnetic stirring bar containing 50 mL $SOCl_2$ and the content was stirred for 5 h at 90 ℃. After filtration, the obtained solid was washed four times with benzene (under a hood) and dried in the air under a hood.

Preparation of MWCNT@COOEt

In a 100 mL round bottom flask equipped with a magnetic stirring bar containing 20 mL ethanol and 3 mL concentrated H_2SO_4 was added MWCNT (1 g) and the content was refluxed for 20 h. After evaporation of the solvent, the obtained solid was washed with 2:1 mixture of $MeOH/H_2O$. The filtrate solution was checked with tornosol paper and the washing of solid was continued

until that the filtrate solution neutralized. Then the obtained solid was dried in air.

Preparation of MWCNT@CONHCH₂CH₂NH₂

In a 50 mL round bottom flask equipped with a magnetic stirring bar containing 20 mL ethylene diamine was added MWCNT@COCl (1g). After stirring at 80 ℃ for 15 h the content was filtered off and the solid washed with methanol and dried in air.

Preparation of MWCNT@CO(acac)MoO₂(acac)

MWCNT@COOEt (1 g) and $MoO_2(acac)_2$(1.5 g) were added in a 100 mL round bottom flask equipped with a magnetic stirring bar containing 50 mL benzene After refluxing for 24 h the content was filtered off and the solid was washed with $CHCl_3$ until the filtered solvent was cleared and after that it was dried in air (caution: all these works must be done under a hood).

Preparation of MWCNT@CONHCH₂CH₂N(acac)MoO₂(acac)

MWCNT@CONHCH₂CH₂NH₂ (1g) and $MoO_2(acac)_2$(1.5 g) were added in a 100 mL round bottom flask equipped with a magnetic stirring bar containing 50 mL DMF. After stirring for 20 h at 110 ℃ the content was filtered off and the obtained solid was washed with $CHCl_3$ until the filtrate solvent was cleared and then it was dried in air.

General procedures of epoxidation of alkenes

To a 25 mL round-bottom flask equipped with a magnetic stirring bar were added CCl_4(4 mL), alkene (0.5 mmol), tert- butylhydroperoxide(TBHP) (1.5 mmol) and catalyst (0.0075 g) and refluxed. The progress of the reaction was monitored by GLC.

RSULTS AND DISCUSION

Scheme 1 shows the preparation procedures of the functionalized MWCNT. The (MWCNT(MWCNT@COOH) was reacted with SO_2Cl_2, resulted in preparing the MWCNT@COCl. In the other reaction for the preparation of the MWCNT@COOEt, it was reacted with $NaOC_2H_5$ in HOC_2H_5 in the refluxed conditions.

The MWCNT@CONHCH₂CH₂NH₂ was also prepared by reaction of MWCNT@COOEt and ethylenediamine. The FT-IR spectroscopy was used to confirm the functional groups' production or transformation.
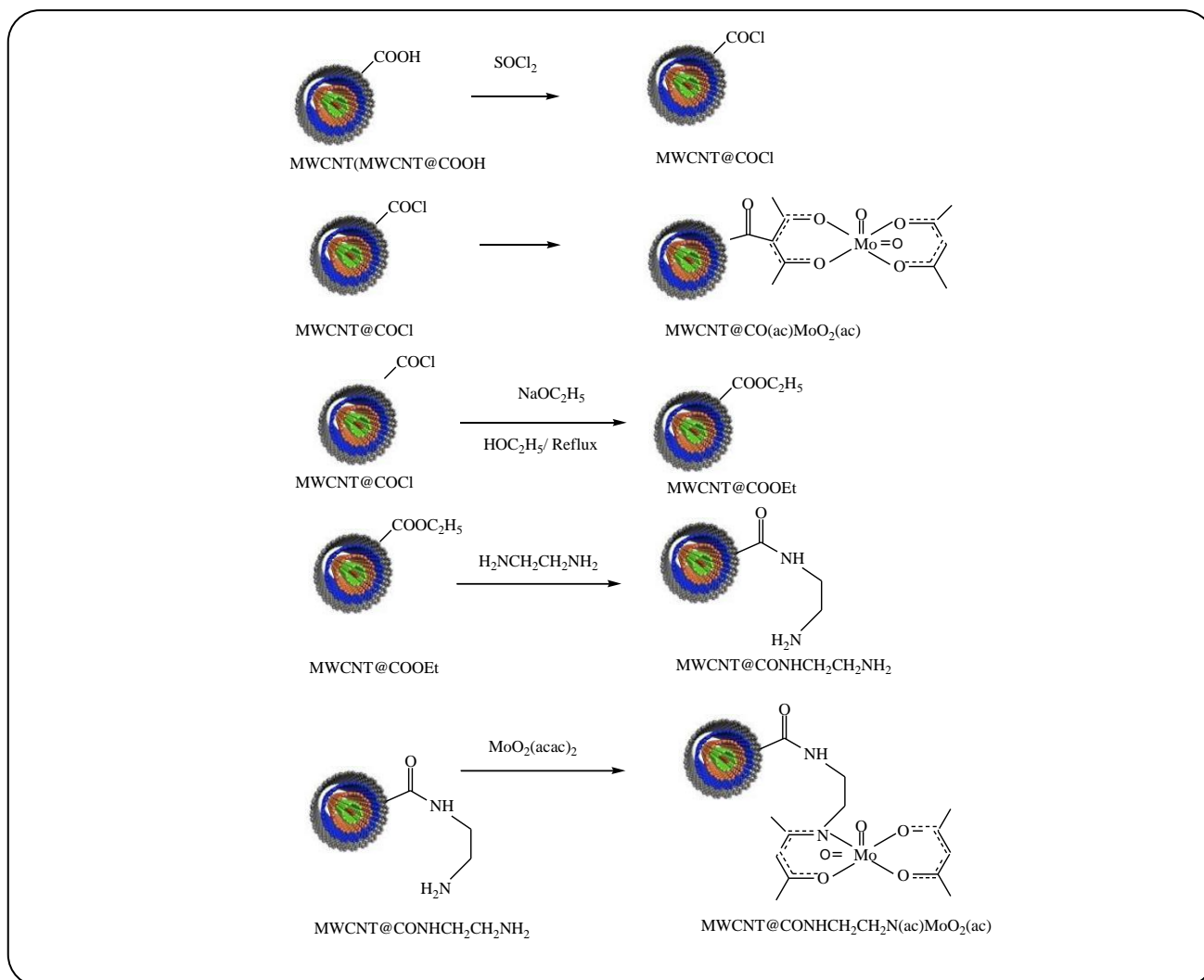
Scheme 1: Preparation procedures of the MWCNT@CO(ac)MoO₂(ac) and MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac).

The principal evidence for the construction of functional groups onto MWCNT is the appearance and the loss of IR peaks that corresponded to the introduction or transformation of distinct functional groups in each stage. Along the above functional group conversions, appreciable changes appeared in the FT-IR spectrum of them respect to the originated CNT. The MWCNT@COOH shows a sharp band at 1716 cm^{-1} and a very broad band in the region of 3200-3500 cm^{-1} due to the carbonyl(C=O) and hydroxyl(O-H) stretching vibration frequencies, respectively. By chlorination of the MWCNT@COOH the $v_{C=O}$ was shifted to the higher frequencies and appeared at 1776 cm^{-1} and the intensity of the broad band was very decreased. By contrast in the esterification reaction the $v_{C=O}$ was shifted to the lower frequencies

and appeared at 1580 cm^{-1} as a very sharp band. In the FT-IR spectrum of the MWCNT@CONHCH₂CH₂NH₂ a new sharp band at 1654 cm^{-1} and a broad band at the region of 3200-3500 cm^{-1} appeared that corresponded to the $v_{C=O}$ and v_{N-H}, respectively. The two functionalized MWCNT@COCl and MWCNT@CONHCH₂CH₂NH₂ were used to immobilization of the MoO₂(acac)₂ by C-C and C=N (imine) bond formation, respectively (scheme 1) resulting to preparing the MWCNT@CO(ac)MoO₂(ac) and MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac). In the FT-IR spectrum of the MWCNT@CO(ac)MoO₂(ac) the characteristic bands of the MoO₂$^{2+}$ moiety appeared as two bands at the 931 cm^{-1} and 901 cm^{-1} due to the asymmetric and symmetric vibration frequencies of Mo=O bonds whereas these bands

Table 1: Epoxidation of the cyclooctene in different oxidant media by the catalytic amount of the MWCNT@CO(ac)MoO₂(ac)
and MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac) catalysts in the presence of TBHP in CCl₄*

Run	Solvent	Oxidant	Time (min)	Epoxide yield(%)	
				MWCNT@CO(ac)MoO$_2$(ac)	MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac)
1	CCL$_4$	TBHP	60	81	81
2	CH$_3$CN/H$_2$O (3 : 2)	H$_2$O$_2$	60	No reaction	No reaction
3	n-Hexan	H$_2$O$_2$	60	No reaction	No reaction
4	n-Hexan	TBHP	60	35	35
5	THF	H$_2$O$_2$	60	4.5	4.5
6	CH$_3$CN	H$_2$O$_2$	60	9	7
7	CH$_3$CN/H$_2$O (3 : 2)	NaIO$_4$	60	9	9.5

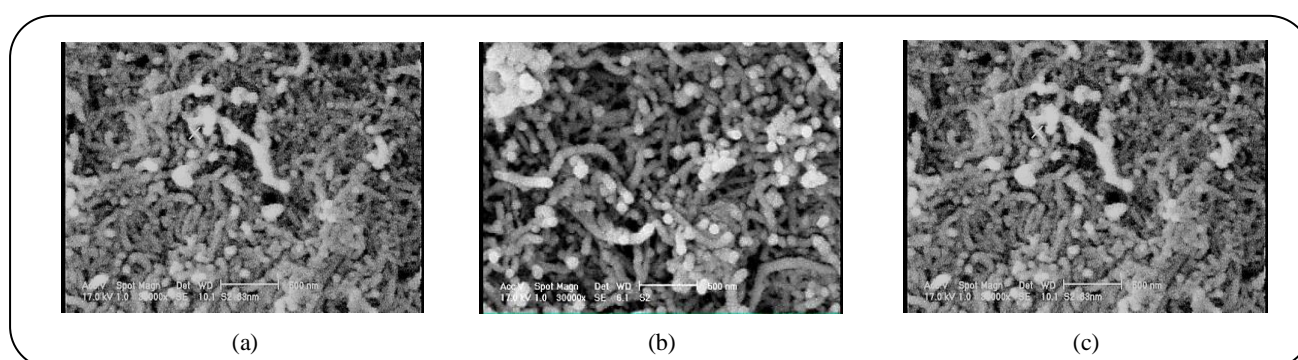(a)   (b)   (c)

Fig 1: a) The SEM of the MVCNT, b) MWCNT@CO(ac)MoO₂(ac) and c). MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac).

were finely seen at 928 and 892 cm^{-1} for the MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac). All of the FT-IR spectra were given as supplementary materials as SF1-SF7. The SEMs of the MWCNT(MWCNT@COOH and two immobilized catalysts were given in Fig 1 that confirm the preservation of the nano tube structures during the functionalization. The nitrogen content of the MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac) was determined by elemental analysis that showed the 1.73% N. The molybdenum loading of the two immobilized catalysts (MWCNT@CO(ac)MoO$_2$(ac) and MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac)) were determined by ICP analysis which showed 2.26% and 1.67% of Mo, respectively. In order to investigate the catalytic activity of the two immobilized MWCNT@CO(ac)MoO$_2$(ac) and MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac) catalysts in epoxidation reaction, the cyclooctene was used as a model substrate and different reaction parameters were investigated and optimized. Different oxygen donors

(TBHP, H$_2$O$_2$, NaIO$_4$) in different media were used in this reaction (Table 1).

The results showed that the TBHP in the CCl$_4$ was the suitable media for the catalytic epoxidation of the cyclooctene because of the high epoxide yield in the presence of the two supported catalysts.

This may be related to the ability of TBHP and the inability of H$_2$O$_2$ and NaIO$_4$ to mix with the organic substrate phase. The cyclooctene/oxidant ratio in the epoxidation reaction of cyclooctene by the MWCNT@CO(ac)MoO$_2$(ac) and MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac) catalysts were also investigated (Fig 2 and Fig 3). According to these plots, the 1:3 and 1:2 ratios of cyclooctene/oxidant were chosen as an optimal ratio because high epoxide yield was obtained in these ratios by the MWCNT@CO(ac)MoO$_2$(ac) and MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac) catalysts, respectively. The effect of catalyst amount in epoxidation of the cyclooctene in CCl$_4$ as a solvent and in the presence of TBHP as an oxidant was showed in Fig. 4
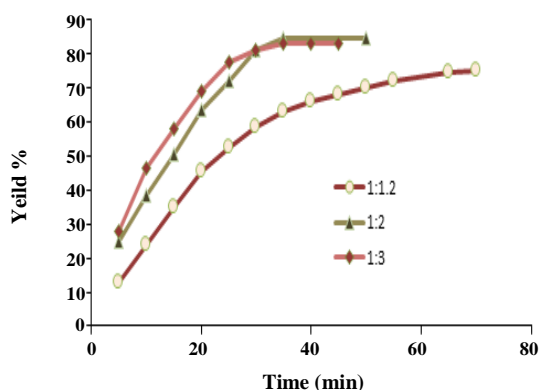
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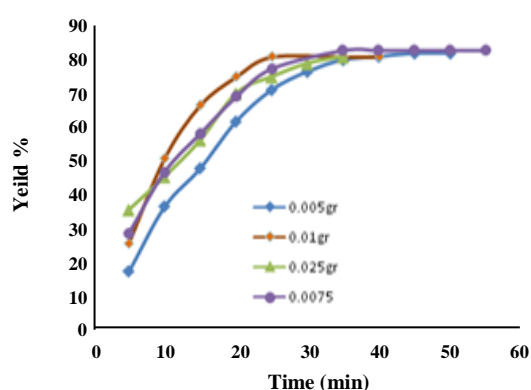*Fig. 2: Epoxidation of the cyclooctene in different alkene/oxidant ratio by the catalytic amount of MWCNT@CO(ac)MoO$_2$(ac)in the presence of TBHP in CCl$_4$.*

Fig. 4: Epoxidation of the cyclooctene by the different amounts of MWCNT@CO(ac)MoO$_2$(ac) in the presence of TBHP in CCl$_4$.
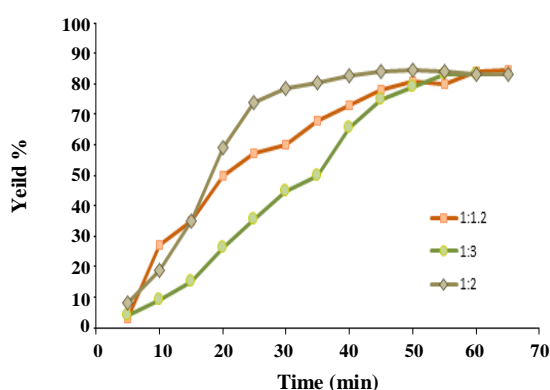

Fig. 3: Epoxidation of the cyclooctene in different alkene/oxidant ratio by the catalytic amount of MWCNT@CONHCH$_2$CH$_2$N (ac)MoO$_2$(ac)in the presence of TBHP in CCl$_4$.
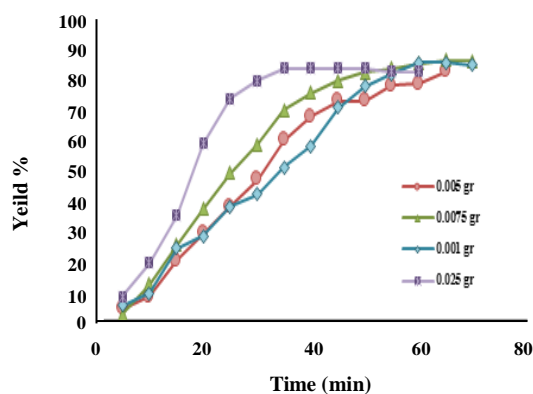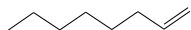

Fig. 5: Epoxidation of the cyclooctene by the different amounts of MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac) in the presence of TBHP in CCl$_4$.

and Fig. 5. The epoxidation reaction was carried out by using four amounts of catalysts (0.0025, 0.005, 0.0075, and 0.01g) with the keeping of other conditions. According to these plots it is clear that the increasing of catalyst amount from 0.0025g to 0.0075g resulted in increasing the epoxide yield but increasing this amount from 0.0075 g to 0.01g has no appreciable effect on the epoxide yield and at the end of the reaction the epoxide yield by these two amounts is near the same. Thus the optimal amounts of 0.0075g of the two catalysts can be chosen as the optimal amounts providing the highest epoxide yields. Figs. 6 and 7 illustrate the results of the epoxidation of cyclooctene in different solvents. in the presence of TBHP as an oxidant with a catalytic amount of the supported catalysts of MWCNT@CO(ac)MoO$_2$(ac)

and MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac). The observed trend for two catalysts was CCl$_4$ > CHCl$_3$ > CH$_3$CN > MeOH > THF. The high epoxide yield was found in the solvents with low coordination ability and low dielectric constant such as CCl$_4$, CHCl$_3$. Recently the mechanistic aspects of molybdenum(VI)-catalysed epoxidation reaction in the presence of TBHP were investigated by many researchers [15-18]. In the mechanism cycle, they generally believed that the TBHP coordinated to the molybdenum center and activated by the metal center and then oxygen transformed to the substrate.

In addition, the high epoxide yields obtained in the chlorinated solvents such as CCl$_4$, CHCl$_3$, 1,1,2,2-tetrachloroethane, and 1, 2, dichloroethane [16-19]. The observed trends for solvent effect in this research

Table 2: Epoxidation of the cyclooctene in different oxidant media by the catalytic amount of the MWCNT@CO(ac)MoO₂(ac) and MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac) catalysts in the presence of TBHP in CCl₄*.

Alkene	MWCNT@CO(ac)MoO$_2$(ac)		MWCNT@CONHCH$_2$CH$_2$N(ac)MoO$_2$(ac)	
	Time (min)	Epoxide yield(%)	Time(min)	Epoxide(yield)
(alkene structure)	440	53	440	58
(alkene structure)	270	72	300	78
(alkene structure)	240	12	290	17
(alkene structure)	95	59	110	68
(alkene structure)	100	54	120	58

*Ration conditions: cyclooctene (0.5 mmol), TBHP Oxiant (1.5mmol in the case of MWCNT@CO(ac)MoO₂(ac) but 1 mmol in the case of MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac)), catalyst(0.0075g), Solvent (5 mL)
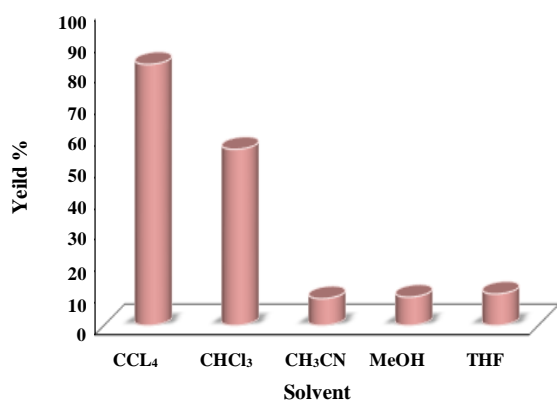

Fig. 6: Epoxidation of the cyclooctene by the catalytic amount of MWCNT@CO(ac)MoO₂(ac) in the presence of TBHP in different solvents.
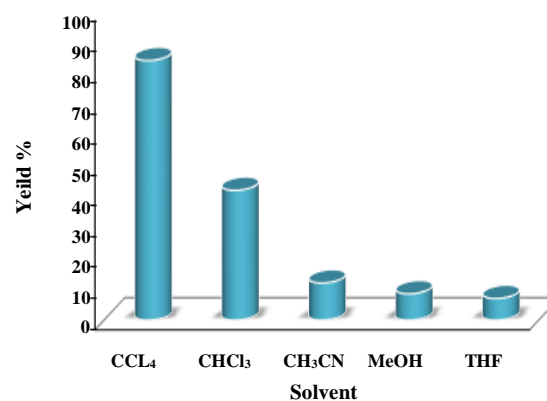

Fig. 7: Epoxidation of the cyclooctene by the catalytic amount of MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac) in the presence of TBHP in different solvents.

also, agree with this mechanism. Based on the mechanism cycle, it can be explained by hard-soft acid–base theory.

The solvents such as methanol, THF, and acetonitrile containing hard coordinate donating atoms (O and N as hard bases) tend strongly to link to the hard metal centers such as Mo(VI) (as hard acid). On the other hand, all of chlorinated solvents do not have any coordination ability to the metal (molybdenum(VI)) center. As the coordination ability of the solvent increases, the solvent competes with TBHP for coordination to the molybdenum(VI) and inhibits the TBHP coordination and retards the reaction progress, resulting in decreasing the epoxide yield [20]. In order to characterization of the epoxidation reaction

product, in a typical reaction, after completion of the reaction in the optimized conditions in the presence of MWCNT@CO(ac)MoO₂(ac) catalyst, the reaction mixture was filtered off and the cyclooctene epoxide was isolated by column chromatography method and characterized by ^{1}HNMR spectroscopy. The [1]NMR spectrum of the cyclooctene epoxide isolated by column chromatography from reaction of cyclooctene in optimized conditions by the MWCNT@CO(ac)MoO₂(ac)) catalyst was given in supplementary material(F8). After obtaining the optimal conditions the epoxidation of the alkenes was done in these conditions (Table 2). The results showed that these two catalysts convert the alkenes to their epoxids in good

Table 3: The reusability of the MWCNT@CO(ac)MoO₂(ac) and MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac).*

Run	Time(min)	Epoxide yield (%)	
		MWCNT@CO(ac)MoO₂(ac)	MWCNT@CONHCH₂CH₂N(ac)MoO₂(ac)
1	60	84	84
2	60	84	84
3	60	83	84.5
4	60	83	83
5	60	81	83
6	60	81	81
7	60	73	79
8	60	56	68
9	60	48	50

yields. The reusability of the catalysts was also investigated (Table 3). The results showed that the activity of these two supported catalysts was maintained for three times but by using in the other sequential reactions the activity of the catalysts was decreased after 8 times and the epoxide yield dropped to about 50%. In comparison to our recent works [20-22] it can be mentionedthat the reusability of these supported catalysts is lower than those polymer-supported molybdenum catalysts.

CONCLUSIONS

In conclusion, we functionalized the MVCNT with different reagents and immobilized the MoO₂(acac)₂ onto the MVCNT via these functionalized MVCNTs and used as epoxidation catalysts. Different reaction parameters were optimized. The obtained results showed that the supported molybdenum based catalysts on MVCNT showed sufficient activity and reusability in epoxidation of the alkenes.

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