

## Multi-wall Carbon Nanotubes Supported Molybdenum Acetylacetonate: Efficient and Highly Reusable Catalysts for Oxidation of Sulfides with *Tert*-butyl Hydroperoxide

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In the present work, highly efficient oxidation of sulfides catalyzed by  $\text{MoO}_2(\text{acac})_2$  supported on multi-wall carbon nanotubes, MWCNTs, modified with 1,2-diaminobenzene (DAB) and 2-aminophenol (AP), at room temperature are reported. The effects of various parameters such as reaction time, solvent, catalyst amount, oxidant, *etc.*, were studied. These heterogenized catalysts showed high activity in the oxidation of a variety of linear, cyclic and aromatic sulfides with *tert*-butyl hydroperoxide (TBHP) in 1,2-dichloroethane as solvent under mild conditions. In these systems sulfides have been selectively oxidized to the corresponding sulfoxides and sulfones with short reaction times and high yields. In the case of aromatic sulfides, sulfoxide was produced as major product and in the case of linear sulfides only sulfoxide was produced. The  $[\text{MoO}_2(\text{acac})_2/\text{amines-MWCNT}]$  catalysts are stable under the reaction conditions and While, the homogeneous  $\text{MoO}_2(\text{acac})_2$  cannot recovered even one time, the MWCNT supported catalysts can be filtered and reused several times without significant loss of their activity.

**Keywords:** Molybdenum acetylacetonate, Multi-wall carbon nanotubes, Heterogeneous catalyst, Oxidation

### INTRODUCTION

Catalytic oxidation processes play a key role in the manufacture of bulk and fine chemicals [1-3]. Sulfoxides and sulfones are potential intermediates for the synthesis of chemically and biologically important molecules which are generally prepared *via* oxidation of the corresponding sulfides [4-13]. However, some of these methods have drawbacks such as the use of corrosive acids, toxic metallic compounds and the formation of environmentally unfavorable by-products. Consequently, safer and simple protocols are required [14], towards selective products, such as the efficient conversion of sulfide to sulfoxides and sulfones [15].

Molybdenum(VI) complexes are good catalysts for the oxidation of organic compounds, usually employing *tert*-butyl hydroperoxide (*t*-BuOOH) as the mono-oxygen source [16-22]. Despite the good results obtained for oxomolybdenum(VI) complexes in homogeneous catalysis, increasing attention is being drawn to developing heterogeneous catalysts since these can be easily separated from a reaction mixture and recycled, which is of significant industrial interest. Different methods have been used to immobilize molybdenum on various supports to obtain heterogeneous catalysts [123-37].

Carbon nanotubes (CNTs) have attracted enormous interest these years due to their extraordinary properties, such as excellent mechanical, electrical, thermal and optical properties [38-40]. Since CNTs are insoluble in the most solvents and provide high surface areas, these materials can be used as catalysts support [41-43]. The use of CNTs as

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catalyst supports, especially in liquid-phase reactions, seems to be one of the most promising fields among all their applications. Inorganic nanomaterials supported on CNTs present unusual catalytic behavior comparing with those loaded on other normally used supports. Because of their small sizes, CNT-supported catalytic nanoparticles can be uniformly dispersed in organic solvents by stirring. Recycling CNT-supported catalysts can be accomplished by gravitational sedimentation. The special structured topology of the CNTs surface introducing a characteristic periodicity and play a positive role when these materials are used as supports in heterogeneous catalysis. The CNT-supported catalysts show excellent catalytic activities for many organic reactions [44-55].

Recently, [MoO<sub>2</sub>(acac)@DAB-MWCNT] and [MoO<sub>2</sub>(acac)@AP-MWCNT] have been used for epoxidation of alkenes with *tert*-butyl hydroperoxide [54, 55]. Here, we report the use of these catalysts in oxidation of sulfides with *tert*-BuOOH (Scheme 1). The stability and reusability of these catalysts were also investigated in the oxidation reactions.

## EXPERIMENTAL

All materials were of commercial reagent grade. Sulfides (entries 1, 8, 9 and 10) were purchased from Merck chemical company and the others were prepared according to the reported procedure [56]. [MoO<sub>2</sub>(acac)@DAB-MWCNT] and [MoO<sub>2</sub>(acac)@AP-MWCNT] were prepared as previously published [54,55]. FT-IR spectra were obtained as potassium bromide pellets in the range 500-4000 cm<sup>-1</sup> with a Bomen-Hartmann instrument. <sup>1</sup>H 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). The specifications of multi-wall carbon nanotubes containing carboxylic acid groups, MWCNT-

COOH, are as follows: outside diameter 20-30 nm, inside diameter 5-10 nm, length 30 μm, COOH content 1.5% and specific surface area >110 m<sup>2</sup> g<sup>-1</sup>.

### General Procedure for Oxidation of Sulfides with TBHP Catalyzed by [MoO<sub>2</sub>(acac)@DAB-MWCNT] and [MoO<sub>2</sub>(acac)@AP-MWCNT]

In a 25 ml round bottom flask equipped with a magnetic stirrer bar, sulfide (1 mmol), *tert*-BuOOH (2 mmol, 80% solution in di-*tert*-butylperoxide), [MoO<sub>2</sub>(acac)@DAB-MWCNT] (40 mg, 0.0074 mmol) or [MoO<sub>2</sub>(acac)@AP-MWCNT] (50 mg, 0.0013 mmol) and 1,2-dichloroethane (5 ml) were mixed under stirring at room temperature. The reaction progress was monitored by GC or TLC. At the end of the reaction, the reaction mixture was diluted with Et<sub>2</sub>O (20 ml) and filtered. The catalyst was thoroughly washed with Et<sub>2</sub>O and the combined washing and filtrates were purified on a silica gel plate to obtain the pure product. FT-IR and <sup>1</sup>H NMR spectral data confirmed the identities of the products. Blank experiment in the absence of catalyst and using the same experimental conditions was also performed.

### Reusability of the Catalysts

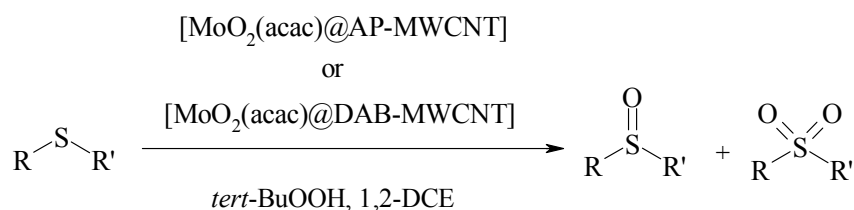
The reusability of the catalysts was studied in the repeated oxidation reaction of diphenyl sulfide. The reactions were carried out as described above. At the end of each reaction, the catalysts were filtered, washed thoroughly with Et<sub>2</sub>O and dried before using in the next run.

## RESULTS AND DISCUSSION

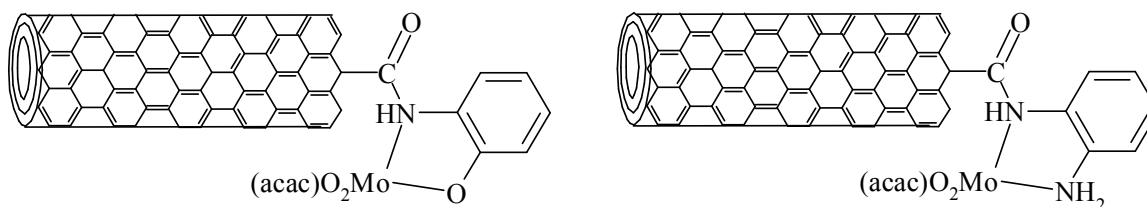
### Catalytic Experiments

The structures of the two catalysts are exhibited in Fig. 1. The prepared catalysts were used for oxidation of sulfides with *tert*-BuOOH at room temperature. First, the reaction parameters such as catalyst amount, oxidant and kind of solvent were optimized in the oxidation of diphenyl sulfide.

**The effect of catalyst amount on the oxidation of diphenyl sulfide catalyzed by [MoO<sub>2</sub>(acac)@DAB-MWCNT] and [MoO<sub>2</sub>(acac)@AP-MWCNT].** Different amounts of catalyst were used to optimize the catalyst amount and the best results were obtained in the presence of



*Scheme 1.* Oxidation of sulfides with *tert*-BuOOH catalyzed by [MoO<sub>2</sub>(acac)@DAB-MWCNT] and [MoO<sub>2</sub>(acac)@AP-MWCNT]



**Fig. 1.** Molecular structures of [MoO<sub>2</sub>(acac)@AP-MWCNT] (left) and [MoO<sub>2</sub>(acac)@DAB-MWCNT] (right).

**Table 1.** Optimazation of the Catalyst Amount on the Oxidation of Diphenyl Sulfide with *tert*-BuOOH<sup>a</sup>

Catalyst amount (mg)	[Mo(O) <sub>2</sub> (acac)@DAB-MWCNT]		[Mo(O) <sub>2</sub> (acac)@AP-MWCNT]	
	Conversion (%) <sup>b</sup>	Time (min)	Conversion (%) <sup>b</sup>	Time (min)
0	5	35	7	50
10	45	35	40	50
20	63	35	56	50
30	87	35	74	50
40	100	35	92	50
50	100	35	100	50
60	-	35	100	50

<sup>a</sup>Reaction conditions: Diphenyl sulfide (1 mmol), *tert*-BuOOH (2 mmol), 1,2-dichloroethane (5 ml).

<sup>b</sup>GC yield based on the starting diphenyl sulfide.

40 mg (0.0074 mmol) of [MoO<sub>2</sub>(acac)@DAB-MWCNT] and 50 mg (0.0013 mmol) of [MoO<sub>2</sub>(acac)@AP-MWCNT]. Control experiments in the absence of catalysts and using MWCNT-DAB and MWCNT-APy as catalysts were also performed and the results showed that the amount of conversion was less than 15% (Table 1).

**The effect of oxidant on the oxidation of diphenyl sulfide.** The effect of different oxidants such as *tert*-BuOOH, Urea-H<sub>2</sub>O<sub>2</sub> (UHP) and H<sub>2</sub>O<sub>2</sub> on the catalytic

activity of [MoO<sub>2</sub>(acac)@DAB-MWCNT] in the oxidation of diphenyl sulfide was also studied. The conversion with UHP and H<sub>2</sub>O<sub>2</sub> in the presence of [MoO<sub>2</sub>(acac)@DAB-MWCNT] was only a trace even after 3 h, while in the presence of *tert*-BuOOH the reaction was complete after just 35 min. Therefore, *tert*-Butylhydroperoxide was chosen as the best oxidant.

Using different molar ratios of diphenyl sulfide to the oxidant (Table 2) shows that the 1:2 molar ratio has been

**Table 2.** Effect of Various TBHP/Sulfide Molar Ratios on the Oxidation of Diphenyl Sulfide Catalyzed by [MoO<sub>2</sub>(acac)@DAB-MWCNT] at Room Temperature

TBAP/sulfide	Time (min)	Conversion (%) <sup>a</sup>	Sulfoxide (%) <sup>a</sup>	Sulfone (%) <sup>a</sup>
1:2	35	100	90	8
1:1	35	85	80	5
2:1	35	40	40	-

<sup>a</sup>GC yield based on the starting diphenyl sulfide.

**Table 3.** The Effect of Solvent on the Oxidation of Diphenyl Sulfide with *tert*-BuOOH<sup>a</sup>

Solvent	[Mo(O) <sub>2</sub> (acac)@DAB-MWCNT]		[Mo(O) <sub>2</sub> (acac)@AP-MWCNT]	
	Conversion (%) <sup>b</sup>	Time (min)	Conversion (%) <sup>b</sup>	Time (min)
ClCH <sub>2</sub> CH <sub>2</sub> Cl	100	35	100	50
CCl <sub>4</sub>	70	35	66	50
CHCl <sub>3</sub>	65	35	67	50
CH <sub>2</sub> Cl <sub>2</sub>	55	35	51	50
CH <sub>3</sub> CN	30	35	31	50
CH <sub>3</sub> COCH <sub>3</sub>	20	35	18	50

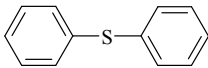
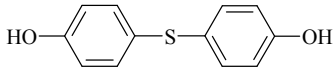
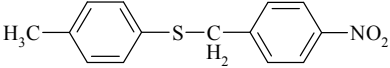
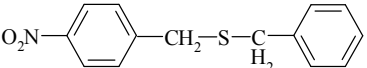
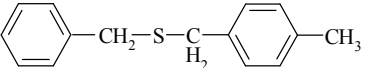
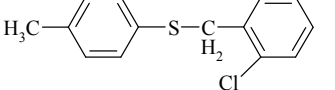
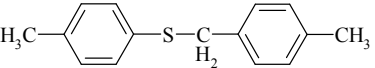
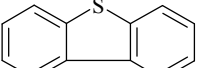
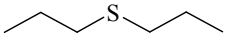
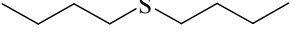
<sup>a</sup>Reaction conditions: Diphenyl sulfide (1 mmol), *tert*-BuOOH (2 mmol), [Mo(O)<sub>2</sub>(acac)@DAB-MWCNT] (40 mg, 0.0074 mmol), [Mo(O)<sub>2</sub>(acac)@AP-MWCNT] (50 mg, 0.0013 mmol), 5 ml solvent. <sup>b</sup>GC yield based on the starting diphenyl sulfide.

found to be the optimized one to obtain the highest conversion. While higher ratios of TBHP to the diphenyl sulfide increase the total conversion of the reaction (Table 2), the over-oxidation of sulfoxide to sulfone decreases the chemoselectivity of the reaction. However, the use of a 2:1 molar ratio leads to the selective oxidation of diphenyl sulfide to the corresponding sulfoxide.

#### The effect of solvent on the oxidation of diphenyl

**sulfide.** The effect of different solvents on the catalytic activity of the resulting catalyst was investigated in the oxidation of diphenyl sulfide with *tert*-BuOOH. Among the different solvents such as acetonitrile, acetone, 1,2-dichloroethane, chloroform and carbon tetrachloride, 1,2-dichloroethane was chosen as the best reaction medium, because the higher catalytic activity was observed in this solvent (Table 3). As reported previously, in the oxidation

**Table 4.** Oxidation of Sulfides with *tert*-BuOOH Catalyzed by [MoO<sub>2</sub>(acac)<sub>3</sub>@DAB-MWCNT] at Room Temperature<sup>a</sup>

Entry	Sulfide	Time (min)	Conversion (%) <sup>b</sup>	Sulfoxide (%) <sup>b,c</sup>	Sulfone (%) <sup>b,c</sup>	TOF (h <sup>-1</sup> )
1		35	100	90	8	231.8
2		40	98	80	18	198.8
3		50	96	96	-	155.7
4		65	96	91	5	119.8
5		35	98	93	5	227.2
6		50	95	95	-	154.1
7		30	98	98	-	264.9
8		40	94	10	84	190.7
9		15	100	100	-	540.5
10		25	100	100	-	324.8

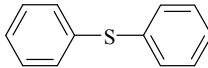
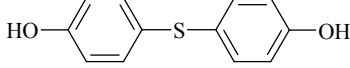
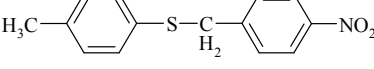
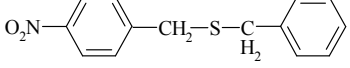
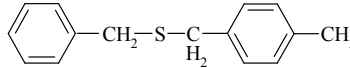
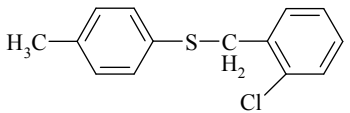
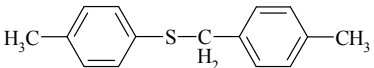
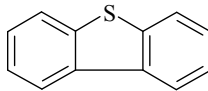
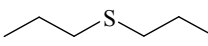
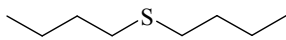
<sup>a</sup>Reaction conditions: sulfide (1 mmol), *tert*-BuOOH (2 mmol), catalyst (40 mg, 0.0074 mmol) and 1,2-dichloroethane (5 ml). <sup>b</sup>GC (entries 1, 9 and 10) or Isolated yield. <sup>c</sup>All products were identified by comparison of their physical and spectral data with those of authentic samples.

of hydrocarbons catalyzed by molybdenum-based catalysts, non-coordinating solvents such as chlorinated ones are the best solvents [55].

**Oxidation of sulfides with *tert*-BuOOH catalyzed by [MoO<sub>2</sub>(*acac*)@DAB-MWCNT] and [MoO<sub>2</sub>(*acac*)@AP-MWCNT].** Under the optimized conditions, both catalytic systems were applied for oxidation of sulfides (Tables 4 and 5). The obtained results in the presence of [MoO<sub>2</sub>(*acac*)@DAB-MWCNT] and [MoO<sub>2</sub>(*acac*)@AP-MWCNT] showed that these catalysts are efficient catalysts in the oxidation of

a wide range of sulfides, including linear, cyclic and aromatic ones. In both catalytic systems, sulfides were converted to their corresponding sulfoxides and sulfones in excellent yields at room temperature. In the case of aromatic sulfides, sulfoxide was produced as major product. In the case of dibenzothiophene, the major product was sulfone which was obtained in 84% and 53% yield in the presence of [MoO<sub>2</sub>(*acac*)@DAB-MWCNT] and MoO<sub>2</sub>(*acac*)@AP-MWCNT], respectively. In the case of linear sulfides such as dipropyl and dibutyl sulfides, only

**Table 5.** Oxidation of Sulfides with *tert*-BuOOH Catalyzed by [MoO<sub>2</sub>(*acac*)@AP-MWCNT] at Room Temperature<sup>a</sup>

Entry	Sulfide	Time (min)	Conversion (%) <sup>b</sup>	Sulfoxide (%) <sup>b,c</sup>	Sulfone (%) <sup>b,c</sup>	TOF (h <sup>-1</sup> )
1		50	100	85	13	923.4
2		55	98	75	23	823.0
3		60	96	96	-	738.5
4		70	95	90	5	626.7
5		45	98	90	8	1005.1
6		70	92	80	12	606.9
7		45	98	90	8	1005.1
8		60	93	40	53	715.4
9		30	100	100	-	1538.5
10		30	100	100	-	1538.5

<sup>a</sup>Reaction conditions: sulfide (1 mmol), *tert*-BuOOH (2 mmol), catalyst (50 mg, 0.0013 mmol) and 1,2-dichloroethane (5 ml). <sup>b</sup>GC (entries 1, 9 and 10) or isolated yield. <sup>c</sup>All products were identified by comparison of their physical and spectral data with those of authentic samples.

**Table 6.** Comparison of the Results Obtained for Oxidation of Diphenyl Sulfide Catalyzed by [Mo(O)<sub>2</sub>(acac)@AP-MWCNT] and [Mo(O)<sub>2</sub>(acac)@DAB-MWCNT] with some of those Reported in the Literature

Entry	Catalyst	Support	Oxidant	Conditions (°C)/Solvent	TOF (h <sup>-1</sup> )	Ref.
1	MoO <sub>2</sub> (acac) <sub>2</sub>	AP-MWCNT	TBHP	RT/DCE	923.4	This work
2	MoO <sub>2</sub> (acac) <sub>2</sub>	ATP-MWCNT	TBHP	RT/DCE	231.8	This work
3	Mn(T <sub>4</sub> PyP)	Polystyrene	NaIO <sub>4</sub>	RT/CH <sub>3</sub> CN-H <sub>2</sub> O	29.8	[3]
4	Mn(TPP)Cl	Silica	NaIO <sub>4</sub>	RT/CH <sub>3</sub> CN-H <sub>2</sub> O	40.1	[4]
5	Mn(TPP)Cl	Silica	NaIO <sub>4</sub>	US/CH <sub>3</sub> CN-H <sub>2</sub> O	196.1	[4]
6	Mn(Br <sub>8</sub> TPP)Cl	Silica	NaIO <sub>4</sub>	RT/CH <sub>3</sub> CN-H <sub>2</sub> O	33.3	[4]
7	Mn(Br <sub>8</sub> TPP)Cl	Silica	NaIO <sub>4</sub>	US/CH <sub>3</sub> CN-H <sub>2</sub> O	133.3	[4]
	VOCl <sub>3</sub>	Silica	H <sub>2</sub> O <sub>2</sub>	RT/CH <sub>3</sub> CN	33.68	[5]
8	[Mn(salophen)Cl]	Polystyrene	NaIO <sub>4</sub>	US/CH <sub>3</sub> CN-H <sub>2</sub> O	86.81	[6]

**Table 7.** Investigation of Catalyst Reuse and Stability in the Oxidation of Diphenyl Sulfide with *tert*-BuOOH at Room Temperature<sup>a</sup>

Run	MoO <sub>2</sub> (acac)@DAB-MWCNT			MoO <sub>2</sub> (acac)@AP-MWCNT		
	Conversion (%) <sup>b</sup>	Time (min)	Mo leached (%) <sup>c</sup>	Conversion (%) <sup>b</sup>	Time (min)	Mo leached (%) <sup>c</sup>
1	100	35	1.3	100	50	1.1
2	98	35	0	98	50	0
3	98	35	0	96	50	0
4	96	35	0	95	50	0
5	96	35	0	95	50	0
6	95	35	0	94	50	0
7	94	35	0	92	50	0
8	94	35	0	90	50	0

<sup>a</sup>Reaction conditions: sulfide (1 mmol), *tert*-BuOOH (2 mmol), MoO<sub>2</sub>(acac)@DAB-MWCNT (40 mg, 0.0074 mmol), MoO<sub>2</sub>(acac)@AP-MWCNT (50 mg, 0.0013 mmol) and 1,2-dichloroethane (5 ml). <sup>b</sup>GC yield based on starting diphenyl sulfide. <sup>c</sup>Determined by ICP.

sulfoxidewas produced. These catalytic systems show high activity in the oxidation of sulfides with *tert*-BuOOH at room temperature. One reason for this behavior may be related to the nano-particle nature of the MWCNTs with high specific surface area which leads to isolation of catalytic active site and increases the catalytic activity [50]. To check the effect of atmospheric oxygen on the conversion and products distribution, the reaction of diphenyl sulfide was carried out under inert atmosphere in the presence of [MoO<sub>2</sub>(acac)@DAB-MWCNT]. No changes were observed in the conversion and selectivity under these conditions.

During the reaction, the catalysts are suspended in the solvent. This is due to the bundled agglomerates of MWCNT 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. While, other heterogeneous catalysts were aggregated more rapidly in comparison with CNTs.

In order to show the efficiency of these catalysts, the result on the oxidation of diphenyl sulfide was compared with several other recorded catalytic systems (Table 6). These comparisons show that the present catalytic systems are more efficient than the others.

### Catalyst Reuse and Stability

The reusability of a heterogeneous catalyst is of great importance from synthetic and economical points of view. While, the homogeneous MoO<sub>2</sub>(acac)<sub>2</sub> cannot recovered even one time, the MWCNT supported catalysts can be filtered and reused several times without significant loss of their activity. The reusability of [MoO<sub>2</sub>(acac)@DAB-MWCNT] and [MoO<sub>2</sub>(acac)@AP-MWCNT], were investigated in the multiple sequential oxidation of diphenyl sulfide with *tert*-BuOOH. At the end of each reaction, the catalysts were separated by simple filtration, washed with acetone and dried carefully before using in the next run. The reused catalysts were used with fresh diphenyl sulfide. The results showed that the catalysts reserve their catalytic activity for eight consecutive runs (Table 7). The filtrates were collected for determination of Mo leaching by ICP. The results showed that the amount of Mo leached is very low which confirms the strong attachment of molybdenum to the MWCNT. Also, the catalytic behavior of the

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

CNT is highly recommended for the catalyst's support because of its nanometric size, high surface area and poor solubility. Therefore, it is easily recovered and recycled without significant loss of its unique properties, while the homogeneous catalyst cannot be recovered even one time.

## CONCLUSIONS

We immobilized molybdenum acetylacetonate on MWCNTs modified with 1,2-diaminobenzene and 2-aminophenol and found that these supported catalysts were active in the oxidation of sulfides with *tert*-BuOOH. Supported catalysts are highly reactive in the oxidation of a wide range of sulfides such as linear and aromatic ones. The catalysts were highly reusable and were recycled eight times without appreciable decrease in its initial activity.

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