



Full paper/Mémoire

Efficient oxidation of alcohols with *tert*-butyl hydroperoxide catalyzed by Mo(CO)₆ supported on multiwall carbon nanotubes

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ABSTRACT

Efficient oxidation of alcohols with *tert*-butyl hydroperoxide catalyzed by Mo(CO)₆ supported on multiwall carbon nanotubes modified with 4-aminopyridine is reported. The effect of various parameters such as catalyst amount, solvent and oxidant was studied. The catalyst, [Mo(CO)₅@APy-MWCNT], showed high activity not only in the oxidation of benzylic and linear alcohols but also in the oxidation of secondary alcohols. The catalyst can be reused several times without significant loss of its activity.

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1. Introduction

Oxidation of alcohols to carbonyl compounds as crucial precursors of drugs, dyes and fine chemicals has attracted much attention in chemical research during last decades. Recently, more and more efforts have been paid in highly efficient catalytic processes for oxidation of alcohols. Successful examples include both homogeneous (e.g. Ru, Pd, Cu complexes; bi-metallic complexes systems) and heterogeneous catalysts (e.g. metal catalysts and supported catalysts, including mesoporous materials, zeolites, etc.) [1–5]. However, the common methods of alcohol oxidation may use toxic, corrosive, expensive oxidants such as chromium(VI), and setting up a severe condition, like high pressure or temperature, using strong mineral acids. Alcohols could be transformed into their corresponding ketones with good yields using Fe(III) catalysts and *t*-butyl hydroperoxide [6].

Molybdenum compounds are considered to be very effective catalysts for the oxidation of organic compounds

with TBHP [7]. A number of soluble molybdenum complexes bearing different ligands have been synthesized and employed as homogeneous catalysts for epoxidation of alkenes [8–10]. In the field of catalytic oxidations, great efforts have been made to convert homogeneous processes to selective heterogeneous ones, including the use of clean and safe oxidants such as O₂, H₂O₂ and alkyl hydroperoxides [11,12]. The immobilization of homogeneous catalysts allows overcoming the problems with separation and reuse and, thus, greatly amends the properties of the catalysts and their commercial value. Different approaches have been used for immobilization of molybdenum complexes on various supports such as silica [13–17], modified MCM-41 [18–26], zeolites [27] and layered double hydroxides [28].

Carbon nanotubes (CNTs) represent a technologically important class of nanostructure materials. These materials are regarded as highly interesting materials for heterogeneous catalysis applications due to their high thermal and chemical stability, the possibility of functionalization and high surface area [29–33]. In this regard, several CNT supported catalysts have been used for chemical transformations. For example, Pt nanoparticles supported on CNTs have been used for methanol oxidation

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[34], palladium nanoparticles supported on CNTs for semihydrogenation of phenylacetylene [35], chiral vanadyl salen complex supported on single-wall CNTs for enantioselective cyanosilylation of aldehydes [36,37], manganese(III) porphyrin supported on MWCNTs for epoxidation of alkenes with NaO_4 [38], manganese(III) salophen supported on multiwall carbon nanotubes for epoxidation of alkenes with NaO_4 [39] and molybdenum hexacarbonyl supported on amines modified multiwall carbon nanotubes, for epoxidation of alkenes with *tert*-butyl hydroperoxide [40–42].

Recently, $[\text{Mo}(\text{CO})_5@APy\text{-MWCNT}]$ has been used for epoxidation of alkenes with *tert*-butyl hydroperoxide [40]. Here, we report the use of this catalyst in oxidation of alcohols with *tert*-BuOOH.

2. Experimental

All materials were of commercial reagent grade. Alcohols were obtained from Merck or Fluka. $[\text{Mo}(\text{CO})_5@APy\text{-MWCNT}]$ was prepared as previously published [40]. A 400 W Hg lamp was used for activation of metal carbonyl. FT-IR spectra were obtained as potassium bromide pellets in the range 500–4000 cm^{-1} with a Bomen-Hartmann instrument. Scanning electron micrographs of the catalyst were taken on SEM Philips XL 30. Gas chromatography experiments (GC) were performed with a Shimadzu GC-16A instrument using a 2 m column packed 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. The products were identified by comparison of their retention times with known samples. MWCNTs containing carboxylic acid groups (multiwall carbon nanotubes with diameters between 20 and 30 nm) were purchased from Shenzhen NTP Factory (Table 1).

2.1. General procedure for oxidation of alcohols with *tert*-BuOOH catalyzed by $[\text{Mo}(\text{CO})_5@APy\text{-MWCNT}]$

In a 25 mL round bottom flask equipped with a magnetic stirrer bar and a condenser, alcohols (1 mmol), *tert*-BuOOH (2 mmol, 80% solution in di-*tert*-butylperoxide), catalyst (90 mg, 0.015 mmol) and CCl_4 (4 mL) were mixed and refluxed. The progress of the reaction was monitored by GLC. At the end of the reaction, the reaction mixture was diluted Et_2O (20 mL) and filtered. The products were extracted with CH_2Cl_2 (2×10 mL) and were purified on silica-gel plates or a silica-gel column ($\text{CCl}_4\text{-Et}_2\text{O}$, 4:1). FT IR and ^1H NMR spectral data was used to confirm the identities of the products.

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

2.2. Reusability of the catalyst

The reusability of the catalyst was studied in the repeated oxidation reaction of 4-chlorobenzyl alcohol as model substrate. The reactions were carried out as described above. When each of the repeated reactions was completed, the catalyst was filtered, washed with diethyl ether and dried before using with fresh 4-chlorobenzyl alcohol and *tert*-BuOOH. The amount of molybdenum leached into the filtrates was determined by ICP.

3. Results and discussions

3.1. Oxidation of alcohols with *tert*-BuOOH catalyzed by $[\text{Mo}(\text{CO})_5@APy\text{-MWCNT}]$

The catalytic activity of the $[\text{Mo}(\text{CO})_5@APy\text{-MWCNT}]$ was initially investigated in the oxidation of 4-chlorobenzyl alcohol with *tert*-BuOOH. First, the reaction parameters such as catalyst amount, solvent and oxidant were optimized. Different solvents were used to find the reaction media. Among the different solvents such as acetonitrile, acetone, carbon tetrachloride, chloroform and 1,2-dichloroethane; carbon tetrachloride was chosen as the reaction medium, because the higher yield was observed in this solvent (Table 2). This is due to the non-coordinating nature of this solvent which the higher catalytic activity of molybdenum-based catalysts is observed in these solvents. Different amounts of catalyst were used to optimize the catalyst amount. The best results were obtained using 90 mg (0.015 mmol) of $[\text{Mo}(\text{CO})_5@APy\text{-MWCNT}]$. Control experiments in the absence of catalyst and using MWCNT-APy as catalyst were also performed and the results showed that the amount of carbonyl compound was less than 10%.

Under the optimized conditions, the $[\text{Mo}(\text{CO})_5@APy\text{-MWCNT}]/\textit{tert}\text{-BuOOH}$ catalytic system was applied for oxidation of a wide range of primary and secondary alcohols. As shown in Table 3, benzyl alcohol and substituted benzyl alcohols are converted to their corresponding aldehydes efficiently. In the case of benzyl alcohol, after 40 min, only benzaldehyde was obtained in 100% yield. In longer reaction times (1 h), the obtained products are 60% benzaldehyde and 40% benzoic acid. The results show that the substituents have no significant

Table 2
Oxidation of 4-chlorobenzyl alcohol with *tert*-BuOOH catalyzed by $[\text{Mo}(\text{CO})_5@APy\text{-MWCNT}]$ under reflux conditions in different solvents.^a

Solvent	Yield (%) ^b	T (°C)
CCl_4	100	72
CHCl_3	72	57
$\text{ClCH}_2\text{CH}_2\text{Cl}$	68	78
CH_2Cl_2	54	38
CH_3CN	15	77
THF	5	61
$(\text{CH}_3)_2\text{CO}$	5	53

^a Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), *tert*-BuOOH (2 mmol), catalyst (90 mg, 0.015 mmol), 4 mL solvent.

^b GC yield based on the starting 4-chlorobenzyl alcohol after 50 min.

Table 3
Oxidation of alcohols with *tert*-BuOOH catalyzed by [Mo(CO)₅@APy-MWCNT] in refluxing CCl₄.

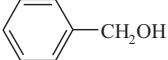
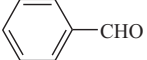
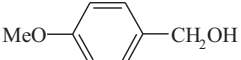

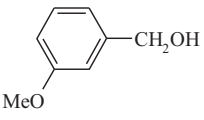
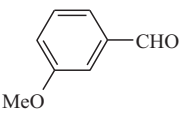

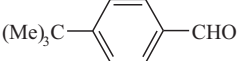
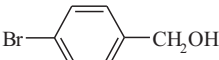
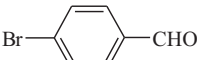
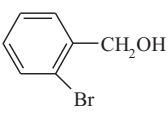
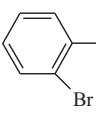
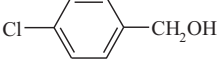
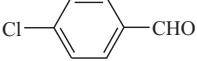
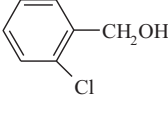
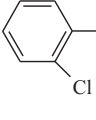
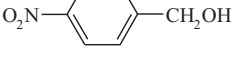
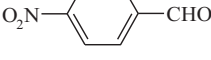
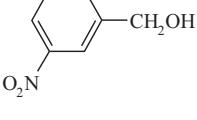
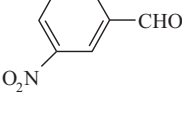
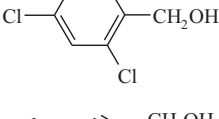
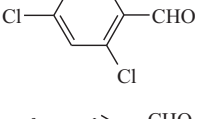


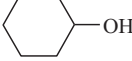
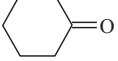
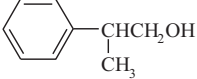
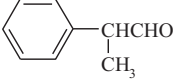
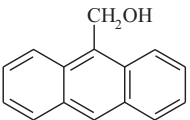
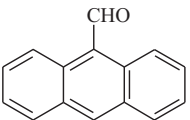
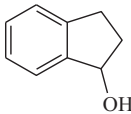
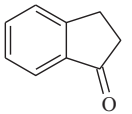

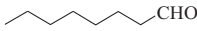
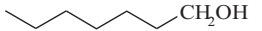
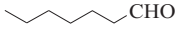
Entry	Alcohol	Product	Yield (%) ^a	Time (min)
1			100	40
2			100	35
3			100	40
4			96	90
5			100	40
6			100	45
7			100	50
8			100	50
9			94	60
10			92	65
11			100	75
12			84	80
13			88	100
14			95	90
15			87	100

Table 3 (Continued)

Entry	Alcohol	Product	Yield (%) ^a	Time (min)
16			77	90
17			71	140
18			75	140

^a GLC yield based on starting alcohol.

effect on the oxidation of benzylic alcohols. In the case of linear alcohols such as *n*-octanol, the result showed that, octanal was obtained in 71% yield. A good selectivity observed in the case of cinnamyl alcohol and only alcoholic group is oxidized and no epoxide was obtained.

[Mo(CO)₅@APy-MWCNT] was also used for oxidation of secondary alcohols and their corresponding ketones were obtained in good yields.

3.2. Catalyst reuse and stability

Heterogeneous catalysis is of great practical importance in modern industry due to the numerous advantages it involves. On the other hand, the reusability of a supported catalyst is of great importance from economical and environmental points of view, because transition metal complexes are often expensive and very toxic. Therefore, heterogenization of homogeneous catalysts makes them useful for commercial applications. The reusability of [Mo(CO)₅@APy-MWCNT] was monitored by using multiple sequential oxidation 4-chlorobenzyl alcohol with *tert*-butyl hydroperoxide (Table 4). The catalyst was consecutively reused several times (10 times were checked) without loss of its initial activity. The amount of molybdenum, which was detected in the filtrates in first two runs, was low and after third run no molybdenum was detected in the filtrates. These results demonstrated the strong attachment of molybdenum to the MWCNT. The catalytic behavior of the separated liquid was also tested

Table 4
Reusability of [Mo(CO)₅@APy-MWCNT] in the oxidation of 4-chlorobenzyl alcohol with *tert*-BuOOH under reflux conditions.^a

Run	4-Chlorobenzaldehyde (%) ^b	Time (min)	Mo leached (%) ^c
1	100	50	0.5
2	100	50	0.3
3	100	50	0
4	100	50	0
5	100	50	0
6	100	50	0
7	100	50	0
8	100	50	0
9	100	50	0
10	100	50	0

^a Reaction conditions: 4-chlorobenzyl alcohol (1 mmol), *tert*-BuOOH (2 mmol), catalyst (90 mg, 0.015 mmol), CCl₄ (4 mL).

^b GC yield based on starting 4-chlorobenzyl alcohol.

^c Determined by ICP.

by addition of fresh 4-chlorobenzyl alcohol and *tert*-BuOOH to the filtrates after each run. Continuation of the oxidation reaction under the same reaction conditions as with catalyst showed that the obtained results were as same as for the blank experiments.

4. Conclusion

In this article we have demonstrated the utility of [Mo(CO)₅@APy-MWCNT] catalyst in the oxidation of primary and secondary alcohols to carbonyl compounds with *tert*-butyl hydroperoxide. This supported catalyst is highly reactive in the oxidation of a wide range of primary and secondary alcohols. It showed the expected advantages of heterogenous catalysts, namely, easy handling and recyclability. The catalyst was highly reusable and recycled 10 times without appreciable decrease in its initial activity.

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