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# Molybdenum hexacarbonyl supported on amine modified multi-wall carbon nanotubes: an efficient and highly reusable catalyst for epoxidation of alkenes with *tert*-butylhydroperoxide

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In the present work, highly efficient epoxidation of alkenes catalyzed by  $Mo(CO)_6$  supported on multi-wall carbon nanotubes modified by 2-aminopyrazine, APyz-MWCNTs, is reported. The prepared catalyst was characterized by elemental analysis, scanning electron microscopy, FT IR and diffuses reflectance UV-vis spectroscopic methods. This new heterogenized catalysts,  $[Mo(CO)_6@APyz-MWCNT]$ , was used as a highly efficient catalyst for epoxidation of alkenes with *tert*-BuOOH. This robust catalyst was reused several times without loss of its catalytic activity. Copyright © 2010 John Wiley & Sons, Ltd.

Keywords: multi-wall carbon nanotubes; molybdenum hexacarbonyl; heterogeneous catalyst; epoxidation; tert-butylhydroperoxide

### Introduction

Epoxidation of alkenes catalyzed by metal complexes is an important reaction in organic synthesis because these compounds serve as useful intermediates in the synthesis of a wide variety of valuable compounds such as polyethers, diols and aminoalcohols.<sup>[1]</sup> Transition metals such as rhenium,<sup>[2]</sup> titanium,<sup>[3]</sup> vanadium,<sup>[4]</sup> manganese and molybdenum<sup>[5-10]</sup> have been used for alkene epoxidation. Among them, Mo (VI) compounds are the most versatile catalysts for the epoxidation of alkenes.<sup>[5-10]</sup> An important example is the Halcon process, for the industrial synthesis of propylene oxide, which is carried out by liquid-phase epoxidation of propylene with alkyl hydroperoxides catalyzed by a homogeneous Mo(VI).<sup>[11]</sup> The homogeneous catalysts of transition metals are often more difficult to prepare and expensive to purchase. 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.

Therefore, attention is now being drawn to the synthesis of heterogeneous catalysts based on these complexes, which can be easily separated from reaction mixture and recycled. Different approaches have been used to immobilize molybdenum on various supports to obtain heterogeneous catalysts. Sherrington and coworkers have reported efficient epoxidation of alkenes with *tert*-butylhydroperoxide catalyzed by reusable Mo(VI) supported on imidazole containing polymers.<sup>[12–15]</sup> Other organic polymers including modified polystyrenes,<sup>[16–20]</sup> polyaniline,<sup>[21]</sup> ion-exchange resins,<sup>[22]</sup> ethylene-propylene rubber and modified poly(ethylene oxide)<sup>[23]</sup> have been used as

$$= \left\langle \underbrace{ [Mo(CO)_6@APyz-MWCNT]}_{tert-BuOOH, CCl_4} \right\rangle^{O}$$



support for immobilization of molybdenum compounds. On the other hands, molybdenum catalysts have been supported on silica,<sup>[24-28]</sup> modified MCM-41,<sup>[29-37]</sup> zeolites<sup>[38]</sup> and layered double hydroxides.<sup>[39]</sup>

Carbon nanotubes (CNTs) have attracted much attention in synthesis, characterization and other applications because of their unique structural, mechanical, thermal, optical and electronical properties. Since CNTs are insoluble in the most solvents, these materials can be used as catalysts support.<sup>[40-43]</sup>

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

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Figure 1. The FT IR spectrum of (A) MWCNT-APyz and (B) [Mo(CO)<sub>6</sub>@APyz-MWCNT].

## 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 500–4000 cm<sup>-1</sup> with a Bomen–Hartmann instrument. Scanning electron micrographs of the catalyst were taken on SEM Philips XL 30. <sup>1</sup>H NMR spectra were recorded on a Bruker–Avance AQS 400 MHz. Gas chromatography experiments (GC) 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



**Figure 2.** The UV-Vis spectrum of: (A) [Mo(CO)<sub>6</sub>]; (B) [Mo(CO)<sub>6</sub>@APyz-MWCNT]; and (C) MWCNT-APyz.

instrument. The products were identified by comparison of their retention times with known samples and also with their <sup>1</sup>H NMR spectra.

## Preparation of Multi-wall Carbon Nanotubes-supported Molybdenum Hexacarbonyl

### Preparation of MWCNT-APyz

The carboxylic acid groups (MWCNT-COOH) in MWCNTs were converted to acid chloride (MWCNT-COCI) as reported.  $^{\rm [43]}$  In a

50 ml round-bottom flask equipped with a magnetic stirring bar, MWCNT-COCI (1 g) and Et<sub>3</sub>N (1 ml) were added to a solution of 2-aminopyrazine (0.5 g) in dimethyl formamide (DMF) (10 ml) and heated at 80 °C for 72 h. Then, the reaction mixture was filtered, washed with CH<sub>3</sub>CN and dried at 60 °C. CHN analysis of MWCNT-APyz: C, 84.83%; H, 1.53%; N, 6.15%.

### Preparation of the catalyst, [Mo(CO)<sub>6</sub>@APyz-MWCNT]

First, the metal carbonyl was activated by stirring a mixture of  $Mo(CO)_6$  (2 g, 7.5 mmol) in tetrahydrofuran (THF; 60 ml) under UV irradiation for 15 min.<sup>[44]</sup> Then, MWCNT-APyz (1 g) was added to this solution and refluxed for 1 h. At the end of the reaction, the catalyst was filtered, washed thoroughly with THF and dried in vacuum. The unreacted  $Mo(CO)_6$  was recovered after evaporation of the solvent

## General Procedure for Epoxidation of Alkenes with *tert*-BuOOH Catalyzed by [Mo(CO)<sub>6</sub>@APyz-MWCNT]

In a 25 ml round bottom flask equipped with a magnetic stirrer bar and a condenser, alkene (1 mmol), *tert*-BuOOH (2 mmol, 80% solution in di-*tert*-butylperoxide), catalyst (100 mg, 0.042 mmol) and CCl<sub>4</sub> (6 ml) were mixed and refluxed. The reaction progress was monitored by GC. At the end of the reaction (since different alkenes has different reactivity toward oxidation, the reactions were continued until no further progress was observed), 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.

### **Reusability of the Catalyst**

The reusability of the catalyst was studied in the repeated epoxidation reaction of *cis*-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.

## **Results and Discussion**

## Preparation and Characterization of catalyst, $[{\rm Mo}({\rm CO})_6@{\rm APyz-MWCNT}]$

The specification of MWCNT-COOH used in this study is presented in Table 1. Scheme 2 shows the preparation procedure of MWCNT-supported molybdenum catalyst. In this scheme, the probable modes for coordination of  $[Mo(CO)_6]$  are shown. The modified MWCNT, APyz-MWCNT, was prepared by covalent attachment of 2-aminopyrazine to MWCNT-COCI via an amide linkage. The [Mo(CO)<sub>6</sub>@APyz-MWCNT] catalyst was prepared by the reaction of APyz-MWCNT with a solution of Mo(CO)<sub>5</sub>THF. The catalyst was characterized by elemental analysis, scanning electron microscopy, FT-IR and diffuses reflectance UV-vis spectroscopic methods. The nitrogen content of support was 6.14% (4.38 mmol/g). The metal loading of [Mo(CO)<sub>6</sub>@APyz-MWCNT], measured by ICP, was 0.42 mmol/g. The FT-IR spectra of MWCNT-APyz and [Mo(CO)6@APyz-MWCNT] are shown in Fig. 1. The C=O stretching band of the amide group had appeared at 1656 cm<sup>-1</sup>. The band at 1961 cm<sup>-1</sup> was assigned to terminal carbonyl stretching band. These observations proved the coordination of [Mo(CO)<sub>6</sub>] to APyz-MWCNT. Further evidence

Table 1. Th	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%	$> 110 m^2/g$		

for attachment of  $[Mo(CO)_6]$  to APyz-MWCNT was obtained by diffuse reflectance UV-vis spectroscopy. The  $[Mo(CO)_6]$  showed absorption peaks at 230 and 280 nm (Fig. 2A). In the supported catalyst, these peaks had appeared at 226 and 278 nm and were attributed to  $Mo \rightarrow CO$  charge transfer bands (Fig. 2B), while MWCNTs showed no absorption peak in this region (Fig. 2C). These observations indicated that molybdenum hexacarbonyl has been supported on MWCNTs. The SEM images of the  $[Mo(CO)_6@APyz-MWCNT]$  showed that the nanotubes were aggregated and had retained their nanotube nature (Fig. 3).

## Epoxidation of Alkene with *tert*-BuOOH Catalyzed by [Mo(CO)<sub>6</sub>@APyz-MWCNT]

The  $[Mo(CO)_6@APyz-MWCNT]$  was used as catalyst for epoxidation of alkenes with *tert*-BuOOH. First, the reaction parameters were optimized in the oxidation of cyclooctene. Different solvents were



Figure 3. SEM image of [Mo(CO)<sub>6</sub>@APyz-MWCNT].

used to find the reaction media. The results showed that a higher epoxide yield was observed in CCl<sub>4</sub> (Table 2). It seems that noncoordinate solvents such as chlorinated ones are the best solvents for oxidation reactions by molybdenum-based catalysts. Different amounts of catalyst were used to optimize the catalyst amount. The best results were obtained using 100 mg (0.042 mmol) of [Mo(CO)<sub>6</sub>@APyz-MWCNT]. Control experiments in the absence of catalyst and using MWCNT-Apyz as catalyst were also performed and the results showed that the amount of epoxide was less than 5%.



Scheme 2. Preparation of [Mo(CO)<sub>6</sub>@APyz-MWCNT],

Table 2.	Epoxidation of <i>cis</i> -cyclooctene with <i>tert</i> -BuOOH catalyzed by
[Mo(CO) <sub>6</sub> @	PAPyz-MWCNT] under reflux conditions in different solvents <sup>a</sup>

Solvent	Epoxide (%) <sup>b</sup>	Temperature (° C)
(CH <sub>3</sub> ) <sub>2</sub> CO	No reaction	53
THF	No reaction	61
CH <sub>3</sub> CN	21	77
CICH <sub>2</sub> CH <sub>2</sub> CI	57	78
CHCl₃	65	57
CCl <sub>4</sub>	97	72
CH <sub>2</sub> Cl <sub>2</sub>	48	38
Neat reaction (solvent free)	41 <sup>c</sup>	-

<sup>a</sup> Reaction conditions: *cis*-cyclooctene (1 mmol), *tert*-BuOOH (2 mmol),

catalyst (100 mg, 0.042 mmol), 6 ml solvent.

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

<sup>c</sup> 10 mmol of cyclooctene was used.

Under the optimized conditions, the  $[Mo(CO)_6@APyz-MWCNT]/tert$ -BuOOH catalytic system was used for epoxidation of a wide range of alkenes (Table 3). In this system, both cyclic and linear alkenes were efficiently converted to their corresponding epoxides using *tert*-BuOOH as oxidant. 1-Octene and 1-dodecene as linear alkenes were efficiently converted to their corresponding epoxides by  $[Mo(CO)_6@APyz-MWCNT]$ . In the case of stilbenes, the epoxidation of *cis* isomer was associated with some loss of stereochemistry and a 7.4:1 mixture of *cis/trans*-epoxides was produced while epoxidation of *trans*-stilbene led to *trans*-epoxide in 90% yield with complete retention of configuration (Table 3).

#### **Catalyst Recovery and Reuse**

The reusability of a supported catalyst is of great importance from economic and environmental points of view. Heterogenization of homogeneous catalysts makes them useful for commercial applications. The reusability of [Mo(CO)<sub>6</sub>@APyz-MWCNT] was investigated in the sequential epoxidation of cyclooctene with *tert*-BuOOH (Fig. 4). The catalyst was consecutively reused several times (20 times was checked) without significant loss of its initial activity. In the 11 first runs, the initial catalytic activity was observed, but then the catalytic activity decreased in 25 min. The elongation of reaction times gave the higher epoxide yield in which, after 20 consecutive runs, the epoxide yield was 90% (Fig. 4). The amount of molybdenum detected in the filtrates in

Table 3 [Mo(CO]	• Epoxidation of ) <sub>6</sub> @APyz-MWCNT] in	alkenes with refluxing CCl <sub>4</sub> <sup>a</sup>	tert-BuOOH	catalyzed	
Entry	Alkene	Conversion (%) <sup>b</sup>	Epoxide (%) <sup>b</sup>	Time (min)	
1		97	97	25	
2	$\bigcirc$	95	95	45	
3		97	90	210	
4		95	60	90	
5	$\sim$	90	90	200	
6	$\sim \sim \sim$	75	75	160	
7	$\checkmark \sim \sim \sim \sim \sim$	85	85	240	
8		100 <sup>c</sup>	99 <sup>c</sup> (trans)	150	
	$\bigcirc$				
9	$\overline{}$	100 <sup>c</sup>	96 (cis), 3 (trans)	° 150	
<sup>a</sup> Reaction conditions: alkene (1 mmol), <i>tert</i> -BuOOH (2 mmol), catalyst (100 mg, 0.042 mmol), CCl <sub>4</sub> (6 ml). <sup>b</sup> GC yield based on starting alkene. <sup>c</sup> Both <sup>1</sup> HNMR and GC data approved the reported yields.					

the first two runs was low and after the third run no molybdenum was detected in the filtrates. These results demonstrate the strong attachment of molybdenum to the MWCNT. The catalytic behavior of the separated liquid was also tested by addition of fresh cyclooctene and *tert*-BuOOH to the filtrates after each run. Execution of the oxidation reaction under the same reaction conditions as with the catalyst showed that the obtained results were the same as for the blank experiments.

## Conclusion

We immobilized molybdenum hexacarbonyl on MWCNTs modified by 2-aminopyrazine and found that this supported catalyst was active in the epoxidation of alkenes with *tert*-BuOOH. This



Figure 4. Reusability results for [Mo(CO)<sub>6</sub>@APyz-MWCNT] in the epoxidation of cyclooctene with tert-BuOOH.

supported catalyst is highly reactive in the epoxidation of a wide range of alkenes such as linear and cyclic ones. The catalyst was highly reusable and was recycled 20 times without appreciable decrease in its initial activity.

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