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Molybdenum hexacarbonyl supported on functionalized multi-wall carbon nanotubes: Efficient and highly reusable catalysts for epoxidation of alkenes with *tert*-butyl hydroperoxide

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ABSTRACT

In the present work, highly efficient epoxidation of alkenes catalyzed by $Mo(CO)_6$ supported on amines modified multi-wall carbon nanotubes, MWCNTs, is reported. The prepared catalysts were characterized by elemental analysis, scanning electron microscopy, FT-IR and diffuse reflectance UV–Vis spectroscopic methods. These new heterogenized catalysts, [$Mo(CO)_6$@amines-MWCNT], were used as highly efficient catalysts for epoxidation of alkenes with *tert*-BuOOH. These robust catalysts could be reused several times without loss of their catalytic activities.

1. Introduction

Epoxidation of alkenes is of academic and industrial interest, because epoxides are one of the most widely used intermediates in organic synthesis. Epoxides undergo ring-opening reactions with a variety of reagents to produce mono- or bi-functional organic products [1–3].

Molybdenum complexes have been known as versatile and useful catalysts for the epoxidation of alkenes by organic hydroperoxides. The most important example of industrial application of molybdenum base catalysts is liquid-phase epoxidation of propylene with alkyl hydroperoxides catalyzed by homogeneous Mo(VI) compounds which is known as Halcon process. A number of soluble molybdenum complexes with different ligands have been synthesized and employed as homogeneous catalysts for epoxidation of various alkenes [4–8].

The homogeneous catalysts of transition metals are often more difficult to prepare and expensive to purchase. On the other hand, 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.

Different approaches have been used for immobilization of molybdenum complexes on various supports to obtain heterogeneous catalysts. Sherrington and coworkers have reported efficient epoxidation of alkenes with *tert*-butyl hydroperoxide catalyzed by reusable Mo(VI) supported on imidazole containing polymers [9–12]. Other organic polymers including modified polystyrenes [13–17], polyaniline [18], ion-exchange resins [19], ethylene–propylene rubber and modified poly(ethylene oxide) [20] have been used as support for immobilization of molybdenum compounds. On the other hands, several approaches have been reported for supporting of molybdenum catalysts on silica [21–25], modified MCM-41 [26–34], zeolites [35] and layered double hydroxides [36].

Recently, molybdenum complexes have been used for epoxidation of alkenes and oxidation of alcohols with hydrogen peroxide [37,38].

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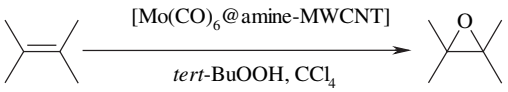


Scheme 1.

Carbon nanotubes (CNTs) have attracted much attention in the synthesis, characterization, and other applications because of their unique structural, mechanical, thermal, optical and electronical properties [39–41].

Since CNTs are insoluble in the most solvents, these materials can be used as catalysts support. For example, Pt nanoparticles supported on CNTs have been used for methanol oxidation [42], palladium nanoparticles supported on CNTs for semihydrogenation of phenylacetylene [43], chiral vanadyl salen complex supported on single-wall CNTs for enantioselective cyanosilylation of aldehydes [44,45] and manganese(III) porphyrin supported on MWCNTs for epoxidation of alkenes with $NaIO_4$ [46].

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

2. 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^{-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-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 Shenzen NTP Factory (China).

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

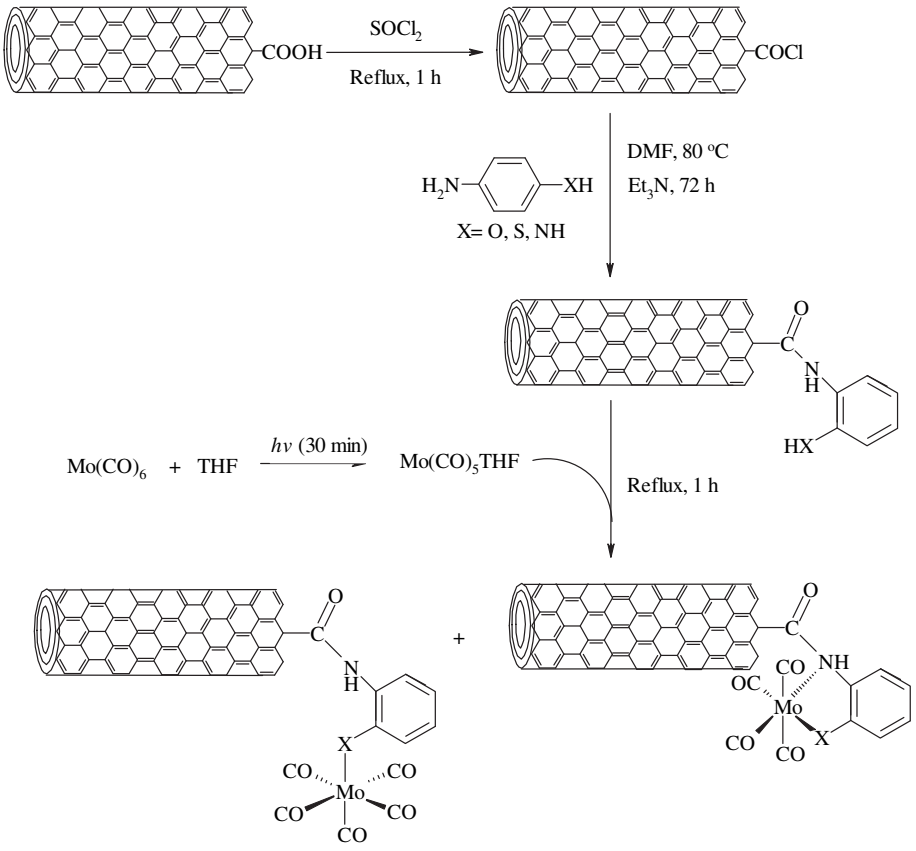
MWCNT-COOH				
Outside diameter	Inside diameter	Length	COOH content	Specific surface area
20–30 nm	5–10 nm	30 μm	1.5%	>110 m^2/g

2.1. Preparation of multi-wall carbon nanotubes supported molybdenum hexacarbonyl

2.1.1. Modification of MWCNT-COCl with amines

The carboxylic acid groups (MWCNT-COOH) in MWCNTs were converted to acid chloride (MWCNT-COCl) according to the reported procedure [46].

To a suspension of MWCNT-COCl (5 g) in DMF (50 mL), were added 1,2-diaminobenzene (DAB), 2-aminophenol (AP) or 2-aminothiophenol (ATP) (2.5 g) and triethylamine (5 mL). The mixtures were vigorously stirred at 80 °C for 72 h. After cooling the mixtures,



Scheme 2.