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## Article

# Epoxidation of alkenes efficiently catalyzed by Mo salen supported on surface-modified halloysite nanotubes



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## ARTICLE INFO

## Article history:

Received 13 September 2014

Accepted 3 November 2014

Published 20 March 2015

## Keywords:

Salen molybdenum

Alkene epoxidation

Halloysite nanotube

Surface modification

High-efficiency catalyst

## ABSTRACT

Halloysite-nanotube-supported Mo salen (HNTs-Mo-SL) catalysts were successfully prepared using a facile chemical surface modification and self-assembly method. The morphologies, sizes, structure, and dispersion of the as-prepared catalysts were investigated by transmission electron microscopy, X-ray diffraction, and Fourier-transform infrared, inductively coupled plasma, and X-ray photoelectron spectroscopy, which confirmed the existence of the Mo salen structure and successful synthesis of the HNTs-Mo-SL catalyst. The immobilized catalyst was found to be highly reactive in the epoxidation of a wide range of alkenes, including linear, cyclic, and aromatic alkenes. The immobilized catalyst exhibited a higher catalytic activity for alkene epoxidation than homogeneous Mo. In contrast experiments, it was determined that the salen structure played an important role in immobilizing  $\text{MoO}(\text{O}_2)_2(\text{DMF})_2$  and improving the conversion and efficiency of alkene epoxidation, which could not be obtained using other ligands, such as the N atom as a single ligand. Furthermore, the bonding between Mo and the salen ligands and the possible mechanism of alkene epoxidation catalyzed by the catalyst were determined. The catalyst could be reused several times without significant loss of catalytic activity. Given that halloysite nanotubes are cheap and easy to obtain, this catalyst offers a novel alternative for the rational design of catalysts with desired features.

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## 1. Introduction

The epoxidation of alkenes is one of the most widely studied reactions in organic chemistry. The resultant epoxides are important intermediates in organic synthesis and essential precursors in the synthesis of various important substances, such as plasticizers, perfumes, and epoxy resins. Catalyzing these epoxidation reactions by transition metal complexes has attracted much attention [1–5]. A number of soluble Mo complexes with different ligands have been synthesized and used as homogeneous catalysts for the epoxidation of various alkenes [6,7]. However, homogeneous catalysts have some industrial problems, such as deposition on the reactor wall and

difficulty in separation and recovery of the catalysts from the reaction products. One way to overcome these problems is to immobilize homogeneous catalysts on solid supports.

In recent years, various types of supported catalysts have been reported in organic transformations. Many approaches have been used to load Mo complexes on different supports, such as silica [8–12], modified MCM-41 [13–16], zeolites [17,18], and multi-wall carbon nanotubes (MWNs) [19,20], to obtain heterogeneous catalysts. However, much cheaper clay minerals have not been reported as supports for Mo complexes. Clay minerals are attractive inorganic hosts for functional inorganic-organic hybrids because of their swelling properties and charged surfaces, which can be easily modified. Clays have

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been successfully used in different fields, even as vectors for delivery of DNA to cells [21–23]. As a naturally abundant clay, halloysite nanotubes (HNTs,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ ) have a tubular structure similar to that of MWNTs, and they are cheap, non-toxic, and biocompatible. The tubular structure of HNTs is composed of one silica sheet with one alumina sheet on each silicate layer, and they have a diameter of 50 nm and a lumen of 15 nm [23]. HNTs have been used in various fields, such as nanocontainers for active anticorrosion coatings [28–31] and supports for catalysts in different types of reactions [32–36], and have useful structural properties [24–27].

Herein, we report the synthesis of Mo catalysts on modified HNT supports. To the best of our knowledge, the synthesis of Mo salen (Mo-SL) supported on surface-modified HNTs has not been previously reported. We investigated the stability and catalytic activity for epoxidation reactions of a variety of alkenes with the *tert*-butyl hydroperoxide oxidant. In addition, we investigated the coordination between Mo and salen ligands and the possible mechanism of alkene epoxidation using this catalyst.

## 2. Experimental

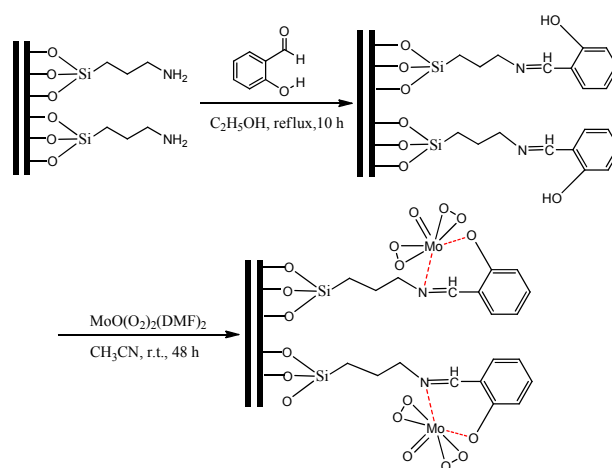
### 2.1. Materials

Halloysite was obtained from Hebei, China. 3-Aminopropyltrimethoxysilane (APTMS) and [3-(2-aminoethyl)aminopropyl]trimethoxysilane (AAPTMS) were purchased from Alfa Aesar and used without further purification. Molybdenum trioxide, *N,N*-dimethylformamide (DMF), *tert*-butyl hydroperoxide (TBHP), and solvents were all analytical grade reagents purchased from Shanghai Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification. Deionized water was used for all of the experiments.

### 2.2. Preparation of catalysts

The HNTs-SL-Mo catalysts were prepared by a facile chemical surface modification and self-assembly method. APTMS (0.5 mL) and HNTs (1 g) were dispersed in toluene (25 mL). The system was vacuumized in the process of ultrasonic dispersion for 1 h. Then, refluxing was performed at 110 °C for 24 h in a nitrogen environment. We obtained HNTs-APTMS after the solid was filtered out and dried under vacuum after washing with toluene several times. HNTs-APTMS (0.5 g) was dissolved in tepid ethanol (40 mL). Then, while stirring at 40 °C, ethanol (70 mL) containing salicylaldehyde (0.55 mL) was added in 2 h. This system was refluxed at 80 °C for 10 h. After filtering, washing, and drying, we obtained a yellow solid, which was HNTs supporting salen ligands (HNTs-APTMS-SL). A mixture of HNTs-APTMS-SL (300 mg) and  $\text{MoO}(\text{O}_2)_2(\text{DMF})_2$  (30 mg) synthesized according to a procedure described in the literature [37,38] was stirred in acetonitrile (15 mL) at room temperature for 48 h. Afterwards, the solid was filtered out and dried under vacuum after washing with acetonitrile. This gave the HNTs-APTMS-Mo-SL catalyst.

The complete synthesis process of the catalyst is shown in



**Fig. 1.** Synthesis process and structure of the HNTs-APTMS-Mo-SL catalyst.

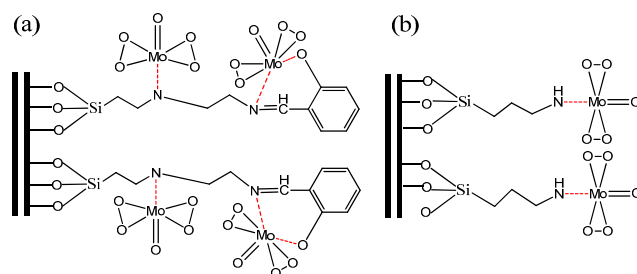
Fig. 1. We used AAPTMS instead of APTMS using the same method to obtain another catalyst, HNTs-AAPTMS-Mo-SL (Fig. 2(a)). The catalyst without the salen structure (HNTs-APTMS-Mo, Fig. 2(b)) was also prepared.

### 2.3. Characterization of catalysts

The size and morphology of the HNTs was observed by a Tecnai G2 F30 transmission electron microscope (TEM). The samples were obtained by placing a drop of a colloidal solution onto a copper grid and evaporating the solvent in air at room temperature. X-ray powder diffraction (XRD) patterns were obtained with a Shimadzu XRD-6000 diffractometer using  $\text{Cu } K\alpha$  radiation at 40 kV. Elemental analysis (EA) was carried out to analyze the elemental composition of the catalysts using an elemental analyzer (Vario EL, Elementar Analysensysteme GmbH, Hanau, Germany). Fourier-transform infrared (FT-IR) spectra were recorded on an Impact 400 FT-IR spectrometer (Nicolet, Waltham, MA, USA), and the samples were measured with KBr pellets. X-ray photoelectron spectra (XPS) were recorded on a PHI-5702 photoelectron spectrometer, and the C 1s line at 284.8 eV was used as the binding energy reference. The Mo content was measured with an inductively coupled plasma-atomic emission spectrometer (ICP-AES).

### 2.4. Catalytic epoxidation of alkenes by TBHP

The epoxidation of alkenes was carried out using TBHP as



**Fig. 2.** Structure of HNTs-AAPTMS-Mo-SL (a) and HNTs-APTMS-Mo (b).

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