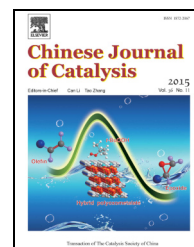


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Article

Catalytic epoxidation of olefin over supramolecular compounds of molybdenum oxide clusters and a copper complex



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ABSTRACT

The catalytic epoxidation of olefin was investigated on two copper complex-modified molybdenum oxides with a 3D supramolecular structure, $[\text{Cu}(\text{bipy})]_4[\text{Mo}_{15}\text{O}_{47}] \cdot 2\text{H}_2\text{O}$ (**1**) and $[\text{Cu}^{\text{I}}(\text{bix})][\text{Cu}^{\text{II}}(\text{bix})](\delta\text{-Mo}^{\text{VI}}_8\text{O}_{26})_{0.5}$ (**2**) (bipy = 4,4'-bipyridine, bix = 1,4-bis(imidazole-1-ylmethyl)benzene). Both compounds were catalytically active and stable for the epoxidation of cyclooctene, 1-octene, and styrene with *tert*-butyl hydroperoxide (*t*-BuOOH) as oxidant. The excellent catalytic performance was attributed to the presence of stable coordination bonds between the molybdenum oxide and copper complex, which resulted in the formation of easily accessible Mo species with high electropositivity. In addition, the copper complex also acted as an active site for the activation of *t*-BuOOH, thus improving these copper complex-modified polyoxometalates.

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1. Introduction

The design and synthesis of inorganic-organic hybrid materials based on polyoxometalates (POMs) have become a significant research area due to their interesting structures and numerous potential applications in material science, medicine, magnetism, electrochemistry, and catalysis [1–6]. Recently, a new class of supramolecular compound composed of a transition metal (e.g., Cu, Ni, and Ag) complex (TMC) and POM units have drawn considerable attention because the combination of a transition metal complex with POMs can help construct versatile intriguing supramolecular structures, and have novel physicochemical properties for various applications [7–14].

In the catalytic application of POM-based compounds, more recent studies have focused on developing highly active and

stable heterogeneous POM-based catalysts for the epoxidation of olefins, which are important processes for the production of fine chemicals [15]. Recently, Ali's group [16] synthesized two novel copper complex-modified Anderson type POMs, $[(\text{Na}_4(\text{H}_2\text{O})_{14})(\text{Cu}(\text{gly}))_2][\text{TeMo}_6\text{O}_{24}]$ (gly = glycine) and $[(\text{Cu}(\text{en})_2)_3(\text{TeW}_6\text{O}_{24})] \cdot 6\text{H}_2\text{O}$ (en = ethylene-diamine), and found that these compounds showed moderate catalytic activity for the epoxidation of styrene and cyclohexene with *tert*-butylhydroperoxide (*t*-BuOOH). In a work reported by Cui and co-authors [17], it was found that a few hybrid compounds composed of POMs, transition metal ions (Ni^{2+} , Cu^{2+} , and Cd^{2+}), and a 4,4'-bipyridine organic ligand were active for the epoxidation of styrene. Currently, it is still a very attractive subject to develop more efficient and stable TMC-modified POMs as catalysts for olefin epoxidation.

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Previously, we reported that some *N*-heterocyclic ligands-modified octamolybdate-based supramolecular compounds were active heterogeneous catalyst for the epoxidation of cyclooctene and 1-octene with *t*-BuOOH. The formation of a multidimensional supramolecular structure using multiple weak interactions, such as hydrogen bonds and π - π interactions, plays a key role in fabricating active and stable POM-based catalysts. The catalytic properties varied considerably with the organic ligand and the multidimensional supramolecular structure [18]. As a continuation of the work, we investigated the catalytic epoxidation properties of two copper complexes used to modify molybdenum oxides, $[\text{Cu}(\text{bipy})]_4[\text{Mo}_{15}\text{O}_{47}]\cdot 2\text{H}_2\text{O}$ (**1**) (bipy = 4,4'-bipyridine) and $[\text{Cu}^{\text{I}}(\text{bix})][(\text{Cu}^{\text{I}}\text{bix})(\delta\text{-Mo}^{\text{VI}}_8\text{O}_{26})_{0.5}]$ (**2**) (bix = 1,4-bis(imidazole-1-ylmethyl)benzene). The structures and electrochemical properties of these two compounds have recently been studied by two research groups [13,14]. In the present work, it was found that both compounds **1** and **2** exhibited excellent catalytic activity and stability for the epoxidation of olefins. The role of the copper complexes was discussed on the basis of the structural characteristics and catalytic properties of these transition metal complex-modified POMs catalysts.

2. Experimental

2.1. Synthesis of the catalysts

2.1.1. $[\text{Cu}(\text{bipy})]_4[\text{Mo}_{15}\text{O}_{47}]\cdot 2\text{H}_2\text{O}$ (**1**)

Bipy (0.5 mmol, 0.0961 g), $\text{Cu}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (0.5 mmol, 0.099 g), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.2 mmol, 0.248 g), and triethylamine (0.02 mL) were added into 15 mL of distilled water at room temperature. The pH of the mixture was adjusted to 3.0 with HCl solution (1 mol/L). After stirring for 1 h at room temperature, the mixture was transferred to a sealed Teflon-lined autoclave (25 mL) and heated at 170 °C for 5 d. When the mixture was slowly cooled (10 °C/h) to room temperature, brown block crystals of **1** were obtained after washing with distilled water. The crystals were dried at room temperature and gave a yield of 40% based on Mo.

2.1.2. $[\text{Cu}^{\text{I}}(\text{bix})][(\text{Cu}^{\text{I}}\text{bix})(\delta\text{-Mo}^{\text{VI}}_8\text{O}_{26})_{0.5}]$ (**2**)

$\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.5 mmol, 0.085 g), bix (0.5 mmol, 0.119 g), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (0.1 mmol, 0.124 g), and triethylamine (0.02 mL) were added into 15 mL of distilled water. The pH of the mixture was adjusted to 5.0 with HCl or NaOH solution (1 mol/L). After stirring for 1 h at room temperature, the mixture was transferred into a sealed Teflon-lined autoclave (25 mL) and heated at 170 °C for 5 d. Red block crystals of **2** were collected after the mixture was slowly cooled (10 °C/h) to room temperature. The crystals were washed with distilled water and dried at room temperature to give a yield of 45% based on Mo.

2.1.3. Reference sample $(\text{H}_2\text{bix})[(\text{Hbix})_2(\gamma\text{-Mo}_8\text{O}_{26})]_2\cdot 2\text{H}_2\text{O}$ (**3**)

The synthesis of **3** was similar to that of **2**, but without the addition of triethylamine and $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$. The crystals of **3** were collected with a yield of 49% based on Mo.

2.2. Characterization of the catalysts

Crystallographic data for all compounds were collected at 120 °C on a Siemens SMART CCD using graphite-monochromatized Mo K_α radiation ($\lambda = 0.071073$ nm). Absorption corrections were carried out with the SADABS program. The structure was solved by direct methods and refined on F_2 by the full matrix least squares technique with the SHELXL-97 program software [19]. Geometric calculations were used to locate the positions of the hydrogen atoms. Fourier transform infrared (FT-IR) spectra (KBr pellets) were recorded with a Nicolet Impact 410 spectrometer. Powder X-ray diffraction (XRD) patterns were obtained on a Shimadzu XRD-6000 diffractometer with Cu K_α radiation range from 5° to 70° at a scan rate of 6°/min. X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Thermo ESCALAB 250 spectrometer with an Mg K (1253.6 eV) achromatic X-ray source.

2.3. Catalytic test

The activity and selectivity of all the catalysts were studied using the epoxidation of various olefins with *t*-BuOOH as oxidant and chloroform or acetonitrile as the solvent. Typically, the epoxidation of olefins was performed in a 10 mL round-bottomed flask equipped with a reflux condenser at a temperature of 35, 45, or 61 °C. The catalyst (0.005 mmol), substrate (1.0 mmol), *t*-BuOOH (1.0 mmol), and solvent (chloroform or acetonitrile, 2 mL) were added into the flask. Samples were withdrawn at regular intervals and filtered before measurement by a gas chromatograph (Shimadzu GC-14C FID). The catalytic performance of catalyst was evaluated by the conversion of olefin and selectivity to its epoxide using toluene as the internal standard.

3. Results and discussion

3.1. Synthesis and structure of the catalysts

The procedures for the synthesis of compounds **1** and **2** were similar to those in the literature [13,14]. Minor modification such as using different reagents and synthesis conditions (pH values, heating temperatures) were used in order to get crystalline products with high quality and yield. For instance, the reagent NH_4VO_3 was used for the synthesis of compound **1** in the literature [13], but our present work confirmed that the introduction of this V-containing reagent was not necessary and a relatively high yield of **1** can be achieved by the optimized synthesis conditions described in the experimental section.

Single crystal XRD analysis revealed that compound **1** has an open multitrack Cu–N coordination polymeric chain-modified molybdenum oxide 3D supramolecular structure (Fig. 1(a)), which is consistent with the previously reported structure in the literature [13]. The molecular structure unit of **1** consists of one molybdenum oxide chain of $[\text{Mo}_{15}\text{O}_{47}]^{4-}$, four $[\text{Cu}(\text{bipy})]^+$ cations, and two water molecules (Fig. 2). Compound **2** showed a 3D (4,4)-connected framework with the

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