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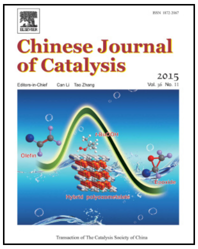

Article

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, $[Cu(bipy)]_4[Mo_{15}O_{47}]\cdot 2H_2O$ (**1**) and $[Cu^I(bix)][(Cu^Ibix)(\delta\text{-}Mo^{VI}_8O_{26})_{0.5}]$ (**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.

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, $[(Na_4(H_2O)_{14})(Cu(gly))_2][TeMo_6O_{24}]$ (gly = glycine) and $[(Cu(en)_2)_3(TeW_6O_{24})]\cdot 6H_2O$ (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, $[Cu(bipy)]_4[Mo_{15}O_{47}]\cdot 2H_2O$ (**1**) (bipy = 4,4′-bipyridine) and $[Cu^{I}(bix)][(Cu^{I}bix)(\delta\text{-}Mo^{VI}{}_8O_{26})_{0.5}]$ (**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. $[Cu(bipy)]_4[Mo_{15}O_{47}]\cdot 2H_2O$ (1)

Bipy (0.5 mmol, 0.0961 g), $Cu(OAc)_2\cdot H_2O$ (0.5 mmol, 0.099 g), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (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. $[Cu^{I}(bix)][(Cu^{I}bix)(\delta\text{-}Mo^{VI}{}_8O_{26})_{0.5}]$ (2)

$CuCl_2\cdot 2H_2O$ (0.5 mmol, 0.085 g), bix (0.5 mmol, 0.119 g), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (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 $(H_2bix)[(Hbix)_2(\gamma\text{-}Mo_8O_{26})]2\cdot H_2O$ (3)

The synthesis of **3** was similar to that of **2**, but without the addition of triethylamine and $CuCl_2\cdot 2H_2O$. 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 (λ = 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 $[Mo_{15}O_{47}]^{4-}$, four $[Cu(bipy)]^{+}$ cations, and two water molecules (Fig. 2). Compound **2** showed a 3D (4,4)-connected framework with the

$(6^4 8^2)(8^4 12^2)$ topology, which is constructed from δ-octamolybdates [20,21], copper cations, and bix ligands. The structure of **2** has been reported in the literature [14]. The main feature of this compound is that its 3D framework is penetrated by copper-organic polymeric chains to form a 3D polythreaded framework (Fig. 1(b)). The unit cell of **2** shows the presence of a $[\delta\text{-Mo}_8\text{O}_{26}]^{4-}$ anion, two Cu^{I} (Cu1 and Cu2) cations and two bix1 (Z-type) and bix2 (U-type) ligands (Fig. 2(c)).

The reference sample of compound **3** exhibited a 3D supramolecular framework based on hydrogen bond interactions and π-π stacking interactions between the bix ligands and $[(\text{Hbix})_2(\gamma\text{-Mo}_8\text{O}_{26})]^{2-}$ units (Fig. 3). The molecular structure of **3** consists of one $[(\text{Hbix1})_2(\gamma\text{-Mo}_8\text{O}_{26})]^{2-}$ unit, one $(\text{H}_2\text{bix2})^{2+}$ cation, and one lattice water.

3.2. Catalytic properties

The catalytic properties of catalysts **1** and **2** and reference sample **3** were investigated for the epoxidation of cyclooctene and 1-octene with *t*-BuOOH as the oxidant. As shown in Table 1, all catalysts were active for the epoxidation of olefins with nearly 100% selectivity to the corresponding epoxides. Among these, catalyst **1** showed the highest activity, and 96% conversion of cyclooctene was reached after 8 h reaction at the low temperature of 35 °C.

Catalyst **2** was also active, and 92% conversion of cyclooctene was achieved after 10 h. Both the copper complex-modified POM catalysts exhibited much higher activity than the reference sample **3** (39% conversion of cyclooctene after 10 h). In addition, the relatively inert terminal olefin of 1-octene can be also converted rapidly to the corresponding epoxide (77% conversion, nearly 100% epoxide selectivity, reaction time 12 h) when **1** was used as catalyst. It should be mentioned here that some byproducts like 1,2-octanediol and 1-octanal were also detected when the reaction time was further prolonged (data not given).

The epoxidation of styrene was also investigated over the above catalysts (Table 2). When chloroform was chosen as the solvent, the catalytic activity of these three catalysts decreased in the order of **1** > **2** > **3**. A significant amount of byproducts like benzaldehyde and penylacetaldehyde were observed over these catalysts, thus considerably decreasing the selectivity to epoxide (particularly seriously on the two copper complex-modified POM catalysts). Changing the solvent from chloroform to acetonitrile did not change the activity order of the catalysts, but the selectivity to epoxide decreased notably with the in-

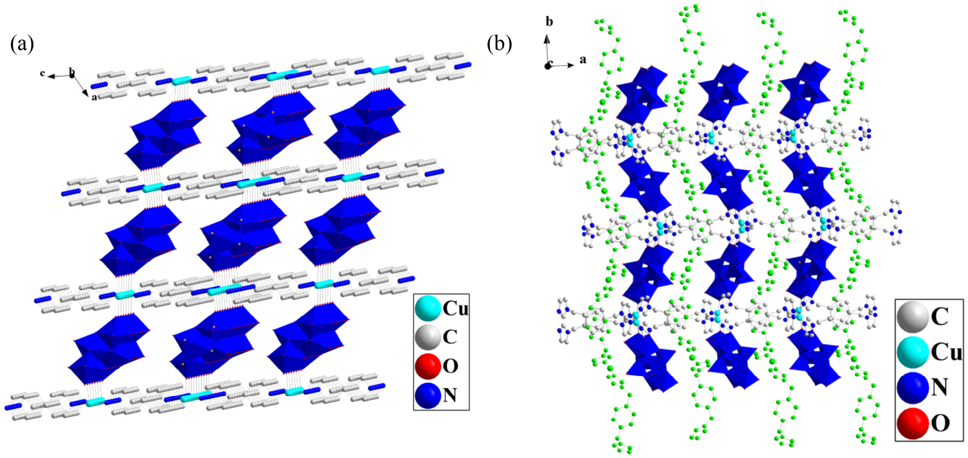


Fig. 1. (a) View of the infinite-track Cu(bipy) chain-modified $[\text{Mo}_{15}\text{O}_{47}]_n^{4n-}$ in compound **1**; (b) The 3D polythreaded supramolecular structure along the given directions in compound **2** (green represents penetrated $[\text{Cu}^{\text{I}}2(\text{bix2})]_n^{n+}$ chains).

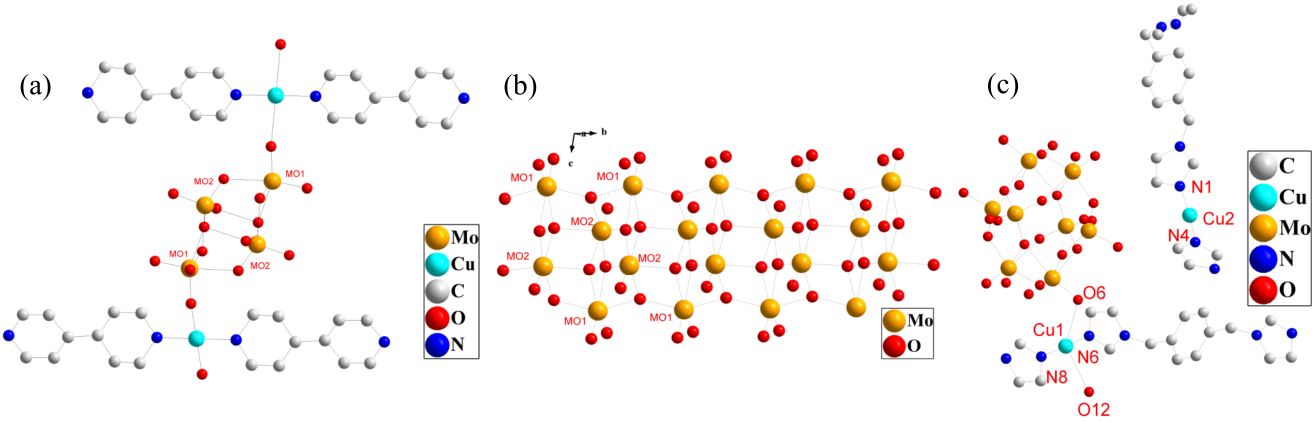


Fig. 2. Ball and stick representation of the molecular unit (a) and $[\text{Mo}_{15}\text{O}_{47}]_n^{4n-}$ chains (b) of compound **1**; (c) Ball and stick representation of the molecular unit of compound **2** (all hydrogen atoms and lattice water molecules were omitted for clarity).

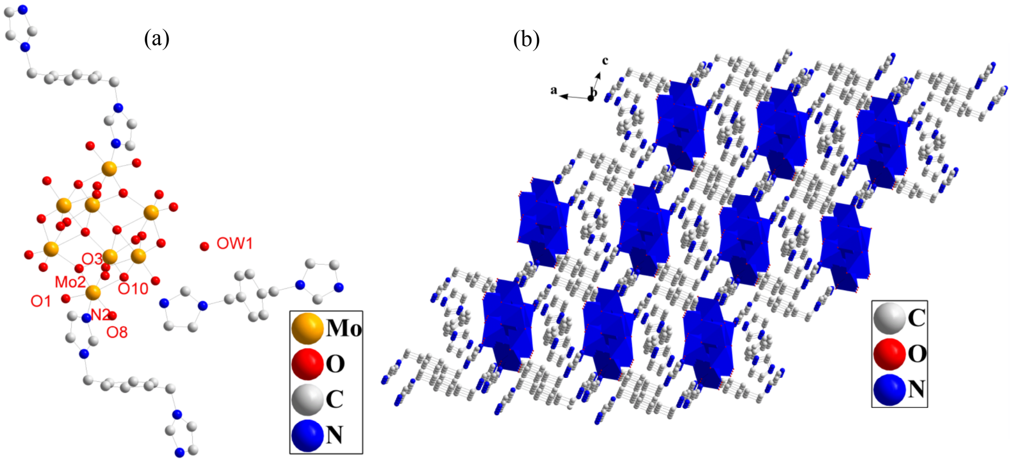


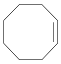
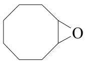
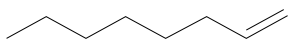
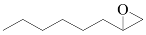
Fig. 3. (a) Ball and stick representation of the molecular unit of compound **3**; (b) 3D supramolecular framework in compound **3.**

crease of benzaldehyde selectivity. Very high benzaldehybe selectivity (up to 96%) was found over the copper-free catalyst **3**. These results suggest that the catalytic performance of these POM-based catalysts was solvent dependent [22].

To verify the heterogeneity of the catalytic process, a leaching test was performed for the epoxidation of 1-octene over the two copper complex-modified POM catalysts. As shown in Fig. 4, both catalyst **1** and catalyst **2** show very high stability against leaching of the active species. Besides, it was also found that these catalysts are recyclable, and no loss in catalytic activity was detected after five reaction cycles (Fig. 5). These results suggested that the copper complex-modified POM compounds are truly heterogeneous catalysts under the reaction conditions employed.

Table 1

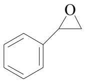
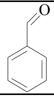
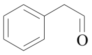
Epoxidation of olefins catalyzed by catalysts **1**, **2**, and **3**.

Catalyst	Substrate	Product	*t* (°C)	Time (h)	Conversion (%)
1			35	8	96
2			35	10	92
3			35	10	39
1			61	12	77
2			61	12	44
3			61	12	43

Reaction conditions: substrate 1.0 mmol; *t*-BuOOH 1.0 mmol; catalyst 0.005 mmol; chloroform 2.0 mL. All selectivities for the epoxide were nearly 100%.

Table 2

Epoxidation of styrene over the three catalysts after 12 h reaction time.

Catalyst	Solvent	Conversion (%)	Selectivity (%)		
					
1	chloroform	98	37	48	15
2		77	40	47	13
3		67	63	10	26
1	acetonitrile	91	9.0	73	17
2		70	11	77	10
3		21	2.5	96	1.3

Reaction conditions: styrene 1.0 mmol; *t*-BuOOH 1.0 mmol; catalyst 0.005 mmol; solvent 2.0 mL; temperature 61 °C.

FT-IR and XRD measurements were carried out to investigate the structural stability of catalyst **1**. The FT-IR spectra showed that there was no obvious difference between the used catalyst (after the 5th reaction of 1-octene epoxidaiton) and the

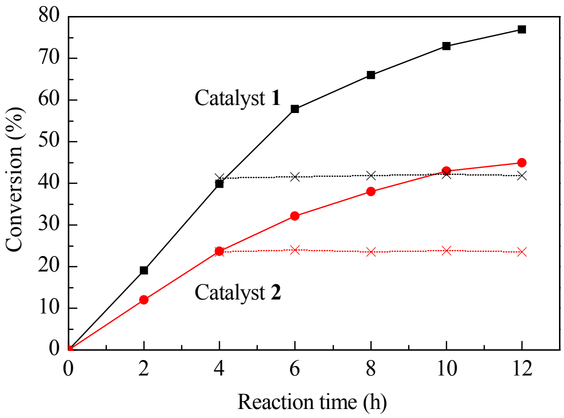


Fig. 4. Kinetic profiles of the epoxidation of 1-octene with *t*-BuOOH over the catalysts. (×) Leaching experiments of the catalysts indicating conversion of 1-octene with the catalysts removed after 4 h at reaction temperature. Reaction conditions: 1-octene 1.0 mmol; *t*-BuOOH 1.0 mmol; catalyst 0.005 mmol; chloroform 2.0 mL; temperature 61 °C. All selectivities for the epoxide were nearly 100%.

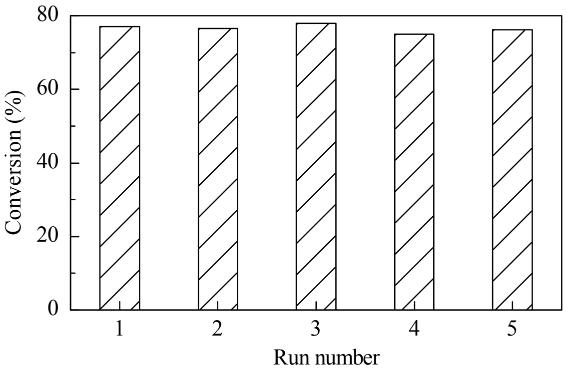


Fig. 5. Recycling experiments of catalyst **1** for the conversion of 1-octene after 12 h reaction. Reaction conditions: 1-octene 1.0 mmol; *t*-BuOOH 1.0 mmol; catalyst 0.005 mmol; chloroform 2.0 mL; temperature 61 °C. All selectivities for the epoxide were nearly 100%.

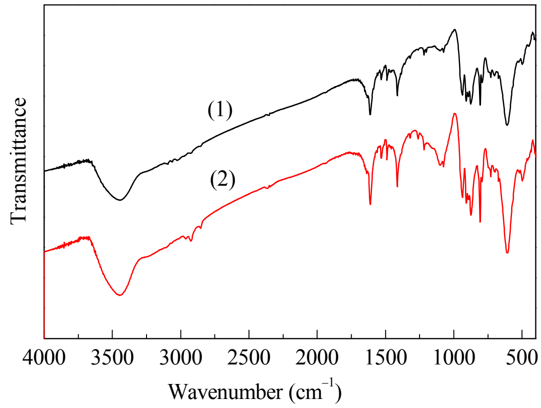


Fig. 6. FT-IR spectra of fresh catalyst **1** (1) and used one after the fifth cycle in 1-octene epoxidation (2).

fresh one (Fig. 6). The XRD patterns indicated that the characteristic diffraction peaks for the used catalyst were consistent with the fresh catalyst **1** (Fig. 7). These results suggested that the molecular structure geometry of catalyst **1** was kept during the reaction process. The high catalytic stability of the copper complex modified POM compounds can be attributed to the formation of the stable 3D supramolecular structure. It was discussed above that the copper complex and molybdenum oxide clusters were coordinately connected via the terminal oxygen atoms of the molybdenum oxide cluster (as active coordination sites) and the copper ions.

XPS measurements were also carried out for the two copper complex-modified POM catalysts (Fig. 8). The XPS spectrum of catalyst **1** showed two peaks at 235.9 and 232.6 eV, which were assigned to Mo $3d_{3/2}$ and Mo $3d_{5/2}$, respectively. For catalyst **2**, a slightly lower binding energy of the Mo species (235.3 and 232.1 eV) was detected. The higher electropositivity of Mo species is associated with the higher catalytic activity of molybdenum-containing catalysts [23]. This may be the main reason why catalyst **1** was more active than **2**. The high electropositivity of catalyst **1** originated from the nature of the molybdenum oxide, i.e., $[Mo_{15}O_{47}]^{4-}$.

Furthermore, the introduction of the copper complex into the framework of the POM-based compounds also considerably influenced the electropositivity of the Mo species by a strong interaction (i.e., forming a coordination bond) between the POM units and the copper complex. This interaction can change the nature of the active Mo species, thus resulting in that the copper complex-modified POM catalysts (**1** and **2**) showed different catalytic activity and selectivity for the epoxidation of olefins compared to the copper-free POM catalyst (**3**). In addition, the introduced copper complex can also act as a new active site for the activation of *t*-BuOOH to form the active intermediate, like the Cu-hydroperoxo species, which has been proposed in the literature [16,24–27]. This may be another important contribution from the copper complex to the improvement of the catalytic activity of the POM-based catalysts.

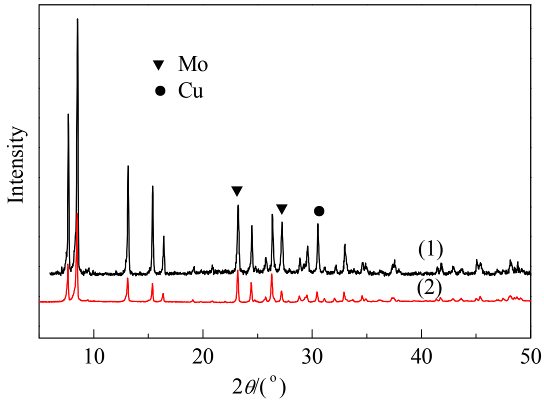


Fig. 7. XRD patterns of fresh catalyst **1** (1) and the used one after the fifth cycle in 1-octene epoxidation (2).

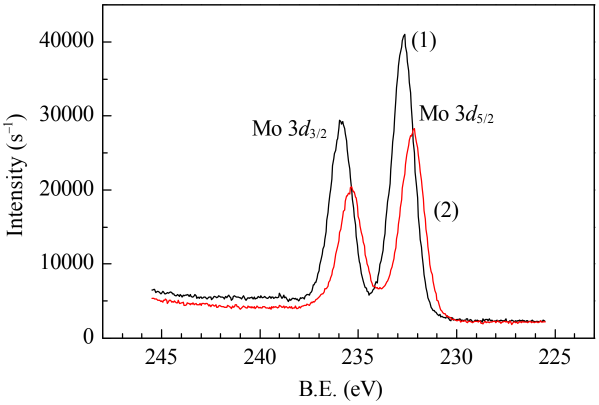


Fig. 8. XPS spectra of catalysts **1** (1) and **2** (2).

Other factors such as the structural characteristics of the POM-based catalysts may also influence its catalytic property. Compared with the polythreaded structure of catalyst **2**, catalyst **1** has a more open framework, which is more suitable for the diffusion of the reactants to increase the substrate contact with the catalyst active sites, thus helping to improve the catalytic activity of catalyst **1**.

4. Conclusions

Two supramolecular compounds based on molybdenum oxide clusters and copper complexes showed excellent catalytic activity and selectivity for the epoxidation of olefins. Both catalysts are heterogeneous in nature and can be easily recycled without decrease in activity. The presence of relatively strong coordination bonds between the copper complex and the molybdenum oxide clusters played a critical role in fabricating the stable supramolecular structure and in forming an active and stable heterogeneous catalyst for the epoxidation of olefins.

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Graphical Abstract

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

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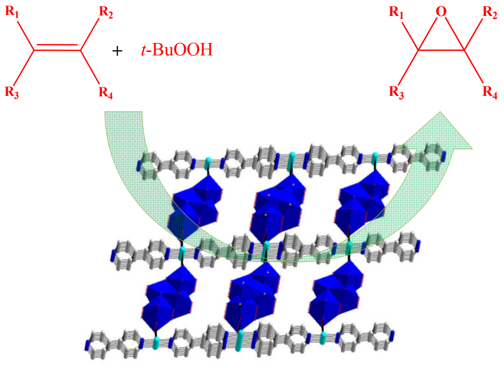
Chengde Petroleum College; Jilin University; Daqing Oilfield General Hospital



Copper complexes modified **POMs**

Copper complex-modified polyoxometalates showed high catalytic activity and stability in the catalytic epoxidation of olefin with *tert*-butyl hydroperoxide (*t*-BuOOH) as oxidant.

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