

A novel hybrid containing two kinds of polyoxometalates for catalyzing olefin epoxidation

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Vanadium-substituted Keggin-type polyoxometalates exhibit a higher negative charge compared to parent polyoxometalates, which not only enhances their ability to coordinate with metals but also endows them with significant potential for oxidative catalysis due to the intrinsic high oxidative catalytic capacity of vanadium. In this study, by incorporating vanadium-substituted Keggin-type polyoxometalates and sodium molybdate, an inorganic-organic hybrid compound, $[\text{Cu}_6(\text{phen})_6(\text{Mo}_6\text{O}_{22})](\text{HPMo}_{10}\text{V}_2\text{O}_{40})\cdot\text{H}_2\text{O}$ (phen = 1,10-phenanthroline), was successfully constructed under hydrothermal conditions. This compound is composed of two kinds of polyoxometalates, $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ and $[\text{Mo}_6\text{O}_{22}]^{8-}$, in which $\{\text{PMo}_{10}\text{V}_2\}$ and $\{\text{Mo}_6\}$ represent $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ and $[\text{Mo}_6\text{O}_{22}]^{8-}$, respectively. In the catalytic epoxidation of olefins, this hybrid efficiently oxidized cyclooctene to 1,2-epoxycyclooctane within 4 hours at 35 °C using oxygen as the oxidant (conversion rate of 98.6% and a selectivity greater than 99%). Moreover, it retained high catalytic activity after five successive cycles and demonstrated broad substrate scope, effectively catalyzing the epoxidation of various olefins.

vanadium-substituted Keggin-type polyoxometalates; inorganic-organic hybrids; olefin epoxidation

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1. Introduction

Epoxides serve as key raw materials and intermediates in fine chemical synthesis. The epoxidation of olefins represents a significant oxidation reaction in industrial processes and organic synthesis, constituting the primary route for epoxide production^[1-6]. Through selective ring-opening or functional group transformation, these compounds can be converted into diverse high-value derivatives with extensive applications in medicinal chemistry, natural product synthesis, the functional polymer industry, and fine chemical fields^[7]. In traditional industries, commonly used oxidants are typically sodium hypochlorite^[8], *m*-chloroperoxybenzoic acid^[9], and alkyl peroxides^[10]. However, these oxidants are not only expensive but also generate pollutants and waste that pose significant threats to the environment^[11]. O_2 being readily available, inexpensive, and environmentally friendly, has gained favor among researchers. Using O_2 as the ox-

idant, catalysts employing transition-metal complexes^[12-15], transition metal substituted heteropolyanions^[16-18], and supported catalysts^[19-22] have been developed. However, these catalysts often exhibit limitations: single catalytic sites, difficulty in reuse after reaction and unclear structures. Therefore, developing heterogeneous catalysts with high catalytic efficiency, recyclability, and synergistic effects at multiple sites for olefin epoxidation reactions remains a noteworthy research topic.

Keggin-type polyoxometalates (POMs) represent the most quintessential example among polyoxometalate structures, being the class of heteropoly compounds that has been studied most extensively and holds the greatest potential for practical applications. They exhibit strong Brønsted acidity and oxidative properties. Vanadium-substituted Keggin-type polyoxometalates retain the composition, structural characteristics, and advantages of Keggin-type polyoxometalates while exhibiting additional properties such as enhanced the negative charge density on the surface of polyoxometalate anions, increased coordination ability, and better oxidative activity. Consequently, they hold application potential across

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numerous fields, particularly in catalysis^[23-29]. However, practical catalytic applications inevitably encounter challenges. For instance, high solubility in polar solvents hinders catalyst separation, reuse, and recovery; while agglomeration and poor dispersibility in nonpolar solvents diminish catalytic activity. To effectively address the aforementioned challenges, we constructed an inorganic-organic hybrid system based on vanadium-substituted Keggin-type POMs, transition metal and organic ligands as basic unit. The approach not only resolves the technical difficulties associated with recycling pure polyoxometalates but also combines the advantages of inorganic components and organic components, ensuring outstanding catalytic performance in the epoxidation of olefins.

This study employed vanadium-substituted Keggin-type polyoxometalate ($\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$) and sodium molybdate as precursors, introducing CuCl_2 and 1,10-phenanthroline (phen) to synthesize a novel polyoxometalate-based hybrid compound, $[\text{Cu}_6(\text{phen})_6(\text{Mo}_6\text{O}_{22})(\text{HPMo}_{10}\text{V}_2\text{O}_{40})\cdot\text{H}_2\text{O}]$, under hydrothermal conditions. This compound contains two distinct types of polyoxometalates, $\{\text{PMo}_{10}\text{V}_2\}$ and $\{\text{Mo}_6\}$. It was employed to catalyze the epoxidation reaction of cyclooctene. The results demonstrated that, at 35 °C with O_2 as the oxidant, the synergistic catalytic effect between the polyoxometalates and Cu^{2+} centers enabled efficient conversion of cyclooctene to 1,2-epoxycyclooctane within 4 hours, achieving a conversion rate of 98.6% and selectivity greater than 99%. Moreover, the compound retained its catalytic activity after five successive cycles and exhibited broad substrate scope, effectively catalyzing the epoxidation of various olefins.

2. Experimental section

2.1 Synthesis of $[\text{Cu}_6(\text{phen})_6(\text{Mo}_6\text{O}_{22})(\text{HPMo}_{10}\text{V}_2\text{O}_{40})\cdot\text{H}_2\text{O}]$

$\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ (0.034 g, 0.2 mmol), phen (0.023 g, 0.125 mmol), $\text{Na}_2\text{MoO}_4\cdot 2\text{H}_2\text{O}$ (0.024 g, 0.1 mmol) and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ (0.174 g, 0.1 mmol) were sequentially dissolved in H_2O (10 mL) with stirring for 1 h. The pH of the solution was adjusted to about 3.1 with $1\text{ mol}\cdot\text{L}^{-1}$ NaOH. The emulsion mixture was then transferred into a 23 mL teflon reactor and heated at 160 °C for 3 d, followed by cooling to room temperature at a rate of $10\text{ }^\circ\text{C}\cdot\text{h}^{-1}$. Brownish-yellow blocky crystals were obtained after filtration and washing, with a yield of 46.2% (based on Cu). Elemental analysis calcd: C 20.86%, H 1.16%, N 4.06%, O 24.34%, P 0.75%, Mo 37.09%, Cu 9.27%; Found: C 20.84%, H 1.19%, N 4.08%, O 24.31%, P 0.78%, Mo 37.07%, Cu 9.26%.

2.2 Epoxidation of olefins in title compound

The catalytic activity of the synthesized compound as a heterogeneous catalyst was investigated using cyclooctene as a model substrate. Prior to the reaction, the catalyst was

dried for 12 h at 50 °C in a vacuum oven to activate it. A mixture of cyclooctene (1 mmol), acetonitrile (5 mL), and biphenyl (internal standard) was added to a 25 mL round-bottom flask. The flask was placed in an oil bath at a set temperature and stirred until the mixture dissolved. Subsequently, the catalyst and isobutyraldehyde (IBA) were added. A condenser was installed, with an oxygen balloon connected at its top to provide oxygen. Stirring was maintained, and the reaction was initiated. Samples were taken at regular intervals, diluted with an equal volume of acetonitrile, and then centrifuged to separate the catalyst. The supernatant was quantitatively analyzed by gas chromatography to determine conversion rate and selectivity. After reaction completion, the catalyst was washed and recovered. It was dried in an oven at 50 °C and reused in subsequent experiments.

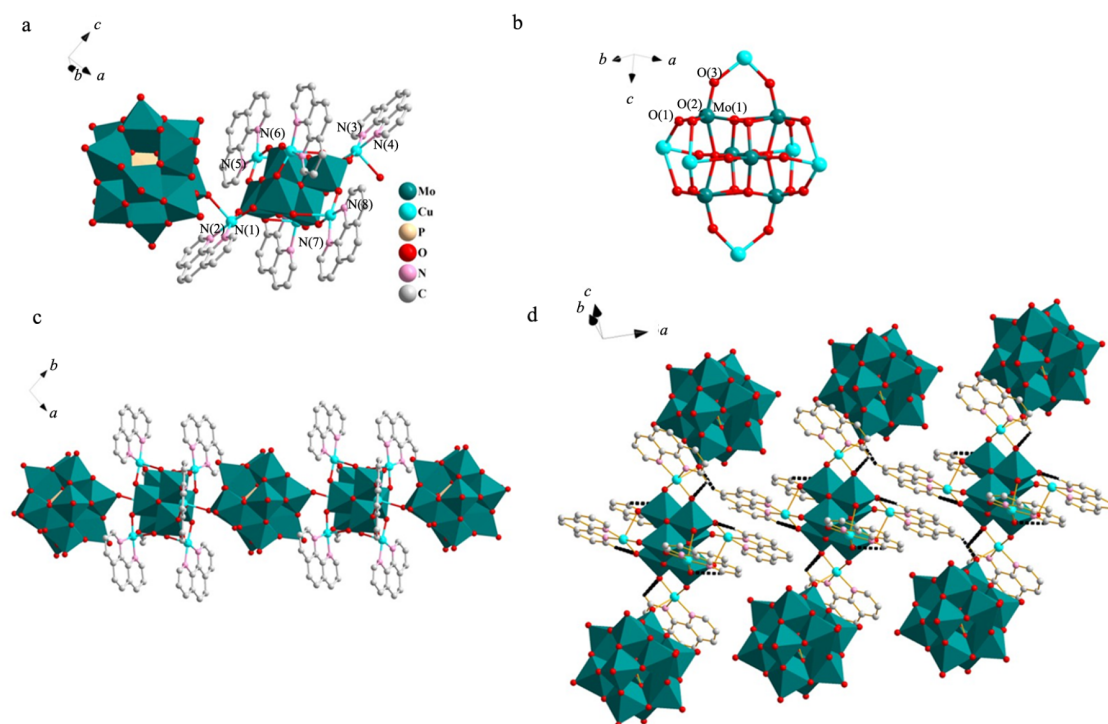
2.3 Reusability test of catalyst

Using cyclooctene as the reaction substrate, we evaluated the recycling performance of the synthesized compound as a catalyst. After each catalytic reaction, the catalyst was recovered by centrifugal separation and washed three times with an appropriate amount of acetonitrile to remove residues. Subsequently, the treated catalyst was dried for reuse in the next recycling experiment.

3 Results and discussion

3.1 Crystal structure of title compound

Single-crystal X-ray diffraction (SCXRD) analysis revealed that synthesized compound is composed of $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$, $\{\text{Mo}_6\}$, Cu(II), and phen ligands (See Figure 1a). Within the $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$, the central P atom is surrounded by a cube of eight oxygen atoms, with each position being half-occupied, a common phenomenon in Keggin-type structures^[30-31]. It crystallizes in the triclinic crystal system with the space group $P\bar{1}$ (See Table 1). All Cu(II) are penta-coordinated but exhibit two distinct coordination modes. One mode involves coordination with a terminal oxygen from $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$, two terminal oxygens of the $\{\text{Mo}_6\}$ cluster, and two nitrogen atoms from the phen ligand. The other mode features coordination with three oxygen atoms from the $\{\text{Mo}_6\}$ cluster and two nitrogen atoms from the phen ligand. This is due to the fact that steric hindrance effect dictates that Cu(II) can only coordinate with one terminal oxygen of the POMs, thereby forming a penta-coordination. The polymerization of NaMoO_4 leads to the formation of $\{\text{Mo}_6\}$ clusters (See Figure 1b). This cluster has a total of 16 terminal oxygen atoms, all of which are coordinated. We attribute this to the obtuse bond angles between the two terminal oxygen atoms connected to Mo, such as the O(1)—Mo(1)—O(2) angle of $103.9(11)^\circ$, O(1)—Mo(1)—O(3) angle of $106.4(10)^\circ$, and O(2)—Mo(1)—O(3) angle of $105.6(10)^\circ$. These obtuse angles result in a



the hydrogen atoms and lattice water molecules are omitted for clarity

Figure 1 The molecular structure diagram of the synthesized compound (a), the structure of the $\{\text{Mo}_6\}$ cluster (b), the 1D chain of the compound viewed along c -axis (c), and the 2D layer structure connected by hydrogen bonds (d)

Table 1 Crystal data and structure refinement for title compounds

Parameter	Property	Parameter	Property
Chemical formula	$\text{C}_{72}\text{H}_{48}\text{Cu}_6\text{Mo}_{16}\text{N}_{12}\text{O}_{63}\text{PV}_2$	Reflections collected	38 379
a/nm	1.3080(3)	Unique reflections	8731
b/nm	1.3504(2)	R_{int}	0.1428
c/nm	1.4971(3)	Data/restraints/parameters	8731/138/787
$\alpha/^\circ$	92.889(7)	GOF on F^2	1.058
$\beta/^\circ$	95.645(7)	$\rho_{\text{calc}}/(\text{g}\cdot\text{cm}^{-3})$	1.323
$\gamma/^\circ$	98.570(7)	μ/mm^{-1}	1.674
Volume/ nm^3	2.5963(8)	$F(000)$	976.1
2θ range	5.18° to 50.06°	$R_1, wR_2 [I \geq 2\sigma(I)]$	0.1562, 0.4285
$h_{\text{min,max}}; k_{\text{min,max}}; l_{\text{min,max}}$	$-15, 15; -16, 16; -17, 17$	$R_1, wR_2 [\text{all data}]$	0.1808, 0.4412

relatively stretched space, enabling the terminal oxygen atoms on the $\{\text{Mo}_6\}$ to coordinate with nitrogen atoms on ligands or oxygen atoms on POMs successfully. We also measured the distances between atoms in two symmetrically positioned ligands. Taking nitrogen atoms as an example, the distance between N(1) and N(3) is 1.3007 nm, and the same goes for the distance between N(2) and N(4), which is also 1.3007 nm; similarly, the distance between N(5) and N(7) is 1.1189 nm, and the distance between N(6) and N(8) is equally 1.1189 nm. This indicates that the atoms within the ligands are parallel to each other, and there exists π - π interactions between the ligands. The bond lengths of Cu—O range from 0.188(2) to 0.264(3) nm, while the bond lengths of Cu—N are 0.196(3) and 0.202(3) nm, all of which are consistent with the bond lengths reported in most literature. To balance the charge, one proton need to be added to $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$, allowing this compound to be defined as $[\text{Cu}_6(\text{phen})_6(\text{Mo}_6\text{O}_{22})(\text{HPMo}_{10}\text{V}_2\text{O}_{40})] \cdot \text{H}_2\text{O}$. Cu(II) ions are

connected to the terminal oxygens of the $\{\text{PMo}_{10}\text{V}_2\}$ and the $\{\text{Mo}_6\}$, forming a one-dimensional (1D) chain (See Figure 1c). Adjacent chains form two-dimensional (2D) layers through hydrogen bonds (See Figure 1d).

3.2 Characterization of title compound

The synthesized compound was characterized using Fourier transform infrared (FT-IR) spectroscopy and X-ray powder diffraction (PXRD). The FT-IR spectrum of the compound is shown in Figure 2a, displaying characteristic vibration peaks of the Keggin-type polyoxoanion in the range of 700 to 1100 cm^{-1} . The peaks at 1057, 947, 866, and 781 cm^{-1} can be assigned to the vibrational modes $\nu(\text{P}=\text{O}_a)$, $\nu(\text{Mo}=\text{O}_d)$, $\nu(\text{Mo}=\text{O}_b-\text{Mo})$, and $\nu(\text{Mo}=\text{O}_c-\text{Mo})$ within the polyoxoanion structure, respectively. The characteristic vibration peaks of the ligand phen are observed in the range of 1100 to 1700 cm^{-1} . The PXRD results show a high degree

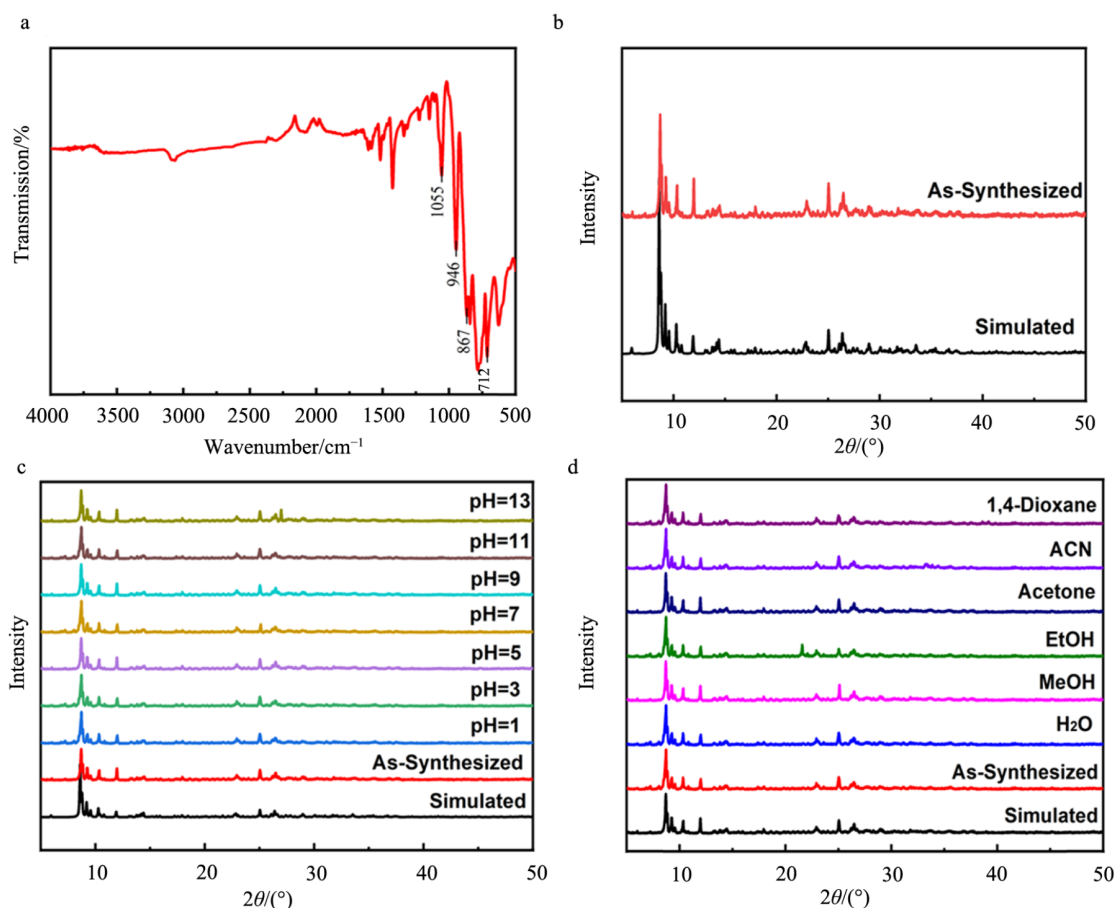


Figure 2 The FT-IR spectra (a), PXRD patterns (b), PXRD patterns in different pH values aqueous solutions for 24 h (c) and in different solvents for 7 d (d) of the synthesized compound

of agreement between the synthesized compound and the PXRD spectrum obtained from single-crystal data fitting (See Figure 2b), confirming the phase purity of the compound. Finally, we investigated its solvent stability by immersing the compound in different aqueous solutions with pH values ranging from 1 to 13 for 24 h and in common solvents (H₂O, MeOH = methanol, EtOH = ethanol, acetone, ACN = acetonitrile, and 1,4-dioxane) at room temperature for 7 d. As shown in Figures 2c and 2d, the PXRD patterns of the recovered samples match well with those of the freshly prepared samples, indicating that the compound possesses good solvent stability and acid-base stability.

3.3 Catalytic activity of the synthesized compound

We evaluated the catalytic activity of the synthesized compound under oxygen as the oxidant, using the epoxidation of cyclooctene as a model reaction (See Figure 3). Firstly, we screened different solvents and the results revealed that the conversion rate and selectivity of cyclooctene were significantly higher in aprotic solvents (1,4-dioxane, CHCl₃, ethyl acetate, and CH₃CN) compared to those in protic solvent (ethanol). Among them, acetonitrile exhibited the highest conversion rate for cyclooctene (See Table 2, entries 1–5). Therefore, we selected acetonitrile as the optimal

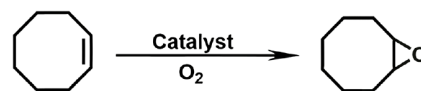


Figure 3 Model reaction of cyclooctene epoxidation using oxygen as an oxidizing agent

reaction solvent. Subsequently, we examined the effect of temperature on the catalytic rate. As the temperature was increased from room temperature to 55 °C (entries 5–8), the results indicated that the selectivity of cyclooctene remained above 99% under four different temperature conditions, while the conversion rate increased as the temperature rose from room temperature to 35 °C. However, with further temperature elevation, the conversion rate began to decline, dropping to 93.6% at 55 °C. This is because the increased temperature reduced the solubility of oxygen in the liquid phase, leading to a decrease in conversion rate. Hence, we chose 35 °C as the optimal reaction temperature. Next, we further investigated the influence of catalyst dosage on the reaction while keeping other reaction parameters constant (entries 6 and 9–11). When the catalyst dosage was 10 mg, the conversion rate of cyclooctene was 85.4%. However, as the catalyst dosage was gradually increased to 20 mg, the number of active sites on the catalyst increased and the conversion rate was optimal. However, when the catalyst

Table 2 The conversion and selectivity of cyclooctene epoxidation catalyzed by the synthesized compound with O₂ as oxidant

Entry	Solvent	<i>m</i> _{Cat} /mg	<i>n</i> _{IBA} /mmol	<i>t</i> /°C	Conv./%	Sel./%
1	1,4-dioxane	20	4	RT	16.5	–
2	EtOH	20	4	RT	4.6	–
3	CHCl ₃	20	4	RT	75.3	> 99
4	Ethyl acetate	20	4	RT	63.9	> 99
5	CH ₃ CN	20	4	RT	82.5	> 99
6	CH ₃ CN	20	4	35	98.6	> 99
7	CH ₃ CN	20	4	45	95.3	> 99
8	CH ₃ CN	20	4	55	93.6	> 99
9	CH ₃ CN	10	4	35	85.4	> 99
10	CH ₃ CN	15	4	35	94.3	> 99
11	CH ₃ CN	25	4	35	95.2	> 99
12	CH ₃ CN	20	2	35	67.3	> 99
13	CH ₃ CN	20	3	35	89.2	> 99
14	CH ₃ CN	20	5	35	98.6	97.4

dosage was further increased to 25 mg, the conversion rate of cyclooctene slightly decreased. This could be due to excessive catalyst addition, resulting in catalyst aggregation and a reduction in the effective contact area between the catalyst and the substrate, thereby weakening the reaction activity. Therefore, we selected 20 mg as the optimal catalyst dosage. Under the optimized solvent system, reaction temperature, and catalyst dosage, we further explored the effect of isobutyraldehyde (IBA) dosage on the epoxidation of cyclooctene. As the IBA dosage increased from 2 mmol to 4 mmol, the conversion rate of the reaction gradually increased. However, when the IBA dosage was increased to 5 mmol, the conversion rate of cyclooctene did not further increase, and the selectivity of the product decreased. Therefore, the optimal IBA dosage was determined to be 4 mmol (See Table 2, entries 6 and 12–14). In summary, we studied the effects of different solvents, reaction temperatures, catalyst dosages, and IBA additions on the epoxidation of cyclooctene and determined the optimal reaction

conditions: a conversion rate of 98.6% and a selectivity of over 99% were achieved after 4 h of reaction at 35 °C using 20 mg of catalyst and 4 mmol of IBA in 5 mL of acetonitrile.

3.4 Substrate scope

Given the excellent catalytic activity of the synthesized compound, we further investigated its catalytic performance in the epoxidation reactions of various olefins. As shown in Figure 4, cyclopentene exhibited a conversion rate of 98.1% and a selectivity of 83.6% after a 4-hour reaction, while cyclohexene showed a conversion rate of 83.4% and a selectivity of 71.5% after an 8-hour reaction. The decrease in selectivity was attributed to the formation of by-products from the dissociation of carbon-carbon double bonds. We also selected aromatic olefins as reaction substrates. Due to the benzene ring is connected to the C=C bond in the olefin, it exerts an electron-donating effect through conjugation, thereby accelerating the reaction rate. Styrene ex-

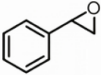
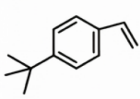
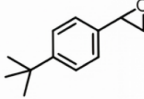
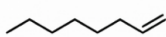
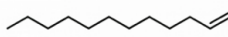
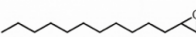
Substrate	Product	<i>t</i> /h	Conv./%	Sel./%
		4	98.1	83.6
		8	83.4	71.5
		4	93.6	89.3
		4	> 99	67.9
		8	59.9	> 99
		8	48.6	> 99

Figure 4 The conversion and selectivity of different olefins catalyzed by the synthesized compound

hibited a conversion rate of 93.6% and a selectivity of 89.3% after a 4-hour reaction. Notably, tert-butylstyrene demonstrated higher reactivity (> 99% conversion) compared to unsubstituted styrene after a 4-hour reaction, albeit with a lower selectivity of 67.9%. This enhanced reactivity was attributed to the electron-donating effect of the tert-butyl group, which increased the electron cloud density of the carbon-carbon double bond, further accelerating the reaction rate. However, the corresponding lower selectivity of the epoxy compound might be due to over-oxidation, leading to the formation of by-products such as aldehydes and carboxylic acids. When linear olefins, such as 1-octene and 1-dodecene, were used as reaction substrates, the product selectivity exceeded 99%. Despite extending the reaction time to 8 h, the conversion rates were only 59.9% and 48.6%, respectively. The lower conversion rates were attributed to the lower electron cloud density of the carbon-carbon double bond at the terminal position of linear olefins, which slowed down the reaction rate. Additionally, we observed a decrease in catalytic efficiency when the number of carbon atoms in linear olefins increased from 8 to 12. This can be attributed to the decrease in molecular polarity as the carbon number increases, leading to reduced solubility in acetonitrile, which in turn affects the catalytic performance. The aforementioned analysis demonstrates that the synthesized compound exhibits broad applicability in catalyzing the epoxidation of olefins, showing good catalytic activity towards cyclic olefins, aromatic olefins, and linear olefins.

3.5 Mechanism study

To investigate the mechanism of the synthesized compound

in catalyzing the epoxidation of cyclooctene, we conducted control experiments to identify the active sites of the catalytic system (See Figure 5a). In the absence of a catalyst, cyclooctene showed almost no reaction, indicating the necessity of adding a catalyst. When using two POMs, $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$, as catalysts in the optimal reaction system, the conversion rates of cyclooctene were 45% and 58.4% respectively. This demonstrates that POMs are active in the epoxidation of olefins, and their oxidative catalytic ability improves with the number of vanadium substitutions increasing. When CuCl_2 was used as a catalyst, the substrate conversion rate was 75.2%, indicating that Cu(II) also has a catalytic effect on the reaction. When a simple physical mixture of $\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and CuCl_2 (abbreviated as $\text{PMo}_{10}\text{V}_2 + \text{CuCl}_2$) was used as a catalyst, the conversion rate of cyclooctene was 86.8%, which was significantly lower than that of the synthesized compound. This suggests that the excellent catalytic activity of the compound is attributed to the synergistic effect between $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and the metal center CuCl_2 rather than a simple addition of their catalytic activities.

To explore the potential active species and ascertain their functions in the catalytic process of the synthesized compound, we carried out radical trapping experiments, as shown in Figure 5b. First, the addition of 2,2,6,6-tetramethylpiperidinyl-1-oxyl (TEMPO, a carbon radical scavenger) almost completely inhibited the reaction, indicating the presence of carbon-centered free radicals in the reaction system. Then, the addition of the oxygen radical scavenger diphenylamine (DPA) resulted in a conversion rate of only 15.9% for the product, suggesting the presence of oxygen-active free radicals in the reaction system. To further de-

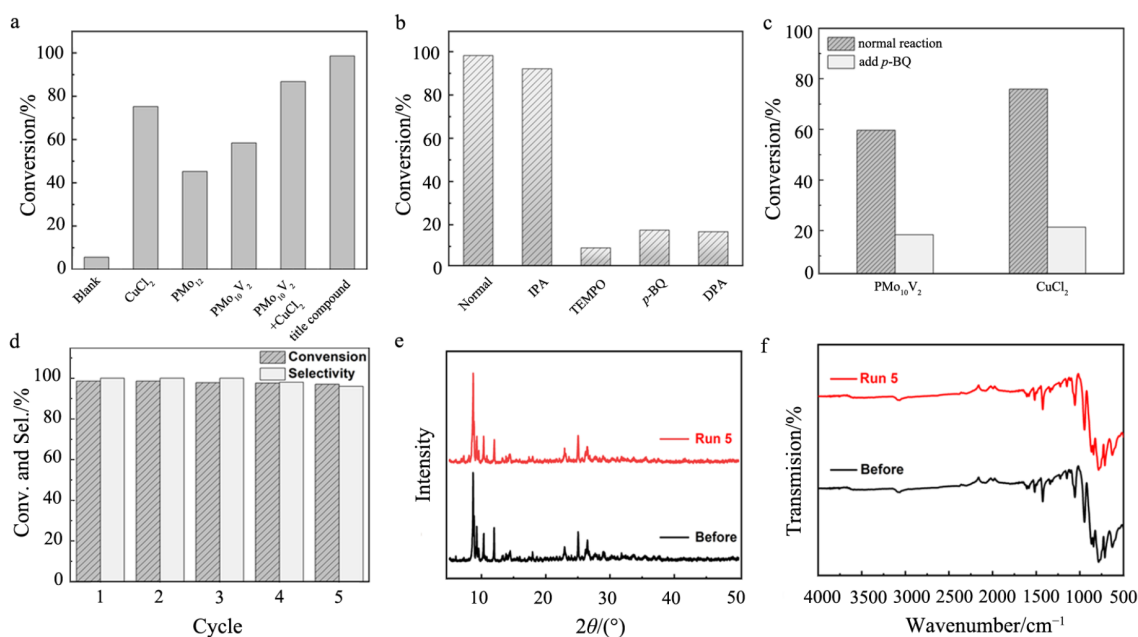


Figure 5 Conversion of different catalysts for the epoxidation of cyclooctene (a), conversion of cyclooctene epoxidation catalyzed by the synthesized compound in the presence of different trapping species (b), conversion over $\text{PMo}_{10}\text{V}_2$ and CuCl_2 in the presence of *p*-BQ (c), recycling performance of the synthesized compound as catalyst for the oxidation of cyclooctene (d), PXRD patterns (e) and FT-IR spectra (f) of the synthesized compound before and after catalytic reactions

monstrate the type of oxygen free radicals, we added isopropyl alcohol (IPA, a hydroxyl radical scavenger) and *p*-benzoquinone (*p*-BQ, a superoxide radical scavenger) to the reaction. The addition of IPA had no significant inhibitory effect on the reaction, with a conversion rate of 92.4% for cyclooctene, indicating the absence of hydroxyl radicals in the system. However, the addition of *p*-BQ reduced the conversion rate of cyclooctene to 16.6%, suggesting that the oxygen-active radicals in the system are superoxide radicals. To explore the mechanism of $\cdot\text{O}_2^-$ formation, we introduced *p*-BQ into the reaction system, employing $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and CuCl_2 as catalysts individually. This led to a reduction in the conversion rate of cyclooctene to 15.8% and 18.9% (See Figure 5c). These findings suggest that both $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and CuCl_2 are capable of activating O_2 to generate $\cdot\text{O}_2^-$ and contributing to the epoxidation process of cyclooctene.

Based on the above experimental results and existing literature, we proposed a possible reaction mechanism for the epoxidation of cyclooctene to epoxycyclooctane catalyzed by the synthesized compound, as shown in Figure 6. First, V^{V} in $\{\text{PMo}_{10}\text{V}_2\}$ promotes the rapid oxidation of isobutyraldehyde to an isobutyryl radical, while itself is reduced to V^{IV} . Subsequently, V^{IV} is oxidized back to V^{V} by O_2 , generating $\cdot\text{O}_2^-$. Meanwhile, the metal active site Cu^{II} oxidizes isobutyraldehyde to an isobutyryl radical, reducing itself to Cu^{I} , which is then oxidized back to Cu^{II} by O_2 , also producing $\cdot\text{O}_2^-$. The isobutyryl radical generates isobutyl peroxyacid through two pathways: the first pathway involves direct reaction with O_2 and isobutyraldehyde to form isobutyl peroxyacid; the second pathway involves the combination of the isobutyryl radical with $\cdot\text{O}_2^-$ and H^+ to form isobutyl peroxyacid. Finally, cyclooctene is converted to epoxycyclooctane under the action of isobutyl peroxyacid.

3.6 Recyclability and stability of the synthesized compound

The reusability of a catalyst is a crucial factor in evaluating

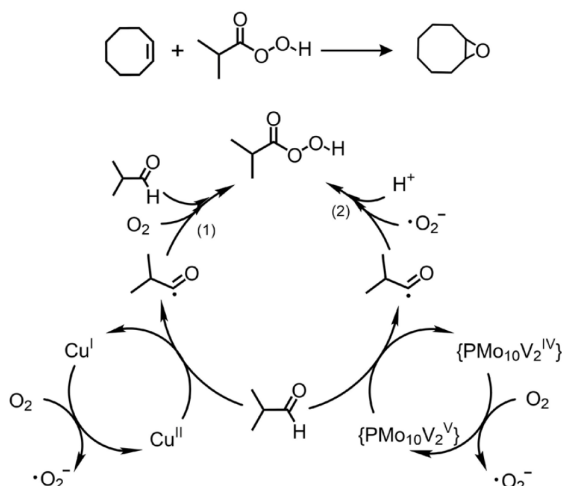


Figure 6 Possible mechanism for the epoxidation of cyclooctene catalyzed by the synthesized compound

its practical application. To assess the recyclability and stability of the synthesized compound, cyclic experiments were conducted on the catalytic epoxidation of cyclooctene under optimal conditions (See Figure 5d). After each experiment, the catalyst was separated by centrifugation, washed with acetonitrile, and dried for use in the next cycle. The experimental results showed that after five cycles, there was no significant decrease in the catalyst's activity, and both the conversion rate and selectivity of the product remained largely unchanged. Characterization of the catalyst after recycling using PXRD and FT-IR revealed that the peak positions in the PXRD patterns (See Figure 5e) and FT-IR spectra (See Figure 5f) of the recovered catalyst closely matched those of the freshly prepared catalyst, indicating good agreement. These results demonstrate that the synthesized compound, as a heterogeneous catalyst, not only exhibits structural stability but can also be recycled efficiently.

4 Conclusion

In this work, utilizing vanadium-substituted Keggin-type polyoxometalate and sodium molybdate as a precursor, we introduced metal $\text{Cu}(\text{II})$ ions and the organic ligand phen to synthesize a novel polyoxometalate-based hybrid compound, $[\text{Cu}_6(\text{phen})_6(\text{Mo}_6\text{O}_{22})(\text{HPMo}_{10}\text{V}_2\text{O}_{40})\cdot\text{H}_2\text{O}]$, via a hydrothermal method and explored its oxidative activity. We analyzed the possible reasons for the formation of the $\{\text{Mo}_6\}$ cluster structure. Subsequently, we employed this compound to catalyze the epoxidation of cyclooctene using O_2 as the oxidant. Under conditions of 35 °C for 4 h, the conversion rate of cyclooctene oxide reached 98.6% with a selectivity greater than 99%. After five cycles, the catalyst maintained high conversion and selectivity, indicating that the synthesized compound exhibits excellent recyclability and stability. Mechanistic studies revealed that the outstanding catalytic performance of the synthesized compound is attributed to the synergistic catalysis of multiple sites from the metal center $\text{Cu}(\text{II})$ and $\text{PMo}_{10}\text{V}_2$, which promoted the generation of $\cdot\text{O}_2^-$ active species upon reaction with O_2 , accelerating the reaction. Furthermore, the synthesized compound demonstrated good catalytic activity for the epoxidation of several other types of olefins, exhibiting excellent substrate universality. This work provides new insights into the design and synthesis of polyoxometalate-based hybrid catalysts with multiple-site synergistic catalysis for promoting olefin epoxidation reactions.

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一种包含两类多金属氧簇的新型杂化物用于催化烯烃环氧化反应

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摘要 钒取代的Keggin型多酸相较于其母体多酸具有更高的负电荷, 这一方面增强了其与金属的配位能力, 另一方面由于钒元素具有较高的氧化催化能力, 使其在氧化催化方面具有极大的发展潜力。本研究通过加入钒取代的Keggin型多酸和钼酸钠, 在水热条件下成功地构建了一例无机有机杂化合物: $[\text{Cu}_6(\text{phen})_6(\text{Mo}_6\text{O}_{22})(\text{HPMo}_{10}\text{V}_2\text{O}_{40})\cdot\text{H}_2\text{O}]$ ($\text{phen} = 1,10\text{-菲咯啉}$), 分别由两类不同的多金属氧簇 $[\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$ 和 $[\text{Mo}_6\text{O}_{22}]^{8-}$ ($\{\text{PMo}_{10}\text{V}_2\} = [\text{PMo}_{10}\text{V}_2\text{O}_{40}]^{5-}$; $\{\text{Mo}_6\} = [\text{Mo}_6\text{O}_{22}]^{8-}$)组成。在烯烃环氧化反应中, 该化合物表现出优异的催化性能。以氧气为氧化剂, 在35 °C下反应4小时, 即可将环辛烯高效转化为1,2-环氧环辛烷, 转化率高达98.6%, 选择性超过99%。此外, 该催化剂具有良好的循环稳定性, 连续使用5个循环后仍保持高活性, 并展现出广泛的底物适用性, 可有效催化多种烯烃的环氧化反应。

关键词 钒取代的Keggin型多金属氧酸盐; 无机-有机杂化物; 烯烃环氧化