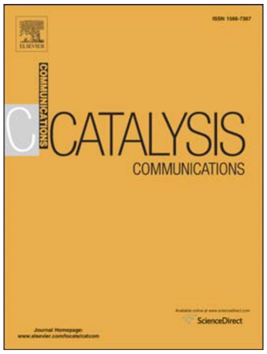

Recyclable, green and efficient epoxidation of olefins in water with hydrogen peroxide catalyzed by polyoxometalate nanocapsule

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Recyclable, Green and Efficient Epoxidation of Olefins in Water with Hydrogen Peroxide Catalyzed by Polyoxometalate Nanocapsule

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Abstract

A practical method for the selective epoxidation of alkenes was discovered using $H_xPMo_{12}O_{40}\subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ as a catalyst in the presence of H_2O_2 as a green oxidant. However, the simple catalyst system involving polyoxometalates and H_2O_2 exercised the most successful system in obtaining high to excellent yields of epoxide products for different alkenes, including aromatic and aliphatic alkenes at room temperature in water. The effectiveness of this catalyst is evidenced by 99% selectivity to epoxide and 97-99% efficiency of H_2O_2 utilization. The stability of $PMo\subset Mo_{72}Fe_{30}$ under a catalytic reaction has been confirmed by XRD, FT-IR and Raman spectroscopies.

Keywords: Keplerate Polyoxometalates, Catalysis, Epoxidation, Hydrogen Peroxide, Alkenes

1. Introduction

In recent years, the epoxidation of alkenes has achieved a remarkable level of popularity from both scientific and industrial researchers. Epoxides play an extremely important role as intermediates and building blocks in organic synthesis [1]. Different epoxides have been widely used in paints, epoxy resins, surfactants, and intermediates such as glycols, glycol ethers, alkanolamines and polymers. For example, annually 4.5 million and 70,000 tons of propylene and butene oxides are produced, respectively [2].

Divergent compounds such as organometallic and inorganic metal oxides have been employed as catalysts for alkene epoxidations utilizing various oxidants, for instance, oxygen, ozone and hydrogen peroxide or organic peroxides [3]. In particular, a hydrogen peroxide-based catalytic epoxidation has received considerable attention because hydrogen peroxide is generally safe in storage and operation. In addition, it is not only a cheap, mild and environmentally benign reagent generating only harmless water as a by-product, but also it has high and effective oxygen content [4].

These advantages have accelerated the progress of substantial procedures for the epoxidation of olefins with aqueous hydrogen peroxide and various catalyst systems such as manganese and cobalt complexes [5], porphyrin [6], salen systems [7], $FeCl_3 \cdot 6H_2O$ [8], titanosilicates [9] methyltrioxorhenium [10], tungsten compounds [11] and manganese complexes [12].

In many of these systems, the efficiency of H_2O_2 usage and their selectivity to epoxides are low. The types of usable olefins are confined, requiring efficiency or high reaction temperatures, which sometimes reduce selectivity to epoxide. Moreover, a major problem in many catalytic systems is to perform such a process in non-toxic solvents, particularly in aqueous media.

Polyoxometalates (POMs) are a large family of anionic metal−oxygen clusters with structural diversity, showing many applications in analytical chemistry, medicinal chemistry, electrochemistry, photochemistry, and catalyst chemistry [13].

POMs have shown to be efficient Brønsted acid catalysts and highly selective oxidation catalysts due to both their stability to oxidation and compatibility with diverse oxygen sources [14].

Müller et al. synthesized new giant molecular spheres with the general formula of $[(\text{pentagon})_{12}(\text{linker})_{30}]$ or $[\text{Mo}(\text{Mo})_5]_{12}(\text{Linker})_{30}]$ and because of their structural features, so-called Keplerates, they could be generated in variable sizes by linking the fundamental pentagonal {(Mo)Mo5} building block with different linkers such as $HCOO^-$, CH_3COO^-, SO_4^{2-}, $Fe^{III}(H_2O)\}^{3+}$, etc [15-17].

Furthermore, Müller synthesized a marvelous structure of polyoxometalates containing a core–shell hybrid made of Keggin-type heteropolyoxomolybdates encapsulated into $\{Mo_{72}Fe_{30}\}$-type Keplerates and $H_xPMo_{12}O_{40}\subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$(abbreviation = $PMo\subset Mo_{72}Fe_{30}$)[18].

The unique structures and topologies of Keplerates have gained a remarkable consideration in solid state chemistry [19, 20]. Izarova et al. discovered the catalytic efficiency of keplerate polyoxometalates for the selective oxidation of sulfides [21]. However, the catalytic activity of these compounds in the oxidation of organic compounds really lags behind [22].

The use of $PMo\subset Mo_{72}Fe_{30}$ as highly efficient catalysts in the selective oxidation of alkenes to epoxide has not been previously reported. As a continuous improvement, the present work reports a simple, recyclable and green method for the selective oxidation of a series of alkenes using 30% aqueous hydrogen peroxide as an oxidant and $PMo\subset Mo_{72}Fe_{30}$ as a catalyst to the corresponding epoxides in excellent selectivity and yield under mild reaction conditions.

2. General methods and materials:

$Mo^{VI}_{72}Fe^{III}_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}].150H_2O$ $\{Mo_{72}Fe_{30}\}$ and $PMo\subset Mo_{72}Fe_{30}$ were prepared according to the literature methods (see supporting information) [18]. All common laboratory chemicals were of reagent grade quality acquired from commercial resources and used without further purification. The techniques and methods applied for the synthesis of Keplerate POMs, as well as the typical procedure used for the oxidation of alkenes have been compiled into the supporting information.

3. Results and discussion

In this work, cyclooctene was selected as a model of the substrate for initial catalytic tests. Epoxidation under mixture conditions using $Mo_{72}Fe_{30}$ did not form any cyclooctenoxide with an appropriate yield. Similarly, the use of $H_3PMo_{12}O_{40}$ represented the conversion of cyclooctene to produce the corresponding epoxide in a low yield (Table 1, entry 2). Using $PMo\subset Mo_{72}Fe_{30}$ as a catalyst for the oxidation of cyclooctene gave rise to the conversion of cyclooctene into cyclooctene oxide with a desirable yield only after 3 h.

Table1. Epoxidation of cyclooctene with $Mo_{72}Fe_{30}$, $H_3PMo_{12}O_{40}$ and $PMo\subset Mo_{72}Fe_{30}$ [a]

Entry	Catalyst	Time(h)	Yield [b] (%)
1	$Mo_{72}Fe_{30}$	5	6
2	$H_3PMo_{12}O_{40}$	5	18
3	$PMo\subset Mo_{72}Fe_{30}$	3	99

[a] Reaction conditions: catalyst (2.5µmol), substrate (5 mmol), 30% H_2O_2 (2 mmol), water (5 mL), 25 ºC. [b] Yield (%) is calculated as products (mmol) per initial H_2O_2 (mmol)×100

After this, the effect of different parameters such as oxidant and catalyst amounts, solvent type and temperature in the catalytic performance of PMo⊂$Mo_{72}Fe_{30}$ in the epoxidation of cyclooctene were studied. Initially, the epoxidation reaction was performed using PMo⊂$Mo_{72}Fe_{30}$ as a catalyst and cyclooctene or cyclohexene as a standard substrate in various solvents and different amounts of oxidant or catalyst at room temperatures (Figure1, 2 and table 1 in the supporting information).

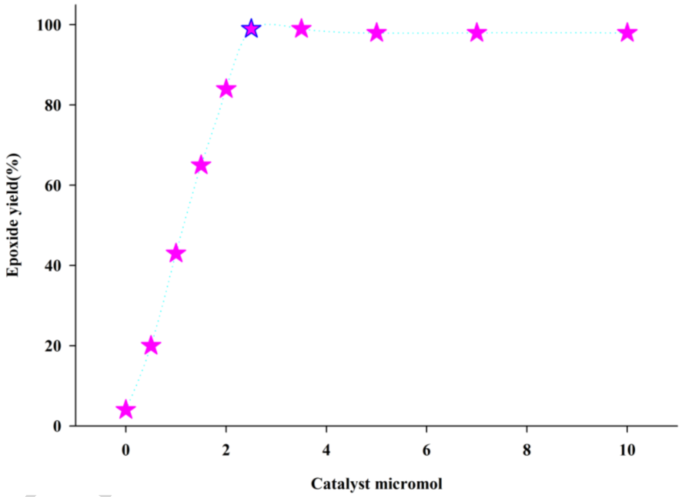


Figure 1. Influence of the catalyst µmol ratio on the oxidation of cyclooctene

Reaction conditions: catalyst (0-10 µmol), substrate (5 mmol), 30% H_2O_2 (2 mmol), water (5 mL), 25 ºC , 3h. Yields were determined by gas chromatography using an internal standard technique.

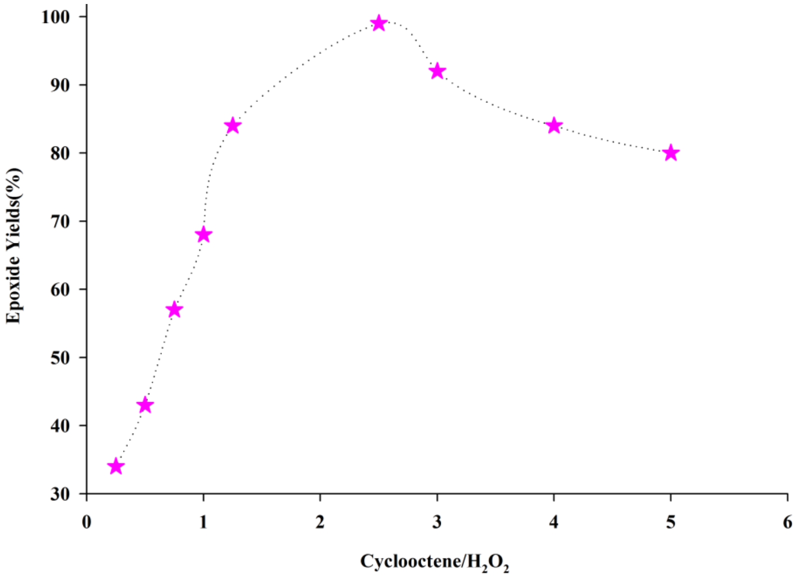
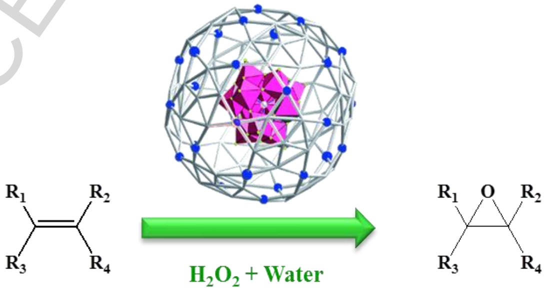


Figure 2. Influence of the Cyclooctene/H_2O_2 ratio on the oxidation of cyclooctene

Reaction conditions: catalyst (2.5µmol), substrate (5 mmol), 30% H_2O_2 (0.2-10 mmol), water (5 mL), 25 ºC, 3h. Yields were determined by gas chromatography using an internal standard technique.

After the optimization of reaction conditions for the model reaction in hand, the selective epoxidation of several alkenes was studied (Scheme 1).

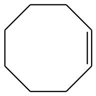
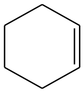
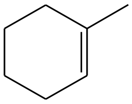


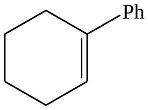
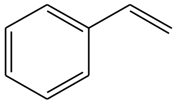
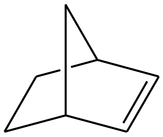
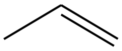
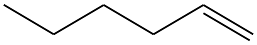
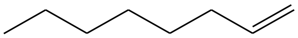
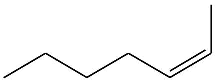
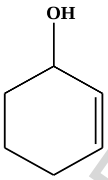
Scheme 1. Green epoxidation of different alkenes in optimized reaction conditions

Under optimum experimental conditions, various alkenes were subjected to the oxidation method using 5 mmol of alkenes, 2 mmol of H_2O_2 and 2.5 µmol of catalysts at 25 °C in water (Table 2). It is generally assumed that the oxidation of terminal alkenes is difficult owing to the presence of an electron-deficient double bond. Importantly, the relevant catalytic networks were equally effective in the epoxidation of terminal alkenes (Table 2). Various cyclic alkenes such as cyclohexene, 1-methyl-cyclohexene, 1-phenyl cyclohexene and cyclooctene were epoxidized with high yields (entries 1-4). The applied method resulted in a styrene (entry 5) of 90% yield within 5 h. Bulky cyclic olefins (norbornene) were epoxidized with 97% yield (entry 6). However, the poor reactivity of 1, 1, 2- trisubstituted and those of E-olefins (entries 3, 4) were identified, demonstrating the steric hindrance around the active site of the catalyst.

The present method led to an excellent chemoselectivity. Different alkenes containing hydroxyl groups were converted into the corresponding epoxy alcohols with high selectivity and only obtained small amounts of aldehydes and ketone (entries 12, 13). Terminal alkenes such as propylene, 1-butene, 1-hexene, and 1-octene could be transformed into the corresponding epoxide with high conversion and selectivity. PMo⊂$Mo_{72}Fe_{30}$ oxidized propylene (94%), 1-butene (91%), 1-hexene (89%), and 1-octene (87%) easily. The reaction mechanism of alkenes' epoxidation over polyoxometalates using H_2O_2 as an oxidant has been extensively investigated by several groups (see supporting information).

Table 2. The selective epoxidation of various substrates with aqueous H_2O_2 catalyzed by PMo⊂$Mo_{72}Fe_{30}$ [a]

Entry	Substrate	Time(h)	Yield (%)[b]	H_2O_2 efficiency (%)[c]
1		3	99	99
2		3.5	98	99
3		5	87	99

4		5	83	99
5[d]		5	90	99
6		6	97	98
7[e]		7	94	97
8[e]		7	91	97
9		7	89	
10		7	87	97
11		4	92	99
12[f]		5	60	97
13[f]		4.5	75	98

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[a] Reaction conditions: catalyst (2.5µmol), substrate (5 mmol), 30% H_2O_2 (2 mmol), water (5 mL), 25 ºC.

[b] Yields were determined by gas chromatography using an internal standard technique (Yield (%) is calculated as products (mmol) per initial H_2O_2 (mmol)×100).

[c] E_{ox}(H_2O_2 efficiency) = [products (mol)/consumed H_2O_2 (mol)] × 100.
The remained H_2O_2 after reaction completion was estimated by potential difference titration of Ce^{3+}/Ce^{4+} [0.1 M aqueous $Ce(NH_4)_4(SO_4)_4.2H_2O$].

[d] Benzaldehyde (select. 8%) was formed.

[e] Propylene (6 atm), 1-butene (3 atm) and 1,3-butadiene (2.5 atm).

[f] Cyclohexenone (select. 10%) and 3-methyl-2-buten-1-ol (select. 19%) were formed as a by-product.

To show the ability and efficiency of PMo⊂$Mo_{72}Fe_{30}$ in the epoxidation of alkenes compared to other polyoxometalates, the results of the cyclooctene epoxidation in the presence of other polyoxometalates were examined (Table 3). Rezaeifard reported the epoxidation of different alkenes catalyzed by $(NH_4)_{42}[Mo^{VI}_{72}Mo^{V}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ (abbreviation= Mo_{132}) in various reaction conditions [22]. Furthermore, the epoxidation reaction was performed using ethanol as a solvent and as a result epoxide products with yields of 90-94% and excellent chemoselectivities were generated (entry 1). In this work, it was reported that the epoxidation procedure presented an excellent chemoselectivity. Kholdeeva described that $PW_{12}O_{40}$/MIL-101 as a true heterogeneous catalyst can be recycled several times without loss of activity and selectivity with the retention of both POM and MIL-101 structures [23]. Moreover, it was revealed that $PW_{12}O_{40}$/MIL-101 material indicates similar catalytic activity in H_2O_2-based alkene epoxidation reaction compared to the activity of the corresponding homogeneous PW_{12}, while the catalytic activity of $PW_{12}O_{40}$/MIL-101 material is significantly higher than the activity of the known supported PW_4 catalyst. Zhou applied $Mo_8O_{26}^{n-}$ as a catalyst for the olefin epoxidation using hydrogen peroxide (H_2O_2) as an oxidant in CH_3CN(entry 4) [24]. These catalysts are not only self-separating, but also brought about excellent catalytic reactivities, which are a great advantage for the catalyst recycling. Leng *et al.* synthesized POM-based ionic hybrids which proved to be highly efficient heterogeneous catalysts for the epoxidation of alkenes with H_2O_2 (entry 5) [25]. In addition, Mizuno and co-workers identified $[\gamma\text{-}SiW_{10}O_{34}]^{4-}$ presenting a high catalytic performance for the epoxidation of different olefins with a hydrogen peroxide oxidant (entry 6) [26]. In these catalytic systems, the epoxidation proceeded with ≥99% selectivity to epoxide formation, high efficiency of H_2O_2 utilization (≥99%), high stereospecificity and the straightforward recovery of the catalyst [26].

Sharma and Patel have carried out the epoxidation of styrene catalyzed by 12-molybdophosphoric acid and hydrous zirconia under organic solvent-free conditions with H_2O_2 as an oxidant. Conversion and selectivity toward the epoxide were 85% and 70%, respectively (entry 7) [27]. Jalilian *et al*. reported the catalytic activity of three Keplerate polyoxometalates and $Mo_{72}M_{30}$ (M = V, Cr, Fe) in the epoxidation of various alkenes [28]. It was demonstrated that among the three Keplerate POM catalysts, in the epoxidation of different alkenes under the same reaction conditions, $Mo_{72}Cr_{30}$ exercised a higher catalytic activity than the other two (entries 8-10). In this work, $Mo_{72}Fe_{30}$ lacks a catalytic activity for the epoxidation reaction. As a result, the catalyst "$PMo\subset Mo_{72}Fe_{30}$" gave rise to an excellent catalytic activity for the epoxidation of alkenes compared to other polyoxometalates. In addition, the epoxidation of different alkenes was conducted in mild reaction conditions with green oxidants and solvents (entry 11). The future aim of this work is to explore the factors affecting the low catalytic activity of $Mo_{72}Fe_{30}$ and the high catalytic performance of $PMo\subset Mo_{72}Fe_{30}$ in the oxidation reaction.

Table 3. Catalytic activity of various catalysts for the epoxidation of cyclooctene with H_2O_2

Entry	Catalyst	Conversion (%)	Ref
1	Mo_{132}	90-94	21
2	$PW_{12}O_{40}$/MIL-101	76	22
3	PW_{12}	78	22
4	$Mo_8O_{26}^{n-}$	99	24
5	MimAM(H)-PW	95	25
6	γ-$SiW_{10}O_{34}^{4-}$	100	26
7	ZPM	85	27
8	$Mo_{72}Cr_{30}$	97	28
9	$Mo_{72}V_{30}$	86	28
10	$Mo_{72}Fe_{30}$	7	28
11	$PMo\subset Mo_{72}Fe_{30}$	99	Present work

Due to the importance of the catalyst specific features such as stability and reusability in the catalyst evaluation, these features of the PMo$\subset$Mo$_{72}$Fe$_{30}$ were also investigated. After the completion of the catalytic epoxidation of cyclooctene with PMo$\subset$Mo$_{72}$Fe$_{30}$ as a catalyst, ethyl acetate was added to the reaction mixture as a safe solvent for isolating hydrophobic organic products. Then, an aqueous solution of the catalyst was reused directly for the next run of the oxidation reactions without further purification. The easy recovery combined with the inherent stability of the PMo$\subset$Mo$_{72}$Fe$_{30}$ permits the catalyst to be reused over 5 times in the epoxidation of cyclooctene with a negligible decrease in the catalyst activity after 5 runs (see supporting information). The IR and Raman spectra and XRD pattern of the recycled compound "PMo$\subset$Mo$_{72}$Fe$_{30}$" illustrated a slight change after many recoveries, indicating a desirable stability of the catalyst (see supporting information).

4. Conclusion

Polyoxometalate nanocapsule was employed as catalysts for the selective epoxidation of various alkenes using hydrogen peroxide as the oxidant in water. The polyoxometalate nanocapsule showed a high catalytic performance for the epoxidation of different olefins with a hydrogen peroxide at room temperature in water. The catalyst can be reused for at least 5 runs without significant loss of activity. These systems demonstrated a straightforward and safe procedure and established that the high reusability of the catalysts is environmentally benign.

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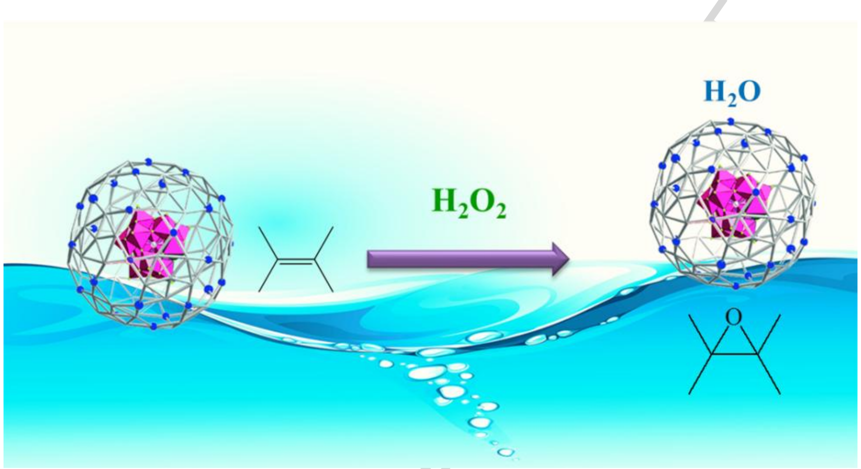
Graphical abstract



Highlights

PMo⊂ $Mo_{72}Fe_{30}$ showed a high catalytic activity for the epoxidation of various alkenes with H_2O_2.

For different alkenes, 99% selectivity to epoxide and 97-99% efficiency of H_2O_2 were observed.

PMo⊂ $Mo_{72}Fe_{30}$ exercised an excellent catalytic activity, stability and reusability.