



Short communication

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 $H_xPMo_{12}O_{40} \cdot C_4H_4Mo_{72}Fe_{30} (CH_3COO)_{15}O_{254}$ 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 $PMo \cdot C_4H_4Mo_{72}Fe_{30}$ under a catalytic reaction has been confirmed by XRD, FT-IR and Raman spectroscopies.

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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], titanasilicates [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 $[(pentagon)_{12}(linker)_{30}]$ or $[Mo(Mo)_5]_{12}(Linker)_{30}$ and because of their structural features, so-called Keplerates, they could be generated in variable sizes by linking the fundamental pentagonal $\{(Mo)Mo_5\}$ 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

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and $H_3PMo_{12}O_{40} \subset H_4Mo_{72}Fe_{30}(CH_3COO)_{15}O_{254}$ (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

$Mo^{VI}_{72}Fe^{III}_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}\cdot 150H_2O \{Mo_{72}Fe_{30}\}$ 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.

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

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

Reaction conditions: catalyst (2.5 μ mol), substrate (5 mmol), 30% H_2O_2 (0.2–10 mmol), water (5 mL), 25 °C, 3 h. 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).

Table 1
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 (2.5 μ mol), substrate (5 mmol), 30% H_2O_2 (2 mmol), water (5 mL), 25 °C.

^b Yield (%) is calculated as products (mmol) per initial H_2O_2 (mmol) \times 100.

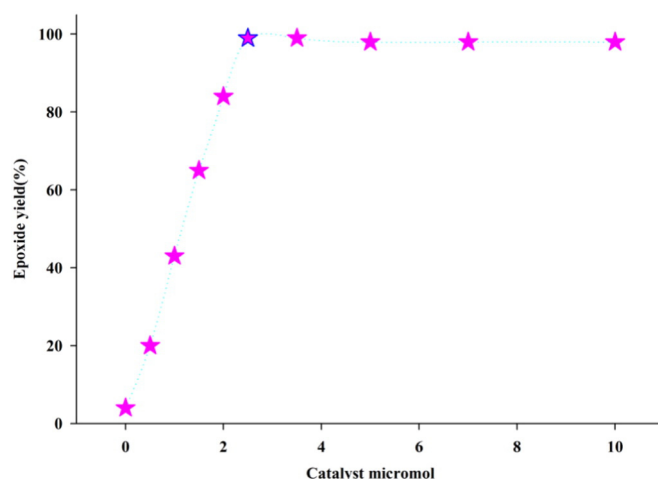


Fig. 1. Influence of the catalyst μ mol ratio on the oxidation of cyclooctene.

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 μ mol 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. $PMo \subset Mo_{72}Fe_{30}$ 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).

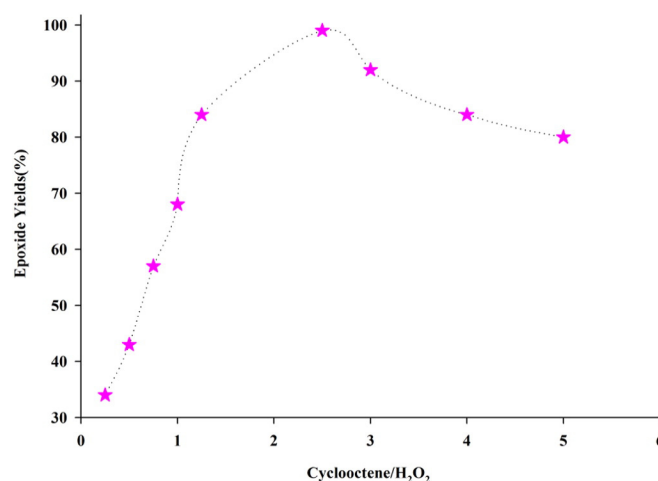


Fig. 2. Influence of the Cyclooctene/ H_2O_2 ratio on the oxidation of cyclooctene.

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