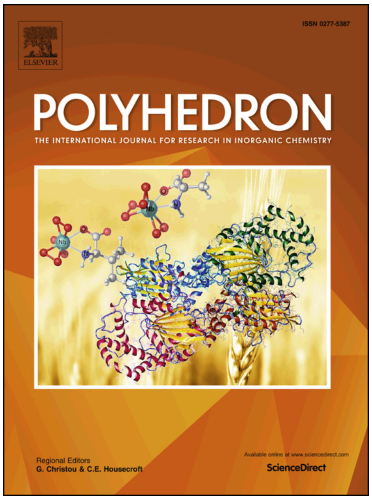

New perspective to catalytic epoxidation of olefins by Keplerate containing Keggin polyoxometalates

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New perspective to catalytic epoxidation of olefins by Keplerate containing Keggin polyoxometalates

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Abstract

Different Keggin encapsulated in Keplerate polyoxometalates ($Mo_{72}Fe_{30}$, $PMo_{12}\subset Mo_{72}Fe_{30}$, $SiMo_{12}\subset Mo_{72}Fe_{30}$ and $BW_{12}\subset Mo_{72}Fe_{30}$) have been synthesized and their catalytic efficiency in the epoxidation of olefins with hydrogen peroxide investigated. Results were confirmed that Keggin encapsulated in Keplerates could show higher catalytic activity than parent ones. These POM catalysts lead to heterogeneous epoxidation of alkenes by hydrogen peroxide with green features of convenient recovery, steady reuse, high conversion and selectivity, and simple preparation.

Keywords: Polyoxomolybdates; Keplerate; Keggin anions; host–guest chemistry; catalysis; oxidation of olefins

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Declarations of interest: none

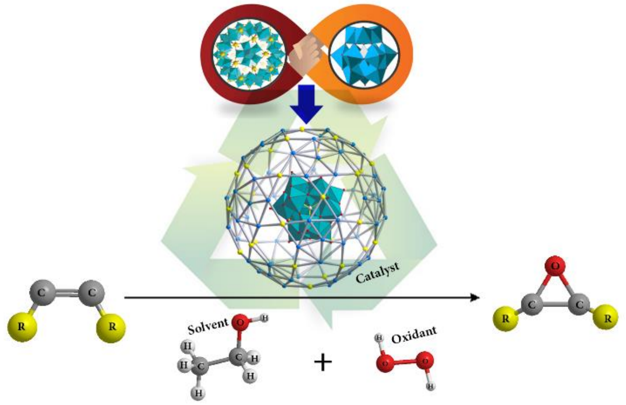
1. Introduction

Oxidation reactions play an important role in both of fine and bulk chemicals manufacturing [1]. Epoxides, which are important intermediates in the synthesis of fine chemicals and pharmaceuticals, form a particularly important and versatile class of products in chemical and industrial processes for the production of epoxy resins, paints, and surfactants [2, 3]. Different catalytic systems have been used for the synthesis of these valuable chemicals. Among them, polyoxometalates (POMs) have been used extensively due to their unique properties and structural variations.

POMs as anionic early transition metal oxygen clusters are unique in terms of molecular and electronic structural versatility, catalysis, medicine, biology, material science, electron-transfer processes and nanochemistry [4-9]. Keplerates with the formula of $\{(M^{VI})M^{VI}_5\}5_{12}(\text{linker})_{30}$ (M = Mo or W) are a highly symmetrical class of POMs that for the first time were synthesized and defined by Müller [10-14]. Among them, $\{Mo_{72}Fe_{30}\}$-type species – comprising 12 molybdenum-oxide-based pentagonal units linked by 30 Fe^{III} spacers that span an icosidodecahedron – have attracted considerable attention such as their magnetic and catalytic properties [15-19]. This Keplerate can act as a unique host for the other POMs like Lindqvist- or Keggin-type POMs [20-22].

Numerous organic processes could be catalyzed by POMs due to their acid/base characterization or ability to readily accept electrons and form electrochemically reduced clusters [23-25]. Nowadays, requirements for green and clear oxidation of olefins caused a great number of studies in the olefin epoxidation with POMs as cheap and effective catalysts and hydrogen peroxide as a green oxidant [26-35].

Considering the importance of epoxides and high efficiency of Keplerate and Keggin POMs as catalyst and in continuation of our previous works [8, 19, 25, 36], in this work the synthesis and catalytic effect of three Keggin-type POM encapsulated in molybdenum-iron-type Keplerate have been investigated. In this way, following **1–4** POMs $[Mo_{72}Fe_{30}O_{251}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O\}_{91}]$ ($Mo_{72}Fe_{30}$ ≡ **1**), $[H_xPMo_{12}O_{40}\subset H_4Mo_{72}Fe_{30}O_{254}(CH_3COO)_{15}(H_2O)_{98}]$ ($PMo_{12}\subset Mo_{72}Fe_{30}$ ≡ **2**), $Na_6[SiMo_{12}O_{40}\subset Mo_{72}Fe_{30}O_{252}(CH_3CO_2)_{16}(H_2O)_{100}]$ ($SiMo_{12}\subset Mo_{72}Fe_{30}$ ≡ **3**) and $Na_3K_4[BW_{12}O_{40}\subset H_4Mo_{72}Fe_{30}O_{254}(CH_3COO)_{16}(H_2O)_{96}]$ ($BW_{12}\subset Mo_{72}Fe_{30}$ ≡ **4**) were synthesized and used as catalyst in the epoxidation of various olefins with hydrogen peroxide (Scheme 1).



Scheme 1. Epoxidation of olefins by Keggins encapsulated in molybdenum-iron-type Keplerate as catalysts

2. Experimental Section

2.1. General remarks

The chemicals used in this work were purchased from Aldrich, Fluka and Merck chemical companies and used without further purification. Melting points were determined with a Stuart Scientific SMP2 apparatus. Conversion and yields of the products were accomplished by GC-FID on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m column and toluene as the internal standard. ^1H NMR spectra were recorded in $CDCl_3$ solvent on a Bruker AC 400 MHz spectrometer using TMS as an internal standard. FT-IR spectra were recorded using potassium bromide pellets from 400 to 4000 cm^{-1} by a Jasco FT/IR-6300 instrument. Powder X-ray diffraction patterns were obtained on a D_8 Advanced Bruker using Cu K_α radiation (2θ = 10–80°).

2.2. Preparation of $Mo_{72}Fe_{30}$ catalyst

This POM cluster was prepared according to the method reported by Müller and coworkers [15]. The NH_4^+ salt of $\{Mo_{132}\}$ (1.4 g, 0.05 mmol) was added to a solution of $FeCl_3 \cdot 6H_2O$ (1.1 g, 4.1 mmol) and $CH_3COONa \cdot 3H_2O$ (1.1 g, 8.1 mmol) in H_2O (75 mL). The resulting solution was vigorously stirred in open 100-mL Erlenmeyer flask for 24 h. After acidification with HCl (1 mL, 1 M) and addition of NaCl (2.0 g), the stirred reaction solution was heated to 90-95 ºC and then filtered whilst still hot. The golden yellow filtrate was cooled to 20 ºC formed over a period of 2-3 d. The crystals were collected by filtration through a glass frit, washed twice with a little iced water, and dried in air. Elemental analysis for $C_{24}H_{526}Fe_{30}Mo_{78}O_{547}$ (%); calcd: C, 1.54; Fe, 8.95; Mo, 39.96; found: C, 1.50; Fe, 8.83; Mo, 38.67; Characteristic IR bands: υ=1622 (m, (H_2O)), υ=1535 (m, COO), υ=1402 (m, COO), υ=965 (m, Mo=O), υ=851 (m), υ=776 (vs), υ=621 (m), υ=571 (s), υ=435 cm^{-1}.

2.3. Preparation of $PMo_{12}\subset Mo_{72}Fe_{30}$ catalyst

The $PMo_{12}\subset Mo_{72}Fe_{30}$ cluster was prepared following previously reported protocol [20]. $NaH_2PO_4 \cdot 2H_2O$ (0.21 g, 1.35 mmol) was added to a solution of $FeCl_2 \cdot 4H_2O$ (1.0 g, 5.03 mmol), $Na_2MoO_4 \cdot 2H_2O$ (5.0 g, 20.66 mmol) and CH_3COOH (100%, 10 mL) in H_2O (75 mL). After acidification to pH 2 with about 3 mL of 32% HCl, the solution was stirred for 15 min at 20 ºC and filtered. The filtrate was kept for one week in an open 250 mL beaker for crystallization. The crystals were filtered, washed with water, and dried at room temperature. Elemental analysis: calcd

(%) for $C_{30}H_{365}Fe_{30}Mo_{84}O_{482}P$: C, 1.98; H, 2.02; Fe, 9.2; P, 0.17; found: C, 2.1; H, 2.8; Fe, 8.6; P, 0.2; Characteristic IR bands for $PMo_{12}\subset Mo_{72}Fe_{30}$: υ=1617 (m, (H_2O)), υ=1539 (m, COO), υ=1420 (m, COO), υ=1068 (w, PO_4), υ=952 (m, Mo=O), υ=827 (s), υ=775 (vs), υ=630 (m), υ=566 (s), υ=435 cm^{-1}.

2.4. Preparation of $SiMo_{12}\subset Mo_{72}Fe_{30}$ catalyst

The cluster was prepared according to previously procedure [21]. $H_4SiMo_{12}O_{40}\cdot xH_2O$ (1.0 g, 0.5 mmol) was added to a solution of $FeCl_2\cdot 4H_2O$ (0.5 g, 2.5 mmol), $Na_2MoO_4\cdot 2H_2O$ (2.0 g, 8.3 mmol) and CH_3COOH (100%, 10 mL) in H_2O (30 mL). After acidification with about 2.5 mL of 1 M hydrochloric acid (pH of the reaction mixture was ~2.0), the solution was stirred for 1 h at room temperature. After adding NaCl (0.5 g, 8.6 mmol), the solution was stirred for 15 min more and then kept in an open 100 mL flask for one week at room temperature. The crystals were filtered, washed with water, and dried at room temperature. Elemental analysis: calcd (%) for $C_{32}H_{364}Fe_{30}Mo_{84}Na_6O_{482}Si$: C, 2.09; H, 2.00; Fe, 9.12; Mo, 43.89; Na, 0.75; Si, 0.15; found: C, 2.3; H, 2.4; Fe, 8.3; Mo, 41.0; Na, 0.4; Si, 0.15; Characteristic IR bands for $SiMo_{12}\subset Mo_{72}Fe_{30}$: υ=1617 (m, (H_2O)), υ=1539 (m, COO), υ=1420 (m, COO), υ=950 (m, Mo=O), υ= 975, 909 (s, SiO_4), υ=855 (s), υ=780 (vs), υ=629 (m), υ=565 (s), υ=440 cm^{-1}.

2.5. Preparation of $BW_{12}\subset Mo_{72}Fe_{30}$ catalyst

The cluster was prepared according to the literature procedure [22]. $K_5[BW_{12}O_{40}]\cdot 11H_2O$ (1.67 g, 0.5 mmol) was added to a solution of $Na_2MoO_4\cdot 2H_2O$ (2.0 g, 8.3 mmol) and acetic acid (15 mL, 100%) with $FeCl_2\cdot 4H_2O$ (1 g, 5 mmol) in H_2O (60 mL). After acidification with about 11.5 mL of 1 M hydrochloric acid (pH of the reaction mixture was ~2.0), the solution was stirred for 1 h at room temperature and then kept in an open 100 mL flask for one week at room temperature. The crystals were filtered off, washed with water and dried at room temperature under nitrogen.

Elemental analysis: calcd (%) for $C_{32}H_{364}BFe_{30}K_4Mo_{72}Na_3O_{482}W_{12}$: C, 1.97; B, 0.06; Fe, 8.60; K, 0.80; Mo, 35.45; Na, 0.35; W, 11.32. Found: C, 2.0; B, 0.05; Fe, 7.9; K, 0.5; Mo, 34.8; Na, 0.2; W, 10.3. Characteristic IR bands for $BW_{12}\subset Mo_{72}Fe_{30}$: ʋ=1623 (m, ($H_2O$)), ʋ=1537 (m, COO), ʋ=1420 (m, COO), ʋ=952 (m, Mo=O), ʋ= 905 (s), ʋ=831 (s), ʋ=776 (vs), ʋ=630 (m), ʋ=565 (s), ʋ=440 cm^{-1}.

2.6. General procedure for the epoxidation reaction

All reactions were performed in a 25 mL round-bottom flask equipped with a magnetic stirrer bar. The catalyst (2 µmol) was added to a solution of olefin (1 mmol) in 2 mL of ethanol. Then, H_2O_2 (30%, 0.3 mL, 3 mmol) was added to the mixture and closed the flask under air at 75 °C for the required time. The progress of the reaction was monitored by TLC and GC, and the yield of products was determined by GC analysis using toluene as the internal standard. At the end of reaction, the catalyst was filtered and washed with ethanol (5 mL).

3. Results and Discussion

Investigation on the catalytic efficiency of **1**, **2**, **3**, and **4** POM compounds were initiated by testing the effect of {$Mo_{72}Fe_{30}$}-type Keplerate (**1**) in the epoxidation of olefins with H_2O_2 30% using cyclohexene as a model compound. Considering its importance, the influence of different solvents such as *n*-hexane, acetonitrile, acetone, ethyl acetate, THF, chloroform, dichloromethane, methanol, ethanol, and water in the oxidation of cyclohexene were studied. From the results in Fig. 1, the highest conversion was obtained in ethanol. Although, the oxidation reaction in some of the other solvents such as acetone and methanol was a little more selective. Consequently, ethanol was selected as optimal solvent in our catalytic epoxidation system.

As expected, solvents of higher polarity and high basicity such as ethanol gave higher conversion in epoxidation of cyclohexene (Fig. 1). These are in agreement with previously reported Kamlet–Taft plot for estimating the physicochemical properties of solvents [26, 37-39].

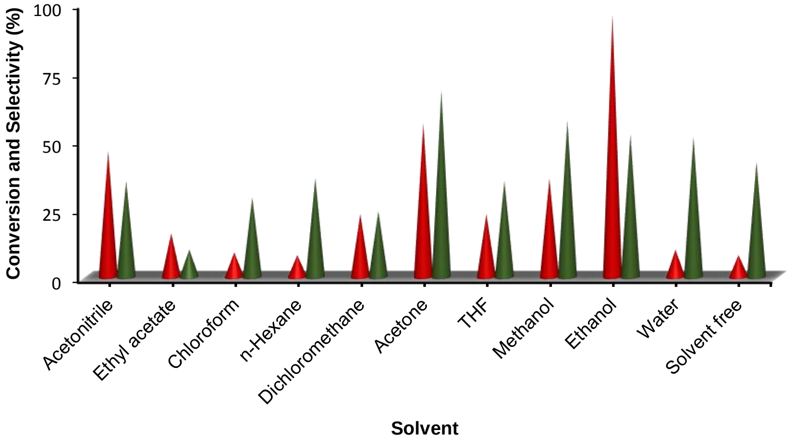


Figure 1. The effect of different solvents (2 mL) on the epoxidation of cyclohexene (1 mmol) with H_2O_2 (3 mmol) in the presence of **1** (2 μmol) after 5 h reaction under reflux (Conversion red and selectivity for epoxide green)

In the next step, to obtain the optimum amount of catalyst **1** in the epoxidation of cyclohexene, the effect of different catalyst amounts was investigated (Fig. 2). It was observed that the conversions were increased by increasing in the catalyst **1** amounts. Further increments of catalyst slightly improved conversions when the amount of catalyst **1** was over 2 μmol. Different amounts of catalyst **1** were only shown a little change in the selectivity. As a result, 2 μmol catalyst was chosen as the optimal catalyst amount for further catalytic studies.

In the oxidation of cyclohexene by different volumes of H_2O_2, the optimum amount of oxidant was obtained in the presence of 2 μmol catalyst (Fig. 3). The results showed that 3 mmol of 30% H_2O_2 is sufficient for completion of the reaction after 5 h oxidation reaction. Thus, 3 mmol of hydrogen peroxide was chosen as the best amount of oxidant in this catalytic epoxidation system.

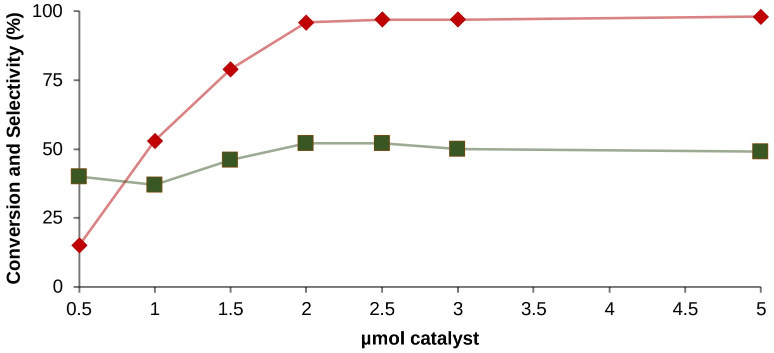


Figure 2. Epoxidation of cyclohexene (1 mmol) by H_2O_2 (3 mmol) in the presence of different catalyst **1** amounts in ethanol (2 mL) under reflux conditions for 5 h (Conversion red and selectivity for epoxide green)

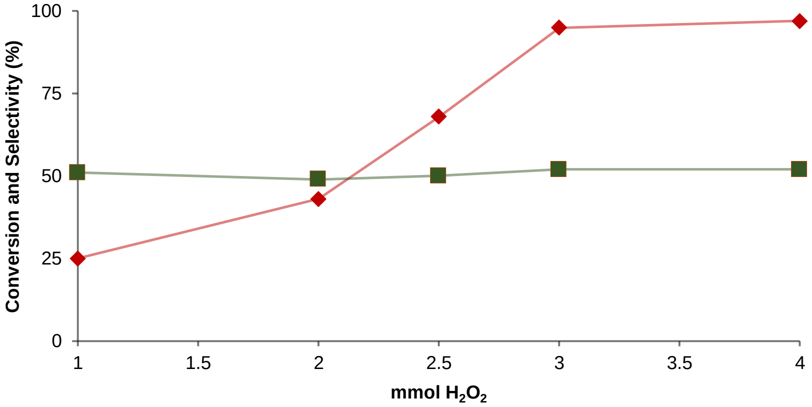


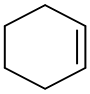
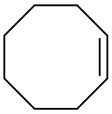
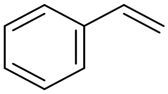
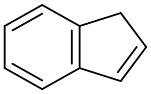
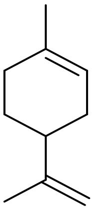
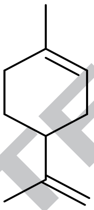
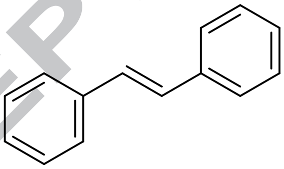
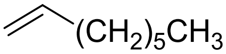
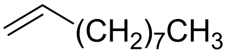
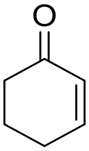
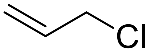
Figure 3. Epoxidation of cyclohexene by various amounts of H_2O_2 in the presence of 2 µmol **1** under reflux conditions for 5 h (Conversion red and selectivity for epoxide green)

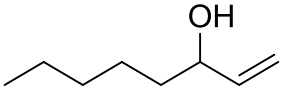
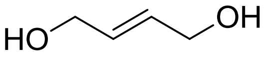
In order to establish the general applicability of the method, the catalytic system was extended to the oxidation of other olefins by the optimal reaction conditions – 2 µmol of catalyst, 3 mmol of 30% H_2O_2, under reflux condition and ethanol as solvent. The results with $Mo_{72}Fe_{30}$ and Keggin POMs encapsulated in $Mo_{72}Fe_{30}$ (**1**, **2**, **3** and **4**) as catalysts were shown in Table 1. From the results, cyclic olefins such as cyclohexene and cyclooctene were converted with very good to excellent yields into their corresponding epoxides (Table 1, entries 1 and 2). In homogeneously catalyzed oxidation reaction of cyclohexene, selectivity for product is often low and cyclohexane-

1,2-diol and 2-cyclohexene-1-one are commonly generated byproducts [40, 41]. Moreover, in this catalytic system 2-cyclohexene-1-one could be converted into the corresponding epoxide in high to excellent conversion and selectivity especially with **3** (Table 1, entry 10). The major product in the oxidation of styrene was benzaldehyde (Table 1, entry 3) and indene was converted into the corresponding aromatic epoxide (Table 1, entry 4). Because of the using from limonene oxide as a raw material for polycarbonate synthesis [42], this new green process of epoxidation was also used for the epoxidation of limonene. Under optimized epoxidation reaction, 48-66% conversion was obtained for different **1**, **2**, **3** and **4** catalysts and the major product was monoepoxide (limonene oxide). After 6 h reaction, di-epoxide was the main product (Table 1, entries 5 and 6). In the case of *trans*-stilbene, epoxidation was done in a stereospecific manner with complete retention of configuration (Table 1, entry 7). Conversion and selectivity became less when the bulkiness or chain length of the substrates is increased. This may be explained on the basis of steric hindrance caused by the substrates. So, although terminal alkenes need higher activation energy, highly conversion (73–93%) of these olefins was obtained in our catalytic systems (Table 1, entries 8 and 9). In general, the epoxidation of allylic alcohols and allylic chlorides compared to cyclic olefins is difficult, since the C=C double bond in allyl moieties is relatively electron deficient by the electron-withdrawing group of hydroxyl (–OH) and –Cl. But, this compounds in our catalytic system were converted into the corresponding epoxides in high to excellent yields (Table 1, entries 11–13).

As it could be seen in Table 1, among **1**, **2**, **3** and **4** POM catalysts, $SiMo_{12}\subset Mo_{72}Fe_{30}$ (**3**) and $BW_{12}\subset Mo_{72}Fe_{30}$ (**4**) under the same reaction conditions were shown higher catalytic activities in the epoxidation of various olefins than two others. Moreover, at this reaction condition $PMo_{12}\subset Mo_{72}Fe_{30}$ (**2**) demonstrated a better catalytic activity respect to $Mo_{72}Fe_{30}$ (**1**), too [43].

Table 1. Catalytic epoxidation of various olefins using 30% aqueous H_2O_2 in the presence of **1, 2, 3**, and **4** catalysts[a]

Entry	Olefin	Conversion (%)[b] [Selectivity (%)]				Time (h)
		1	2	3	4	
1		64 [52]	74 [59]	95 [46]	89 [71]	3.5
2		73 [97]	82 [98]	91 [99]	93 [99]	3.25
3[c]		69 [91]	75 [81]	89 [85]	85 [89]	3.5
4		45 [85]	57 [93]	66 [81]	82 [85]	3.5
5[d]		48 [89]	57 [85]	85 [68]	66 [79]	3.5
6[e]		65 [45]	76 [54]	92 [46]	89 [58]	6
7		68 [92]	81 [94]	87 [99]	95 [96]	9
8		73 [95]	87 [94]	85 [97]	93 [97]	3.75
9		75 [97]	79 [91]	86 [87]	86 [93]	4.25
10		65 [72]	86 [88]	95 [93]	93 [85]	3.5
11		47 [91]	54 [96]	68 [97]	74 [91]	8

12		79 [85]	82 [69]	85 [75]	90 [79]	5
13		73 [76]	84 [72]	86 [91]	81 [77]	4

[a] Reaction conditions: olefin (1 mmol), H_2O_2 (3 mmol), and catalyst (2 μmol) in ethanol (2 mL) under reflux.

[b] Yields refer to GC yields.

[c] Product was benzaldehyde.

[d] Product was 1,2-epoxide.

[e] Product was diepoxide.

By MoO_3, $Na_2MoO_4·4H_2O$, and $(NH_4)_6MO_7O_{24}·4H_2O$ as simple salts of Mo (VI) and $FeCl_3·6H_2O$ as a simple salt of Fe (III), epoxidation product was not observed even after 24 h reaction under the same conditions. Furthermore, the catalytic effect of PMo_{12}, $SiMo_{12}$ and BW_{12} as Keggin POMs were examined in this epoxidation system (Table 2, entries 1–3) and low to moderate conversions and selectivity were observed.

Table 2. Catalytic epoxidation of cyclohexene in the presence of **1**, PMo_{12}, $SiMo_{12}$, BW_{12} and the physical mixture of **1** with PMo_{12}, $SiMo_{12}$, or BW_{12}[a]

Entry	Catalyst	Conversion (%)[b]	Selectivity (%)[c]
1	PMo_{12}	18	58
2	$SiMo_{12}$	26	45
3	BW_{12}	23	69
4	$Mo_{72}Fe_{30}$ (**1**)	64	52
5	PMo_{12} + **1**[d]	68	50
6	$SiMo_{12}$ + **1**[d]	70	52
7	BW_{12} + **1**[d]	68	54

[a] Reaction conditions: cyclohexene (1 mmol), H_2O_2 (3 mmol), and catalyst (2 μmol) in ethanol (2 mL) under reflux condition for 3.5 h.

[b] Conversion based on olefin substrate.

[c] Selectivity for epoxy cyclohexane.

[d] Reaction conditions: cyclohexene (1 mmol), H_2O_2 (3 mmol), and catalysts (2 + 2 μmol) in ethanol (2 mL) under reflux condition for 3.5 h.

Another catalytic investigation was carried out by physical mixings of $Mo_{72}Fe_{30}$ Keplerate (**1**) and PMo_{12}, $SiMo_{12}$ and BW_{12} with the same ratio. Results (Table 2, entries 5–7) indicated that the mixtures of **1** and Keggin POMs have not been shown considerable improvement in the catalytic epoxidation reaction. So, exceeded catalytic activity of Keggins encapsulated in Keplerate than parent ones were confirmed by these results.

The inhibitory effect of radical scavengers such as 2,6-di-*tert*-butyl-4-methylphenol (BHT) and diphenyl amine in this oxidation system was also studied. This purpose was done by cyclohexene epoxidation in the presence of BHT or diphenyl amine (>10 equiv. rather than catalyst **1**). In this oxidation systems, cyclohexene epoxide was produced after 5 h reaction in 90 and 51% yields, respectively. So, in the present system our results demonstrated that non-radical processes prevail to a high extent, although some contribution of free radicals may be existed. This behavior of **1** is also similar to previously reported works by $\{Mo_{132}\}$ [44, 45].

Interestingly, these POM catalysts are stable even for months in various solvents due to inertness of the spherical solutes and the presence of hard Fe^{III} and Mo^{VI} centers [46, 47]. Since the structure of POMs is pH dependent, the effect of different pH values in the epoxidation of olefins was also studied (Fig. 4). According to previous works, $Mo_{72}Fe_{30}$ (**1**) in dilute aqueous solutions can act as a nanosized weak inorganic acid that deprotonate differently depending on the pH [47]. As follows, their sizes decrease with increasing deprotonation, monotonically that is relevant to cluster surface charges. Also, it should be noted that all POMs decomposes at high pH values while smaller species are formed. From Fig. 4, when the pH value was adjusted to less than or equal to 6, the same conversions and selectivity were obtained. However, owing to the lesser stability of **1**, **2**, **3** and **4** POM catalysts at higher pH values, lower oxidation activities were observed at pH > 6.

Additionally, these Keggins encapsulated in Keplerate catalysts could be easily recovered by filtration and reused without loss of catalytic activities. At least eight times reusability of as mentioned POM catalysts without any significant loss of catalytic activity is one of the major advantages in these systems (Fig. 5). The XRD patterns and FT-IR spectra for **1**, **2**, **3** and **4** catalysts after 8 times recycling were stated that the structure of catalysts are preserved.

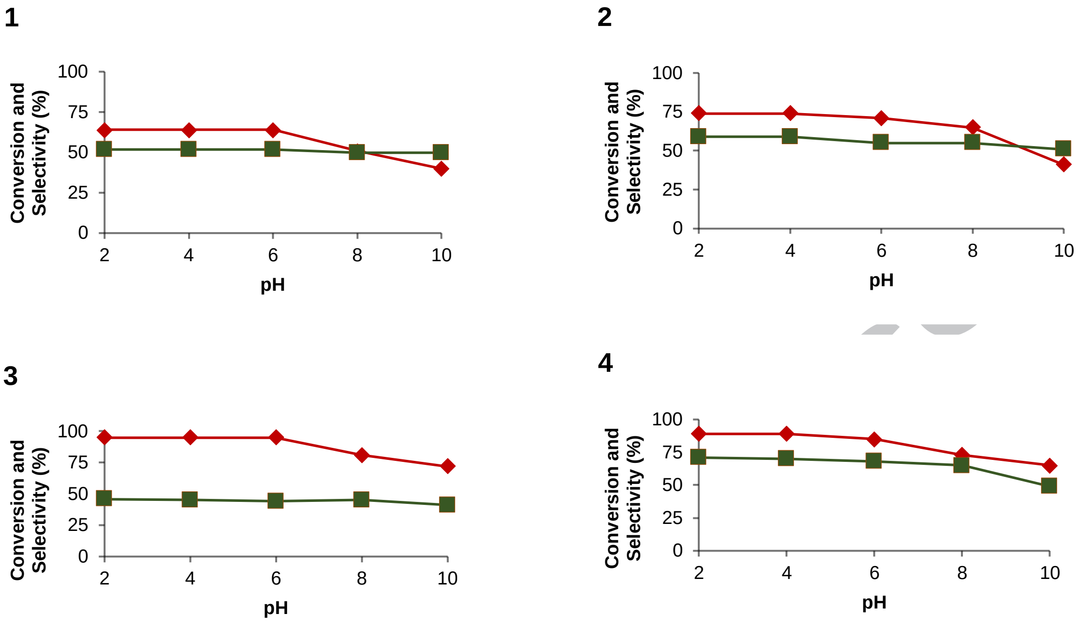


Figure 4. The effect of pH in the epoxidation of cyclohexene by H_2O_2 in the presence of **1**, **2**, **3** and **4** as catalyst

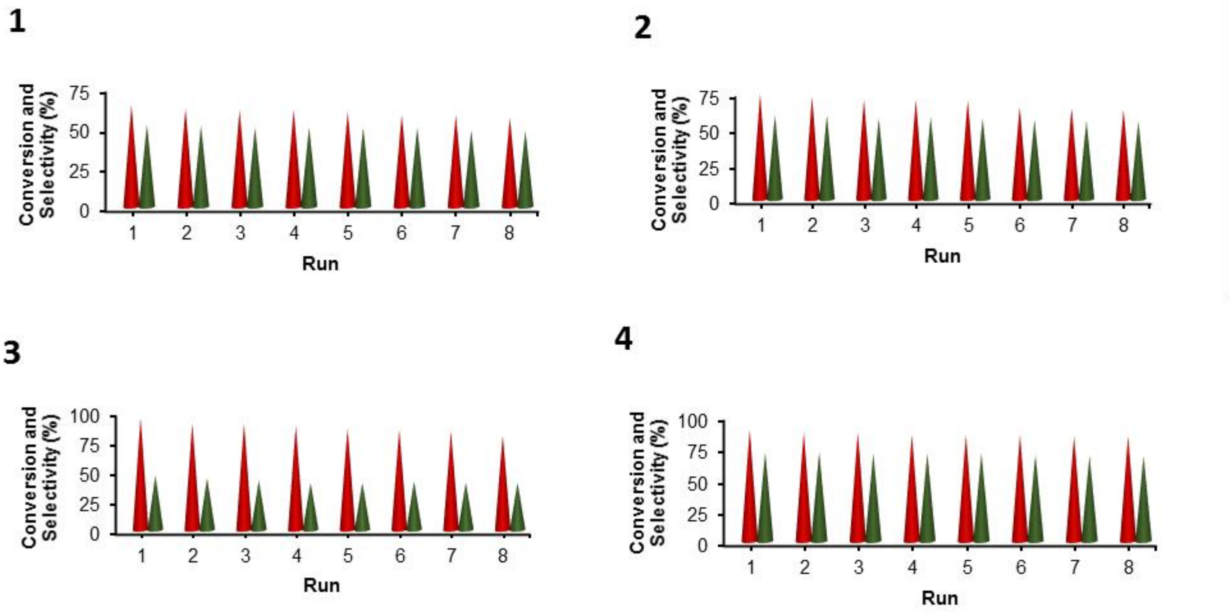


Figure 5. The reusability of **1**, **2**, **3** and **4** catalysts in the epoxidation of cyclohexene by H_2O_2

4. Conclusion

In this work, $Mo_{72}Fe_{30}$ and encapsulated Keggin anions in $Mo_{72}Fe_{30}$ were prepared and used as catalyst for epoxidation of olefins by hydrogen peroxide. Optimum reaction conditions such as the type of solvent and catalyst, amount of oxidant and catalyst, pH and temperature were obtained and the oxidation of various olefins was performed at this catalytic reaction conditions. Keggin encapsulated Keplerates were shown higher catalytic activity than parent ones and among them, by $SiMo_{12}\subset Mo_{72}Fe_{30}$ (**3**) and $BW_{12}\subset Mo_{72}Fe_{30}$ the highest conversions and selectivity were obtained. These catalysts were also showed high reusability after eight times usage without any appreciable decrease in catalytic activity and selectivity.

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New perspective to catalytic epoxidation of olefins by Keplerate containing Keggin polyoxometalates

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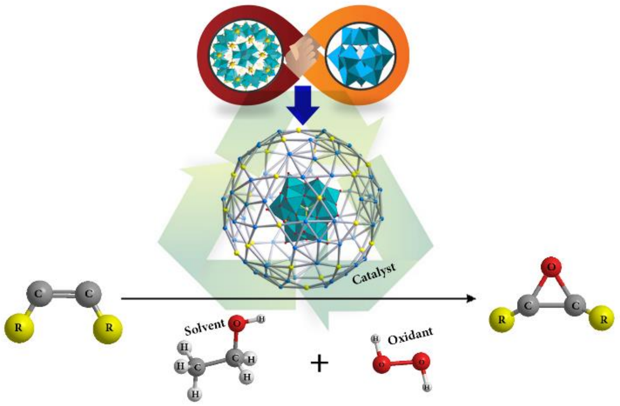

New perspective to catalytic epoxidation of olefins by Keplerate containing Keggin polyoxometalates

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Different Keggin encapsulated in Keplerate polyoxometalates have been used as catalyst in the epoxidation of olefins with hydrogen peroxide. These POM catalysts show higher catalytic activity than parent ones with green features of convenient recovery, steady reuse, high conversion and selectivity, and simple preparation.

Using from Keggin encapsulated in Keplerate polyoxometalates as catalyst

Green catalytic epoxidation by hydrogen peroxide

Higher catalytic activity of Keggin encapsulated Keplerates than parent ones