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Catalytic performance of Keplerate polyoxomolybdates in green epoxidation of alkenes with hydrogen peroxide

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Abstract

In this work, the catalytic perspective of three Keplerate polyoxometalates, $Mo_{72}M_{30}$ (M = V, Cr, Fe) in the epoxidation of various alkenes are considered. The catalytic reactions were performed in water at mild conditions and high to excellent conversions and selectivity was obtained using H_2O_2 as oxidant and $Mo_{72}Cr_{30}$ as the best catalyst. Keplerate POM catalysts have been shown a very good recyclability, up to five times, without any appreciable decreases in catalytic activity and selectivity.

Keywords: Keplerate polyoxometalates, catalysis, epoxidation, hydrogen peroxide, alkenes, water

1. Introduction

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Selective oxidation of olefins to epoxides is among the important reactions in chemical industry and organic chemistry.[1–2] To develop environmentally benign synthetic methodologies, there is a great interest in new and more efficient catalytic oxidations based on low-cast, accessible and environmentally benign catalysts and oxidants.[3–5] The oxidation of olefins with aqueous hydrogen peroxide has received much attentions, since H_2O_2 is clean, inexpensive, safe, readily available, high content of active oxygen species and gives water as the sole by-product.[6] Furthermore, using from nontoxic solvents such as water, which is safer, cheaper, and more environmentally friendly compared to other solvents in use today, is a major problem in these reactions.[7]

Polyoxometalates (POMs), as a class of metal-oxygen clusters, because of the different structures and the diversity in shapes, charges, compositions, solubility and reactivity showed a lots of applications.[8–9] Increasing in POMs usage are evidently revealed in various literatures in the fields of catalysis, material science, medicine, analytical chemistry and so on.[10–12] In the last decades various types of POMs have drawn wide attention as effective and important catalysts for epoxidation of alkenes.[13–24]

Metal oxide based nanocapsules of the type $\{(\mathrm{Mo^{VI}})\mathrm{Mo^{VI}}_5\}_{12}(\mathrm{linker})_{30}$ which called Keplerates was firstly reported by Müller and coworkers.[25] Keplerate POMs have attracted considerable interest and indicated a lot of applicability in various fields such as chemical science, molecular physics, magnetochemistry, biological sciences, materials science, and even mathematics.[26] However, despite extremely promising potential in different fields of science the catalytic properties of Keplerate POMs in the oxidation of organic compounds really needs to be further investigations.[27] For the first time, the catalytic activity of Keplerate POMs in the oxidation of sulfides was reported.[28] Selective epoxidation of an aqueous suspension of olefins under mild

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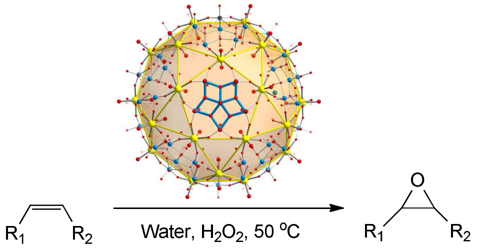
reaction conditions catalyzed by $(NH_4)_{42}[Mo^{VI}{}_{72}Mo^{V}{}_{60}O_{372}(CH_3COO)_{30}(H_2O)_{72}]$ was the other work.[29–30] It was also reported that $Mo_{72}M_{30}$ is thermodynamically stable to oxidation and contains transition metals (molybdenum and iron) capable of activating various oxidants.[28] Furthermore, $Mo_{72}M_{30}$ have been shown very well stability in various solvents.[31] In continuation of our current research,[32] a novel method for oxidation of organic compounds with hydrogen peroxide as a green oxidant in the presence of Keplerate POMs and especially in sustainable media was developed. In this regard, for the first time, the catalytic epoxidation of different alkenes using 30% H_2O_2 catalyzed by three Keplerate POMs, $Na_8K_{14}(VO)_2[\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_3\}_{10}\{(Mo^{VI})Mo^{VI}{}_5O_{21}(H_2O)_3(SO_4)\}_2\{V^{IV}O(H_2O)\}_{20}\{V^{IV}O\}_{10}(\{KSO_4\}_5)_2].150H_2O$ $\{Mo_{72}V_{30}\}$, $Mo^{VI}{}_{72}Fe^{III}{}_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}_2\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}].150H_2O$ $\{Mo_{72}Fe_{30}\}$ and $[\{Na(H_2O)_{12}\}[Mo^{VI}{}_{72}Cr^{III}{}_{30}O_{252}(CH_3COO)_{19}(H_2O)_{94}\}].120H_2O$ $\{Mo_{72}Cr_{30}\}$, in aqueous media are described (Scheme 1).



Scheme 1. Catalytic epoxidation of alkenes with H_2O_2 catalyzed by $Mo_{72}V_{30}$, $Mo_{72}Cr_{30}$ and $Mo_{72}Fe_{30}$

2. Results and discussion

In our previous work, the catalytic activity of Keplerate POMs, $Mo_{72}M_{30}$ (M = V, Cr, Fe), in successfully conversion of different sulfides into the corresponding sulfones under mild reaction conditions with high to excellent yields were showed. Also, the reusability of these catalysts was

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very good and spectral results showed that the structure of recycled catalyst is preserved and it is stable since catalytic recycling.[33]

In this work, at first, the catalytic efficiency of three Keplerate POMs ($Mo_{72}Fe_{30}$, $Mo_{72}Cr_{30}$, and $Mo_{72}V_{30}$) in the epoxidation of olefins was tested using cyclooctene as a model compound. In order to obtain the optimum amounts of Keplerate POM catalysts, the epoxidation of cyclooctene was studied by various amounts of $Mo_{72}Cr_{30}$. From the results in Figure 1, by increasing in the catalyst amounts up to 10 µmol of $Mo_{72}Cr_{30}$ the yields of epoxide was improved. In the presence of higher amounts of Keplerate catalyst the selectivity for epoxide was decreased. In this system, it was also showed that the presence of catalyst is crucial for the oxidation reaction. So, 10 µmol of $Mo_{72}Cr_{30}$ which provides the highest yields for epoxidation of cyclooctene was chosen as the best amount of catalyst.

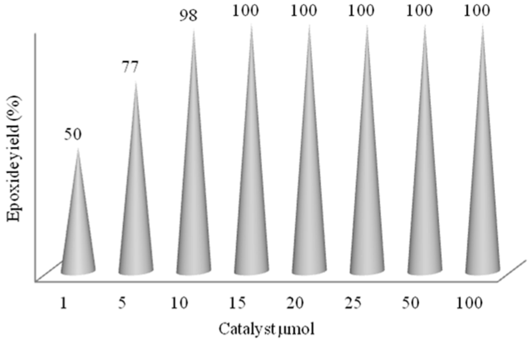

Figure 1. The effect of $Mo_{72}Cr_{30}$ amounts in the epoxidation of cyclooctene by 30% hydrogen peroxide in water after 2.5 h reaction. Reaction conditions: cyclooctene (1 mmol), H_2O_2 (1 mmol) and catalyst at 50 °C. Yields refer to GC yield.

In the oxidation reaction of cyclooctene by different amounts of H_2O_2, the optimum amount of hydrogen peroxide was obtained in the presence of 10 µmol catalyst after 2.5 h reaction. The results in Figure 2 show that 1 mmol of 30% H_2O_2 is sufficient for completion of the reaction at

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request time. Thus, 1 mmol of hydrogen peroxide was chosen as the best amount of oxidant in this catalytic epoxidation system.

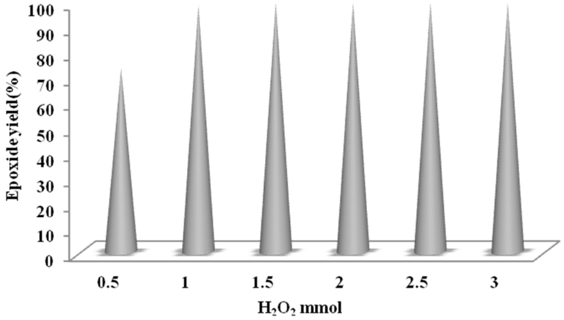

Figure 2. The effect of hydrogen peroxide amounts in the epoxidation of cyclooctene (1 mmol) catalyzed by $Mo_{72}Cr_{30}$ (10 µmol) at 50 °C after 2.5 h reaction. Yields refer to GC yield.

By the optimal reaction conditions – 10 µmol of catalyst, 1 mmol of 30% H_2O_2, 50 °C temperature, and water as solvent – selective epoxidation of various alkenes with $Mo_{72}V_{30}$, $Mo_{72}Cr_{30}$, and $Mo_{72}Fe_{30}$ as catalyst were investigated (Table 1). As it could be seen in Table 1, epoxidation of styrene was gave styrene oxide as the main product by 98% selectivity (Table 1, entry 4). The catalytic epoxidation of cyclic alkenes such as cyclohexene, cyclooctene, and indene were efficiently proceeded to afford the corresponding epoxides in high to excellent yields (Table 1, entries 1-3, 5). Also, nonactivated aliphatic alkenes such as 1-octene has been converted into the corresponding epoxide selectively (Table 1, entry 6). In 2-cylohexene-1-ol (Table 1, entry 7) C=C double bond was selectively oxidized into corresponding epoxide and hydroxyl functional groups remained intact.

Among three Keplerate POM catalysts in epoxidation of various alkenes under the same reaction conditions, $Mo_{72}Cr_{30}$ was shown higher catalytic activity than two others. Albeit, $Mo_{72}V_{30}$ was also demonstrated a better catalytic activity respect to $Mo_{72}Fe_{30}$.

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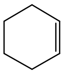
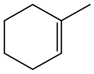
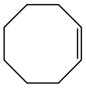
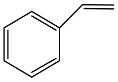
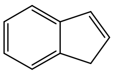
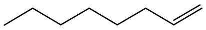
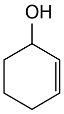
Table 1. Epoxidation of different alkenes with 30% H_2O_2 catalyzed by $Mo_{72}M_{30}$ (M = V, Fe, Cr) in water[a]

Entry	Alkene	Time (h)	Epoxide (%)[b]		
			$Mo_{72}Fe_{30}$	$Mo_{72}V_{30}$	$Mo_{72}Cr_{30}$
1		5	10	83	92
2		5	7	63	75
3		2.5	7	86	97
4[c]		3	8	85	96
5		6	7	80	91
6		6	6	79	87
7		6.5	6	83	92

[a]Reaction conditions: the reactions were run at 50 °C in 3 mL of aqueous suspension of olefin (1 mmol), 10 μmol of $Mo_{72}M_{30}$ (M = V, Fe, Cr) as catalyst and 1 mmol of 30% H_2O_2.
[b]Yields refer to isolated yields.
[c]The selectivity of epoxides was 98% and 2% benzaldehyde was also produced.

It was reported that the catalytic activity of POMs could be inversely correlated to the rate of hydrogen peroxide dismutation.[34] So, in this work hydrogen peroxide dismutation by $Mo_{72}Cr_{30}$, $Mo_{72}V_{30}$, and $Mo_{72}Fe_{30}$ was also studied. Our results showed that in the presence of $Mo_{72}Cr_{30}$ decomposing of hydrogen peroxide was performed with lower rate compared to $Mo_{72}V_{30}$ and also $Mo_{72}Fe_{30}$. Thus, this is rationale for $Mo_{72}Cr_{30}$ which shows a better catalytic activity than the two other Keplerate catalysts. From Figure 3 the inversely correlations between catalytic activity of $Mo_{72}M_{30}$ (V, Cr, and Fe) catalysts and the rate of hydrogen peroxide decomposition in the absence of substrate could be deduced. It was also demonstrated that Keplerate structure of $Mo_{72}Fe_{30}$ could be preserved in the presence of a large excess of H_2O_2.[30]

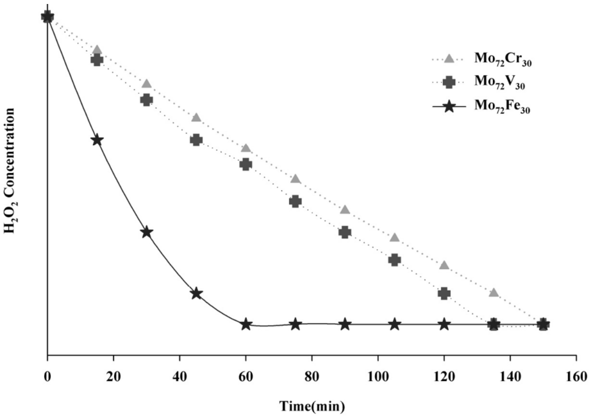


Figure 3. H_2O_2 decomposition in the presence of $Mo_{72}M_{30}$ (V, Cr and Fe) catalysts. Reaction conditions: H_2O_2 (10 mmol), catalysts (100 μmol), water (3 mL) at 50 °C.

The epoxidation reaction of cyclooctene was used for studying the recyclability of these Keplerate POM catalysts. In this regard, the catalysts was simply recovered after each run of the oxidation reaction and using ethyl acetate, as a safe solvent, the organic products were isolated. Aqueous solution of the Keplerate catalyst was recycled for the next round of the reaction without further purification. The reusability of as mentioned POM catalysts, for at least five times, without any significant loss of catalytic activity is one of the advantages in this catalytic system (Table 2).

Table 2. Recycling of $Mo_{72}M_{30}$ (Cr and V) catalysts in the epoxidation of cyclooctene by H_2O_2 according to the procedure mentioned in Table 1[a]

Run	Epoxide (%)	
	$Mo_{72}Cr_{30}$	$Mo_{72}V_{30}$
1	97	86
2	97	86
3	97	85
4	95	85
5	95	83

[a] Yields refer to GC yields.

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As it could be seen in Figure 4, similar XRD patterns for fresh and recycled $Mo_{72}Cr_{30}$ catalysts in the epoxidation of alkenes were obtained. This stated that the structure of catalyst is preserved and it is stable since catalytic recycling.

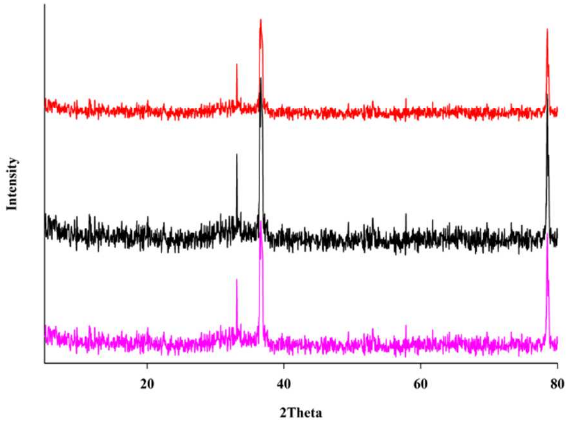

Figure 4. The XRD pattern of $Mo_{72}Cr_{30}$ fresh (red) and recovered in run 3 (black) and run 5 (pink)

Sustainable oxidation of olefins by H_2O_2 in water as solvent shows lot of potential advantages for this catalytic system in both environmental and economic aspects. The applicability and efficiency of this green system was shown by comparing the catalytic results with some of the reported methods on the epoxidation of cyclohexene. From Table 3, it could be seen that the proposed catalytic system has superior results in comparison to most of the other methods. Additionally, our catalytic system has a very well reusability along with using a nontoxic solvent.

Table 3. Catalytic results for the oxidation of cyclohexene in the presence of different POM catalysts[a]

Entry	Catalyst	Solvent	Conv. (Yields) (%)	Ref.
1	$[\gamma\text{-SiW}_{10}O_{34}]^{4-}$	CH_3CN	84 (>99)	17
2	$[\gamma\text{-1,2-H}_2SiV_2W_{10}O_{40}]^{4-}$	CH_3CN/*t*-BuOH	90 (99)	17
3	(diperoxotungsto)phosphates	C_6H_6	88 (100)	14
4	$[NMe_4]_3[(MePO_3)\{MePO_2(OH)\}W_6$	C_6H_6	36 (100)	20

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	$O_{13}(O_2)_4(OH)_2(OH_2)]$			
5	$[\pi\text{-}C_5H_5N(CH_2)_{15}CH_3]_3[PW_4O_{16}]$	$CHCl_3$	95 (97)	24
6	$[P_2W_{17}MnO_{61}]^{8-}$	CH_2Cl_2/CH_3CN	48 (16)	18
7	$(CPB)_3[PW_{12}O_{40}]$	CH_3CN	80 (97)	23
8	$Mo_{72}Cr_{30}$	H_2O	92 (>99)	-

[a] The oxidant for entries 1–5 and 8 was H_2O_2, $F_5PhI(TFAc)_2$ for entry 6 and UHP for entry 7.

The mechanism of alkenes epoxidation in the presence of POM catalysts using H_2O_2 as oxidant has been extensively investigated by several groups. In this regard, different active species such as $Q_2[HPO_4\{WO(O_2)_2\}_2]$, $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$, $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$, $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$, and some of the other hydroperoxo intermediates have been proposed.[35] In this work, the favor reaction path for the oxidation reaction by $Mo_{72}M_{30}$ Keplerates could also be as above.

3. Experimental

3.1. General Methods and Materials: Mo_{132}, $Mo_{72}V_{30}$, $Mo_{72}Fe_{30}$ and $Mo_{72}Cr_{30}$ prepared according to the literature methods.[36] All common laboratory chemicals were reagent grade, commercially prepared and used without further purification. Elemental analyses for C, S, Cr, Fe, V, Mo and K were carried out on a Perkin-Elmer 7300 DV and Leco CHNS-932 elemental analyzer. Infrared spectra (KBr pellets) were recorded on a JASCO FT/IR-6300 instrument. ^1H NMR spectra were recorded on a Bruker 400 (296 K) using $CDCl_3$ as solvent and TMS as an internal reference. The oxidation products were quantitatively analyzed by gas chromatography (GC) on a Chrompack CP 9001 instrument using a SIL-5CB column (50m, 32mm, 5μm) and FID detector. UV-vis spectra were recorded on a JASCO V-670 UV-vis spectrophotometer (190-2700 nm). Powder X-ray diffraction (XRD) data were obtained on a D8 Advanced Bruker using Cu Kα radiation (2θ = 5-80°).

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3.2. Synthesis of $Mo_{72}Cr_{30}$: $CrCl_3\cdot 6H_2O$ (8.6 g, 32.27 mmol) was added to a solution of $Na_2MoO_4\cdot 2H_2O$ (9.0 g, 37.2 mmol) in a H_2O (80 mL)/CH_3COOH (100%; 35 mL) mixture. After stirring for 5 min it was acidified with 1M HCl (17 mL; resulting pH ~2), and the solution was heated under reflux for 45 min. The cooling of resulting green solution to room temperature gave the pale green precipitate. Elemental analysis: Found: C, 2.53; Cr, 8.86; Mo, 38.80. Calc. for $Mo_{72}Cr_{30}$: C, 2.58; Cr, 8.81; Mo, 38.99%. IR (KBr pellet, cm^{-1}): 1622 (m, H_2O), 1547 (m, COO), 1423 (w, COO), 953 (m, (Mo=O)), 796 (s), 635 (w), 580 (s), 455 (w).

The synthesis method for $Mo_{72}Fe_{30}$ and $Mo_{72}V_{30}$ are presented in Supplementary Material. The XRD patterns of these three Keplerate POM are also shown in Figure S1.

3.3. General procedure for epoxidation of alkenes: The Keplerate catalyst (10 µmol), an alkenes (1 mmol) and water (3 mL) were added to a glass tube under air. Then, hydrogen peroxide (1 mmol, 30%) was added and the reaction mixture was stirred for appropriate time in a preheated oil bath at 50 °C. The reaction progress was monitored by TLC and GC, and the yield of products was determined by GC analysis using toluene as the internal standard. After completion of the reaction ethyl acetate, 3 × 2 mL was added, and the extraction of organic phase was followed by evaporation of solvent. Higher purification of products was achieved by chromatography over silica gel (eluent: n-hexane/ethyl acetate 80:20). For the recyclability reactions, an aqueous solution of catalyst was used for the next runs.

4. Conclusion

In summary, the Keplerate catalysts $Mo_{72}M_{30}$ (M = V, Cr and Fe) were used as efficient catalysts for epoxidation of various olefins to epoxides at 50 °C in water using 30% H_2O_2. Among three Keplerate POM catalyst, $Mo_{72}Cr_{30}$ showed the highest conversions and selectivity for epoxidation of alkenes. In this system, $Mo_{72}M_{30}$ (M = V and Cr) catalysts efficiently reused

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many times without any loss of activity. Furthermore to the above-mentioned advantageous, the use of nontoxic and eco-friendly reagents, green solvents, and safe workup procedures makes this catalytic methodology appropriate for industrial goals.

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