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Complete List of Authors:	Haddadi, Hedayat; Department of Chemistry, Faculty of Sciences, Shahrekord University, P.O. Box 115, Moradpour Hafshejani, Shahrbanou; Chemical Nanoscience Laboratory, School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK Riahi Farsani, Mostafa; Department of Chemistry, Islamic Azad University, Shahrekord branch, Kazemi babaheydari, Ali; Department of Chemistry, Islamic Azad University, Shahrekord branch,

Heterogeneous Epoxidation of Alkenes with H_2O_2 Catalyzed by a Recyclable Organic–Inorganic Polyoxometalate-based Frameworks Catalyst

Hedayat Haddadi[a], Shahrbanou Moradpour Hafshejani [b, c], Mostafa Riahi Farsani*[c], Ali Kazemi Babahydari [c]

[a]*Department of Chemistry, Faculty of Sciences, Shahrekord University, P.O. Box 115, Shahrekord, Iran*
[b]*Chemical Nanoscience Laboratory, School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK*
[c] *Department of Chemistry, Islamic Azad University, Shahrekord Branch, Shahrekord , Iran*

∗Corresponding author: Tel: *+98 9133831017*
E-mails: *Riahim91@gmail.com, Riahim91@yahoo.com*

Abstract

Four organic–inorganic polyoxometalate-based frameworks(HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF) were synthesised and characterized by Elemental analysis, UV-vis, FT-IR cyclic voltammetry and XRD. Organic–inorganic polyoxometalate-based frameworks could act as effective and reusable heterogeneous catalysts for selective epoxidation of alkenes with aqueous hydrogen peroxide in acetonitrile. In the presence of PW-MOF, various kinds of alkenes could selectively be converted into the corresponding epoxides with high conversion and selectivity. The PW-MOF was stable to leaching, behaved as true heterogeneous catalysts, were easily recovered by filtration, and reused four times with the maintenance of the catalytic performance.

Keywords: Polyoxometalates, Epoxidation, Metal organic frameworks, H_2O_2

Introduction

Selective epoxidation of alkenes are of high interest in industrial organic synthesis. Different epoxides have been used widely in paints, epoxy resin, surfactants, and intermediates in various organic syntheses and industries (For example, 4.5 million tons and 70,000 tons of propylene and butene oxides, respectively, are produced each year), [1, 2]. H_2O_2 is an attractive and clean oxidant for different oxidation reactions because it has high content of active oxygen species and can be safely stored and used [3]. Polyoxometalates (POMs) are appealing compounds whose versatility and accessibility have led to the use of these compounds for various applications of science[4, 5].

Heteropoly compound of Keggin structure are widely used as catalysts for oxidative type reactions due to their unique properties, such as Brønsted acids, stronger than the conventional solid acids and fast and reversible multielectron redox transformations under rather mild condition[6, 7].

In recent decades, many catalytic systems with various types of POMs as the effective catalysts for the epoxidation of alkenes have been used for example $[\{\gamma\text{-SiTi}_2W_{10}O_{36}(OH)_2\}_2(\mu\text{-O})_2]^{8-}$, $[\gamma\text{-SiW}_{10}O_{34}(H_2O)_2]^{4-}$,$[\gamma\text{-PW}_{10}O_{38}V_2(\mu\text{-OH})_2]^{3-}$,$H_2Na_{14}[Fe^{III}_2(NaOH_2)_2(P_2W_{15}O_{56})_2]$, $([TM^{II}Fe^{III}_2(P_2W_{15}O_{56})(P_2TM^{II}_2W_{13}O_{52})]^{16-}$,TM=Cu,Co),$[WZnM_2(H_2O)_2(ZnW_9O_{34})_2]^{12-}$ (M=Mn^{II}, Zn^{II}), and so on[8-14]. Kholdeeva et al. have demonstrated the catalytic performance of $(TBA)_4[PTi(OH)W_{11}O_{39}]$, in the oxidation of alkenes[15]. Furthermore, the immobilization of polyoxometalates on solid supports such as silica has attracted great research interest because solid catalysts have the advantages of being easier to recover and recycle[16-23]. However, a few examples of using heterogeneous catalysts with polyoxometalates in alkene epoxidation with

H_2O_2 were also reported [24]. Mizuno reported that the epoxidation hardly proceeded with $[\gamma\text{-}H_2PV_2W_{10}O_{40}]^{3-}$ or SiW_{12} alone but the $[\gamma\text{-}H_2PV_2W_{10}O_{40}]$-$[SiW_{12}]$ composite and $[\gamma\text{-}H_2PV_2W_{10}O_{40}]$-$[SiW_{12}]$ supported on different compounds, showed a much higher catalytic activity than those of $[\gamma\text{-}H_2PV_2W_{10}O_{40}]^{3-}$ and SiW_{12}[25].

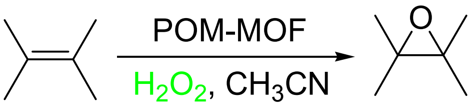
The mechanistic pathway for the epoxidation of alkenes has been reported by diffrent groups [26]. Radical chain processes, including those associated with O_2 and H_2O_2, and non-radical mechanisms and peroxometal intermediates are more commercially significant.

Metal-organic frameworks (MOFs) have been shown to be efficent supports to incorporate polyoxometalates to formation of efficient heterogeneous catalysts. In recent years, MOFs have attracted considerable attention because of their unique combination of properties such as high surface area, crystalline open structures, tunable pore size, and functionality, and so forth [27, 28]. All these properties allow considering MOFs as prospective catalytic materials and supports for immobilization of homogeneous catalysts[29-31]

In addition, different polyoxometalate structures catalyzed various oxidation reactions [32-34]. Nevertheless, such reactions are still rare and lack generality.

The present work on the development of novel oxidation methods for the oxidation of organic compounds[35] reports a heterogeneous epoxidation with hydrogen peroxide catalyzed by POM hybrid materials based on Keggin polyanion building blocks and copper organic frameworks with pyrazine derivatives[36] (Scheme 1) $[Cu_3(4,4'\text{-bpy})_3]$ $[HSiW_{12}O_{40}].(C_3H_4N_2)$ (abbreviation: HSiW-MOF),$[Cu_3(4,4'\text{-bpy})_3]$ $[PMo_{12}O_{40}].(C_5H_6N_2).0.5H_2O$(abbreviation: PMo-MOF), $[Cu_2(4,4'\text{-bpy})_2][HPMo_{12}O_{40}].(C_5H_6N_2)$(abbreviation: HPMo-MOF) and $[Cu(Phen)(4,4'\text{-bpy})(H_2O)]_2[PW_{12}O_{40}].(4,4'\text{-bpy})$, (abbreviation: PW-MOF) $C_3H_4N_2$ = imidazole, $C_5H_6N_2$ = 2-

aminopyridine, bpy =bipyridine, Phen = 1,10-phenanthroline). Moreover, the catalyst was reused in the procedure for four times without any loss of activity.



Scheme 1. Epoxidation of alkenes catalyzed by POM-MOF

Experimental section

All common laboratory chemicals were reagent grade, purchased from commercial sources, and used without further purification.

Preparation of the catalysts

HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF were prepared and fully characterized according to the procedure already published in the literature(see supporting information figures 1-10) [36].

Preparation of HSiW-MOF

HSiW-MOF was synthesized hydrothermally from a mixture of $H_4SiW_{12}O_{40}\cdot xH_2O$ (FW ≈ 2878.17, 0.4 g, 0.14 mmol), $CuCl_2.2H_2O$ (0.23 g, 1.33 mmol), $H_2C_2O_4.2H_2O$ (0.41 g, 3.25 mmol), im (im = imidazole, 0.027 g, 0.4 mmol), 4,4′-bpy (0.101 g, 0.65 mmol) and distilled water (20 ml). The pH of the mixture was necessarily adjusted to 4 with $NH_3.H_2O$ solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Dark red block crystals could be isolated. in about 51% yield (based on W). Elemental analyses (%) calcd.: W, 61.24; Si, 0.78; Cu, 5.29; C, 11.00; H, 0.81; N, 3.11. Found: W, 62.2; Si, 0.87; Cu, 5.04; C, 9.85; N, 2.94, H, 0.75

Preparation of PMo-MOF

PMo-MOF was synthesized hydrothermally from a mixture of $H_3PMo_{12}O_{40}.xH_2O$ (FW≈1825.25, 0.5 g, 0.274mmol), NH_4VO_3 (0.234 g, 2.0mmol), $C_8H_6O_4$ (isophthalic acid) (0.30 g, 1.81mmol), $CuCl_2.2H_2O$ (0.333 g, 1.953 mmol), 4,4′-bpy (0.166 g, 0.864 mmol), $C_5H_6N_2$ (2-aminopyridine) (0.10 g, 1.062mmol) and distilled water (25 ml). The pH of the mixture was necessarily adjusted to 6.5 with $NH_3.H_2O$ solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Dark block crystals could be isolated in about 61% yield (based on Mo). Elemental analyses (%) calcd.: Mo, 44.54; P, 1.20; Cu, 7.38; C, 16.26; H, 1.21; N, 4.34. Found: Mo, 43.75; P, 1.02; Cu, 7.14; C, 16.7; N, 4.25; H: 1.18

Preparation of HPMo-MOF

HPMo-MOF was synthesized hydrothermally from a mixture of $H_3PMo_{12}O_{40}.xH_2O$ (FW ≈ 1825.25, 0.5 g, 0.274 mmol), $C_6H_5NO_2$ (2-picolinic acid) (0.16, 1.357 mmol), $CuCl_2.2H_2O$ (0.333 g, 1.953 mmol), 4,4′-bpy (0.20 g, 1.04 mmol), $C_5H_6N_2$(2-aminopyridine) (0.10 g, 1.062 mmol) and distilled water (25 ml). The pH of the mixture was necessarily adjusted to 6 with $NH_3.H_2O$ solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Dark block crystals could be isolated in about 58% yield (based on Mo). Elemental analyses (%) calcd.: Mo, 48.85; P, 1.31; Cu, 5.39; C, 12.74; H, 0.98; N, 3.57. Found: Mo, 48.70; P, 1.18; Cu, 5.11; C, 12.87; N, 3.54; H, 0.89

Preparation of PW-MOF

PW-MOF was synthesized hydrothermally from a mixture of $Na_2WO_4.2H_2O$(0.5g, 1.516 mmol), H_3PO_4 (0.20 ml, 85%), $C_6H_5NO_2$ (isonicotinic acid) (0.1 g, 0.812 mmol), $CuCl_2.2H_2O$ (0.201 g, 1.179 mmol), Phen (0.133 g, 0.671 mmol), 4,4′-bpy (0.052 g, 0.271 mmol) and distilled water (25 ml). The pH of the mixture was necessarily adjusted to 5 with $NH_3.H_2O$ solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Blue block crystals could be isolated in about 45% yield (based on W). Elemental analyses (%) calcd.: W, 57.02; P, 0.80; Cu, 3.28; C, 16.76; H, 1.15; N, 3.62. Found: W, 56.12; P, 0.81; Cu, 3.51; C, 16.47; N, 3.37; H, 0.99.

A typical procedure for the catalytic oxidation of alkenes

The catalytic reactions were performed in a 10 mL round bottom flask equipped with a magnetic stirring bar, and a reflux condenser. The desired catalyst (HSiW - MOF, PMo - MOF , HPMo-MOF and PW-MOF), alkenes and 1.25 mmol H_2O_2 in acetonitrile were charged in the reaction flask at the set constant temperature for the whole duration of reactions. The same reaction was carried out by varying different parameters such as effect of molar ratio of H_2O_2 to substrate, amount of the catalyst, reaction time, and reaction temperature. After completion of the reaction, the catalyst was removed by filtration. The progress of the reaction was detected by gas chromatography (GC). Conversion = 100% × (mol epoxide product + mol byproducts)/mol initial H_2O_2. Selectivity = 100% × mol epoxide product/(mol epoxide product + mol byproducts). The concentration of H_2O_2 in the reacted mixture was determined by the titration with sodium thiosulfate (starch as the indicator) in the presence of potassium iodide, sulfuric acid and ammonium molybdate. No remaining H_2O_2 was detected due to the self-decomposition of H_2O_2 accompanying with the oxidation of the alkene. In this case, the conversion of the substrate based on H_2O_2 calculated by the formula above also reflects the H_2O_2 utilization efficiency.Other alkene substrates were tested accordingly.

Results and discussion

Synthesis and Structure

In this study, HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF were obtained by hydrothermal reactions according to the published procedure by Prof. Cui [36]. His reported that all compounds synthesis by mixing polyoxometalates or polyoxometalates precursors, $CuCl_2$ and organic linker with different molar ratio in water solution. Also, the pH of the mixture was necessarily adjusted in specific pH with $NH_3 \cdot H_2O$ solution. Furthermore, his reported that, $H_2C_2O_4.2H_2O$ plays an important role in the synthesis of HSiW-MOF as a reducing agent. Interestingly, Cui et al. reported that preparation of PMo-MOF without adding isophthalic acid or NH_4VO_3 resulted in only amorphous powders. The roles of NH_4VO_3 and isophthalic acid are still elusive[36]. After synthesing of four compounds with above method, purity and structure of all compounds was confirmed by infrared spectroscopy, UV-vis, cyclic voltammetry, elemental analysis and XRD (see supporting information Fig. 1-10). This is in complete agreement with the observations by Cui et al. for HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF [36].

Effect of the nature of catalyst

At first, the catalytic activity of $CuCl_2$, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF was evaluated for the epoxidation of cyclooctene using 1.25 mmol of H_2O_2 as an oxidant at 50 °C in acetonitrile. With the results shown in entries 1–9 (Table 1) it could be observed that the HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF could be applied to the epoxidation of cyclooctene using H_2O_2 and as a result of this in all cases beneficial to excellent activities and selectivities were obtained. However, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ were inactive or exhibited extremely low catalytic activities for cyclooctene in homogeneous systems, which further confirms the promotional role of MOF structure for the high epoxidation activity of POM-MOF in heterogeneous systems. The $CuCl_2$ was also used as catalyst for the epoxidation of cyclooctene and no conversion was found. The epoxidation of cyclooctene was carried out without catalyst. It was identified that no oxidation occurs and among all catalysts PW-MOF caused a heterogeneous epoxidation system and showed an 83.5% conversion with 99% selectivity (entry 7). In addition, pure $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ (entries 1-3), despite of being a homogeneous catalyst, only gave a 5.1-37% conversion with desirable selectivity. Regarding PW-MOF as a more effective catalyst, detailed reaction parameters such as reaction temperature, amount of catalyst and H_2O_2 amounts were taken into account on the epoxidation of cyclooctene to optimize the conditions.

Table 1. The epoxidation of cyclooctene with H_2O_2 in the presence of various catalysts[a]

Entry	Catalyst	Weight of catalyst (mg)	Conv (%)[b]	Sel(%)[c]
1	$H_3PW_{12}O_{40}$	29	37	92
2	$H_4SiW_{12}O_{40}$	29	5.1	71
3	$H_3PMo_{12}O_{40}$	18	17	73
4	HSiW-MOF	36	44.7	86
5	PMo-MOF	26	68.5	95.5
6	HPMo-MOF	24	66.4	93.7
7	PW-MOF	39	83.5	99
8	$CuCl_2$	0.2	4.5	12
9	Without catalyst	-	1	-

[a] Reaction conditions: catalyst (0.01mmol POM), substrate (1 mmol), 30% H_2O_2 (1.25 mmol), acetonitrile (3 mL), 50 ºC for 5 h for cyclooctene.

[b] Conversion and selectivities were determined by gas chromatography using an internal standard technique and are based on alkenes.

[c] Selectivity for the epoxide product

Effect of temperature

Temperature can also be important for achieving the optimum result. To study the relevant effect, the reaction was studied at four different temperatures of 25, 50, 60, and 85 °C, with 39 mg PW-MOF contain 0.01mmol of PW_{12}, 1 mmol of cyclooctene, 1.25 mmol hydrogen peroxide, and 3 ml CH_3CN. The results for the same are presented in Figure 1. The outcomes indicated that the conversion of cyclooctene increased with the rise of temperature while selectivity to epoxide decreased.

Although, increase of the reaction temperature improved the conversion of cyclooctene but in higher temperature selectivity to epoxide decrease.

Therefore, the temperature of 50 °C was found optimal for the higher conversion of cyclooctene to the corresponding epoxide.

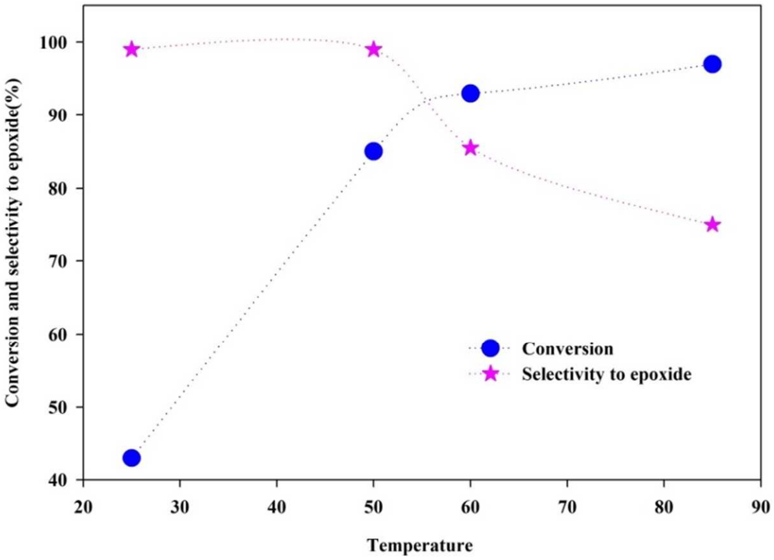


Fig. 1. The epoxidation of cyclooctene catalyzed by PW-MOF in various temperatures

Effect of the amount of catalyst

The effect of the catalyst amount on the epoxidation of cyclooctene is represented in Figure 2. The reaction was performed with various amounts of PW-MOF with 1 mmole of cyclooctene and 1.25 mmol of H_2O_2 for 5 h at 50 °C. The conversion and selectivity for the epoxidation of cyclooctene are reported in Figure 2. It is observed from Figure 2 that the conversion increases with a rise in the amount of PW-MOF from 0.001mmol to 0.1mmol but higher selectivity was noted with 0.01mmol of catalyst. Furthermore, with 0.01mmol of PW-MOF, the conversion was 83.5%. Thus, further optimization of the conditions was conducted with 0.01mmol of PW-MOF.

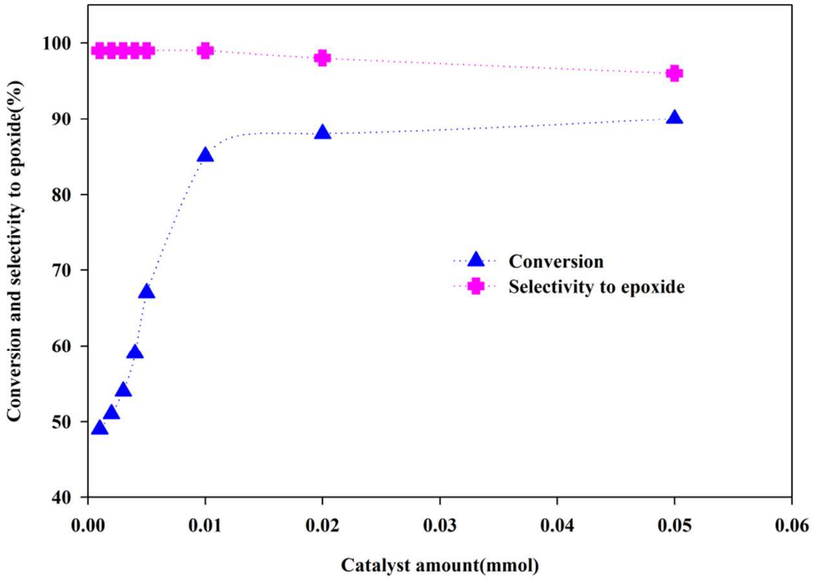


Fig. 2. The epoxidation of cyclooctene with different amounts of catalyst

Effect of the amount of H_2O_2

In order to determine the role of H_2O_2 in the epoxidation of cyclooctene, this epoxidation was studied with different concentrations of H_2O_2 from 0.5 to 5 mmol maintaining a constant catalyst amount 39 mg (0.01mmol), temperature (50 °C) and reaction time (5 h). The results are shown in Figure 3. Molar ratios of H_2O_2 to cyclooctene 1:10 and 1.25:1 resulted in 7 and 83.5% conversions, respectively, and when the molar ratios of H_2O_2 to cyclooctene were changed to 1.4:1, 1.6:1, 1.8:1 and 2:1 then the conversion increased to 88-95.5. However, selectivity to epoxide decreased with increasing the mmol of H_2O_2.

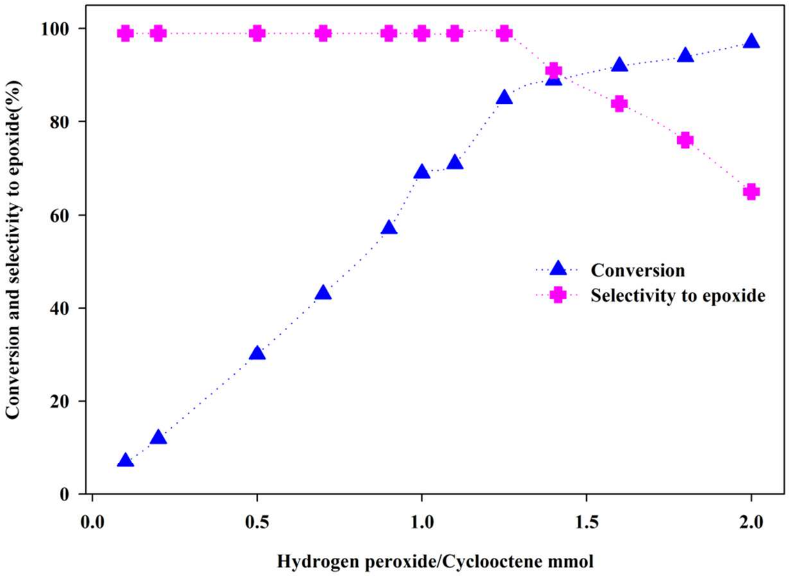


Fig. 3. The epoxidation of cyclooctene with different amounts of H_2O_2

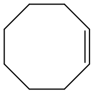
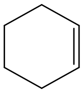
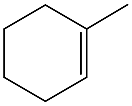
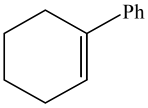
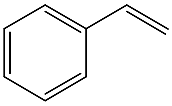
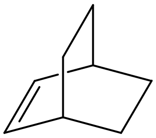
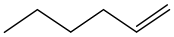
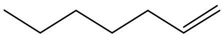
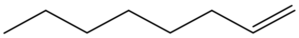
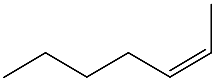
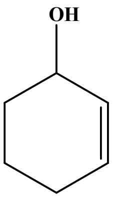
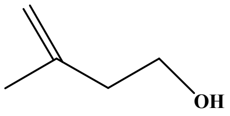
Epoxidation of different alkenes

In the presence of PW-MOF, different terminal, internal, and cyclic alkenes were epoxidized with high selectivity's using a 1.25equimolar amount of H_2O_2 in acetonitrile(Table 2). Various cyclic alkenes such as cyclohexene, 1-methyl-cyclohexene, 1-phenyl cyclohexene and cyclooctene were epoxidized with good conversion and selectivity (entries 1-4). The applied method resulted in a 73% conversion of styrene (entry 5) within 6 h.

Bulky cyclic olefins (norbornene) was epoxidized with 77.5%conversion and 91% epoxide selectivity(entry 6). In addition, non-activated terminal alkenes such as 1-hexzene, 1- hepten, 1-octene could be converted into the corresponding epoxides with 67-70% conversion and 86-92% selectivity to epoxide (entries 7-9). For the epoxidation of cis-2-heptene (entry 10), the configuration around the C=C bond was retained in the corresponding epoxide (cis-2,3-epoxyheptane was obtained with a 97% selectivity). The method possesses novelty regarding chemoselectivity. The hydroxyl group which is sensitive to oxidation remained completely intact under the influence of the catalyst, producing the pertinent epoxides in good selectivity (entries

11,12). It could be perceived that the present catalyst could be applied to the epoxidation of different alkenes using H_2O_2. In all cases, beneficial to excellent activities and selectivities were achieved.

Table 2. The **s**elective epoxidation of various substrates with aqueous H_2O_2 catalyzed by PW-MOF[a]

Entry	Substrate	Time(h)	Conversion (%)[b]	selectivity (%)[c]
1		5	83.5	99
2		6	80	94
3		5.5	61.4	95.5
4	 Ph	6	50.5	97
5		6	73	83
6		5.5	77.5	91
7		4.5	67	86
8		6.5	71.5	93
9		8	70	92
10		5	79.1	97
11	 OH	7.5	74	81
12	 OH	7	71.4	85

[a]Reaction conditions: catalyst 39 mg (0.01mmol POM), substrate (1 mmol), 30% H_2O_2 (1.25 mmol), acetonitrile (3 mL), Reaction temperature: 50 ºC.

[b] Conversion and selectivities were determined by gas chromatography using an internal standard technique and are based on alkenes.

[c]Selectivity for the epoxide product

Comparison with Other Catalysts

Comparative data of the cyclooctene epoxidation for previously-reported catalysts and present catalysts is given in Table 3. Leng et al. Identified that the epoxidation of alkenes was catalyzed by heteropolyanion-based amino-containing cross-linked ionic copolymers[37]. This group of researchers performed the oxidation reaction using acetonitrile as a solvent and 98.5% conversion and 100% selectivity of epoxide was reported (Table 3, entry 1). In addition, Kholdeeva et al. carried out the epoxidation of alkenes catalyzed by PW_{12} and hybrid Polyoxotungstate/MIL-101 using CH_3CN as a solvent with H_2O_2 as an oxidant (Table 3, entries 2, 3) [33]. Furthermore, Kholdeeva et al. reported that PW_{12}/MIL-101 materials behave as true heterogeneous catalysts and can be recycled several times without loss of activity and selectivity with the retention of both POM and MIL-101 structures [33]. Moreover, Pac et al. found out that heterogeneous catalysts prepared by the immobilization of polyoxometalates on chemically-modified hydrophobic mesoporous silica gel have been successfully applied to the selective epoxidation of olefins with 15% aqueous H_2O_2 without the use of organic solvent (Table 3, entry 4) [38]. In the present work, PW-MOF gives 83.5% conversion and 99% selectivity toward the epoxide (Table 3, entry 5). Hill et al. conducted the epoxidation of alkenes catalyzed by Phosphotungstic acid using $H_2O/CHCl_3$ as a solvent with H_2O_2 as an oxidant and 78% conversion with 98% selectivity of the epoxide was observed [39] (Table 3, entry 6).

Therefore, the present catalyst (PW-MOF) provides a desirable catalytic activity for the epoxidation of alkenes compared to PW_{12}.

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

Entry	Catalyst	Substrate	Solvent	Conv(%)	Sel (%)	Ref
1	AM–BM–PW	Cyclooctene	CH_3CN	98.5	100	37
2	PW_{12}/MIL-101	Cyclooctene	CH_3CN	76	99	33
3	PW_{12}	Cyclooctene	CH_3CN	78	95	33
4	PW_{12}/Modified SiO_2	Cyclooctene	-	97	100	38
5	PW-MOF	Cyclooctene	CH_3CN	83.5	99	-
6	PW_{12}	Cyclooctene	$CHCl_3$	78	98	39

Proposed mechanism

In this work, the mechanism of the oxidation reaction was not studied. However, the reaction mechanism of the epoxidation of alkenes over polyoxometalates using H_2O_2 as an oxidant was extensively investigated by several groups. For example, Brégeaul et al. Discovered that several salts of the general formula $Q_2[HPO_4\{WO(O_2)_2\}_2]$ were obtained by the reaction of $H_3PW_{12}O_{40}$ with hydrogen peroxide [40]. Hill et al. [39] and Griffith et al. [41] reported that the $[PW_{12}O_{40}]^{3-}$ and its lacunary derivative $[PW_{11}O_{39}]^{7-}$ can also form smaller active species $[(PO_4)\{WO(O_2)_2\}_4]^{3-}$, $[(PO_4)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]^{3-}$, and $[(PO_3(OH))\{WO(O_2)_2\}_2]^{2-}$ in the presence of hydrogen peroxide.

Recycling of the catalyst

Stability of polyoxometalates in oxidation reaction by using H_2O_2 as an oxidant was extensively investigated by several groups. Previous work suggested that PW_{12} partially transformed to lower nuclearity peroxotungstates, such as PW_4 and PW_2. PW_{12} and PW_4 could be transformed to each other under the reaction conditions, and most of PW_4 was transformed to PW_{12} after the reaction[33, 42-46]. The epoxidation of cyclooctene was performed with the recycled catalyst under the optimized conditions. It can be observed that the performance of PW-MOF was considerably stable during three runs, but the catalytic activity of PW-MOF slightly decreased after the third run (Table 4). The IR spectrum and XRD pattern of PW-MOF run after four cycles of cyclooctene epoxidation (Figure 4, 5) indicated the same IR spectrum and XRD pattern for the new and reused catalysts.

The recycled catalyst PW-MOF was characterized by FT-IR and XRD. The FT-IR spectra for the fresh as well as regenerated catalysts (four cycles) are represented in Figure 4. The IR spectrum of fresh and reused PW-MOF shows similar peaks at 807-1100 cm^{-1} corresponding to (W–O$_t$), (W–O$_b$) , (W–O$_c$), (P-O)[36]. Furthermore, XRD patterns of fresh catalysts indicated impressive similarity with the reused catalyst XRD patterns (Figure 5). Hot catalyst filtration tests were performed and no further substrate conversion was found in the filtration after the removal of PW-MOF. This proves the true heterogeneous nature of the oxidation catalysis over the PW-MOF catalyst. Additionally, the ICP analysis data confirmed that no evident tungsten or copper leaching occurred under the conditions employed. After the hot filtration experiment, the separated catalysts were washed with acetonitrile and dried at 100 °C. A minor reduction was observed in the catalytic activity of PW-MOF (83% conversion and 99% selectivity to epoxide). We found no further substrate conversion in the filtrate after the removal of PW-MOF (Figure 6). These results determine that the framework structures of PW-MOF can still be retained after the catalytic performance [36].

Table 4. The catalytic activity of PW-MOF in different runs[a]

Run	Conversion(%)[b]	Selectivity(%)[c]
1	83.5	99

2	83.5	99
3	83	99
4	83	98
5	80	98

[a] Reaction conditions: catalyst (0.01mmol), substrate (1 mmol), 30% H_2O_2 (1.25 mmol), acetonitrile (3 mL), 50 °C for 5 h for cyclooctene.

[b] Conversion of the substrate based on alkenes.

[c] Selectivity for the epoxide product

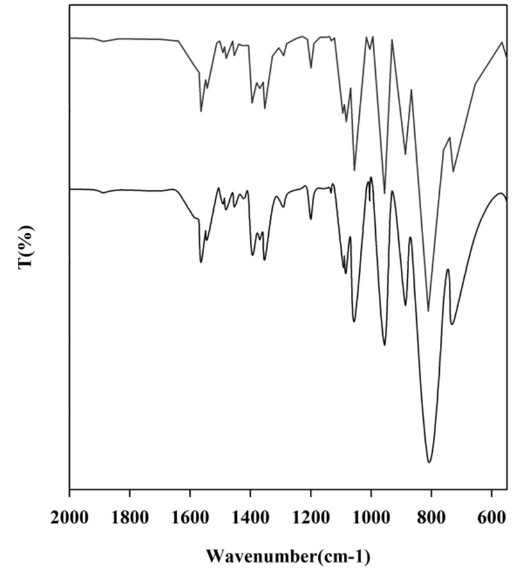


Fig. 4. FT-IR spectrum of the PW-MOF recovered in run 1 (up) and 4 (down)

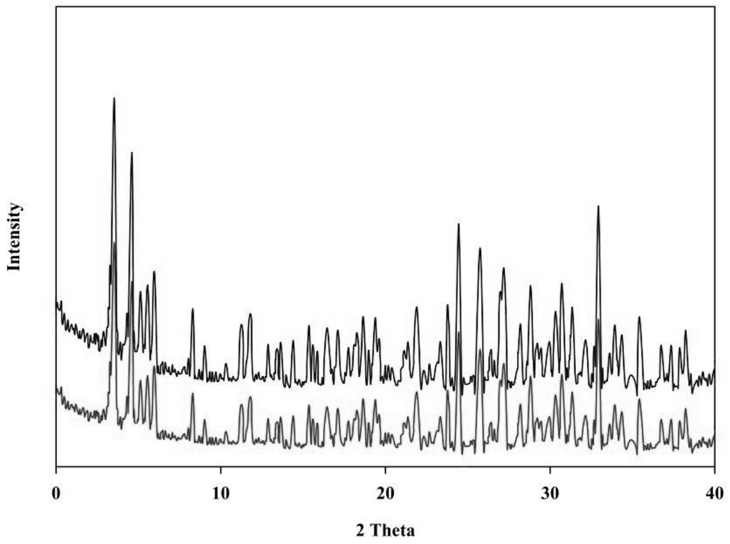


Fig. 5. XRD pattern of the PW-MOF recovered in run1 (up) and 4 (down)

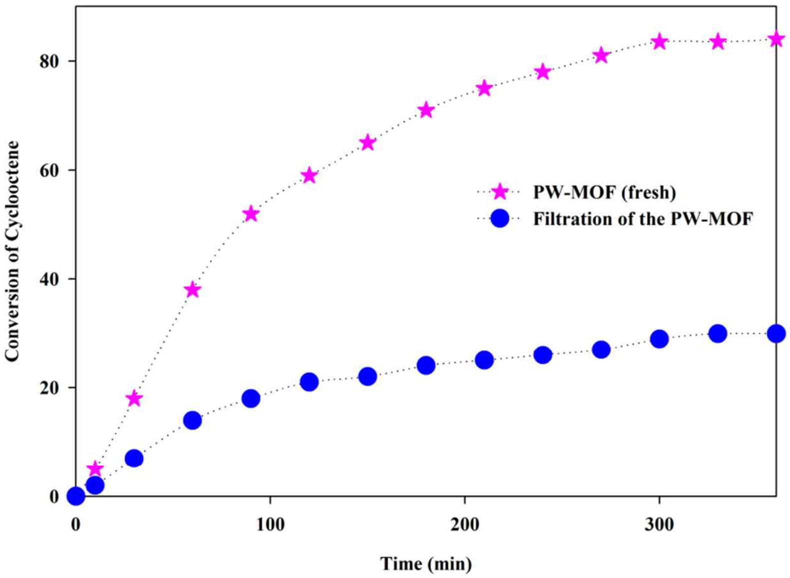


Fig. 6. Hot catalyst filtration experiments for cyclooctene oxidation with H_2O_2 over PW-MOF and Filtration of the PW-MOF

Conclusion

In this work, the catalytic performance of organic–inorganic polyoxometalate-based frameworks in the epoxidation of different olefins with H_2O_2 as an oxidant in acetonitrile was demonstrated. A comparison between the catalytic activity of the heterogeneous and homogeneous catalysts indicated that heterogeneous catalysts exercised higher catalytic activities in the epoxidation of alkenes with hydrogen peroxide compared to the corresponding homogeneous catalysts. Diffrent aromatic and aliphatic alkenes were oxidized to the corresponding epoxide with excellent selectivity (81-99%) and often high conversion. Moreover, the epoxidation method showed excellent chemoselectivity. The hydroxyl group which is sensitive to oxidation remained completely intact under the influence of the catalyst. The catalyst is recyclable and stable and can be reused at least for four times in the epoxidation of cyclooctene without significant loss in its catalytic activity, which indicates the high stability of the catalyst.

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Graphical abstract:

Heterogeneous Epoxidation of Alkenes with H_2O_2 Catalyzed by a Recyclable Organic–Inorganic Polyoxometalate-based Frameworks Catalyst

Hedayat Haddadi[a], Shahrbanou Moradpour Hafshejani [b], Mostafa Riahi Farsani*[c], Ali Kazemi Babahydari [c]

[a]*Department of Chemistry, Faculty of Sciences, Shahrekord University, P.O. Box 115, Shahrekord, Iran*
[b]*Chemical Nanoscience Laboratory, School of Chemistry, Bedson Building, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK*
[c] *Department of Chemistry, Islamic Azad University, Shahrekord Branch, Shahrekord , Iran*

∗Corresponding author: Tel: *+98 9133831017*
E-mails: *Riahim91@gmail.com, Riahim91@yahoo.com*

PW-MOF as an efficient, recyclable and stable catalyst for the selective oxidation of alkenes with hydrogen peroxide