Published on 22 October 2015. Downloaded by University of Iowa on 25/10/2015 16:37:13.

NJC

PAPER

View Article Online
View Journal

Cite this: DOI: 10.1039/c5nj01661d

Heterogeneous epoxidation of alkenes with H_2O_2 catalyzed by a recyclable organic–inorganic polyoxometalate-based framework catalyst†

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

Received (in Victoria, Australia)
27th June 2015,
Accepted 13th October 2015

DOI: 10.1039/c5nj01661d

www.rsc.org/njc

Four organic–inorganic polyoxometalate-based frameworks (HSiW-MOF, PMo-MOF, HPMo-MOF and PW-MOF) were synthesised and characterized by elemental analysis, UV-vis and FT-IR spectroscopy, cyclic voltammetry and XRD analysis. 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. PW-MOF was stable to leaching, behaved as true heterogeneous catalysts, easily recovered by filtration, and reused four times with maintenance of the catalytic performance.

Introduction

Selective epoxidation of alkenes is of high interest in industrial organic synthesis. Different epoxides have been used widely in paints, epoxy resins, 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 compounds 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 conditions.[6,7]

In recent decades, many catalytic systems with various types of POMs as 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 much higher catalytic activity than those of $[\gamma\text{-H}_2PV_2W_{10}O_{40}]^{3-}$ and SiW_{12} used alone.[25]

The mechanistic pathway for the epoxidation of alkenes has been reported by different 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 efficient supports to incorporate polyoxometalates for the 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, 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]

---

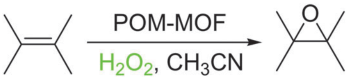
[a] *Department of Chemistry, Faculty of Sciences, Shahrekord University, P. O. Box 115, Shahrekord, Iran*

[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. E-mail: Riahim91@gmail.com, Riahim91@yahoo.com; Tel: +98 9133831017*

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c5nj01661d

Published on 22 October 2015. Downloaded by University of Iowa on 25/10/2015 16:37:13.



Scheme 1 Epoxidation of alkenes catalyzed by POM-MOF.

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), $[Cu_3(4,4'\text{-bpy})_3]$ $[HSiW_{12}O_{40}]\cdot(C_3H_4N_2)$ (abbreviation: HSiW-MOF), $[Cu_3(4,4'\text{-bpy})_3]$ $[PMo_{12}O_{40}]\cdot(C_5H_6N_2)\cdot0.5H_2O$ (abbreviation: PMo-MOF), $[Cu_2(4,4'\text{-bpy})_2][HPMo_{12}O_{40}]\cdot(C_5H_6N_2)$ (abbreviation: HPMo-MOF) and $[Cu(Phen)(4,4'\text{-bpy})(H_2O)]_2[PW_{12}O_{40}]\cdot(4,4'\text{-bpy})$, (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 four times without any loss of activity.

Experimental section

All common laboratory chemicals were of 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 ESI,† Fig. S1–S10).[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), $CuCl_2\cdot2H_2O$ (0.23 g, 1.33 mmol), $H_2C_2O_4\cdot2H_2O$ (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 $NH_3\cdot H_2O$ 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 analysis (%) 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 $H_3PMo_{12}O_{40}\cdot xH_2O$ (FW ≈ 1825.25, 0.5 g, 0.274 mmol), NH_4VO_3 (0.234 g, 2.0 mmol), $C_8H_6O_4$ (isophthalic acid) (0.30 g, 1.81 mmol), $CuCl_2\cdot2H_2O$ (0.333 g, 1.953 mmol), 4,4′-bpy (0.166 g, 0.864 mmol), $C_5H_6N_2$ (2-aminopyridine) (0.10 g, 1.062 mmol) and distilled water (25 ml). The pH of the mixture was necessarily adjusted to 6.5 with $NH_3\cdot H_2O$ 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 analysis (%) 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 $H_3PMo_{12}O_{40}\cdot xH_2O$ (FW ≈ 1825.25, 0.5 g, 0.274 mmol), $C_6H_5NO_2$ (2-picolinic acid) (0.16, 1.357 mmol), $CuCl_2\cdot2H_2O$ (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 $NH_3\cdot H_2O$ 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 analysis (%) 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 $Na_2WO_4\cdot2H_2O$ (0.5 g, 1.516 mmol), H_3PO_4 (0.20 ml, 85%), $C_6H_5NO_2$ (isonicotinic acid) (0.1 g, 0.812 mmol), $CuCl_2\cdot2H_2O$ (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 $NH_3\cdot H_2O$ 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 analysis (%) 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 of 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 the effect of molar ratio of H_2O_2 to substrate, the amount of 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 reaction mixture was determined by the titration with sodium thiosulfate (with 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 the oxidation of alkene. In this case, the conversion of the substrate based on H_2O_2 calculated using the

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2015

Published on 22 October 2015. Downloaded by University of Iowa on 25/10/2015 16:37:13.

above formula 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 of Prof. Cui.[36] He reported that all compounds are synthesised by mixing polyoxometalates or polyoxometalate precursors, $CuCl_2$ and an organic linker with different molar ratios in water solution. Also, the pH of the mixture was necessarily adjusted to specific pH with $NH_3 \cdot H_2O$ solution. Furthermore, he reported that $H_2C_2O_4 \cdot 2H_2O$ plays an important role in the synthesis of HSiW-MOF as a reducing agent. Interestingly, Cui *et al.* reported that preparation of the 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 synthesizing the four compounds using the above method, the purity and structure of all compounds were confirmed by infrared spectroscopy, UV-vis spectroscopy, cyclic voltammetry, elemental analysis and XRD analysis (see ESI,† Fig. S1–S10). They are in complete agreement with the observations of 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 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, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ were inactive or exhibited extremely low catalytic activities for cyclooctene in homogeneous systems, which further confirm the promotional role of MOF structure in the high epoxidation activity of POM-MOF in heterogeneous systems. $CuCl_2$ was also used as a catalyst for the epoxidation of cyclooctene and no conversion was found. Epoxidation of cyclooctene was carried out without a catalyst. It was identified that no oxidation occurs and among all catalysts PW-MOF produced a heterogeneous epoxidation system and showed an 83.5% conversion with 99% selectivity (entry 7). In addition, pure $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, and $H_3PMo_{12}O_{40}$ (entries 1–3), despite being homogeneous catalysts, gave only 5.1–37% conversion with desirable selectivity. Regarding PW-MOF as a more effective catalyst, detailed reaction parameters such as reaction temperature, the amount of catalyst and H_2O_2 concentration were taken into account in the epoxidation of cyclooctene to optimize the conditions.

Table 1 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 (0.01 mmol POM), substrate (1 mmol), 30% H_2O_2 (1.25 mmol), acetonitrile (3 ml), 50 °C 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 results. To study the relevant effect, the reaction was studied at four different temperatures of 25, 50, 60, and 85 °C with 39 mg of PW-MOF containing 0.01 mmol of PW_{12}, 1 mmol of cyclooctene, 1.25 mmol of hydrogen peroxide, and 3 ml of CH_3CN. The results of the same are presented in Fig. 1. The outcomes indicated that the conversion of cyclooctene increased with the increase of temperature while selectivity to epoxide decreased.

Although the increase of the reaction temperature improved the conversion of cyclooctene at higher temperatures selectivity to epoxide decreased.

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

Effect of the amount of catalyst

The effect of the amount of catalyst on the epoxidation of cyclooctene is presented in Fig. 2.

The reaction was performed with various amounts of PW-MOF with 1 mmol 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 Fig. 2. It is observed from Fig. 2 that the conversion increases with an increase in the amount of

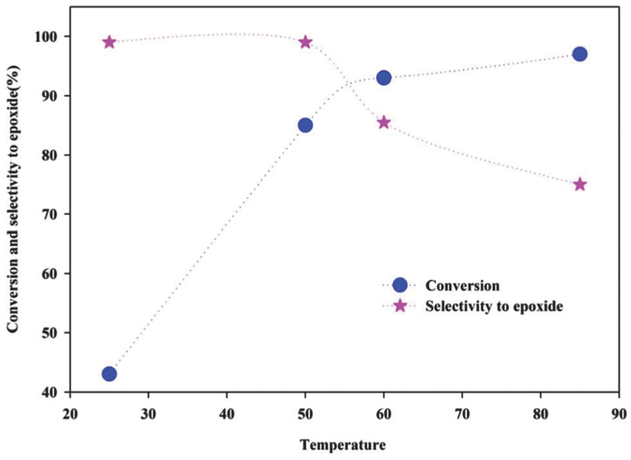


Fig. 1 Epoxidation of cyclooctene catalyzed by PW-MOF at various temperatures.

Published on 22 October 2015. Downloaded by University of Iowa on 25/10/2015 16:37:13.

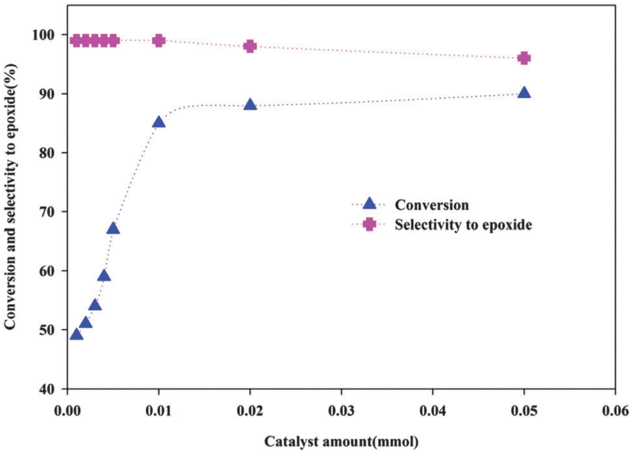


Fig. 2 Epoxidation of cyclooctene with different amounts of catalyst.

PW-MOF from 0.001 mmol to 0.1 mmol but higher selectivity was noted with 0.01 mmol of catalyst. Furthermore, with 0.01 mmol of PW-MOF, the conversion was 83.5%. Thus, a further optimization of the conditions was performed with 0.01 mmol of PW-MOF.

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 amount of catalyst of 39 mg (0.01 mmol), temperature (50 °C) and reaction time (5 h). The results are shown in Fig. 3. The 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 concentration 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 using 1.25 equimolar 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 73% conversion of styrene (entry 5) within 6 h.

Bulky cyclic olefins (norbornene) were epoxidized with 77.5% conversion and 91% epoxide selectivity (entry 6). In addition, non-activated terminal alkenes such as 1-hexene,

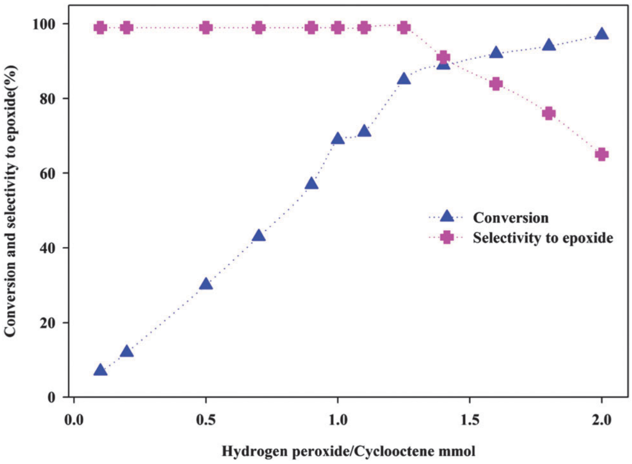
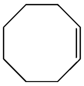
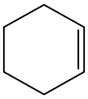
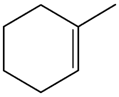
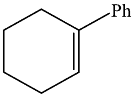
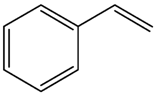
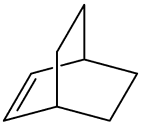
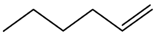
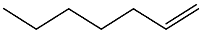
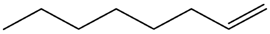
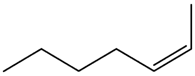
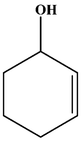
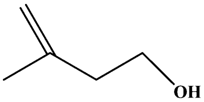


Fig. 3 Epoxidation of cyclooctene with different amounts of H_2O_2.

Table 2 The selective 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		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		7.5	74	81
12		7	71.4	85

[a] Reaction conditions: catalyst 39 mg (0.01 mmol POM), substrate (1 mmol), 30% H_2O_2 (1.25 mmol), acetonitrile (3 ml); reaction temperature: 50 °C. [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.

Published on 22 October 2015. Downloaded by University of Iowa on 25/10/2015 16:37:13.

1-heptene, and 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 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 and 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.

Comparison with other catalysts

Comparative data on the cyclooctene epoxidation with previously-reported catalysts and present catalysts are 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 were 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 and 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 an organic solvent (Table 3, entry 4).[38] In the present work, the PW-MOF gives 83.5% conversion and 99% selectivity toward the epoxide (Table 3, entry 5). Hill *et al.* performed 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 epoxide were observed[39] (Table 3, entry 6).

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

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 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 $[PW_{12}O_{40}]^{3-}$ 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.

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

Recycling of the catalyst

The stability of polyoxometalates in the oxidation reaction by using H_2O_2 as an oxidant was extensively investigated by several groups. Previous work suggested that PW_{12} partially transformed into lower nuclearity peroxotungstates, such as PW_4 and PW_2. PW_{12} and PW_4 could be transformed into each other under the reaction conditions, and most of PW_4 transformed into PW_{12} after the reaction.[33,42–46] 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 the XRD pattern of the PW-MOF run after four cycles of cyclooctene epoxidation (Fig. 4 and 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 analyses. The FT-IR spectra of the fresh as well as regenerated catalysts (four cycles) are presented in Fig. 4. The IR spectra of fresh and reused PW-MOF show similar peaks at 807–1100 cm^{-1} corresponding to ($W–O_t$), ($W–O_b$), ($W–O_c$), and (P–O).[36] Furthermore, XRD patterns of the fresh catalyst show an impressive similarity to the XRD patterns of the reused catalyst (Fig. 5). Hot catalyst filtration tests were performed and no further substrate conversion was found in the filtrate after the removal of PW-MOF. This proves the true heterogeneous nature of 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 (Fig. 6).

Table 4 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 (0.01 mmol), 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.

Published on 22 October 2015. Downloaded by University of Iowa on 25/10/2015 16:37:13.

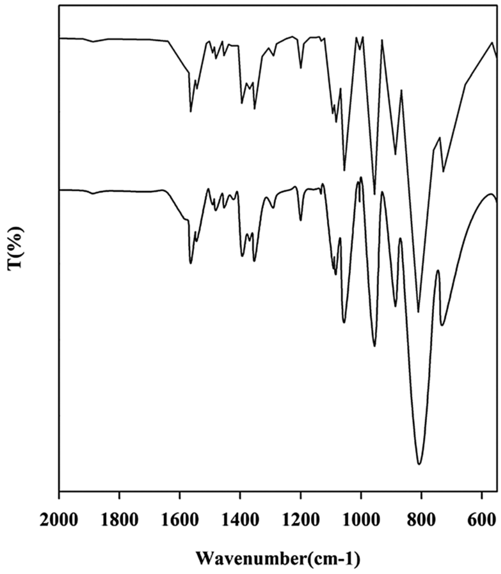


Fig. 4 FT-IR spectrum of PW-MOF recovered in runs 1 (up) and 4 (down).

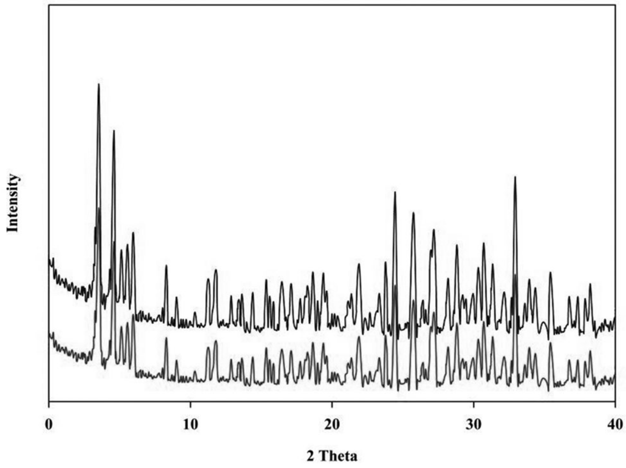


Fig. 5 XRD pattern of PW-MOF recovered in runs 1 (up) and 4 (down).

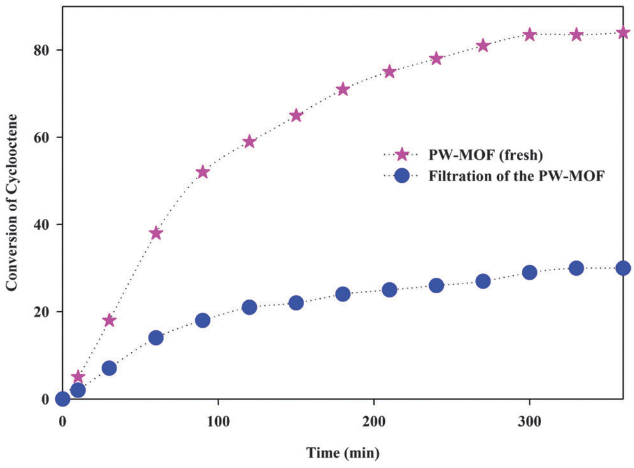


Fig. 6 Hot catalyst filtration experiments for cyclooctene oxidation with H_2O_2 over PW-MOF and filtration of PW-MOF.

These results demonstrate that the framework structures of PW-MOF can still be retained after the catalytic performance.[36]

Conclusion

In this work, the catalytic performance of organic–inorganic polyoxometalate-based frameworks in the epoxidation of different olefins using H_2O_2 as an oxidant in acetonitrile was demonstrated. A comparison between the catalytic activity of 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. Different 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 four times in the epoxidation of cyclooctene without significant loss in its catalytic activity, which indicates the high stability of the catalyst.

Acknowledgements

The authors gratefully acknowledge the support of the Research Council of Shahrekord University for this study.

References

1 R. A. Sheldon and J. K. Kochi, *Metal Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981.
2 X. Zuwei, Z. Ning, S. Yu and L. Kunlan, *Science*, 2001, **292**, 1139.
3 *Catalytic Oxidations with Hydrogen Peroxide as Oxidant*, ed. G. Strukul, Kluwer Academic, Dordrecht, The Netherlands, 1992.
4 Y. Kikukawa, S. Yamaguchi, K. Tsuchida, Y. Nakagawa, K. Uehara, K. Yamaguchi and N. Mizuno, *J. Am. Chem. Soc.*, 2008, **16**, 5472.
5 V. M. Pandya, U. Kortz and S. Joshi, *Dalton Trans.*, 2015, **44**, 58.
6 N. Mizuno and M. Misono, *Chem. Rev.*, 1998, **98**, 199.
7 I. V. Kozhevnikov, *Chem. Rev.*, 1998, **98**, 171.
8 Y. Goto, K. Kamata, K. Yamaguchi, K. Uehara, S. Hikichi and N. Mizuno, *Inorg. Chem.*, 2006, **45**, 2347.
9 K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi and N. Mizuno, *Science*, 2003, **300**, 964.
10 K. Kamata, M. Kotani, K. Yamaguchi, S. Hikichi and N. Mizuno, *Chem. – Eur. J.*, 2007, **13**, 639.
11 K. Kamata, K. Sugahara, K. Yonehara, R. Ishimoto and N. Mizuno, *Chem. – Eur. J.*, 2011, **17**, 7549.
12 X. Zhang, T. M. Anderson, Q. Chen and C. L. Hill, *Inorg. Chem.*, 2001, **40**, 418.
13 R. Neumann and M. J. Gara, *J. Am. Chem. Soc.*, 1994, **116**, 5509.

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2015

Published on 22 October 2015. Downloaded by University of Iowa on 25/10/2015 16:37:13.

14 R. Neumann and M. J. Gara, *J. Am. Chem. Soc.*, 1995, **117**, 5066.

15 O. A. Kholdeeva, *Top. Catal.*, 2006, **40**, 229.

16 S. Damyanova, L. Dimitrov, R. Mariscal, J. L. G. Fierro, L. Petrov and I. Sobrados, *Appl. Catal., A*, 2003, **256**, 183.

17 V. M. Mastikhin, S. M. Kulikov, A. V. Nosov, I. V. Kozhevnikov, I. L. Mudrakovsky and M. N. Timofeeva, *J. Mol. Catal.*, 1990, **60**, 65.

18 T. Sakamoto and C. Pac, *Tetrahedron Lett.*, 2000, **41**, 10009.

19 H. J. Kim, Y. G. Shul and H. Han, *Appl. Catal., A*, 2006, **299**, 46.

20 Y. Izumi, K. Hisano and T. Hida, *Appl. Catal., A*, 1999, **181**, 277.

21 I. V. Kozhevnikov, A. Sinnema, R. J. J. Jansen and H. V. Bekkum, *Catal. Lett.*, 1994, **27**, 187.

22 M. Hasik, W. Turek, E. Stochmal, M. Lapkowski and A. Pron, *J. Catal.*, 1994, **147**, 544.

23 K. R. Mohana, R. Gobetto, A. Iannibello and A. Zecchina, *J. Catal.*, 1989, **119**, 512.

24 P. Sharma and A. Patel, *Appl. Surf. Sci.*, 2009, **255**, 7635.

25 Y. Wang, K. Kamata, R. Ishimoto, Y. Ogasawara, K. Suzuki, K. Yamaguchi and N. Mizuno, *Catal. Sci. Technol.*, 2015, **5**, 2602.

26 C. Venturello, R. D. Aloisio, J. C. J. Bart and M. Ricci, *J. Mol. Catal.*, 1985, **32**, 107; C. Venturello and R. D. Aloisio, *J. Org. Chem.*, 1988, **53**, 1553; C. L. Hill and C. M. Prosser-McCartha, *Coord. Chem. Rev.*, 1995, **143**, 407; R. Neumann and M. Dahan, *J. Am. Chem. Soc.*, 1998, **120**, 11969; Y. Lenga, W. Zhanga, J. Wang and P. Jiang, *Appl. Catal., A*, 2012, **446**, 306; R. Prabhakar, K. Morokuma, C. L. Hill and D. G. Musaev, *Inorg. Chem.*, 2006, **45**, 5703.

27 G. Ferey, *Chem. Soc. Rev.*, 2008, **37**, 191.

28 S. Kitagawa, R. Kitaura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.

29 J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Leon and K. Kim, *Nature*, 2000, **404**, 982.

30 M. H. Alkordi, Y. Liu, R. W. Larsen, J. F. Eubank and M. Eddaoudi, *J. Am. Chem. Soc.*, 2008, **130**, 12639.

31 J. Y. Lee, O. K. Farha, J. Roberts, K. A. Sheidt, S. T. Nguyen and J. T. Hupp, *Chem. Soc. Rev.*, 2009, **38**, 1450.

32 N. V. Maksimchuk, M. N. Timofeeva, M. S. Melgunov, A. N. Shmakov, Y. A. Chesalov, D. N. Dybtsev, V. P. Fedin and O. A. Kholdeeva, *J. Catal.*, 2008, **257**, 315.

33 N. V. Maksimchuk, K. A. Kovalenko, S. S. Arzumanov, Y. A. Chesalov, M. S. Melgunov, A. G. Stepanov, V. P. Fedin and O. A. Kholdeeva, *Inorg. Chem.*, 2010, **49**, 2920.

34 J. Song, Z. Luo, D. K. Britt, H. Furukawa, O. M. Yaghi, K. I. Hardcastle and C. L. Hill, *J. Am. Chem. Soc.*, 2011, **133**, 16839.

35 R. Afrasiabi, F. Jalilian, B. Yadollahi and M. R. Farsani, *Inorg. Chem. Commun.*, 2014, **50**, 113; M. R. Farsani and B. Yadollahi, *J. Mol. Catal. A: Chem.*, 2014, **392**, 8; R. Afrasiabi, M. R. Farsani and B. Yadollahi, *Tetrahedron Lett.*, 2014, **55**, 3923; F. Jalilian, B. Yadollahi, M. R. Farsani, S. Tangestaninejad, H. Amiri Rudbari and R. Habibi, *Catal. Commun.*, 2015, **66**, 107.

36 L. Xiao, L. Wang, X. Shan, H. Guo, L. Fu, Y. Hu, X. Cui, K. Li and J. Xu, *CrystEngComm*, 2015, **17**, 1336.

37 Y. Leng, W. Zhang, J. Wang and P. Jiang, *Appl. Catal., A*, 2012, **445**, 306.

38 T. Sakamoto and C. Pac, *Tetrahedron Lett.*, 2000, **41**, 10009.

39 D. C. Duncan, R. C. Chambers, E. Hecht and C. L. Hill, *J. Am. Chem. Soc.*, 1995, **117**, 681.

40 L. Salles, A. Catherine, T. Rene, R. Francis, D. Claudine, C. Genevieve, L. Henry, J. Yves and M. B. Jean, *Inorg. Chem.*, 1994, **33**, 871.

41 N. M. Grecley, W. P. Griffith, A. C. Laemmel, H. S. Nogueira and B. C. Parkin, *J. Mol. Catal. A: Chem.*, 1997, **117**, 185.

42 S. Zhang, G. Zhao, S. Gao, Z. Xi and J. Xu, *J. Mol. Catal. A: Chem.*, 2008, **289**, 22.

43 H. Su and C. Yang, *Chin. J. Catal.*, 2014, **35**, 1224.

44 H. Wang, R. Hu, Y. Yang, M. Gao and Y. Wang, *Catal. Commun.*, 2015, **70**, 6.

45 X. Dong, D. Wang, K. Li, Y. Zhen, H. Hu and G. Xue, *Mater. Res. Bull.*, 2014, **57**, 210.

46 Y. Chen, R. Tan, W. Zheng, Y. Zhang, G. Zhaoa and D. Yin, *Catal. Sci. Technol.*, 2014, **4**, 4084.