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Synthesis and characterization of supported heteropolymolybdate nanoparticles between silicate layers of Bentonite with enhanced catalytic activity for epoxidation of alkenes

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ABSTRACT

A new heterogeneous catalyst (PVMo/Bentonite) consisting of vanadium substituted heteropolymolybdate with Keggin-type structure $Na_5[PV_2Mo_{10}O_{40}]\cdot 14H_2O$ (PVMo) supported between silicate layers of bentonite has been synthesized by impregnation method and characterized using X-ray diffraction, Fourier-transformed infrared spectroscopy, scanning electron microscopy, UV–vis diffuse reflectance spectroscopy, transmission electron microscopy and elemental analysis. X-ray diffraction and scanning electron microscopy analysis indicated that PVMo was finely dispersed into layers of bentonite as support. The PVMo/Bentonite used as an efficient heterogeneous catalyst for epoxidation of alkenes. Various cyclic and linear alkenes were oxidized into the corresponding epoxides in high yields and selectivity with 30% aqueous H_2O_2. The catalyst was reused several times, without observable loss of activity and selectivity. The obtained results showed that the catalytic activity of the PVMo/Bentonite was higher than that of pure heteropolyanion (PVMo).

1. Introduction

Polyoxometalates (POMs) have been widely studied in relation to their expressive conductive, catalytic, antiviral, photochromic and many other properties [1–3]. Unlike metal oxides and zeolites, polyoxometalates possess a discrete and mobile ionic structure. Moreover, POMs display strong Brønsted acidity and appropriate redox properties, which can be tuned by varying the chemical composition of the catalyst [4–6]. Among various structural classes, Keggin-type polyoxometalates have received considerable attention due to their acid–base and redox properties, and ease of preparation [7]. POMs are soluble in water and polar solvents and have low surface area. These disadvantages can be overcome by incorporation of the polyoxometalate into various stable porous supports by formation of different composites [8–18]. Among these materials, clay is an excellent support due to its thermal stability, relative high surface area, large pore volume and uniform pore size distribution. Bentonite is a clay mineral, which is mainly composed of montmorillonite with chemical composition of SiO_2, Al_2O_3, CaO, MgO, Fe_2O_3, Na_2O and K_2O. It is a 2:1 aluminosilicate, the unit layer structure of which consists of one Al^{3+} octahedral sheet between two Si^{4+} tetrahedral sheets [19].

Oxidation of organic compounds through ultrasonic irradiation of liquids is due to acoustic cavitation. In the presence of dissolved gases and tiny particles with dissolved gases in their crevices, ultrasound wave consisting of cycles of compression and expansion produce cavitation bubbles. Cavitation bubbles are produced when applied sound pressure overcomes surface tensile forces. Once a cavitation bubble is formed in a liquid, it absorbs the ultrasound energy until the bubble grows to a critical size where it collapses violently during sound compression cycles. These collapsing bubbles can have temperatures and pressures as high as 5000 K and 1000 atm, respectively. Under such extreme conditions during bubble collapse, organic compounds are oxidized by direct pyrolysis and hydroxyl free radical oxidation (°OH) reactions. With direct pyrolysis an organic compound absorbed in a cavitation bubble is converted to by-products due to the extremely high temperature and pressure inside the bubble. Under these extreme conditions free radicals are also formed when water molecules are split:

$$H_2O \rightarrow H^\circ + {}^\circ OH \quad (1)$$

$$H^\circ + O_2 \rightarrow HO_2{}^\circ \quad (2)$$

$$HO_2{}^\circ + HO_2{}^\circ \rightarrow H_2O_2 + O_2 \quad (3)$$

$$H^\circ + HO_2{}^\circ \rightarrow H_2O_2 \quad (4)$$

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$$^{\circ}OH + {^{\circ}OH} \rightarrow H_2O_2 \quad (5)$$

$$^{\circ}OH + {^{\circ}HO_2} \rightarrow H_2O + O_2 \quad (6)$$

$$^{\circ}OH + H_2O_2 \rightarrow HO_2{^{\circ}} + H_2O \quad (7)$$

These radicals can react with organic compounds to form products. The main oxidation pathway is direct pyrolysis, but in the presence of oxidants such as $HO_2{^{\circ}}$ and H_2O_2, radicals produced in implosive bubbles can also be an important reaction pathway [20–22].

In the present study, vanadium substituted heteropolymolybdate supported into bentonite (PVMo/Bentonite nanocomposite) was synthesized. To the best of our knowledge, this is the first report about synthesis of heteropolymolybdate with layered structure such as bentonite. The PVMo/Bentonite exhibited an excellent catalytic activity for epoxidation of alkenes. Also, the catalytic activity of the PVMo/Bentonite nanocomposite for epoxidation of alkenes was improved as compared with the unsupported heteropolymolybdate (PVMo).

2. Experimental

2.1. Chemicals

All chemicals were of analytical grade and used without further purification. The $Na_5[PV_2Mo_{10}O_{40}]\cdot 14H_2O$ (PVMo) was prepared as described in the literature [23]. Also, The PVMo/Bentonite with 20% loading of PVMo was prepared. The UV–vis spectrum of solution before and after impregnation showed that more than 99% of PVMo was supported on the bentonite.

2.2. Preparation of the PVMo/Bentonite nanocomposite

The typical preparation method of PVMo/Bentonite is as follows: PVMo (1.0 g) and bentonite (4.0 g) were mixed and put into an agate mortar. The mixture was thoroughly ground for 20 min, washed in a supersonic washing machine using absolute alcohol as dispersant and centrifuged. The washing and centrifuging processes were repeated five times. The wet PVMo/Bentonite were obtained and dried at 60 °C.

2.3. Catalyst characterization

Elemental analysis was performed on a Perkin–Elmer 2400 instrument. Atomic absorption analyses were carried out on a Shimadzu 120 spectrophotometer. Compositional and elemental investigations were performed by backscattered electrons and EDX analysis, respectively. UV–vis diffuse reflectance spectra were recorded on a Shimadzu UV-265 instrument using optical grade $BaSO_4$ as reference. FT-IR spectra were obtained as potassium bromide pellets in the range 400–4000 cm^{-1} with Nicollet-Impact 400D instrument. Scanning electron micrographs of the heterogeneous catalyst and support were taken on SEM Philips XL 30. Powder X-ray diffraction data were obtained on a D_8 Advanced Bruker using Cu K_{α} radiation ($2\theta = 5–70^{\circ}$). Gas chromatography experiments (GC) were performed on a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20 m. In all experiments the n-decane was used as the internal standard. ^1H NMR spectra were recorded on a Bruker–Arance AQS 300 MHz using $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal reference. Conversions and yields were obtained by GC experiments and the products were identified after isolation and purification.

2.4. General oxidation procedure catalyzed by PVMo/Bentonite nanocomposite under reflux

The catalytic reaction was performed in a 25 mL round-bottomed flask equipped with a magnetic stirring bar and a reflux condenser. In a typical experiment, hydrogen peroxide (30%) (1 mL), acetonitrile (5 mL), alkene substrate (0.8 mmole) and catalyst (2.86 μmol of PVMo) were added in the flask. The reaction was performed at 78 °C and was monitored by GC analysis. After 10 h, conversion of the substrate was measured by GC with the internal standard method. At the end of reaction, the mixture was diluted with Et_2O (20 mL) and filtered. The catalyst was thoroughly washed with Et_2O and combined washings and filtrates were purified on a silica gel plate or silica gel column. The catalyst alone did not show any activity in the reactions studied.

2.5. General oxidation procedure catalyzed by PVMo/Bentonite nanocomposite under ultrasonic irradiation

A UP 400S ultrasonic processor equipped with a 3 mm wide and 140 mm long probe, which was immersed directly into the reaction mixture was used for sonication. The operating frequency was 24 kHz and the output power was 0–400 W through manual adjustment. The final volume of solution was 6 ml and the temperature of the solution reached 60 °C during sonication.

To a mixture of alkene (0.8 mol) and the catalyst (containing 2.86 μmol of PVMo) in acetonitrile (5 mL) was added H_2O_2 (1 mL, 30%) and the mixture was exposed to ultrasonic irradiation. The reaction was monitored by GC. After the reaction was completed, the reaction mixture was diluted with Et_2O (20 mL) and filtered. The catalyst was thoroughly washed with Et_2O and the combined washings and filtrates were purified on a silica gel plates or silica gel column.

3. Results and discussion

3.1. Characterization of the PVMo/Bentonite nanocomposite

The size of the PVMo nanoparticles were calculated from the data of broadened XRD peaks by the Scherrer equation: $D = 0.89\lambda/\beta \cos\theta$. The bentonite has pores, whose diameters range from 10 to 50 nm and the heteropolyanions of the Keggin type structure have molecular diameter of ~1–2 nm. Therefore, it is feasible to insert polyoxometalates such as $Na_5[PV_2Mo_{10}O_{40}]$ between the silicate layers of bentonite [24,25]. Also, the presence of the heteropolymolybdate (PVMo) was confirmed by X-ray diffraction. As shows in Fig. 1, the insertion of heteropolymolybdate nanoparticles into the silicate layers of bentonite would make the later expand, which results in the shift of the according diffraction peak to smaller angle in the XRD patterns (Bragg's equation), but due to the strong interactions between PVMo and the bentonite surface, the XRD patterns showed little angle shift, which the heteropolymolybdate (PVMo) exhibited typical peaks at 2θ: 8.89°, 9.26°, 10.15°, 27.16° and 29.44° [15], while the as-prepared PVMo/Bentonite composite showed peaks at 2θ: 8.78°, 26.72° and 28.88° that showed the PVMo was introduced in the substitutional position of bentonite.

FT-IR spectrum of the PVMo/Bentonite catalyst in the range 700–1100 cm^{-1} showed absorption bands at 1052, 952, 873 and 787 cm^{-1}, corresponding to the four typical skeletal vibrations of the Keggin polyoxometalate (PVMo), which indicated that PVMo has been supported into layeres of bentonite (Fig. 2). These peaks could be attributed to $\nu(P{=}O_a)$, $\nu(Mo{=}O_t)$, $\nu(Mo–O_b–Mo)$ and $\nu(Mo–O_c–Mo)$, respectively (O_t = terminal oxygen, O_b = bridged oxygen of two octahedral sharing a corner and O_c = bridged oxygen sharing an edge) [25]. The FT-IR spectra indicated that the

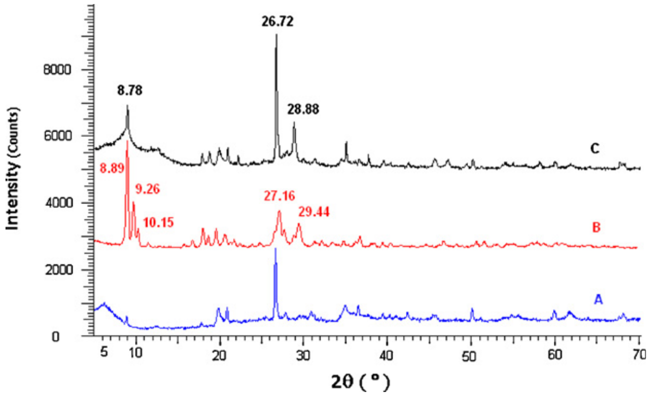


Fig. 1. XRD patterns of: (A) Bentonite, (B) PVMo and (C) PVMo/Bentonite nanocomposite.

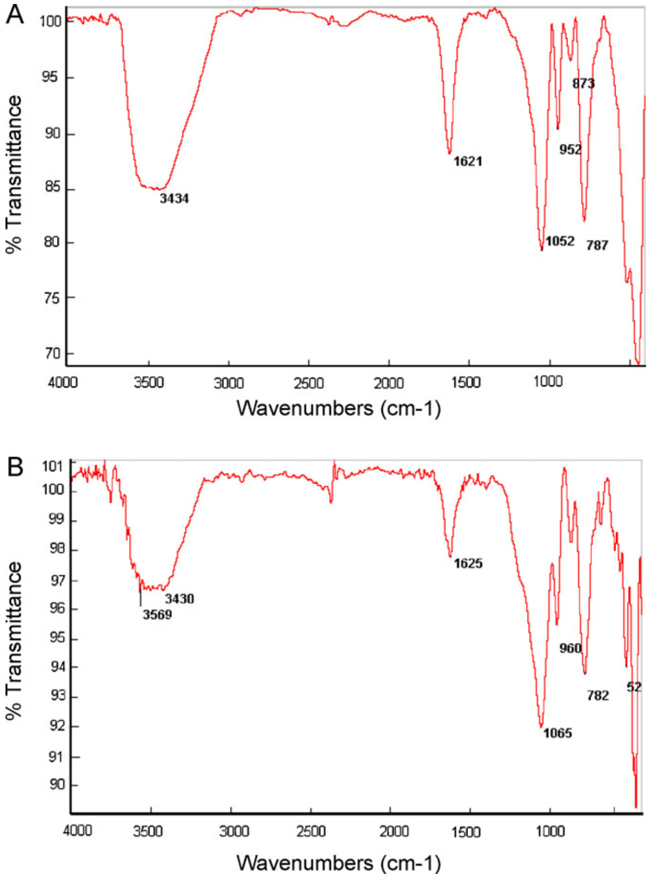


Fig. 2. FT-IR spectrum of: (A) PVMo/Bentonite composite and (B) recovered PVMo/Bentonite nanocomposite.

structure of the polyoxometalate (PVMo) remains unchanged upon impregnation method.

The UV–vis spectra of PVMo in CH_3CN displayed absorption bands at 246 and 308 nm, which are due to the Mo–O and V–O charge-transfer absorptions in the heteropolycompound cage [26,27]. These two absorption bands appeared in the diffuse reflectance UV–vis spectrum of the heterogeneous catalyst and since pure bentonite shows no UV absorption, then these results indicated that PVMo was introduced into the layered framework of bentonite (Fig. 3).

According to the SEM images, the particles are approximately spherical and the average diameter of particles is estimated to be about 50 nm (Fig. 4). A clear change in the morphology of the PVMo/Bentonite nanocomposite indicated that the PVMo has been supported into the layers of bentonite. TEM analysis was also performed to determine the location and the particle size of the PVMo/Bentonite which can be distinguished as dark dots in TEM (Fig. 5). Also, the particle size obtained by this method was less than 80 nm.

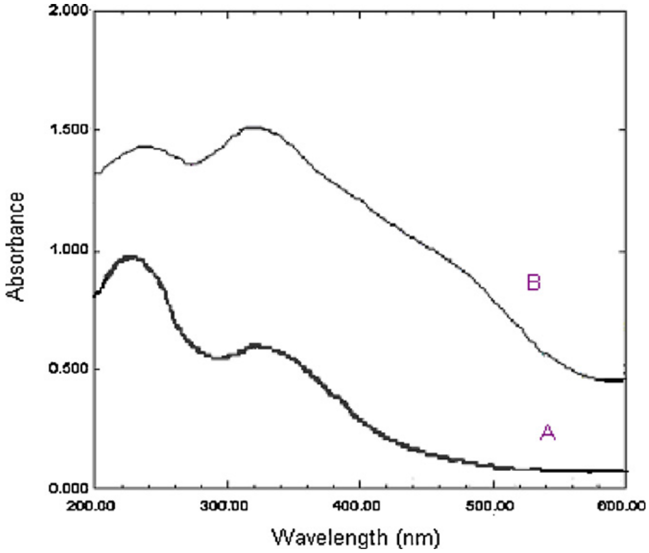


Fig. 3. UV–vis (DRS) spectrum of: (A) PVMo and (B) PVMo/Bentonite nanocomposite.

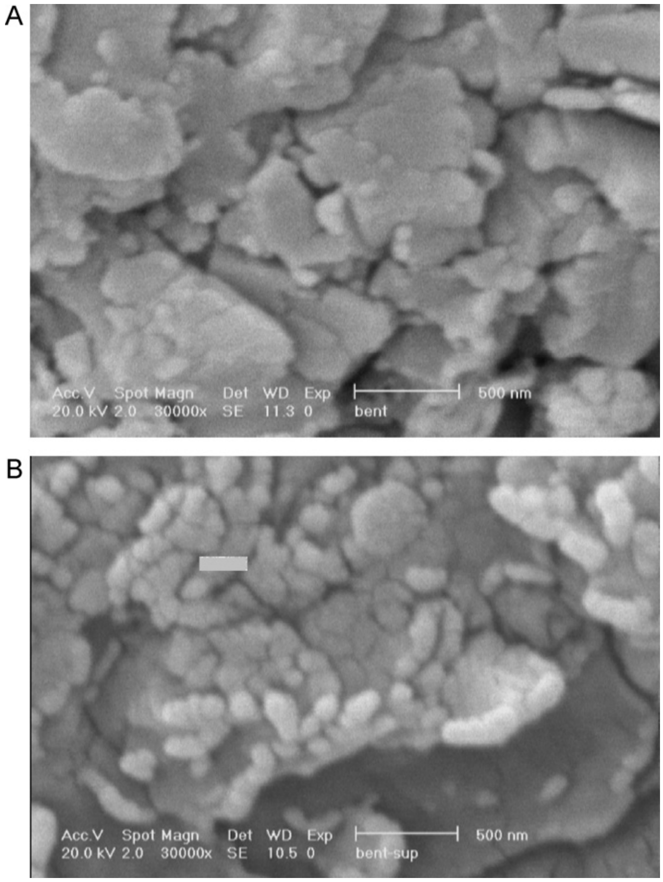


Fig. 4. SEM images of: (A) Bentonite and (B) PVMo/Bentonite nanocomposite.

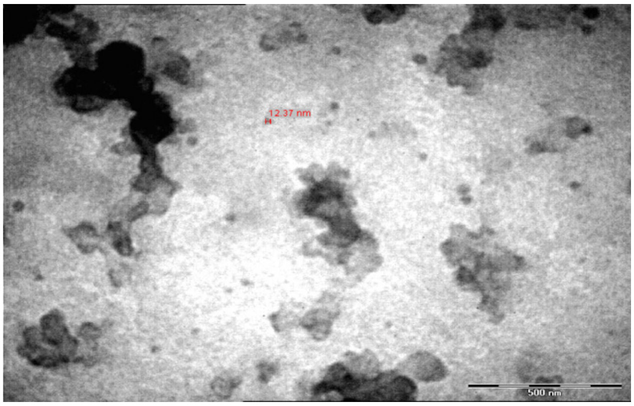


Fig. 5. TEM images of: PVMo/Bentonite nanocomposite.

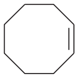
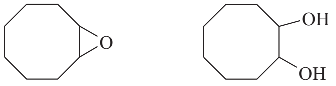
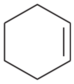
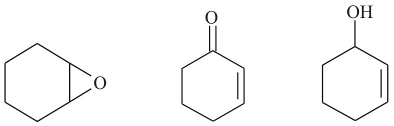
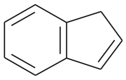
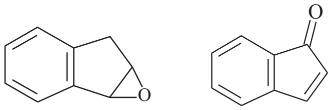
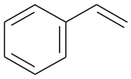
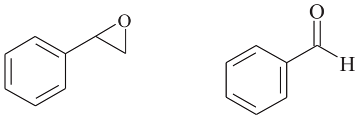
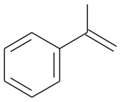
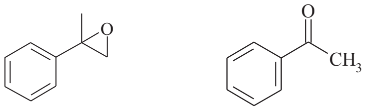
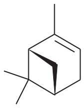
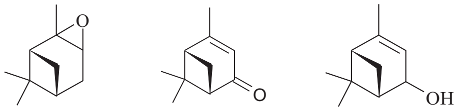
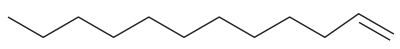
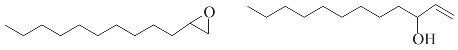
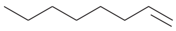
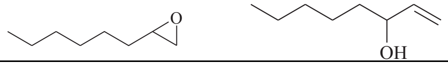
3.1.1. Catalytic performance of the PVMo/Bentonite nanocomposite

At first, the ability of the prepared PVMo/Bentonite was investigated in the epoxidation of cyclooctene as a model reaction with H_2O_2 as oxidant in acetonitrile. The reactions were continued until no further progress was observed. The results showed that the conversion was 60% with 64% epoxide selectivity. In order to clarify the catalytic active sites for epoxidation of alkenes, blank reactions are carried out with bentonite support under identical conditions. Also, a blank experiment in the absence of the catalyst showed only small amounts of products in the epoxidation of cyclooctene with H_2O_2. Epoxidation of cyclohexene with 80% conversion produced cyclohexene oxide as major product (with 78% epoxide selectivity), and allylic oxidation products (cyclohexene-1-one and cyclohexene-1-ol) were obtained as minor products. In the case of indene, styrene and α-methyl styrene, the corresponding epoxides were obtained in 60%, 58% and 72% epoxide selectivity (In the oxidation of α-pinene the major product was α-pinene oxide, while verbenone and verbenol were also produced as minor products). Oxidation of linear alkenes such as 1-octene and 1-dodecene was accompanied by allylic oxidation (Table 1). As shown in Table 2, the behavior of the catalyst with other oxidants reduced epoxide selectivity.

3.1.2. Epoxidation of alkenes catalyzed by PVMo/Bentonite nanocomposite under ultrasonic irradiation

Due to the effect of ultrasonic irradiation on the product yield and selectivity, we decided to investigate the effect of ultrasonic waves on the epoxidation of alkenes with H_2O_2 catalyzed by PVMo/bentonite. As shown in Table 3, application of ultrasonic waves in this catalytic system reduced the reaction times and improved the

Table 1
Epoxidation of alkenes with H_2O_2 catalyzed by PVMo/Bentonite nanocomposite under reflux conditions.[a]

Entry	Substrate	Products	Time (h)	Conversion (%)[b,c]	Epoxide selectivity (%)[b]	TOF (h^{-1})
1			10	60	64	16.8
2			10	80	78	22.4
3			10	64	60	17.9
4			10	60	58[d]	16.8
5			10	65	72[e]	18.2
6			10	35	32[f]	9.8
7			10	15	24[g]	4.2
8			10	30	28[h]	8.4

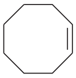
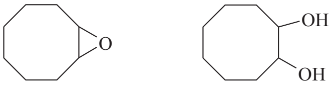
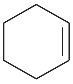
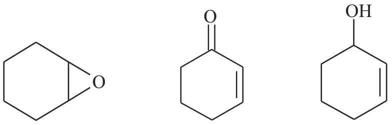
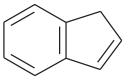
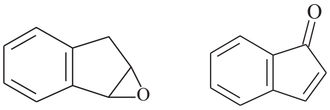
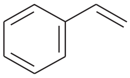
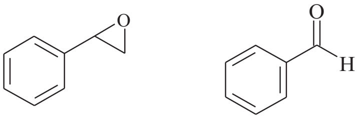
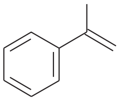
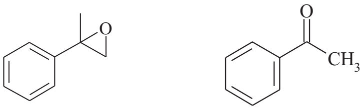
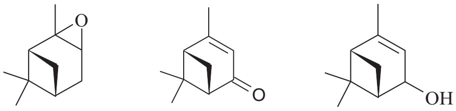
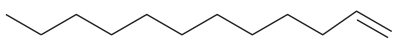
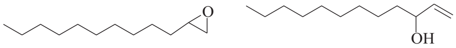
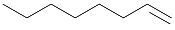
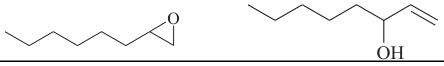
[a] Reaction conditions: alkene (0.8 mmol), catalyst (2.86 μmol), H_2O_2 (1 mL), CH_3CN (5 mL).
[b] Based on the starting alkene.
[c] GC yield.
[d] 25% benzaldehyde was produced.
[e] 18% acetophenone was detected as by product.
[f] 15% verbenone and 9% verbenol were produced.
[g] 11% alcohol was produced.
[h] 21% alcohol was detected.

Table 2
Epoxidation of cyclooctene with oxygen donors catalyzed by PVMo/Bentonite[a] nanocomposite under reflux conditions.

Entry	Oxygen donor	Solvent	Epoxide selectivity (%)[b] after (10 h)		
			PVMo	PVMo/Bentonite (MS)	PVMo/Bentonite (US)
1	$NaIO_4$	CH_3CN/H_2O	61	33	60
2	Oxone ($KHSO_5$)	CH_3CN/H_2O	54	31	56
3	H_2O_2	CH_3CN	90	64	92
4	NaOCl	CH_3CN	32	27	39
5	Tert-BuOOH	CH_3CN	39	32	41
6	Bu_4NIO_4	CH_3CN	41	36	45
7	O_2	CH_3CN	28	25	32

[a] Reaction conditions: cyclooctene (0.8 mmol), catalyst (2.86 μmol), H_2O_2 (1 mL), CH_3CN (5 mL).
[b] GC yield based on the starting cyclooctene.

Table 3
Epoxidation of alkenes with H_2O_2 catalyzed by PVMo/Bentonite nanocomposite under ultrasonic irradiation.[a]

Entry	Substrate	Products	Time (min)	Conversion (%)[b,c]	Epoxide selectivity (%)[b]	TOF (h^{-1})
1			40	85	92	360
2			40	100	98	424
3			40	82	79	347
4			40	85	82[d]	360
5			40	87	84[e]	369
6			40	68	65[f]	288
7			40	18	26[g]	76
8			40	75	28[h]	318

[a] Reaction conditions: alkene (0.8 mmol), catalyst (2.86 μmol), H_2O_2 (1 mL), CH_3CN (5 mL).
[b] Based on the starting alkene.
[c] GC yield.
[d] 15% benzaldehyde was produced.
[e] 14% acetophenone was detected as by product.
[f] 16% verbenone and 8% verbenol were produced.
[g] 13% alcohol was produced.
[h] 54% alcohol was detected.

product yield and selectivity. The system under ultrasonic irradiation showed a good catalytic activity in the epoxidation of linear alkenes such as 1-octene and 1-dodecene (Table 4).

It is reported that peroxo radicals were generated at the PVMo sites (Scheme 1). Subsequent epoxidation of the alkenes can occur both within the pores and in the bulk liquid solution [15–17,28–31].

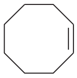
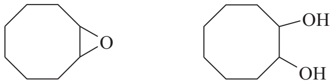
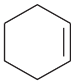
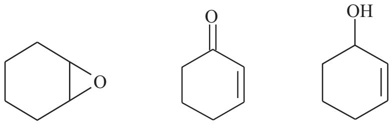
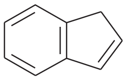
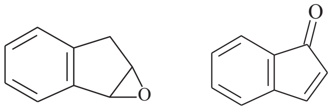
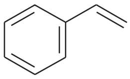
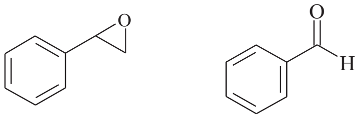
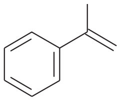
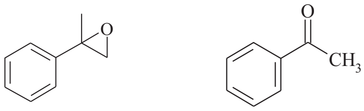
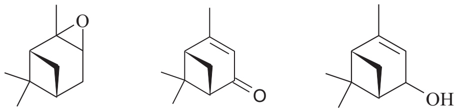
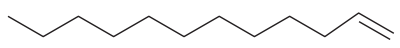
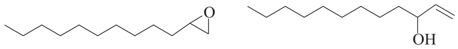
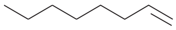
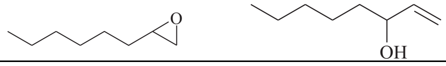
The results indicated that the increase of ultrasound power improved the extent of epoxidation of cyclooctene and the highest conversion was observed at a power of 400 W (Fig. 6).

Fig. 7 shows systems under ultrasonic irradiation and under agitation with magnetic stirring, which indicate that the catalytic activity of PVMo/Bentonite nanocomposite has been enhanced by ultrasonic irradiation.

The blank experiments in the absence of the catalyst showed that ultrasonic irradiation has a poor ability to epoxidize the alkenes with hydrogen peroxide.

In order to show the effect of supporting on the catalytic activity, all reactions were repeated in the presence of PVMo as catalyst under the same reaction conditions. It is clear from Tables 1 and 3 that the catalytic activity of the PVMo/Bentonite nanocomposite was much higher than that of unsupported heteropolyanion (PVMo). The TOFs are higher for PVMo/Bentonite nanocomposite in comparison with the parent PVMo. By disper-

Table 4
Epoxidation of alkenes with H_2O_2 (30%) catalyzed by PVMo under reflux conditions.[a]

Entry	Substrate	Products	Time (h)	Conversion (%)[b,c]	Epoxide selectivity (%)[b]	TOF (h^{-1})
1			20	65	90	9.1
2			20	67	85	9.4
3			20	35	49	4.9
4			20	43	29	6.0
5			20	27	42	3.8
6			20	20	52	2.8
7			20	26	58	3.7
8			20	30	31	4.2

[a] Reaction conditions: alkene (0.8 mmol), catalyst (2.86 μmol), H_2O_2 (1 mL), CH_3CN (5 mL).
[b] Based on the starting alkene.
[c] GC yield.

sion of the vanadium-substituted heteropolymolybdate on bentonite, the available vanadium active sites were isolated which in turns increased the catalytic activity. On the other hand, the ability of bentonite alone as support of catalyst was checked in the epoxidation of cyclooctene with H_2O_2. The obtained results showed that bentonite has a poor ability to catalyze the epoxidation of cyclooctene and the amount of epoxide was less than 4%.

3.1.3. The stability and reusability of PVMo/Bentonite nanocomposite

The reusability of the supported catalyst was investigated in the epoxidation of cyclooctene with hydrogen peroxide under reflux and ultrasonic irradiation. At the end of each consecutive run, the heterogeneous catalyst was filtered, washed thoroughly with acetonitrile and 1,2-dichloroethane successively, and dried before being used with fresh cyclooctene and hydrogen peroxide. In both cases, the catalysts were consecutively reused four times. The amount of leaching of catalyst after each run was determined by ICP analysis. In this manner the filtrates were collected after each run and used for determining of the amounts of vanadium leached (Table 5). Addition of fresh alkene and oxidant to the filtrates showed that the amount of epoxide is comparable to the blank experiments. These results are in accordance with the leaching data. The nature of the recovered catalyst was followed by FT-IR. After reusing the catalyst for several times, no change in the FT-IR spectrum was observed (Fig. 2).

$$V^{V} + H_2O_2 \longrightarrow V^{V}\text{----}H_2O_2$$

$$V^{V}\text{----}H_2O_2 \longrightarrow V^{IV} + HOO^{\bullet} + H^{+}$$

Scheme 1.

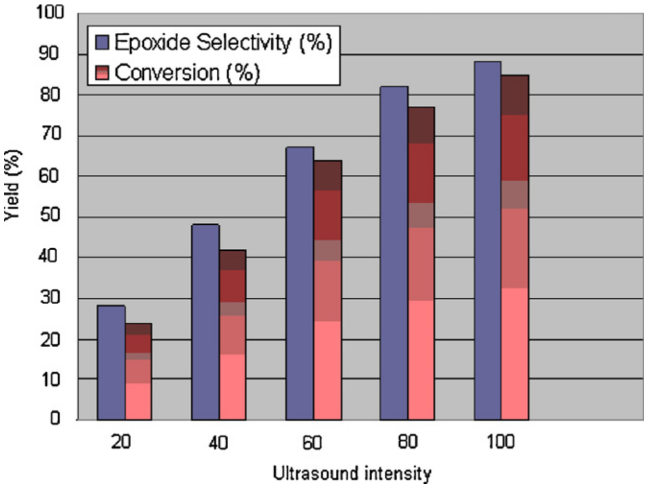


Fig. 6. The effect of ultrasonic irradiation intensity on the epoxidation of cyclooctene with H_2O_2 catalyzed by PVMo/Bentonite.

Table 5
The results obtained from the reusability and stability of catalyst under magnetic stirring (MS) and ultrasonic irradiation (US).[a]

Run	Time		Conversion (%)[b]		Epoxide selectivity (%)		Vanadium leaching (%)[c]	
	MS (h)	US (min)	MS	US	MS	US	MS	US
1	10	40	60	85	64	92	1.0	1.0
2	10	40	59	84	63	91	0.8	0.7
3	10	40	58	84	62	90	0.4	0.5
4	10	40	58	83	62	89	0.3	0.4

[a] Reaction conditions: cyclooctene (0.8 mmol), catalyst (2.86 μmol), H_2O_2 (1 mL), CH_3CN (10 mL).
[b] GC yield based on the starting cyclooctene.
[c] Determined by ICP.

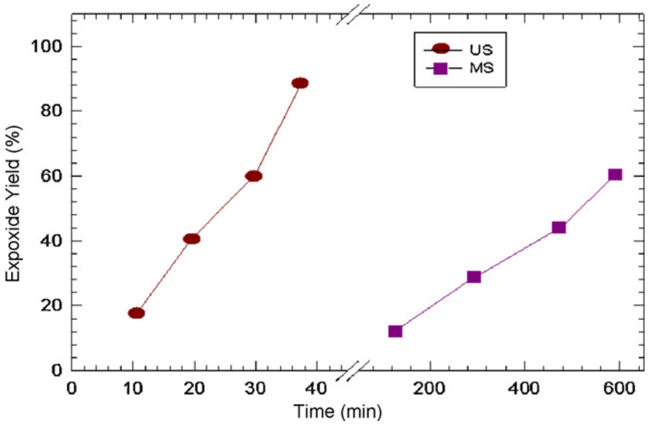


Fig. 7. Comparison of ultrasonic irradiation and magnetic agitation in the oxidation of cyclooctene with H_2O_2 catalyzed by PVMo/Bentonite.

4. Conclusions

We successfully synthesized the PVMo/Bentonite nanocomposite by simple impregnation method. The as-prepared nanocomposite showed higher catalytic activity for epoxidation of alkenes than parent heteropolymolybdate (PVMo). The use of ultrasonic irradiation increased the conversion and reduced the reaction times. The results showed that good catalytic activity of the heteropolymolybdate, especially under ultrasonic irradiation make them useful catalysts for further applications in the area of catalysis. Moreover, the H_2O_2 is a green and eco-friendly oxidant in these systems.

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