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Sonocatalytic epoxidation of alkenes by vanadium-containing polyphosphomolybdate immobilized on multi-wall carbon nanotubes

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ABSTRACT

A Keggin type polyoxometalate (POM) has been immobilized in the unique network structure of multi-wall carbon nanotubes (CNTs). The vanadium-containing polyphosphomolybdate (PVMo) supported on CNTs, which was prepared by a one-step solid-state reaction, was characterized by FT-IR, XRD, SEM and elemental analyses. These uniform nanoparticles have an average size 20–30 nm. Furthermore, due to the chemical interaction between PVMo and carboxylic acid groups, PVMo nanoparticles were successfully immobilized on the CNTs. Moreover, the obtained composite was found as an efficient catalyst for oxidation of hydrocarbons under reflux and ultrasonic irradiation (US) conditions.

1. Introduction

Nanosystems, with characteristic lengths (1–100 nm), have become one of the most attractive subjects in materials science, chemistry, physics and biology. Therefore, the exploration of new nanostructure materials for various applications is still the first and one of the most significant challenges in nano science [2]. In the last decade, carbon nanotubes (CNTs) have attracted wide interest because of their unique physical properties and many potential applications such as one dimension quantum wires, optical switches, nano-transistors and other essential electronic components [1].

Polyoxometalates (POM) can also be practically used as solid catalysts if they could be physically immobilized on solid supports. Recently, Müller et al. have reported the synthesis of many POMs with nanometer size, including novel kinks, of large rings and wheel-shaped systems with 176 or even more Mo atoms [3]. In another work, the growing process of $[(NH_4)_3PW_{12}O_{40}]$ nanoparticles has been reported [4]. Due to the unique properties of POMs, the preparation of POMs nanocrystals and nano/micro-systems is of great interest [5]. Kang and co-workers reported the immobilization of POMs on carbon nanotube by direct synthesis of these molecules in the CNTs [6].

In this work, the chemical modification of CNTs by PVMo nanoparticles is reported. Based on the novel properties of both PVMo and CNTs, such structures may find a wide field of applications [6]. Recently, various efficient catalytic systems have been reported for epoxidation of alkenes with H_2O_2 using homogeneous or heterogeneous polyoxometalates as catalyst [7–12]. However, an important disadvantage associated with heterogeneous catalytic systems is their lower catalytic activity in comparison with homogeneous counterparts. In most cases the use of ultrasonic (US) wave (sonocatalysis) is recommended for solving this problem.

In general US has chemical and mechanical effects. The chemical effects of ultrasound do not derive from a direct coupling of the acoustic field with chemical species on a molecular level. Instead, sonochemistry and sonoluminescence derive principally from acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquids irradiated with high-intensity ultrasound. Bubble collapse during cavitation serves as an effective means of concentrating the diffuse energy of sound: compression of a gas generates heat. When the compression of bubbles occurs during cavitation, heating is more rapid than thermal transport, creating a short lived localized hot spot. There is a nearly universal consensus that this hot spot is the source of homogeneous sonochemistry [13,14].

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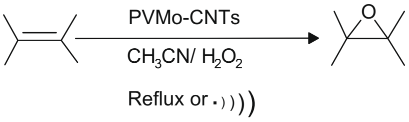
The most successful applications of ultrasound have been found in the field of heterogeneous chemistry involving solids and metals. This is due to the mechanical impact of ultrasound on solid surfaces. In conventional chemistry there are several problems associated with reactions involving solids or metals: small surface area of the solid/metal may limit reactivity, penetration of reactants into deeper areas is not possible, oxide layers or impurities can cover the surface, reactants/products have to diffuse onto and from the surface and reaction products can act as deposit on the surface and prevent further reactions.

The mechanical effects of ultrasound offer an opportunity to overcome the following types of problem associated with conventional solid/metal reactions: break up of the surface structure allows penetration of reactants and/or release of materials from surface, degradation of large solid particles due to shear forces induced by shock waves and microstreaming leads to reduction of particle size and increase of surface area and accelerated motion of suspended particles leads to better mass transfer [15].

Recently, we reported the sonocatalytic oxidation of organic compounds catalyzed by vanadium-containing polyphosphomolybdate supported on MCM-41 and TiO_2 nanoparticles [7,8]. In this paper, we wish to report the sonocatalytic oxidation of alkenes with H_2O_2 catalyzed by $Na_5PV_2Mo_{10}O_{40}$ (PVMo) supported on multi-wall carbon nanotubes (CNTs). The effect of US irradiation on the catalytic activity of this catalyst was also investigated (Scheme 1).

2. Experimental

All chemicals were of analytical grade and were used without further purification. Elemental analysis was performed on a Perkin–Elmer 2400 instrument. Atomic absorption analysis was carried out on a Shimadzu 120 spectrophotometer. 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 Nicolet-Impact 400D instrument. Scanning electron micrographs of the 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 Kα radiation ($2\theta = 5–70°$). 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. ^1H NMR spectra were recorded on a Bruker-Arance AQS 300 MHz. Conversions and yields were obtained by GC experiments and the products were identified after isolation and purification.



Scheme 1.

The $Na_5[PV_2Mo_{10}O_{40}]\cdot 14H_2O$ salt was prepared as described in the literature [16].

2.1. Preparation and characterization of PVMo–CNTs composite

The unmodified carbon nanotubes (multi-wall carbon nanotubes with diameters between 20 and 30 nm) were purchased from Shenzen NTP Factory and modified. Multi-wall carbon nanotubes containing carboxylic acid groups were the predominant groups expected to be acquired [17]. Subsequently, the CNTs were dispersed in *N,N*-dimethylformamine (DMF), yielding a black–brown suspension.

The typical preparation of PVMo/CNTs nanoparticles is as follows: PVMo (0.1 g) and CNTs (0.4 g) were put into an agate mortar and the surfactant Triton-X-100 (0.5 ml) was added drop-wise to the mixture. The mixture was thoroughly ground for 20 min, washed in a supersonic washing machine using absolute alcohol as dispersant, and centrifuged. The washing and centrifugalizing processes were repeated five times. The wet nanoparticles of PVMo–CNTs obtained and were dried in vacuum drying oven for 5 h (60–80 °C).

2.2. General procedure for oxidation reactions with H_2O_2 under reflux conditions

Reactions were carried out in a 50 ml thermostated glass reactor equipped with a magnetic stirrer. In a typical experiment, the reaction vessel was loaded with the supported catalysts (30 mg, containing 2.86 μmol of PVMo), alkene or alkane (0.8 mmol) in acetonitrile (5 ml). H_2O_2 (1 ml, 30%) was added and the mixture was refluxed. The progress of the reaction was monitored by GC. At the end of the reaction, the mixture was diluted with Et_2O

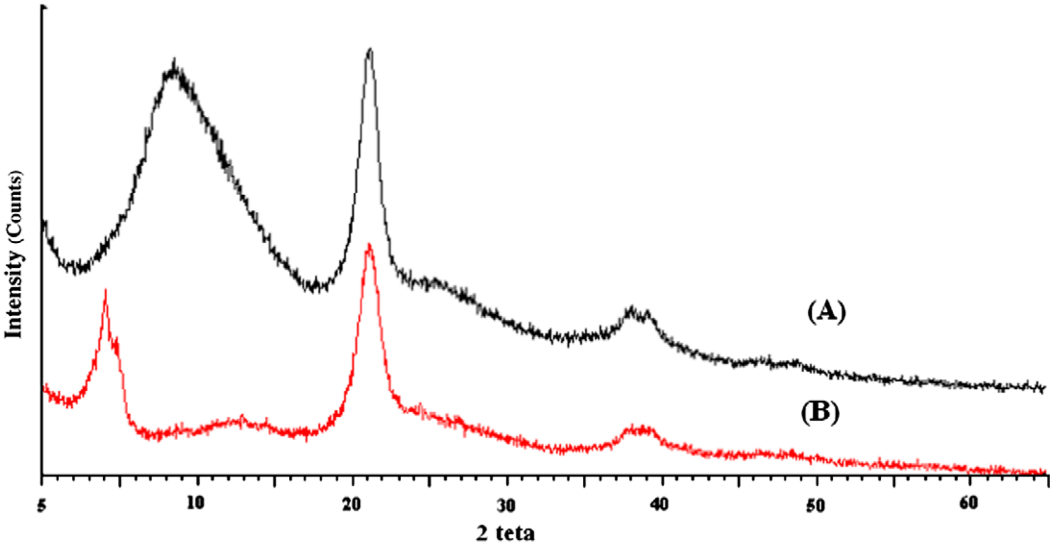


Fig. 1. XRD patterns of (A) CNTs and (B) PVMo–CNTs composite.

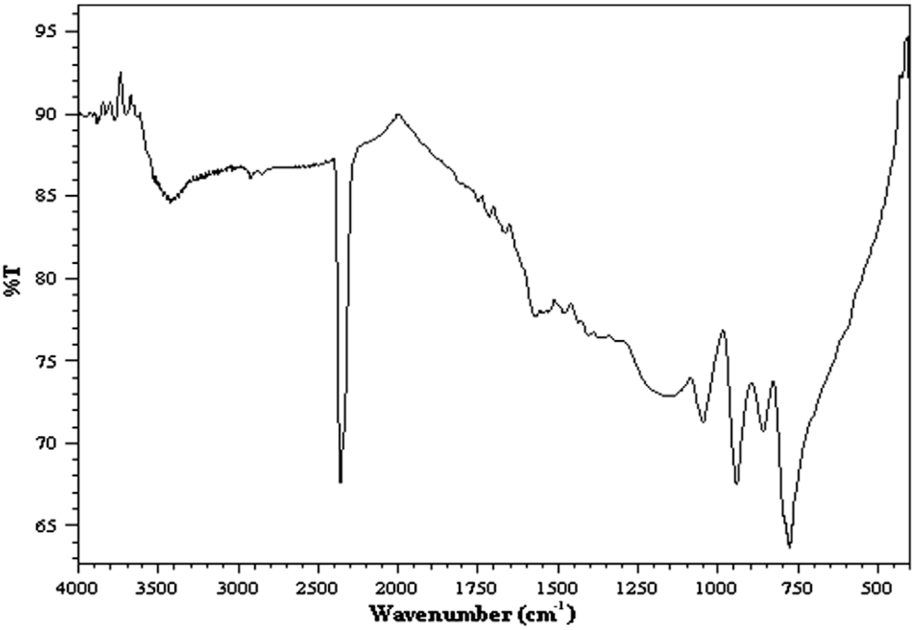


Fig. 2. FT-IR spectrum of PVMo–CNTs composite.

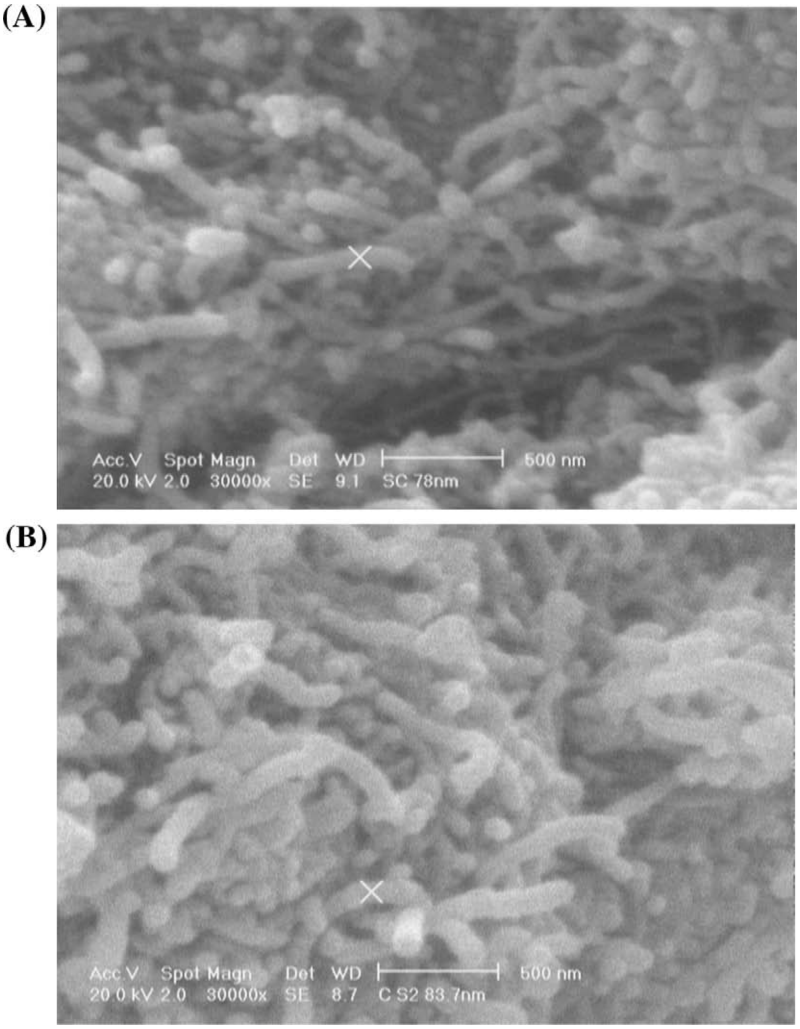


Fig. 3. SEM images of (A) CNTs and (B) PVMo–CNTs composite.

(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 a silica gel column. IR and ^{1}HNMR spectral data confirmed the identities of the products.

2.3. General procedure for oxidation reactions with H_2O_2 under US 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. The temperature of the solution reached to 60 °C during sonication.

To a mixture of alkene or alkane (0.8 mmol) and the supported catalysts (30 mg, containing 2.86 μmol of PVMo) in acetonitrile (5 ml) was added hydrogen peroxide (1 ml, 30%) and the mixture was exposed to US 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 combined washings and filtrates were purified on a silica gel plates or a silica gel column. IR and ^{1}HNMR spectral data confirmed the identities of the products.

3. Results and discussion

3.1. Preparation and characterization of PVMo–CNTs composite

Since heteropolyanions of the Keggin structure have molecular diameters of ~12 Å, it is feasible to support polyoxometalates such as PVMo on CNTs. Fig. 1 shows the XRD patterns of CNTs and PVMo–CNTs. However, PVMo–CNTs pattern indicated that PVMo was introduced in the substitutional position of CNTs.

The FT-IR spectrum of the prepared catalyst in the range 700–1100 cm^{-1} showed absorption bands at 1045, 943, 858 and 783 cm^{-1}, corresponding to the four typical skeletal vibrations of the Keggin polyoxoanions, which indicated that PVMo has been supported on CNTs (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) [18]. IR spectra show a peak at about 1578 cm^{-1}, corresponding to the IR active phonon mode of CNTs [19]. The IR spectra indicated that the structure of the polyoxometalate retain upon impregnation. It is reported that supporting of PVMo nanoparticles on CNTs is due to the chemical adsorption between carboxylic acid groups on CNTs and PVMo nanoparticles, in which PVMo nanoparticles tend to be preferably attached to the ends, the curves, and the connection points of CNTs [6].

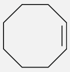
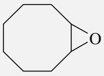
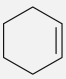
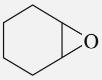
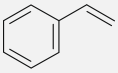
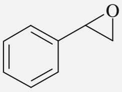
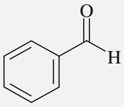
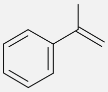
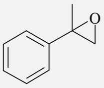
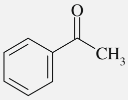
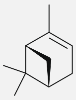
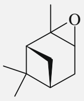
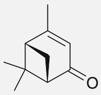
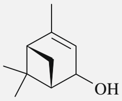
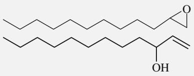
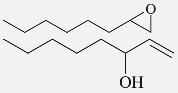
Fig. 3 shows SEM images of nanoparticles. The morphologies and microstructure of the nanoparticles are approximately spherical. Some nanoparticles are importantly aggregated. Assuming that a nanoparticle is spherical, the average diameter of nanoparticles is estimated to be about 20–30 nm by averaging its diameters measured in several directions in the SEM images. A clear change in the morphology of catalysts indicated that the PVMo has been supported on the CNTs.

3.2. Catalytic activity

Since heterogeneous catalysts are recoverable, hence, heterogenization of homogenous catalysts is of great interest. Therefore, we

Table 1

Epoxidation olefins with H_2O_2 catalyzed by PVMo–CNTs under reflux conditions.[a]

Entry	Substrate	Products	Time (h)	Conversion (%)[b,c]	Epoxide selectivity (%)	TOF (h^{-1})
1			10	80	100	22.4
2			10	72	96	20.2
3		 	10	47	58[d]	13.2
4		 	10	57	70[e]	15.9
5		  	10	70	62[f]	19.6
6	1-Dodecene		10	31	73[g]	8.7
7	1-Octene		10	44	67[h]	12.3

[a] Reaction conditions: olefin (0.8 mmol), catalyst (2.86 μmol), H_2O_2 (1 ml), CH_3CN (5 ml).

[b] Based on the starting olefin.

[c] GC yield.

[d] 20% benzaldehyde was produced.

[e] 17% acetophenone was detected as by product.

[f] 17% verbenone and 10% verbenol were produced.

[g] 8% alcohol was produced.

[h] 14.5% alcohol was detected.

decided to immobilize PVMo on CNTs nanoparticles, and investigate its catalytic activity in the epoxidation of alkenes with H_2O_2 under agitation with magnetic stirring and under US irradiation.

3.2.1. Alkene epoxidation with H_2O_2 catalyzed by PVMo–CNTs under reflux conditions

First, the ability of the prepared catalyst, PVMo–CNTs, was investigated in the epoxidation of cyclooctene with H_2O_2 in acetonitrile. The reactions were continued until no further progress was observed. The results (Table 1) showed that the conversion was 80% with 100% epoxide selectivity. Epoxidation of cyclohexene with 72% conversion and 96% epoxide selectivity, and only small amounts of allylic oxidation products (cyclohexene-1-one and cyclohexene-1-ol) were detected in the reaction mixture. In the case of styrene and α-methyl styrene, the corresponding epoxides were obtained in 47% and 57% epoxide selectivity. In the oxidation of α-pinene, the major product was α-pineneoxide, while verbenone and verbenol were produced as minor products. Oxidation of linear alkenes such as 1-octene and 1-dodecene was accompanied by allylic oxidation. A blank experiment in the absence of the catalyst showed only small amounts of products in the oxidation of cyclooctene with H_2O_2.

3.2.2. Alkene epoxidation with H_2O_2 catalyzed by PVMo–CNTs under US irradiation

As mentioned in the previous works, US irradiation can be used as an efficient tool to influence the product yield and selectivity [7,8]. Therefore, we decided to investigate the effect of US waves on the epoxidation of different alkenes with H_2O_2 catalyzed by PVMo–CNTs.

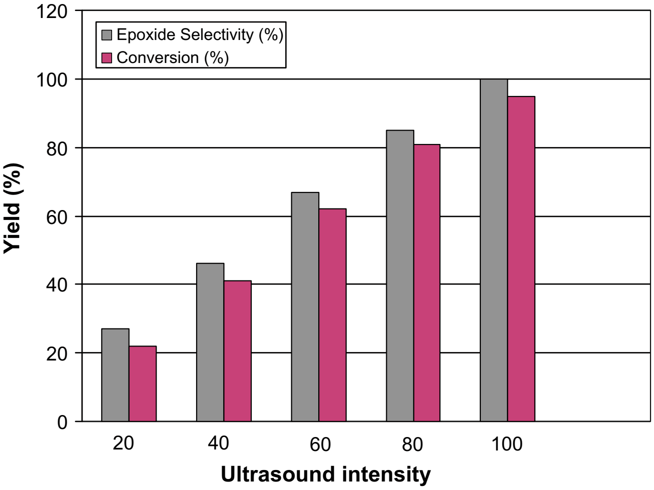
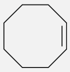
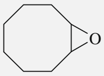
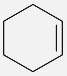
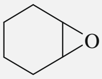
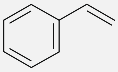
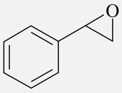
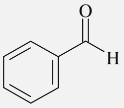
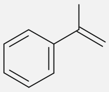
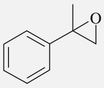
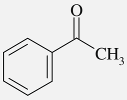
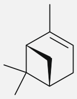
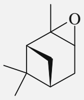
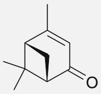
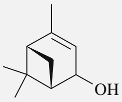
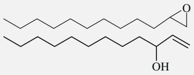
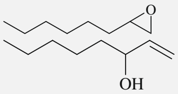


Fig. 4. The effect of ultrasonic irradiation intensity on the oxidation of cyclooctene with H_2O_2 catalyzed by PVMo–CNTs.

As shown in Table 2, application of US waves in this catalytic system has reduced the reaction times and improved the yields and product selectivities. The system under US irradiation showed a good catalytic activity in the oxidation of linear alkenes such as 1-octene and 1-dodecene.

The US processor used in this study works at low frequency and it is well known that low frequency does not produce important radicals. Radicals can come from the reactions at the surface of the catalyst. In this case, it seems that this is the "ultrasonic

Table 2
Epoxidation of olefins with H_2O_2 catalyzed by PVMo–CNTs under ultrasonic irradiation.[a]

Entry	Substrate	Products			Time (min)	Conversion (%)[b,c]	Epoxide selectivity (%)	TOF (h^{-1})
1					40	95	100	402.6
2					40	88	95	373.0
3					40	71	60[d]	301.0
4					40	78	82[e]	330.6
5					40	82	62[f]	347.5
6	1-Dodecene				40	48	82[g]	203.4
7	1-Octene				40	64	62[h]	271.2

[a] Reaction conditions: olefin (0.8 mmol), catalyst (2.86 μmol), H_2O_2 (1 ml), CH_3CN (5 ml).
[b] Based on the starting olefin.
[c] GC yield.
[d] 28% benzaldehyde was produced.
[e] 14% acetophenone was detected as by product.
[f] 20% verbenone and 11% verbenol were produced.
[g] 9% alcohol was produced.
[h] 24% alcohol was detected.

mechanical effect" which is involved. Shock waves induce by the collapsing bubble conduct to strong movement in the liquid and to particles collision. This will reduce particles size; it also increases the mass transfer and reduces the diffusion layer at the surface of the particles [13–15]. On the other hand, collapse of the produced bubbles results in generation of high temperatures. As the reaction under mechanical stirring requires a temperature of about 80 °C, therefore, the reaction can be also accelerated under US irradiation. To confirm the influence of the mechanical effects in breaking up the agglomerates and reducing the particles size during the oxidation reactions, a sample of catalyst was exposed to US waves and then used for oxidation of cyclooctene under reflux conditions. The results showed that the reaction time reduced from 10 to 7 h. These observations showed that both chemical and mechanical effects of US are effective in the acceleration the reaction.

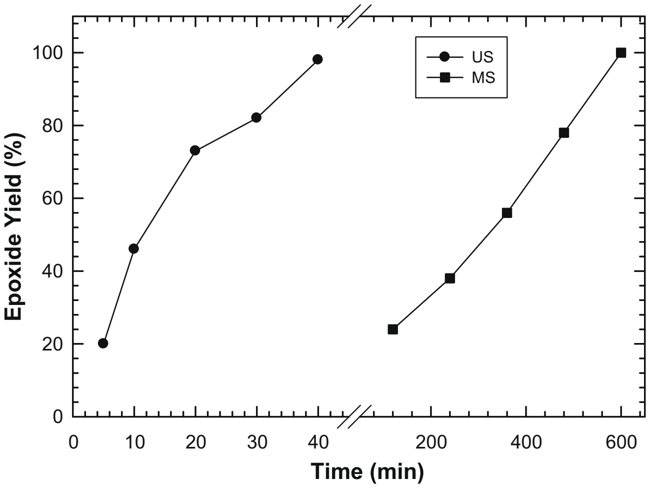


Fig. 5. Comparison of ultrasonic irradiation and magnetic agitation in the oxidation of cyclooctene with H_2O_2 catalyzed by PVMo–CNTs.

The power of ultrasound is a very important parameter and also has a great influence on the phenomena of acoustic cavitation and efficiency of ultrasound treatment. Fig. 4 shows the effect of irradiation power on the epoxidation of cyclooctene, which indicates that increasing of ultrasound power will improve the extent of oxidation and the highest conversion was observed at a power of 400 W.

Fig. 5 comprises systems under US irradiation and under agitation with magnetic stirring, which indicating that the catalytic activity of PVMo–CNTs catalyst has been enhanced by US irradiation.

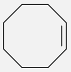
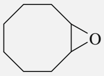
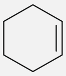
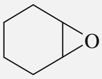
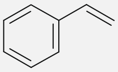
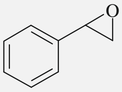
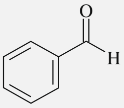
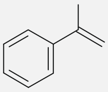
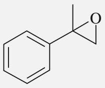
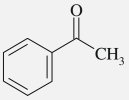
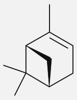
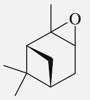
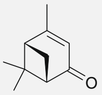
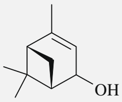
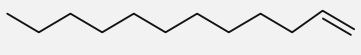
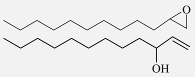
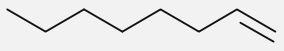
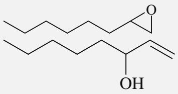
The blank experiments in the absence of catalyst showed that US irradiation has poor ability to epoxidize the alkenes with hydrogen peroxide.

In order to show the effect of supporting on the catalytic activity, all reactions were repeated in the presence of homogeneous PVMo catalyst and under the same reaction conditions. It is clear from Tables 1 and 3 that the catalytic activity of PVMo–CNTs was much higher than that of unsupported heteropolyanion. The conversions, selectivities and TOFs are higher for heterogeneous PVMo–CNTs in comparison with the homogeneous one. Therefore, the catalytic activity increases by dispersing of the catalyst on the nanotubes. On the other hand, the ability of CNTs, as catalyst, was checked in the oxidation of cyclooctene with H_2O_2. The obtained results showed that CNTs has poor ability to catalyze the epoxidation of cyclooctene and the amount of epoxide was less than 3%.

3.2.3. Catalyst reuse and stability

The stability of the supported catalyst was monitored using multiple sequential oxidation of cyclooctene with hydrogen peroxide under reflux or US irradiation. For each of the repeated reactions, the catalyst was recovered, washed thoroughly with

Table 3
Epoxidation of olefins with H_2O_2 (30%) catalyzed by homogeneous PVMo.[a]

Entry	Substrate	Products	Time (h)	Conversion (%)[b,c]	Epoxide selectivity (%)	TOF (h^{-1})
1			20	78	96	10.9
2			20	70	85	9.8
3		 	20	43	49	6.0
4		 	20	27	29	3.8
5		  	20	20	28	2.8
6			20	26	59	3.6
7			20	38	31	5.3

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

Table 4
The results obtained from catalyst reuse and stability in the oxidation of cyclooctene with H_2O_2 by PVMo–CNTs under agitation with magnetic stirring and under ultrasonic irradiation.[a]

Run	Time		Conversion (%)[b,c]		Epoxide selectivity (%)		*V* leaching (%)[d]	
	MS (h)	US (min)	MS	US	MS	US	MS	US
1	10	40	80	95	100	100	1.0	1.0
2	10	40	79	94	100	100	0.8	0.7
3	10	40	78	93	100	100	0.4	0.5
4	10	40	78	92	100	100	0.3	0.4

[a] Reaction conditions: olefin (1 mmol), catalyst (2.86 μmol), H_2O_2 (1 ml), CH_3CN (10 ml).
[b] Based on the starting olefin.
[c] GC yield.
[d] Determined by ICP.

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. Since the vanadium-containing catalysts usually show the leaching phenomena, the amounts of catalyst leaching after each run, was determined by ICP. In this manner the filtrates were collected after each run and used for determining of the amounts of *V* leached (Table 4). 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 IR. After reusing the catalyst for several times, no change in the IR spectra was observed.

4. Conclusion

Supporting of polyoxometalates on nanoparticle materials such as CNTs gave a catalyst, which was recoverable and reusable in the oxidation of alkenes with hydrogen peroxide. The use of US irradiation increased the conversions and reduced the reaction times. The results showed that good catalytic activity of the vanadium polyoxometalate, especially under US irradiation; make them as useful catalysts for further applications in the area of catalysis.

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