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Sonocatalytic oxidation of olefins catalyzed by heteropolyanion-montmorillonite nanocomposite

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1. Introduction

Heteropolyanion (HPO), a class of molecularly defined inorganic metal-oxide clusters, has interesting structures and unexpected properties, and attracts increasing attention worldwide [1-4]. Also, HPOs have some properties related to developing functional materials, such as catalytic activity for chemical transformations [5], molecule-based conductivity [6], and so on. Recently, HPOs-polyelectrolyte multilayer films have been fabricated by the layer-bylayer (LbL) self-assembly method [7,8]. Such multilayer films shows electrochromism, photoluminescence and nonlinear optical properties [9-11], which suggest that the functional properties of HPOs can be successfully incorporated into the multilayer film materials. However, the joining force between layers in the film was only electrostatic interaction. so that film's stability is insufficient. It was well-known that heteropolyanion is generally an anionic cluster, in which its negative charges mostly distribute on the surface oxygen atoms of HPO anion, thus photoinduced reactions can occur by activation of these surface oxygen atoms [12].

Intercalation of clays is known to transform the unstable clay structures into highly porous and stable structures. The robust oxide particles, which form the pillars in between the clay layers, prevent the collapse of the expanded layers and simultaneously

ABSTRACT

A Keggin-type heteropolyanion compound (HPO) was doped within the montmorillonite (MMT) structure by impregnation method. The synthesized catalyst was characterized by FT-IR, XRD, UV-vis, CV, SEM and elemental analysis. Based on chemical adsorption between HPO, and hydroxyl surface groups, HPOs nanoparticles were successfully located on the MMT. Moreover, the obtained nanocomposite was found as an efficient catalyst for oxidation of hydrocarbons under reflux and ultrasonic irradiation conditions.

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lead to the formation of large pores with dimensions of >2.0 nm, depending up on the extent of pillaring and the pillared material [13,14]. The presence of such large pores in montmorillonite-K10 is expected to facilitate the introduction and stabilization of the heteropolyanions. Montmorillonite is an interesting support for the immobilization of charged complexes [15].

Supported heteropolyanions are important for many applications, because bulk HPO have low specific surface area $(1-10 \text{ m}^2)$ g). In the case of unsupported heteropolyanions, when the reactants have a polar character, the catalytic reactions occur not only at the surface but also in the bulk of the solid heteropolyanions [16]. This is the reason why despite their low surface areas they demonstrate quite high catalytic activity. When non-polar reactants are used, it is important to increase the surface area or even better to increase the number of accessible acid sites of the HPO. This can be achieved by dispersing the heteropolyanions on solid supports with high surface areas [15]. It is known, that HPO strongly interact with supports at low loading levels, while the bulk properties of heteropolyanions prevail at higher loadings. Acidic or neutral substances like SiO₂, active carbons or aluminosilicates are suitable as supports. Due to the interaction of HPO and the OH surface groups protons are transferred to the silica surface which results in a decrease of acidity and the appearance of redox properties of HPOs. Interacting with the surface occurs very readily for samples with loadings lower than 20 wt.% [16].

The main effect of ultrasonic in liquids is cavitation phenomenon, which involves numerous tiny gas bubbles called cavitation



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Fig. 1. XRD patterns of: (A) MMT and (B) PVMo-MMT nanocomposite.



Fig. 2. FT-IR spectrum of: (A) PVMo-MMT and (B) recovered PVMo-MMT.

bubbles. The collapse of the bubbles generates high temperature and pressures at the centre of the bubbles. These local effects produce a variety of radicals and highly active intermediates, which initiate other secondary chemical reactions in the bulk liquid. These radicals can react with contaminants to form by products.

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 lead to excessive 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 [17].

Recently, we reported the sonocatalytic oxidation of organic compounds catalyzed by vanadium containing polyphosphomolybdate supported on MCM-41 and TiO₂ nanoparticles [18,19]. 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) deposited on montmorillonite. The effect of ultrasonic irradiation on the catalytic activity of this catalyst was also investigated.

2. Experimental

All reagents were purchased commercially and used without further purification. Elemental analysis was performed on a Perkin–Elmer 2400 instrument. The amount of Mo was measured by a Leaman inductively coupled plasma (ICP) spectrometer. Diffuse reflectance spectra were recorded on a Shimadzu UV-265 instrument using optical grade BaSO₄ as reference. FT-IR spectra were



Fig. 3. UV-vis spectrum of: (A) PVMo and (B) PVMo-MMT.

obtained as potassium bromide pellets in the range 400-4000 cm⁻¹ with a Nicollet-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 D₈ Advanced Bruker using Cu K α radiation (2 θ = 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 using *n*-decane as internal standard. ¹H NMR spectra were recorded on a Bruker-Arance AOS 300 MHz. Conversions and yields were obtained by GC experiments and the products were identified after isolation and purification. 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 was kept at 40 °C by a thermostat bath during sonication.

The $Na_5[PV_2Mo_{10}O_{40}]$ ·14H₂O was prepared according to the literature [20].

2.1. Preparation and characterization of HPO-MMT nanocomposite

The typical preparation of PVMo–MMT nanoparticles is as following: PVMo (1 g) and MMT (5 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 centrifugalized. The washing and centrifuging processes were repeated 5 times. The wet nanoparticles of HPO– MMT were obtained and dried in vacuum for 5 h (60–80 °C).



Fig. 4. SEM images of: (A) MMT and (B) PVMo-MMT nanocomposite.

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

In a typical experiment, the reaction vessel was loaded with the supported catalyst (30 mg, containing 4.76 mmol of PVMo), alkene (0.8 mmol) in acetonitrile (5 ml). H_2O_2 (1 ml) was added and the mixture was refluxed or exposed to ultrasonic waves. The progress of 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 ¹H NMR spectral data confirmed the identities of the products.

3. Results and discussion

3.1. Catalyst characterization

Since heteropolyanions of the Keggin structure have molecular diameters of \sim 12 A°, it is feasible to support the polyoxometalates such as PVMo on MMT. Fig. 1 shows the XRD patterns of MMT and

Table 1

Epoxidation olefins with H₂O₂ catalyzed by PVMo-MMT under reflux conditions.^a



^a Reaction conditions: olefin (0.8 mmol); catalyst (2.86 μmol); H₂O₂ (1 ml); CH₃CN (5 ml).

^c GC yield.

- ^e 16% Acetophenone was detected as by product.
- ^f 15% Verbenone and 10% verbenol were produced.

^g 25% Alcohol was produced.

h 4% Alcohol was detected.

^b Based on the starting olefin.

^d 26% Benzaldehyde was produced.

PVMo–MMT. These patterns indicated that PVMo has been introduced in the substitutional position of MMT. PVMo has a striking effect on the width and intensity of the main reflection at the high d_{100} spacing and this line becomes broader and weaker as the catalyst loading increases. At higher loadings, interactions between PVMo and the MMT surface may have a negative effect on the activity of these materials, as they appear to be responsible for severe distortion of the structural wall [21,22].

FT-IR spectrum of the prepared catalyst showed absorption bands at 1056, 957, 867 and 798 cm⁻¹, corresponding to the four typical skeletal vibrations of the Keggin polyoxoanions, which indi-

cated that PVMo has been supported on MMTs (Fig. 2). These peaks could be attributed to v(P = Oa), v(Mo = Ot), $v(Mo-O_b-Mo)$ and $v(Mo-O_c-Mo)$, respectively (Ot = terminal oxygen, O_b = bridged oxygen of two octahedral sharing a corner and O_c = bridged oxygen sharing an edge) [23].

The UV–vis spectra of PVMo in CH₃CN displayed absorption bands at 266 and 308 nm, which are associated with octahedrally coordinated Mo⁶⁺ and arise due to the Mo–O and V–O charge– transfer absorptions in the heteropoly cage [23–25]. These two absorption bands were appeared in the solid-state UV–vis spectra of catalyst and since pure MMT show no UV absorption; therefore,

Table 2

Epoxidation of olefins with H₂O₂ catalyzed by PVMo-MMT under ultrasonic irradiation.^a



^a Reaction conditions: olefin (0.8 mmol); catalyst (2.86 µmol); H₂O₂ (1 ml); CH₃CN (5 ml).

^b Based on the starting olefin.

c GC yield.

- ^d 14% Benzaldehyde was produced.
- ^e 5% Acetophenone was detected as by product.
- ^f 10% Verbenone heteropolyanion and 5% verbenol were produced.

^g 26% Alcohol was produced.

^h 20% Alcohol was detected.

these results indicated that primary Keggin structure has been introduced into the nanostructure framework (Fig. 3).

Fig. 4 shows the 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 between 50 and 250 nm by averaging its diameters measured in several directions in the SEM images. The larger size may be due to the aggregation of particles.

3.2. Catalytic activity

Since heterogeneous catalysts are recoverable, hence, heterogenization of homogenous catalysts is of great interest. Therefore, we decided to immobilize PVMo on MMT nanoparticles, and investigate its catalytic activity in the epoxidation of alkenes with H_2O_2 under agitation with magnetic stirring and under ultrasonic irradiation.

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

First, the ability of the prepared catalyst, PVMo–MMT, 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 showed that the conversion was 58% with 65% epoxide selectivity. Epoxidation of cyclohexene showed 58% conversion and 72% epoxide selectivity, and 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



Scheme 1. Mechanism for generation of peroxo radicals at PVMo sites.





Fig. 5. The particle size distribution PVMo-MMT before and after sonication.

in 58% and 78% epoxide selectivity. In the oxidation of α -pinene, the major product was α -pinene oxide, 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. Blank experiments in the absence of the catalyst showed that H₂O₂ has low ability in the epoxidation of alkenes.

3.2.2. Alkene epoxidation with H_2O_2 catalyzed by PVMo–MMT under ultrasonic irradiation

As mentioned in the previous works, ultrasonic irradiation can be used as an efficient tool to influence the product yield and selectivity [18,19]. Therefore, we decided to investigate the effect of ultrasonic waves on the epoxidation of different alkenes with H_2O_2 catalyzed by PVMo–MMT.

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

It is reported that peroxo radicals are generated at the PVMo sites (Scheme 1). Subsequent oxidation of the hydrocarbon can occur both within the pores and in the bulk liquid solution [3,26].



Fig. 6. The effect of ultrasonic irradiation intensity on the oxidation of α -methyl styrene with H₂O₂ catalyzed by PVMo–MMT.



Fig. 7. Comparison of ultrasonic irradiation and magnetic agitation in the oxidation of α -methyl styrene with H₂O₂ catalyzed by PVMo–MMT (the reactions were carried out as described in the Section 2).

Ultrasonic irradiation promotes the generation of radicals in the reaction media and this can accelerate the reaction. 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 ultrasonic irradiation.

In order to show the effect of ultrasonic irradiation on the catalytic activity enhancement, the particle size distribution of the catalysts was determined before and after sonication. The results showed that the catalyst agglomerates break-up during the sonication process (Fig. 5). It seems that a part of ultrasonic irradiation effect is due to this phenomenon. To stress this point, the catalytic activity of a sonicated sample catalyst was studied in the epoxidation of cyclooctene under conventional mechanical stirring. It was found that the reaction time reduced from 10 to 6 h for epoxidation of cyclooctene to its corresponding epoxide. These results show that in addition to break-up of the agglomerates, other factors such as thorough mixing of the reactants and producing of hot spots are

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

the main reasons for catalytic enhancement by ultrasonic irradiation.

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. 6 shows the effect of irradiation power on the epoxidation of α -methyl styrene, 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. 7 comprises the systems under ultrasonic irradiation and under agitation with magnetic stirring, which indicating that the catalytic activity of PVMo–MMT catalyst has been enhanced by ultrasonic irradiation.

The blank experiments in the absence of catalyst showed that ultrasonic irradiation has poor ability to epoxidize the alkenes with hydrogen peroxide (about 10%).

In order to show the effect of supporting on the catalytic activity, all reactions were repeated in the presence of homogeneous

Entry	Substrate	Products	Time (h)	Conversion (%) ^{b,c}	Epoxide selectivity (%)	TOF (h^{-1})
1	\bigcirc	ОН ОН	20	55	96	7.7
2	\bigcirc		20	53	85	7.4
3			20	38	49	6.9
4		CH ₃	20	27	29	3.8
5			20	20	28	2.8
6	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	→→→→→→ →→→→→→ OH	20	26	59	3.6
7	$\sim\sim\sim\sim$		20	32	31	4.6

 a Reaction conditions: olefin (0.8 mmol); catalyst (2.86 μ mol); H₂O₂ (1 ml); CH₃CN (5 ml).

^b Based on the starting olefin.

^c GC yield.

Table 4

Run	Time		Conversion (%) ^{b,c}		Epoxide selectivity (%)		V leaching (%) ^d	
	MS (h)	US (min)	MS	US	MS	US	MS	US
1	10	35	72	92	78	95	1.0	1.0
2	10	35	71	91	77	94	0.8	0.7
3	10	35	70	90	76	94	0.4	0.5
4	10	35	69	89	76	93	0.3	0.4

The results obtained from catalyst reuse and stability in the oxidation of α -methyl styrene with H₂O₂ by PVMo–MMT under agitation with magnetic stirring and under ultrasonic irradiation.^a

^a Reaction conditions: olefin (0.8 mmol); catalyst (2.86 µmol); H₂O₂ (1 ml); CH₃CN (10 ml).

^b Based on the starting olefin.

^c GC yield.

^d Determined by ICP.

PVMo catalyst and under the same reaction conditions. It is clear from Tables 1 and 3 that the catalytic activity of PVMo–MMT was much higher than that of unsupported heteropolyanion. The conversions, selectivities and TOFs are higher for heterogeneous PVMo–MMT in comparison with the homogeneous one. Therefore, the catalytic activity increases by dispersing of the catalyst on the montmorillonite. On the other hand, the ability of MMT, as catalyst, was checked in the oxidation of cyclooctene with H_2O_2 .

Recently, we have reported the use of polymer supported molybdenum hexacarbonyl in the alkene epoxidation with *tert*-BuOOH [26–28]. No doubt, these methods are good in terms of reactivity and reusability; but the present method is superior in terms of thermal stability, ease of preparation and lower cost of the catalyst. On the other hand, the H_2O_2 is a green and eco-friendly oxidant in comparison with *tert*-BuOOH. Also all metal carbonyls are more toxic than polyoxometalate. Finally, this catalyst can be considered as a nanocatalyst.

3.2.3. Catalyst reuse and stability

The stability of the supported catalyst was monitored using multiple sequential oxidation of α -methyl styrene with hydrogen peroxide under reflux or ultrasonic irradiation. For each of the repeated reactions, the catalyst was recovered, washed thoroughly with acetonitrile and 1,2-dichloroethane, successively, and dried before being used with fresh α-methyl styrene 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. Conclusions

Supporting of heteropolyanion nanoparticle on materials such as MMT gave a catalyst, which was recoverable and reusable in the oxidation of alkenes with hydrogen peroxide. The use of ultrasonic irradiation increased the conversions and reduced the reaction times. The results showed that good catalytic activity of the vanadium heteropolyanion, especially under ultrasonic irradiation; make them as useful catalysts for further applications in the area of catalysis. We have directly observed the attachment of heteropolyanion nanoparticles to MMT due to the chemical adsorption between hydroxyl groups of MMTs and PVMOs nanoparticles. This method can be readily extended to label defects on MMT by using PVMOs nanoparticles as a marker.

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