CSM

Chemistry of Solid Materials
Vol. 2 No. 1 2014

Nano composite mixed-addenda vanadium substituted polyoxometalate-TiO_2 as a green, reusable and efficient catalyst for rapid and efficient synthesis of symmetric disulfides under ultrasound irradiation

M. A. Rezvani*[1], M. Ali Nia Asli[2], L. Abdollahi[3], M. Oveisi[4]

[1,2]Assistant Professor, Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran
[3,4]MSc Student, Department of Chemistry, Faculty of Science, University of Zanjan, Zanjan, Iran
**Corresponding author; E-mail: marezvani@znu.ac.ir*

Article history:
(Received*:* 5 Nov 2014, Revised: 21 Jan 2015, Accepted: 17 Feb 2015)

ABSTRACT

Mixed-addenda vanadium substituted polyoxometalate supported on anatase TiO_2 crushed nano leaf was synthesized by an unusual reaction with titanium tetraisopropoxide at 100 ºC via sol–gel method under oil-bath condition. The materials characterized by XRD, TEM, IR and UV–vis techniques. In the present work, efficient oxidative of thiols with polyoxometalate-TiO_2/hydrogen peroxide system using ultrasound irradiation is reported. The Keggin type polyoxometalate-TiO_2/H_2O_2, sandwich type POM-TiO_2 and Wells Dowson type POM-TiO_2/H_2O_2 systems showed completely different reactivity ordering for the same oxidation of thiols. Ultrasonic irradiation increased the catalytic activity of the catalyst, reduced the reaction times and increased the products yields.

Keywords: Polyoxometales; Desulphurization; Anatase; Keggin; Dowson.

1. INTRODUCTION

Disulfides plays an important role in synthetic organic chemistry as well as biology, notably to control cellular redox potential in biological systems in which thiols are oxidized to prevent oxidative damage [1-3]. Disulfides have also found industrial applications as vulcanizing agents and as important synthetic intermediates in organic synthesis [4]. Various reagents and oxidants have been employed for oxidation of thiols to homodisulfides [4-6]. Some of these methods suffer from obvious disadvantages such as long reaction times, limited availability of the oxidant, toxicity of reagents and difficult isolation of products. Consequently, the introduction of readily available, safe and stable reagents for the oxidation of thiols to disulfide is still a necessity. The application of heteropolyacids (HPAs) as catalytic materials is growing continuously in the catalytic field. These compounds possess unique properties such as: well-defined structure, Brönsted acidity, possibility to modify their acid–base and redox properties by changing their chemical composition (substituted HPAs), ability to accept and release electrons, high proton mobility, being environmentally benign and presenting fewer disposal problems [7, 8]. Supporting the heteropolyacids on solids with high surface areas improve their catalytic performance in heterogeneous reactions. In this article in continuation of our group research [8-12], we describe the synthesis and crystal structure of a mixed-addenda vanadium-containing heteropolyanion supported on TiO_2 by an unusual reaction. Homogeneous catalysts cannot be separated from the reaction media and subsequently, cannot be reused. Fixation of the homogeneous catalysts onto a solid support may be a strategy to overcome this problem. The catalyst easily separated and reused at the end of reaction without a significant loss of its catalytic activity, which suggests that the catalyst is stable under different conditions. The ultrasound irradiation is applicable to a broad range of practical syntheses. Some advantages of ultrasound procedure are short reaction times and mild reaction conditions, formation of purer products and waste minimization. Ultrasound irradiation can also be used to influence selectivity and yields of reactions [13-16]. Despite the vast advantages of this technique, the use of ultra sound in synthesis of organic compounds is not fully developed. The reactions proceeded smoothly under mild and green ultrasound-accelerated conditions to afford the products in high yields. Application of ultrasound in a so-called ‘‘sonochemistry’’ has received enormous interests since it offers a versatile and challenging technique in organic synthesis. Recently, ultrasonic irradiation technique has been employed not only to decrease reaction times but also to improve yields in a large variety of organic reactions. To develop the applications of ultrasound in organic reaction herein we wish to report a very efficient and simple method for oxidative of thiols under ultrasound irradiation.

2. EXPERIMENTAL

2.1 Materials

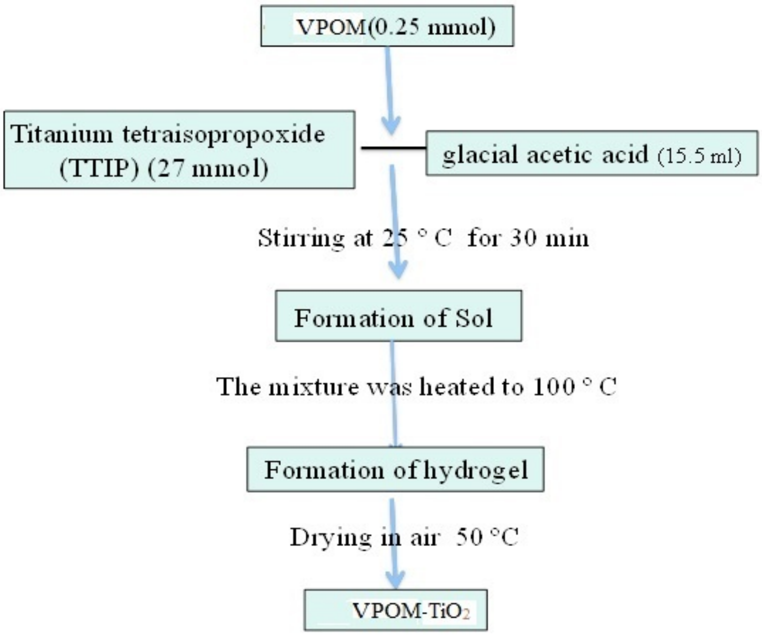
All the chemicals were obtained from Merck Company and used as received. All reagents and solvents used in this work are available commercially and were used as received, unless otherwise indicated. Hydrogen peroxide (30 vol%) were obtained from Aldrich Chemical Company. $Na_5[PV_2Mo_{10}O_{40}]–TiO_2$ and other polyoxometalate were prepared according to our previous work [8-11]. The compound A-β-$Na_8HPW_9O_{34}$. $24H_2O$ (abbreviated as A-PW9) and other catalysts were prepared as previously described [10, 11]. Ultra sound apparatus was Wiseclear (Seol, Korea), with a frequency of 40 kHz, nominal power of 770W and output of 200 W.

2.2 Preparation of $H_5[PMo_{10}V_2O_{40}]$ (VPOM)

Sodium metavanadate (12.2 g, 100 mmol) was dissolved by boiling in 50 mL of water and then mixed with (3.55 g, 25 mmol) of Na_2HP0_4 in 50 mL of water. After the solution was cooled, (5 mL, 17 M, 85 mmol) of concentrated sulfuric acid was added, and the solution developed a red color. An addition of (60.5 g, 250 mmol) of $Na_2MoO_4.2H_2O$ dissolved in 100 mL of water and then was added to the red solution with vigorous stirring, followed by slow addition of concentrated sulfuric acid (42 mL, 17 M, 714 mmol). The hot solution was allowed to cool to room temperature. The 10-molybdo-2-vanadophosphoric acid was then extracted with 500 mL of ethyl ether. Air was passed through the heteropoly etherate (bottom layer) to free it of ether. The solid remaining behind was dissolved in water, concentrated to first crystal formation, as already described, and then allowed to crystallize further. The large red crystals that formed were filtered, washed with water, and air-dried [9].

2.3 Preparation of nano catalyst VPOM-TiO_2

The VPOM–TiO_2 nanoparticle was prepared as following: First, titanium tetraisopropoxide was added into glacial acetic acid with stirring. Next, a solution of VPOM in water was drop wised in it. The mixture was stirred to dissolve any solid. Then, the sol was heated to 100 °C under oil bath condition until a homogenous VPOM –TiO_2 hydrogel was formed. Finally, the gel was filtered, washed with deionized water-acetone and dried in oven at 50 ºC overnight (Scheme 1).



Scheme 1. Chart of synthesis of nanocomposite.

2.4. General procedure for oxidation reactions with H_2O_2 under ultrasonic irradiation

To a mixture of thiol (0.5 mmol) and nano catalysts (16 mg, containing 2.20 μmol of VPOM –TiO_2) in EtOH (8 mL) was added 2 mL of 30% hydrogen peroxide and the mixture was exposed to ultrasonic irradiation. The reaction was monitored by TLC. After the reaction was completed, the reaction mixture was diluted with CH_2Cl_2 (30 mL) and filtered. The nano catalyst was thoroughly washed with CH_2Cl_2 and combined washings and filtrates were purified on a silica gel plates or a silica- gel column.

2.5. Characterization methods

X-ray diffraction (XRD) patterns were recorded by a D8 Bruker Advanced, X-ray diffractometer using Cu Kα radiation (α=1.54 A). The patterns were collected in the range 2θ = 20–70° and continuous scan mode. Transmission electron microscope (TEM) images were obtained on a Philips CM10 transmission electron microscope with an accelerating voltage of 100 kV. The electronic spectra of the synthesized catalysts were taken on a RAYLEIGH (UV-1800) ultraviolet–visible (UV–vis) scanning spectrometer. Infrared spectra were recorded as KBr disks on a Buck 500 scientific spectrometer.

2.6. Recycling of the nano catalyst

At the end of the oxidation of the thiols, the catalyst was filtered, washed with dichloromethane. In order to know whether the catalyst would succumb to poisoning and lose its catalytic activity during the reaction, we investigated the reusability of the catalyst. For this purpose we carried out the oxidation reaction of 4-Chlorothiophenol in the presence of catalyst. Even after three runs for the reaction, the catalytic activity of (VPOM-TiO_2) was almost the same as that freshly used catalyst. The results are summarized in Table 1.

Table 1. Reuse of the catalyst for oxidation of 4-Chlorothiophenol (Table 2, entry 4)

Entry	Isolated yield (%)
1	96
2	94
3	94

3. RESULTS AND DISCUSSION

3.1 Characterization of synthesized catalysts

XRD patterns of TiO_2, VPOM and VPOM-TiO_2 are shown in Figure 1. XRD patterns (a) and (b) in Figure 1 are corresponded to pristine TiO_2 and VPOM, respectively. The XRD pattern corresponding to pure TiO_2 was found to match with that of fully anatase phase. No peaks from any else impurities or rutile phase were observed, which indicates the high purity of the obtained powders. The sharp diffraction peaks manifest that the obtained TiO_2 have high crystallinity. When VPOM is bound to the TiO_2 surface, (VPOM -TiO_2), all of signals corresponding to VPOM is disappeared and the final pattern matched to fully anatase phase of TiO_2 (JCPDS No. 21-1272), which is most likely due to VPOM forming only a thin coating on the TiO_2 surface and thus the majority of the observed signals are due to the crystal phases of anatase TiO_2. Using the Scherrer equation, the crystallite diameter of VPOM -TiO_2 is about 9 nm.

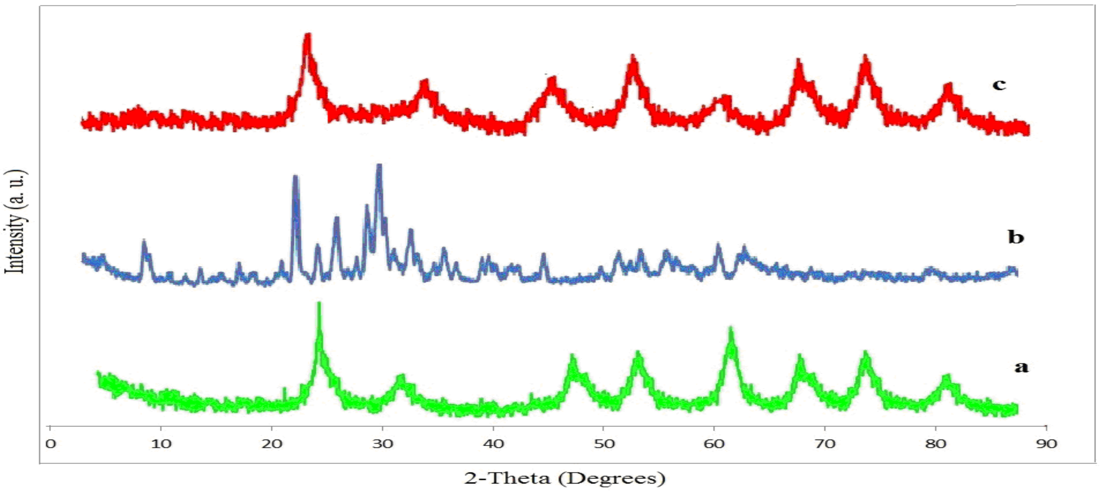


Fig. 1. XRD pattern of (a) TiO_2, (b) VPOM and (c) VPOM-TiO_2.

Figure 2 depicts the transmission electron micrographs of obtained powders. Figure 2(a) shows TEM image of obtained fully anatase phase of TiO_2 as crushed nano leaf with average size of about 20 nm. It is observed from the TEM image, after modification of anatase with VPOM a significant change in morphology and size was occurred. It can be seen that in the TEM image, most of the obtained powders are nano particles with average size about 10 nm and there are some nano rods.

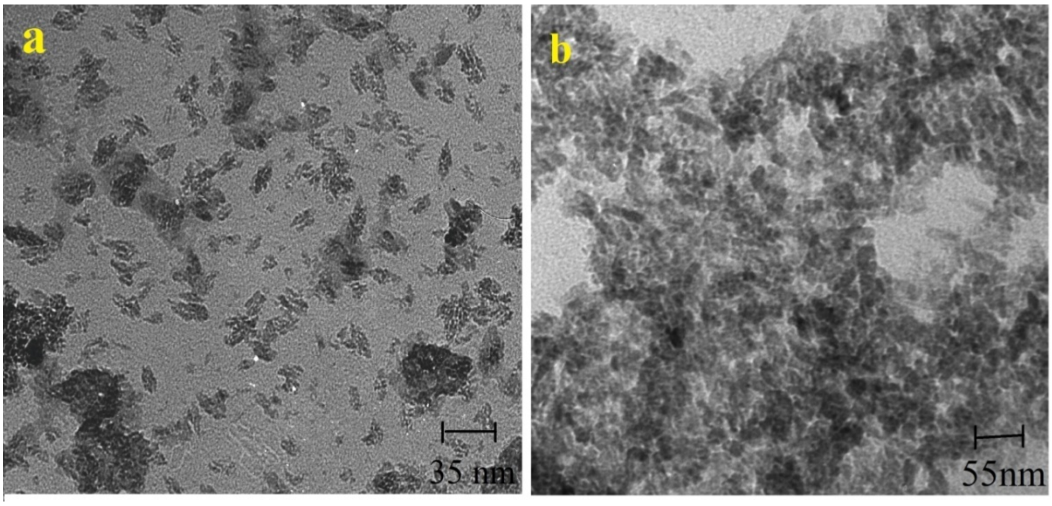


Fig. 2. TEM image of (a) TiO_2 and (b) VPOM-TiO_2.

Also UV-visible spectroscopy of obtained powders was studied. UV-vis spectra of TiO_2, VPOM and VPOM -TiO_2 nanocomposite are shown in Figure 3. In ultraviolet light regions, which are shorter than 350 nm, pure nano TiO_2 whose band gap energy equivalent to around 275 nm (3.70 eV) shows the highest absorbance due to charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d t_2g orbitals of the Ti^{4+} cations) [12]. In addition, some hyper fine structure in the range from 280 to 330 nm observed in VPOM spectrum. The inset of the figure shows the UV-vis spectrum of the VPOM -TiO_2 indicating there are two peaks around 220 and 260 nm. The above UV–vis results indicate that introduction of VPOM into TiO_2 framework has an influence on coordination environment of TiO_2 crystalline [7].

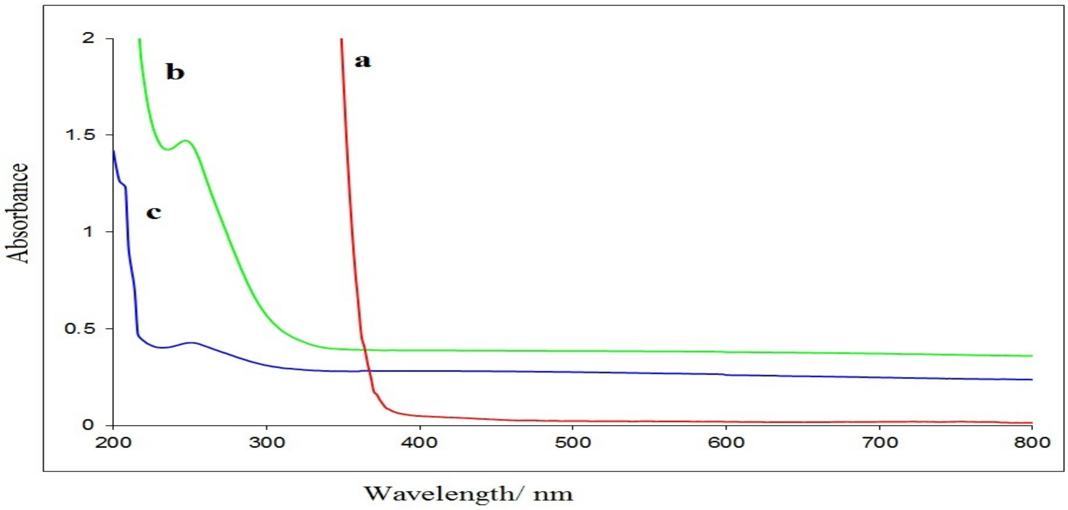


Fig. 3. UV-vis spectra of (a) TiO_2, (b) VPOM and (c) VPOM-TiO_2.

IR spectrum of the prepared catalyst in the range 700–1100 cm^{-1} showed absorption bands at 1078, 968, 879 and 763 cm^{-1}, corresponding to the four typical skeletal vibrations of the Keggin polyoxoanions, which indicated that VPOM has been supported on TiO_2 (Fig. 4). These peaks could be attributed to ν(P–O), ν(Mo–O), ν(Mo–O_b–Mo) and ν(Mo–O_c–Mo) (O_b: corner-sharing oxygen, O_c: edge-sharing oxygen), respectively [8, 17].

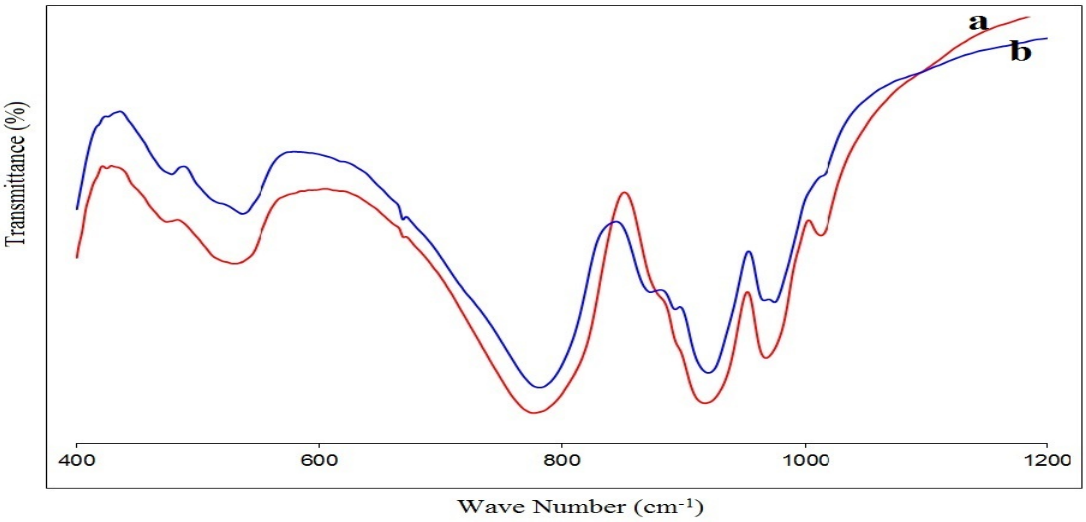


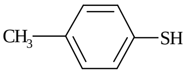
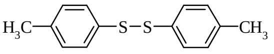
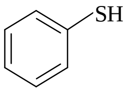
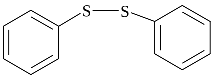
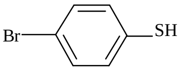
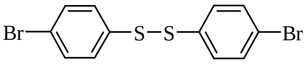
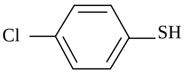
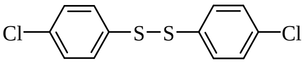
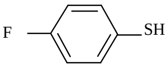
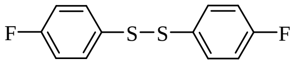
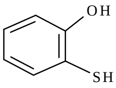
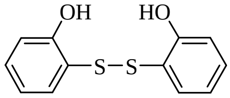
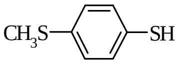
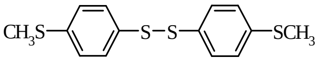
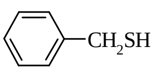
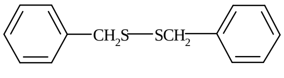
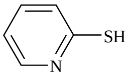
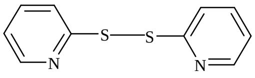
Fig. 4. IR spectrum of (a) VPOM and (b) VPOM-TiO_2.

3.2. Catalytic results

3.2.1. Effect of the substituent

The effects of various substituents on the yields of produced disulfides have been examined in the presence of VPOM-TiO_2 as a nano catalyst. The results are given in Table 2. Halogens were chosen as electron-withdrawing groups (entries 3–5), while methyl, phenolic hydroxyl and methylthiol groups (entries 1, 6 and 7, respectively) were chosen as electron-donating substituents. One heteroaromatic thiol, *i.e.*, pyridine-2-thiol, was successfully oxidized in good yield (entry 9) as well as benzylthiol (entry 8) as a benzylic aliphatic representative. The yields were generally very good (>75 %) to excellent (>90 %) with no obvious relationship between the aromatic substituent and yield (compare entries 4 with 5 and 2 with 10). A highlight of the method is the ease by which the product may be isolated *via* simple filtration followed by removal of the solvent.

Table 2. Oxidation of different thiols using $H_5PV_2Mo_{10}O_{40}$-TiO_2 as a catalyst under ultrasound irradiation.

Entry	Thiol	Disulfide	Time (min)	Yield [a,b] (%)	M.P (°C) found	M.P(°C) Literature [9, 12]
1			10	96	43-44	44-45
2			15	96	60-61	61
3			20	94	90-92	91-93
4			20	97	72-73	70-71
5			30	84	49-51	--
6			30	92	Liquid[29]	--
7			30	83	40-43	40-43
8			40	78	69-71	69-70
9			30	81	55-56	55-57

---

[a] Isolated yield on the basis of the weight of the pure product obtained.

[b] The products were identified by comparison of physical and spectroscopic properties with authentic compounds.

3.2.2. Effect of the catalyst structure

The effect of the structure of the catalyst on the oxidation of 4-chlorothiophenol, as a model compound, is presented in Table 3. It was studied using Keggin, Wells Dowson and sandwich type polyoxometalate-anatase nanoparticle as a catalyst and hydrogen peroxide as an oxidant. POMs-TiO_2 nanocomposite has presented higher catalytic activity than that of the unsupported polyoxometalates. The VPOM -TiO_2 nano particle was very active catalyst systems for the model compound oxidation, while other polyoxometalates systems were less active. In the Keggin-type polyoxometalates series, $H_5PV_2Mo_{10}$-O_{40}-TiO_2 showed the highest catalytic activity. The results of Table 3 show that the heteropoly salt type catalysts were less efficient than the heteropolyacids. The Keggin-type polyoxometalates led to more effective reactions in comparison with the sandwich and Wells–Dawson type polyoxometalates. However, $H_6P_2Mo_{18}$-O_{62} was more effective than $H_6P_2W_{18}O_{62}$ in the oxidation of thiols, possibly due to the difference in tungsten and molybdenum reduction potentials. The compression of efficiency of TiO_2-supported mixed addenda heteropolyacid (VPOM-TiO_2) with mixed addenda heteropolyacid (VPOM) has been carried out. The results are shown in Table 3. It is clear that Nano composite VPOM-TiO_2 gave the better yields than VPOM.

Table 3 . Effect of different catalyst in oxidation of 4-Chlorothiophenol (Table 2, entry 4) [a]

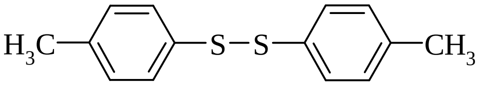
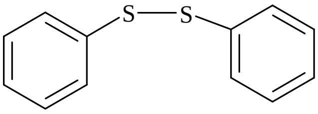
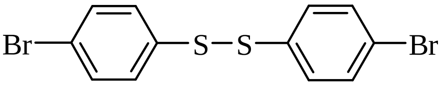
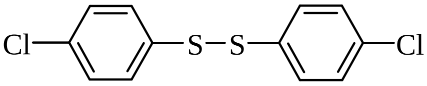
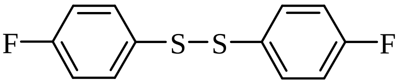
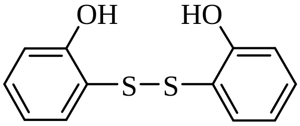
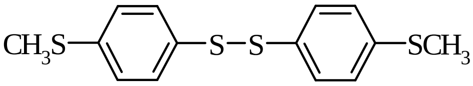
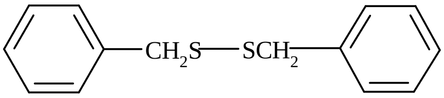
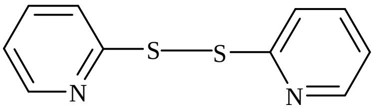
Entry	Catalyst	Time (min.)	Yeild (%)
1	$H_5PV_2Mo_{10}O_{40}$-TiO_2	20	97
2	$(Bu_4N)_7H_3[P_2W_{18}Cd_4]$-$TiO_2$	25	97
3	$H_5PV_2Mo_{10}O_{40}$	20	95
4	$H_4PVMo_{11}O_{40}$	20	93
5	$(Bu_4N)_7H_3[P_2W_{18}Cd_4]$	20	90
6	$(NH_4)_{10}[P_2W_{18}Cd_4]$	20	87
7	$K_5PV_2Mo_{10}O_{40}$	30	86
8	$K_4PVMo_{11}O_{40}$	35	84
9	$K_{10}[P_2W_{18}Zn_4]$	35	83
10	$H_6P_2Mo_{18}O_{62}$	20	82
11	$H_6P_2W_{18}O_{62}$	20	80

[a] Condition for oxidation: 2 ml H_2O_2 as an oxidant, 2.20 μmol mmol catalyst, 30 ml CH_2Cl_2 as an extraction solvent and ultrasonic irradiation.

3. 2. 3. Effect of ultrasound irradiation

To investigate the role of ultrasound irradiation in this method, the reactions were carried out in the presence of the same amount of nanocomposite VPOM -TiO_2 under stirring condition in EtOH at room temperature. The results are summarized in Table 4. It is clear that in the same reaction condition reactions under ultrasound irradiation led to relatively higher yields and shorter reaction times (Table 2 and 3). 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.

Table 4. Oxidation of different thiols using $H_5PV_2Mo_{10}O_{40}$-TiO_2 as catalyst under refluxing condition.

Entry	Disulfide	Time (h)	Yield [a](%)
1		2	98
2		2	94
3		2	96
4		2	98
5		3	95
6		3	91
7		3	84
8		3	83
9		3	80

[a] Isolated yield on the basis of the weight of the pure product obtained.

Figure 5 shows the effect of irradiation power on the oxidation of thiols, 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.

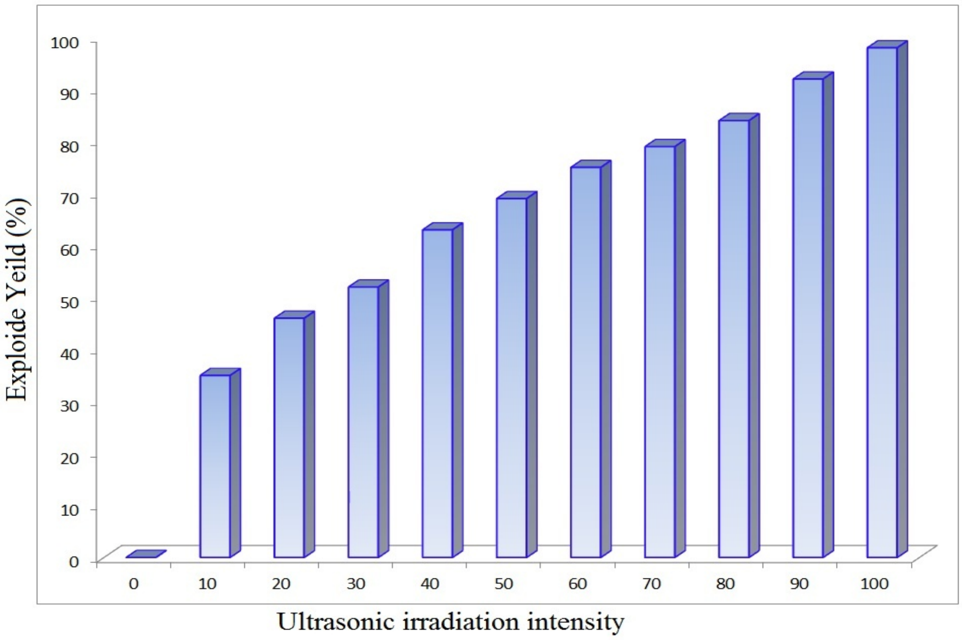


Fig. 5. Effect of ultrasound irradiation intensity on the oxidation of thiol with H_2O_2 catalyzed by VPOM–TiO_2.

4. CONCLUSION

VPOM-TiO_2 nanocomposite has been synthesized at low temperature via sol–gel method under oil-bath condition. Fixing of VPOM into TiO_2 decreases the particle size of crushed nano leaf of anatase phase. The VPOM-TiO_2 nano composite was very active catalyst systems for the model compound oxidation, while unmodified VPOM showed much lower activity.

REFERENCES

[1] J. Langer, R. Fischer, H. Gorls, *Am. J. Physiol. Renal Physiol.* 278, 2952 (**2000**).

[2] D.C. Jocelyn, Biochemistry of the Thiol Groups, Academic press, New York, (**1992**).

[3] R.J. Cremlyn, An Introduction to Organosulfur Chemistry, Wiley and Sons, New York, (**1996**).

[4] S. Oae, Organic Sulfur Chemistry: Structure and Mechanism, CRC Press, Boca Raton, FL, (**1991**).

[5] G. Ledung, M. Bergkvist, J. Carlsson, S. Oscarsson, *Langmuir* 17, 6056 (**2001**).

[6] Y. Nishiyama, K. Maehira, J. Nakase, N. Sonoda, *Tetrahedron Lett.* 46, 7415 (**2005**).

[7] F.M. Collins, A.R. Lucy, C. Sharp, *J. Mol. Catal. A: Chem.* 117, 397 (**1997**).

[8] M. A. Rezvani, A. F. Shojaie, M. H. Loghmani, *Catal. Commun.* 25, 36 (**2012**).

[9] A. Fallah Shojaei, M.A. Rezvani, M. Heravi, *J. Serb. Chem. Soc.* 76, 955 (**2011**).

[10] A. F. Shojaie, M. A. Rezvani, M. H. Loghmani, *Fuel Process. Technol.*,118, 1 (**2014**).

[11] A. Fallah Shojaei, M.A. Rezvani, M. Heravi, *J. Serb. Chem. Soc.* 76, 1513 (**2011**).

[12] R. Harutyunyan; M. A. Rezvani; Majid M. Heravi, Synth. *React. Inorg. Met.-Org. Chem.,* 41, 94 (**2011**).

[13] W. Bonrath, *Ultrason. Sonochem.* 10, 55 (**2003**).

[14] K.S. Suslick, Ultrasound: its Chemical, Physical and Biological Effect, VCH, Weinheim, (**1988)**.

[15] M. M. Heravi, S. Sadjadi, *Ultrason. Sonochem.,* 16, 708 (**2009**).

[16] M. M. Heravi, S. Sadjadi, *Ultrason. Sonochem.,* 16, 718 (**2009**).

[17] Y. Yang, Q. Wu, Y. Guo, C. Hu, E. Wang, *J. Mol. Catal. A: Chem.* 225, 203 (**2005**).

[18] M. M. Khodaei, I. Mohammadpoor, *Bull. Korean Chem. Soc.* 24, 885 (**2003**).

[19] A. McKillop, D. Koyuncu, and M. Trabelsi, *Tetrahedron Lett*. 31, 5007 (**1990**).

[20] H. Golchoubian, F. Hosseinpoor, *Catal. Commun*. 8, 697 (**2007**).