A comparative study between transition-metal-substituted Keggin-type tungstosilicates supported on anatase leaf as catalyst for synthesis of symmetrical disulfides

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ABSTRACT

Transition-metal-substituted (TMS) polyoxometalates of the general formula $[SiW_9M_3O_{39}]$, (where M = first row transition metal), has been synthesized and supported on anatase by sol–gel method under oil-bath condition. The tetrabutylammonium (TBA) salts of the Keggin-type polyoxotungstates $[SiW_9M_3O_{39}]$, (M = V^{II}, Cr^{II}, Mn^{II}, Fe^{II} Co^{II} and Ni^{II}), proved to be green, reusable, and highly efficient catalysts for the oxidation of thiols and dithiols into the corresponding disulfides using hydrogen peroxide as an oxidizing reagent. This article will be focused on the discovery of other transition metal substituted silicotungstate structures with a potential for homogeneous and heterogeneous oxidation catalysis. We will focus on red/ox active 3d metals (e.g. Fe^{2+}, Cr^{2+}).The catalytic activity of these transition-metal-substituted polyoxometalates (TMSPOMs) was strongly influenced by the type of transition metal in the TMSPOMs. Among them, the ($TBA_7SiV_3W_9O_{40}$) catalytic system showed the highest activity. Nanoparticle ($TBA_7SiV_3W_9O_{40}$-TiO_2) has been synthesized by sol–gel method under oil-bath condition at 100 °C. The materials were characterized by IR, XRD, TEM and UV–vis techniques.

Keywords: Transition-metal, Polyoxometalate, Sol–gel method, Keggin, Thiol.

1. INTRODUCTION

The catalytic functions of transition-metal-substituted (TMS) polyoxometalates and related polyoxometalate compounds have attracted much attention, particularly over the last two decades [1]. In this context, heteropoly acids (HPAs) are promising catalysts. A common and important class of these acids and those used in the majority of catalytic applications is the Keggin compounds, with the general formula $H_nXM_{12}O_{40}$ (X = P, Si, As, Ge, B; M = Mo, W) [2-4].

These solid acids are us-ually insoluble in non-polar solvents but highly soluble in polar ones. They can be used in bulk or supported forms in both homogeneous and hetero-geneous systems. Furthermore, these POMs have several advantages, including high flexibility in modification of the acid strength, ease of handling, environ-mental compat-ibility, non-toxicity, and experimental simplicity [3-5]. Keggin type poly-oxoanions (Figure 1) have widely been studied as homogeneous and hetero-geneous catalyst for the oxi-dation of organic compounds [4].
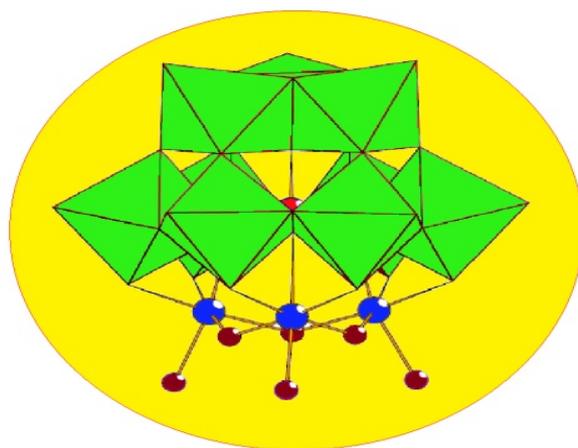
Fig. 1: Polyhedral representation of $SiMo_3W_9O_{40}$. Color coding for octahedra: WO_6 (green), for balls: Si (red), Mo (blue), O (brown).

Further catalytically important sub-classes of the Keggin compounds are the mixed-addenda vanadium (V) substituted polyoxometalates with the general formula of $TBA_{3+n}SiM_{12-n}V_nO_{40}$ (M = Mo and W; n = 1–6). It has been well known that one or three addenda units are generally removed from the Keggin-type polyoxometalate to form so-called lacunary anions as $XM_{11}O_{39}^{n-}$ and $A-XM_9O_{34}^{n-}$ and that the other metal ions are incorporated to the vacant sites of these lacunary anions to form metal-substituted polyoxometalates [6]. These compounds exhibit high activity in acid-base type catalytic reactions; hence they are used in many catalytic areas as homogeneous and hetero-geneous catalysts. In continuation of our group research on the syntheses and application of polyoxometalates in organic syntheses [5-13] and due to the importance of derivatives of disulfides in biological and chemical processes, we hereby report the applicability of POM-TiO_2 for efficient oxidation of thiols to the corresponding disulfides. Supporting the heteropolyacids on solids with high surface areas improve their catalytic performance in various liquid–solid and solid–solid surface heterogeneous reactions. Titanium dioxide is a wide band-gap semi-conductor material that has received intense scrutiny for a broad range of applications, thanks to its intriguing physical-chemical properties and cheap, abundant, and reasonably nontoxic nature [6-8]. TiO_2, also a widely used catalyst support as well as a catalyst is known to enhance the catalytic activity in many cases because of the strong interaction between the active phase and the support [6-8, 11]. Disulfide plays an important role in biology and synthetic organic chemistry [15-17]. In order to control cellular redox potential in biological systems, thiols are oxidized to prevent oxidative damage. Disulfide is used as a protecting group under oxidative conditions for thiol, and can be regenerated by S-S bond cleavage [18]. Disulfides have also found industrial applications as vulcanizing agent and are important synthetic intermediates in organic synthesis. Thiol can also be over-oxidized to sulphoxide and sulphone, therefore controlled and selective studies were carried out for their oxidation [19]. Various reagents and oxidants have been employed for conversion of thiols to disulfides [17-

19]. 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.In continuation of our group research on the syntheses and application of heteropolyacids in organic syntheses and due to the importance of derivatives of disulfides in biological and chemical processes, we hereby report the applicability of TBAPOMs for efficient oxidation of thiols to the corresponding disulfides. We wish to report a very efficient and simple method for oxidative of thiols into the corresponding disulfides using hydrogen peroxide as an oxidizing reagent catalyzed by the TBA_7Si-$V_3W_9O_{40}$-TiO_2 nanocomposite under mild conditions. Supporting the heteropolyacids on solids with high surface areas improves their catalytic performance in various heterogeneous reactions [6-9]. We designed anatase TiO_2 crushed nano leaf coupled by mixed-addenda vanadium-containing keggin type polyoxometalate at 100 °C via sol–gel method under oil-bath condition, as a nano catalyst for oxidative of thiols.

2. EXPERIMENTAL

2.1 Materials

All solvents and reagents used in this work are available commercially and were used as received, unless otherwise indicated. Previously reported methods were used to purify the thiols [9]. Preparation of mixed heteropolyacids and salts were based on a literature procedure with the following modifications [6, 8]. Titanium (IV) tetraisopropoxide was obtained from Merck Chemical Company. All chemicals were purchased from Merck and used without purification.

2.2 Catalyst Synthesis

2.2.1 Preparation of $TBA_7SiCr_3W_9O_{40}$

First, in 40 ml of distilled water (10 °C), $Na_9H[SiW_9O_{34}].16H_2O$, (5 g) was dissolved. An aqueous solution of $Cr(NO_3)_3.9H_2O$ was added stoichio-metrically to the above suspension.The solution was heated for 30 min on awater bath. KCl (12.5 g) was then added to thesolution. The green crystals were isolated and recrystallized in water. The potassium salt wasfiltered and washed with a dilute solution of KCl,then EtOH and Et_2O-dried, respectively. Tetrabutylammonium (TBA) salts were obtained by adding n-Bu_4NCl in solution, to the solution of $K_{10}SiCr_3W_9O_{40}$.

2.2.2 Preparation of $TBA_7SiFe_3W_9O_{40}$

In 25 ml of distilled water, $Na_9H[SiW_9O_{34}]. 16H_2O$ (6.5 g) was stirred, and an aqueous solution of $Fe(NO_3)_3.9H_2O$ (3.2 g) was added dropwise to the resulting suspension. The yellow-brown clear solution which formed was heated (30 min.) on a water-bath after adjusting the pH =4 with 1 M NaOH. The insoluble solid resulting was filtered off, and the pH of the filtrate was readjusted to4. Solid KCl was then added to the filtrate toprecipitate a yellow-brown salt, which was recrystallized thrice from a buffer solution of HOAc-NaOAc. Tetrabutylammonium (TBA) salts were obtained by adding n-Bu_4NCl in solution (pH = 2), to the solution of $K_{10}SiFe_3W_9O_{40}$.

2.2.3 Preparation of $TBA_7SiV_3W_9O_{40}$

First, in 30 ml of distilled water, sodium vanadate (0.05 g; 0.43 mmol) is dissolved. To the stirred solution is added $Na_{10}[SiW_9O_{34}].18H_2O$ (4.03 g; 1.4 mmol), followed by 20 mL of 6 M sulfuric acid. Then, for 30 min, the solution is maintained under stirring.

By addition of solid potassium carbonate, the pH is adjusted between 6 and 7. By addition of solid potassium chloride (2.2g) an orange potassium salt (2.5g) is precipitated and recrystallized in water. Tetrabutyl-ammonium (TBA) salts were obtained by adding n-Bu_4NCl in solution (pH = 2), to the solution of $K_{10}SiV_3W_9O_{40}$.

2.3 Preparation of catalyst

The TBASiW$_9$V$_3$–TiO$_2$ nanoparticle was prepared as following: First, titanium tetraisopropoxide was added into glacial acetic acid with stirring.

Next, a solution of TBA$_7$SiV$_3$W$_9$O$_{40}$ [10] 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 TBASiW$_9$V$_3$–TiO$_2$ hydro-gel was formed. Finally, the gel was filtered, washed with deionized water-acetone and dried in oven at 50 ℃ overnight (Scheme 1).
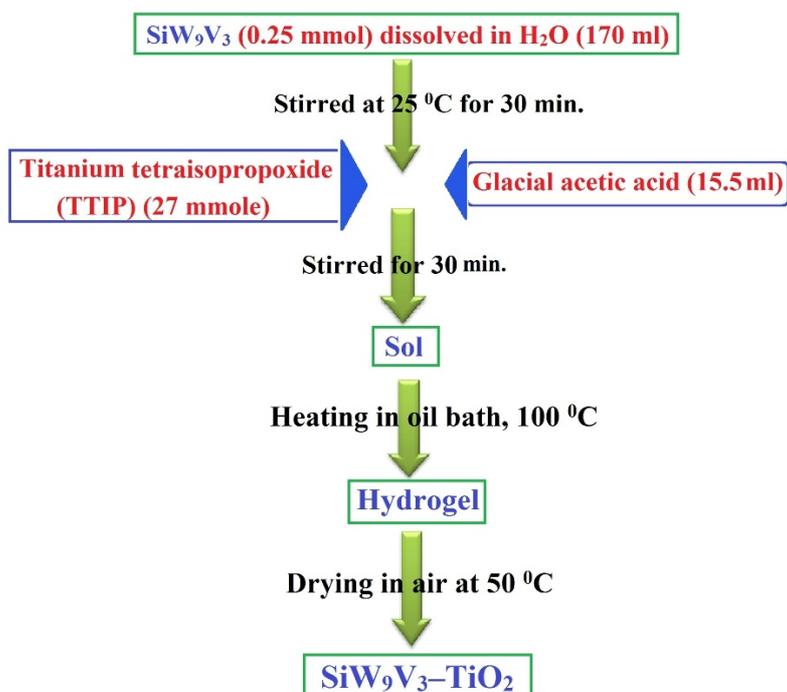
Scheme 1. Chart of synthesis of nanocatalyst.

2.4 General procedure for oxidation of thiols

The TBA$_7$SiW$_9$V$_3$–TiO$_2$ (0.3 g, 0.1 mmol) was dissolved in the mixture of 17 ml of ethanol and 3 ml of H$_2$O. The substrate, (thiol) (4 mmol) and 5 mL H$_2$O$_2$ were added to solution. The reaction mixture was stirred at room temperature until thin layer chromatography, TLC, indicated the reaction was complete. The solvent was then removed and the resulting residue was then washed with CH$_2$Cl$_2$. After completion of the reaction, the solid product was filtered off and recrystallized. The products were isolated and identified by comparison of their physical and spectral data with authentic samples prepared according to a previous method [12].

2.5 General procedure for oxidation of dithiols to cyclic disulfides

TBA$_7$SiW$_9$V$_3$–TiO$_2$ (1.5 g, 0.5 mmol) was dissolved in the mixture of 26 ml of ethanol and 4 ml of H$_2$O in a small beaker. Then dithiol (4 ml, 40 mmol) and H$_2$O$_2$ (10 ml, 330 mmol) was added. The reaction mixture was stirred at room temperature until TLC indicated the reaction was complete. The solvent was then removed and the resulting residue (white precipitate) was then washed with CH$_2$Cl$_2$.

2.6 Characterization methods

By a D8 Bruker Advanced, X-ray diffractometer using Cu Kα radiation (α=1.54 A), X-ray diffraction (XRD) patterns were recorded. The patterns were collected in the range 2θ = 20–70° and continuous scan mode. On a Philips CM10 transmission electron microscope with an accelerating voltage of 100 kV, transmission electron microscope (TEM) images were obtained. 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.

3. RESULTS AND DISCUSSION

3.1 Characterization of synthesized nano-catalysts

As distinct from other M-O vibrations, the antisymmetricstretching between terminal oxygen (unsharedoxygen) and tungsten [υ_{as}(W-O$_a$)] is a pure stretchingvibration mode. Its frequency increases as the cation-size increases, show that the W-O$_a$ distance shortens with theincrease in cation-size. In the K$_7$SiW$_9$M$_3$,theantisymmetric vibrational frequences, between tungstenatoms and corner-sharing oxygen atoms linking the twoW$_3$O$_{13}$groups [υ_{as} (W--O$_b$--W)], shift to higher wavenumberas the cation-size increases. The [υ_{as} (W--O$_b$--W)], of the intergroup bridging oxygen atoms is related to theW--O$_b$--W angle; the bigger the cations, the larger theangle. As the cation-size increases, the tungsten and edgesharingoxygen vibrations in the W$_3$O$_{13}$ group decreaseto some extent, showing that the W-O$_c$-W angle decrease. In the tetrabutylammonium (TBA) salts of the Keggin-type polyoxotungstates [SiW$_9$M$_3$O$_{39}$], M = V^{II}, Cr^{II}, Mn^{II}, Fe^{II} Co^{II} and Ni^{II}), the vibrational frequences of the SiO$_4$ tetrahedron increase as cation-size increases. The main IR spectral bands are characteristic of the Keggin structure. It was confirmed that the various salts of SiW$_9$M$_3$ have an identical Keggin structure. The band at ~960 cm^{-1}, the broader band at ~ 900 cm^{-1}, and the very broad band at ~ 800 cm^{-1}were assigned to the vibrations ofW-O$_d$, Si-O$_a$, overlapping of corner-sharing octahedral W-O-W, and edge-sharing octahedral W-O-W, respectively. The main vibrational frequencies increased with the cation-size increase (Figure 2).
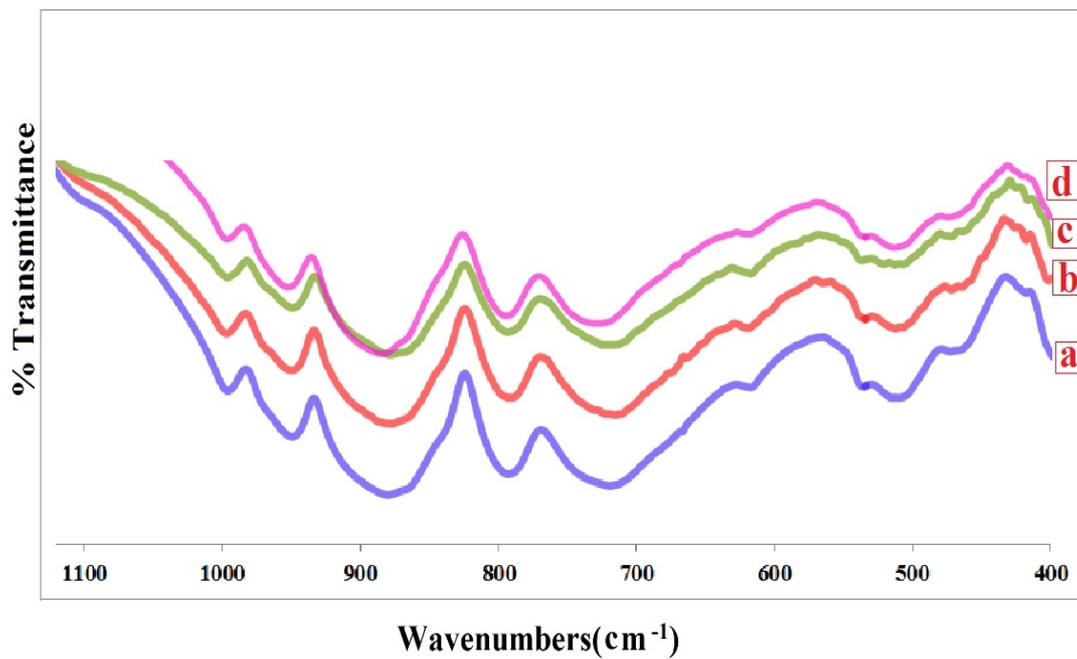
Fig 2: IR spectra of **(a)** $TBA_7SiV_3W_9O_{40}$ **(b)** $TBA_7SiV_3W_9O_{40}$-TiO_2**(c)** $TBA_7SiFe_3W_9O_{40}$ **(d)** $TBA_7SiCr_3W_9O_{40}$.

XRD patterns of $TBA_7SiV_3W_9O_{40}$-TiO_2,$TBA_7SiV_3W_9O_{40}$, $TBA_7SiFe_3W_9O_{40}$, $TBA_7SiCr_3W_9O_{40}$, $TBA_7SiNi_3W_9O_{40}$ and TiO_2 are shown in Figure 3. 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 $TBA_7SiV_3W_9O_{40}$ is bound to the TiO_2 surface, $TBA_7SiV_3W_9O_{40}$-TiO_2, approximately all of signals corresponding to $TBA_7SiV_3W_9O_{40}$ is disappeared (Figure 3(f)) and the final pattern matched to fully anatase phase of TiO_2 (JCPDS No. 21-1272), which is most likely due to $TBA_7SiV_3W_9O_{40}$ 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.
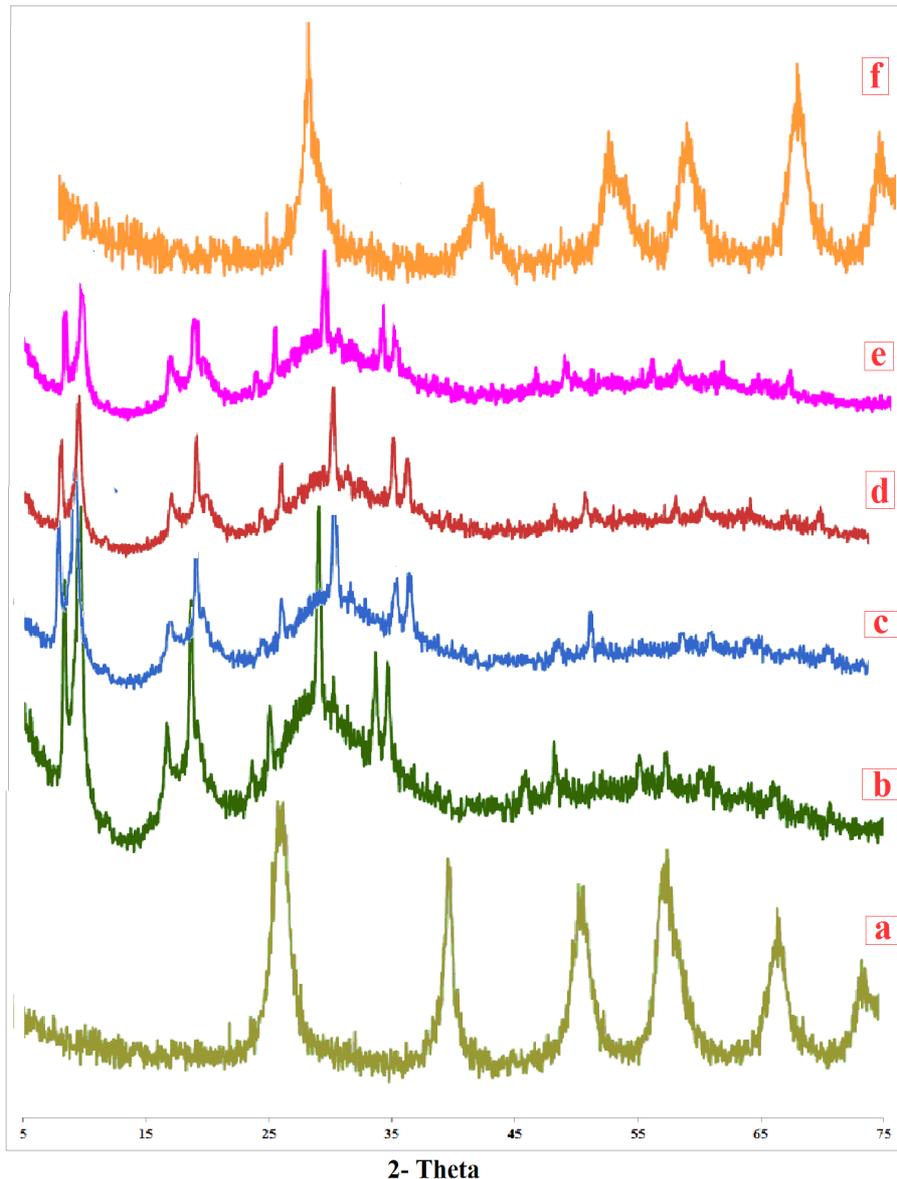
Fig. 3. XRD pattern of (**a**) TiO_2, (**b**) $TBA_7SiV_3W_9O_{40}$, (**c**) $TBA_7SiFe_3W_9O_{40}$, (**d**) $TBA_7SiCr_3W_9O_{40}$, (**e**) $TBA_7SiMn_3W_9O_{40}$ and (**f**)$TBA_7SiV_3W_9O_{40}$-TiO_2.

The UV spectra were characteristic of 12-heteropoly tungstosilicate anions with Keggin structure and were assigned to O → W charge-transfer bands. In the heteropolyanion Fe^{3+} is located in an octahedral field and has a high-spin d^5 configuration. The d-d transition is both spin and orbital forbidden and hence very weak. In $(K_7SiW_9Fe_3)$ at 267 cm^{-1}, an intense absorption band is characteristic of the 9-heteropoly tungstosilicate anion. For $K_7SiW_9Cr_3$, an intense absorption band at 250 nm was observed. It was assigned as d-d transition arising from the d^3 configuration in a near-octahedral crystal field. UV-vis spectra of $TBA_7SiV_3W_9O_{40}$-TiO_2 nanocomposite, $TBA_7SiV_3W_9O_{40}$ and TiO_2 are shown in (Figure 4). UV-vis spectra showed broad and strong absorption in range of 200-400 nm for $TBA_7SiV_3W_9O_{40}$-TiO_2 crystallite, which was different from original $TBA_7SiV_3W_9O_{40}$ and anatase TiO_2. The $TBA_7SiV_3W_9O_{40}$-TiO_2 nanocomposite shows a red shift compared with the parent anatase, and a blue shift

compared with $TBA_7SiV_3W_9O_{40}$. The inset of the figure shows the UV-vis spectrum of the $TBA_7SiV_3W_9O_{40}$-TiO_2 indicating there is one peak around 320 nm. The above UV–vis results indicate that introduction of $TBA_7SiV_3W_9O_{40}$ into TiO_2 framework has an influence on coordination environment of TiO_2 crystalline [11]. In ultraviolet light regions, which are shorter than 340 nm, pure nano TiO_2 whose band gap energy equivalent to around 335nm (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) [11].
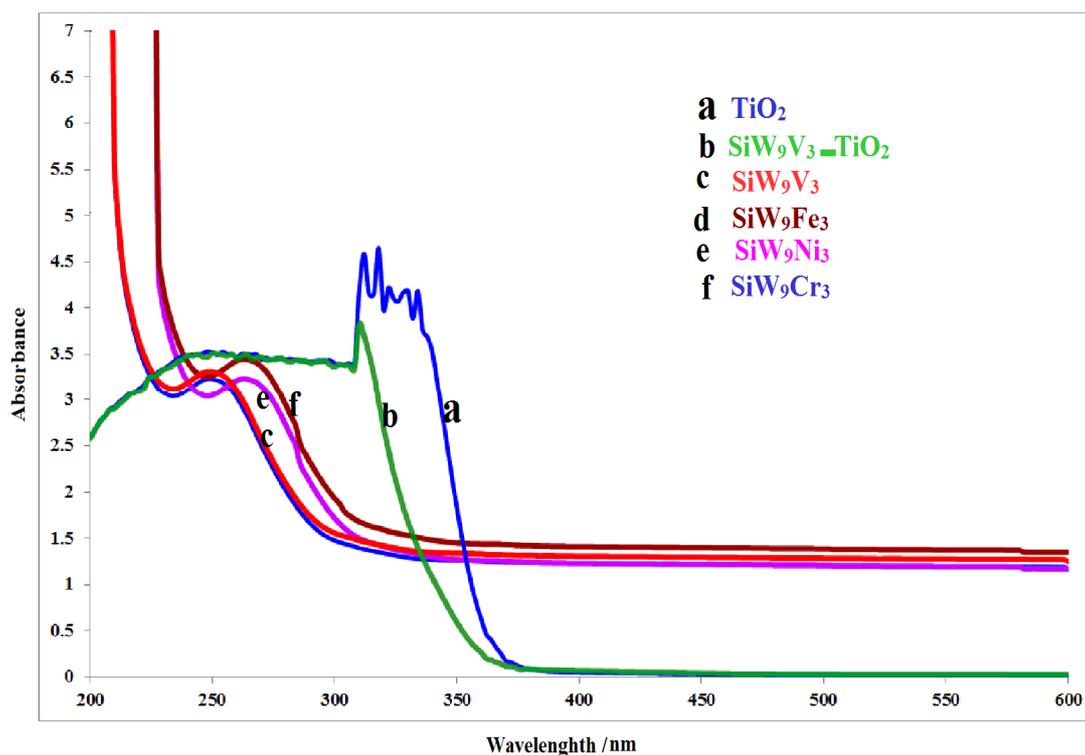

Fig. 4. UV-vis spectra of obtained catalysts.

3.2 Effects of the catalyst structure

In this article we focused on the discovery of other transition metal substituted silicotungstate structures with a potential for homogeneous and heterogeneous oxidation catalysis. We focused on red/ox active 3d metals (e.g. Fe^{2+}, Cr^{2+}, V^{2+} and Ni^{2+}). Transition-metal-substituted (TMS) polyoxo-metalates of the general formula $[SiW_9M_3O_{40}]$, where (M = first row transition metal), has been synthesized and comparative catalytic activity of them. The tetrabutylammonium (TBA) salts of the Keggin-type polyoxo-tungstates $[SiW_9M_3O_{40}]$, M = V^{II}, Cr^{II}, Mn^{II}, Fe^{II} Co^{II} and Ni^{II}), proved to be green, reusable, and highly efficient catalysts for the oxidation of thiols and dithiols into the corresponding disulfides using hydrogen peroxide as an oxidizing reagent. Table 1 was shown effect of catalyst on oxidation of thiols by H_2O_2. 4-chlorothiophenol was taken as a model compound. The TBA_7Si-$V_3W_9O_{40}$-TiO_2 nanoparticle was very active catalyst system for

oxidative of thiols, while other polyoxometalates systems were much less active. The amount of each catalyst was constant throughout the series. The Keggin-type polyoxometalates led to more effective reactions in comparison with the Wells–Dawson type polyoxometalates [12, 13].

Table 1. Effect of different catalyst in Oxidation of 4-Chlorothiophenol[a]

Entry	Catalyst	Time (min)	Temperature (^{o}C)	Yield (%)
1	$TBA_7SiV_3W_9O_{40}\text{-}TiO_2$	15	25	98
2	$TBA_7SiV_3W_9O_{40}$	20	25	94
3	$TBA_7SiFe_3W_9O_{40}$	20	25	94
4	$TBA_7SiCr_3W_9O_{40}$	20	25	93
5	$TBA_7SiMn_3W_9O_{40}$	20	25	92
6	$TBA_7SiCo_3W_9O_{40}$	20	25	91
7	$TBA_7SiNi_3W_9O_{40}$	20	25	91
8	$Na_4SiW_{12}O_{40}$	25	30	85
9	$Na_3PMo_{12}O_{40}$	25	30	84
10	$Na_3PW_{12}O_{40}$	25	30	83
11	$Na_6P_2Mo_{18}O_{62}$	25	30	79
12	$Na_6P_2W_{18}O_{62}$	30	30	78

[a] Condition for oxidation: 4 mmol substrate, 5 ml H_2O_2 as an oxidant, 1.0 mmol catalyst, 20 ml solvent 25 ml CH_2Cl_2 as an extraction solvent.

3.3 Effect of temperature
The reaction was carried out at different temperatures under the same conditions by $TBA_7SiV_3W_9O_{40}\text{-}TiO_2$ as a nanocatalysts and H_2O_2 system. 4-chlorothiophenol was taken as a model compound. The results are shown in Table 1, 2.

Table 2. Oxidation of dithiols using $TBA_7SiV_3W_9O_{40}$-TiO_2 and $TBA_7SiV_3W_9O_{40}$ as catalysts

	Catalyst ($TBA_7SiV_3W_9O_{40}$)					NanoCatalyst ($TBA_7SiV_3W_9O_{40}$-TiO_2)		
Entry	Yield %	Conversion %	Time (min.)	Substrate	Product	Time (min.)	Conversion %	Yield %
1	92	94	30	1,2-Dithiolane	1,3-Propanedithiol	20	99	98
2	91	93	30	1,2-Dithiane	1,4-Butanedithiol	30	98	96
3	93	94	40	1,2-Dithiepane	1,5-Pentanedithiol	30	97	96
4	95	97	40	1,2-Dithiacyclooctane	1,6-Hexanedithiol	20	99	98
5	90	93	40	1,2-Dithiacyclodecane	1,8-Octanedithiol	20	96	95

The results in Table 3 showed that yields of products are a function of temperature. The results show that yield increased as the reaction temperature was raised. Table 2 and 3 show % conversion of model compound increased as the temperature and time raised. In Table 4, % conversion of 1, 8-Octanedithiol at 60 ºC is higher than that at 50 ºC. 98% conversion of 1, 8-Octanedithiol ($SHCH_2(CH_2)_6CH_2SH$) was obtained at 60 ºC. The catalytic activities of the $TBA_7SiV_3W_9O_{40}$-TiO_2 nanocatalysts in the oxidation of 1, 8-octanedithiol at different temperatures, 10 - 60 °C were compared.

Table 3. Effect of temperature on oxidation of different thiol and dithiol using $TBA_7SiV_3W_9O_{40}$-TiO_2 catalyst [a]

Entry	Temperature (°C)	Conversion %				
		4-florothiophenol	4-methylethiophenol	1,2-Dithiolane	1,2-Dithiane	1,2-Dithiacyclodecane
1	10	55	46	44	36	31
2	20	79	79	75	60	52
3	30	91	98	89	76	66
4	40	92	--	98	89	74
5	50	--	--	--	96	87
6	60	--	--	--		95

[a] Condition for oxidation: 4 mmol substrate, 5 ml H_2O_2 as an oxidant, 1.0 mmol catalyst, 20 ml solvent 25 ml CH_2Cl_2 as an extraction solvent.

Table 4. Oxidation of thiols with different substituents by $TBA_7SiV_3W_9O_{40}$-TiO_2 as catalyst with H_2O_2 as oxidant

Entry	Dithiol	Cyclic Disulfide	Disulfide	Time (min)	Temperature (°C)	Yield (%)[a]
1	1,3-Propanedithiol ($SHCH_2CH_2CH_2SH$)	1,2-Dithiolane		20	40	98
2	1,4-Butanedithiol ($SHCH_2CH_2CH_2CH_2SH$)	1,2-Dithiane		30	50	96
3	1,5-Pentanedithiol ($SHCH_2CH_2CH_2CH_2CH_2SH$)	1,2-Dithiepane		30	50	96
4	1,6-Hexanedithiol ($SHCH_2(CH_2)_4CH_2SH$)	1,2-Dithiacyclooctane		20	30	98
5	1,8-Octanedithiol ($SHCH_2(CH_2)_6CH_2SH$)	1,2-Dithiacyclodecane		20	60	95

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

3.4 Effect of dithiols substituent

The effects of various substituents on the yields of produced cyclic disulfides have been examined in the presence of $TBA_7SiV_3W_9O_{40}$-TiO_2 catalyst. The structural formulas of different dithiols are shown in Table 4. The first of dithiols was oxidized with great speed than others. The most notable feature is that we have been able to apply this procedure successfully in the oxidation of dithiols to cyclic disulfides. Large ring disulfides are difficult tosynthesize due to competing intermolecular reaction.

3.5 Recycling of the catalyst

At the end of the oxidation of thiols to disulfides, 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. All products are soluble in dichloromethane but the catalyst is not. Thus, it could be separated by a simple filtration and washed with dichloromethane and dried at 90 °C for 1 h, and reused in another reaction with the same substrate. Even after five runs for the reaction, the catalytic activity of $TBA_7SiV_3W_9O_{40}$ was almost the same as that freshly used catalyst. The results are summarized in Table 5.

Table5. Reuse of the catalyst for oxidation of 4-Chlorothiophenol (Table 2, entry 4)

Entry	Isolated yield (%)
1	96
2	94
3	94
4	92
5	91

4. CONCLUSION

The $TBA_7SiV_3W_9O_{40}$-TiO_2 nanoarticle was very active catalyst system for the models compound oxidation, while unmodified $TBA_7SiV_3W_9O_{40}$ showed much lower activity. This TiO_2/ poly-oxometalates/H_2O_2 system provides an efficient, convenient and practical method for the syntheses of symmetrical disulfides.

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