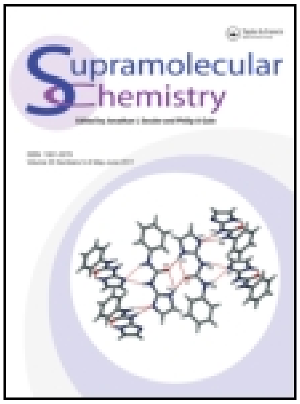
This article was downloaded by: [Moskow State Univ Bibliote]
On: 20 February 2014, At: 03:57
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gsch20

Synthesis, characterisation and catalytic activity of non-crystalline organic-inorganic hybrid material comprising Keggin-type manganese(II)-substituted phosphotungstate and salen

Ketan Patel [a] , Pragati Shringarpure [a] & Anjali Patel [a]
[a] Chemistry Department , Faculty of Science, M.S. University of Baroda , Vadodara , 390 002 , India

Published online: 02 Dec 2011.

To cite this article: Ketan Patel , Pragati Shringarpure & Anjali Patel (2012) Synthesis, characterisation and catalytic activity of non-crystalline organic-inorganic hybrid material comprising Keggin-type manganese(II)-substituted phosphotungstate and salen, Supramolecular Chemistry, 24:3, 149-156, DOI: 10.1080/10610278.2011.636445

To link to this article: http://dx.doi.org/10.1080/10610278.2011.636445

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Supramolecular Chemistry
Vol. 24, No. 3, March 2012, 149–156

Synthesis, characterisation and catalytic activity of non-crystalline organic–inorganic hybrid material comprising Keggin-type manganese(II)-substituted phosphotungstate and salen

Ketan Patel, Pragati Shringarpure and Anjali Patel*

Chemistry Department, Faculty of Science, M.S. University of Baroda, Vadodara 390 002, India

(*Received 25 May 2011; final version received 24 October 2011*)

A new inorganic–organic hybrid material comprising Keggin-type mono manganese-substituted phosphotungstate and salen was synthesised. The synthesised hybrid material was systematically characterised by various physicochemical techniques such as elemental analysis, thermal gravimetric analysis, FT-IR, UV–vis, electron spin resonane, ^{1}H NMR, ^{13}C MAS NMR and ^{31}P NMR. The catalytic activity was evaluated for non-solvent liquid phase oxidation of styrene using O_2. The novelty of the present work lies in obtaining 42% conversion with 41% selectivity for styrene oxide with O_2 under solvent-free mild reaction conditions only in 4 h.

Keywords: Keggin; polyoxometalates; manganese-substituted phosphotungstate; hybrid material; oxidation; catalysis

1. Introduction

Polyoxometalates (POMs) are inorganic and discrete multimetal clusters that have found applications in catalysis, material sciences and medicine (*1–7*). Their properties may be modified depending on the elemental composition, structure and counteractions (*1*). In addition, the presence of organic substituents anchored on the POM surface offers the possibility to tune the electronic features of the resulting complexes, as well as their solubility, reactivity and hydrolytic stability (*4, 8, 9*). The merging of organic and inorganic domains is a developing field of investigation focusing on the design of new hybrid materials (*10*). In this respect, surface-appended organic moieties carrying suitable functional groups are introduced to foster the extended organisation of the POM molecular units (*7, 11, 12*). This strategy was successfully employed to obtain polymerisable (*13*), dendrimeric (*14*) and supramolecular derivatives (*15, 16*).

The development of organic–inorganic hybrid materials remains a challenge and is an emerging field. The organic–inorganic hybrid materials are categorised into two classes. Those formed due to the non-covalent interactions involving hydrogen bonds or van der Waals interactions form the class I type; those involving strong covalent or iono-covalent bonds form the class II type of compounds (*1d*).

The synthesis of hybrid materials can result in the formation of non-crystalline or crystalline materials that are isolated under mild conditions, following the room temperature synthesis or under hydrothermal conditions. In the field of catalysis, the study of organic–inorganic hybrids with POMs can lead to the development of more efficient recyclable multifunctional catalysts.

Recently, Wang et al. reported organic–inorganic hybrid aggregates based on Anderson-type POMs and metal – schiff base (*2c*). To the best of our knowledge, only one research article involving quaternary ammonium salt of Keggin-type silicotungstate and metallosalen has been reported (*17*). The catalytic activity has also been evaluated for hybrid compounds involving metallosalen and silicotungstates (*18*). Thus, most of the work has been reported on silicotungstates, and studies on the phosphotungstates are very scarce. Moreover, it has also been observed that no literature is available on the catalytic aspects of hybrid compounds comprising phosphotungstates and metallosalen.

Recently, we have reported one pot synthesis of manganese(II)-substituted phosphotungstate and its catalytic activity towards liquid phase aerobic oxidation of styrene (*19*). It is known that the functionalisation of POM can lead to the formation of new hybrid material with an improved catalytic activity. It appears to be of interest to functionalise the Mn(II)-substituted phosphotungstate with an organic ligand, like salen, which would result in interesting catalytic properties.

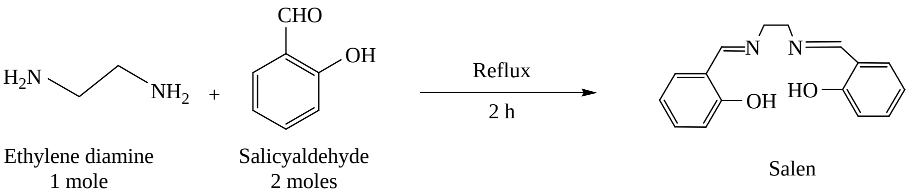
In the present paper, an attempt was made to synthesise a new non-crystalline organic–inorganic hybrid material, of class I type, comprising Keggin-type manganese-substituted phosphotungstate and salen. The synthesised hybrid compound was systematically characterised by elemental analysis, thermal gravimetric analysis (TGA), FT-IR, UV–vis, electron spin resonance (ESR), multinuclear NMR (^{1}H, ^{13}C MAS and ^{31}P NMR). The catalytic

---

*Corresponding author. Email: aupatel_chem@yahoo.com

ISSN 1061-0278 print/ISSN 1029-0478 online

http://dx.doi.org/10.1080/10610278.2011.636445
http://www.tandfonline.com



Scheme 1. Synthesis of salen.

activity of the synthesised complex was evaluated for non-solvent liquid phase oxidation of styrene using molecular oxygen.

2. Experimental section

2.1 Materials

All chemicals used were of A.R. grade. Sodium tungstate dihydrate, disodium hydrogen phosphate, sodium hydroxide, $MnCl_2{\cdot}4H_2O$, caesium chloride, acetone, ethylene diamine, salicyaldehdyde and styrene were obtained from Merck (Bombay, India).

2.2 Synthesis of salen

The salen ligand (Schiff base) was synthesised followed by the reported method (*20*), by refluxing the ethanolic solution of the ethylenediamine and salicylaldehyde for 1 h. The isolated yellow solid was designated as S (Scheme 1).

2.3 Synthesis of inorganic–organic hybrid material

The synthesis of the hybrid material was carried out as shown in Scheme 2. The $PW_{11}MnO_{39}$ was synthesised by using the method as reported by us (*19*). The caesium salt of $PW_{11}MnO_{39}$ (0.8985 g, 0.04 mmol) was dissolved in a minimum amount of water, and S (0.067 g, 0.04 mmol) was dissolved in a minimum amount of absolute alcohol. The alcoholic solution of S was added dropwise to the aqueous solution of $PW_{11}MnO_{39}$. The resultant mixture was refluxed for 10 h with constant stirring, filtered to obtain pale yellow powder. The isolated material was washed with water as well as ethanol and dried at room temperature (35–40°C). The obtained hybrid material (yield 0.88 g) was designated as $PW_{11}MnO_{39}$–S.

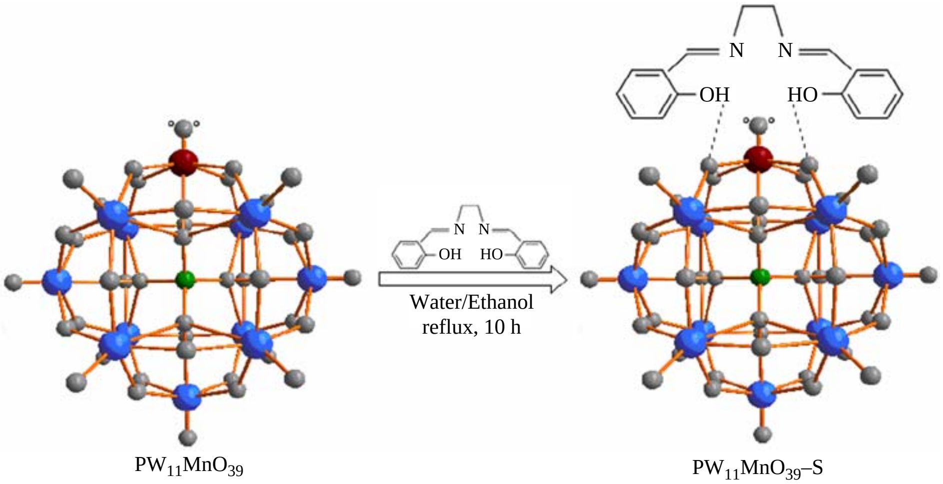
The values of elemental analysis data for $PW_{11}Mn$–S are in good agreement with the theoretical values. Anal. calcd: Cs, 14.32; W, 54.50; P, 0.84; Mn, 1.48; O, 21.98; C, 5.1; H, 0.43; N, 0.75. Found: Cs, 14.28; W, 54.45; P, 0.81; Mn, 1.47; O, 21.49; C, 5.0; H, 0.43; N, 0.74.

2.4 Synthesis of manganese(III) salen

The Mn(III) salen was synthesised by the method reported by Freire et al. (*20*). The observed values for *S* are in good agreement with the theoretical values. Anal. calcd: C, 71.64; H, 5.97; N, 10.44. Found: C, 71.53; H, 5.94; N, 10.40.

2.5 Synthesis of physical mixture of $PW_{11}MnO_{39}$ and salen

The physical mixture was synthesised by mixing equimolar amount of $PW_{11}MnO_{39}$ and salen. Salen



Scheme 2. Synthesis of $PW_{11}MnO_{39}$–S.

(0.067 g, 0.04 mmol) and the caesium salt of $PW_{11}MnO_{39}$ (0.8985 g, 0.04 mmol) were mixed and grinded properly in a mortar and pestle till it becomes homogeneous in nature. The obtained mixture was designated as $PW_{11}Mn+S$.

2.6 Characterisation

Elemental analysis was carried out using JSM 5610 LV combined with INCA instrument for EDX-SEM analyser for the quantitative identification of metal ions. C, H and N analyses were carried out using PerkinElmer 2400. The total weight loss was calculated by the TGA method on the Mettler Toledo Star SW 7.01 upto 600°C. FT-IR spectra of the samples were recorded as the KBr pellet on the PerkinElmer instrument. The UV–visible spectrum was recorded at an ambient temperature on PerkinElmer 35 LAMDA instrument using the 1 cm quartz cell. The ESR spectra was recorded on a Varian E-line Century series X-band ESR spectrometer (liquid nitrogen temperature and scanned from 2000 to 3200 Gauss). ^1H solution NMR was recorded in DMSO on Varian Mercury plus 300 instruments. ^{13}C MAS NMR was recorded on Bruker DSX 300 MHz instrument. ^{31}P solution NMR was recorded in D_2O on Bruker ACF 300 MHz instrument.

2.7 Catalytic activity

The catalytic activity was evaluated for the oxidation of styrene using molecular oxygen as oxidant and tert-butyl hydro peroxide (TBHP) as co-oxidant. Oxidation reaction was carried out in a batch-type reactor operated under atmospheric pressure. In a typical reaction, a measured amount of catalyst was added to a three-necked flask containing styrene and initiator TBHP (0.2 ml) at 80°C. The reaction was started by bubbling O_2 into the liquid with constant stirring on magnetic plate. The reaction was carried out by varying different parameters such as the amount of the catalyst and reaction time. After completion of the reaction, the liquid product was extracted with dichloromethane, dried with magnesium sulphate and analysed on a gas chromatograph (Nucon 5700 model) having a flame ionisation detector and an SE-30 packed column (2 m length and 10% silica-based stationary phase). Product identification was done by comparison with authentic samples and finally by a combined gas chromatography mass spectrometer (Hewlett Packard) using an HP-1 capillary column (30 m, 0.5 mm ID) with EI (70 eV).

3. Results and discussion

The number of water molecules calculated from TGA curve shows 4.6% weight loss corresponding to loss of 10 water molecules. From the elemental as well as the thermal techniques, the chemical formula of the isolated hybrid material is proposed as $Cs_5[PW_{11}O_{39}Mn(H_2O)]\cdot 9H_2O-(S)$ ($PW_{11}MnO_{39}-S$).

The FT-IR stretching vibration for S, $PW_{11}MnO_{39}$ and $PW_{11}MnO_{39}-S$ are presented in Table S1 (Supplementary Information, available online). $PW_{11}MnO_{39}$ shows stretching vibration at 1078, 1053, 956, 882 and 820 cm^{-1} corresponding to P—O, W═O and W—O—W (*21–23*). The $\Delta\upsilon$ difference of P—O stretching is 24 cm^{-1}, which is the typical $\Delta\upsilon$ split value for Mn-substituted phosphotungstate, indicating the presence of Mn in the octahedral environment (*19, 22, 23*). The FT-IR spectrum of $PW_{11}MnO_{39}-S$ shows that all the stretching vibrations correspond to P—O, W═O and W—O—W without any significant shift except in the W—O—W bridges. These was a slight shift from 820 to 813 cm^{-1} observed in case of $PW_{11}MnO_{39}-S$.

In addition to these vibrations, FT-IR spectrum can be helpful in obtaining structural information concerning the organic groups. A pair of the weak peaks at 1496 and 1460 cm^{-1} was obtained for S and $PW_{11}MnO_{39}-S$, which is attributed to both symmetric- and asymmetric-stretching vibrations of aliphatic C—H bonds. Furthermore, the stretching vibration of $PW_{11}MnO_{39}-S$ for C—N, C═N and aliphatic as well as for aromatic CH_2 region can also be observed. The results ensure a successful functionalisation of $PW_{11}MnO_{39}$ with salen. At the same time it has also been observed that there is a shift in the peak position from 1525 to 1545 cm^{-1} corresponding to the C—O stretching vibration. This interesting observation indicates some interaction of salen with the $PW_{11}MnO_{39}$. It is well known that the POMs is polydentate ligand with high negative charge, which may be favoured by the formation of hydrogen bond. Hence, in the present case, it may be possible that the salen ligand gets bind to the large cluster of POMs *via* hydrogen bond.

The UV–vis spectra of Mn(III)-salen (MnS) and $PW_{11}MnO_{39}-S$ are shown in Figures 1 and 2. It is well known that metalation of salen ligand with Mn(II) yields the corresponding MnS complex distinctly identified by UV–vis as well as by colour (brown) (*18*). As seen from the UV–vis spectra for MnS (Figure 1), two absorption bands were observed at 500 and 420 nm corresponding to the typical d–d transition band for MnS complex, indicating the presence of Mn(III) in the square pyramidal environment/geometry. Whereas the UV–vis spectrum for $PW_{11}MnO_{39}-S$ (Figure 2) shows two absorption bands, one strong at 291 nm corresponding to the $[PW_{11}O_{39}]^{7-}$ species. The other broad and weak absorption band at around 393 nm, associated with d–d transition, which is a typical value for Mn(II). The absence of any absorption bands at 420 and 500 nm, which is the typical region for MnS complex, indicates that salen moiety is not covalently coordinated to the Mn centre. The presence of Mn(II) species was further confirmed by ESR spectroscopy.

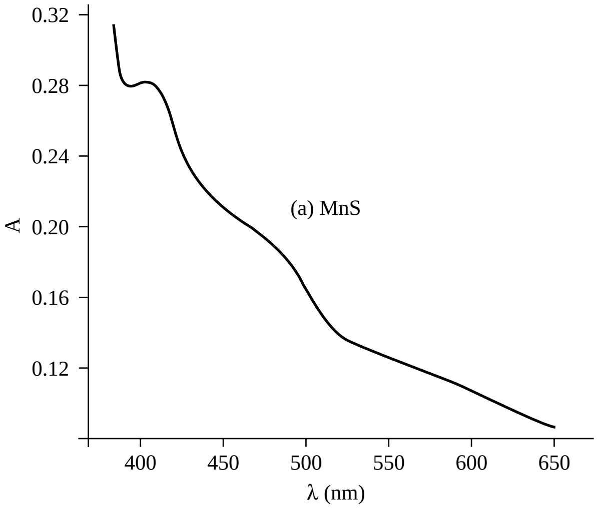


Figure 1. UV–vis spectra of MnS.

Paramagnetic compounds have different relaxation times. If the electronic relaxation is slow, good ESR spectra can be obtained at room temperature while, if the electronic relaxation is fast, good ESR spectra can be obtained only at low temperature. Mn(III)-salen compounds are known to be ESR silent in the normal X-band mode but absorb at $g = 8$ in the high-field ESR spectroscopy (*18*). If salen is covalently coordinated to Mn, ESR is expected to be silent. However, a well resolved six line hyperfine spectrum for $PW_{11}MnO_{39}$–S indicating the presence of Mn (II) species.

Thus UV–vis and ESR studies indicate the presence of salen in the synthesised material and support the observation drawn from FT-IR, i.e. the formation of the hydrogen bond.

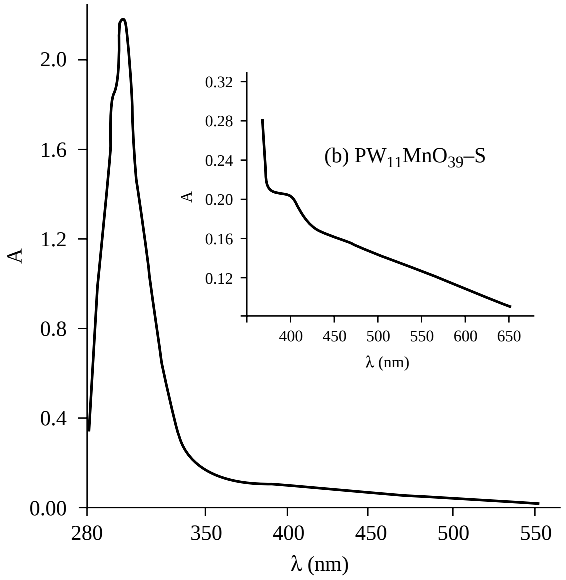


Figure 2. UV–vis spectra of $PW_{11}MnO_{39}$–S.

Table 1. ^{13}C MAS NMR chemical shifts for $PW_{11}MnO_{39}$–S and S.

	Chemical shift (ppm)	
Functional group	S	$PW_{11}MnO_{39}$–S
CH_2 (bridge carbon)	54.81	57.82
CH_2 (ring carbon)	121.53	116.22
	124.4	119.20
	135.08	130.84
C—O	171.52	161.91
C═N	166.51	165.91

3.1 *Magnetic spectroscopy*

It is known that the presence of paramagnetic metal centre generally results in a poorly defined NMR spectrum. As mentioned earlier, for paramagnetic compounds electronic relaxation is fast, good ESR spectrum cannot be obtained at room temperature, while good NMR spectrum can be obtained at room temperature.

In order to study the interaction between $PW_{11}MnO_{39}$ species and the salen moiety, solution (^1H and ^{31}P) and solid (^{13}C) NMR spectra were recorded. The ^1H NMR spectrum of $PW_{11}MnO_{39}$–S and S was recorded in D_2O and $CDCl_3$ respectively. The chemical shifts for all protons of the organic moiety (i.e. salen) in $PW_{11}MnO_{39}$–S did not show any significant shift as compared to S. However, broadening of the signal in case of $PW_{11}MnO_{39}$–S is observed. If the Mn centre forms the covalent bond with the salen moiety, significant chemical shift is expected. The absence of any shift in the signals indicate that S is not coordinate to Mn but is present in the chemical environment of $PW_{11}MnO_{39}$ as an individual moiety.

The chemical shift of the ^{13}C MAS NMR values for S and $PW_{11}MnO_{39}$–S is presented in Table 1. As shown in Table 2, the ring C atoms (—CH_2—) as well as C—OH were significantly shielded and appeared upfield with respect to the salen moiety. A very significant shifting from +171.5 to +161.9 ppm can be attributed to the shift

Table 2. Effect of amount of $PW_{11}MnO_{39}$–S on oxidation of styrene.

		Selectivity (%)	
Amount of catalyst (mg)	Conversion (%)	BA	StyO
15	15	60	40
25	42	59	41
50	46	84	16
75	49	89	11
100	52	93	7
200	55	91	9

Note: Styrene, 100 mmol; oxidant, O_2 (1 atm); TBHP, 0.15 mmol; reaction time, 4 h; temperature, 80°C.

of the electron density from O—H of salen to the bridging O of $PW_{11}MnO_{39}$. It is known that for transition metal-substituted POMs, the bridging O atom is expected to generate basic sites (*1*) and as a consequence they attract the protonated species towards them.

In the present case, O—H of the S is attracted towards oxygen atoms of the $PW_{11}MnO_{39}$ and form hydrogen bond. Hence upfield shifts for the C atom of the C—OH are observed. In addition to this, NMR signal of the C=N does not show any shift from the parent value. This indicates that the N atom of the salen does not coordinate with the Mn centre of $PW_{11}MnO_{39}$.

Upon comparison of the ^1H and ^{13}C NMR spectrum of $PW_{11}MnO_{39}$–S, it was observed that the proton of the C—O—H group is not deprotonated. This observation indicates that the S moiety is not coordinated with the Mn of the $PW_{11}MnO_{39}$, but is intactly attracted towards $PW_{11}MnO_{39}$ *via* some chemical interaction.

From the above study, it may be proposed that salen is present in the complex *via* H-bonding. The H of C—O—H from salen forms hydrogen bond with the bridging O of the Mn of the $PW_{11}MnO_{39}$ without disturbing the Mn-substituted Keggin structure. The presence of intact Keggin unit is further supported by ^{31}P solution NMR (Figure 3). A strong single-line ^{31}P NMR spectrum $\delta = -13.7$ ppm was obtained. The value of -13.7 ppm is the typical region for the mono metal-substituted Keggin-type POM, indicating the presence of intact Keggin unit.

Thus spectral as well as the magnetic studies confirm the presence of strong H-bonding between S and $PW_{11}MnO_{39}$.

3.2 Catalytic activity

A detailed study on the oxidation of styrene with O_2 and TBHP (co-oxidant) was carried out to optimise conditions. A neat reaction (without catalyst) was carried out and it showed no conversion for the substrate, indicating that there is no auto-oxidation taking place.

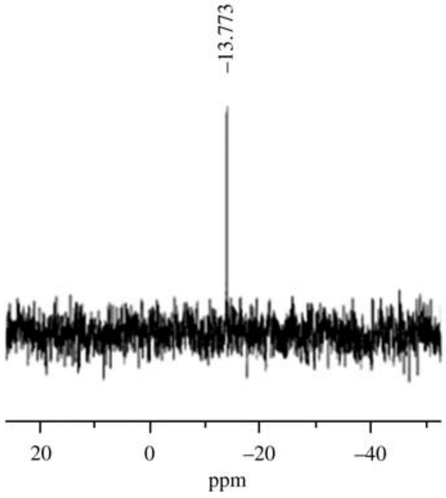


Figure 3. ^{31}P solution NMR of $PW_{11}MnO_{39}$–S.

3.3 Effect of amount of catalyst

The effect of the amount of catalyst on the conversion of styrene is represented in Table 2. It is seen from the table that the conversion increases up to 75 mg, after that it stays almost constant.

The non-polar molecules such as hydrocarbons just adsorb on the surface without entering the bulk. Thus, on further increase in the amount, there may be blocking of the active sites and thus increase in conversion is not significant. This shows that it follows the adsorption phenomenon rather than the typical pseudo-liquid behaviour. In the present catalytic system, as the concentration of the catalyst increases the number of active sites available for the reaction to progress increases which results in a difference in the selectivity of products. On further increase in the concentration of the catalyst the distribution of selectivity of products towards the more stable product (i.e. benzaldehyde, BA). Due to the known importance of epoxide, the amount of the catalyst was optimised at 25 mg (*24*). Furthermore, the effect of reaction time on oxidation of styrene was also studied.

3.4 Effect of reaction time

It is seen from Table 3 that with the increase in reaction time the conversion also increases. Initially, the increase in the conversion is fast, and after 16 h a slow increase in the conversion is observed. This may be due to the fact that the alkene is consumed during the reaction, as a result the amount of the reactant decreases, which then requires time to reversibly bind with the oxidant. Furthermore, the rate of desorption of the products formed from the catalyst surface is faster, as a result the overall rate of the reaction slows down resulting in a slow increase in the conversion with time (*24*).

Table 3. Effect of reaction time on oxidation of styrene over $PW_{11}MnO_{39}$–S.

		Selectivity (%)	
Reaction time (h)	Conversion (%)	BA	StyO
2	25	50	50
4	42	59	41
8	62	79	21
12	71	83	17
16	84	95	5
20	89	>99	–
24	100	>99	–

Note: Styrene, 100 mmol; oxidant, O_2 (1 atm); TBHP, 0.15 mmol; reaction time, 4 h; temperature, 80°C.

As a result the overall rate of the reaction slows down and results in a slow increase in the percentage conversion with time. The distribution of the product changes with increase in the reaction time. Initially, after the completion of 2 h, the equimolar of both products was observed. As the reaction time increases the product selectivity shifts towards BA. With an increase in the reaction time the unstable intermediate, epoxide, is converted to the more stable product BA. Due to the known industrial importance of styrene oxide, the reaction time was optimised at 4 h.

3.5 Effect of salen

Oxidation of styrene involves the formation of styrene oxide and BA. It is known that if the oxidation reaction is fast the product selectivity shifts towards the more stable product (BA) rather than the less stable intermediate (styrene oxide). While if the reaction is slow and controlled, one styrene oxide is obtained as a major product.

In order to see the effect of salen and to confirm the chemical interaction, the catalytic activity of $PW_{11}MnO_{39}$, MnS and the physical mixture ($PW_{11}Mn + S$) was evaluated for oxidation of styrene under the optimised conditions of $PW_{11}Mn{-}S$. The obtained results are represented in Table 4.

As seen from Table 4, in case of MnS, only 24% conversion with 71% selectivity for styrene oxide and 29% selectivity for BA was obtained in 4 h (Table 4). However, 61% conversion with single selective product (i.e. BA) was obtained when $PW_{11}MnO_{39}$ was used as a catalyst in 4 h. On the other hand, moderate conversion of 42% was obtained for $PW_{11}MnO_{39}{-}S$ with 41% selectivity towards styrene oxide and 59% selectivity towards BA (Table 4). The difference in the conversion as well as selectivity for the hybrid material can be explained in the basis of S. Mn(II) sites are the catalytic active sites which are responsible for effective oxidation of styrene. In case of $PW_{11}MnO_{39}{-}S$, these active sites Mn(II) are surrounded by S moiety. As a result, the Mn(II) centre becomes sterically hindered. This steric hindrance around the active metal centre leads to the partial prevention of the oxidation process. Hence, the overall reaction becomes a controlled reaction, resulting in the formation of styrene oxide.

Furthermore, the almost same conversion as well as selectivity towards BA for $PW_{11}MnO_{39}{+}S$ and $PW_{11}Mn$ indicates the presence of salen as a separate moiety. Thus, for $PW_{11}MnO_{39}{+}S$, the salen moiety is free and not attached to $PW_{11}MnO_{39}$ *via* chemical interaction, as a result the Mn(II) active sites are easily available for oxidation which results in a single selective product with almost the same percentage conversion as that of $PW_{11}MnO_{39}$.

The above data clearly indicates that the formed hydrogen-bonded molecular assembly (formed by salen and $PW_{11}MnO_{39}$) is the real active species responsible for selectivity towards styrene oxide.

As seen from Table 4, $PW_{11}MnO_{39}{-}S$ gives higher conversion as compared to MnS, while better selectivity towards epoxide than $PW_{11}MnO_{39}$. It is also observed from Table 3 that the hybrid material gives 100% conversion with single selective product in 24 h. So the present catalyst is superior as compared to MnS and $PW_{11}MnO_{39}$. Thus, there is a choice for the chemists to select the reaction, with 100% conversion and single selective product or with 42% conversion and 41% selectivity towards styrene oxide.

3.6 Test for leaching and heterogeneity

Any leaching of the active species from the support makes the catalyst unattractive and hence it is necessary to study the stability as well as leaching of $PW_{11}Mn{-}S$. The catalyst was filtered after the completion of the reaction and the filtrate was characterised for UV–vis spectroscopy. For comparison, UV–vis spectra of $PW_{11}MnO_{39}{-}S$ in water were also recorded (Figure 4). The absence of characteristic peaks in filtrate (Figure 5) indicates that there is no leaching of $PW_{11}MnO_{39}{-}S$, and the catalyst remains completely insoluble under reaction condition and could be reused.

Furthermore, for the rigorous proof of heterogeneity, a test was carried out by a filtering catalyst from the reaction mixture at 80°C after 2 h and the filtrate was allowed to

Table 4. Comparative data for oxidation of styrene using different catalysts.

Catalyst[a]	Amount of catalyst (mg)	Amount of active species, i.e. $PW_{11}Mn$ (mg)	Conversion (%)	Selectivity (%) BA	Selectivity (%) StyO
MnS	23	23	24	29	71
$PW_{11}MnO_{39}$	23	23	58	>99	
$PW_{11}MnO_{39}{-}S$	25	23	42	59	41
$PW_{11}MnO_{39}{+}S$	25	23	56	>99	

Notes: [a] Styrene, 100 mmol; oxidant, O_2 (1 atm); TBHP, 0.2 ml; reaction time, 4 h; temperature, 80°C; BA, benzaldehyde; StyO, styrene oxide.

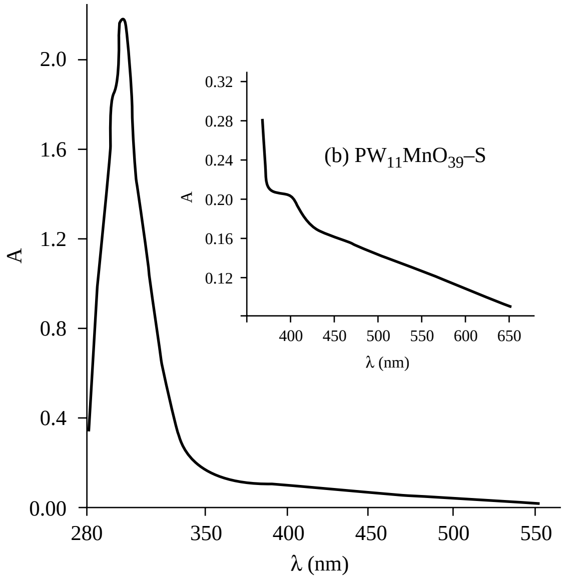


Figure 4. UV–vis spectra of $PW_{11}MnO_{39}$–S.

react up to 4 h. The reaction mixture was kept for 2 h and filtrate was analysed on gas chromatogram. No change in percentage conversion as well as percentage selectivity was found. On the basis of the results, it can be concluded that there is no leaching of the $PW_{11}MnO_{39}$–S, and the present catalysts are truly heterogeneous in nature and fall into the category C (*25*).

3.7 Regeneration and recycling

The catalyst remains insoluble in the present condition and hence can be easily separated by simple filtration followed by washing. As in present case, the amount of catalyst is very less (25 mg), hence recycling of the catalyst was not very efficient. There is difficulty in the collection of catalyst due to the loss during filtration. But if a large amount of catalyst is used, the recycling of the catalyst was significant. The recycle catalyst shows a decrease in the conversion value upto 3%, whereas the distribution of the products remains the same.

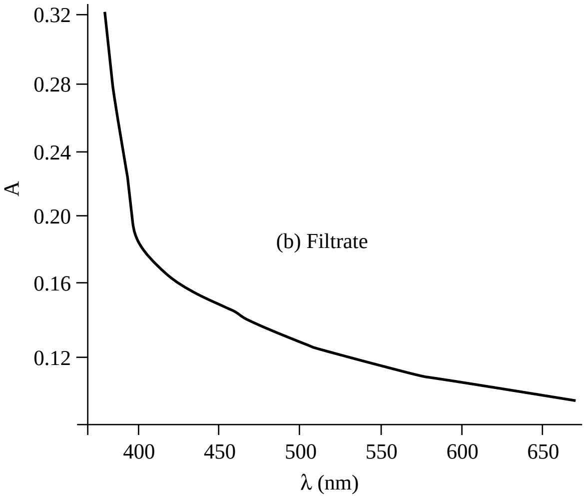


Figure 5. UV–vis spectra of filtrate.

4. Conclusions

The present paper reports synthesis of a new inorganic–organic hybrid material. Spectral and magnetic studies show that the Keggin unit retains its structure even after the introduction of S. The heterogeneous nature of the present hybrid material makes it attractive for the oxidation of styrene. The superiority of the present catalyst lies in obtaining 41% selectivity for styrene oxide using molecular oxygen in a short period of time (4 h). The catalyst was regenerated and reused up to three cycles after simple workup. The present catalyst is multifunctional.

Acknowledgements

We are thankful to Indian Institute of Science (IISc), Bangalore, for recording ^{13}C MAS NMR spectra. Mr Ketan Patel and Ms Pragati Shringarpure are thankful to Department of Science and Technology (SR/S1/IC-13/2007), New Delhi, and Council of Industrial and Scientific Research (CSIR, New Delhi) for providing financial support.

References

(1) (a) Pope, M.T.; Muller, A.; Eds.; *Polyoxometalate Chemistry from Topology via Self-Assembly to Applications*; Kluwer Academic Publishers: Dordrecht, 2001; (b) Borrás-Almenar, J.J.; Coronado, E.; Müller, A.; Pope, M.T.; *Polyoxometalate Molecular Science*; Kluwer Academic Publishers: Dordrecht, 2003; (c) Long, D.L.; Burkholder, E.; Cronin, L. *Chem. Soc. Rev.* **2007**, *36*, 105–121; (d) Dolbecq, A.; Dumas, E.; Mayer, C.R.; Mialane, P. *Chem. Rev.* **2011**, *110*, 6009–6048.

(2) (a) Kamata, K.; Yonehara, K.; Sumida, Y.; Yamaguchi, K.; Hikichi, S.; Mizuno, N. *Science* **2003**, *300*, 964–966; (b) Sartorel, A.; Carraro, M.; Bagno, A.; Scorrano, G.; Bonchio, M. *Angew. Chem. Int. Ed.* **2007**, *46*, 3255–3258; (c) Wu, Q.; Chen, W.L.; Liu, D.; Liang, C.; Li, Y.G.; Lin, S.W.; Wang, E. *Dalton Trans.* **2011**, *40*, 56–61.

(3) (a) Bonchio, M.; Carraro, M.; Scorrano, G.; Kortz, U. *Adv. Synth. Catal.* **2005**, *347*, 1909–1912; (b) Sartorel, A.; Carraro, M.; De Zorzi, R.; Geremia, S.; McDaniel, N.D.; Bernhard, S.; Scorrano, G.; Bonchio, M. *J. Am. Chem. Soc.* **2008**, *130*, 5006–5007.

(4) Proust, A.; Thouvenot, R.; Gouzerh, P. *Chem. Commun.* **2008**, 1837–1852.

(5) Carraro, M.; Sandei, L.; Sartorel, A.; Scorrano, G.; Bonchio, M. *Org. Lett.* **2006**, *8*, 3671–3674.

(6) (a) Judd, D.A.; Nettles, J.H.; Nevins, N.; Snyder, J.P.; Liotta, D.C.; Tang, J.; Ermolieff, J.; Schinazi, R.F.; Hill, C.L. *J. Am. Chem. Soc.* **2001**, *123*, 886–897; (b) Shigeta, S.; Mori, S.; Kodama, E.; Kodama, J.; Takahashi, K.; Yamase, T. *Antiviral Res.* **2003**, *58*,

265–271; (c) Wang, X.; Liu, J.; Pope, M.T. *Dalton Trans.* **2003**, 957–968; (d) Tajima, Y. *Microbiol. Immunol.* **2003**, *47*, 207–212.

(7) Sanchez, C.; de Soler-Illia, G.J.; Ribot, F.; Lalot, T.; Mayer, C.R.; Cabuil, V. *Chem. Mater.* **2001**, *13*, 3061–3083.

(8) Gouzerh, P.; Proust, A. *Chem. Rev.* **1998**, *98*, 77–112.

(9) Peng, Z. *Angew. Chem. Int. Ed.* **2004**, *43*, 930–935.

(10) Longa, J.R.; Yaghib, O.M. *Chem. Soc. Rev.* **2009**, *38*, 1213–1214.

(11) Zhang, Z.; Song, Y.F.; Cronin, L.; Liu, T. *J. Am. Chem. Soc.* **2008**, *130*, 14408–14409.

(12) Carraro, M.; Sartorel, A.; Scorrano, G.; Maccato, C.; Dickman, M.H.; Kortz, U.; Bonchio, M. *Angew. Chem. Int. Ed.* **2008**, *47*, 7275–7279.

(13) Mayer, R.C.; Thouvenot, R. *Chem. Mater.* **2000**, *12*, 257–260.

(14) Nlate, S.; Plault, L.; Astruc, D. *Chem. Eur. J.* **2006**, *12*, 903–914.

(15) Favette, S.; Hasenknopf, B.; Vaissermann, J.; Gouzerh, P.; Roux, C. *Chem. Commun.* **2003**, 2664–2665.

(16) Reinoso, S.; Vitoria, P.; Lezama, L.; Luque, A.; Gutiérrez-Zorrilla, J.M. *Inorg. Chem.* **2003**, *42*, 3709–3711.

(17) Bar-Nahum, I.; Cohenand, H.; Neumann, R. *Inorg. Chem.* **2003**, *42*, 3677–3684 and references therein.

(18) (a) Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Moammadpoor-baltork, I.; Rasouli, N. *Catal. Commun.* **2008**, *9*, 219–233; (b) Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Moammadpoor-baltork, I.; Rasouli, N. *Inorg. Chem. Commun.* **2007**, *10*, 1537–1540; (c) Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Moammadpoor-baltork, I.; Rasouli, N. *Appl. Catal. A; Gen.* **2008**, *334*, 106–111.

(19) Patel, K.; Shringarpure, P.; Patel, A. *Trans. Met. Chem.* **2011**, *36*, 171–177.

(20) Silva, A.R.; Freire, C.; de Castro, B. *New. J. Chem.* **2004**, *28*, 253–260.

(21) Zhang, X.; Pope, M.T.; Chance, M.R.; Jameson, G.B. *Polyhedron* **1995**, *14*, 1381–1392.

(22) Deltcheff, R.; Thouvenot, R. *J. Chem. Res. Synop.* **1977**, *2*, 46–47.

(23) Deltcheff, C.R.; Thouvenot, R. *J. Chem. Res. (M)* **1977**, 0555–0563.

(24) Shringarpure, P.; Patel, A. *Dalton Trans.* **2010**, *39*, 2615–2621.

(25) Sheldon, A.; Walau, M.; Arends, I.W.C.E.; Schurdt, U. *Acc. Chem. Res.* **1998**, *31*, 485–493.