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# Keggin type inorganic–organic hybrid material containing Mn(II) monosubstituted phosphotungstate and S-(+)-sec-butyl amine: Synthesis and characterization

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#### ABSTRACT

A new inorganic–organic POM-based hybrid material comprising Keggin type mono manganese substituted phosphotungstate and enantiopure S-(+)-sec-butyl amine was synthesized in an aqueous media by simple ligand substitution method. The synthesized hybrid material was systematically characterized in solid as well as solution by various physicochemical techniques such as elemental analysis, TGA, UV–vis, FT-IR, ESR and multinuclear solution NMR (<sup>31</sup>P, <sup>1</sup>H, <sup>13</sup>C). The presence of chirality in the synthesized material was confirmed by CD spectroscopy and polarimeter. The above study reveals the attachment of S-(+)-sec-butyl amine to Keggin type mono manganese substituted phosphotungstate through N  $\rightarrow$  Mn bond. It also indicates the retainment of Keggin unit and presence of chirality in the synthesized material. An attempt was made to use the synthesized material as a heterogeneous catalyst for carrying out aerobic asymmetric oxidation of styrene using molecular oxygen. The catalyst shows the potential of being used as a stable recyclable catalytic material after simple regeneration without significant loss in conversion.

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#### 1. Introduction

The tailoring and synthesis of inorganic–organic hybrid materials constructed from distinctive building blocks represents an outstanding research area in material science, crystal engineering, magnetic materials, photosensitive material and catalysis [1]. All these reflect a current interest in combining different inorganic and organic moieties by molecular assemblies to produce hybrid materials, which combines the unique feature of both inorganic and organic components. In this regards, polyoxometalates (POMs) can act as excellent inorganic multidentate O-donor ligands [2] to assemble various inorganic–organic hybrid compounds. Polyoxometalates (POMs) are metal oxygen anion clusters and their properties may be modified depending on the elemental composition, structure as well as counteractions [3].

Transition metal substituted polyoxometalates (TMSPOMs) are of excellent candidate in POMs chemistry due to their unique electrochemical, magnetic, medicinal and catalytic properties [2– 4]. Further, they can also be rationally modified on the molecular level including shape, size, charge density, redox states as well as stability. In the TMSPOMs the transition metal is coordinated with available five oxygen atoms of the POMs, while the sixth coordination site on the metal is occupied by an aqua ligand. Thus aqua ligand is labile and can be replaced by any organic group or even by organometallic groups [5]. The obtained material is the so-called inorganic–organic hybrid material based on POMs, which have potential application in various fields from material science to biology [6,7].

A number of strategies have been reported for the synthesis of hybrid compounds based on POMs [8,9]. This includes transition metal-substituted POMs [10], lacunary POMs [11], saturated POMs and simple inorganic units as the starting materials [12]. Since the POMs and organic moiety have different chemical and structural properties, their synthesis remains a challenge. The reported syntheses include hydrothermal conditions [13], self-assembly reactions starting with the minimal building blocks [12] or the use of organic solvent [14]. Recently Peng et al. has synthesized such hybrid materials, containing functionalized manganese substituted silicotungstate and imidazol as well as cobalt substituted silicotungstate and 4,4'-bipyridine as an antenna ligand and fully characterized spectroscopically as well as crystallographically [9b,15]. They have carried out the synthesis in aqueous media under normal bench conditions using coordination competition approach.

At the same time, synthesis using *ligand substitution approach* was not used at all. Further, it was also found that no reports are available on the derivatization of the Mn-substituted phosphotungstate with S-(+)-sec-butylamine (SBA). So, it was thought of



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interest to synthesize POMs based hybrid material containing SBA using ligand substitution approach. Mn(II)-substituted phosphotungstate(PW<sub>11</sub>Mn) was selected as inorganic building block based on two reasons. Recently we have reported the single crystal X-ray analysis of PW<sub>11</sub>Mn [16] and expertise in using such inorganic building block. As SBA having N atom as potential coordination sites which may play important role to extend the structure with chiral centre, it was select as an organic ligand.

The present paper consists of synthesis of a new inorganicorganic hybrid material containing Keggin type manganese substituted phosphotungstate and SBA by ligand substitution method. The synthesized hybrid material was systematically characterized by elemental analysis, TGA, UV–vis, ESR, FT-IR, multinuclear NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P), CD spectroscopy and polarimeter. An attempt was made to use the synthesized hybrid material for carrying out aerobic oxidation of styrene at ambient temperature under mild reaction condition.

# 2. Materials

All chemicals used were of A.R. grade. 12-Tungstophosphoric acid,  $H_3PW_{12}O_{40}$ · $nH_2O$  (Loba Chemie, Mumbai), sodium hydroxide, MnCl<sub>2</sub>·4H<sub>2</sub>O and cesium chloride were obtained from Merck and used as received. S-(+)-sec-butyl amine was obtained from Sigma and used as received.

#### 2.1. Synthesis

The synthesis was carried out in two steps.

# 2.1.1. Synthesis of mono manganese substituted phosphotungstate $(PW_{11}Mn)$

 $PW_{11}MnO_{39}$  was synthesized by reported method by us recently [16]. 2.88 g of  $H_3PW_{12}O_{40}$ · $nH_2O$  was dissolved in 10 ml of water and the pH of the solution adjusted to 4.8 using NaOH solution. The solution was heated to 90 °C with stirring. To this hot solution was added 0.197 g of  $MnCl_2$ · $4H_2O$  solution dissolved in 10 ml water. The final pH of the solution was 4.8. The solution was heated at 90 °C with stirring for 1 h and filtered hot. 10 ml saturated solution of CsCl was added to the hot filtrate. The resultant mixture was allowed to stand overnight at room temperature. The solution was filtered and the orange colored crystals (87.9%) were dried at 50 °C. The isolated solid was designated as  $PW_{11}Mn$ .

# 2.1.2. Synthesis of POMs based hybrid material ( $PW_{11}Mn$ -SBA)

0.8985 g of PW<sub>11</sub>Mn was dissolved in 10 ml of distilled water. 0.1314 g of SBA was dissolved in 15 ml of ethanol. The ethanolic solution of SBA was added drop wise to the aqueous solution of PW<sub>11</sub>Mn. The pH of the solution was found to be 6.4. This resulted mixture was refluxed for 10 h and then allowed to cool, filtered and washed with water:ethanol (1:1) mixture. The obtain powder was designed as PW<sub>11</sub>Mn-SBA.

#### 2.2. Characterization

Elemental analysis was carried out using JSM 5610 LV combined with INCA instrument for EDX-SEM analyzer for the quantitative identification of metal ions. Thermo gravimetric analysis was carried out on the Mettler Toledo Star SW 7.01 upto 600 °C in air with the heating rate of 5 °C/min. FT-IR spectra of the samples were recorded as the KBr pellet on the Perkin Elmer instrument. The UV–vis spectrum was recorded at ambient temperature on Perkin Elmer 35 LAMDA instrument using the 1 cm quartz cell. The ESR spectra were recorded on a Varian E-line Century series X-band ESR spectrometer (liquid nitrogen temperature and scanned from 2000 to 3200 Gauss). Solution NMR (<sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P) was recorded in D<sub>2</sub>O as well as in CDCl<sub>3</sub> on Bruker ACF 300 MHz instrument. Optical activity was carried out using JASCO (J-815 CD Spectrometer, model no.: J-815-150L) and JASCO (P-2000 Digital Polarimeter). The optical rotation was carried out for neat S-SBA as well as for PW<sub>11</sub>Mn-SBA in methanol and water respectively. The 5% solution was used to carry out optical rotation.

### 2.3. Catalytic activity

The catalytic activity was evaluated for the non-solvent oxidation of styrene using molecular oxygen as an oxidant and TBHP as a 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 alkenes and initiator TBHP (0.014 g) at 80 °C (for styrene). The reaction was started by bubbling O<sub>2</sub> into the reaction medium and was continuously stirred on magnetic hot plate.

In the oxidation of styrene, after completion of reaction the reaction mixture was allowed to cool to room temperature and then 10% aqueous solution Na<sub>2</sub>CO<sub>3</sub> was added with constant stirring. The resultant mixture (organic and aqueous) was allowed to stand for 15–20 min in order to separate the two distinct layers. The aqueous layer was collected and concentrated HCl was added slowly with constant stirring. No precipitates of benzoic acid were separated. The remained organic layer was extracted with dichloromethane and analyzed by Agilent Technologies 6890N gas chromatography (FID, 19091G-B213 chiral capillary column  $(30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}))$  using nitrogen as a carrier gas with flow rate 30 ml/min. The injector temperature, detector temperature, and oven temperature were 250°, 250°, and 100°C, respectively. The authentic samples of benzaldehyde, R- and Sconfiguration styrene epoxides were used as the standard product to determine the yields by comparison of peak height and area.

The percentage-conversion of the substrate and the percentageselectivity of the products in the epoxidation reaction are calculated as:

 $\label{eq:conversion} \text{Conversion } (\%) = \frac{(initial \ mol\%) - (final \ mol\%)}{initial \ mol\%} \times 100$ 

 $Selectivity (\%) = \frac{product \ formed \ (moles)}{substrate \ converted \ (moles)} \times 100$ 

# 3. Results and discussion

The observed values for the elemental analysis in the isolated complex ( $PW_{11}Mn$ ) are in good agreement with the theoretical values. Anal calc: Cs, 19.1; W, 57.9; P, 0.89; Mn, 1.57; O, 20.2. Found: Cs, 19.8; W, 56.68; P, 0.86; Mn, 1.53; O, 20.06. The number of water molecules calculated from TGA curve, based on total weight loss (2.5%), corresponds to loss of 5 water molecules. From the elemental as well as the thermal analysis the chemical formula of the isolated complex is proposed as: Cs<sub>5</sub>[PW<sub>11</sub>O<sub>39</sub>Mn(H<sub>2</sub>O)]-4H<sub>2</sub>O (PW<sub>11</sub>Mn).

The observed values for the elemental analysis in the isolated complex (PW<sub>11</sub>Mn-SBA) are in good agreement with the theoretical values. Anal calc: Cs, 18.11; W, 55.13; P, 0.84; Mn, 1.49; O, 21.81; C, 1.30; H, 0.89; N, 0.38. Found: Cs, 17.92; W, 54.84; P, 0.83; Mn, 1.47; O, 21.49; C, 1.20; H, 0.80; N, 0.35. The number of water molecules calculated from TGA curve, based on total weight loss (4.3%), corresponds to loss of 11 water molecules. From elemental as well as thermal analysis the chemical formula of the isolated complex is proposed as:  $Cs_5[PW_{11}O_{39}Mn(C_4H_{11}N)] \cdot 11H_2O$  (PW<sub>11</sub>Mn-SBA).

Table 1FT-IR frequency data.

Materials	FT-IR frequencies						
	P-O	W=0	W-O-W	Mn–N	C-N	N-H	C-H
PW <sub>11</sub> Mn	1078 1053	955	884 813	-	-	-	-
SBA	-	-	-	-	1290 1259 1148	1598	2928 2850 1450
PW <sub>11</sub> Mn-SBA	1075 1054	952	880 812	672	1200 1173	1541	2922 2852 1448
R <sub>1</sub> -PW <sub>11</sub> Mn-SBA	1078 1055	953	882 815	670	1201 1171	1541	2920 2848 1451

The frequencies of FT-IR bands for  $PW_{11}Mn$ ; SBA and  $PW_{11}Mn$ -SBA are shown in Table 1.  $PW_{11}Mn$  displays a characteristic IR fingerprint [16] in the region of 1000–700 cm<sup>-1</sup>, attributed to the stretching vibration of the tetrahedral P–O bonds (1078 and 1053 cm<sup>-1</sup>), terminal W=O bonds (955 cm<sup>-1</sup>) and the two types of bridging W–O–W bonds of the cluster (884 and 813 cm<sup>-1</sup>). SBA gives characteristic IR fingerprint region for C–N vibration (1290, 1259 and 1148 cm<sup>-1</sup>), symmetric and asymmetric stretching vibrations of aliphatic C–H bonds (2928, 2850 and 1450 cm<sup>-1</sup>) and N–H stretching vibration (1598 cm<sup>-1</sup>).

 $PW_{11}Mn$ -SBA complex shows IR vibration bands correspond to  $PW_{11}Mn$  as well as SBA. It displays a characteristic IR fingerprint in the region of 1000–700 cm<sup>-1</sup>, attributed to the stretching vibration of the tetrahedral P–O bonds (1075 and 1054 cm<sup>-1</sup>), terminal W=O bonds (952 cm<sup>-1</sup>) and the two types of bridging W–O–W bonds of the cluster (880 and 812 cm<sup>-1</sup>). These characteristic IR data indicate the retainment of Keggin structure even after introduction of SBA. However, little shift was observed which may due to the introduction of SBA in the coordination sphere of PW<sub>11</sub>Mn.

In addition, from the FT-IR spectra we can obtain the structural information about the organic ligand. A pair of weak peaks at 2922 and 2852 cm<sup>-1</sup> for the synthesized material is attributed to the symmetric and asymmetric stretching vibrations of aliphatic C–H bonds. These results ensure the successful formation of POMs based hybrid material with PW<sub>11</sub>Mn and SBA.

It is interesting to note that after introduction of an organic moiety (i.e. for PW<sub>11</sub>Mn-SBA), the vibration bands that originated from C–N bond gives two broad bands at 1200 and 1273 cm<sup>-1</sup> instead of three characteristic bands. Further a very significant shift, from 1598 cm<sup>-1</sup> to 1541 cm<sup>-1</sup> for N–H stretching is observed. This indicates the formation of dative bond from N  $\rightarrow$  Mn. As a result of decreases in electron density on N atom, N–H bond length decreases which leads to the significant shift. In addition, the formation of new band at 672 cm<sup>-1</sup> also supports the formation of N  $\rightarrow$  Mn bond. Further, Raman spectra of PW<sub>11</sub>Mn-SBA indicate the single line at 374, which may indicate the formation of N  $\rightarrow$  Mn bond in the synthesized material.

The UV-vis spectrum of PW<sub>11</sub>Mn and in water, shows a W  $\rightarrow$  O charge-transfer peak at 291 nm accompanied by another  $\lambda_{max}$  at 398 nm (Fig. 1a), which can be attributed to the d-d electronic transition of the Mn center in the [PW<sub>11</sub>O<sub>39</sub>Mn(H<sub>2</sub>O)] anion. The observed values are in good agreement with the reported one [16]. The UV-vis spectrum of PW<sub>11</sub>Mn-SBA in water shows two peaks: one at 289 nm corresponding to the W  $\rightarrow$  O charge-transfer and another  $\lambda_{max}$  at 407 nm (Fig. 1b) which can be attributed to the d-d electronic transition of the Mn center in the [PW<sub>11</sub>O<sub>39</sub>Mn(SBA)] anion. The shift in  $\lambda_{max}$  from 398 nm to 407 nm may be due to the replacement of the labile aquo ligand by SBA. The ability of the manganese polyoxometalate to coordinate with the organic ligand is well documented in the literature [9b] and it was reported that, changes in the position or shape or increase in intensity of ligand



Fig. 1. UV-vis spectra of (a) PW<sub>11</sub>Mn, and (b) PW<sub>11</sub>Mn-SBA.



Fig. 2. ESR spectra of (a) PW<sub>11</sub>Mn, and (b) PW<sub>11</sub>Mn-SBA.

field band was observed when aquo ligand was replaced by any ligand. The change of the ligand field band was observed for number of ligand in case of Co(II) undecatungstocobalto(II) by Weakly [17]. The obtained result is as expected.

Thus the UV–vis spectrum supports the formation of N  $\rightarrow$  Mn. 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. The low temperature ESR for PW<sub>11</sub>Mn and PW<sub>11</sub>Mn-SBA were recorded in the range of 3200–2000 G. The low temperature ESR shows (Fig. 2a and b) a well resolved six lines ESR spectrum with  $g \sim 2.3$  and 2.1 which is as expected and confirms the presence of Mn(II) in the synthesized material. The slight shift in g value may be due to the change in the environment around the Mn(II) centre.

Thus the FT-IR, UV-vis and ESR spectrum support the formation of inorganic–organic hybrid material through  $N \rightarrow Mn$  bond.

#### 4. Nuclear magnetic resonance spectra

It is known that the presence of paramagnetic metal centre generally results in a poorly defined NMR spectrum. In the present case, well resolved NMR spectra ( $^{13}$ C,  $^{31}$ P) are obtained. This may be due to the two facts: the concentration of paramagnetic metal centre (present case 1.53% Mn(II)); and the electronic relaxation for paramagnetic compound is fast. So ESR spectra cannot be obtained

at room temperature but NMR spectrum can be obtained at room temperature.

 $^{31}$ P NMR spectra for PW<sub>11</sub>Mn and PW<sub>11</sub>Mn-SBA are shown in Fig. 3a and b. <sup>31</sup>P NMR spectroscopy is a useful method to identify the change in the environment around the transition metal centre incorporated into the POMs. Further, it also showed the purity of the formed product. However many a time it is well documented that in case of preparing such kind hybrid material there is lack of getting pure product in aqueous media resulting into the two to three line in <sup>31</sup>P NMR spectrum [18]. Such kind of material exhibiting spectrum corresponds to the formed product along with presence of other species (i.e. monolacunary POMs and TMSPOMs). In the present case only single peak is observed confirming the formation of single pure products. The significant upfield shift in PW<sub>11</sub>Mn-SBA as compared to PW<sub>11</sub>Mn may be due to the change in the environment around the Mn(II)-centre. This also changes the central P environment, i.e. PO<sub>4</sub>-Mn-H<sub>2</sub>O becomes PO<sub>4</sub>-Mn-SBA. Thus <sup>31</sup>P NMR indicates the successful replacement of aquo ligand bv SBA.

Fig. 4 shows the structure of SBA. The chemical shift of  ${}^{13}$ C NMR spectrum for SBA as well as PW<sub>11</sub>Mn-SBA is presented in Table 2. As shown in Table 2, no significant shift in  ${}^{a}$ CH<sub>3</sub> carbon indicates that the amine remains intact in the synthesized material. The considerable upfield shift was observed for  ${}^{b}$ CH<sub>3</sub> and  ${}^{c}$ CH<sub>2</sub> and downfield shift was observed for  ${}^{d}$ CH. This may be due to the bond formation between N atom of SBA and Mn of PW<sub>11</sub>Mn. Once, dative bond forms between Mn and N, the electron density on N atom



Fig. 3. <sup>31</sup>P NMR of (a) PW<sub>11</sub>Mn, (b) PW<sub>11</sub>Mn-SBA, and (c) R1-PW<sub>11</sub>Mn-SBA.



**Hg. 4.** 5-(+)-see-butyr an

Table 2Chemical shift for <sup>13</sup>C NMR.

Chemical shift	SBA	PW <sub>11</sub> Mn-SBA	
<sup>a</sup> CH <sub>3</sub>	10.8	10.6	
<sup>b</sup> CH <sub>3</sub>	23.6	18.83	
<sup>c</sup> CH <sub>2</sub>	33.8	28.76	
<sup>d</sup> C–H	48.6	50.84	

decreases, which leads to the downfield shift for  ${}^dCH$  carbon. The result is as expected. The NMR study confirms the formation of  $N\to Mn$  bond.

<sup>1</sup>H NMR spectra of the  $PW_{11}Mn$ -SBA (Fig. 5) show broadened peaks or very poorly defined spectra corresponding to the  $CH_3$  and  $CH_2$  protons. This indicates the presence of SBA moiety into the coordination sphere of PW11Mn. Presence of paramagnetic centre will be responsible to give broadened peaks or very poorly defined spectra.

To examine the chiroptical and stable activities of synthesized material in the solution state, the CD spectra were carried out in water (Fig. 6). The spectrum of the synthesized material exhibits Cotton effect at 250 nm. This is region for characteristic of the oxygen-to-tungsten charge-transfer bands of Keggin polyoxoanions [19]. The induced circular dichroism in the POM clusters can be clearly seen in the CD spectra. Optical rotation of SBA and PW<sub>11</sub>Mn-SBA was found to be  $[\alpha]20/D + 1.49$  and  $[\alpha]20/D + 0.4$  respectively. This result ensures that the formed hybrid material is chiral.



Fig. 5. <sup>1</sup>H NMR spectra of PW<sub>11</sub>Mn-SBA.



Fig. 6. CD spectra of PW<sub>11</sub>Mn-SBA.

# 4.1. Catalytic activity

A neat reaction (without catalyst) was carried out and it showed no conversion for the substrate indicating that there is no autooxidation taking place. In order to study the role of TBHP the same sets of reactions were carried under two different conditions: (i) alkene + oxidant + TBHP and (ii) alkene + oxidant + PW<sub>11</sub>Mn-SBA. In both the cases the reaction did not progress significantly. These observations indicate that the liberation of O<sub>2</sub> from TBHP was not sufficient to induce the reaction as well as the activation of manganese. Hence it may be concluded that in the present study TBHP acts as an initiator only.

# 4.2. Effect of amount of catalyst

The effect of concentration of the catalyst amount on the conversion and selectivity is shown in Table 3. In the present study epoxidation of styrene gives styrene oxide as well as benzaldehyde. However with an increase in the amount of catalyst, % conversion also increases. This suggests that the manganese centre functions as active sites for oxidation. It is very interesting to observe the difference in the selectivity of the products with an increase in the amount of the catalyst. As shown in Table 3, up to 25 mg of catalyst, epoxide was observed. On further increasing the amount of the catalyst, the product selectivity shifts from the less stable intermediate (epoxide) to the more stable product (benzaldehyde). This may be due to the fact that with increase in the amount of the active species the reaction becomes very fast which favours the conversion of the formed styrene oxide to benzaldehyde. Due to the known importance of epoxide, the amount of the catalyst was optimized at 25 mg.

# 4.3. Effect of reaction time

It is seen from the Table 4 that the distribution of the product changes with increase in the reaction time. Initially, after the completion of 2 h the 21% of styrene oxide is observed. As the

Table	3		
Effect	of amou	nt of ca	talys

Catalyst	Amount (mg)	Conversion (%)	Selectivity (%)		ee (S) (%)
			Benzaldehyde	Styrene oxide	
PW <sub>11</sub> Mn-SBA	5	6	75	25	6
	10	19	78	22	8
	15	32	83	17	7
	20	41	86	14	9
	25	52	89	11	10
	30	58	>99		

Substrate; styrene (100 mmol); oxidant,  $O_2$  (4 ml/min); TBHP, 0.15 mmol; reaction time, 4 h; temperature, 80  $^\circ\text{C}.$ 

## 430

# Table 4Effect of reaction time.

Catalyst	Reaction time (h)	Conversion (%)	Selectivity (%)		ee (S) (%)
			Benzaldehyde	Styrene oxide	
PW <sub>11</sub> Mn-SBA	2	29	79	21	9
	4	52	89	11	10
	6	56	>99		

Substrate; styrene (100 mmol); oxidant, O<sub>2</sub> (4 ml/min); TBHP, 0.15 mmol; catalyst, 25 mg; temperature, 80 °C.

#### Table 5

Oxidation of styrene using PW11Mn and PW11Mn-SBA (under optimized condition).



<sup>a</sup> Epoxidation of alkenes catalyzed by PW<sub>11</sub>Mn-SBA.

<sup>b</sup> Epoxidation of alkenes catalyzed by  $Cs_5[PMn(H_2O)W_{11}O_{39}] \cdot 4H_2O$ .

<sup>c</sup> Conversion based on substrate; styrene, 100 mmol; oxidant, O<sub>2</sub> (4 ml/min); TBHP, catalyst, 25 mg; reaction time, 4h.

<sup>d</sup> Turnover number based on conversion.

reaction time increases the product selectivity shifts towards BA. With 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 optimized at 4 h.

## 4.4. Effect of SBA

To examine the effect organic ligand, the oxidation of styrene was carried out using  $PW_{11}Mn$  as well as  $PW_{11}Mn$ -SBA in optimized condition and the distribution of products are reported in Table 5.  $PW_{11}Mn$  showed 61% conversion for styrene with >99% selectivity towards benzaldehyde whereas  $PW_{11}Mn$ -SBA showed 52% conversion with 11% selectivity towards 89% selectivity towards benzaldehyde. The difference in the catalytic activity can be explained on the basis of the structural difference between  $PW_{11}Mn$  and  $PW_{11}Mn$ -SBA. This could be explained on the basis of the nature of the catalyst. The excellent catalytic performances of the  $PW_{11}Mn$ -SBA catalysts are mainly due to the easy electron-donating ability of

the organic ligand, which facilitates the formation of stabilization of the formed styrene oxide.

# 4.5. Leaching as well as heterogeneity test

Any leaching of the active species makes the catalyst unattractive and hence it is necessary to study the stability as well as leaching of  $PW_{11}Mn$ -SBA. The catalyst was filtered after completion of reaction and the filtrate was characterized for UV–vis spectroscopy. For comparison, UV–vis spectrum of  $PW_{11}Mn$ -SBA was recorded (Fig. 7). The absence of characteristic peaks in filtrate indicates that there is no leaching of  $PW_{11}Mn$ -SBA and the catalyst remains completely insoluble under reaction condition and could be reused.

For rigorous proof of heterogeneity, a test was carried out by filtering catalyst from the reaction mixture at 80 °C after 2 h and the filtrate was allowed to react up to completion of reaction (4 h). The reaction mixture of 2 h and filtrate was analyzed on gas chromatogram. The results are presented in Table 6. No change in %



Fig. 7. UV-vis spectra of (a) PW<sub>11</sub>Mn-SBA, and (b) filtrate.

#### Table 6

% conversion and % selectivity for oxidation of styrene (with and without catalyst).

Catalyst	Reaction Conversion Sele time (h) (%)		Selectivity (%)		ee (S) (%)
			Benzaldehyde	Styrene oxide	
PW <sub>11</sub> Mn-SBA (2 h) Filtrate (4 h)	2 4	27 27	81 81	19 19	10 10

Substrate; styrene (100 mmol); oxidant, O<sub>2</sub> (4 ml/min); TBHP, 25 mg catalyst; reaction time, 4 h; temperature, 80  $^\circ$ C.

#### Table 7

Recycling of the catalyst.

Catalyst	Reaction time (h)	Conversion (%)	Selectivity (%)	ee (S) (%)	
			Benzaldehyde	Styrene oxide	
PW <sub>11</sub> Mn-SBA R1-PW <sub>11</sub> Mn-SBA	4 4	52 50	89 90	11 10	10 9

Substrate; styrene (100 mmol); oxidant, O\_2 (4 ml/min); TBHP, 25 mg catalyst; reaction time, 4 h; temperature, 80  $^\circ C.$ 

conversion as well as % selectivity was found. On the basis of the results, it can be said that the present catalysts are truly heterogeneous in nature.

# 4.6. Regeneration and recycling of the catalyst

In order to investigate the stability of the catalyst during oxidation reaction, the catalyst was separated by simple filtration after completion of reaction. The separated catalyst was washed with dichloromethane and dried at 100 °C (designated as  $R_1$ -PW<sub>11</sub>Mn-SBA). Oxidation of styrene was then carried out with the recycled catalyst, under the optimized conditions ( $R_1$ -PW<sub>11</sub>Mn-SBA). The obtained results are presented in Table 7. As seen from Table 7, the recycled catalyst did not show any appreciable change in the activity, indicating that the catalyst is stable and can be regenerated for repeated use.

Further, the recycled catalyst (R1-PW<sub>11</sub>Mn-SBA) was characterized by FT-IR (Table 1) and <sup>31</sup>P NMR (Fig. 3c) spectroscopy. The FT-IR spectra of the R1-PW<sub>11</sub>Mn-SBA display all the characteristic bands for the C-N, N-H stretching and N  $\rightarrow$  Mn bond.

Further, the <sup>31</sup>P NMR spectra of  $R_1$ -PW<sub>11</sub>Mn-SBA show the chemical shift at -11.56 ppm (Fig. 3c). No shift in FT-IR bands and the chemical shift indicate that the PW<sub>11</sub>Mn-SBA remains stable in the present reaction condition.

#### 5. Conclusion

In conclusion, we have developed chiral POM-based materials utilizing enantiopure SBA ligand and Keggin-type mono-manganese substituted phosphotungstate via ligand substituted method. Spectral studies show that the Keggin unit retains its structure even after the introduction of SBA. The multinuclear NMR (<sup>13</sup>C and <sup>31</sup>P) studies indicate the formation of N  $\rightarrow$  Mn bond. The presence of chirality in the synthesized material was confirmed by CD spectroscopy and polarimeter. The above studies reveal the attachment of SBA to the PW<sub>11</sub>Mn without any distortion of structure as well as with retainment of chirality. The synthesized hybrid material was successfully used as heterogeneous catalyst. Our future aspect would be to increase the % selectivity and % ee for the styrene oxide.

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