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## Short Communication

## Cesium salts of manganese based lacunary phosphotungstate supported mesoporous silica: An efficient catalyst for solvent free oxidation reaction



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#### 1. Introduction

The oxidation of alcohols to the corresponding carbonyl compounds, i.e., benzyl alcohol to benzaldehyde is one of the most important and vital transformations in synthetic organic chemistry. Benzaldehyde is a valuable chemical in the perfumery, dyestuffs, and agrochemical industries [1]. Numerous catalyzed methods have been reported for alcohol oxidations [2,3], but many are either expensive or involving toxic chemicals or solvents. Solvent free approach is an attractive green process for selective oxidation of benzyl alcohol and oxidants like molecular oxygen, hydrogen peroxide and TBHP are in the order as green options. Molecular oxygen as oxidant generates significant amount of inorganic waste and is not very active, while hydrogen peroxide is a good oxygen donor in catalytic oxygen-transfer reactions. However, most of the catalyst systems using hydrogen peroxide are based on noble metals such as Pt, Pd, and Ru and are expensive and difficult to synthesize [4–7]. Thus, polyoxometalates (POMs) are definitely an attractive alternative in terms of economic viability and easy-tomanufacture alternative with a heterogeneous nature.

The general formula of Keggin type heteropoly acids is  $[X^{n+}M_{12}O_{40}]^{(8\ -n)-},$  where  $X^{n+}$  is a central hetero atom  $(P^{5+},Si^{4+}$ 

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## ABSTRACT

Keggin-type Cs salt of Mn (II)-substituted mono-lacunary phosphotungstate supported on mesoporous silica, a novel catalyst exhibited excellent activity towards solvent free oxidation reactions. The catalyst materials were fully characterized by different techniques including XRD, BET analysis, TG–DTA, Raman spectra, FT-IR and XPS. While XPS study shown the presence of Mn (II) on the material, the existence of Keggin structure even after modification was confirmed by XRD and FT-IR data. Excellent conversion and selectivity were achieved in selective oxidation of benzyl alcohol to benzaldehyde. Optimum reaction conditions were established with respect to various parameters that influence the selective oxidation.

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etc.) and M is an addenda atom ( $W^{6+}$ ,  $Mo^{6+}$ ,  $V^{5+}$ , etc.) [8]. When one or more addenda atoms from polyoxometalates are replaced they are known as lacunary polyoxometalates. The removal of one or two MO units from the fully occupied polyoxometalates [ $XM_{12}O_{40}$ ]<sup>n-</sup>, gives rise to mono-lacunary [ $XM_{11}V_{1}O_{39}$ ]<sup>(n + 4)-</sup> and di-lacunary [ $XM_{10}V_2O_{36}$ ]<sup>(n + 5)-</sup> polyoxometalates respectively. The reducing ability of these materials can be enhanced by creation of lacuna in them. Lacunary and di-lacunarypolyoxometalates are gaining more importance because of their unique structural properties [9]. The reduced oxidizing ability of these materials can further be boosted by simply substituting an appropriate transition metal in their skeleton. Hence, we developed interest in the synthesis of Mn substituted monolacunary polyoxometalates and to investigate their scope as catalysts.

Recently, Nagai et al. reported Fe inclusion in the Keggin anion of heteropoly acid catalysts for selective oxidation of isobutene [10]. Patel et al. have reported the detailed synthesis and characterization of Keggin-type manganese (II)-substituted phosphotungstate and its activity towards liquid phase oxidation of styrene [11]. Excellent activity of single-site iron catalysts towards epoxidation as well as oxidation reaction was reported by Thomas and Raja [12]. So far there is little or no literature available on the catalytic aspects of supported Cs salt of Mn substituted lacunary anions. Earlier, Parida et al. have reported the synthesis of Pd and Fe substituted lacunary polyoxometalates supported on mesoporous silica [13,14]. Choice of the support material is vital for activity, as support materials can provide high surface area and active sites, which are crucial in enhancing conversion and selectivity efficiencies. Mesoporous silica (MCM-41) contains high surface area, uniform and controllable pore sizes and the periodic orders of their pore packing which provides a tremendous dispersion of the active

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species over it. In this communication, we report the synthesis of novel materials containing varied wt% of manganese substituted monolacunary phosphotungstates supported on mesoporous silica and their catalytic activity and selectivity towards partial oxidation of benzyl alcohol.

## 2. Experimental section

In the preparation of catalyst, physico-chemical characterization and procedure of oxidation reaction are provided in supplementary content.

## 3. Results and discussion

## 3.1. Physicochemical characterization of the catalyst

#### 3.1.1. XRD

The SXRD patterns of MCM-41 and 50LMn@MCM-41 are shown in Fig. 1a. Both the materials exhibit a strong peak at  $2\theta = 2.2^{\circ}$  due to (100) plane and also small peaks due to higher order (110), (200) and (210) plane reflections within 5° indicate the formation of well-ordered mesoporous materials. Thus, the mesoporosity remains intact after the modification of the silica network with manganese lacunary polyoxometalates. Marginal reduction and broadening of the (100) peak of 50LMn@MCM-41 after modification with manganese lacunary on the support surface observed, suggest a slight disturbance in hexagonal symmetry. The high angle XRD spectra of LMn and 50LMn@MCM-41 are shown in Fig. 1b. In that figure shows very high dispersion of LMn in a non-crystalline form on the surface of MCM-41.



**Fig. 1.** a: Low angle XRD spectra of MCM-41 (a) and 50LMn@MCM-41. b: High angle XRD spectra of 50LMn@MCM-41 (a) and MCM-41 (b).

#### 3.1.2. BET

The nitrogen adsorption–desorption isotherm was carried for MCM-41 and 50 wt.% loaded Mn(II)-substituted mono-lacunary phosphotungstate on MCM-41 is shown in Fig. 2. The isotherm of the parent shows a H4 type hysteresis loop (according to IUPAC nomenclature) with well-developed step in the relative pressure range  $\approx 0.9$ . Modification of MCM-41 framework with LMn, it seems to lower the P/P0 for capillary condensation step, indicating the shift in pore size to lower value due to incorporation of manganese lacunary acid in the pore of that support and also pore volume is found to decrease with increasing LMn content over the MCM-41 surface (Fig. 2). The BET surface area of parent MCM-41 sample was 1380 m<sup>2</sup>/g. After loading different wt % of LMn, the surface area and pore volume gradually decrease as shown in Table 1. This may be due to the fact that the Mn(II)-substituted a mono-lacunary phosphotungstate molecules that block the pores on the silica matrix.

## 3.1.3. FT-IR

The FT-IR spectra of LMn and 50LMn@MCM-41 are shown in Fig. 3. The CsPTA shows prominent bands at 1080, 985, 890 and 800 cm<sup>-1</sup> which are characteristic of Keggin structure and are assigned to cornersharing and edge-sharing respectively [15]. In the case of lacunary structure LW, the 1080 cm<sup>-1</sup> band is split into two components (1084–1044 cm<sup>-1</sup>), due to the symmetry decrease of the PO4 tetrahedron. Other bands found are 953 ( $n_{as}(W-O_d)$ ), 860 ( $n_{as}(W-O_b-W)$ ), 809 and 742 cm<sup>-1</sup> ( $n_{as}(W-O_c-W)$ ), and differ from those of PW<sub>12</sub> [15]. After modification with Mn, the spectra for LMn showed characteristic splitting for the P–0 bond frequency at 1073 and 1052 cm<sup>-1</sup>, which was slightly shifted towards lower frequency as compared to LW confirming the exchange of W atom by Mn. Both LMn and LMn modified MCM-41 support displayed similar bands.

#### 3.1.4. TG-DTA

The TG–DTA of the MCM-41 and 50LMn@MCM-41 are shown in Fig. 4. The TGA of MCM-41 shows weight loss in the temperature range 100–200 °C due to the loss of crystalline water. It also shows weight loss at 500 °C. This may be due to desorption of several organic species. TGA of LMn@MCM-41 shows weight loss in the temperature range 70–200 °C due to loss of adsorbed water. It does not show any weight loss up to 400 °C, indicating the synthesized catalyst is stable up to 400 °C. The DTA of the MCM-41 shows an endothermic peak around 100 °C due to water loss. The exothermic peak above 500 °C is due to surfactant removal. DTA of the 50LMn@MCM-41 sample (Fig. 4b) shows an endothermic peak with maximum at 80 °C ascribed to loss of adsorbed water. A wide exothermic peak with maximum at



Fig. 2. N2-adsorption & desorption study of MCM-41 (a) and 50LMn@MCM-41 (b).

Table 1

1	Surface properties of Elvine Mein-41.					
	Catalyst	Surface area $(m^2 g^{-1})$	Pore volume (cm <sup>3</sup> /g)			
	MCM-41	1380	1.28			
	LMn	3	0.041			
	30 LMn@MCM-41	820	0.71			
	40 LMn@MCM-41	740	0.68			
	50 LMn@MCM-41	625	0.56			
	60 LMn@MCM-41	585	0.51			

around 520 °C was observed, which is assigned to decomposition of metal-modified lacunary Keggin anion.

#### 3.1.5. Raman spectra

Fig. 5 indicates the Raman scattering spectra of LMn (a) and 50 LMn@MCM-41 (b). The bulk LMn gives peaks at 966 for P–O, 921 for  $W-O_b-W$ , 885 for  $W-O_c-W$  and 824 cm<sup>-1</sup> for  $W-O_t$  stretching vibrations. The band at about 220 cm<sup>-1</sup> may be attributed to symmetric stretching vibration of  $W-O_a$  band [16]. The 50 wt.% of LMn loaded on MCM-41 shows all the above described peaks of LMn, but the intensity of the peaks is low, compared to the bulk LMn and slightly shifted towards higher wave number values due to strong interactions between the MCM-41 support and lacunary Keggin unit. These results confirm the incorporation of un-degraded LMn on MCM-41 surface.

#### 3.1.6. XPS

The Mn 2p XPS spectrum of 50 LMn@MCM-41 is shown in Fig. 6. The catalyst shows two peaks at 641.03 and 652.64 eV. In the reported literature [17], the binding energy of about 640.6 eV was attributed for Mn  $2p^{3/2}$ . The Mn  $2p^{3/2}$  peaks are shifted towards a higher binding energy i.e., 0.4 eV, which indicated the strong interaction of Mn within the lacunary structure and with the support.

## 3.2. Catalytic activity

Phosphomolybdic acid supported vanadium–alumina mixed oxide as catalyst for the oxidation of alcohol with toluene as the solvent (93% conversion) was reported by Manyar et al. [18]. Parida et al. reported oxidation of benzyl alcohol over PMA/ZC catalyst with 85% conversion and 96% selectivity at 80 °C in 5 h reaction time [19]. Sawant et al. [20] reported that oxidation of benzyl alcohol with hydrogen peroxide over ammonium molybdate and tungstic acid catalyst gives <78% conversion of benzyl alcohol, at 90 °C in 5 h. Both the methods have inherent disadvantage of organic solvent. In this communication, we report a new catalyst LMn@MCM-41, which displays excellent activity in terms of conversion and selectivity to benzaldehyde (89% conversion, 98% selectivity) under solvent free conditions. Reaction was investigated under different wt% (30–60) LMn@MCM-41 and LMn as catalyst conditions and the results of the oxidation reaction are summarized in



Fig. 3. FT-IR spectra of LMn (a) and 50LMn@MCM-41 (b).



Fig. 4. TG-DTA spectra of 50LMn@MCM-41 (a) and MCM-41 (b).

Table 2. Out of those catalysts, 50 wt.% LMn@MCM-41 gave better results relative to that of others. So, a detailed study was carried out on the oxidation of benzyl alcohol using 50 wt.% LMn@MCM-41 as catalysts, and reactions were carried out under optimized conditions.

#### 3.2.1. Effect of temperature

Reaction was investigated at four temperatures, 70, 80, 90 and 100 °C, while other parameters are kept fixed (Fig. 7). The conversion % increased with increasing temperature from 70 to 100 °C, but the selectivity towards benzaldehyde drastically decreased. This might be due to the self-decomposition of H<sub>2</sub>O<sub>2</sub> at higher temperatures or further oxidation of benzaldehyde to benzoic acid at elevated temperatures.



Fig. 5. Raman spectra of LMn (a) and 50LMn@MCM-41 (b).



Fig. 6. XPS spectra of Mn 2p of 50LMn@MCM-41.

## 3.2.2. Effect of catalyst amount

The effect of 50 wt.% LMn@MCM-41 catalyst loading on the progress of benzyl alcohol oxidation is illustrated in Fig. 8. With the increase of the catalyst amount from 0.05 g to 0.20 g, the benzyl alcohol conversion increased from 67% to 94%, but the selectivity towards benzaldehyde reduced slightly from 99% to 89%. This may be due to the increase in active sites resulting from higher amount of catalyst which facilitate the further oxidation of benzaldehyde to benzoic acid.

## 3.2.3. Effect of time

When the reaction time was increased from 2 h to 6 h, the % conversion of benzyl alcohol increased too, but the selectivity towards benzaldehyde declined. Fig. S1 shows the influence of reaction time on the conversion of benzyl alcohol and product selectivity over the 50 wt.% LMn@MCM-41 catalyst (0.1 g). Thus, optimum reaction time was found to be 5 h, when catalyst gave the highest conversion and selectivity, i.e. 89% conversion of benzyl alcohol and 98% selectivity towards benzaldehyde. With an increase of the reaction time from 5 h to 6 h, the conversion marginally increased from 89% to 91%, but the selectivity dropped from 98% to 87%, due to further oxidation of benzaldehyde to benzoic acid.

## 3.2.4. Effect of oxidant

The efficiencies of three different oxidants  $H_2O_2$ , TBHP and  $O_2$  were compared under otherwise similar conditions (Fig. S2). The results indicate that after 5 h reaction, the % conversion of benzyl alcohol with the oxidants was in the order of  $H_2O_2 > TBHP > O_2$ , while the selectivity was in the order of  $H_2O_2 > TBHP$ . Relative to molecular oxygen, selectivity was poor in presence of TBHP. The LMn supported on mesoporous silica reacts with TBHP to form LMn-OOH peroxo surface species. In peroxo surface species, the O - O bond is polarized, which facilitates the attack by hydroxyl group on the nucleophilic center of aldehyde again, resulting in further oxidation and formation of benzoic acid. Thus, optimized conditions for oxidation of benzyl alcohol (89% conversion, 98% selectivity of benzaldehyde) are as follows: amount of the catalyst (0.1 g), temperature (80 °C), oxidant (H<sub>2</sub>O<sub>2</sub>) and time (5 h).

#### Table 2

Conversion and selectivity of various catalysts towards the oxidation of benzyl alcohol.

Catalyst	Conversion of benzyl alcohol	Selectivity (%)	
		Benzaldehyde	Benzoic acid
LMn	58	88.2	11.8
30 LMn@MCM-41	62	90	10
40 LMn@MCM-41	78	92	8
50 LMn@MCM-41	89	98	2
60 LMn@MCM-41	81	94.6	5.4



Fig. 7. Effect of temperature on the conversion of benzyl alcohol using 50 LMn@MCM-41 as the catalyst.

## 3.3. Recyclability of the catalyst

Recovery and reutilization of catalyst are the main advantages of heterogeneous catalysis. The activity of the recovered catalyst provides useful information about its stability during the catalytic cycle. In order to regenerate, catalyst was separated by filtration after reaction and washed several times with distilled water. It was further dried at 100 °C for 12 h followed by calcination at 200 °C for 3 h. The regenerated catalyst was then used in the reaction with a fresh reaction mixture and products were analyzed after the reaction. When the regenerated catalyst was used in three consecutive cycles, selectivity remained unaltered at 98%, but conversion decreased by marginal 2% in the third cycle.

## 4. Conclusions

We have developed a Cs salt of Mn substituted mono-lacunary phosphotungstate material and supported it on MCM-41 to obtain a new and robust heterogeneous catalyst. The Keggin structure does not break after modification which is confirmed by XRD and FT-IR. From the XPS studies Mn (II) was present on the materials. The 50 wt.% LMn@MCM-41 was found to be an excellent catalyst towards oxidation reaction under solvent free conditions. The N<sub>2</sub> adsorption–desorption studies revealed that the modified samples retained the mesoporosity. The advantage new catalyst is selective conversion of benzyl alcohol to benzyl alcohol under solvent free conditions with excellent yield. Furthermore, the removal of the catalysts consists of a single filtration step and the catalyst can be re-used for up to two cycles without any significant loss in conversion or selectivity.



Fig. 8. Effect of catalyst on the conversion of benzyl alcohol using 50 LMn@MCM-41 as the Catalyst.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2014.09.038.

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