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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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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.

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-to-manufacture 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+} 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 $[XM_{12}O_{40}]^{n-}$, gives rise to mono-lacunary $[XM_{11}V_1O_{39}]^{(n+4)-}$ and di-lacunary $[XM_{10}V_2O_{36}]^{(n+5)-}$ 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 mono-lacunary 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 mono-lacunary 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 $2\theta = 2.2°$ 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.

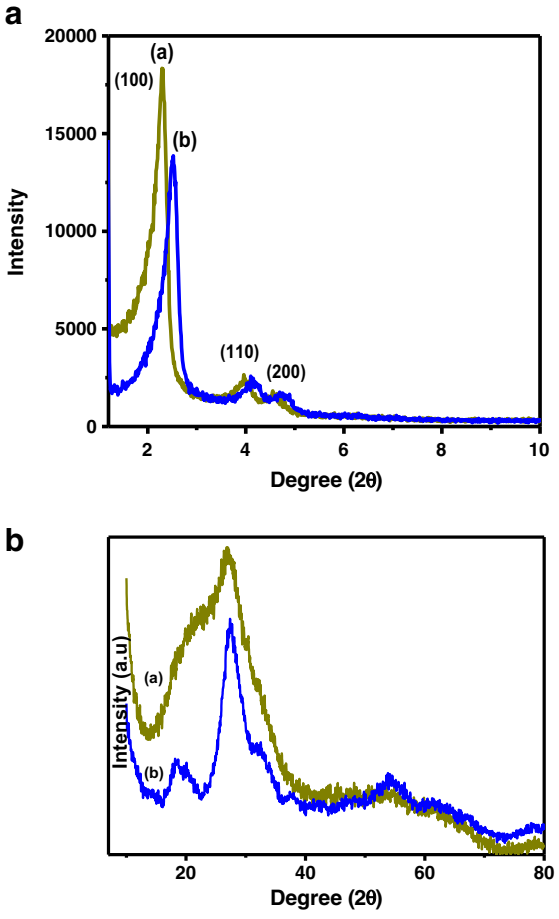

Fig. 1. a: Low angle XRD spectra of MCM-41 (a) and 50LMn@MCM-41. b: High angle XRD spectra of 50LMn@MCM-41 (a) and MCM-41 (b).

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 ≈ 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^2/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^{-1} which are characteristic of Keggin structure and are assigned to corner-sharing and edge-sharing respectively [15]. In the case of lacunary structure LW, the 1080 cm^{-1} band is split into two components (1084–1044 cm^{-1}), 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^{-1} ($n_{as}(W-O_c-W)$), and differ from those of PW_{12} [15]. After modification with Mn, the spectra for LMn showed characteristic splitting for the P–O bond frequency at 1073 and 1052 cm^{-1}, 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

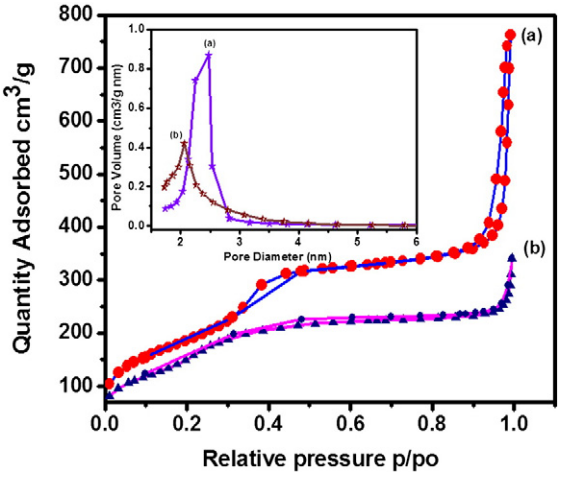

Fig. 2. N2-adsorption & desorption study of MCM-41 (a) and 50LMn@MCM-41 (b).