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A facile method for synthesis of Keggin-type cesium salt of iron substituted lacunary phosphotungstate supported on MCM-41 and study of its extraordinary catalytic activity

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ABSTRACT

A novel catalyst, Keggin-type Cs salt of Fe substituted mono lacunary phosphotungstate supported MCM-41 was synthesized from $H_3PW_{12}O_{40}$, FeCl₂ and Cs₂CO₃ and characterized by different techniques like X-ray diffraction, UV-vis diffused reflectance spectroscopy (UV-vis DRS), nitrogen adsorption-desorption, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectra and Fourier-Transform Infrared Spectroscopy (FT-IR). Diffused reflectance spectra and FT-IR studies confirmed the undegraded Keggin structure of the lacunary salt after supporting it on MCM-41. The material showed its amazing catalytic activity toward two different types of reactions. Among various samples prepared, 50 wt% Fe substituted lacunary salt supported MCM-41 showed remarkable catalytic performances. In acid catalyzed bromination of phenol, it showed 95% conversion obtaining p-bromophenol with 99% selectivity and in case of oxidation of trans-stilbene using hydrogen peroxide oxidant, the same catalyst gave 52% conversion with 99% trans-stilbene oxide selectivity.

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1. Introduction

Polyoxometalates are polyionic metal oxide clusters that have attracted the interest of scientists for many decades. Their interesting properties include high thermal stability, rich redox chemistry and photochemical efficiency etc. These properties help them to be catalytically active towards several industrially and biologically significant reactions [1–5]. So, polyoxometalates (POMs) have applications in fields such as materials science [6,7], analytical chemistry [8] and medicine [9]. An efficient approach to the synthesis of new polyoxometalate architectures is mainly based on lacunary POMs, i.e. species with defect structures.

The most investigated Keggin type heteropoly acids are represented by the general formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$, where X^{n+} is a central hetero atom (Si⁴⁺, P⁵⁺ etc.) and M is an addenda atom (W⁶⁺, Mo⁶⁺, V⁵⁺, etc.) [10]. Polyoxometalates containing replaced one or more addenda atoms are called lacunary polyoxometalates. Removal of one or two MO units from the fully occupied polyoxometalates $[XM_{12}O_{40}]^{n-}$, gives rise to mono-lacunary $[XM_{11}^{VI}O_{39}]^{(n+4)-}$ and di-lacunary $[XM_{10}^{VI}O_{36}]^{(n+5)-}$ polyoxometalates are gaining more importance because of their unique structural properties [11]. It is well known that when the lacunary of Keggin anions

 $[XW_{11}O_{39}]^{(n+4)-}$ is substituted by other transition metal cations, it gives rise to transition metal-modified lacunary heteropoly compounds having the general formula $[XW_{11}O_{39}M]^{n-}$ (where M = first row transition metal). These species have recently attracted considerable attention [12], because of their thermal and chemical stability and the range of possibilities for their modification of electro catalytic property without affecting the primary Keggin structure [13].

Recently, Patel et al. reported the detailed synthesis and characterization of Keggin-type manganese (II)-substituted phosphotungstate and its activity toward liquid phase oxidation of styrene [12]. However, iron is a low-cost and less hazardous metal compared with other transition metals [14]. Therefore a great deal of works has already been carried out on Fe metal substituted heteropoly acids. Mizuno et al. [15] reported synthesis of Fe, Ni substituted Keggin-type heteropoly anion, and evaluated its catalytic activity toward oxidation reaction. Nagai et al. reported iron in the Keggin anion of heteropoly acid catalysts for selective oxidation of isobutene [16]. Dai et al. reported that out of various transition metals in the supported system, Fe is the best metal for oxidation reactions [17]. The excellent activity of single-site iron catalysts for epoxidation as well as oxidation reaction was reported by Thomas and Raja [18]. But so far there is no literature available on the catalytic aspects of supported Cs salt of iron substituted lacunary anions.

According to literature, among various heteropoly acids, phosphotungstic acid is more acidic and generally used for acid



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catalyzed reactions [19]. Its acidity can be enhanced more by converting it into its corresponding acidic Cs salt. Therefore, creation of lacuna in the skeleton of the salt as well as its modification with a transition metal will make it a suitable catalyst for both acid catalyzed as well as oxidation reactions. With these concepts in mind, for the first time we prepared a Cs salt of Fe metal modified lacunary phosphotungstate supported on MCM-41 and studied its catalytic activity toward acid catalyzed bromination of phenol as well as oxidation of trans-stilbene. Our rationale in choosing MCM-41 support lies in the fact that it is endowed with a high surface area, uniform and controllable pore sizes and the periodic orders of their pore packing which provides a tremendous dispersion of the active species over it. What we found from the results is that, the catalyst is incredibly efficient toward both the reactions.

2. Experimental

2.1. Catalyst preparation

Synthesis of the catalyst was carried out in different steps. Since direct impregnation of Cs salt of Fe metal modified lacunary phosphotungstate to MCM-41 is not possible because of the insolubility of the Cs salts in any solvent, in the first step sodium salt of iron substituted lacunary phosphotungstate was prepared. The second step involved the impregnation of Cs⁺ ion on MCM-41, followed by the desired lacunary anion produced from sodium salt of iron substituted lacunary phosphotungstate. The detailed procedure is given below.

For comparison purpose during various characterizations, a plain Cs salt of lacunary phosphotungstate without Fe substitution and a Cs salt of Fe substituted lacunary phosphotungstate have also been prepared.

2.2. Synthesis of sodium salt of iron substituted lacunary phosphotungstate (Na₅FePW₁₁O₃₉)

The sodium salt of lacunary heteropoly compound modified with iron ion was prepared by the alkalization of a solution of dodecatungstophosphoric acid with an aqueous solution of NaHCO₃. First $H_3PW_{12}O_{40}$ · nH_2O (2.88 g) was dissolved in water (10 mL) and the pH of the solution was adjusted to 4.8 using NaHCO₃ solution. This resulted in the formation of lacunary heteropoly anion $[PW_{11}O_{39}]^{7-}$. The solution having pH 4.8 was heated to 90 °C with constant stirring. A solution of FeCl₂ (0.197 g, 1 mmol) in water (10 mL) was added to this hot solution. The Na₅FePW₁₁O₃₉ was obtained by solvent evaporation, and recrystallization from water, followed by subsequent drying at 110 °C for 12 h.

2.3. Synthesis of Cs salt of iron substituted lacunary phosphotungstate supported onto MCM-41 (xLFeW/MCM-41)

The parent MCM-41 was synthesized by sol-gel method [20]. A series of catalysts having different loading of Cs salt of Fe modified lacunary phosphotungstate (30–60 wt%) were synthesized by incipient weight impregnation method by adopting the following procedure.

MCM-41 was first impregnated with aqueous solution of the Cs⁺ precursor (Cs₂CO₃), dried at 110 °C for 12 h [21]. Following this, an aqueous solution of Na₅FePW₁₁O₃₉ was impregnated, dried at 110 °C for 12 h and calcined at 200 °C for 3 h. The catalysts are designated as *x*LFeW/MCM-41 (x = 30–60 wt%).

2.4. Synthesis of cesium salt of iron substituted lacunary phosphotungstate (LFeW) and Cs salt of lacunary phosphotungstate (LW)

The preparation procedure for LFeW was same as described in the section for the preparation of $Na_5FePW_{11}O_{39}$ up to the addition of FeCl₂. After which a saturated solution of the Cs₂CO₃ was added to the hot filtrate and the resulting mixture was allowed to stand overnight at room temperature. The mixture was filtered and the residue was dried at 110 °C for 12 h, which resulted in LFeW. The filtrate was used for the estimation of W and Fe, in order to see the loss during synthesis.

The preparation procedure of LW is almost same with that of LFeW. The only difference is that no $FeCl_2$ was added to it. The rest parts of the preparatory steps are completely same.

2.5. Physico-chemical characterization

Micromeritics ASAP 2020 instrument determined the specific surface area, pore size distribution and pore volume. The samples were degassed at 250 °C for 4 h. Powder X-ray diffraction (PXRD) patterns of the samples were taken in the 2θ range of 1 to 10° at a rate of 2° /min in steps of 0.01° (Rigaku Miniflex set at 30 kV and 15 mA) using Cu K α radiation. The high angle XRD patterns of powdered samples were taken in the 2θ range of 10° - 80° at a rate of 1.2° /min (Philips analytical 3710) using Cu K α radiation. The FT-IR spectra of the samples were recorded using Varian FTIR-800 in KBr matrix in the range of 4000–400 cm⁻¹. Diffuse reflectance UV-vis (DRUV-vis) spectra of the photo catalyst samples were recorded with a Varian Cary 100 spectrophotometer equipped with a diffuse reflectance accessory in the region 200-800 nm. Raman measurements were made using a Jobin-Yvon T64000 Raman spectrometer, configured in a single spectrograph mode. The spectra were recorded against the boric acid background. The acid character of the samples was studied by NH₃-TPD AutoChem-II, (micromeritics) Chemisorption analyzer equipped with a thermal conductivity detector (TCD). About 1 g of powdered sample contained in a quartz "U" tube was degassed at 250 °C for 1 h with ultra-pure nitrogen gas. After cooling the sample to room temperature, NH₃ (20% NH₃ balanced with helium) gas was passed over the sample while it was heated at a rate of 10 °C min⁻¹ and the profile was recorded. The scanning electron microscopic figures of the sample were recorded using a Hitachi S3400 N. Elemental analysis was performed by AAS using PerkinElmer Analysis 300 with acetylene flame and by ICP-OES using PerkinElmer Optima 2100 DV. The X-ray photoelectron spectra of Fe, W, Si and O were recorded using KRATOS apparatus with Mg, Al and Cu K α as X-ray sources.

2.6. Catalytic activity toward bromination of phenol and oxidation of trans-stilbene

Bromination of phenol was carried out in a 50 ml two-necked round bottom flask, charged with 0.2 g catalyst, phenol (2 mmol) in acetic acid (4 ml) and KBr (2.2 mmol). Then 30% H₂O₂ (2.2 mmol) was added drop wise to the reaction mixture and the contents in the flask was stirred continuously at room temperature for 5 h [22]. After 5 h of the reaction, the catalyst was filtered and the solid was washed with ether. The combined filtrates were washed with saturated sodium bicarbonate solution and then shaken with ether in a separating funnel. The organic extract was dried over anhydrous sodium sulfate. The products were analyzed by GC, through capillary column.

The oxidation of trans-stilbene was carried out in a 50 ml twonecked round bottom flask, provided with a mercury thermometer for measuring the reaction temperature and a reflux condenser. The reaction mixture containing 0.015 g catalyst, 1.82 g trans-stilbene



Fig. 1. N_2 adsorption-desorption isotherm of MCM-41 (a) and 50 LFeW/MCM-41 (b).

(10 mmol) and 30% H_2O_2 (20 mmol), 20 ml of acetonitrile was heated at 60 °C for 4 h in an oil bath with stirring. The reaction products were analyzed by gas chromatograph using capillary column (ZB MAX).

3. Results and discussion

Elemental analysis for W and Fe was carried out on the filtrate by gravimetric and volumetric methods [23], the other elements by ICP-OES and AAS methods respectively. The observed values for the elemental analysis of the isolated complex were in good agreement with the theoretical values. Found: Cs, 19.21; W, 58.33; P, 0.91; Fe, 1.64; Calc: Cs, 19.35; W, 59.52; P, 0.91; Fe, 1.64.

The nitrogen adsorption–desorption isotherms for MCM-41 and 50 LFeW/MCM-41 are shown in Fig. 1. N₂ adsorption–desorption resulted in typical type IV isotherm which is defined by Brunauer et al. [24]. It is observed that there are three different well-defined stages in the isotherm of MCM-41. The initial increase in nitrogen uptake at low p/p_0 may be due to monolayer adsorption on the pore walls, a sharp steep increase at intermediate p/p_0 indicates the capillary condensation in the mesopores and a plateau portion at higher p/p_0 is associated with multilayer adsorption on the external surface of the materials [24].

Parent MCM-41 sample exhibits N₂ uptake at a relative pressure of 0.32 which corresponds to the pre-condensation loop. The isotherm shows a H4 type hysteresis loop (according to IUPAC nomenclature) with well-developed step in the relative pressure range \approx 0.9. The incorporation of LFeW in the MCM-41 framework is found to lower the p/p_0 value for capillary condensation step, indicating the shift in pore size to lower value due to incorporation of lacunary acid. The pore diameter is found to decrease with increase in loading of LFeW content over the MCM-41 surface (Fig. 2).

The textural properties such as BET surface area, pore diameter and pore volume derived from the N_2 adsorption–desorption measurements are included in Table 1. The parent MCM-41 has a surface area of 1250 m²/g. But there is a gradual decrease in the value with increasing LFeW content in MCM-41.

As can be seen from Fig. 1, there are considerable number of micropores present in MCM-41. Therefore we suppose, during impregnation, LFeW goes to the micropores present in MCM-41, thereby blocking them. After filling the micropores, it occupies the mesopore walls of MCM-41. Therefore, though there is a decrease in surface area with increase in loading of LFeW on MCM-41, the trend of reduction in surface area and pore volume is not proportional to the decrease in pore size.

Total acidity of the samples was measured from NH₃-TPD and is presented in Table 1. It shows that the total acidity of MCM-41 increases with the increase in loading of LFeW.



Fig. 2. Pore size distribution curve of MCM-41 (a) and 50 LFeW/MCM-41 (b).

The PXRD patterns of MCM-41 and 50 LFeW/MCM-41 are shown in Fig. 3(A). The XRD patterns indicate that the samples exhibited hexagonal structures with a high degree of structural ordering, since the materials like MCM-41 exhibit a strong peak at $2\theta = 2.2^{\circ}$ due to (100) plane and small peaks due to (110), (200) and (210) plane reflections within 5° indicate the formation of well ordered mesoporous materials [25]. The XRD patterns of both the samples are nearly same indicating that the mesoporosity remain intact after introduction of the LFeW on the silica network. So it is considered that LFeW salt was highly dispersed on MCM-41. There is a little bit reduction in intensity, shifting and broadening of the (100) peak in case of 50 LFeW/MCM-41 sample, indicating a slight disturbance in hexagonal symmetry after modification with LFeW [26].

The wide angle XRD of LFeW and LFeW/MCM-41 is shown in Fig. 3(B). The XRD pattern of LFeW shows that it is crystalline in nature. But in case of 50 LFeW/MCM-41 sample, the XRD pattern shows a broad peak showing no characteristic peaks of LFeW,



Fig. 3. (A) Low angle $(0-10^{\circ})$ XRD patterns of MCM-41 (a) and 50 LFeW/MCM-41 (b). (B) Wide angle $(10-80^{\circ})$ XRD patterns of (a) 50 LFeW/MCM-41 and (b) LFeW.

| Table 1 | |
|----------|--------------------------------|
| Textural | properties of different sample |

Tabla 1

| Catalyst | Surface area (m ² g ⁻¹) | Pore volume (cm ³ /g) | Pore diameter (Å) | Acidity (mmol g^{-1}) |
|----------------|--|----------------------------------|-------------------|--------------------------|
| MCM-41 | 1250 | 0.85 | 22.3 | 0.238 |
| 30 LFeW/MCM-41 | 850 | 0.72 | 21.9 | 45.8 |
| 40 LFeW/MCM-41 | 715 | 0.68 | 21.4 | 48.2 |
| 50 LFeW/MCM-41 | 610 | 0.59 | 21.0 | 52.7 |
| 60 LFeW/MCM-41 | 575 | 0.53 | 20.6 | 49.4 |

indicating an undegraded and very high dispersion of LFeW in a non-crystalline form on the surface of MCM-41.

The FT-IR spectra of various samples are shown in Fig. 4. In case of LFeW/MCM-41 the broad band around 3500 cm⁻¹ may be attributed to surface silanols and adsorbed water molecules, while deformational vibrations of adsorbed molecules cause the absorption bands at 1623–1640 cm⁻¹ [20]. The spectrum of the Keggin anion $[PW_{12}O_{40}]^{3-}$, shows prominent bands at 1080, 985, 890 and 800 cm⁻¹ which are characteristic of Keggin structure and are assigned to $\nu_{(P-O)}$, $\nu_{(W=O)}$, corner-sharing $\nu_{(W-O-W)}$, and edgesharing $v_{(W-O-W)}$, respectively [27]. In case of LW the 1080 cm⁻¹ band has been splitted into two components (1084–1044 cm⁻¹), due to the symmetry decrease of the PO₄ tetrahedron. The other bands found are 953 ($\nu_{as(W-O_d)}$), 860 ($\nu_{as(W-O_b-W)}$), 809 and 742 cm⁻¹($\nu_{as(W-O_c-W)}$), and differ from those of $[PW_{12}O_{40}]^{3-}$ [27]. The spectra for LFeW showed characteristic splitting for the P-O bond frequency at 1074 and 1052 cm⁻¹, which faced a slight shifting toward lower frequency compared to bulk lacunary unit. This clearly indicated that Fe was introduced into the octahedral lacuna. The slight shifting of bands in FT-IR spectra of LFeW sample compared to bulk LW may be due to formation of pseudo-symmetric environment that resulted from the replacement of a W atom with a Fe atom. It can be observed that 50 LFeW/MCM-41 sample has similar vibration bands to those of the corresponding pure LFeW,



Fig. 4. FT-IR spectra of LW (a), LFeW (b) and 50 LFeW/MCM-41(c).

which suggests that the LFeW structures remained intact regardless of their functionality. The shifting in the positions of the IR absorption peaks are due to both hydrogen bonding and chemical interactions that exist between the surface of LFeW and the MCM-41.

The UV–vis DRS gives information about the non-reduced heteropoly anion due to charge transfer from oxygen to metal. The UV–vis DRS spectra of the LW, 50 LFeW/MCM-41 and LFeW are shown in Fig. 5. The LFeW sample exhibits two absorption maxima at 200–206 nm and 260–320 nm (λ_{max}), which are attributed to oxygen-to-tungsten charge-transfer (OMCT) at W=O and W–O–W bonds, respectively. A broad peak at 680 nm was obtained in LFeW which arises due to ${}^{4}T_{2} \leftarrow {}^{6}A_{1}$ transition and a similar weak absorption peak was observed for LFeW in the range of around 540 nm may be the presence of ${}^{4}T_{1} \leftarrow {}^{6}A_{1}$ transition of iron [28]. The λ_{max} of 50 wt% loading of LFeW on MCM-41 is same as that for LFeW (Fig. 5). This confirms the presence of the undegraded LFeW on the surface of MCM-41 which is online with the XRD results.

To study the surface morphology and to assess the dispersion of the active components over the surface of MCM-41, SEM investigation was performed for 50 LFeW/MCM-41 (Fig. 6). The sample does not have a well-defined hexagonal structure like MCM-41. Further, aggregates without regular shapes are observed, which is in agreement with the reported literature for metal incorporated materials [29], indicating a slight reduction in hexagonal symmetry of MCM-41 due to metal incorporated lacunary salt modification, which is in line with the low angle XRD results.

The XPS investigation of binding energies and intensities of the surface elements provides information on the chemical states and relative quantities of the outermost surface compounds. Fig. 7a displays the XPS survey spectrum obtained for 50 LFeW/MCM-41. The main peaks indicate the presence of W,O, P, Cs, Si and Fe in the sample. One distinct peak can be observed at binding energy 724 eV for the 50 LFeW/MCM-41 samples. The binding energy of about 724 eV for the Cs $3d_{5/2}$ peak is characteristic of Cs⁺. The W 4f XPS spectrum of 50 LFeW/MCM-41 is shown in Fig. 7b. The catalyst shows two peaks at 35.62 and 37.15 eV. The shifting of W 4f peaks toward a higher BE indicates the flow of electron density toward silica from LFeW through the Si–O–W linkages [30].



Fig. 5. UV-vis DRS of LW (a), 50 LFeW/MCM-41 (b) and LFeW (c).



Fig. 6. SEM image of 50 LFeW/MCM-41.

The Fe 2p XPS spectrum of 50 LFeW/MCM-41 samples is shown in Fig. 7c. Two distinct iron peaks can be observed at binding energies 709.76 and 723.59 eV for the 50 LFeW/MCM-41 samples. The binding energy of about 709.5 eV for the Fe $2p_{3/2}$ main peak is in agreement with the typical values for the iron oxides reported in the literature [31,32]. The peaks are shifted toward a higher binding energy, which indicated the strong interaction of iron within the lacunary structure and with the support.

Raman scattering spectroscopy is considered to be an effective technique for studying the structure of LFeW and its incorporation on MCM-41. The Raman scattering spectra of LFeW and 50 LFeW/MCM-41 are shown in Fig. 8. The bulk LFeW gives peaks at 966, 921, 885 and 824 cm^{-1} which are attributed to the stretching vibrations of P–O, W–O_b–W, W–O_c–W and W–O_t bonds of metal modified mono lacunary Keggin unit, respectively. The band at 716 cm⁻¹ may be due to WO₃ [33]. The band at about 220 cm⁻¹ may be attributed to symmetric stretching vibration of W–O_a band [34]. The 50 LFeW/MCM-41 sample shows all the above described peaks of LFeW, but the intensity of the peaks are low, compared to the bulk LFeW and slightly shifted toward higher wave

number values due to strong interactions between the MCM-41 support and lacunary Keggin unit [35]. These results confirm the incorporation of undegraded LFeW on MCM-41 surface.

3.1. Catalytic activity

Many studies were already carried out on oxidation of transstilbene as well as bromination of phenol using various catalysts. Maurya and Kumar [36] reported oxidation of trans-stilbene. But the inherent disadvantages associated were higher temperature, and longer reaction time. Our group (Parida and co-workers [37]) reported bromination of phenol over heteropoly acid (HPA)impregnated zirconium phosphate (ZrP), with 86% conversion. But the most enchanting part of the present study is that, this single catalyst is showing its superlative catalytic activity toward both the reactions.

We have investigated the use of various LFeW/MCM-41 as catalysts in the acid catalyzed bromination of phenol as well as in the oxidation of trans-stilbene. The bromination of phenol was carried out in acetic acid medium with KBr and hydrogen peroxide at room

Table 2

Conversion and selectivity of various catalysts toward bromination of phenol.

| Catalyst | Conversion (%) | Selectivity (%) | | Yield (%) of p-bromophenol |
|----------------|----------------|-----------------|---------------|----------------------------|
| | | o-Bromophenol | p-Bromophenol | |
| MCM-41 | 32 | 35 | 65 | 21 |
| LFeW | 59 | 40 | 60 | 35 |
| 30 LFeW/MCM-41 | 76 | 38 | 62 | 47 |
| 40 LFeW/MCM-41 | 85 | 29 | 71 | 60 |
| 50 LFeW/MCM-41 | 95 | 1 | 99 | 94 |
| 60 LFeW/MCM-41 | 89 | 19 | 81 | 72 |

Condition: Phenol (2 mmol), KBr (2.2 mmol), catalyst (0.02 g), time (5 h).

Table 3

Conversion and selectivity of various catalysts toward oxidation of trans-stilbene.

| Catalyst | Conversion (%) | Selectivity (%) | | Yield (%) Of Trans-stilbene oxide |
|---------------|----------------|----------------------|--------------|-----------------------------------|
| | | Trans-stilbene oxide | Benzaldehyde | |
| MCM-41 | 5 | 43 | 57 | 2 |
| LFeW | 14 | 63 | 37 | 9 |
| 30LFeW/MCM-41 | 16 | 75 | 25 | 12 |
| 40LFeW/MCM-41 | 36 | 87 | 13 | 31 |
| 50LFeW/MCM-41 | 52 | 99 | 1 | 51 |
| 60LFeW/MCM-41 | 46 | 90 | 10 | 41 |

Condition: Trans-stilbene (10 mmol), H2O2 (20 mmol), catalyst (0.015 g), time (4 h).



Fig. 7. (a) XPS spectra of 50 LFeW/MCM-41. (b) XPS of W4f_{7/2} and W4f_{5/2} of 50 LFeW/MCM-41. (c) XPS of Fe2p_{3/2} and Fe2p_{1/2} of 50 LFeW/MCM-41.



Fig. 8. Raman spectra of LFeW (a) and 50LFeW/MCM-41 (b).

temperature. The results show that all the catalysts were efficient for catalyzing the reaction. The selectivities of para- and orthobromo phenol obtained are shown in Table 2. Among the catalysts with different LFeW loading, 50 LFeW/MCM-41 showed highest conversion 95% with 99% selectivity toward p-bromophenol. Further, increase in the LFeW loading decreased the phenol conversion. The acid sites of the catalysts are given in Table 1. It is evident from the data that there is an initial increase in the acidity up to 50 wt% loading, and thereafter the acidity decreases. The highest acidity for 50 wt% loading may be due to the formation of monolayer coverage of LFeW on MCM-41. The decrease in the surface acidity at high LFeW concentration is probably due to the formation of poly layer coverage of LFeW on MCM-41.

When the reaction was carried out without catalyst the conversion was only 25% with nearly equal ortho and para selectivity.

From the selectivity data, it is supposed that phenol may interact with the Lewis acid sites of the catalyst, as a result, the electron density at ortho positions of the aromatic ring decreases, which hinders the attack of incoming electrophile (Br⁺) at two ortho position and preferred to attack on para position [38,39].

Various solvents including carbon tetrachloride, hexane, dichloromethane, methanol, acetonitrile and acetic acid were used for this reaction. The best results were obtained when acetic acid was used as a solvent compared to others. In presence of H_2O_2 , acetic acid gives peracetic acid, which is a stronger oxidant than H_2O_2 and efficiently oxidizes the Br⁻ to Br⁺, which could not be observed in case of other solvents. It is assumed that the catalyst LFeW/MCM-41 reacts with hydrogen peroxide and forms peroxo species in presence of acetic acid [40]. The formed peroxo metal species then enhances the oxidation of Br⁻ (KBr) to Br⁺ (HOBr), which reacts in presence of active centers of LFeW/MCM-41 with the phenol to give, brominated compounds.

In order to establish the oxidative nature of the synthesized catalyst, oxidation of trans-stilbene was carried out using hydrogen peroxide as oxidant and the results are shown in Table 3. It is found that pure MCM-41 showed 5% conversion. The conversion of trans-stilbene increases with increase in loading of LFeW up to 50 wt%. An optimum 52% conversion with 99% selectivity toward trans-stilbene oxide was observed using 50 LFeW/MCM-41 which decreased on further increase in LFeW loading.

3.2. Heterogeneity test

Since LFeW is water tolerant at room temperature, we carried out a heterogeneity test only for the oxidation reaction which was carried out at a higher temperature in order to know whether the catalyst was truly behaving heterogeneously or not toward this reaction. During the catalytic oxidation of trans-stilbene, the solid catalyst was separated from the reaction mixture by filtration after 2 h of the reaction and the filtrate obtained was continuously stirred under same reaction conditions for further 3 h. GC analysis showed no increment in the conversion. This fact suggests that there is no loss of catalyst components during the course of the reaction which confirmed the heterogeneity of the catalyst.

3.3. Recyclability of the catalyst

The catalyst with 50 wt% loading was used for recycling experiments. In order to regenerate the catalyst after completion of reaction, it was separated by filtration, washed several times with conductivity water and dried at 110 °C. The material was used for further run in the bromination of phenol with a fresh reaction mixture. In the regenerated sample after two cycles, the yield decreased by 3%. The activity loss observed with the regenerated catalyst could be due to partial loss of acid sites of the catalyst during reaction/regeneration.

4. Conclusion

We have developed a Cs salt of Fe substituted mono lacunary phosphotungstate material and supported it on MCM-41 to obtain a new and robust heterogeneous catalyst. The XRD and nitrogen adsorption–desorption studies revealed that the modified samples retained the mesoporosity. The pore diameter and pore volume decreased with an increase in LFeW loading. FT-IR, UV–vis DRS and XPS studies revealed the presence of Fe atoms in lacunary unit and also indicated the presence of undegraded lacunary unit on MCM-41. The material proved to be an efficient catalyst for acid catalyzed bromination of phenol as well as oxidation of trans-stilbene. Good catalytic activity and recycling efficiency for acid catalyzed as well as oxidation reaction suggests the potential application of this Cs salt of Fe substituted mono lacunary phosphotungstate supported MCM-41 material for the synthesis of additional organic molecules.

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