

# Characterization of novel Cs and K substituted phosphotungstic acid modified MCM-41 catalyst and its catalytic activity towards acetylation of aromatic alcohols

SURJYAKANTA RANA, SUJATA MALLICK, DHARITRI RATH and K M PARIDA\*

Colloids and Materials Chemistry Department, Institute of Minerals and Materials Technology, Bhubaneswar 751 013, India

e-mail: kmparida@yahoo.com

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**Abstract.** The MCM-41 supported  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  and  $\text{K}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  salts were synthesized by incipient wetness impregnation method. The solids were characterized by  $\text{N}_2$  adsorption–desorption isotherms, FT-IR, XRD, and temperature programmed desorption, etc. This catalyst has been found to exhibit excellent activity for acetylation of phenolic compounds. The catalyst is stable and reusable giving 96% conversion with 100% selectivity towards acetate products.

**Keywords.** Acetylation; MCM-41; phenol; Cs and K salt of phosphotungstic acid.

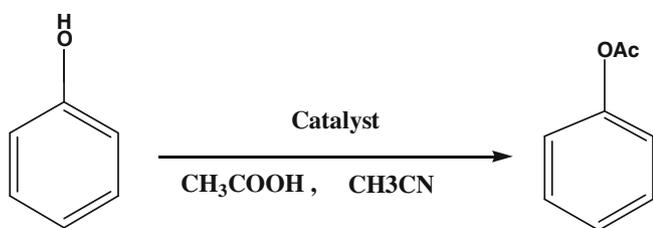
## 1. Introduction

Mesoporous molecular sieves designated as M41S have attracted the attention of many researchers since their discovery at Mobil Oil Corporation in 1992.<sup>1</sup> These materials possess well-defined mesopores, the diameters of which can be tailored to the desired value (18–100 Å) by the proper choice of surfactants, auxiliary organics and synthesis parameters.<sup>2</sup> Mesoporous silica of the MCM-41 type is an important class of a hexagonal arrangement of cylindrical pores between which an amorphous  $\text{SiO}_2$  network is interposed.<sup>3</sup> The MCM-41 structure exhibits high thermal stability (up to 900°C), a large surface area (about 1000 m<sup>2</sup>/g) and a large adsorption capacity. Pure silica mesoporous molecular sieves comprise silanol -OH groups, which are practically non-acidic. Acidic sites can be generated in this material by introduction of some heteroatoms such as aluminium<sup>4</sup> or zinc<sup>5</sup> into the MCM-41 framework. However, the acidity of these materials is moderate and the thermal stability of modified molecular sieves is always lower than that of pure silica ones. Attempts have also been undertaken to generate the catalytically active centres by means of encapsulation of transition metal complexes or heteropoly acids into MCM-41 channels.

The heteropoly acids having Keggin anion structures have received much attention due to their simple preparation and strong acidity.<sup>6,7</sup> Especially phosphotungstic acid (PTA) has been extensively studied<sup>8–10</sup> since it possesses super acidity.<sup>11</sup> However, some of the major problems associated with HPAs in the neat form are their low efficiency due to low surface area, rapid deactivation, and relatively poor stability. Supporting the heteropoly acids on solids with high surface area is a useful method for improving catalytic performance in liquid–solid and gas–solid surface heterogeneous reactions. For instance, Hu *et al.*<sup>12</sup> have used heteropoly acids supported on silica and alumina for the preparation of octyl phenol and nonyl phenol, through the alkylation reaction of phenol with 1-octene and nonene, respectively. Although the surface area of HPA is low, salts of large alkaline ions as  $\text{Cs}^+$  and  $\text{K}^+$  displayed high surface area and microporous structure.<sup>13</sup> The wet impregnation of HPA on these salts can be considered as an alternative method to prepare supported HPA catalysts to improve surface activity of the catalysts. Pizzio *et al.* reported  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  on their partially substituted Cs or K salts as catalyst for the production of Isoamyl acetate.<sup>14</sup>

In this work we have studied the activity, selectivity and deactivation behaviour of cesium and potassium salts of phosphotungstic acid supported MCM-41 for the liquid phase acetylation of phenols and substituted phenols.

\*For correspondence



**Scheme 1.** Schematic presentation of acetylation of aromatic alcohols.

## 2. Materials and methods

### 2.1 Material preparation

**2.1a Synthesis of MCM-41:** In a typical synthesis method 1.988 g of cetyltrimethyl ammonium bromide (CTAB, 98%, S.D. fine chem.) was dissolved in 120 g of water at room temperature. After complete dissolution, 8 ml of aqueous  $\text{NH}_3$  (32% in water, Merck) was added to the above solution. Then 10 ml of tetraethyl orthosilicate (TEOS, 99%, Aldrich) was added to the solution under vigorous stirring (300 rpm). The hydrolysis of TEOS takes place during the first 2 min at room temperature (the solution becomes milky and slurry forms) where as the condensation of the mesostructured hybrid material is achieved after 1 h of reaction. The material was then filtered and allowed to dry under static air at  $80^\circ\text{C}$  for 12 h. The mesoporous material was finally obtained by calcination of the hybrid structure at  $550^\circ\text{C}$  for 5 h.<sup>15</sup>

**2.1b Synthesis of Cs and K salt of phosphotungstic acid:** Cesium or potassium salt of phosphotungstic acid ( $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  and  $\text{K}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ) were prepared by adding pre-determined amounts of aqueous solution of the corresponding carbonates to the phosphotungstic acid (PTA) solution with stirring.<sup>16</sup> The resulting precipitate was dried at  $110^\circ\text{C}$  overnight in vacuum and calcined at  $300^\circ\text{C}$  for 3 h.

**2.1c Synthesis of catalyst:** In our preliminary studies we have found that 50wt% HPA promoted MCM-41

shows highest acidity, surface area.<sup>17</sup> So the present study is confined to 50wt% PTA promoted MCM-41. Appropriate quantity of PTA, Cs and K salt solution in 50wt% was taken with 1 g of neat MCM-41 in a beaker. It was heated with continuous stirring till complete dryness. Then it was dried at  $110^\circ\text{C}$  for 24 h and then calcined at  $500^\circ\text{C}$  for 3 h. The catalysts are here after referred to as 50PTA/MCM-41, 50CsPTA/MCM-41 and 50KPTA/MCM-41.

### 2.2 Characterization

Low angle XRD patterns of powdered samples were taken in the  $2\theta$  range of 1 to  $30^\circ$  at a rate of  $2^\circ/\text{min}$  in steps of  $0.01^\circ$  (Rigaku Miniflex set at 30 kV and 15 mA) using  $\text{Cu K}\alpha$  radiation. The wide angle XRD patterns of powdered samples were taken in the  $2\theta$  range of  $20$  to  $80^\circ$  at a rate of  $1.2^\circ/\text{min}$  (Philips analytical 3710) using  $\text{Cu K}\alpha$  radiation.

The BET surface area, average pore diameter and pore volume of all the samples were determined by multipoint  $\text{N}_2$  adsorption–desorption method at liquid  $\text{N}_2$  temperature (77 K) by an ASAP 2020 (Micromeritics). Prior to analyses, all the samples were degassed at  $200^\circ\text{C}$  and  $10^{-4}$  Torr pressure for 2 h to evacuate the physically adsorbed moisture. The mesopore structure was characterized by the distribution function of mesopore volume calculated by applying the Barrett–Joyner–Halenda (BJH) method.

The FT-IR spectra of the samples were recorded using Varian FTIR-800 in KBr matrix in the range of  $4000\text{--}400\text{ cm}^{-1}$ .

The  $\text{NH}_3$ -TPD of both MCM-41 and Cs salt of phosphotungstic acid supported MCM-41 samples was carried out in a CHEM BET-3000 (Quantachrome, USA) instrument. About 0.1 g powdered sample was taken inside a quartz ‘U’ tube and degassed at  $350^\circ\text{C}$  for 1 h with nitrogen gas flow. The sample was then cooled to  $30^\circ\text{C}$  and the gas flow was changed to  $\text{NH}_3$  for 30 min. The  $\text{NH}_3$  adsorbed sample was then purged with nitrogen flow for another 30 min at the same temperature to

**Table 1.** Textural parameters of various salt of PTA loaded MCM-41 and its catalytic activity towards acetylation of phenol.

Catalysts	Surface area ( $\text{m}^2/\text{g}$ )	Pore diameter (nm)	Pore volume ( $\text{cm}^3/\text{g}$ )	Acidity <sup>a</sup> ( $\text{mmol g}^{-1}$ )	Yield (%)	SA after regeneration	Yield (%) after regeneration
MCM-41	987	3.74	0.92	0.238	79	980	77
50PTA/MCM-41	525	3.25	0.42	25.6	89	522	86
50KPTA/MCM-41	561	2.68	0.37	38.9	90	559	87
50CsPTA/MCM-41	700	2.96	0.51	50.6	96	695	93

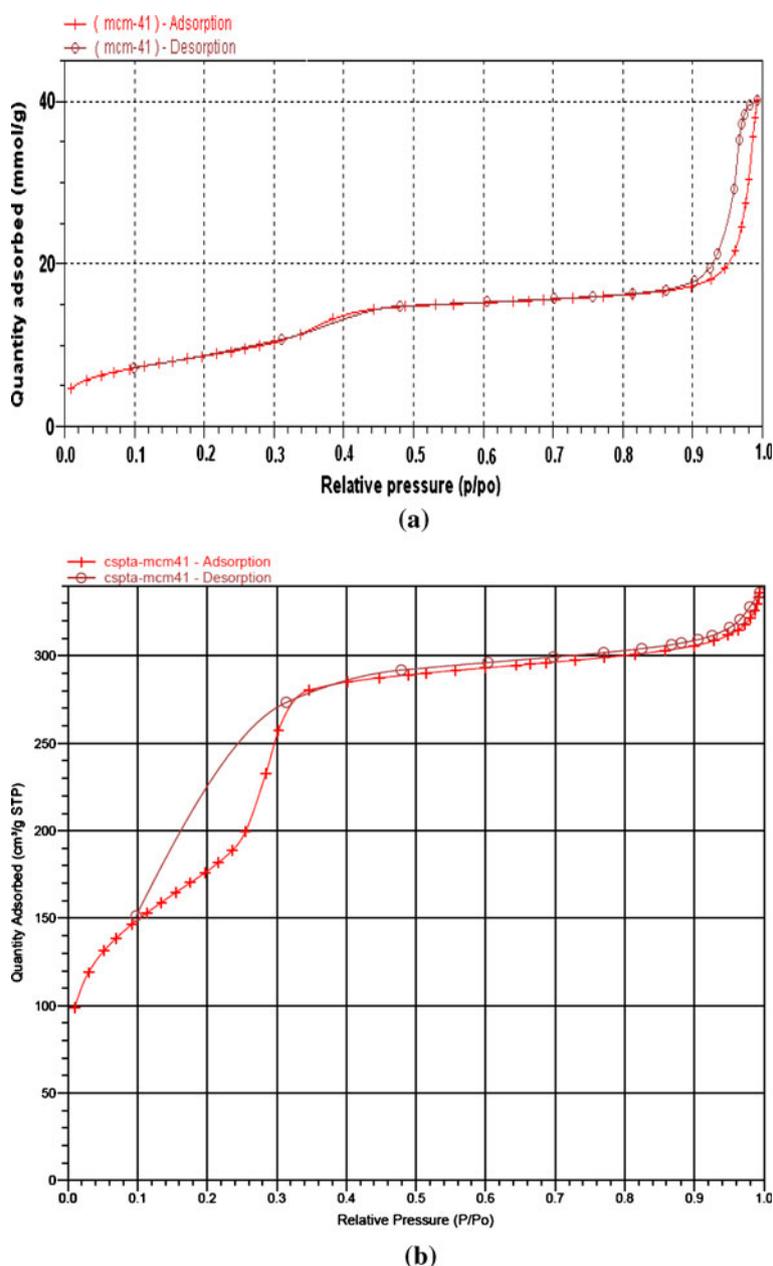
<sup>a</sup> Acidity determined from TPD study

remove any weakly adsorbed  $\text{NH}_3$  on the catalyst surface. It was then heated up under nitrogen flow at a heating of  $10^\circ\text{C}/\text{min}$  up to  $600^\circ\text{C}$  and the spectra were recorded.

### 2.3 Catalytic activity towards acetylation of phenol

In a round-bottom flask (25 mL) equipped with a magnetic stirrer, a solution of Benzyl alcohol or phenol and their substrate (1.0 mmol) in acetic acid (1.0 mol) and  $\text{CH}_3\text{CN}$  (2 mL) was prepared. The catalyst (0.01g) was added to this solution and the reaction mixture was

stirred at  $50^\circ\text{C}$  for 30 min. Upon completion of the reaction, the reaction mixture was filtered and washed with sodium bicarbonate and extracted with  $\text{CH}_2\text{Cl}_2$ . Combined organic layers were dried over  $\text{Na}_2\text{SO}_4$ , the solvent was removed by evaporation to afford the acetylated compound (scheme 1). The product was analysed through gas chromatograph using capillary column of ZB MAX connected with a FID detector. The conversion was calculated on the basis of mole percent of aromatic alcohol divided by initial area percent (olefin peak area from GC) to get the response factor. The unreacted moles of aromatic alcohol remained in the



**Figure 1.** (a)  $\text{N}_2$  adsorption–desorption isotherms of MCM-41 sample. (b)  $\text{N}_2$  adsorption–desorption isotherms of 50 wt% CsPTA/MCM-41 sample.

reaction mixture were calculated by multiplying response factor with the area percentage of the GC peak for olefins obtained after the reaction. The conversion and selectivity were calculated as follows:

$$\text{Yield (\%)} = \frac{\text{Selectivity (\%)}}{\text{Conversion (\%)}} \times 100.$$

Conversion (mol%)

$$= \left[ \frac{\text{initial mol\%} - \text{final mol\%}}{\text{initial mol\%}} \right] \times 100$$

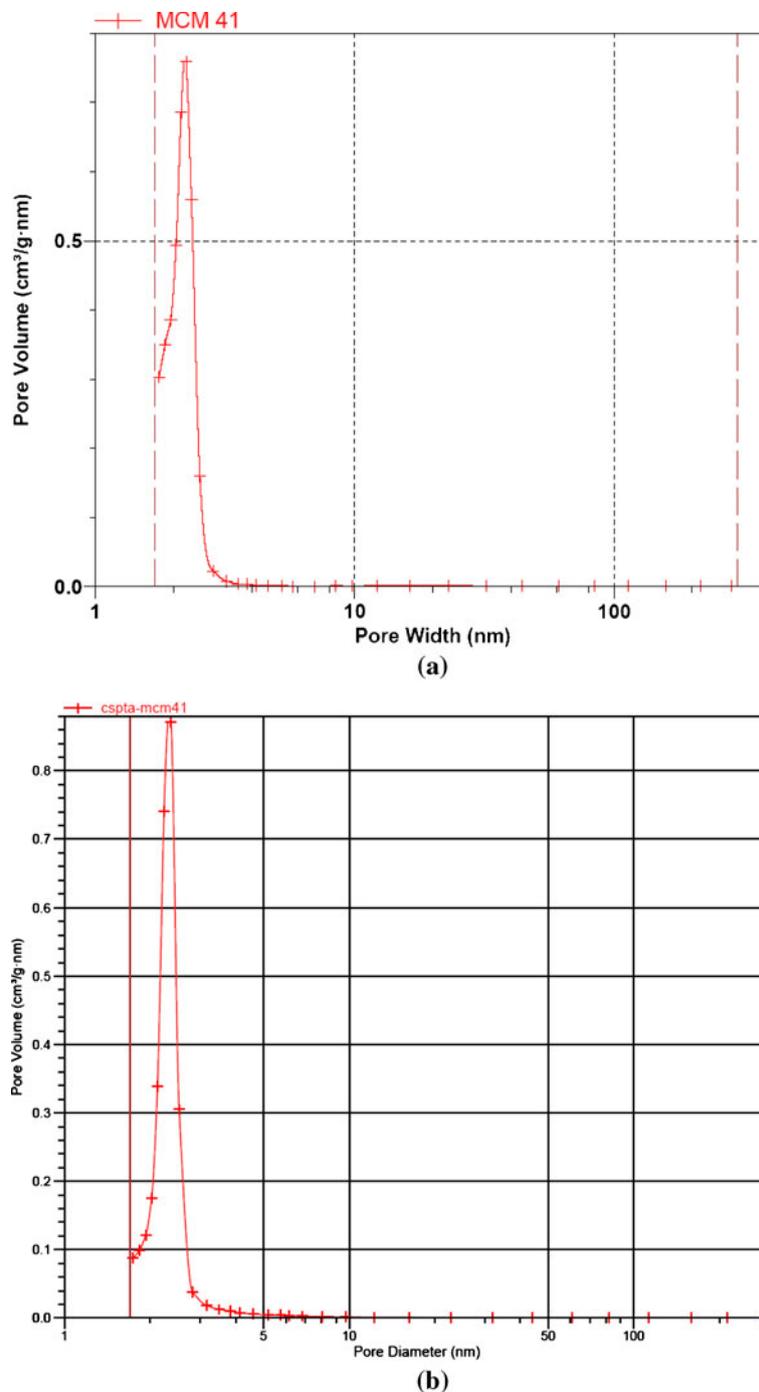
Acetate selectivity

$$= \left( \frac{\text{GC peak area of acetate}}{\text{GC peak area of all product}} \right) \times 100$$

### 3. Results and discussion

#### 3.1 Characterization

The BET surface area of the solids determined from N<sub>2</sub> adsorption–desorption isotherms are shown in table 1. The partially substituted salts presented high surface



**Figure 2.** (a) Pore size distribution of MCM-41 sample. (b) Pore size distribution of 50wt% CsPTA/MCM-41 sample.

area compared to the bulk acid as already reported by several authors.<sup>18–20</sup> The potassium salts displayed lower surface area than the cesium salts and the proton containing heteropoly acid showed lower surface area than both potassium and cesium salt. The Pore size and pore volume of modified sample is decreased than the parent MCM-41.

The nitrogen adsorption–desorption isotherm was carried out over the above catalysts and the typical isotherms are shown in (figure 1 and figure S1). Parent MCM-41 shows a sharp increase at  $P/P_0 = 0.3$  whereas the HPA modified MCM-41 samples show the increase at  $P/P_0 = 0.1–0.15$ . The modification of the MCM-41 framework with HPA is found to lower the  $P/P_0$  for capillary condensation step, indicating the shift in pore size to lower value. The pore diameter and pore volume is found to decrease with modification of HPA on MCM-41 (figure 2 and figure S2).

The powder X-ray diffraction patterns of MCM-41, 50wt% of PTA, Cs and K salt of PTA loaded MCM-41 are shown in figure 3. The XRD figures showed a strong peak at  $2\theta = 2.2^\circ$  due to d100 plane. Other two weak peaks below  $5^\circ$  suggest the hexagonal symmetry of the materials.<sup>2,21</sup> The modification of MCM-41 with Cs and K with PTA considerably reduces the intensities of the XRD peaks and shifted towards higher angle. But the structure of the modified MCM-41 is still mesoporous and similar to that of MCM-41.

The FT-IR spectra of MCM-41 and modified MCM-41 are shown in figure S3. The Keggin anion structure of PTA consists of a  $PO_4$  tetrahedron surrounded by twelve  $WO_6$  octahedra, which share edges in  $W_3O_{13}$  triad groups and corners between each triad through oxygen atoms.<sup>22</sup> From the structure, it is possible to

deduce four types of oxygens, which provide four characteristics bands in the range of  $1200–700\text{ cm}^{-1}$ . The exact position of these bands depends upon the hydration degree<sup>23,24</sup> and the type of counter cation present.<sup>25</sup>

The spectra showed a broad band around  $3100–3600\text{ cm}^{-1}$  for all samples, which is due to adsorbed water molecules. The absorption band due to H–O–H bending vibration in water is at  $1620–1640\text{ cm}^{-1}$ . The absorption band around  $1087–1092\text{ cm}^{-1}$  is due to Si–O asymmetric stretching vibrations of Si–O–Si bridges. The PTA and PTA salts ( $Cs_{2.5}H_{0.5}PW_{12}O_{40}$  and  $K_{2.5}H_{0.5}PW_{12}O_{40}$ ) supported MCM-41 show the characteristic IR bands at  $1080\text{ cm}^{-1}$  (P–O in the central tetrahedra),  $984\text{ cm}^{-1}$  (terminal W=O),  $897\text{ cm}^{-1}$ ,  $812\text{ cm}^{-1}$  (W–O–W) and  $595\text{ cm}^{-1}$  (Oa–P–Oa,) associated with the asymmetric vibrations in the Keggin polyanion; however, the CsPTA/MCM-41 and KPTA/MCM-41 catalysts are distinctively characterized by a split in the W=O band. This doublet becomes more prominent as the Cs stoichiometry in the catalyst increases (not shown here), suggesting a direct interaction between the  $[PW_{12}O_{40}]^{3-}$  anions and  $Cs^+$  or  $K^+$  cations. Similar observations have been reported for the case of W=O vibrations in  $Cu_{1.5}PW_{12}O_{40}$  anions.<sup>26</sup>

The adsorption–desorption technique permits to determine the strength of acid sites present in the catalyst surface together with total acidity. The  $NH_3$ -TPD profile of parent MCM-41 and different salts of phosphotungstic acid are shown in figure S4, and the amounts of  $NH_3$  desorbed are presented in table 1. The MCM-41 sample gives broad peak about  $100^\circ\text{C}$  to  $300^\circ\text{C}$ , indicating broad distribution of surface acid sites (figure S4a). The 50CsPTA/MCM-41 sample shows a large broad pattern of TPD profile in

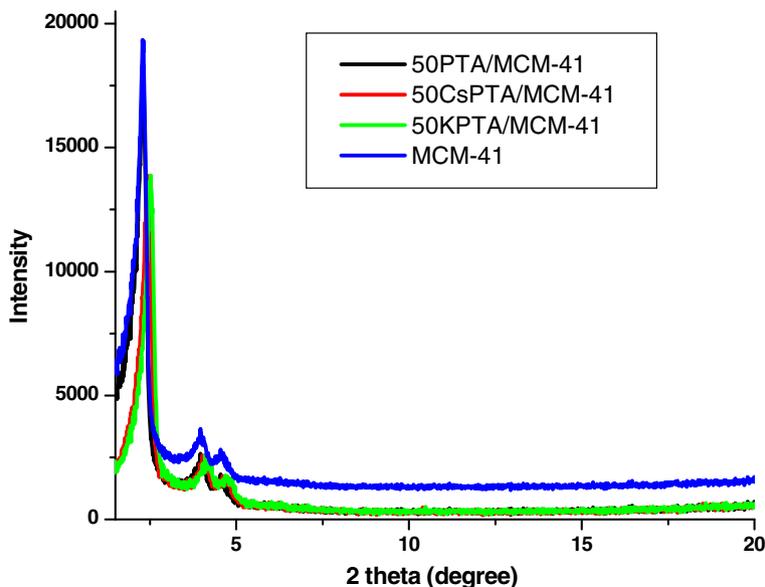
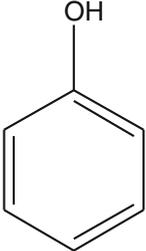
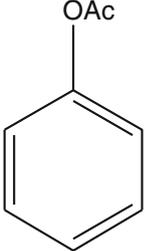
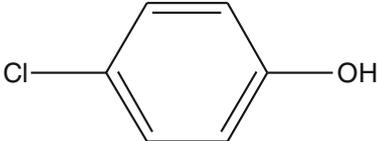
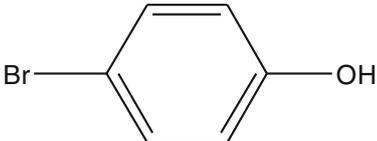
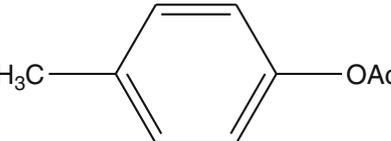
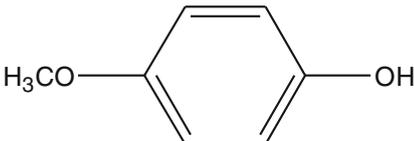
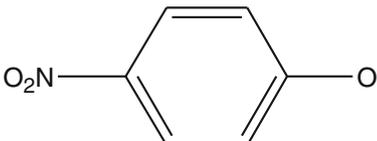
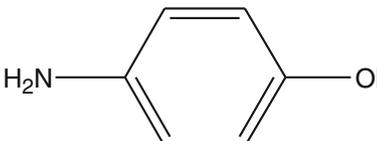
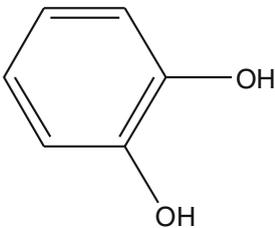
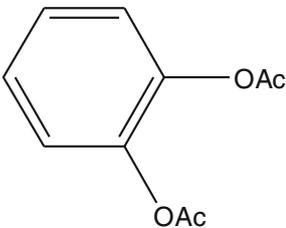
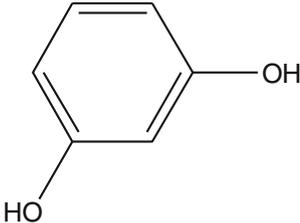
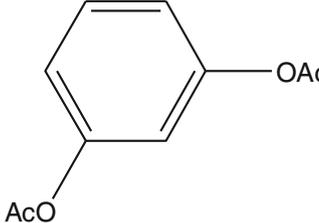
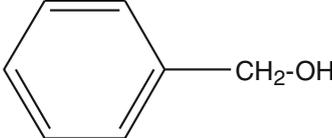
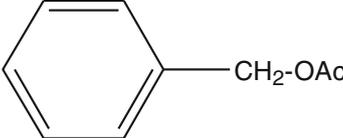
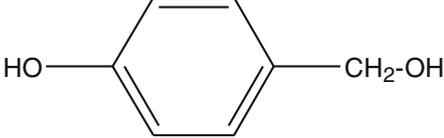
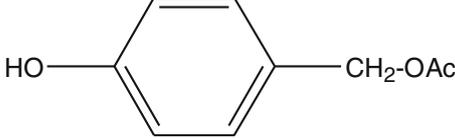
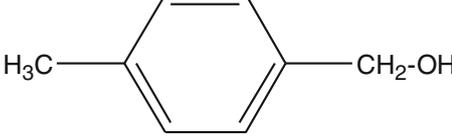
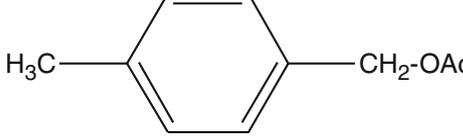
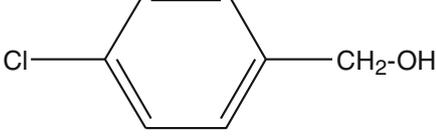
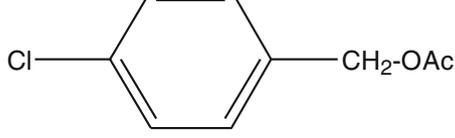


Figure 3. XRD patterns of MCM-41 and modified MCM-41.

**Table 2.** Acetylation of aromatic alcohol with acetic acid catalysed by 50CsPTA/MCM-41.

Substrate	Product	Time (min)	Yield(%)
		30	96
		30	97
		30	97
		30	98
		30	99
		30	91
		30	94
		30	97
		30	96

**Table 2.** (Continued).

Substrate	Product	Time (min)	Yield(%)
		30	96
		30	97
		30	98
		30	99
		30	97

comparison to 50KPTA/MCM-41 and 50PTA/MCM-41, revealing the highest number of acid sites. It is also evident from table 1 that the total acidity increased in the following order, MCM-41 < 50PTA/MCM-41 < 50KPTA/MCM-41 < 50CsPTA/MCA-41.

### 3.2 Catalytic activity evaluation

The liquid-phase acetylation of phenol and benzyl alcohol with acetic acid gives the corresponding acetate as the only product. The influence of Cs and K salt

of phosphotungstic acid on acetylation of phenol and the product selectivity is presented in table 1. Among the catalysts studied, 50CsPTA/MCM-41 showed highest conversion having 96% yields. The catalytic activity of various salt of PTA supported on MCM-41 in acetylation of phenol is decreased in the following order, 50CsPTA/MCA-41 > 50KPTA/MCM-41 > 50PTA/MCM-41. Similar trend was reported by Pizzio *et al.*<sup>14</sup> for isopropanol dehydration reaction taking  $H_3PW_{12}O_{40}$  on their partially substituted Cs or K salts as catalyst. The higher activity as well as

**Table 3.** Acetylation of benzyl alcohol over recently reported catalysts.

Catalyst	Substrate	Time (min)	Yield (%)	Reference
50CsPTA/MCM-41	Acetic acid	30	96	Present study
Sn(tpp)(BF <sub>4</sub> ) <sub>2</sub>	Acetic anhydride	2	99	27
H <sub>6</sub> [P <sub>2</sub> W <sub>18</sub> O <sub>62</sub> ]	Acetic anhydride	400	95	28
H <sub>14</sub> [NaP <sub>5</sub> W <sub>29</sub> MoO <sub>110</sub> ]	Acetic anhydride	10	95	28
Sn <sup>IV</sup> (tpp)(OTf) <sub>2</sub>	Acetic anhydride	1	94	29
H <sub>14</sub> [NaP <sub>5</sub> W <sub>30</sub> O <sub>110</sub> ]	Acetic anhydride	60	95	30
Ferric perchlorate	Acetic acid	900	95	31

selectivity of 50CsPTA/MCM-41 was due to higher number of acid sites and surface area.

The conversion was only 5% without catalyst, suggesting the influence of solid acid catalyst on the conversion. Several organic substrates including phenol were subjected to the acetylation reaction using 50CsPTA/MCM-41 as catalyst and the results are summarized in table 2. The presence of electron withdrawing substituents (nitro group and halo group) on the aromatic ring substantially decreases the rate of acetylation while an electron-donating group (-CH<sub>3</sub>, -OCH<sub>3</sub>, -NH<sub>2</sub>, etc.) increases it. Similar types of observations were found for substituted benzyl alcohol as substrate towards acetylation reaction.

In order to show the advantage of the presented method in the acetylation reactions, we have compared the obtained results in the acetylation of phenol with acetic acid catalysed by heteropoly acid modified MCM-41 with some of those reported in the literature (table 3).

### 3.3 Recyclability of the catalyst

In order to regenerate the catalyst after 30 min of reaction, it was separated by filtration, washed several times with conductivity water and dried at 110°C. The material calcined at 500°C was used in the acetylation 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 surface area which is confirmed from surface area data (table 1).

## 4. Conclusions

Phosphotungstic acid and its cesium and potassium salts supported on MCM-41 are found to be very active and an efficient catalyst for acetylation of aromatic alcohols using inexpensive and easily available acetic acid as acetylating agent but 50CsPTA/MCM-41 showed highest conversion having 96% yields. From the XRD study, we have confirmed that the mesoporosity of parent MCM-41 remain intact after heteropoly acid modification. FTIR spectra confirmed that the heteropoly acids retain their Keggin type structure when supported on MCM-41.

### Supporting material

Figures S1–S4 can be seen in [www.ias.ac.in/chemsci](http://www.ias.ac.in/chemsci) Website.

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