# HPW and supported HPW catalyzed condensation of aromatic aldehydes with aniline: Synthesis of DATPM derivatives

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## Abstract

The mesoporous Si-MCM-41 was synthesized by hydrothermal method and various wt.% (20 and 30 wt.%) of HPW were loaded on Si-MCM-41 by wet impregnation method. The synthesized Si-MCM-41 and HPW-loaded catalysts were characterized by XRD, BET surface area, FT-IR, TEM and TGA–DTG techniques. The catalytic activity of the catalyst was tested over the condensation reaction of aniline with various aromatic aldehydes at refluxing temperature under liquid-phase condition, which yields highly commercial product namely diamino triphenyl methanes (DATPMs). The effects of various parameters like catalyst, mole ratio, solvents and substituent effect on the formation of DATPMs were optimized. The catalytic activity of the catalysts showed the following order: $H_3PW_{12}O_{40} \cdot nH_2O > H_3PMo_{12}O_{40} \cdot nH_2O > H_4SiW_{12}O_{40} \cdot nH_2O > 20$ wt.% HPW/MCM-41 > 30 wt.% HPW/MCM-41 > HM (12) > Hβ (8) > HY (4) > HZSM-5 (15) > Al-MCM-41 (25). The results showed that mole ratio of 4:1 (aniline:aldehyde) gave higher yield than the other mole ratios. Acetonitrile and ethyl acetate shows better activity especially in the supported materials than toluene was used as a solvent. The product thus obtained was analyzed by $^1$H NMR, FT-IR techniques.
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*Keywords:* HPW; HPW/MCM-41; Aniline; Aromatic aldehydes; DATPMs

## 1. Introduction

Triphenyl methane and its amino substituted derivatives are widely employed as dyes [1] and as antifungal agents in commercial fish hatcheries [2]. These compounds have also been employed as precursors in high performance polymer synthesis [3], in host–guest chemistry [4] and in material science [5]. Several DATPMs have been evaluated as copper corrosion inhibitors [6]. DATPMs present a number of interesting structural properties in solid and solution that have been much studied [7]. One of the most competitive industrial processes for the production of DATPMs is through acid-catalyzed condensation of aniline with aromatic aldehydes [8]. Many researchers reported in the literature that the condensation of aniline with aromatic aldehydes is carried out using various catalysts namely dry HCl [9,10], ion-exchange resin (Nafion XR) [11], ZnCl$_2$ (reactant aniline hydrochloride) [12], perfluorinated sulfonic acid resin [13], H$_3$PO$_4$ [14] and microwave conditions [15]. So the present

industrial practice of the condensation reaction requires large quantities of aqueous mineral acids as a homogeneous catalyst, which causes environmental problems associated with catalyst recovery and large amount of waste. Most methods described so far are lengthy procedures involving high catalyst/substrate ratios and high temperatures.

The use of relatively stable and strongly acidic heteropoly acids (HPWs) in acid-catalyzed reactions has attracted increasing attention for processes requiring higher acidity than that of the traditional catalysts [16–18]. 12-Tungstophosphoric acids, with the crystal structure of Keggin style [19], molecular of H$_3$PW$_{12}$O$_{40}$, was one kind of the widely applied catalytic species with high catalysis efficiency [20,21]. Until now, 12-tungstophosphoric acids had been employed widely for catalyst in the field of alkylation, acylation, esterification, polymerization and redox type organic reactions of both homogeneous and heterogeneous acid [22–24]. HPW having significantly higher Brönsted acidity, compared with the acidity of traditional mineral acid catalysts, is of great importance for catalysis [18,25–27]. The HPW has several advantages, such as the supported materials are reusable and very useful for commercial process. Several recent reports have been published on

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HPW/MCM-41 systems that catalyze reactions such as the esterification of acetic acid with isoamyl alcohol [28] and alkylation of 4-*tert*-butylphenol by isobutene and styrene [29], and synthesis of MTBE [30]. So the use of heterogeneous solid acid catalysts could provide much cleaner technology for the production of triphenyl methane derivatives. However, HPW, HPW/MCM-41 catalysts have not yet been used in the condensation of this typical work. Using HPW-based catalysts, it is frequently possible to obtain higher selectivity and successfully solve ecological problems. In this study, the catalytic activity of 12-tungstophosphoric acids that is used for the condensation of aniline with various aromatic aldehydes is studied, and the possible mechanism is also discussed.

Our work was initiated by the unique catalytic properties of HPWs observed using condensation of aniline with various aromatic aldehydes, and later was extended to other acid catalysts including Al-MCM-41, ZSM-5, HY, Hβ and mordenite. HPWs are promising solid acids to replace environmentally harmful liquid acid catalysts such as $H_2SO_4$ [25–27,31]. The condensation reactions only yield the DATPMs as the desired product. The emphasis is put on the optimization of catalytic performance, product yield and on catalyst deactivation. The results for HPW are compared with those for zeolites.

## 2. Experimental

### 2.1. Materials

The chemicals used for the synthesis of Si-MCM-41 and Al-MCM-41 (25) were sodium meta silicate ($Na_2SiO_3 \cdot 5H_2O$), aluminium sulfate ($Al_2SO_4 \cdot 18H_2O$), cetyltrimethylammonium bromide (CTAB) ($C_{16}H_{33}(CH_3)_3N^+Br^-$), and sulfuric acid ($H_2SO_4$). All chemicals used were A.R. grade, purchased from Aldrich & Co., USA. Aniline and various aldehydes and ketones used for the reaction are received from Merck with a claimed purity.

### 2.2. Synthesis of Si-MCM-41

Si-MCM-41 and Al-MCM-41 (25) samples were synthesized hydrothermally using a gel composition of $SiO_2$:$x$$Al_2O_3$:0.2CTAB:0.89$H_2SO_4$:120$H_2O$ [32]. Sodium meta silicate and aluminium sulfate were used as the sources for silicon and aluminium, respectively. Cetyltrimethylammonium bromide was used as the template. In typical synthesis, 10.6 g of sodium meta silicate in water was combined with an appropriate amount of aluminium sulfate in distilled water and the pH of the solution was adjusted to 10.5 by adding 1 M $H_2SO_4$ with constant stirring to form a gel. After 30 min, an aqueous solution of CTAB was added to it and the mixture was stirred for 1 h at room temperature. The suspension was then transferred into a 300-ml stainless steel autoclave, sealed and heated in a hot air oven at 145 °C for 48 h. After cooling to room temperature, the product formed was filtered, washed with deionised water and dried. The dried materials were calcined at 550 °C for 1 h in nitrogen atmosphere and for 5 h in air.

### 2.3. Preparation of HPW/MCM-41

HPW was supported on Si-MCM-41 by wet impregnation method. One gram of predried Si-MCM-41 was dispersed in 12 ml of deionised water with constant stirring. An aqueous solution of desired amount of Keggin-type heteropoly acid ($H_3PW_{12}O_{40} \cdot xH_2O$, Qualigens) was added. The dispersion was stirred for 6 h and then evaporated to dryness, and the resulting solid was dried overnight at 96 °C, followed by calcination at 300 °C for 5 h in air. Two HPW ($x\%$)/MCM-41 catalysts, where $x\%$ is the respective HPW content of 20 and 30 wt.%, were prepared according to the above procedure. The samples were stored from moisture free atmosphere.

### 2.4. Commercial catalytic materials

HM (Si/Al = 12, PQ), Hβ (Si/Al = 8, PQ), HY (Si/Al = 4, PQ), HZSM-5 (Si/Al = 15, PQ), $H_3PW_{12}O_{40} \cdot nH_2O$, $H_3PMo_{12}O_{40} \cdot nH_2O$, $H_4SiW_{12}O_{40} \cdot nH_2O$ were obtained from Sud Chemie India Ltd.

### 2.5. Catalytic runs and analysis of the product

The condensation of aniline with various aldehydes was carried out in liquid-phase in a 50 ml glass reactor equipped with a condenser and a magnetic stirrer. The reactor was charged with aromatic aldehydes (5 mmol), aniline (20 mmol) and required amount of toluene was used as a solvent. The system was purged with nitrogen to expel air and moisture and heated to reflux temperature (120 °C). An appropriate amount of preactivated catalyst was added to the reactor. The reaction mixture turned into various colours depending upon the aldehydes in the colourless solution and the colour of the reaction mixture deepened dark as the reaction progressed. After the reaction the solid product thus obtained was filtered and washed with excess toluene and purified by using ethyl acetate/hexane mixed solvent. The conditions like the effect of the catalyst, mole ratio and substituent effect were studied on the yield of DATPMs. The products were analyzed by $^1$H NMR (Fig. 1) and FT-IR techniques.

### 2.6. Characterization

The XRD powder diffraction patterns of the mesoporous MCM-41 (Si-MCM-41, 20 and 30% HPW/Si-MCM-41) molecular sieves were obtained with a Stereoscan diffractometer using nickel-filtered Cu Kα radiation and a liquid nitrogen cooled germanium solid-state detector. The diffractograms were recorded in the 2θ range of 1.0–40.0° in the steps of 0.02° with a count time of 15 s at each point for MCM-41 molecular sieves. Surface area, pore volume and pore size distribution were measured by nitrogen adsorption at 77 K with an ASAP-2010 porosimeter from Micromeritics Corporation Noreross, GA. The samples were degassed at 623 K with $10^{-5}$ Torr overnight prior to the adsorption experiments. The mesopore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.5 by assuming that all the mesopores were filled with con-
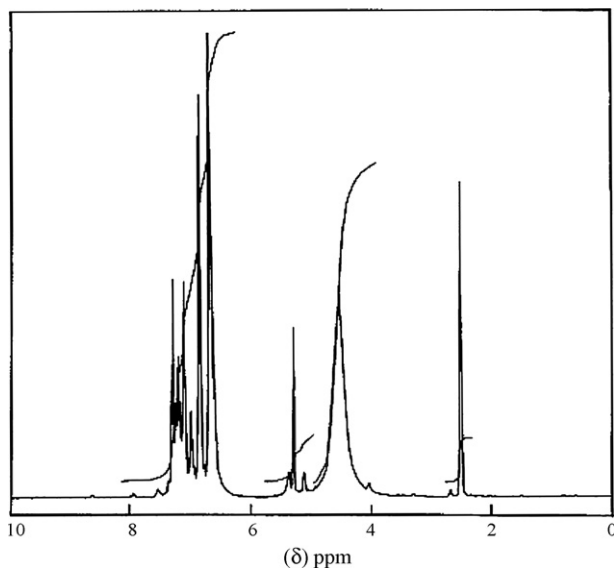
Fig. 1. $^1$H NMR (DMSO-$d^6$, 400 MHz) spectrum of the compound (Table 3, entry [a]): $\delta$ 4.51 (br s, 4H, –NH$_2$), 5.26 (s, 1H, CH), 6.62 (d, 4H Ar, $J$ = 8.3 Hz), 6.81 (d, 4H Ar, $J$ = 8.3 Hz), 7.05–7.26 (m, 5H, Ar).

ing is 20 °C/min at 40–800 °C in air atmosphere. The acidity of the catalysts was studied by temperature-programmed desorption of ammonia (NH$_3$-TPD). About 200 mg of catalyst was placed in a quartz reactor and was activated at 823 K in air for 6 h, followed by 2 h in helium with a flow rate of 50 ml min$^{-1}$. The reactor was then cooled to 373 K and maintained for another hour under the same condition. The desorption of ammonia was carried out by heating the reactor up to 823 K at a uniform rate of 10 K min$^{-1}$. The amount of ammonia desorbed was estimated with the aid of thermal conductivity detector response factor for ammonia. The tungsten content in supported catalyst was recorded using various ICP-AES with Allied Analytical ICAP 9000. The dispersion of the HPW on the support was determined by means of TEM measurements. TEM was performed using a JEOL 3010 electron microscope operated at 300 kV. Samples for TEM were prepared by placing droplets of a suspension of the sample in acetone on a polymer microgrid supported on a Cu grid.

densed nitrogen in the normal liquid state. Pore size distribution was estimated using the built-in Barrett, Joyner and Halenda (BJH) algorithm (ASAP-2010) software from Micromeritics. The acidity of all the catalytic systems was analyzed by pyridine adsorption followed by FT-IR spectroscopy in absorbance mode on a Nicolet 800 (AVATAR) FT-IR spectrometer, fully controlled by the OMNIC software, and an all-glass high-vacuum system. $^{31}$P MAS NMR spectra were measured at room temperature on a Bruker Avance DSX 400 FT-NMR spectrometer in the frequency range of 10 kHz, pulse duration 12 μs, delay between pulses 30 s: the instrument was equipped with a Doty Scientific 5 mm Solids MAS Probe, as described elsewhere. One percent H$_3$PO$_4$ in D$_2$O was used as an external reference. The accuracy of the chemical shift determination was within ±0.4 ppm. Simultaneous TGA–DTG investigation was made on the thermal properties of the samples: A TA Instrument: SDT Q600 instrument was used. The thermogram of pure HPW was recorded for ~5 mg samples: the N$_2$ flow rate is 100 mL/min; the rate of heat-

## 3. Results and discussion

### 3.1. Structure of HPW/MCM-41 catalysts

#### 3.1.1. XRD

The XRD patterns of Si-MCM-41, Al-MCM-41 (25) and HPW/MCM-41 samples show the diffraction peaks below 10° (2$\theta$) which corresponds to the planes (1 0 0), (1 1 0), (2 0 0) and (2 1 0), characteristic for mesoporous materials (Table 1 and Fig. 2). The XRD patterns of supported materials (HPW/MCM-41) retain the long-range ordering of the hexagonal mesostructure. The amount of HPW loading shows a remarkable effect on the intensity of the main (1 0 0) reflection peak of the Si-MCM-41 support and the peak height is inversely proportional to the amount of loaded HPW. The material does not show any bulk HPW crystal phase for the fresh composite catalyst, indicating that HPW is finely dispersed on the MCM-41 support. The XRD peak of supported materials shows lower crystallinity of (1 0 0), (1 1 0) and (2 0 0) plane and shorter $d$-spacing value than the parent material [33].

Table 1
Physico-chemical properties of the supported catalysts and the support

| Catalysts | XRD | | Surface area[a] (m$^2$/g) | Pore size[a] BJH$_{Ads}$ (nm) | Pore volume[a] BJH$_{Ads}$ (cc/g) | Total acidity[b] (mmol g$^{-1}$) | ICP[c] W (wt.%) |
|---|---|---|---|---|---|---|---|
| | $d$ spacing (Å) | $a_0$ (nm) | | | | | |
| Si-MCM-41 ($\infty$) | 40.61 | 4.69 | 1032 | 2.996 | 0.773 | – | – |
| 20% HPW/Si-MCM-41 | 39.97 | 4.62 | 729 | 2.731 | 0.497 | 0.47 | 14.8 |
| 30% HPW/Si-MCM-41 | 38.16 | 4.53 | 540 | 2.721 | 0.367 | 0.43 | 22.5 |
| Al-MCM-41 (25) | 38.86 | 4.49 | 932 | 2.667 | 0.777 | 0.29 | – |
| HM (12) | – | – | 481 | – | – | 1.14 | – |
| Hβ (8) | – | – | 587 | – | – | 0.92 | – |
| HY (4) | – | – | 367 | – | – | 0.58 | – |
| HZSM-5 (15) | – | – | 386 | – | – | – | – |

[a] Measured by BET surface area method.
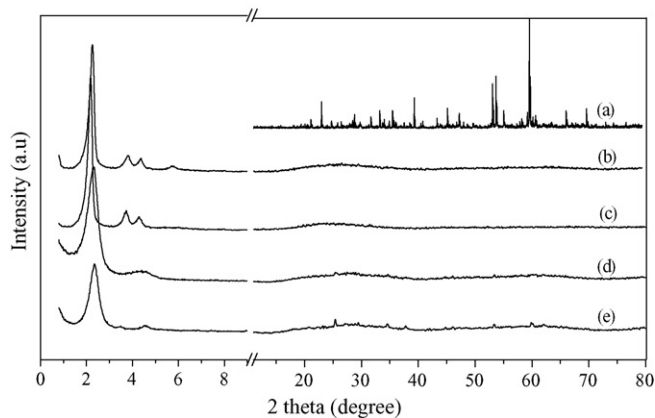[b] Measured by NH$_3$-TPD techniques.
[c] Measured by ICP-AES techniques.

Fig. 2. X-ray diffraction pattern of MCM-41 molecular sieves: (a) pure HPW, (b) Al-MCM-41, (c) Si-MCM-41, (d) 20% HPW/Si-MCM-41 and (e) 30% HPW/Si-MCM-41.

### 3.1.2. Nitrogen adsorption isotherms

Table 1 illustrates that BET surface area, pore volume and pore size of the material decrease with increasing HPW loading [34]. However, the pore size distribution of the mesoporous part is centered at about 26.6–29.9 Å. The pore sizes of the HPW/Si-MCM-41 samples are in the range 27.21 and 27.31 Å, which is smaller than that of Si-MCM-41 (29.9 Å). This shows that HPW has been dispersed on the surfaces of the mesopores of Si-MCM-41, which is due to the blockage of particles in one-dimensional mesopores of Si-MCM-41 by small aggregates of HPW. Fig. 3 shows $N_2$ adsorption–desorption isotherms of Si-MCM-41 and all the HPW/Si-MCM-41 samples. When varying the HPW loading a sharp mesoporous inflection was observed on the isotherms, the higher the HPW loading inflection becomes gradually shorter corresponding to a reduction in the pore volume. As shown in Fig. 4, a notable compression of the pore size distribution was found with increasing HPW loading.



Fig. 3. Nitrogen adsorption–desorption isotherms of the catalysts: (a) Si-MCM-41, (b) 20% HPW/Si-MCM-41 and (c) 30% HPW/Si-MCM-41.



Fig. 4. Pore size distribution of the catalysts: (a) Si-MCM-41, (b) 20% HPW/Si-MCM-41 and (c) 30% HPW/Si-MCM-41.

### 3.1.3. Pyridine FT-IR technique

The distribution of acid sites over supported Si-MCM-41 was given in Fig. 5. It revealed that the characteristic skeletal vibrations of pyridine adsorbed on Lewis acid sites and Brönsted acid sites. The peaks at 1445, 1545 and 1493 $cm^{-1}$ corresponds to Lewis, Brönsted and both Lewis and Brönsted acid sites, respectively [35,36]. The acidity varies depending on the amount of HPW loaded on the support. Acidity of the catalyst increases with increasing HPW loading (from 20 to 30 wt.%), as judged from acidity measurements. Particularly, the Lewis acid peak shows a more intense peak than the Brönsted acid peak. Brönsted and Lewis acidity are quantified into integrated areas of the absorbance bands at 1545 and 1450 $cm^{-1}$, respectively, which increase stepwise with increasing HPW loading.

### 3.1.4. $^{31}P$ MAS NMR spectra

Fig. 6 illustrates the $^{31}P$ MAS NMR spectra of HPW and HPW/Si-MCM-41 (20 and 30 wt.%). The strong resonance at −15 ppm corresponds to the tetrahedral coordination of $PO_4$ in
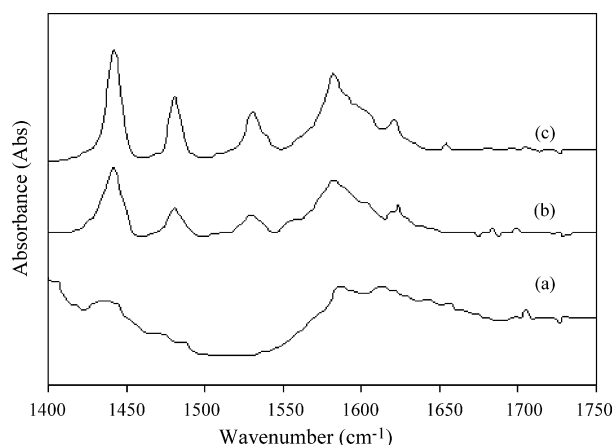


Fig. 5. Pyridine-adsorption FT-IR spectra of the catalysts: (a) Si-MCM-41, (b) 20% HPW/Si-MCM-41 and (c) 30% HPW/Si-MCM-41.
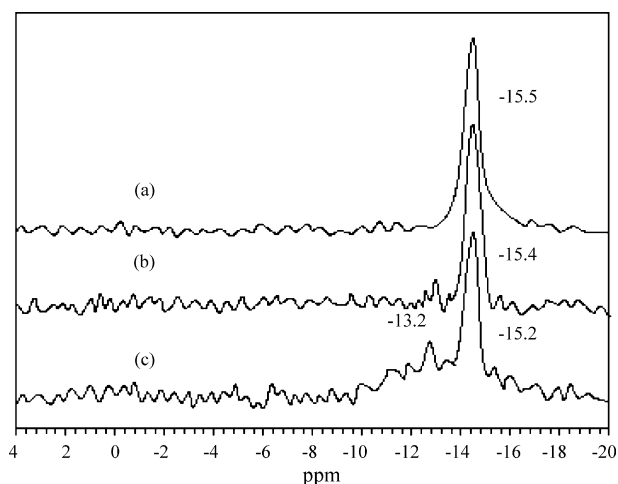
Fig. 6. $^{31}$P MAS NMR spectrum of the catalysts: (a) HPW, (b) 20% HPW/Si-MCM-41 and (c) 30% HPW/Si-MCM-41.

Keggin unit. The supported catalyst also shows a peak around −15.2 ppm, indicating that the Keggin structure of the het-eropolyacid is retained after supporting in the Si-MCM-41. In the case of HPW/Si-MCM-41, another resonance peak with lower intensity observed at −13.3 ppm, indicates the interactions between HPW and the support [31]. This $^{31}$P MAS NMR results revealed that the fine dispersion of HPW on the host material.

### 3.1.5. Thermal analysis

The catalytic activity and structure of the heteropolyacids mainly depend upon the percentage of water content in the HPW. This could be solved by the thermal pretreatment that was carried out at 130–200 °C [25]. Fig. 7 illustrates the derivative TGA spectrum for hydrated bulk HPW. The peak shows three-stage weight loss: (a) the first peak observed at a temperature below 100 °C (2.81%) corresponding to the loss of physisorbed water; (b) a peak in the temperature range of 100–320 °C (3.96%) centered at about 200 °C, accounting for the loss of $6H_2O$ (1a) molecules per Keggin unit; (c) a peak in the range of 370–600 °C (1.32%) centered at about 470 °C due to the loss of $1.5H_2O$ ((1b) and (1c)) molecules corresponding to the loss of all acidic protons and the beginning
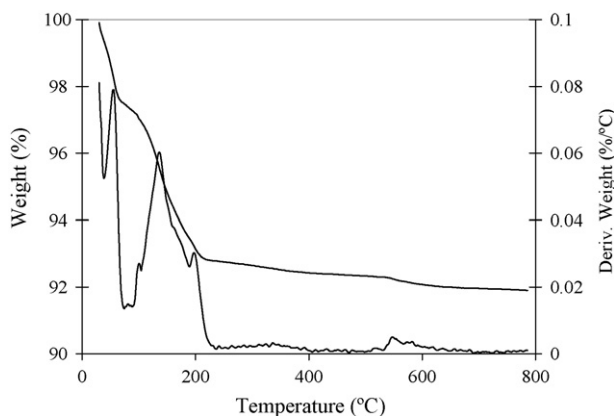


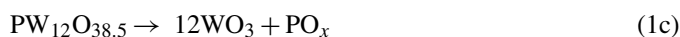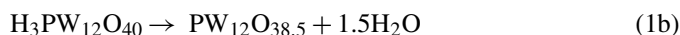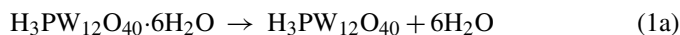Fig. 7. Determination of water content in HPW catalyst by TGA/DTG method.

of decomposition of the Keggin structure [37]:

$$H_3PW_{12}O_{40} \cdot 6H_2O \; \rightarrow \; H_3PW_{12}O_{40} + 6H_2O \tag{1a}$$

$$H_3PW_{12}O_{40} \rightarrow \; PW_{12}O_{38.5} + 1.5H_2O \tag{1b}$$

$$PW_{12}O_{38.5} \rightarrow \; 12WO_3 + PO_x \tag{1c}$$

### 3.1.6. TEM analysis

The morphology of the Si-MCM-41 and supported catalysts was consistent with TEM results (Fig. 8). TEM shows a honey-comb structure of the host material, whereas, 20 and 30% HPW containing Si-MCM-41 shows the uniform dispersion of HPW on the host, which can be distinguished as dark dots in TEM images.

### 3.2. Synthesis of diamino triphenyl methane over various catalysts to the condensation of aniline with aromatic aldehydes

The DATPMs were synthesized by the condensation of aniline with various aromatic aldehydes. The reaction yielded nine products, namely 4,4′-(phenyl methylene) dian-iline (entry [a]), 4,4′-[(2-nitrophenyl) methylene] dianiline (entry [b]), 4,4′-[(3-nitrophenyl) methylene] dianiline (entry [c]), 4,4′-[(2-chlorophenyl) methylene] dianiline (entry [d]), 4,4′-[(4-chlorophenyl) methylene] dianiline (entry [e]), 4,4′-[(4-bromophenyl) methylene] dianiline (entry [f]), 4,4′-[(1-naphthyl methylene] dianiline (entry [g]), 4,4′-(1H-indol-3-ylmethylene) dianiline (entry [h]) and 4,4′-[(2-methoxyphenyl) methylene] dianiline (entry [i]).

This condensation reaction occurs with 2 mol of aniline and 1 mol of aldehyde or ketone. Scheme 1 shows that the conden-sation reactions proceed through two steps: the first step is the adsorption of aldehydes on catalyst active sites which leads to the formation of carbocation on carbonyl group. The carbonium ion undergoes electrophilic attack with 1 mol of aniline and forms an intermediate. The second step of the reaction is the adsorption of intermediate on the catalyst active sites, thereby producing the carbonium ion. The carbonium ion makes further electrophilic attack with another mol of aniline, which leads to the formation of DATPMs.

### 3.2.1. Effect of catalyst

The effect of various catalysts on the yield of DATPM is given in Table 2. The condensation of aniline with various aromatic aldehydes were carried out over HPW and supported HPW. The catalytic activity of HPW and supported HPW are compared with zeo-type solid acid catalysts. The reaction was carried using Dean-stark apparatus, the reactant mole ratio (aniline to aldehyde) are 4:1, 0.5 g of catalyst, amount of solvent is 40 ml (toluene), the reaction period is kept constant for 8 h at refluxing temperature. The activity of the catalysts on the yield of DATPM follow the order $H_3PW_{12}O_{40}$ ·$nH_2O > H_3PMo_{12}O_{40} \cdot nH_2O > H_4SiW_{12}O_{40} \cdot nH_2O > 20$ wt.% HPW/MCM-41 > 30 wt.% HPW/MCM-41 > HM (12) > Hβ (8) > HY (4) > HZSM-5 (15) > Al-MCM-41 (25). The yield of DADPM mainly depends upon the strength of acid sites
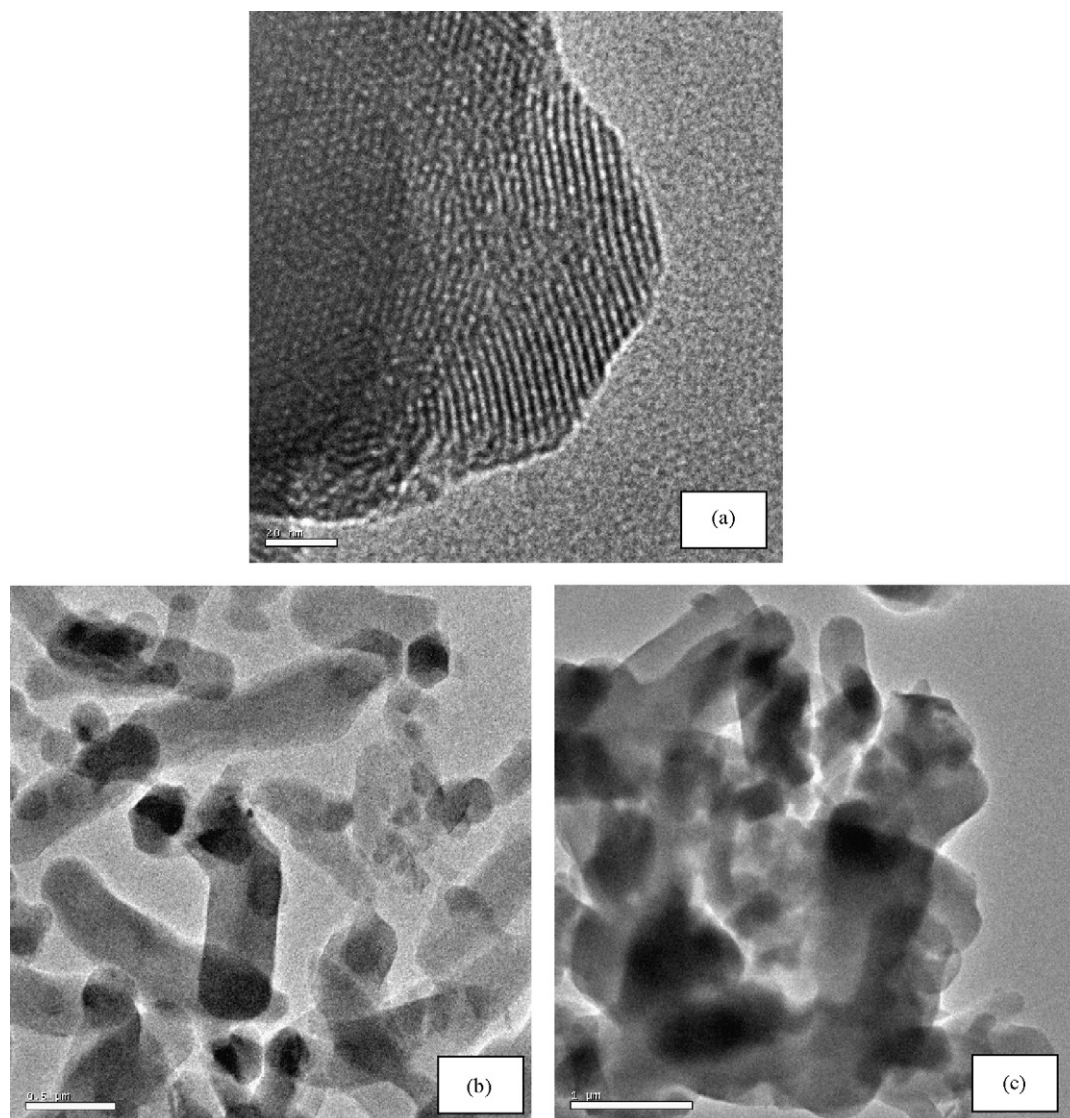
Fig. 8. TEM image of MCM-41 molecular sieves: (a) Si-MCM-41, (b) 20% HPW/Si-MCM-41 and (c) 30% HPW/Si-MCM-41.

Table 2
Effect of various catalysts on condensation of aniline with benzaldehyde

| Sl. no. | Catalysts | Yield (%) |
|---|---|---|
| 1 | Al-MCM-41 (25) | 19 |
| 2 | $H_3PW_{12}O_{40} \cdot nH_2O$ | 85 |
| 3 | $H_3PMo_{12}O_{40} \cdot nH_2O$ | 78 |
| 4 | $H_4SiW_{12}O_{40} \cdot nH_2O$ | 72 |
| 5 | HM (12) | 23 |
| 6 | Hβ (8) | 19 |
| 7 | HY (4) | 16 |
| 8 | HZSM-5 (15) | 14 |
| 9 | Without catalyst | 0 |
| 10 | 20 wt.%HPW/MCM-41 | 66 |
| 11 | 30 wt.%HPW/MCM-41 | 55 |

Reaction conditions: temperature = refluxing; time = 8 h; feed ratio = 4:1 (aniline/benzaldehyde); catalyst loading = 0.5 g; solvent = toluene.

present in the catalyst. The activity order of commercial HPAs lies parallel to the acid strength which is calculated by proton affinity [38]. The proton affinity values of $H_3PW_{12}O_{40} \cdot nH_2O$, $H_3PMo_{12}O_{40} \cdot nH_2O$ and $H_4SiW_{12}O_{40} \cdot nH_2O$ are 1070, 1140 and 1140 kJ/mol, respectively. Among the catalysts bulk HPW shows better activity compared with other solid acid catalysts, which might be due to the presence of more number of Brönsted acid sites. Though the bulk HPW shows better activity, HPW-supported Si-MCM-41 (20, 30 wt.%) shows considerably high yield than other unsupported solid acids like HM, Hβ, HY, HZSM-5, Al-MCM-41. The activity of HPW was further compared with the previous literature. Ghatge and Khune [12] obtained DATPMs with 75–88% yield by the condensation of $PhNH_2 \cdot HCl$ with various substituted aldehydes at 165–170 °C for 4 h with $ZnCl_2$, but in our procedure the same reactions gave 65–91% yield with HPW even at lower temperature. Bulk and supported HPW catalysts shows better yield than the other catalysts.
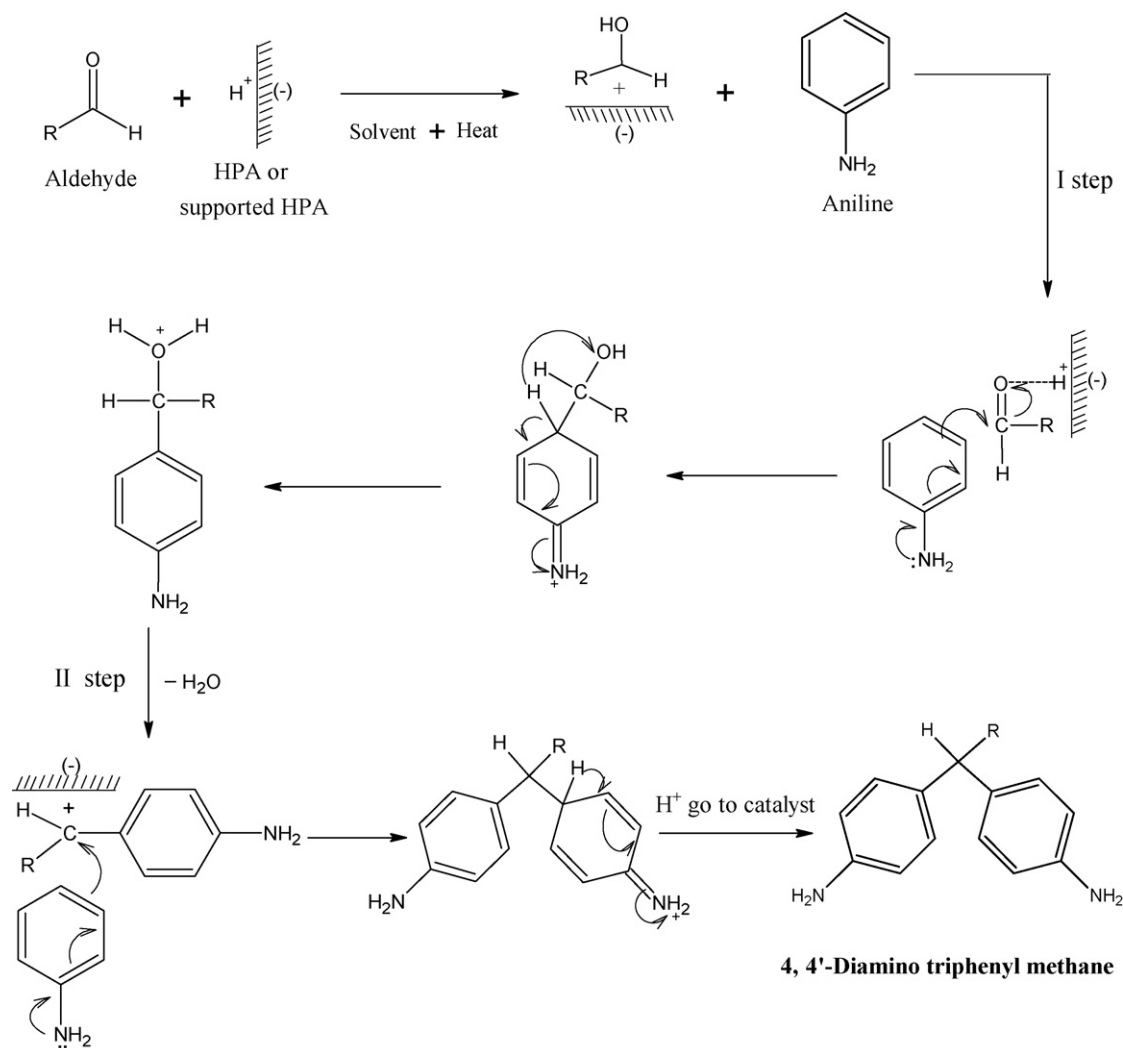
Scheme 1. Mechanism for the formation of diamino triphenyl methane.

The lower yield of DATPM in Al-MCM-41 and other zeo-type catalysts is attributed to its mild acidity, not adequate enough to catalyze the reaction. Though both 20 and 30 wt.% HPW-loaded catalysts have Keggin structure with high dispersion of the HPW on host material, the activity of 20 wt.% HPW/MCM-41 is significantly higher than that of the 30 wt.% HPW/MCM-41 (Table 2, Sl. no. 10, 66% vs. Sl. no. 11, 55%). As given in Table 1, the slow decrease in the pore size with increasing HPW loading and the abrupt decrease in the BET surface area and the pore volume at higher loading of HPW indicate the partial blockage of one-dimensional mesopores of Si-MCM-41 by small aggregates of HPW. Hence, the lowering of pore size in 30 wt.% HPW/MCM-41 shows the less activity compared to 20 wt.% HPW/MCM-41; this might be due to (i) the lower pore size containing material that reduces the formation of bulky intermediate and (ii) the formed product were suffered by diffusion resistance thereby preventing further reaction.

### 3.2.2. Influence of mole ratio of the reactants

The effect of mole ratio on product yield was studied over 0.5 g HPW at refluxing temperature for the period of 8 h. The mole ratio of aniline:benzaldehyde increased from 2:1, 4:1, 6:1 and 8:1 for which the obtained DATPM yields were 70, 85, 74 and 61%, respectively. When the feed increased from 2:1 to 8:1, the product yield increased up to 4:1, above the 4:1 mole ratio the product yield decreased. This is due to increase in aniline concentration up to certain level, which increases the availability of aniline nearer to the Brönsted acid sites thereby enhancing the electrophilic attack of polarized aldehyde species in the Brönsted acid. Further increase in aniline concentration, higher % of aniline decreases the product yield. This is certainly due to much higher initial rates of reaction thereby leading to selective pore blocking due to the precipitation of the product inside the pores. The bulkier product molecules are formed at a faster rate due to more acidity of the catalysts. This tends to overcrowd the pores leading to diffusion resistance. In all the mole ratios of benzaldehyde and aniline, DATPM was observed as the only product.

### 3.2.3. Influence of the substituent

The effect of various substituent on the aromatic aldehydes on the reaction yield were tested at the optimized

Table 3
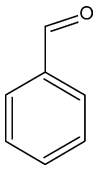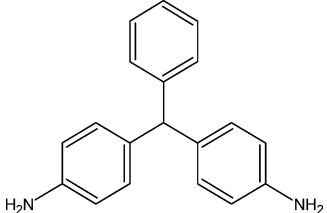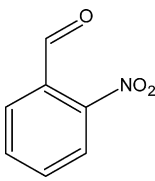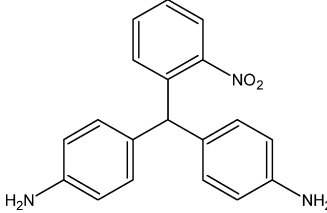Synthesis of DATPMs over various % of HPW and HPW-loaded Si-MCM-41
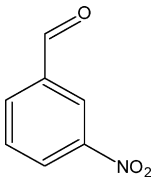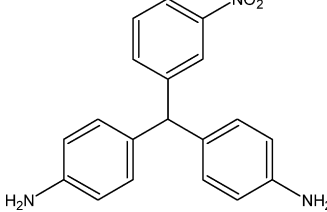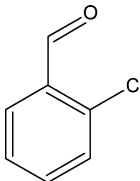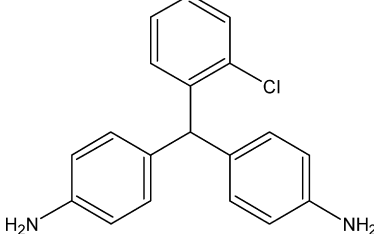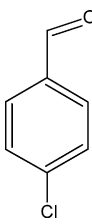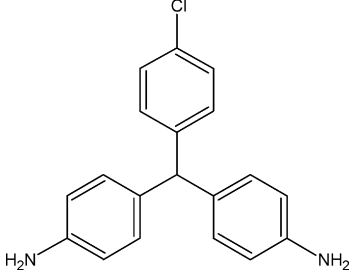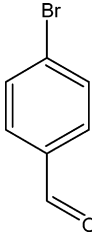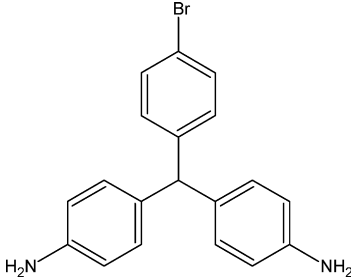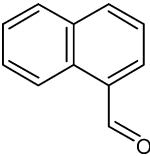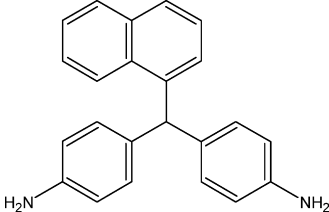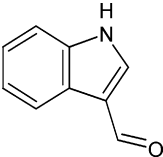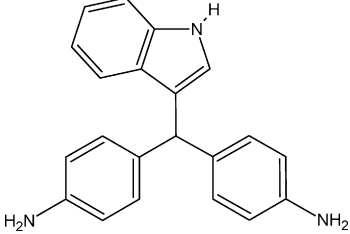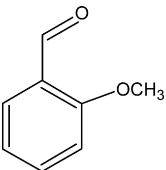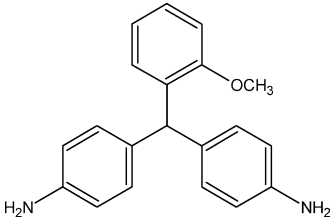
| Entry | Aldehyde | Compound | % Yield | | |
|---|---|---|---|---|---|
| | | | HPW | 20 wt.% HPW/MCM-41 | 30 wt.% HPW/MCM-41 |
| [a] |  |  | 85 | 66 | 55 |
| [b] |  |  | 89 | 68 | 51 |
| [c] |  |  | 91 | 73 | 61 |
| [d] |  |  | 76 | 51 | 39 |
| [e] |  |  | 79 | 54 | 41 |
| [f] |  |  | 83 | 61 | 47 |

Table 3 (*Continued*)

| Entry | Aldehyde | Compound | % Yield | | |
|---|---|---|---|---|---|
| | | | HPW | 20 wt.% HPW/MCM-41 | 30 wt.% HPW/MCM-41 |
| [g] | | | 65 | 33 | 26 |
| [h] | | | 69 | 41 | 31 |
| [i] | | | 47 | 29 | 18 |

Reaction conditions: temperature = 120 °C; reaction vessel = 50 ml; time = 8 h; solvent = toluene (40 ml); mole ratio = 4:1 (aniline/benzaldehyde); catalyst = HPW, 20 wt.% HPW/MCM-41 and 30 wt.% HPW/MCM-41; weight of the catalyst = 0.5 g.

condition over 0.5 g of HPW, 20 wt.% HPW/MCM-41 and 30 wt.% HPW/MCM-41 by refluxing with aniline (Table 3, entries [a]–[i]). When compared with (entries [b] and [i]) the aromatic aldehyde with electron-withdrawing groups such as nitro group at ortho position showed higher reactivity than the electron-donating group such as methoxy group. This can be further evidenced by the reaction with 2-chloro-, 4-chloro- and 4-bromo-benzaldehyde (electron-withdrawing group) which shows higher product yield (entries [d]–[f]) compared with (entry [a]), which confirms the reaction mainly occurs in benzaldehyde containing withdrawing substitution than the benzaldehyde containing donating substitution. From Table 3 (entries [g] and [h]) showed lower yield than the (entry [a]), this is due to the bulky nature of the aldehyde. The results show that steric hindrance plays the major role for the yield of DATPM. Table 3 shows bulk HPW gave better yield than the 20 and 30 wt.% HPW/MCM-41, which confirms that supported porous materials suffer by the % of active substance in the host material as well as the size of product formed during the reaction reduces further reaction due to diffusional constraint.

### 3.2.4. Effect of various solvents on the product yield

Influence of solvents are the important parameter for the determination of yield of the product. Table 4 shows the effect of various solvents on the condensation reaction. The reaction was conducted with various solvents on the condensation reaction of aniline with benzaldehyde over 20 wt.% HPW/MCM-41 with the mole ratio of 4:1 (aniline:benzaldehyde). The performance of various solvents are in the following order: acetonitrile > ethyl acetate > toluene > THF > dichloromethane. Acetonitrile and ethyl acetate shows better yield on DATPM compared with other solvents. This is due to higher solvent polarity of acetonitrile and ethyl acetate when compared to that of other solvents, thus the solvent gets the products from the active surface of the catalyst thereby more polar solvents regenerate the catalyst active sites. The catalyst shows the lower the DATPM yield, when the reaction was carried out using toluene as the solvent. Toluene shows lower product yield due to lower

Table 4

The effect of various solvents on the condensation of aniline with benzaldehyde over 20 wt.% HPW/MCM-41

| Sl. no. | Solvents | Temperature (°C) | Yield of DATPM (%) |
|---|---|---|---|
| 1 | Dichloromethane | 75 | 29 |
| 2 | Ethyl acetate | 75 | 64 |
| 3 | Acetonitrile | 75 | 71 |
| 4 | Toluene | 100 | 59 |
| 5 | DMSO | 100 | – |
| 6 | DMF | 100 | – |
| 7 | THF | 75 | 41 |

Reaction conditions: mole ratio = 4:1 (aniline/benzaldehyde); catalyst = 20 wt.% HPW/MCM-41; time = 16 h; weight of the catalyst = 0.5 g.

Table 5
Recycling of the supported catalyst over condensation of aniline with benzaldehyde

| Cycle | Toluene | | Acetonitrile | |
|---|---|---|---|---|
| | Yield (%) | W[a] (wt.%) | Yield (%) | W[a] (wt.%) |
| Fresh | 59 | 14.8 | 71 | 14.8 |
| First | 55 | 14.5 | 56 | 12.3 |
| Second | 53 | 14.4 | 48 | 10.9 |

Conditions: temperature = 100 °C for toluene and 75 °C for acetonitrile; mole ratio = 4:1 (aniline/benzaldehyde); catalyst = 20 wt.% HPW/MCM-41; time = 16 h; weight of the catalyst = 0.5 g.

[a] W content in catalysts from ICP.

polarity, toluene was not capable to get the products for the catalyst surface thereby the solid products deactivates the active surface of the catalyst. But, DMSO and DMF show no reaction, hence, it can be depicted that the solvent plays a negative role by retarding the condensation reaction. This might be due to neither the adsorption of solvent on the catalyst surface nor the association of the reactant with solvent.

### 3.2.5. Leach out and reusability study of the supported catalyst

To check the leaching of HPW, the reaction was carried out under optimized reaction conditions using 20 wt.% HPW/MCM-41. After each catalytic run, the solids were separated by filtration and regenerated by washing consecutively with methanol and acetone and dried at 100 °C. Finally, the fresh and used catalysts were subjected to elemental analysis by ICP-AES techniques. The results show that there is no significant loss of W content while toluene is used as a solvent where only <2% loss of W is observed at each cycle (Table 5). The stability of the catalyst over the polar solvent (acetonitrile) is also studied where a measurable loss of W is detected. In the first run it shows 16.8% loss of W content and 11.4% loss in the second run. In addition, the product yield was found to be less when toluene was used as a solvent compared to acetonitrile but the stability of the supported catalyst remained unaltered as parent material.

### 4. Conclusion

The bulk HPW and supported HPW show better catalytic activity than the other materials for the synthesis of the industrially important diamino triphenyl methanes. The 20 wt.% HPW is the optimum loading on the support for production of DATPM. The steric hindrance plays an important role in the yield of DATPM. The moderate polar solvents like acetonitrile and ethyl acetate show slightly higher activity than non-polar solvent. The electron-withdrawing groups present in the aldehyde influences the yield, whereas donating group present in the aldehyde reduces the product yield. This work illustrates the activity of various catalysts for the production of DATPM. The stability and reusability of the supported catalysts are higher in toluene than acetonitrile. As a conclusion, MCM-41-supported heteropolyacid, the strongest heteropolyacid in the Keggin series, is a very efficient and environmentally benign heterogeneous catalyst for the liquid-phase synthesis of DATPM derivatives.

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